10 Aromatic Compounds

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1 Introduction

The graph-theoretical approach[1a] to conjugation and resonance energies of hydrocarbons involving the concept of conjugated circuits [see *Ann. Reports (B)*, 1976, **73**, p. 223] has been developed as a new approach to the aromaticity[1b] of polycyclic systems, those having only conjugated circuits with $(4n+2)$ π-electrons, when the Kekulé structures are examined, being defined as aromatic. The approach allows the prediction of the relative aromaticity of some systems containing both $(4n+2)$ and $(4n)$ conjugated circuits. Resonance energies obtained[2a] using Clar's aromatic sextet theory correlate well with the Dewar-type resonance energies from graph theory [see *Ann. Reports (B)*, 1976, **73**, p. 201],[2b] and the latter approach has been applied to a wide range of systems.[2c] An essentially identical graph-theoretical approach, derived, however, as the result of a different line of argument, has also been reported.[3] The degree of electron delocalization in cyclic systems has been proposed,[4] with theoretical justification, to be a function both of orbital phase continuity requirements and of the disposition of donor and acceptor component systems. The condition under which the normal criterion for delocalization, based on the number of π-electrons, becomes invalid in 'effectively discontinuous systems' has been presented.

An interesting polycyclic system with different possible delocalized structures is the dicyclo-octatetraeno[1,2:4,5]benzene dianion, which has been shown[5] not to sustain a localized 14π-electron diamagnetic ring current. It is probably best described by the planar 20π-electron structure (1), where the electrostatic repulsion is adequate to overcome the strain energy and the antiaromatic character of the ion.

The diamagnetic susceptibility exhaltations of several 7-substituted cycloheptatrienes vary as a function of the size of the substituent, are very large, and are indicative of a substantial ring current.[6] It has been suggested that, in view of the low resonance energies and the bond alternation, these systems should simply be

[1] M. Randić, (a) *Tetrahedron*, 1977, **33**, 1905; (b) *J. Amer. Chem. Soc.*, 1977, **99**, 444.

[2] J.-I. Aihara, (a) *Bull. Chem. Soc. Japan*, 1977, **50**, 2010; (b) *ibid.*, p. 3057; (c) *J. Amer. Chem. Soc.*, 1977, **99**, 2048.

[3] I. Gutman, M. Milun, and N. Trinajstić, *J. Amer. Chem. Soc.*, 1977, **99**, 1692.

[4] S. Inagaki and Y. Hirabayashi, *J. Amer. Chem. Soc.*, 1977, **99**, 7418.

[5] L. A. Paquette, G. D. Ewing, S. Traynor, and J. M. Gardlik, *J. Amer. Chem. Soc.*, 1977, **99**, 6115.

[6] R. F. Childs and I. Pikulik, *Canad. J. Chem.*, 1977, **55**, 259.

(1)

(2)

(3) R = p-NO$_2$C$_6$H$_4$
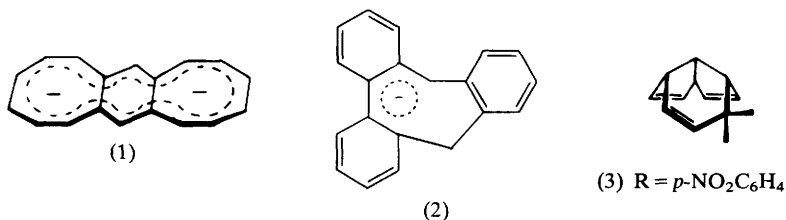
described as diatropic rather than homoaromatic, and the authors question whether diatropicity is a useful or even valid criterion of aromaticity. Two homoaromatic ions have been reported[7] which involve the interruption of the cyclic conjugated system by a three-carbon bridge. The benzannelated homocyclopentadienyl anion (2) is formed by treatment of the parent hydrocarbon with butyl-lithium. Examination of several systems[8] has provided no evidence for trishomoaromatic stabilization. Kinetic and product studies of the hydrolysis of (3), for example, indicate[8b] no participation of the double bonds. A mathematical model has been devised which enables the magnitude of the interaction between homoaromatic centres to be evaluated.[8c]

The sites of protonation of simple substituted benzenes in the gaseous phase have been receiving attention. Ring protonation of phenol has been calculated[9] by *ab initio* MO theory to be 63 kJ mol^{-1} more favourable than *O*-protonation, and a deuterium-exchange experiment gave an approximate value in agreement with this. Measurements of N$_{1s}$ core ionization energy suggest that aniline is protonated on nitrogen in the gaseous phase, but anomalies exhibited by *NN*-dimethylaniline may be due to ring protonation.[10a] Pulsed ion cyclotron resonance spectroscopy confirms[10b] the former result, although *ab initio* MO theory suggests that ring protonation is only 4—13 kJ mol^{-1} less favourable. After comparison of the relative base strengths of some *meta*- and *para*-substituted anilines in the gaseous phase with the values for these compounds in aqueous solutions, it has been suggested that, for *m*-toluidine and *m*-anisidine, protonation occurs on the ring.[10c]

The opposing views concerning the nature of aryl ^{19}F n.m.r. polar field effects have now been largely reconciled. Calculations (CNDO/2) on the 1-substituted 4-*p*-fluorophenylbicyclo[2,2,2]octanes have indicated[11a] the dominance of π-polarization effects, direct field effects accounting for only about 25% of the polar effects on ^{19}F chemical shifts. In this connection, the distinction between π-polarization and the π-inductive effect has been emphasized.[11b] ^{13}C N.m.r. data

[7] A. Dagan, D. Bruck, and M. Rabinovitz, *Tetrahedron Letters*, 1977, 2995.

[8] (*a*) L. A. Paquette, M. J. Kukla, S. V. Ley, and S. G. Traynor, *J. Amer. Chem. Soc.*, 1977, **99**, 4756; L. A. Paquette, H. C. Berk, C. R. Degenhardt, and G. D. Ewing, *ibid.*, p. 4764; (*b*) L. A. Paquette, P. B. Lavrik, and R. H. Summerville, *J. Org. Chem.*, 1977, **42**, 2659; (*c*) L. A. Paquette, T. G. Wallis, T. Kempe, G. G. Christoph, J. P. Springer, and J. Clardy, *J. Amer. Chem. Soc.*, 1977, **99**, 6946.

[9] D. J. DeFrees, R. T. McIver, and W. J. Hehre, *J. Amer. Chem. Soc.*, 1977, **99**, 3853.

[10] (*a*) R. G. Cavell and D. A. Allison, *J. Amer. Chem. Soc.*, 1977, **99**, 4203; (*b*) S. K. Pollack, J. L. Devlin, tert, K. D. Summerhays, R. W. Taft, and W. J. Hehre, *ibid.*, p. 4583; (*c*) K. D. Summerhays, S. K. Pollack, R. W. Taft, and W. J. Hehre, *ibid.*, p. 4585.

[11] (*a*) W. F. Reynolds, *Tetrahedron Letters*, 1977, 675; (*b*) W. Kitching, M. Bullpit, D. Gartshore, W. Adcock, T.-C. Khor, D. Doddrell, and I. D. Rae, *J. Org. Chem.*, 1977, **42**, 2411; (*c*) D. F. Ewing, S. Sotheeswaran, and K. J. Toyne, *Tetrahedron Letters*, 1977, 2041; (*d*) W. Adcock and T.-C. Khor, *ibid.*, p. 3769.

provide unequivocal supporting evidence for π-polarization in the phenyl group of 1-substituted phenylbicyclo[2,2,2]octanes, although there is not quantitative agreement with the above calculations.[11c] The relative importance of the π-polarization and direct field effects has also been estimated by comparison of [19]F n.m.r. data on the *para*-fluoro- and *meta*-fluoro-systems, and the result is in good agreement with the estimate mentioned above.[11d] Reversed [19]F n.m.r. polar field effects are realized in the *ortho*-fluoro-analogues.

The modified version of the general theory of structure–property relationships, previously proposed,[12a] has been applied[12b] to the problem of the relationships between substituent chemical shifts and substituent reactivity parameters, and some success has been achieved in predicting whether a single parameter or a pair of parameters should be utilized in a particular situation. The non-additive behaviour of ^{13}C chemical shifts in *para*-disubstituted benzenes [see *Ann. Reports (B)*, 1976, **73**, p. 203] has been reinterpreted.[13] The data for the 1- and 2-positions are in fact predicted additively, and those for the 4-positions may be accurately described by linear proportionality relationships with the appropriate substituent chemical shifts in monosubstituted benzenes. The proportionality relationships were interpreted in terms of localized changes in the excitation term of the paramagnetic shielding expression for ^{13}C shifts, determined largely by the ionization potential of the 4-substituent. Substituent effects on the ^{13}C shifts of the side-chain C_α atoms in *meta*- and *para*-disubstituted benzenes have also been studied and interpreted.[14]

Further reviews illuminate the reactivity–selectivity debate.[15a,b] Considerations concerning change of solvent and temperature have been emphasized, as has the fact that if substituents influence bond cleavage as well as bond formation, a more reactive species can be more selective than a less reactive one in spite of an 'earlier' transition state. An illustrative example is the competition of aniline and 3-chloroaniline for substituted benzenesulphonyl chlorides, where selectivity increases with reactivity. This argument is similar to that concerning desolvation of ions in reactions of charged species [see *Ann. Reports (B)*, 1976, **73**, p. 203]. This latter effect has, however, been regarded as unimportant.[16]

2 Benzene Isomers, Oxides, and Homobenzenes

The photoelectron spectrum of benzvalene has been reported[17] and this has led to the suggestion that the unusual u.v. absorption (217 nm) may be due to the superimposition of the first member of a low-lying Rydberg series on a valence-shell transition.

Full details of the preparation, separation, and aromatization of *meso*- and *dl*-1,1′-dimethyl-3,3′-bicyclopropenyls have now appeared.[18] The aromatization

[12] M. Godfrey, *J.C.S. Perkin II*, (a) 1975, 1016; (b) 1977, 769.
[13] B. M. Lynch, *Canad. J. Chem.*, 1977, **55**, 541.
[14] N. Inamoto, S. Masuda, K. Tori, and Y. Yoshimura, *Tetrahedron Letters*, 1977, 737; J. Bromilow, R. T. C. Brownlee, and D. J. Craik, *Austral. J. Chem.*, 1977, **30**, 355.
[15] (a) B. Giese, *Angew Chem. Internat. Edn.*, 1977, **16**, 125; (b) A. Pross, *Adv. Phys. Org. Chem.*, 1977, **14**, 69.
[16] C. D. Ritchie and M. Sawada, *J. Amer. Chem. Soc.*, 1977, **99**, 3754.
[17] P. J. Harman, J. E. Kent, T. H. Gan, J. B. Peel, and G. D. Willett, *J. Amer. Chem. Soc.*, 1977, **99**, 943.
[18] J. H. Davis, K. J. Shea, and R. G. Bergman, *J. Amer. Chem. Soc.*, 1977, **99**, 1499.

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passes through an intermediate in which the stereochemical distinction between the diastereoisomers has disappeared. The data are most consistent with Scheme 1 for
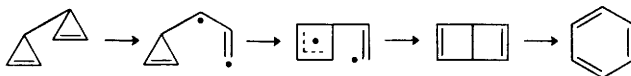
Scheme 1

gas-phase aromatization and probably for reaction in solution also. 1,4-Hexamethylene-Dewar-benzene is formed slowly, and apparently quantitatively, on irradiation of a solution of [6]paracyclophane in cyclohexane; warming the solution to 50—90 °C results in a clean and rapid reversion to the thermodynamically more stable precursor.[19] A polemical reminder of the limitations of the use of correlation diagrams, illustrated by that for the 'allowed' but not spontaneous thermal aromatization of benzvalene, has been given;[20] the words 'allowed' and 'forbidden' are only of use when there is a choice between two stereochemically different modes of reaction. Benzvalene has been shown[21] to undergo a degenerate rearrangement, catalysed by silver(I) ion, in competition with the known catalysed aromatization. Evidence was presented that the reaction of the silver(I) ion with the bicyclobutane moiety is a reversible process involving the intermediacy of (4). Scrambling does not occur with other bicyclobutane derivatives.

(4)   (5) $Ts = p\text{-}MeC_6H_4SO_2$ (6)
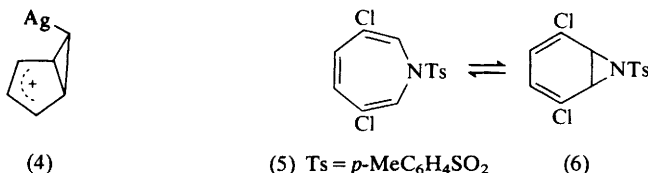
The synthesis of 3-t-butoxycarbonylbenzene oxide has been accomplished[22] and, in contrast to the 4-isomer, it exists mainly as the benzene oxide valence tautomer. Attempts to effect nucleophilic addition on this molecule failed, although the 4-isomer reacts *via* its oxide tautomer. Benzene oxide itself is converted into (Z,Z)-hexa-2,4-dienedial on oxidation with peroxy-acids,[23] the oxidative ring opening involving the oxepin tautomer. The reaction of $[Rh(CO)_2Cl]_2$ with benzene oxide and arene oxides at room or lower temperatures in chloroform or methanol leads to both deoxygenation and the formation of phenol, by mechanisms involving initial Lewis acid catalysis.[24] The equilibrium between the azepine (5) and its bicyclic valence tautomer (6) has been directly observed[25] in the range -70 to $+40\,°C$ $[\Delta G^{\ddagger}, (5)\rightarrow(6) = 46\text{ kJ mol}^{-1}]$.

[19] S. L. Kammula, L. D. Iroff, M. Jones, jun., J. W. van Straten, W. H. de Wolf, and F. Bickelhaupt, *J. Amer. Chem. Soc.*, 1977, **99**, 5815.
[20] J. J. C. Mulder, *J. Amer. Chem. Soc.*, 1977, **99**, 5177.
[21] U. Burger and F. Mazenod, *Tetrahedron Letters*, 1977, 1757.
[22] B. A. Chiasson and G. A. Berchtold, *J. Org. Chem.*, 1977, **42**, 2008.
[23] S. G. Davies and G. H. Whitham, *J.C.S. Perkin I*, 1977, 1346.
[24] R. W. Ashworth and G. A. Berchtold, *Tetrahedron Letters*, 1977, 343.
[25] H. Prinzbach, H. Babsch, H. Fritz, and P. Hug, *Tetrahedron Letters*, 1977, 1355.

A new synthetic pathway to substituted *trans*-bishomobenzenes is now available.[26] Thermolysis of dibromotetracyclo[5,1,0,0^{2,4},0^{3,5}]octanes, readily available from tricyclo[4,1,0,0^{2,7}]hept-3-enes, gave the species (7), which was readily
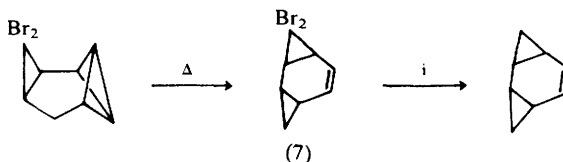
Reagents: i, Li—Bu^{t}OH in THF

Scheme 2

dehalogenated (Scheme 2). Studies of the flash pyrolysis (485 °C) of $^2H_1$-labelled hexahomobenzene (8) have shown[27] that there is not sufficient interaction energy

amongst the three constituent rings to allow for bond shifting, a result in agreement with last year's report concerning trioxahexahomobenzenes [see *Ann. Reports (B)*, 1976, **73**, p. 205].

3 Benzene and its Derivatives

General.—The second part[28] of the review of the organic photochemistry of benzene is concerned with photoreactions with other molecules. The photoaddition of methyl phenylpropiolate to benzene has been shown[29a] to form the tetra-cyclo[3,3,0,0^{2,4},0^{3,6}]oct-7-ene (9) as major product, in addition to the known 1-methoxycarbonyl-8-phenylcyclo-octatetraene, and in proportions which vary with
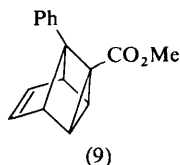
the wavelength of irradiation. The products are also photochemically interconvertible. The presumed precursor to both products, at least in the photoaddition reaction, is the corresponding bicyclo[4,2,0]octatriene, and species with this structure have now been isolated[29b] from the photoaddition of alkynes to hexafluorobenzene.

[26] R. T. Taylor and L. A. Paquette, *J. Amer. Chem. Soc.*, 1977, **99**, 5824.

[27] M. R. Detty and L. A. Paquette, *Tetrahedron Letters*, 1977, 347.

[28] D. Bryce-Smith and A. Gilbert, *Tetrahedron*, 1977, **33**, 2459.

[29] (a) A. H. A. Tinnemans and D. C. Neckers, *J. Amer. Chem. Soc.*, 1977, **99**, 6459; (b) B. Šket and M. Zupan, *ibid.*, p. 3504.

The major product of photocycloaddition of 2,3-dihydropyran to benzene is the *endo*-1,2-adduct formed in a process of surprising selectivity having a quantum efficiency greater than those previously observed for any mode of addition of an ethene to benzene.[30a] The 1,3-photocycloadditions of ethyl vinyl ether to toluene, and in particular those to anisole, are promoted by polar solvents, indicating that the 1,3-addition is not the general homopolar process, as was previously believed.[30b] The synthetic utility of the 1,3-addition of alkenes to anisole has been explored as a route to the bicyclo[3,2,1]octen-8-one system.[30c] 1,3-Cycloadducts are the major products of photochemical reactions[30d] between benzene and both

(10)

ethene [to give (10)] and propene, in contrast to the behaviour expected from the ionization potentials of these alkenes.[28] The authors suggest that electron affinities are more relevant for these alkenes, which are electron acceptors relative to benzene.

2,2-Dimethyl-1,3-dioxole undergoes 1,2-photoaddition to benzene, as expected from its ionization potential, but gives, in contrast to normal alkenes, the *exo*-adduct.[30e] Photoreactions of hexafluorobenzene have been the subject of some attention.[29b,31a—c] The [2+2]cycloaddition of cyclopentene in cyclohexane solution proceeds[31a] to give predominantly the *exo*-adduct (85%), and reaction with norbornadiene gives predominantly (80%) the *exo-syn*-isomer.[31b] It may be that these results reflect the stereochemistry of precursor complexes formed in the absence of irradiation.[28] Studies of the photoaddition of aliphatic amines to benzene have been reported in full.[31c]

An important review[32a] covers the field of cobalt-catalysed cyclo-oligomerization of alkynes, and full details[32b] of the formation of benzocycloalkenes using this approach, and of their synthetic utility, have appeared. The method has also been applied in an elegant synthesis of the steroid nucleus.[32c] The key step involves the reaction of the precursor (11) (Scheme 3), which is available by convergent series of reactions from hexa-1,5-diyne and 2-methylcyclopent-2-enone. The overall yield is 28%, based on the former. Some attention has been paid to the mechanism(s) of the trimerization. Evidence has been presented[33a] that there exist at least two distinct mechanisms for the production of aromatic compounds from the reaction of alkynes with metallocyclopentadienes, if these are intermediates. One path

[30] (a) A. Gilbert and G. Taylor, *Tetrahedron Letters*, 1977, 469; (b) *J.C.S. Chem. Comm.*, 1977, 242; (c) J. A. Ors and R. Srinivasan, *J. Org. Chem.*, 1977, **42**, 1321; (d) M. F. Mirbach, M. J. Mirbach, and A. Saus, *Tetrahedron Letters*, 1977, 959; (e) H.-D. Scharf and J. Mattay, *ibid.*, p. 401.

[31] (a) B. Šket and M. Zupan, *J.C.S. Chem. Comm.*, 1977, 365; (b) *Tetrahedron Letters*, 1977, 2811; (c) M. Zupan, B. Šket, and B. Pahor, *ibid.*, p. 4541; (d) M. Bellas, D. Bryce-Smith, M. T. Clarke, A. Gilbert, G. Klunkin, S. Krestonosich, C. Manning, and S. Wilson, *J.C.S. Perkin I*, 1977, 2571.

[32] (a) K. P. C. Vollhardt, *Accounts Chem. Res.*, 1977, **10**, 1; (b) R. L. Hillard, tert., and K. P. C. Vollhardt, *J. Amer. Chem. Soc.*, 1977, **99**, 4058; (c) R. L. Funk and K. P. C. Vollhardt, *ibid.*, p. 5483.

[33] (a) D. R. McAlister, J. E. Bercaw, and R. G. Bergman, *J. Amer. Chem. Soc.*, 1977, **99**, 1666; (b) P. Caddy, M. Green, E. O'Brien, L. E. Smart, and P. Woodward, *Angew. Chem. Internat. Edn.*, 1977, **16**, 648.

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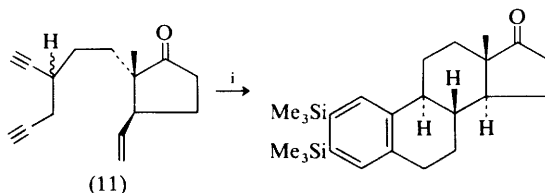
Reagents: i, bis(trimethylsilyl)acetylene–CpCo(CO)$_2$

Scheme 3

involves initial co-ordination of the alkyne and the other direct pathway may involve Diels–Alder addition. Other studies[33b] of η^5-indenylrhodium(I) complexes have, however, suggested the intermediacy of metallocyclopent-2-enes.

Ynamines (R^{1}C≡CNR$_2^2$) undergo cyclotrimerization in moderate yields on warming in acetonitrile solution over Ni^{II} or Ni^0, but not Cu^I, catalysts, and they form the unsymmetrical triaminobenzene (12).[34a] A useful synthesis of hindered

(12)
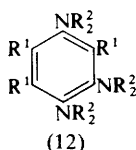
aromatic amines[34b] also involves ynamines which react with α-pyrone, carbon dioxide being lost spontaneously; methyl 2-(*NN*-diethylamino)-3-methylbenzoate, for example, is formed in 79% yield from 1-diethylaminoprop-1-yne.

Two procedures have been reported for the preparation of *meta*-bisannelated benzenes (13). The first procedure[35a] (Scheme 4) utilizes Corey's modified pinacol

$X = (CH_2)_m$
$Y = (CH_2)_n$

(13)
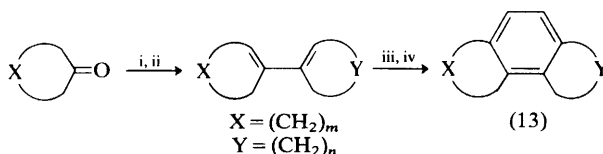
Reagents: i, Mg(Hg)–TiCl$_4$; ii, POCl$_3$–pyridine; iii, acrylic acid; iv, 10% Pd/C, Δ

Scheme 4

reduction, and the second[35b] involves the initial reaction of 2-cyclo-alkenylcycloalkanones with malonodinitrile, acid-catalysed cyclization, and efficient removal of the nitrile function from the *ortho*-amino-nitrile. A simpler, albeit low-yield, preparation of benzo[1,2:3,4]dicyclobutane (13; $n = m = 1$) has been described,[36a] and the procedure of the earlier Diels–Alder method has been

[34] (a) J. Ficini, J. d'Angelo, and S. Falou, *Tetrahedron Letters*, 1977, 1645; (b) T. A. Bryson and D. M. Donelson, *J. Org. Chem.* 1977, **42**, 2930.
[35] (a) M. E. Isabelle, D. H. Lake, and R. H. Wightman, *Canad. J. Chem.*, 1977, **55**, 3268; (b) J. Sepiol, B. Kawalek, and J. Mirek, *Synthesis*, 1977, 701.
[36] (a) E. Giovannini and H. Vuilleumier, *Helv. Chim. Acta*, 1977, **60**, 1452; (b) R. P. Thummell and W. Nutakul, *J. Org. Chem.*, 1977, **42**, 300.

applied[36b] to a series of *meta-* and *para-*bisannelated benzenes involving fused 4-
and 5-membered rings.

Syntheses of benzocyclobutenes abound. The flash vacuum pyrolysis of tolyl
propargyl ethers provides a low-yield source of aromatic-ring-methylated benzo-
cyclopropenes.[37] Full details of the thermal and electron-impact syntheses of
benzocyclobutene itself, and examples having oxygenated substituents on the aryl
ring, have appeared.[38a] The latter type of compound, however, can indeed be
prepared[38b] by the ready and efficient cyclization of the corresponding *ortho-*
lithio(2-bromoethyl)benzenes. 3,4-Bis(trimethylsilyl)benzocylobutene has been
synthesized for the first time.[39] Interestingly, the trimethylsilyl group at the 4-
position is five-hundred times more susceptible to hydrolysis than that at the
3-position. The reaction of $\alpha\alpha\alpha\alpha$-tetrabromo-*o*-xylene with pentacarbonyliron
gave[40] a facile synthesis of mainly *trans-*1,2-dibromobenzocyclobutene.

Pyrolysis (600 °C; 0.3 s) of 2-methylbenzoyl chlorides gave the corresponding
benzocyclobutenones in good yields.[41] Benzocycloalkenones have been
synthesized[42a] in good yield by treatment of *o*-bromophenylalkanoic acids with
butyl-lithium at low temperatures, and the procedure allows for the presence of
some functionality in the ring being formed. An extension of the oxidative rear-
rangement of styrene derivatives by thallium(III) nitrate provides[42b] a general
method for the ring expansion of benzocycloalkanones of this type. They are first
subjected to a Wittig procedure, whereby a methylene carbon, which may be
substituted, is inserted selectively between the aromatic ring and the carbonyl
group.

The reactions of polyfluoro-aromatic compounds with aryl and alkyl radicals
have been reviewed.[43] Some scavenging reactions of phenyl radicals, from the
thermal decomposition of phenylazotriphenylmethane, are nearly diffusion-
controlled in media of low viscosity, and are so controlled in media of high
viscosity, leading to relative rates approaching unity for pairs of scavengers.[44]
Competition with slower reactions at higher viscosities has given absolute rate
constants. The reactions of the phenyl radicals do not show a clear selectivity–
reactivity relationship. Correlations for the rate of hydrogen abstraction from
substituted toluenes by isopropyl and t-butyl radicals by a Hammett equation have
been recorded.[45] The authors suggest that substituent effects on both the structure
of the transition state (consideration of polar resonance structures) and of the initial
state (bond dissociation energy) are important and that, contrary to common
practice, both should be considered. The ability of aromatic nitro-compounds to
increase the yields of biaryls in arylation reactions is now believed[46] to involve

[37] J. M. Riemann and W. S. Trahanovksy, *Tetrahedron Letters*, 1977, 1863.
[38] (*a*) R. J. Spangler, B. G. Beckmann, and J. H. Kim, *J. Org. Chem.*, 1977, **42**, 2989; (*b*) P. D. Brewster,
J. Tagat, C. A. Hergrueter, and P. Helquist, *Tetrahedron Letters*, 1977, 4573.
[39] R. L. Hillard, tert., and K. P. C. Vollhardt, *Angew. Chem. Internat. Edn.*, 1977, **16**, 399.
[40] R. Victor, *Transition Metal Chem. (Weinheim)*, 1977, **2**, 2.
[41] P. Schiess and M. Heitzmann, *Angew. Chem. Internat. Edn.*, 1977, **16**, 469.
[42] (*a*) R. J. Boatman, B. J. Whitlock, and H. W. Whitlock, jun., *J. Amer. Chem. Soc.*, 1977, **99**, 4822; (*b*)
E. C. Taylor, C.-S. Chiang, and A. McKillop, *Tetrahedron Letters*, 1977, 1827.
[43] L. S. Kobrina, *Russ. Chem. Rev.*, 1977, **46**, 348.
[44] R. G. Kryger, J. P. Lorand, N. R. Stevens, and N. R. Herron, *J. Amer. Chem. Soc.*, 1977, **99**, 7589.
[45] W. H. Davis, jun., and W. A. Pryor, *J. Amer. Chem. Soc.*, 1977, **99**, 6365.
[46] R. Henriquez and D. C. Nonhebel, *J. Chem. Res. (S)*, 1977, 253.

oxidation of the intermediate arylcyclohexadienyl radicals by an electron-transfer mechanism, examples having electron-withdrawing substituents being more effective. The authors of the original experimental work on the photobromination of dihalogeno-benzenes have reacted[47] to the suggestion that *ipso*-substitution is involved [see *Ann. Reports (B)*, 1976, **73**, p. 208], and show that such substitution is neither required nor precluded by their results.

A deamination reaction that uses alkyl nitrite and copper(II) halide has been used in several processes that are of synthetic importance.[48] The reagent rapidly converts arylamines into aryl chlorides and bromides in high yield,[48b] and a Meerwein-type arylation of alkenic substrates, giving α-halogeno-β-aryl compounds, occurs if the reaction is carried out in acetonitrile or acetone solutions containing the substrate.[48c] Good to excellent yields of phenols are formed from aryl bromides under basic conditions on reaction of the derived Grignard reagent with molybdenum peroxide–pyridine–hexamethylphosphoramide.[49] A procedure for the formation of phenols from diazonium ions, which avoids the usual highly acidic conditions and is considered to be the method of choice for new cases, consists in adding copper(I) oxide to a dilute solution of the arenediazonium salt in the presence of a large excess of copper(II) nitrate.[50]

Electrophilic Substitution.—Studies of the gas-phase pyrolysis of some 1-arylethyl acetates have led[51] to the conclusion that the Baker–Nathan order of electron release by alkyl groups is a solvation phenomenon, and also that hyperconjugation from C—C bonds is greater than that from C—H bonds. These studies also suggest that the solvolysis of $\alpha\alpha$-dimethylbenzyl chlorides is exceptionally sensitive to steric hindrance to solvation, and that this limits the suitability of the derived σ^+ constants for the description of electrophilic aromatic substitution. The protonations of toluene and ethylbenzene in super-acid media have been reinvestigated[52] and the presence of the *ortho*-protonated species has been established; the results are now in agreement with gas-phase studies.

Details of the gas-phase reaction of the t-butyl cation with phenol and anisole to give initially predominantly t-butylated oxonium ions have appeared.[53a] In contrast to the t-butyl cation, which exhibits both substrate and positional selectivity, the isopropyl cation does not show substrate selectivity in its reactions with arenes.[53b] It does, however, exhibit a measurable degree of positional selectivity, and its reactions are complicated by secondary dealkylation and isomerization processes. Chlorobenzene is isopropylated at a rate only half that of toluene, and the predominant *ortho*-substitution is again attributed[53c] to initial attack at the substituent. The attack of CH_5^+ and $C_2H_5^+$ ions on halogeno-benzenes causes[54]

[47] P. Gouverneur and J. P. Soumillion, *Bull. Soc. chim. belges*, 1977, **86**, 647.

[48] M. P. Doyle, J. F. Dellaria, jun., B. Siegfried, and S. W. Bishop, *J. Org. Chem.*, 1977, **42**, 3494; M. P. Doyle, B. Siegfried, and J. F. Dellaria, jun., *ibid.*, p. 2426; M. P. Doyle, B. Siegfried, R. C. Elliott, and J. F. Dellaria, jun., *ibid.*, p. 2431.

[49] N. J. Lewis, S. Y. Gabhe, and M. R. DeLaMater, *J. Org. Chem.*, 1977, **42**, 1479.

[50] T. Cohen, A. G. Dietz, jun., and J. R. Miser, *J. Org. Chem.*, 1977, **42**, 2053.

[51] E. Glyde and R. Taylor, *J.C.S. Perkin II*, 1977, 678.

[52] D. Fărcaşiu, M. T. Melchior, and L. Craine, *Angew. Chem. Internat. Edn.*, 1977, **16**, 315.

[53] (a) M. Attinà, F. Cacace, G. Ciranni, and P. Giacomello, *J. Amer. Chem. Soc.*, 1977, **99**, 4101, 5022; (b) *ibid.*, p. 2611; (c) M. Attinà and P. Giacomello, *Tetrahedron Letters*, 1977, 2373.

[54] M. Speranza and F. Cacace, *J. Amer. Chem. Soc.*, 1977, **99**, 3051.

extensive dehalogenation by two competitive routes, which lead to pro-
todehalogenation and methyldehalogenation and are a reflection of the ambient
nucleophilic character of the substrates. Mono- and di-substituted benzenes have
been brominated by $^{80}Br^+$ in the gas phase.[55] The relative rates led to good σ^+, ρ^+
plots ($\rho^+ = -0.9$) and the data on toluene agreed with the Brown selectivity rela-
tionship.

Perrin has asserted[56] that aromatic nitration is not always a conventional elec-
trophilic substitution, but that for some reactive substrates the mechanism involves
the transfer of an electron from the aromatic to the nitronium ion, followed by
collapse of the radical pair. Experiments quoted in support of this proposal involve
the determination of anodic half-wave potentials for nitrogen dioxide and some
aromatic compounds, and one involving the generation of the naphthalene radical
cation in the presence of nitrogen dioxide, which gives the normal isomer ratio of
nitro-naphthalenes. The author appears to confuse and combine the different
approaches of others to encounter pairs and π-complexes, and ignores the possi-
bility of catalysis by nitrous acid, which must surely affect the results obtained for
some substrates which are used to support the proposed mechanism. Catalysis by
nitrous acid is evident in the formation of the *ipso*-substituted σ-complex (14) that
is formed on nitration of *NN*-dimethyl-*p*-toluidine in 70—77% sulphuric acid.[57] It
slowly rearranges to the *NN*-dimethyl-4-methyl-2-nitroanilinium ion.

(14)
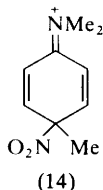
It seems that the problem of the identity of the electrophile for nitration by nitric
acid in acetic anhydride has at last been solved.[58] The observed rates have been
shown to be sensitive to the presence of trace impurities at $[HNO_3] < 0.9$ mol dm^{-3},
and a comparison of the true rate constant for the reaction of the electrophile and
toluene with that for the reaction in acetic acid indicates that reaction indeed
involves the nitronium ion.

A study of some model compounds has led to a reconsideration[59a] of the
nitration of acetanilide, and it now seems clear that this molecule is in fact nitrated
as the unprotonated species by nitric acid in aqueous sulphuric acid. For anisole in
the same medium[59b] the *ortho* : *para* ratio varies considerably, and an explanation
has been offered that involves the combined effects of hydrogen bonding and a
diffusion-controlled reaction. With *o*- and *p*-methylanisole, *ipso*-substitution at
C—Me is of importance, and in the latter case this leads to 4-methyl-2-nitrophenol

[55] E. J. Knust, *J. Amer. Chem. Soc.*, 1977, **99**, 3037.
[56] C. L. Perrin, *J. Amer. Chem. Soc.*, 1977, **99**, 5516.
[57] K. Fujiwara, J. C. Giffney, and J. H. Ridd, *J.C.S. Chem. Comm.*, 1977, 301.
[58] N. C. Marziano, R. Passerini, J. H. Rees, and J. H. Ridd, *J.C.S. Perkin II*, 1977, 1361.
[59] (*a*) R. B. Moodie, P. N. Thomas, and K. Schofield, *J.C.S. Perkin II*, 1977, 1693; (*b*) J. W. Barnett, R. B.
    Moodie, K. Schofield, J. B. Weston, R. G. Coombes, J. G. Golding, and G. D. Tobin, *J.C.S. Perkin II*,
    1977, 248.

as a major product. 4-Methyl-4-nitrocyclohexa-2,5-dienone, a postulated inter-mediate in this reaction, has been observed[60a] as a product from the nitration of *p*-methylanisole and some other *para*-substituted toluenes in acetic anhydride.

Nitration *ipso* to an ethyl group has been observed[60b] in *p*-diethylbenzene, *p*-ethyltoluene, and almost exclusively in ethylmesitylene. Attempts to activate a biphenyl to nitration *ipso* to a phenyl group have, however, failed. The sensitivity of *ipso*-nitration to substituent effects has been examined[60a] by the competitive study of a series of 5-X-hemimellitene derivatives (X = H, F, Br, OAc, OMe, and NHAc), and a ρ^+ value ($-8 > \rho^+ > -12$) has been estimated, showing a satisfactory agreement with that for nitrodeprotonation.

Some synthetic aspects of side-reactions attending aromatic nitration have been reviewed.[61] An interesting example of intramolecular trapping of a Wheland intermediate has been observed[62a] in the isolation of (15) from the nitration of methyl β-(2,3,4-trimethylphenyl)isovalerate. Another reaction involving initial *ipso*-substitution is the conversion[62b] of some *p*-xylonitrile derivatives into 1-imino-1,3-dihydroisobenzofurans [*e.g.* (16) from 2,3,4,6-tetramethylbenzonitrile]. Solvolytic studies[63] of the *ipso*-adducts formed on nitration of hemimellitene have reinforced the view [see *Ann. Reports* (*B*), 1976, **73**, p. 210] that, in >50% sulphuric acid, adducts of this type yield the *ipso*-Wheland intermediate, which is then partitioned between trapping by water and rearrangement by, in this case, sequential 1,2-shifts of the nitro-group. Full details of the reactions of nitronium salts with pentamethylbenzene have been given,[64] confirming that the initially detected species is the 1-nitro-1,2,3,4,6-pentamethylbenzenonium ion. The 1,3-dinitro-1,2,4,5,6-pentamethylbenzenonium ion formed from pentamethyl-nitrobenzene undergoes a degenerate rearrangement of a nitro-group from posi-tion 1 to position 5.

(15)

(16)
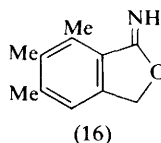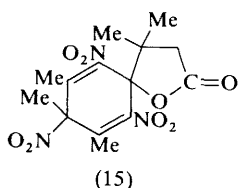
The mercuric-acetate-catalysed nitration of toluene in acetic acid at 80 °C, which produces 36% *o*-, 12% *m*-, and 52% *p*-nitrotoluenes, has been shown[65] to involve initial mercuration followed by nitrosodemercuration and subsequent oxidation of the nitroso-toluenes.

The sulphonations of some polyethyl- and polyisopropyl-benzenes in concen-trated sulphuric acid have been studied.[66] The sulphonic acids from 1,2,3,5- and

[60] A. H. Clemens, M. P. Hartshorn, K. E. Richards, and G. J. Wright, *Austral. J. Chem.*, 1977, **30**, (*a*) p. 113; (*b*) p. 103.

[61] H. Suzuki, *Synthesis*, 1977, 217.

[62] (*a*) M. Shinoda and H. Suzuki, *J.C.S. Chem. Comm.*, 1977, 479; (*b*) H. Suzuki, M. Koge, and T. Hanafusa, *ibid.*, p. 341.

[63] T. Banwell, C. S. Morse, P. C. Myhre, and A. Vollmar, *J. Amer. Chem. Soc.*, 1977, **99**, 3042.

[64] A. N. Detsina, V. I. Mamatyuk, and V. A. Koptyug, *J. Org. Chem.* (*U.S.S.R.*), 1977, **13**, 122.

[65] L. M. Stock and T. L. Wright, *J. Org. Chem.*, 1977, **42**, 2875.

[66] A. Koeberg-Telder and H. Cerfontain, *J.C.S. Perkin II*, 1977, 717; H. Cerfontain, A. Koeberg-Telder, and C. Ris, *ibid.*, p. 720.

1,2,4,5-tetraethylbenzene are unstable, and rearrange into 2,3,4,5-tetraethylbenzenesulphonic acid. With 1,3,5-tri-isopropylbenzene, both rearrangement and dealkylation reactions become of importance. Kinetic and product studies[67a] have shown that the sulphonation of aniline in a large excess of 100—102% sulphuric acid at 25 °C proceeds by direct attack of the electrophile ($H_3S_2O_7^+$) on the aromatic ring of the anilinium ion. Under more aqueous conditions ($\sim 97\%$ sulphuric acid), at higher temperatures, some reaction occurs by the same mechanism, as shown by the formation of *m*-aminobenzenesulphonic acid, but reaction involving the intermediacy of phenylsulphamic acid may also occur. The latter compound itself, at 25 °C, yields[67b] only *o*- and *p*-aminobenzenesulphonic acids, by an intermolecular path involving *C*-sulphonation of the minority *O*-protonated species, $PhNHSO_3H$, and subsequent *N*-desulphonation, although at lower acidities solvolysis to the anilinium ion is a competing process.[67c] The sulphonation of *m*-aminobenzenesulphonic acid in fuming sulphuric acid has also been studied.[68a] Studies of methanesulphonanilide ($PhNHSO_2Me$) indicate[68b] that sulphonation occurs on the unprotonated species, which is in the minority above 84% sulphuric acid.

For non-catalytic bromination reactions the process may follow the power-series rate equation, and involve a reaction pathway in which more than one molecule of bromine is concerned in the transition state. The suggestion [see *Ann. Reports (B)*, 1975, **72**, p. 225] that this will show the same kinetic behaviour as an $A\text{-}S_E2$ process in which the rate of the reverse of the first step becomes significant, and that the rate expressions for these processes are equivalent, is incorrect.[69a] The circumstances under which a distinction may be made have been established and the authors also briefly review the mechanisms available for brominations by molecular bromine. The effect of addition of bromide and perchlorate to the bromination of polymethylbenzenes in 90% aqueous acetic acid shows clearly[69b] that in this case reaction involves a transition state which includes more than one molecule of bromine. Flow ^1H n.m.r. studies have clearly confirmed[70] the generality of the occurrence of cyclohexadienone intermediates in the bromination of substituted phenols in aqueous acetic acid, the lifetime of the intermediates decreasing with the size of alkyl substituents at 2- and 6-positions.

'Free' CT_3^+ cations have been generated from the decay of a radioactive atom in a tritiated methane solution in toluene and benzene.[71] The attack of the cation on the arene is likely to occur in a much shorter time than is necessary for the formation of an organised solvent sphere. The intermolecular selectivity was indicated by an approximate toluene:benzene rate ratio of 2.3:1, and a very low but slightly electrophilic intramolecular selectivity was observed. The vinylation of some aromatic substrates by a variety of vinyl triflates [*e.g.* $PhC(Me){=}C(Ph)OSO_2CF_3$], lacking a β C—H bond, is possible, and it results in

[67] P. K. Maarsen and H. Cerfontain, *J.C.S. Perkin II*, 1977, (*a*) p. 1008; (*b*) p. 921; (*c*) p. 929.

[68] (*a*) P. K. Maarsen, R. Bregman, and H. Cerfontain, *J.C.S. Perkin II*, 1977, 1863; (*b*) P. K. Maarsen and H. Cerfontain, *ibid.*, p. 1003.

[69] (*a*) N. H. Briggs, P. B. D. de la Mare, and D. Hall, *J.C.S. Perkin II*, 1977, 106; (*b*) R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.*, 1977, **99**, 5693.

[70] C. A. Fyfe and L. Van Veen, jun., *J. Amer. Chem. Soc.*, 1977, **99**, 3366.

[71] F. Cacace and P. Giacomello, *J. Amer. Chem. Soc.*, 1977, **99**, 5477.

good yields of styrenes under moderate conditions even in the absence of Friedel–Crafts catalysts.[72]

Nucleophilic Substitution.—Recent developments in the application of linear free-energy relationships between reactivity and physical properties of leaving groups and substrates have been discussed.[73] A comparison of some substitution reactions of both neutral and negative nucleophiles in the 2,4-dinitrohalogeno-benzenes with reactions with organic cations has provided[16] further support for the general applicability of the N_+ nucleophilicity scale. Selectivity again appears not to be a function of reactivity in these reactions.

The photostimulated $S_{RN}1$ reaction between iodobenzene and potassium diethylphosphite in DMSO has been studied,[74a] with particular attention being paid to the initiation and termination stages. The main reaction for the latter is first-order in propagating radical. The initiation, however, may involve initial absorption by iodobenzene or by a molecular complex of iodobenzene with diethylphosphite. An $S_{RN}1$ reaction in aqueous t-butyl alcohol has been identified[74b] in the reaction of halogeno-benzenes with phenoxide ion in the presence of sodium amalgam to form benzene and diphenyl ether. A thermally induced $S_{RN}1$ reaction has been found[74c] in the reaction of bromo- and iodo-benzenes with ketone enolate anions in DMSO at 25 °C in the dark, and in one example this was well separated from the photostimulated process. Large rate accelerations by added oxygen, nitrobenzene, and ferric nitrate were, however, not explained.

The reactions of picryl chloride and bromide with the diethylmalonate anion have been studied[75] by the stopped-flow technique, which enables the stages involving fast formation of σ-complexes followed by slower decomposition to the picryl esters to be identified. In the reaction of 2,4,6-trinitroanisole with n-butylamine to give, in the absence of a large excess of the amine, N-(n-butyl)picramide, the ^{1}H n.m.r spectrum of the intermediate σ-complex has been recorded, using a flow technique.[76] The stable intramolecular σ-complex (17), formed under basic conditions from N-benzyl-N-(2-hydroxyethyl)picramide, cyclizes under the conditions of the Smiles' rearrangement, without prior rearrangement, to form 4-benzyl-5,7-dinitro-2,3-dihydrobenzoxazine.[77] Kinetic and equilibrium data have been reported[78] for the addition of sodium ethoxide to a series of 6-substituted 2,4-dinitrophenetoles to give σ-complexes. The results support the suggestion that interaction with the cation for 1,1-diethoxy-complexes involves the oxygen atoms of the alkoxy-groups attached to C-1 and the *ortho*-substituents.

[72] P. J. Stang and A. G. Anderson, *Tetrahedron Letters*, 1977, 1485.
[73] G. Bartoli and P. E. Todesco, *Accounts Chem. Res.*, 1977, **10**, 125; see also G. Bartoli, P. E. Todesco, and M. Fiorentino, *J. Amer. Chem. Soc.*, 1977, **99**, 6874.
[74] (a) S. Hoz and J. F. Bunnett, *J. Amer. Chem. Soc.*, 1977, **99**, 4690; (b) S. Rajan and P. Sridaran, *Tetrahedron Letters*, 1977, 2177; (c) R. G. Scamehorn and J. F. Bunnett, *J. Org. Chem.*, 1977, **42**, 1449, 1457.
[75] K. T. Leffek and A. E. Matinopoulous-Scordou, *Canad. J. Chem.*, 1977, **55**, 2656, 2664.
[76] C. A. Fyfe, A. Koll, S. W. H. Damji, C. D. Malkiewich, and P. A. Forte, *J.C.S. Chem. Comm.*, 1977, 335.
[77] V. N. Drozd, V. N. Knyazev, and V. M. Minov, *J. Org. Chem. (U.S.S.R.)*, 1977, **13**, 357.
[78] M. R. Crampton, *J.C.S. Perkin II*, 1977, 1442.

R. G. Coombes

(17)   (18)   (19)
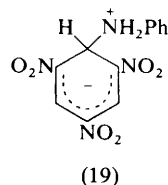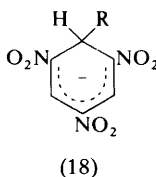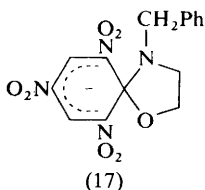
The formation of the σ-complex (18; R = NHPh) from 1,3,5-trinitrobenzene and aniline, catalysed by a tertiary amine in DMSO, has been shown[79a] to involve rate-limiting deprotonation by the catalyst of the zwitterionic intermediate (19), and it shows only a small primary kinetic isotope effect. The magnitude of the effect should have relevance to the identification of rate-limiting stages in S_NAr reactions (see below). The complex (18; R = NHPh) may also be formed by the reaction of aniline with the complex (18; R = OMe), and the full evidence that in this example a dissociative mechanism involving the intermediacy of tri-nitrobenzene is involved has been given.[79b] Methoxide ion acts in a similar fashion to the tertiary amine catalyst in the previous reaction, but in this case the formation of the intermediate (19) is rate-limiting. It seems that the unreactivity of aromatic as opposed to aliphatic amines towards nitro-aromatic compounds is due to ther-modynamic rather than kinetic factors.

Arguments have been presented[80a] that currently available evidence indicates that the specific base–general acid-catalysed mechanism for substitution in activated aromatic compounds by amines, involving fast deprotonation and rate-limiting catalysed expulsion of the leaving group, is not a significant pathway in protic solvents. Instead the mechanism involves a rate-limiting deprotonation of (20), when the expulsion of the leaving group is relatively fast (*e.g.* X = OPh), or a rapid equilibrium deprotonation of (20) followed by a rate-limiting non-catalysed

(20)
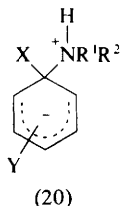
expulsion of a very poor leaving group (*e.g.* on occasions when X = OMe). Catalysis by base in the reaction of piperidine with 2,4-dinitrophenyl 4-nitrophenyl ether in benzene solution has been discussed[80b] in terms of concerted proton transfer and expulsion of the leaving group, the protic base acting as a bifunctional catalyst. Evidence from the uncatalysed reaction of morpholine with 2,4-dinitrophenyl phenyl ether in dipolar aprotic solvents suggests that here also fast deprotonation and slow expulsion of the leaving group does not occur,[80c] and the authors also

[79] (a) E. Buncel, W. Eggimann, and H. W. Leung, *J.C.S. Chem. Comm.*, 1977, 55; E. Buncel and W. Eggimann, *J. Amer. Chem. Soc.*, 1977, **99**, 5958; (b) E. Buncel, J. G. K. Webb, and J. F. Wiltshire, *ibid.*, p. 4429.

[80] (a) C. F. Bernasconi, R. H. De Rossi, and P. Schmid, *J. Amer. Chem. Soc.*, 1977, **99**, 4090; (b) D. Spinelli, G. Consiglio, and R. Noto, *J.C.S. Perkin II*, 1977, 1316; (c) D. Ayediran, T. O. Bamkole, J. Hirst, and I. Onyido, *ibid.*, p. 597.

discuss shortcomings of the concerted mechanism for media of low dielectric constant, and suggest a modification involving the formation of aggregates within which bond-making and -breaking is not synchronous.

Biaryls.—An important modification of the nickel–phosphine-complex-catalysed homo-coupling of aryl halides has been reported,[81] and the reaction proceeds catalytically in nickel in the presence of zinc, which reduces the Ni^{II} species formed to the active Ni^0 species. The molar ratio $PhBr:Zn:PPh_3:Ni(PPh_3)_2Cl_2$ of $1:1:0.3:0.5$ in DMF solution at $50\,°C$ gave an 89% yield of biphenyl. The presence of iodine greatly accelerated the reaction. Efficient formation of the symmetrical biaryl has been observed[82] when some arylcopper cluster compounds [*e.g.* $(4\text{-MeC}_6H_4)_4Cu_4$] react with equimolar quantities of copper triflate. These reactions involve intermediate complexes which may be isolated in some cases. Treatment of a variety of aromatic substrates with thallium(III) trifluoroacetate in trifluoroacetic acid results in oxidative coupling to give[83] biaryls in good yield in the absence of powerfully electron-withdrawing substituents, probably by a radical cation mechanism; 2,5-dimethylanisole, for example, is converted into 2,2′,5,5′-tetramethyl-4,4′-dimethoxybiphenyl. An improved method[84] has been reported for the conversion of arylmercury (II) chlorides into biaryls, using $[ClRh(CO)_2]_2$ as a catalyst in the presence of lithium chloride. Thermal decomposition of tetra-aryl-tellurium compounds at $140\,°C$ forms biaryls by a non-radical pathway.[85]

The preparation of a wide variety of mixed biaryls, in improved yields, is possible by the application of phase-transfer catalysis to a Gomberg reaction.[86] Potassium acetate, in the presence of 18-crown-6, apparently reacts with an arenediazonium ion in non-polar solution to form a diazoanhydride, which then decomposes in the presence of various aromatic compounds to form biaryls. The reaction of some arylzinc derivatives with aryl bromides or iodides in the presence of a small amount of a nickel or palladium catalyst [*e.g.* $Ni(PPh_3)_4$] provides a general and highly selective route to unsymmetrical biaryls.[87] Palladium(II) chloride (< 0.001 mol equivalent) appears[88] to be a preferred catalyst in Kharasch-type reactions of aryl Grignard reagents with iodobenzenes in THF. Aromatic nitrogen compounds (nitroso-, azo-, azoxy-, and nitro-benzenes and *NN*-dialkylaniline *N*-oxides, in addition to aryl-hydroxylamines) are susceptible to nucleophilic attack by benzene to give biphenyls in varying yields under strongly acidic conditions;[89] 5-(*NN*-dimethylamino)-2-methylbiphenyl, for example, is formed in 46% yield from *NN*-dimethyl-*p*-toluidine *N*-oxide.

A comparison of the rates of solvolysis of some α-(7-X-fluoren-2-yl)benzyl chlorides and α-(4′-X-biphenyl-4-yl)benzyl halides is consistent with regarding

[81] M. Zembayashi, K. Tamao, J.-I. Yoshida, and M. Kumada, *Tetrahedron Letters*, 1977, 4089.
[82] G. van Koten, J. T. B. H. Jastrzebski, and J. G. Noltes, *J.C.S. Chem. Comm.*, 1977, 203; *J. Org. Chem.*, 1977, **42**, 2047.
[83] A. McKillop, A. G. Turrell, and E. C. Taylor, *J. Org. Chem.*, 1977, **42**, 764.
[84] R. C. Larock and J. C. Bernhardt, *J. Org. Chem.*, 1977, **42**, 1680.
[85] D. H. R. Barton, S. A. Glover, and S. V. Ley, *J.C.S. Chem. Comm.*, 1977, 266.
[86] S. H. Korzeniowski, L. Blum, and G. W. Gokel, *Tetrahedron Letters*, 1977, 1871.
[87] E.-I. Negishi. A. O. King, and N. Okukado, *J. Org. Chem.*, 1977, **42**, 1821.
[88] A. Sekiya and N. Ishikawa, *J. Organometallic Chem.*, 1977, **125**, 281.
[89] T. Ohta, K. Shudo, and T. Okamoto, *Tetrahedron Letters*, 1977, 101; K. Shudo, T. Ohta, Y. Endo, and T. Okamoto, *ibid.*, p. 105.

fluorene as a planar biphenyl structure, and yields an interplanar angle for biphenyl in accord with other estimates.[90] Both systems respond to substituent effects in a similar way. The overall reactivity to protiodetritiation of 9,10-dihydrophenanthrene relative to that of fluorene is consistent with the differences in coplanarity between the molecules,[91a] and other results confirm that the low reactivity of the α-position of the latter arises from an increase in strain on going to the corresponding transition state. The reversible rearrangement of 1-fluoro-9*H*-fluoren-9-one into the 3-fluoro-isomer in polyphosphoric acid provides the first direct evidence for the complete reversibility of a Friedel–Crafts acylation.[91b]

Quinones and Related Compounds.—A review of photoinitiated reactions of quinones has appeared.[92] A convenient synthesis[93] of 2-alkyl *p*-benzoquinones in 65—70% yields involves the oxidation of the *p*-alkylphenol with thallium(III) perchlorate in perchloric acid. The reaction of allyl-silanes with various *p*-benzoquinones in the presence of titanium tetrachloride gave[94] allyl-substituted hydroquinones, whilst 2,6-disubstituted quinones gave *p*-allyl-quinols, which were presumed also to be intermediates in the former cases. An interesting base-catalysed rearrangement of *p*-peroxyquinol ethers to give *p*-quinoxyacetic acid derivatives has been observed,[95] and is shown formally in (21). The suggested mechanism involves initiation by homolysis of the O—O bond even at $-60\,^\circ$C.

(21)   (22)   (23)
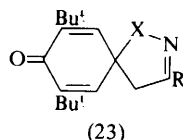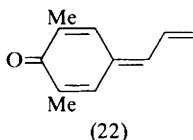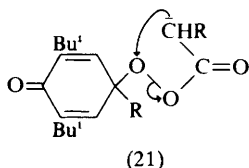
The quinone methide (22), which has a vinyl group in conjugation with the quinone system, forms, in the solid or in concentrated solution in an aprotic solvent, a dimer involving Diels–Alder addition of the terminal double bond of one molecule to the side-chain diene system of another molecule.[96a] The products of nucleophilic addition to (22) have been studied,[96b] and with water and methanol both 1,6- and 1,8-adducts are observed. Kinetic studies of the related methylene compound have also appeared.[96c] Some reactive 1,3-dipoles ($R\overset{+}{-}C{=}N{-}\overset{-}{X}$) add to 2,6-di-t-butyl-4-methylenecyclohexa-2,5-dienone to give the 1 : 1 cycloadducts (23) in high yield, providing ready access to the hetero-spiro[4,5]decatrienone system.[96d]

[90] R. Bolton and R. E. M. Burley, *J.C.S. Perkin II*, 1977, 426.
[91] (a) H. V. Ansell and R. Taylor, *J.C.S. Perkin II*, 1977, 866; (b) I. Agranat, Y. Bentor, and Y.-S. Shih, *J. Amer. Chem. Soc.*, 1977, **99**, 7068.
[92] A. V. El'tsov, O. P. Studzinskii, and V. M. Grebenkina, *Russ. Chem. Rev.*, 1977, **46**, 93.
[93] Y. Yamada and K. Hosaka, *Synthesis*, 1977, 53.
[94] A. Hosomi and H. Sakurai, *Tetrahedron Letters*, 1977, 4041.
[95] A. Nishinaga, K. Nakamura, K. Yoshida, and T. Matsuura, *Chem. Letters*, 1977, 303.
[96] (a) J. A. Hemingson, *Tetrahedron Letters*, 1977, 2967; (b) *J.C.S. Perkin II*, 1977, 616; (c) G. Leary, I. J. Miller, W. Thomas, and A. D. Woolhouse, *ibid.*, p. 1737; (d) A. D. Woolhouse, *Austral. J. Chem.*, 1977, **30**, 1145.

An electron-diffraction study of *p*-xylylene, which is widely accepted to have a singlet structure, has been made,[97a] and the conclusion reached that the molecule does not simply contain conjugated double and single bonds. The average $C=C$ bond length is longer than typical values for conjugated double bonds, and in good agreement with simple HMO theory. The i.r. and Raman spectra of *o*-xylylene have been observed for the first time.[97b] The molecule was generated in the gaseous phase by the reaction of $\alpha\alpha'$-dibromo-*o*-xylene with sodium or potassium vapour, which had been excited by a microwave discharge, and it was then collected in an argon matrix (at 8—30 K). 2,2-Dimethyl-2*H*-indene (24) shows more than a

(24)
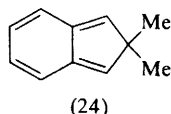
transient existence.[98a] It was generated and isolated in a matrix at 77 K, but was also generated in a solution at room temperature, where it was sufficiently stable for its ^{1}H n.m.r. spectra to be recorded. Transient isoindenes have been observed and studied in the flash photolysis of a series of 1,1-diaryl-indenes.[98b] Isoindene itself has been implicated[98c] as an intermediate in a photobisdecarbonylation reaction which may be suitable for future matrix-isolation studies. *o*-Xylylenes have also been observed as transients in the flash photolysis of methylated indan-2-ones.[99] The intermediacy of the 2*H*-indenes (26) in the thermal rearrangement of the 1-acyl-1,3-diphenyl- and -dimethyl-indenes (25) to the corresponding 2-acyl-indenes (27) has been established,[100a] and migratory aptitudes have been described. Other studies of the related photochemical rearrangement of 3-substituted 1,1-diphenylindenes have been reported.[100b]
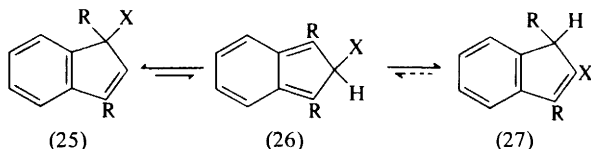
R = Ph or Me; X = *e.g.* CHO, COMe, COPh, or CO_2Me

Oxidation of 4-aryl-2,6-di-t-butylphenols with oxygen in the presence of a cobalt(II) complex followed by decomposition of the intermediate hydroperoxides with toluene-*p*-sulphonic acid gave the 5-aryl-3-t-butyl-*o*-benzoquinones in good yield.[101] Oxidation of a series of *o*-benzoquinones with lead(IV) acetate in methanol to yield the corresponding dimethyl hexa-2,4-dienedioates in 60—90%

[97] (a) P. G. Mahaffy, J. D. Wieser, and L. K. Montgomery, *J. Amer. Chem. Soc.*, 1977, **99**, 4514; (b) K. L. Tseng and J. Michl, *ibid.*, pp. 4840, 6154.

[98] (a) W. R. Dolbier, jun., K. Matsui, J. Michl, and D. V. Horak, *J. Amer. Chem. Soc.*, 1977, **99**, 3876; (b) K. K. de Fonseka, C. Manning, J. J. McCullough, and A. J. Yarwood, *ibid.*, p. 8257; (c) R. N. Warrener, R. A. Russell, and T. S. Lee, *Tetrahedron Letters*, 1977, 49.

[99] K. K. de Fonseka, J. J. McCullough, and A. J. Yarwood, *J.C.S. Chem. Comm.*, 1977, 721.

[100] (a) D. W. Jones and G. Kneen, *J.C.S. Perkin I*, 1977, 1313; (b) W. A. Pettit and J. W. Wilson, *J. Amer. Chem. Soc.*, 1977, **99**, 6372.

[101] A. Nishinaga, K. Nishizawa, H. Tomita, and T. Matsuura, *Synthesis*, 1977, 270.

yield has been reported.[102] A pronounced and unexpected solvent effect has been uncovered[103] in the reaction of some *o*-benzoquinones with butadiene; 4-methoxy-5-methyl-*o*-benzoquinone, for example, gave mainly the abnormal spiro-compound (28) in benzene and (29) in methanol.

(28)　　　　　　　　(29)
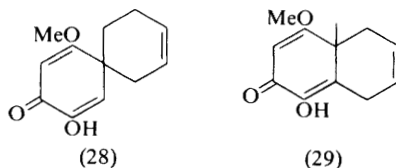
An unusually stable orange-red crystalline *o*-quinone methide, probably (30), has been isolated[104a] from the oxidation of 2-cinnamyl-4,5-methylenedioxyphenol with silver oxide, and the corresponding methide from 2-(4-methoxybenzyl)-4,5-methylenedioxyphenol rapidly dimerizes in polar solvents. Another stable *o*-quinone methide (m.pt. 284—5 °C) is (31), prepared[104b] by the reaction of 2,4-dimethylphenol with two equivalents of 1,3-benzodithiolylium tetrafluoroborate in

(30)　　　　　　　　(31)
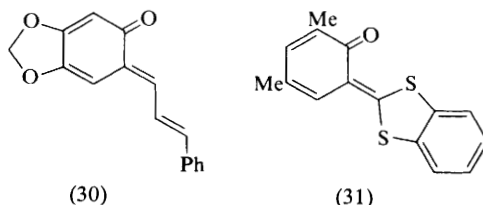
acetonitrile and subsequent addition of triethylamine. 6-Acetoxycyclohexa-2,4-dien-1-ones react with Grignard and lithium reagents to give, in addition to the expected 1,2- and 1,4-addition, an ether which is the product of the formal addition of a carbanion to the carbonyl oxygen.[105a] Ether formation largely supersedes conjugate addition with tertiary and benzylic organometallics. Substituent effects support an electron-transfer mechanism,[105b] and further evidence[105c] suggests that dialkylmagnesium species are concerned in the case of Grignard reagents.

The metallation reaction of electrochemically derived quinone bisacetals [see *Ann. Reports* (*B*), 1976, **73**, p. 215] has been modified[106] to produce organo-copper-lithium derivatives which will react efficiently with allylic halides to provide a route to some isoprenoid natural products (*e.g.* cymopol).

4 Cyclophanes

A review of the information to be gained concerning steric effects of substituents from conformational studies of cyclophanes has appeared.[107] [5]Metacyclophane,

[102] M. Wiessler, *Tetrahedron Letters*, 1977, 233.
[103] S. Danishefsky, P. F. Schuda, and W. Caruthers, *J. Org. Chem.*, 1977, **42**, 2179.
[104] (*a*) L. Jurd, *Tetrahedron*, 1977, **33**, 163; (*b*) J. Nakayama, K. Yamashita, M. Hoshino, and T. Takemasa, *Chem. Letters*, 1977, 789.
[105] (*a*) B. Miller, *J. Org. Chem.*, 1977, **42**, 1402; (*b*) *ibid.*, p. 1408; (*c*) B. Miller, E. R. Matjeka, and J. G. Haggerty, *Tetrahedron Letters*, 1977, 323.
[106] P. W. Raynolds, M. J. Manning, and J. S. Swenton, *J.C.S. Chem. Comm.*, 1977, 499.
[107] H. Förster and F. Vögtle, *Angew. Chem. Internat. Edn.*, 1977, **16**, 429.

the lowest member of this series to date, is a by-product of a synthesis of 3,3'-hexamethylenebicyclopropenyl.[108] Its spectral properties are indicative of unusually high strain and also of high conformational rigidity of the pentamethylene chain. A novel synthesis[109] of [7]- and [8]-paracyclophanes involves flow pyrolysis of the spiroquinodimethanes (32; $n = 6$ and 7), and a simple synthesis[110] of some [10]paracyclophanes [*e.g.* (33)] involves the reaction of methyl propiolate and aluminium chloride with cyclododecene and thermal dehydrogenation of the resulting 2:1 adducts.
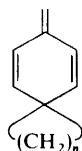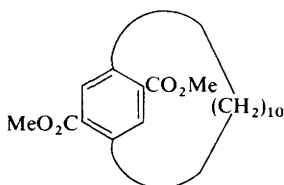
(32)   (33)

[3.3]Paracyclophane is now readily available by a route[111a,b] involving the surprisingly efficient (94%) pyrolysis of the disulphone of 2,13-dithia[4.4]paracyclophane. The dithia[4.4]cyclophanes may also yield[111c] the [3.3]cyclophanes on photodesulphurization in triethyl phosphite. Another approach to [3.3]paracyclophanes, also suitable for higher cyclic oligomers, has involved the construction of aliphatic bridges by a reaction between a bromide and a carbanionic species. Charge-transfer interactions in some [3.3]cyclophanes have been studied.[111b,112a] Such interactions may be transmitted through intervening rings in multilayered cyclophanes.[112b] The general usefulness of the sulphone pyrolysis procedure for the synthesis of many-membered hydrocarbon rings has also been illustrated.[113]

Representatives of the highly strained cyclophanes which have two benzene rings held with three or more ethano-bridges have been synthesized. A new approach to [2.2.2](1,2,4)cyclophane involves the formation of the third bridge in a paracyclophane derivative.[114] The chiral [2.2.2](1,2,4)(1,3,5)cyclophane has been synthesized,[115] and it has a marked tendency to resinify at room temperature. Its skew geometry causes an upfield shift of one aromatic proton to τ 4.96. [2.2.2.2](1,2,3,5)Cyclophane, the first to have a consecutive arrangement of three

[108] J. W. van Straten, W. H. de Wolf, and F. Bickelhaupt, *Tetrahedron Letters*, 1977, 4667.
[109] J. W. van Straten, W. H. de Wolf, and F. Bickelhaupt, *Rec. Trav. chim.*, 1977, **96**, 88.
[110] B. B. Snider and N. J. Hrib, *Tetrahedron Letters*, 1977, 1725.
[111] (a) D. T. Longone, S. H. Küsefoglu, and J. A. Gladysz, *J. Org. Chem*, 1977, **42**, 2787; (b) M. W. Haenel, A. Flatow, V. Taglieber, and H. A. Staab, *Tetrahedron Letters*, 1977, 1733; (c) T. Otsubo, M. Kitasawa, and S. Misumi, *Chem. Letters*, 1977, 977; (d) T. Synmyozu, K. Kumagae, T. Inazu, and T. Yoshino, *ibid.*, p. 43.
[112] (a) T. Shinmyozu, T. Inazu, and T. Yoshino, *Chem. Letters*, 1977, 1347; (b) H. A. Staab, U. Zapf, and A. Gurke, *Angew. Chem. Internat. Edn.*, 1977, **16**, 801; see also H. A. Staab and C. P. Herz, *ibid.*, p. 392; C. P. Herz and H. A. Staab, *ibid.*, p. 394.
[113] J. Grütze and F. Vögtle, *Chem. Ber.*, 1977, **110**, 1978; L. Rossa and F. Vögtle, *J. Chem. Res. (S)*, 1977, 264.
[114] S. Trampe, K. Menke, and H. Hopf, *Chem. Ber.*, 1977, **110**, 371.
[115] M. Nakazaki, K. Yamamoto, and Y. Miura, *J.C.S. Chem. Comm.*, 1977, 206.

ethano-bridges, has been synthesized[116a] by a procedure analogous to that applied to the (1,2,4,5)-isomer [see *Ann. Reports (B)*, 1975, **72**, p. 231]; an *X*-ray structure of the latter has now appeared.[116b]

[2.1.2.1]Paracyclophane has been synthesized in 14% yield by a modified Wurtz reaction, under high dilution, on 4,4'-dichloromethyldiphenylmethane.[117] The application of the Wittig procedure to the synthesis of [2.2.2.2]cyclophanetetraenes [see *Ann. Reports (B)*, 1975, **72**, p. 231] has been extended,[118a] but an attempt to form [2.2.2]paracyclophanediene from 4,4'-bibenzyldicarbaldehyde and the bisphosphonium salt of 1,4-di(bromoethyl)benzene failed, but gave a small yield of all-*cis*-[2⁶]paracyclophanetetraene, providing an improved route to [2⁶]paracyclophane. The Wittig approach has also led to the synthesis[118b] of [2.0.2.0]metacyclophanediene, which, on photolysis in the presence of iodine, gave bi-4,5-phenanthrylene (34), a non-planar analogue of [8]circulene. The reaction of benzene-1,3,5,-tricarbaldehyde and the bisphosphonium salt of 1,4-di(bromomethyl)benzene has given[118c] a route to the bicyclophane (35), which should exist as a rapidly equilibrating mixture of enantiomeric conformations.

(34)

(35)
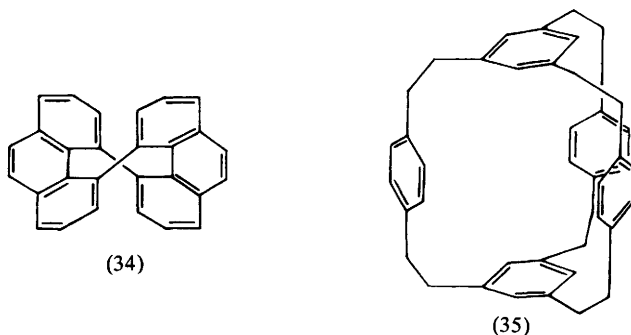
The 'benzene–Stevens' route [see *Ann. Reports (B)*, 1975, **72**, p. 231, Scheme 2] has been applied[119] to the syntheses of both *syn*- and *anti*-[2.2](1,4)naphthalenophane-1,13-dienes. [2](1,5)Naphthaleno[2]paracyclophane and its 2,6-isomer, where the bridging is from one benzene ring of the naphthalene moiety to the other, have been synthesized for the first time.[120a] The naphthaleno-paracyclophane (36) has also been prepared[120b] for the first time by two routes, and, in spite

(36)
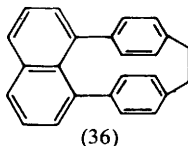
[116] (a) W. Gilb, K. Menke, and H. Hopf, *Angew. Chem. Internat. Edn.*, 1977, **16**, 191; (b) A. W. Hanson, *Acta Cryst.*, 1977, **B33**, 2003.

[117] S. Sergheraert, P. Marcinal, and E. Cuingnet, *Tetrahedron Letters*, 1977, 2879.

[118] (a) B. Thulin, O. Wennerström, I. Somfai, and B. Chmielarz, *Acta Chem. Scand. (B)*, 1977, **31**, 135; (b) B. Thulin and O. Wennerström, *Tetrahedron Letters*, 1977, 929; (c) H. E. Högberg, B. Thulin, and O. Wennerström, *ibid.*, p. 931.

[119] T. Otsubo and V. Boekelheide, *J. Org. Chem.*, 1977, **42**, 1085.

[120] (a) M. W. Haenel, *Tetrahedron Letters*, 1977, 4191; (b) W. Bieber and F. Vögtle, *Angew. Chem. Internat. Edn.*, 1977, **16**, 175.

of the similarity of its u.v. spectrum to that of a 1,8-diarylnaphthalene, the
^{1}H n.m.r. spectrum shows an enhancement of the anisotropic effect due to the
closer approach of the *p*-phenylene rings.

(37)

(38)
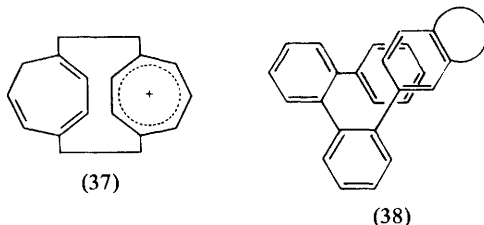
A further synthesis and an *X*-ray structure of [2.2](2,7)pyrenophane have
appeared.[121] [2.2](1,4)tropylio(1,4)cycloheptatrienophane (37) tetrafluoroborate
has been formed[122a] from [2.2]paracyclophane by a route involving ring expansions
using dibromocarbene. In contrast to its normal behaviour, the cycloheptatriene
ring acts as a good intramolecular charge-transfer donor. New cyclophanes having
tropylium rings have been reported.[122b]

A new series of compounds which have the combined attributes of helicenes and
cyclophanes are the 4,4'''-*o*-quaterphenylophanes (38; $n = 2$ and 6), which have
been synthesized[123] by a sulphone-extrusion procedure. Species (38; $n = 2$) exhi-
bits an unexpectedly high conformational flexibility.

5 Molecular Rearrangements

The thermal and acid-catalysed Claisen rearrangements of *N*-allyl-anilines have
been investigated.[124] The rearrangement of *N*-(1',1'-dimethylallyl)-2,6-dimethyl-
aniline into 4-(1',1'-dimethylallyl)-2,6-dimethylaniline cannot be achieved ther-
mally, but occurs readily in 4 mol dm^{-3} sulphuric acid. A new regioselective
synthesis of anilides having carbonyl-functionalized alkyl groups in the *ortho*-
position has been accomplished[125a] in 40—70% yields by decarboxylative 1-aza-1'-
oxa[3.3]sigmatropic[125b] Claisen rearrangements of enolizable or enolized *N*-aryl-
NO-diacyl-hydroxylamines, *i.e.* (39)→(40). *N*-Acyl-*N*-aryl-azasulphonium salts

(39)   (40)
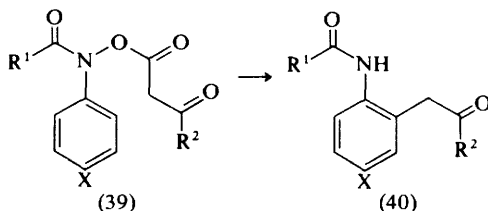
[121] H. Irngartinger, R. G. H. Kirrstetter, C. Krieger, H. Rodewald, and H. A. Staab, *Tetrahedron Letters*,
1977, 1425.
[122] (*a*) J. G. O'Connor and P. M. Keehn, *Tetrahedron Letters*, 1977, 3711; (*b*) H. Horita, T. Otsubo, and S.
Misumi, *Chem. Letters*, 1977, 1309.
[123] F. Vögtle, M. Atzmüller, W. Wehner, and J. Grütze, *Angew. Chem. Internat. Edn.*, 1977, **16**, 325.
[124] S. Jolidon and H.-J. Hansen, *Chimia (Switz.)*, 1977, **31**, 46; *Helv. Chim. Acta*, 1977, **60**, 978.
[125] (*a*) R. M. Coates and I. M. Said, *J. Amer. Chem. Soc.*, 1977, **99**, 2355; (*b*) F. Vögtle and E.
Goldschmidt, *Chem. Ber.*, 1976, **109**, 1; (*c*) P. G. Gassman and R. J. Balchunis, *Tetrahedron Letters*,
1977, 2235.

have been prepared for the first time and, when treated with base, they yield ylides (41), which undergo spontaneous [2,3]sigmatropic rearrangement to produce *o*-methylthiomethyl-anilides, and thus provide another route to *ortho*-substituted anilides.[125c] The assumption that the severe conditions necessary for [3,3]sigmatropic rearrangement of *O*-aryl or *O*-vinyl oximes refer to the preliminary tautomerism stage have been confirmed,[126] and some *N*-aryl-*O*-vinyl-hydroxylamines [*e.g.* (42)] and *O*-aryl-*N*-vinyl-hydroxylamines undergo spontaneous rearrangement, demonstrating the ease of cleavage of N—O bonds when a Cope rearrangement path is available. It has been shown[127] by deuterium labelling that 2-vinyl-phenols, at 143 °C, undergo reversible 1,5-hydrogen shifts to give *o*-quinone methides, and the same process leads to rapid (E,Z) isomerization of, for example, 2-(prop-1-enyl)-phenols.

(41)   (42)
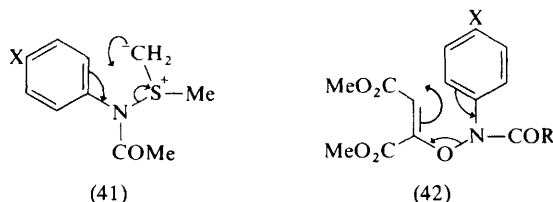
It has been noted that an autoxidation process to form dimethylbenzylamine and benzoic acid occurs during Stevens rearrangement of benzyldimethylphenacylammonium ylide at low temperatures, and that this predominates under an atmosphere of oxygen.[128] The solvent hexamethylphosphoramide enables the extension of the application of the Smiles' rearrangement of 2-aryloxy-2-methyl-propanamides[129a] into *N*-aryl-2-hydroxy-2-methyl-propanamides to examples which possess deactivated aromatic rings.[129b] This reaction is the basis of a new method for the conversion of phenols into anilines.[129b]

The kinetic nitrogen isotope effect for the benzidine rearrangement of hydrazobenzene is $k_{14}/k_{15} = 1.0203$ (± 0.0007), demonstrating, at last unequivocally, that breaking of the N—N bond in this two-proton process is part of the rate-limiting step. This result[130] rules out the recent proposal involving a second protonation at the C-1 atom, but cannot distinguish between the traditional mechanism having pre-equilibria at the two nitrogen atoms followed by rate-limiting rearrangement, or some concerted process involving N—N bond scission and almost complete second protonation in the rate-limiting stage. The synthetic usefulness of the oxygen analogue of the benzidine rearrangement has been examined.[131] The reactions of salts of *N*-aryl-hydroxamic acids with activated halogeno-benzenes yield 4-amino-4'-hydroxybiphenyls *via* intermediate *NO*-diaryl-hydroxylamines. Biaryls are also formed by a new rearrangement[132] of arylhydrazones of aromatic aldehydes and diaryl ketones, which is stated to be of

126 T. Sheradsky, E. Nov, S. Segal, and A. Frank, *J.C.S. Perkin I*, 1977, 1827.
127 H.-J. Hansen, *Helv. Chim. Acta*, 1977, **60**, 2007.
128 S. H. Pine and E. Fujita, *J. Org. Chem.*, 1977, **42**, 1460.
129 R. Bayles, M. C. Johnson, R. F. Maisey, and R. W. Turner, *Synthesis*, 1977, (*a*) p. 31; (*b*) p. 33.
130 H. J. Shine, G. N. Henderson, A. Cu, and P. Schmid, *J. Amer. Chem. Soc.*, 1977, **99**, 3719.
131 T. Sheradsky and E. Nov, *J.C.S. Perkin I*, 1977, 1296.
132 F. Fusco and F. Sannicolo, *Tetrahedron Letters*, 1977, 3163.

general applicability, and which is exemplified by the formation of 4-amino-3'-formyl-6'-methoxy-3,5-dimethylbiphenyl (35%) on heating the 2,6-dimethyl-phenylhydrazone of anisaldehyde in polyphosphoric acid.

The product data from the nitramine rearrangement of *N*-methyl-*N*-nitro-*m*-chloroaniline have been compared[133] with those from the Claisen rearrangement of allyl *m*-chlorophenyl ether, and it is claimed that the 'cartwheel' mechanism for the former is not able to accommodate the findings that isomer formation, except for a small steric effect and the requirement for *ortho,para*-substitution, is random. Photochemical rearrangement of the sulphonyl group has been observed[134] in the conversion of phenyl benzenesulphonate into *o*- and *p*-hydroxyphenyl phenyl sulphones by u.v. irradiation, and a mechanism involving a caged radical pair has been proposed. Further studies[135a] of the Fischer–Hepp rearrangement and concurrent denitrosation have involved methyl-substituted *N*-methyl-*N*-nitroso-anilines, with a view to the evaluation of steric effects; in particular, those on the enigmatic intramolecular rearrangement step. A steric effect was apparent for the 3,5-dimethyl compound. *N*-Nitrosodiphenylamine is denitrosated by various nucleophiles and can also act as a direct ring-nitrosating agent towards anilines.[135b]

6 Condensed Systems

A new route[136] to polymethylated naphthalenes, anthracenes, and phenanthrenes involves the reaction of 3,4-dichloro-1,2,3,4-tetramethylcyclobutene with aromatic hydrocarbons in the presence of aluminium tribromide, and, for example, reaction with naphthalene gave 1,2,3,4-tetramethylphenanthrene (60%). The usefulness of photodehydrocyclization reactions of stilbenes and analogues to give phenanthrenes has been increased, as reaction occurs much more cleanly[137] in the presence of certain π-acceptor molecules (*e.g.* tetracyanoethylene) under anaerobic conditions and, if necessary, at low temperature. The generation of α'-bromo-1,2-naphthoquinodimethane from 1-bromomethyl-2-dibromomethylnaphthalene is involved[138] in an improved one-pot synthesis of phenanthrenes. The species then undergoes Diels–Alder reaction with *N*-phenylmaleimide, elimination of hydrogen bromide, and fortuitous oxidation to give (43). A new phenanthrene synthesis is

(43)

(44)

(45)
$\alpha = 99°$
$\beta = 138°$
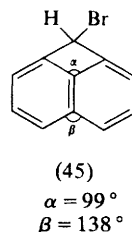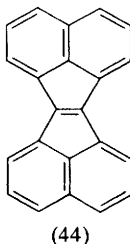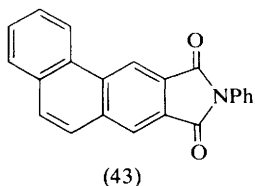
[133] W. N. White and J. R. Klink, *J. Org. Chem.*, 1977, **42**, 166.
[134] Y. Ogata, K. Takagi, and S. Yamada. *J.C.S. Perkin II*, 1977, 1629.
[135] (*a*) I. D. Biggs and D. L. H. Williams, *J.C.S. Perkin II*, 1977, 44; (*b*) J. T. Thompson and D. L. H. Williams, *ibid.*, p. 1932.
[136] A. P. Krysin, N. V. Bodoev, and V. A. Koptyug, *J. Org. Chem. (U.S.S.R.)*, 1977, **13**, 1183.
[137] J. Bendig, M. Beyermann, and D. Kreysig, *Tetrahedron Letters*, 1977, 3659.
[138] G. W. Gribble, E. J. Holubowitch, and M. C. Venuti, *Tetrahedron Letters*, 1977, 2857.

involved[139a] in the direct conversion of a 2,2'-di(chloromethyl)-substituted biphenyl into the phenanthrene with sodamide in ammonia, using an iron catalyst. Vanadium trifluoride oxide has been found[139b] to convert a variety of 1,2-diaryl-ethene derivatives into phenanthrenes in high yield.

Full details of the preparation of 1,1-dichlorocyclopropa[*b*]naphthalene from 1,1,1a,7a-tetrachloro-1a,2,7,7a-tetrahydro-2,7-diphenylcyclopropa[*b*]naphthalene have appeared.[140] The *gem*-dibromo-derivative cannot be formed in an analogous way, but the reaction of the dichloro-compound with a small excess of ethyl- or phenyl-magnesium bromide leads to halogen exchange, the isolable *gem*-diethyl compound only being formed with a large excess of the Grignard reagent. The unisolable *gem*-diphenyl compound undergoes ready cleavage of the cyclopropane ring. Acenaphthylene is formed (41% yield) by the elimination of carbon monoxide from 1*H*-phenalen-1-one on flow pyrolysis at 900 °C.[141] This method is of more general utility and, for example, provides the preferred route to indeno[2,1-*a*]indene (dibenzopentalene). Acenaphth[1,2-*a*]acenaphthylene (44) has been synthesized[142] by a new route, and the increasingly strained compounds obtained by introducing ethano-bridges across the *peri*-positions of (44) have been made for the first time. Spectral effects due to strain were noted, and the authors remark on the lack of calculations on these systems. The structure of 1-bromo-1*H*-cyclo-buta[*de*]naphthalene (45) has been determined[143a] and, surprisingly, the three rings are essentially coplanar. The strain due to *peri*-bridging is accommodated by adjustments, particularly in bond angles [see (45)], throughout the molecule. The first determination of the crystal structure of a Dewar molecule has been per-formed[143b] on 1,3,6,8-tetra-t-butylhemi-Dewar-naphthalene. The molecule has a *syn*-structure, as the substituents cause considerable distortion and the benzo-cyclobutene system is not planar.

Decamethylanthracene has been prepared for the first time,[144] utilizing (in part) the removal of a nitrogen bridge in a 1,4-imine by oxidation with peroxide [see *Ann. Reports (B)*, 1976, **73**, p. 224]. The strain in the structure was illustrated by the ease of photochemical conversion into the 9,10-Dewar-isomer. A convenient method has been found[145] for the introduction of a tertiary carbon carrying an elec-tronegative group into the 9-position of anthracene. The appropriate alkyl radical generated thermally from an azo-compound reacts with anthrone under basic conditions to give the 10-alkyl-anthrone, and the alcohol formed on subsequent reduction could be aromatized to the desired 9-substituted anthracene by phos-phorus pentoxide. Dehydrogenation of a series of mono- and di-t-butyldihy-droanthracenes has been investigated[146] as a potential synthetic route to t-butyl-anthracenes. 1- and 2-t-Butylanthracene were prepared in this way, although rearrangements complicated other cases. 2,6-Di-t-butylanthracene could be pre-pared in high yield by direct t-butylation of anthracene.

[139] (*a*) M. S. Newman and H. M. Dali, *J. Org. Chem.*, 1977, **42**, 734; (*b*) A. J. Liepa and R. E. Summons, *J.C.S. Chem. Comm.*, 1977, 826.
[140] A. R. Browne and B. Halton, *J.C.S. Perkin I*, 1977, 1177.
[141] G. Shaden, *Angew. Chem. Internat. Edn.*, 1977, **16**, 50.
[142] R. H. Mitchell, T. Fyles, and L. M. Ralph, *Canad. J. Chem.*, 1977, **55**, 1480.
[143] (*a*) M. Gessner, P. Card, H. Shechter, and G. G. Christoph, *J. Amer. Chem. Soc.*, 1977, **99**, 2371; (*b*) R. W. Franck, R. Gruska, and J. G. White, *Tetrahedron Letters*, 1977, 509.
[144] H. Hart and B. Ruge, *Tetrahedron Letters*, 1977, 3143.
[145] T. Mitsuhashi, S. Otsuka, and M. Ōki, *Tetrahedron Letters*, 1977, 2441.
[146] P. P. Fu and R. G. Harvey, *J. Org. Chem.*, 1977, **42**, 2407.

Some unusual structures in the anthracene series have been stabilized. 2,4,9-Trichloro-1,10-anthraquinone is a stable crystalline solid prepared[147] by refluxing 9-chloro-10-hydroxy-1,4-anthraquinone with thionyl chloride and triethylamine, and some stable 9,10-quinodimethanes [*e.g.* (46), m.pt. 105 °C] have been prepared[148a] by the initial reaction of the anthraquinone with methylmagnesium iodide followed by treatment with phosphoryl chloride in pyridine. Related compounds (47) have been formed[148b] from the appropriate anthrone. Compounds which had at least two *peri*-methyl–methyl interactions were formed with the alkylidenedihydroanthracene structures shown, whereas simpler compounds were formed as the anthracene tautomer. Other examples have been reported[144,148c] of the ease of loss of aromaticity of the central rings of anthracenes caused by double *peri* interactions.
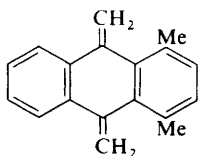
(46)
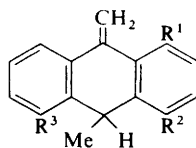
(47) R^1, R^2, R^3 = Me, H, Me; Me, Me, H; H, Me, Me; or Me, Me, Me

A ^{13}C-labelling experiment has revealed[149a] the scrambling of α- and β- (but not angular) carbon atoms in naphthalene at 1035 °C ('automerization'), and a reasonable (but unproven) hypothesis involves the intermediacy of azulene. Mass spectrometric studies indicate[149b] that complete scrambling of the carbon atoms of naphthalene occurs in an energy range between the ionization potential and 18.8 eV, and prior to loss of C_2H_2. The oxidation of naphthalene with *m*-chloroperbenzoic acid under carefully controlled conditions has led[150a] to a synthesis of *anti*-naphthalene 1,2 : 3,4-dioxide, which complements that of the *syn*-isomer reported last year [see *Ann. Reports (B)*, 1976, **73**, p. 225]. A naphthalene pentaoxide has been synthesized[150b] from 1,6-epoxy[10]annulene by two successive sequences of addition of singlet oxygen and thermolysis, and it has been shown to have the *syn,syn,syn,syn*-1,2;3,4;5,6;7,8-*anti*-9,10-structure.

The mechanism proposed for the photocatalysed nitrosation of 2-naphthol appeared unlikely[151a] [see *Ann. Reports (B)*, 1975, **72**, p. 223], but new evidence for acid-catalytic action of singlet excited 2-naphthol on a ground-state reaction has been presented for the production of acetals from the irradiation of alkanals in alcohols.[151b] Although 1-naphthol, in contrast to phenol, does not undergo photodimerization, it has now been reported[152] that irradiation of the 1-naphthoxide ion

[147] M. V. Gorelik, S. P. Titova, and V. A. Trdatyan, *J. Org. Chem. (U.S.S.R.)*, 1977, **13**, 424.

[148] (*a*) B. F. Bowden and D. W. Cameron, *Tetrahedron Letters*, 1977, 383; (*b*) *J.C.S. Chem. Comm.*, 1977, 78; (*c*) H. Hart and H. Wachi, *ibid.*, p. 409.

[149] (*a*) L. T. Scott and G. K. Agopian, *J. Amer. Chem. Soc.*, 1977, **99**, 4506; (*b*) H. Budzikiewicz and R. Stolze, *Monatsh.*, 1977, **108**, 869.

[150] (*a*) K. Ishikawa and G. W. Griffin, *Angew. Chem. Internat. Edn.*, 1977, **16**, 171; see also K. Ishikawa, H. C. Charles, and G. W. Griffin, *Tetrahedron Letters*, 1977, 427; (*b*) E. Vogel, A. Brewer, C.-D. Sommerfeld, R. E. Davis, and L.-K. Liu, *Angew. Chem. Internat. Edn.*, 1977, **16**, 169.

[151] (*a*) E. A. Chandross, *J. Amer. Chem. Soc.*, 1976, **98**, 1053; (*b*) M. Hisaoka and K. Tokumaru, *Chem. Letters*, 1977, 533.

[152] T. Kitamura, T. Imagawa, and M. Kawanisi, *J.C.S. Chem. Comm.*, 1977, 81.

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remarkably gives a dimer (48), probably *via* a photoinduced nucleophilic addition reaction. In a seemingly unprecedented nucleophilic substitution reaction, the formation of 1-piperidinomethyl-4-methyl-3-nitronaphthalene has been recorded[153] from the reaction of 1,4-dimethyl-2,3-dinitronaphthalene with piperidine, and the authors suggest redefining the term '*tele*-substitution' to cover reactions where the entering group occupies a position one or two atoms away from that vacated by the leaving group.

OH

OH

(48)

R O$_2$H

O

(49)
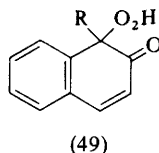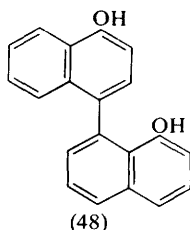
Heating potassium 2-naphthoxide in a primary alcohol (benzyl, or containing more than three carbon atoms) has been found[154] to give a novel route to the 1-alkyl-2-naphthol in good yield. The syntheses of 1-t-butyl- and 1-t-pentyl-2-naphthol have been reported,[155a] and, although these molecules are considerably strained, any ketone tautomer present was undetectable. The bulk of the alkyl group does lead, however, to an extremely rapid autoxidation to the hydroperoxynaphthalenone (49). It has been suggested[155b] that the unreactivity to oxygen of some 1-aryl- and 1-aralkyl-2-naphthols is due to intramolecular hydrogen bonding of the hydroxy-group to the aryl group of the substituent.

The first quantitative determination of the reactivity towards electrophiles of anthracene results from studies of protiodetritiation.[156] The 1- and 2- positions are more reactive than the corresponding positions in naphthalene, but are closer in reactivity than are those in naphthalene.

Irradiation of 2-styrylbenzo[c]phenanthrene in chiral solvents gives[157] the optically active hexahelicene, albeit with low optical yields (0.2—2%). 3,15-Ethano- and 3,15-(2-oxapropano)-[7]helicene have been synthesized,[158] and their conformations

CH

(50)
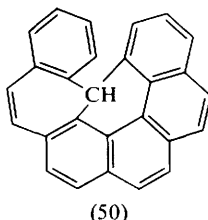
[153] G. Guanti, S. Thea, M. Novi, and C. Dell'Erba, *Tetrahedron Letters*, 1977, 1429.
[154] T. Kito and K. Ota, *J. Org. Chem.*, 1977, **42**, 2020.
[155] (a) J. Carnduff and P. A. Brady, *J. Chem. Res.* (S), 1977, 235; (b) P. A. Brady, J. Carnduff, and F. Monaghan, *Tetrahedron Letters*, 1977, 3295.
[156] H. V. Ansell, M. M. Hirschler, and R. Taylor, *J.C.S. Perkin II*, 1977, 353.
[157] W. H. Laarhoven and Th. J. H. M. Cuppen, *J.C.S. Chem. Comm.*, 1977, 47.
[158] M. Joly, N. Defay, R. H. Martin, J. P. Declerq, and G. Cermain, *Helv. Chim. Acta*, 1977, **60**, 537.

and ^{1}H n.m.r. spectra compared with those of [7]helicene and 3,15-dimethyl[7] helicene. Thermolysis of 1-formyl[6]helicene tosylhydrazone in benzene in the presence of sodium hydride gave[159] the carbene-insertion product (50), which was resolved, using h.p.l.c. [see *Ann. Reports (B)*, 1976, **73**, p. 226].

7 Non-benzene Systems

Three- and Four-membered Rings.—The 11-methyl-11-tricyclo[4,4,1,0^{1,6}]undecyl cation has been formed,[160] below $-60\,°C$, and its ^{13}C n.m.r. spectrum suggests that it has significant 2π-homoaromatic character, leading to an unsymmetrical structure (51). The planar 1-(2,3-diphenylcycloprop-2-enylidenemethyl)-2,3-diphenylcyclopropenium ion has been synthesized[161] by treatment of bis(2,3-diphenylcycloprop-2-enyl)methane with trityl perchlorate. Spectral measurements indicate a significant contribution of (52) to its structure. Tetra(*NN*-dialkyl-amino)triafulvalene dications [*e.g.* (53)] have been synthesized[162] for the first time.
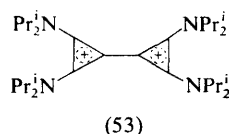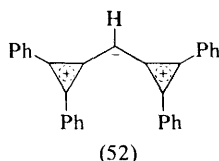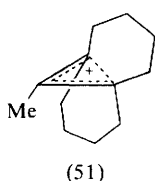
The mono-, bis-, and tris-(*p*-*NN*-di-isopropylamino)triphenylcyclopropenium ions have been formed[163a] by the reaction of *NN*-di-isopropylaniline with the appropriate chlorocyclopropenium ion; the fully substituted ion is one of the most stable cyclopropenium ions yet reported. Studies of these ions allow an interesting comparison to be made with analogous triphenylmethyl cations, showing, for example, the reduced importance of the immonium canonical form in the former cases. The reactions of 1,2-bisdialkylamino-3-halogenocyclopropenium ions and aryl Grignard reagents have been studied,[163b] and reactions of an intermediate cyclopropenium Grignard reagent identified.

Two electrochemical studies[164] have yielded values for 'antiaromatic' destabilization upon the formation of a cyclobutadiene ring. The value for cyclobutenedione upon reduction to the radical anion was at least $59\,kJ\,mol^{-1}$.[164b] Dewar has reinforced[165a] his suggestion that the cyclobutadiene formed by the matrix-isolation technique is a metastable triplet [see *Ann. Reports (B)*, 1975, **72**, p. 240], and he has used MINDO/3 theory to calculate (with apparent success) the i.r.

[159] J. Jespers, N. Defay, and R. H. Martin, *Tetrahedron*, 1977, **33**, 2141.
[160] G. A. Olah, G. Liang, D. B. Ledlie, and M. G. Costopoulos, *J. Amer. Chem. Soc.*, 1977, **99**, 4196.
[161] K. Komatsu, K. Masumoto, and K. Okamoto, *J.C.S. Chem. Comm.*, 1977, 232.
[162] Z.-I. Yoshida, H. Konishi, S.-I. Sawada, and H. Ogoshi, *J.C.S. Chem. Comm.*, 1977, 850.
[163] (a) K. Komatsu, R. West, and D. Stanislawski, *J. Amer. Chem. Soc.*, 1977, **99**, 6286; (b) Z.-I. Yoshida, H. Konishi, Y. Miura, and H. Ogoshi, *Tetrahedron Letters*, 1977, 4319.
[164] (a) M. Horner and S. Hünig, *Angew. Chem. Internat. Edn.*, 1977, **16**, 410; (b) R. D. Rieke, C. K. White, L. D. Rhyne, M. S. Gordon, J. F. W. McOmie, and N. P. Hacker, *J. Amer. Chem. Soc.*, 1977, **99**, 5387.
[165] (a) M. J. S. Dewar and A. Komornicki, *J. Amer. Chem. Soc.*, 1977, **99**, 6174; (b) H. Kollmar and V. Staemmler, *ibid.*, p. 3583.

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spectrum of such a species. The paper seems, however, to have been overtaken in publication by the doubts raised concerning the experimental values [see *Ann. Reports (B)*, 1976, **73**, p. 228]. In contrast to Dewar's calculations, and with relevance to his arguments concerning metastability, another treatment suggests[165b] that, even for a square geometry, the singlet is lower in energy than the triplet, which is in violation of Hund's rule, due to spin polarization effects. Both observed and calculated electron densities for a rectangular cyclobutadiene, for which the structure is known, have shown[166a] that the density maxima for the four-membered ring lie significantly off the lines joining the carbon atoms, indicating that the bonds are 'bent'. The symmetrical and apparently uncomplexed tetrakis(trifluoromethyl)cyclobutadiene has been fully characterized[166b] spectrally in solution and matrix at low temperatures. It has a singlet ground state and appears to be rectangular. Tri-t-butylcyclobutadiene, for which a rectangular structure is to be assumed, has now been shown[166c] to undergo reactions typical of a triplet diradical species; for example, it undergoes addition with carbon tetrachloride. It was suggested that the two structures may be in rapid equilibrium or that the reaction is initiated by transfer of an electron from the cyclobutadiene within a donor–acceptor complex.

Labelling experiments[167] have confirmed the intermediacy of butalene (54) in the reaction of 1-chloro[2,2,0]bicyclohexa-2,5-diene with lithium dialkylamides to give dialkyl-anilines, but this pathway only accounts for about 50% of the product.

(54)   (55)
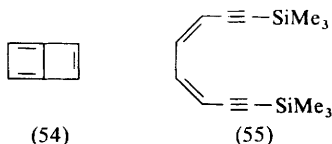
1,2-Bis(trimethylsilyl)benzocyclobutadiene has been prepared[168] by the vacuum pyrolysis of the *cis,cis*-dienediyne (55) as a thermally stable air-sensitive orange-red oil. The ^{1}H n.m.r. spectrum provides convincing evidence of strong paramagnetic ring-current contributions to the induced ring-current. The pathways of oxidation of benzocyclobutadienes have been clarified[169a] by the observation that in solution the tetraphenylbenzo[1,2:4,5]dicyclobutadiene (56) is oxidized initially to the oxide (57). In the solid, however, the stable *o*-quinone methide (58) is formed.

(58)   (56)   (57)
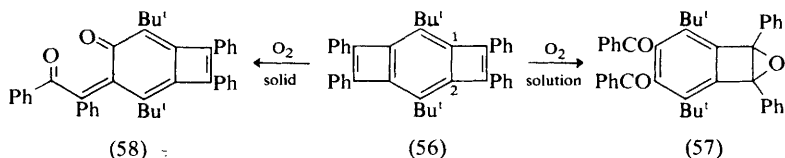
[166] (*a*) H. Irngartinger, H.-L. Hase, K.-W. Schulte, and A. Schweig, *Angew. Chem. Internat. Edn.*, 1977, **16**, 187; (*b*) S. Masamune, T. Machiguchi, and M. Aratani, *J. Amer. Chem. Soc.*, 1977, **99**, 3524; (*c*) G. Maier and W. Sauer, *Angew. Chem. Internat. Edn.*, 1977, **16**, 51.

[167] R. Breslow and P. L. Khanna, *Tetrahedron Letters*, 1977, 3429.

[168] K. P. C. Vollhardt and L. S. Yee, *J. Amer. Chem. Soc.*, 1977, **99**, 2010.

[169] (*a*) F. Toda, N. Dan, K. Tanaka, and Y. Takehira, *J. Amer. Chem. Soc.*, 1977, **99**, 4529; (*b*) F. Toda and T. Yoshioka, *Chem. Letters*, 1977, 561.

Cycloadditions of tetracyanoethylene to substituted analogues of (56) occur in a [2 + 2] manner across the bond indicated (1,2) to give highly strained propellanes.[169b]

Five- and Seven-membered Rings.—A fulvene synthesis has resulted[170] from a study of the reactions of thiobenzophenones with the dicarbonylcyclopentadienyl-iron anion. Yields are improved by the inclusion of *para*-electron-releasing substituents in the aryl group. The synthesis of fulvenes from the reaction of 1-chloroalkyl acetates and sodium pentadienide, followed by base-catalysed elimination, has been extended[171a] to some 6-substituted fulvenes, and 1,2-benzo-fulvene, 1,2,3,4-dibenzofulvene, and the corresponding 6-methyl- and 6-phenyl-derivatives have been prepared by an analogous procedure[171b] from sodium indenide or sodium fluorenide. 1,2-Benzofulvene has also been formed[172] by the flash vacuum pyrolysis of the 11-diphenylmethylene derivative (59), which was prepared from the benzyne adduct of 6,6-diphenylfulvene by selective hydrogenation.
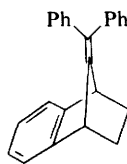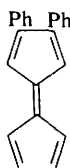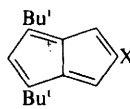
(59)   (60)   (61) $X = CO_2Me$, CHO, or CN

A series of 6,6-disubstituted fulvenes has been protonated under super-acid conditions at low temperatures.[173] Protonation takes place exclusively at the C-2 position of the fulvene ring in accord with calculated electron densities. The crystalline isolable 1,2,3,4-tetraphenyl- and 1,2:3,4-dibenzofulvalenes, and 2,3-diphenylfulvalene (60), which is only stable in solution, have been synthesized.[174] Species (60) readily dimerizes by [4 + 2]addition. The scope of the facile pentalene synthesis from 1,3-di-t-butyl-6-dimethylaminofulvene [see *Ann. Reports* (*B*), 1976, **73**, p. 230] has been extended,[175a] by using other alkynes, to give the pentalenes (61). These pentalenes are formed as dimers, with which the monomers are in rapid equilibrium and which form the monomers in organic solvents. The dimerization reactions and other dimerization products that are formed after longer times have been studied,[175a] as have the reactivities of the pentalene monomers to acids, bases, dienophiles, and dienes.[175b]

3-Amino-tropones have been formed[176] by rapid pyrolysis of a corresponding enamine; 3-amino-4-methyltropone, for example, being formed from (62). 3-Ethoxy- and 3-phenoxy-tropones have been prepared[177] by the reaction of 3-tosyloxytropone with sodium ethoxide and lithium phenoxide respectively. A

[170] H. Alper and H.-N. Paik, *J.C.S. Chem. Comm.*, 1977, 126.
[171] (*a*) M. Neuenschwander and R. Iseli, *Helv. Chim. Acta*, 1977, **60**, 1061; (*b*) M. Neuenschwander, R. Vögeli, H.-P. Fahrni, H. Lehmann, and J.-P. Ruder, *ibid.*, p. 1073.
[172] R. N. Warrener, K. I. Gell, and M. N. Paddon-Row, *Tetrahedron Letters*, 1977, 53.
[172] G. A. Olah, G. K. S. Prakash, and G. Liang, *J. Org. Chem.*, 1977, **42**, 661.
[174] H. Prinzbach, H. Sauter, H.-G. Hörster, H.-H. Limbach, and L. Knothe, *Annalen*, 1977, 869.
[175] M. Suda and K. Hafner, *Tetrahedron Letters*, 1977, (*a*) p. 2449; (*b*) p. 2453.
[176] J. Ficini and A. Duréault, *Tetrahedron Letters*, 1977, 809.
[177] M. Cavazza, R. Cabrino, and F. Pietra, *Synthesis*, 1977, 298.

reported preparation[178a] of 3-hydroxytropone derivatives appears, however, to be incorrect,[178b] the products being 2-hydroxyacetophenones.

(62)   (63)   (64)
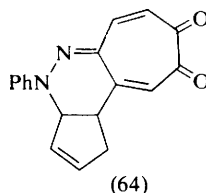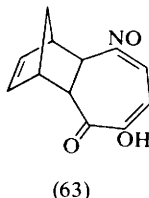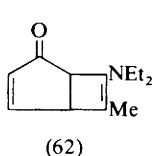
Electrophilic substitution of 5-methyltropolone by arenediazonium ions occurs first at the 3- and then at the 7-position.[179a] 5-Arylazotropolones undergo arylazo exchange (61—92%) on reaction with a different arenediazonium ion.[179b] The reaction of 5-nitrosotropolone with cyclopentadiene gives (63), and provides an example of a stable tropolone derivative reacting as a 2π compound in a [4 + 2]cycloaddition.[179c] 5-Phenylazotropolone, however, which is known to react as its diketo-form, adds to cyclopentadiene, utilizing its $N{=}N{-}C{=}C$ linkage to give (64).[179d] Further reactions with cyclopropene have established the *endo*-stereo-chemistry required for the latter reaction.[179e] An analogous side-chain reaction has also been established[179f] as a minor pathway in one case, in a homodiene system, on reaction of 2-methoxy-6-styryltropone with maleic anhydride.

The first benzo[3,4]cyclobuta[1,2-c]tropolone, the 9-chloro-derivative, has been synthesized[180] and appears to exist predominantly or exclusively as the tautomer (65). The geometrically isomeric 2,3:6,7-dioxa-bis-σ-homotropones [e.g. (66)] have been formed[181] by the direct oxidation of tropone with alkaline hydrogen peroxide. The unreactivity of the remaining double bond, however, limits their synthetic utility. A series of methoxy-substituted heptalene-1,8- and -3,8-diones have been formed[182a] by oxidation of 8H-cyclohepta[d]tropolone.[182b] In solution in fluorosulphonic acid, these compounds are diprotonated, and provide the first examples of the 10π-heptalenium dication structure [e.g. (67)].

(65)   (66)   (67)
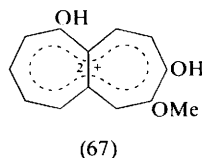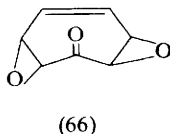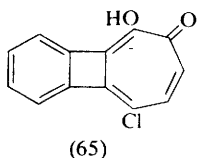
The MINDO/3 method has been applied to the prediction of the rearrangement of benzyl and substituted benzyl cations to tropylium ions and related processes and

[178] (a) J. H. Clark and J. M. Miller, *Tetrahedron Letters*, 1977, 139; (b) H. Takeshita, *ibid.*, p. 1657.
[179] (a) T. Ide, K. Imafuku, and H. Matsumura, *Chem. Letters*, 1977, 717; (b) *ibid.*, p. 511; (c) I. Saito, K. Sakan, and S. Itô, *ibid.*, p. 253; (d) S. Itô and I. Saito, *Tetrahedron Letters*, 1977, 1203; (e) Y. Fujise, M. Sakaino, and S. Itô, *ibid.*, p. 2663; (f) I. Saito, Y. Watanabe, and S. Itô, *ibid.*, p. 3049.
[180] M. Sato, S. Ebine, and J. Tsunetsugu, *Tetrahedron Letters*, 1977, 855.
[181] H. Prinzbach, W. Seppelt, and H. Fritz, *Angew. Chem. Internat. Edn.*, 1977, **16**, 198.
[182] S. Kuroda and T. Asao, *Tetrahedron Letters*, 1977, (a) p. 289; (b) p. 285.

of the properties of these ions.[183] A pure heptamethyltropylium salt has been prepared[184] for the first time by the use of phosphorus pentachloride as a reagent for hydride abstraction from 1,2,3,4,5,6,7-heptamethyltropilidene. The 9,10-dihydro-9-10-(1,2-tropylio)anthracene ion (68) has been synthesized,[185] and the u.v. spectrum is indicative of strong intermolecular charge-transfer interaction despite the small overlap of the orbital systems involved.
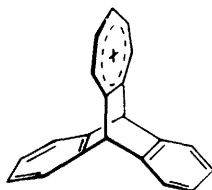
(68)

8-Phenylheptafulvene has been prepared[186] by the reaction of the benzyl-tropylium ion with an equivalent of triethylamine in dichloromethane. It is stable for several days in solution at room temperature under nitrogen. U.v. spectroscopy suggests even less π-electron delocalization than in heptafulvene itself, and only a small contribution of the dipolar canonical form for this system. 8-Amino- and 8-methoxy- 8-(triethylsiloxy)heptafulvene have also been synthesized; they are hygroscopic and thermolabile.[187] A facile synthesis of 8-azaheptafulvenes involves the reaction of tropylium borofluoride with anilines to give 8-aryl-8-azahep-tafulvenium salts, which are deprotonated with aqueous sodium carbonate.[188a] The cycloaddition reactions of these compounds with, *inter alia*, isocyanates and ketens, to give (usually) [8 + 2]cycloadducts, have also been studied.[188b]

Two independent reports[189] have been given of an improved route to azulenes by [6 + 4]cycloaddition of 6-NN-dimethylaminofulvene with thiophen 1,1-dioxides; 3,4-dichlorothiophen, for example, yielding the hitherto unknown 5,6-dichloroazulene in 60%[189a] or 46%[189b] yield. 2,6-Dihydroxyazulene has been prepared[190a] from diethyl 2,6-dihydroxyazulene-1,3-dicarboxylate[190b] and undergoes a heavily solvent-dependent keto–enol tautomerism. In chloroform the species exists mainly as 1,3-dihydroazulene-2,6-dione. 1,3-Dicarbethoxyazulene-2,6-dione has also been synthesized,[190b] but was isolated only in the form of a dimer. 1-Alkyl-azulenes are converted into 1-acyl-azulenes in 59—98% yields by a novel oxidation, using DDQ.[190c]

[183] C. Cone, M. J. S. Dewar, and D. Landman, *J. Amer. Chem. Soc.*, 1977, **99**, 372; M. J. S. Dewar and D. Landman, *ibid.*, pp. 2446, 4633, 7439.
[184] K.-I. Takeuchi, Y. Yokomichi, and K. Okamoto, *Chem. Letters*, 1977, 1177.
[185] T. Nakazawa and I. Murata, *J. Amer. Chem. Soc.*, 1977, **99**, 1996.
[186] K. Komatsu, M. Fujimori, and K. Okamoto, *Tetrahedron*, 1977, 2791.
[187] K. M. Rapp and J. Daub, *Tetrahedron Letters*, 1977, 227.
[188] (a) K.-I. Sanechika, S. Kajigaeshi, and S. Kanemasa, *Synthesis*, 1977, 202; (b) K. Yamamoto, S. Kajigaeshi, and S. Kanemasa, *Chem. Letters*, 1977, 85, 91.
[189] (a) S. E. Reiter, L. C. Dunn, and K. N. Houk, *J. Amer. Chem. Soc.*, 1977, **99**, 4199; (b) D. Copland, D. Leaver, and W. B. Menzies, *Tetrahedron Letters*, 1977, 639.
[190] (a) T. Morita, H. Kanzawa, and K. Takase, *Chem. Letters*, 1977, 753; (b) T. Morita and K. Takase, *ibid.*, p. 513; (c) T. Amemiya, M. Yasunami, and K. Takase, *ibid.*, p. 587.

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Annulenes.—A series of substituted cyclo-octatetraene dications has now been prepared[191] by oxidation of the parent hydrocarbon. Most are stable only at low temperatures, but the *sym*-dibenzocyclo-octatetraene dication is stable even at 0 °C, and spectral evidence suggests that delocalization of all fourteen π-electrons about the sixteen-carbon-atom periphery is occurring. Oxidation of cyclo-octa[*def*]fluorene by a different method gave[192] the protonated cyclo-octa[*def*]fluorenone dication (69), a 14 π-electron aromatic system which is stable at room temperature. The 9,10-diphenylbicyclo[6,2,0]decapentaenes (70) have been synthesized[193] by a route involving initial photoaddition of diphenylacetylene to bicyclo[4,2,0]octa-3,7-diene, and other stages, one of these involving the thermal isomerization of bicyclo[4,2,0]octatriene to cyclo-octatetraene. The preliminary evidence suggests that π-electron delocalization in (70; R = H), but not in (70; R = Me), overcomes the strain involved in attaining (near) planarity.

(69)   (70) R = H, D, or Me
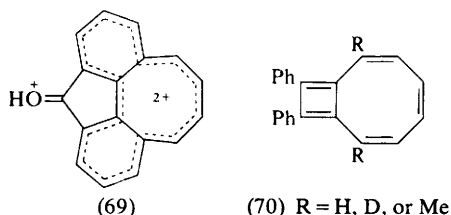
PMO theory has demonstrated[194] that the small variations in the perimeter bond lengths of 1,6-methano[10]annulene are due mainly to transannular 1,6-homoaromatic interaction. This type of interaction is smaller, but still important, for the 1,6-methano[11]annulenium cation [*cf. Ann. Reports* (*B*), 1976, **73**, p. 234]. 1,6-Methano[10]annulene and some hetero-bridged analogues undergo Diels–Alder addition with 4-substituted-1,2,4-triazoline-3,5-diones, giving both mono- and bis-adducts, formed by *anti*-attack.[195a] The methylene bridge also hinders sterically the approach of *NNN'N'*-tetramethyl-*p*-phenylenediamine to 2,7-dinitro-1,6-methano[10]annulene, leading to the formation of only a 1:1 donor–acceptor complex.[195b] Unsubstituted 1,5-methano[10]annulene has been synthesized, and appears to maintain a diamagnetic ring current.[196] In contrast to its 1,6-analogue, however, its electronic spectrum extends into the visible region, and it is an orange crystalline solid.

Two sets of correlations[197] have been reported between experimentally determined properties of annulenes and variously calculated values of 'resonance energies per π-electron' (REPE). In the first case[197a] the correlation involved the rates of formation of some annulenes determined by Sondheimer *et al.* in connection

[191] G. A. Olah, J. S. Staral, G. Liang, L. A. Paquette, W. P. Melega, and M. J. Carmody, *J. Amer. Chem. Soc.*, 1977, **99**, 3349.

[192] I. Willner, A. L. Gutman, and M. Rabinovitz, *J. Amer. Chem. Soc.*, 1977, **99**, 4167.

[193] M. Oda, H. Oikawa, N. Fukazawa, and Y. Kitahara, *Tetrahedron Letters*, 1977, 4409.

[194] R. C. Haddon, *J. Org. Chem.*, 1977, **42**, 2017.

[195] (*a*) P. Ashkenazi, D. Ginsburg, and E. Vogel, *Tetrahedron*, 1977, **33**, 1169; (*b*) J. A. Chudek, R. Foster, and E. Vogel, *J.C.S. Perkin II*, 1977, 994.

[196] S. Masamune and D. W. Brooks, *Tetrahedron Letters*, 1977, 3239.

[197] (*a*) B. A. Hess, jun., and L. J. Schaad, *J.C.S. Chem. Comm.*, 1977, 243; (*b*) B. A. Hess, jun., L. J. Schaad, and M. Nakagawa, *J. Org. Chem.*, 1977, **42**, 1669.

with their 'reactivity criterion' of aromaticity [see *Ann. Reports* (*B*), 1976, **73**, p. 237]. In the second case,[197b] the differences in ^{1}H n.m.r. chemical shifts of the inner (i) and outer (o) protons of some dehydroannulenes (71; $m = p = 0$, 1, 2, or 3) gave a good linear correlation with REPE, suggesting that chemical-shift data, at least if used in this way, can give quantitative information concerning aromaticity.

(71) $n = 1$ or 3

(72)
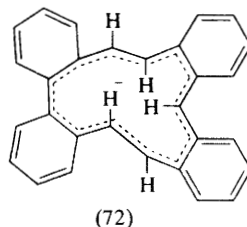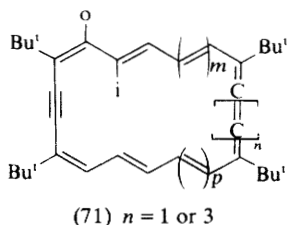
Studies of some newly synthesized model compounds have led to the conclusion that the [12]annulene rings in some previously studied di- and tri-benzannelated bisdehydro[12]annulenes are paratropic.[198a] A necessarily planar benzo-naphtho-analogue was also synthesized,[198b] and the ^{1}H n.m.r. shifts were interpreted in terms of paratropicity of the [12]annulene ring. The 2,3:6,7:8,9:12,13-tetra-benzo[13]annulenyl anion (72), the first such ion to contain only formal double and single bonds, has been prepared[199a] from the corresponding hydrocarbon.[199b] The ^{1}H n.m.r. spectrum is indicative of the reduced diatropicity caused by benzan-nelation, and, in addition, of the considerable change in ring conformation from that of the parent hydrocarbon.

Full details[200a] of the synthesis of 3,7,10,14-tetrasubstituted 1,8-bisdehy-dro[14]annulenes by the method involving cyclic dimerization of 2,3-dien-4-yne ketones, and the details[200b] of the greatly improved synthetic route to bisde-hydrobenzannulenes, have appeared. In the latter publication, the syntheses of bisdehydrobenz-[14]-, -[16]-, -[18]-, and -[20]-annulenes, as well as of some methyl derivatives, are described. It seems that the structural features which allow one to draw equivalent Kekulé structures for some dehydroannulenes [*e.g.* (73)] have little effect on their properties.[201] Diatropicity differences between (73) and


(73)
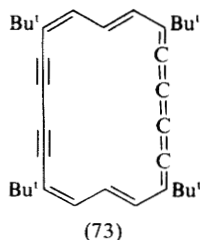
[198] (*a*) H. A. Staab and P. Günthert, *Chem. Ber.*, 1977, **110**, 619; (*b*) H. A. Staab and H. J. Shin, *ibid.*, p. 631.

[199] I. Willner, A. Gamliel, and M. Rabinovitz, (*a*) *Chem. Letters*, 1977, 1273; (*b*) *Synthesis*, 1977, 410.

[200] (*a*) K. Fukui, T. Nomoto, S. Nakatsuji, S. Akiyama, and M. Nakagawa, *Bull. Chem. Soc. Japan*, 1977, **50**, 2758; (*b*) N. Darby, T. M. Cresp, and F. Sondheimer, *J. Org. Chem.*, 1977, **42**, 1960.

[201] (*a*) M. Osuka, S. Akiyama, and M. Nakagawa, *Tetrahedron Letters*, 1977, 1649; (*b*) Y. Yoshikawa, S. Nakatsuji, F. Iwatani, S. Akiyama, and M. Nakagawa, *ibid.*, p. 1737.

(71); $m = 0$, $n = 3$, $p = 1$), for example, appear to be insignificant,[201a] and similar conclusions were also drawn from studies of a paratropic bisdehydro[16]annulene system.[201b] It seems that energy differences between non-equivalent canonical forms [*e.g.* in (71; $m = 1$, $n = 3$, $p = 1$)] are not enough to depress significantly the π-electron delocalization.

(74)

(75)
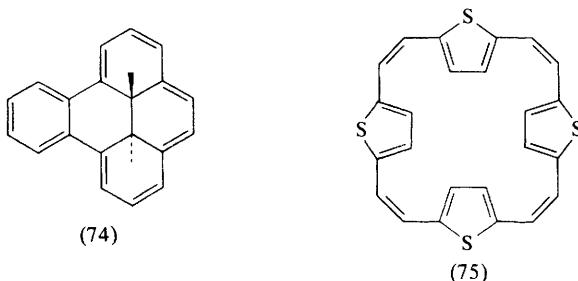
Benzo[18]annulene has been synthesized,[202] in low yield, by a route involving prototropic isomerization of an intermediate 13,14,15,16-bisdehydro-derivative. Again, annelation of the benzene ring reduces the diatropicity of the macrocyclic ring. Two further annulenes have been synthesized[203] where extensive benzannelation has removed the diatropicity of $(4n + 2)\pi$-electron macrocyclic rings, and, for example, tribenzo[*a*,*g*,*m*]-15,17-bisdehydro[18]annulene is atropic. The dimethyldihydrobenzo[*e*]pyrene (74) sustains[204] about 55% of the ring-current of the parent non-benzannelated dimethyldihydropyrene. This amount is much greater than the value for other benzannelated [14]annulenes, and reflects the greater aromaticity of the rigid dihydropyrene nucleus. All-*cis*-[2⁴](2,5)thiophenophanetetraene (75) has been prepared[205] in a one-step reaction from thiophen-2,5-dicarbaldehyde and the Wittig reagent from 2,5-bis(chloromethyl)thiophen. The compound shows a small paramagnetic ring current over the 24π-electron periphery; this is enhanced on cooling, when planar conformations become of more importance. The presence of the thiophen nuclei does not seem to interfere with the paratropicity of the molecule.

The syntheses of the dibenzannulenones (76; $n = 1$, 2, and 3) have been completed[206a] and the results for (76; $n = 1$) and (76; $n = 2$) have now been reported[206b] in full. The paratropicity exhibited by (76; $n = 1$) and (76; $n = 2$), which are, however, less paratropic than monobenzannelated analogues, disappears in (76; $n = 3$), and comparison with an acyclic analogue indicates that the latter is atropic. The first monocyclic large-ring annulenones (77; R = H) and (77; R = Me) have been synthesized.[206c] The introduction of the additional methyl group (77; R = Me) causes a change in conformation at the other *trans* double bond. Both species exhibit paratropicity, and this is enhanced on dissolution in

[202] U. E. Meissner, A. Gensler, and H. A. Staab, *Tetrahedron Letters*, 1977, 3.

[203] J. Ojima, M. Enkaku, and C. Uwai, *Bull. Chem. Soc. Japan*, 1977, **50**, 933.

[204] S. Icli, V. J. Nowlan, P. M. Rahimi, C. Thankachan, and T. T. Tidwell, *Canad. J. Chem.*, 1977, **55**, 3347.

[205] A. Strand, B. Thulin, and O. Wennerström, *Acta Chem. Scand.* (*B*), 1977, **31**, 521.
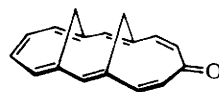
[206] (*a*) J. Ojima, M. Enkaku, and M. Ishiyama, *J.C.S. Perkin I*, 1977, 1548; (*b*) J. Ojima, Y. Yokoyama, and M. Enkaku, *Bull. Chem. Soc. Japan*, 1977, **50**, 1522; J. Ojima, M. Ishiyama, and A. Kimura, *ibid.*, p. 1584; (*c*) T. M. Cresp, J. Ojima, and F. Sondheimer, *J. Org. Chem.*, 1977, **42**, 2130.
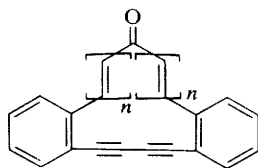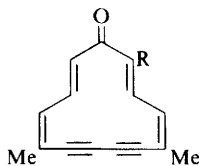
(76)   (77)   (78)

deuteriotrifluoroacetic acid. *syn*-4,13;6,11-Dimethano[15]annulenone (78) has been synthesized as an air-stable red crystalline solid, and an *X*-ray crystallographic analysis has been performed. The molecule is protonated in trifluoroacetic acid to give a delocalized annulenium ion.[207]

The syntheses of the first bridged [22]annulenes, *i.e. syn-* and *anti*-(79), have been accomplished,[208] in one step, by the dimerization of 6,11-methano[11]annulenylidene, followed by ring closure and loss of hydrogen. ¹H N.m.r. measurements show no diatropicity, and suggest that there is localization of bonds as shown in (79). The first derivative to be formed that is derived from the hitherto unknown nonalene skeleton is the planar delocalized diatropic dibenzo[*gh, op*]nonalenide dianion (80), formed[209] from the reaction of 6,14-dihydrodibenzo[*gh, op*]nonalene with butyl-lithium.
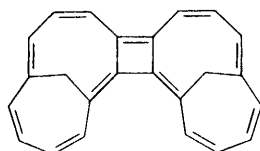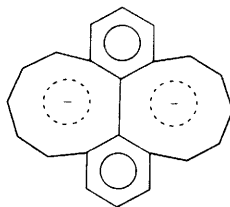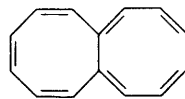

(79)   (80)   (81)

Further bicyclic compounds containing two fused macrocyclic conjugated π-systems have been reported.[210] Octalene (81) has been prepared[210a] from 1,4,5,8-tetrahydronaphthalene as a lemon-yellow air-sensitive compound. Structures involving a central double bond, or aromatic structures, were ruled out. Peripheral C=C bond shifting occurs above 80 °C. *ortho*-Fused [14]annuleno-[16]- and -[18]-annulenes analogous to the original [14]annulene [see *Ann. Reports* (*B*), 1975, **72**, p. 248] have been synthesized.[210b] The diatropicity of the 14-membered ring is reduced as the size of the fused annulene is decreased, irrespective of whether this latter annulene is (4n + 2)- or 4n-membered. Other annuleno-annulenes are (82; m = 1)[210c] and (82; m = 2),[210d] which are both strongly diatropic and quite stable, in

[207] W. Wagemann, K. Müllen, E. Vogel, T. Pilati, and M. Simonetta, *Angew. Chem. Internat. Edn.*, 1977, **16**, 170.

[208] U. H. Brinker, R. W. King, and W. M. Jones, *J. Amer. Chem. Soc.*, 1977, **99**, 3175.

[209] I. Willner and M. Rabinovitz, *J. Amer. Chem. Soc.*, 1977, **99**, 4507.

[210] (*a*) E. Vogel, H.-V. Runzheimer, F. Hogrefe, B. Baasner, and J. Lex, *Angew. Chem. Internat. Edn.*, 1977, **16**, 871; J. F. M. Oth, K. Müllen, H.-V. Runzheimer, P. Mues, and E. Vogel, *ibid.*, p. 872; (*b*) T. M. Cresp and F. Sondheimer, *J. Amer. Chem. Soc.*, 1977, **99**, 194; (*c*) S. Nakatsuji, S. Akiyama, and M. Nakagawa, *Tetrahedron Letters*, 1977, 3723; (*d*) M. Osuka, Y. Yoshikawa, S. Akiyama, and M. Nakagawa, *ibid.*, p. 3719.

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(82)   (83)
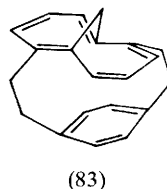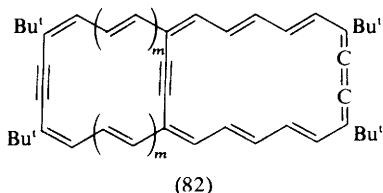
contrast to the appropriate [26]- and [30]-annulenes. In the ^{1}H n.m.r. spectra the
inner protons of the 14-membered ring appear at a much higher field than those of
the 18-membered ring, and the latter and all outer protons shift to higher field as
the distance from the central bridge increases.

Finally, the first examples of annulenophanes, *e.g.* (83), have been reported.[211]
The benzenoid protons of (83) show the expected upfield shift due to the ring
current in the [10]annulene ring. The indications are, however, that in this example
transannular interaction of π-electrons is small.

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[211] M. Matsumoto, T. Otsubo, Y. Sakata, and S. Misumi, *Tetrahedron Letters*, 1977, 4425.