Studies in the Cycloproparene Series: A Theoretical and Experimental Study of the Cyclopropabenzynes[1]

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Abstract: The highly strained cyclopropabenzynes 13 and 15 have been generated by use of the complex base system of tert-butoxide ion/amide ion, commencing with 2- and 3-bromocyclopropabenzene. Benzynes 13 and 15 have been trapped as the furan adducts 14 and 16, respectively. Fully optimized geometries of 13 and 15, their relative energies, and the strain and electronic properties, as well as the regioselectivity of addition of 13, have been examined by ab initio molecular orbital calculations. 13 is predicted to be less stable than 15 by ca. 2.5 kcal·mol⁻¹ (based on a 3-21G* energy difference of 7.4 kcal·mol⁻¹ and on an estimated correction of 5 kcal·mol⁻¹ for the difference in correlation energy). In 15 the strain of either the triple bond or the cyclopropene ring is similar to that in benzyne and cyclopropabenzene, respectively.

The study of strained organic molecules has provided a wealth of fascinating experimental chemistry and significant theoretical challenge.[2] Whilst the chemistry of the cycloproparenes, e.g., 1, has been examined systematically[3] and the bonding and energetics of the parent molecule have been accounted for on a theoretical basis,[4] the limits to which such stress and strain can be imposed upon the benzenoid framework remain to be established.

Compounds 1-3 represent the major structural types of cycloproparenes currently known. Cyclopropabenzene (1) is a surprisingly stable molecule[3] with a strain energy[5] of ca. 68 kcal·mol⁻¹, whereas cyclopropa[a]naphthalene (2)[6] and cyclo-

1

2 R=H

3 RR=benzo-
   fusion

4
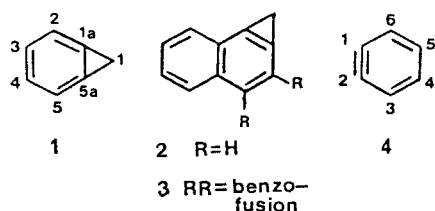
propa[l]phenanthrene (3)[7] decompose in solution at temperatures of -30 and -60 °C, respectively. On the other hand, benzyne (4), the lower homologue of the ortho-bridged aromatic series of compounds, is well established[8] as a reactive intermediate in solution. The juxtaposition of cycloproparenes with stabilities comparable to that of benzyne has encouraged us to search for cycloproparenes more strained than 4. We now report upon the cyclopropabenzynes[9,10] 13 and 15 which have been generated as reaction intermediates in solution and whose structural parameters, energetics, and reactivity have been studied by ab initio molecular orbital calculations.

The existence of highly strained dehydroaromatics has been ably demonstrated[11] with unambiguous syntheses of the cyclobutabenzynes 6 and 9 (Scheme I) which were trapped as the furan adducts 7 and 10, respectively. At the present time, cycloproparenes carrying two substituents in the aromatic ring are unknown,[3] and an analogous pathway to the cyclopropabenzynes 13 and 15 is thus thwarted. However, the existence of 3-halocyclopropabenzenes, e.g., 11, in Scheme II is well established,[12] and their 2-halo isomers, e.g., 12, have become available more recently.[1,13] Consequently, the dehydrohalogenation of 2- and 3-halocyclopropabenzenes offers a potential route to the highly strained cyclopropabenzynes 13 and 15, respectively.

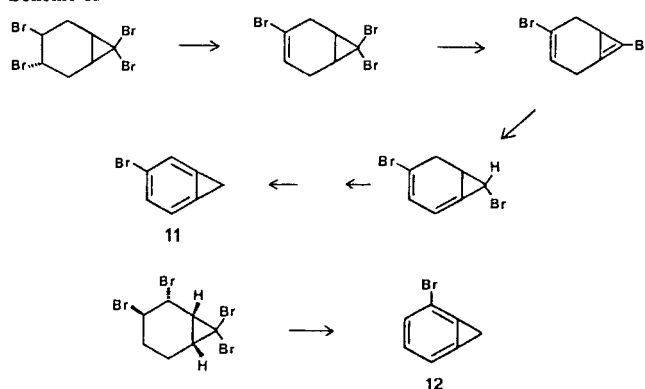## Experimental Studies

Substrates 11[12] and 12[1a,13] were prepared in accord with the published procedures (because of the strong, foul odor of the
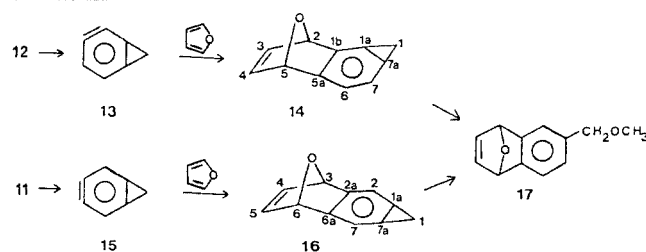
Scheme I
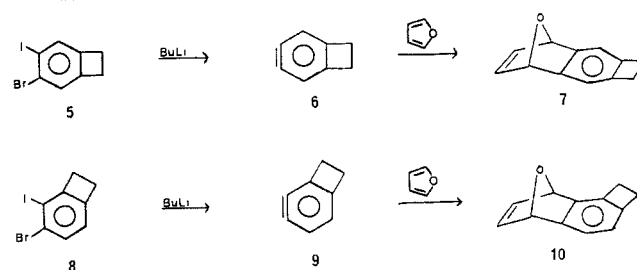
Scheme II

Scheme III

halocyclopropabenzenes, all manipulations were performed in a well-ventillated hood), and halide 12 was examined first because

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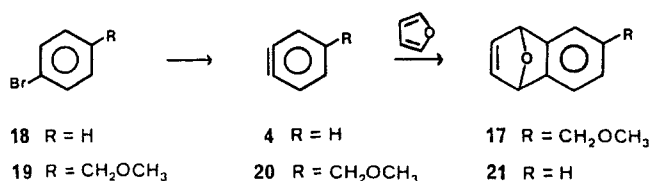
(3) For reviews see: Halton, B. Ind. Eng. Chem. Prod. Res. Dev. 1980, 19, 349-364. Billups, W. E. Acc. Chem. Res. 1978, 11, 245-251.

(4) (a) Apeloig, Y.; Arad, D. J. Am. Chem. Soc. 1986, 108, 3241. (b) Hiberty, P. C.; Ohanessian, G.; Delbecq, F. Ibid. 1985, 107, 3095-3100.

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Scheme IV



18 R = H	**4** R = H	**17** R = CH$_2$OCH$_3$
19 R = CH$_2$OCH$_3$	**20** R = CH$_2$OCH$_3$	**21** R = H

only one dehydroaromatic, namely 2,3-dehydrocyclopropabenzyne (**13**), is possible by 1,2-elimination. Attempted dehydrobromination of **12** with sodium amide in liquid ammonia leads to the consumption of substrate. However, under no circumstances (including the presence of various trapping agents) was characterizable material obtained, and no claim to the intervention of **13** can be made.

The failure of the "classical" 1,2-elimination method[8] for benzyne generation led us to search for other milder and more controllable procedures. The complex base *t*-BuO⁻/NH$_2$⁻ developed by Caubère[14a] and utilized by him for the synthesis of **4** from aryl halides[14b] is particularly effective for syn eliminations[15] and appeared ideally suited to our requirements. In the event, treatment of **12** with the complex base at ambient temperature and in the presence of furan leads to adduct **14** (10%) as an unstable oil together with unchanged **12** (13%) (Scheme III). The absence of a symmetry plane in **14** is evident from the presence of 11 distinct signals in the ^{13}C NMR spectrum and from an aromatic ortho-coupled AB system (J_{ortho} = 6.1 Hz) in the ^{1}H spectrum. Of particular significance is the presence of a single, high-field aromatic carbon doublet (δ 109.0). It is well-known[3] that the three-membered ring in the cyclopropapenes causes shielding of the *adjacent* aromatic carbon atoms by ~14 ppm, e.g., C2(5) of **1** resonate at δ 114.7. Thus, the signal at δ 109.0 is confidently assigned to C7 of **14** which is shielded by δ 15.9 when compared with the analogous carbon resonance (δ 124.9) of **21**, the furan adduct[16] of **4** (Scheme IV). Furthermore, the quaternary C1b of **14** (δ 136.0) likewise is shielded by δ 13.2. These data and the observation of an overlapping methylene AA′ system at δ 3.19 argue convincingly for the retention of the three-membered ring of **12** throughout the elimination-trapping sequence. Confirmation of this has been gained from Ag(I)-catalyzed methanolysis[17] of **14** which gives the epoxynaphthalene **17** (70%) identical with a sample independently prepared from **19** (Scheme IV).

The apparent regiospecificity in the formation of **17** from **14** deserves comment. Garratt and co-workers[17] have examined the regioselectivity of electrophilic substitution involving attack at a σ-bond of the cyclopropabenzenes. These authors have demon-

strated distinct preferences in the direction of three-membered ring cleavage of various subsituted cyclopropabenzenes. For example, cyclopropacyclobutabenzene gives ether **22** exclusively with Ag(I) in ethanol. This is explained[17] by a preference for
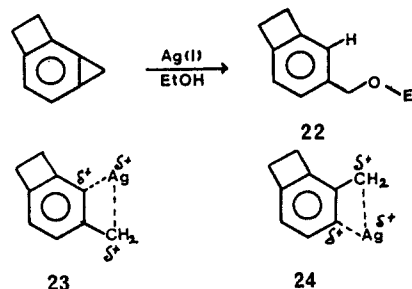
the formation of **23** over **24** since C3 is better able to stabilize positive charge. Applied to the present case, cleavage of the three-membered ring of **14** by silver ion should proceed with cationic charge at C1a to give **17** as is observed.

An analogous sequence of experiments commencing with halide **11**[12] lead to the furan adduct **16** (51%) whose symmetry plane is evident from the appearance of only six ^{13}C NMR resonaces; the protons C2(7) are shielded (δ 109.6) as expected. The ^{1}H spectrum displays a singlet (δ 7.10) for the aromatic protons H2(7) and an AB system at δ 3.18 and 3.22 (J = 2.0 Hz) for the magnetically nonequivalent methylene protons (H1). Adduct **16** is somewhat more stable than its isomer **14**. Silver-ion-catalyzed cleavage of the three-membered ring of **16** in methanol gives **17** (74%).

Similar trapping experiments with 1,3-diphenylisobenzofuran provide analogues of **14** and **16** which have proved to be too unstable for formal characterization.

The formation of **14** from **12** and **16** from **11** requires the intervention of the benzynes **13** and **15**, respectively. Whereas **13** is the only possible product of 1,2-dehydrobromination of **12**, halide **11** could lead to **13** and **15** by removal of H2 and H4, respectively. A careful examination of the NMR spectra recorded for **16** reveals the presence of traces of **14**. From the heights of the ^{13}C NMR signals of the C1 atoms (**14**, δ 18.4; **16**, δ 24.2), the proportion of **14** formed is reasonably estimated as 2%. Assuming that the "angular" benzyne **13** is efficiently trapped when generated from its 2-bromo precursor **12**, the presence of adduct **14** in only 2% yield argues strongly for high regioselectivity in the generation of the "linear" benzyne **15** from **11**. This is in accord with expectations based upon the distortions present in **1**[4,18] (a (C1a–C5a) bond length of ~1.35 Å and ∠1a23 of ~113°) and calculated[19] for benzyne (**4**) (short C1–C2 bond and large ∠123). These distortions complement one another in **15** but not in **13** and thus the "linear" benzyne **15** is expected to be thermodynamically more stable than **13**. This is borne out by our molecular orbital calculations reported below.

Theoretical Studies

Despite our success in generating the isomeric cyclopropabenzynes **13** and **15**, many interesting questions regarding these exciting molecules remain unanswered. For example, the exact geometries of **13** and **15**, their relative energies, and their

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(10) Compound **13** may also be named as bicyclo[4.1.0]hepta-1,5-dien-3-yne and compound **15** as bicyclo[4.1.0]hepta-1,3,4,5-tetraene since "fusion" nomenclature requires cyclopropabenzene (**1**) to be named as bicyclo-[4.1.0]hepta-1,3,5-triene.

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Table I. Calculated Total Energies (in hartrees) of **1, 4, 13, 15,** and Other Molecules Used in the Isodesmic Equations

method	molecule						
	1	**4**	**13**	**15**	C_6H_6	C_2H_4	C_2H_2
3-21G//3-21G	−266.952 82	−228.106 23	−265.629 50	−265.641 77	−229.419 45	−77.600 99	−76.395 96
3-21G*//3-21G	−267.204 23[a]	−228.310 58	−265.882 48	−265.894 28	−229.621 72	−77.666 03	−76.758 22

[a] −267.204 76 using a partially optimized 3-21G* geometry—see ref 4a.

strain and electronic structures are of key importance. Moreover, the reactive nature of these species makes it difficult to obtain such quantitative data experimentally. However, these goals can be achieved computationally by using reliable quantum-mechanical methods. We have therefore studied the cyclopropabenzynes **13** and **15** by standard ab initio molecular orbital methods using the GAUSSIAN 80 series of program.[21] Geometries were fully optimized by using analytical techniques[21] and the split-valence 3-21G basis set.[22] For more accurate energy comparisons at these geometries, we carried out single-point calculations using the fully polarized 3-21G* basis set[23a] (denoted as 3-21G*//3-21G). The 3-21G* basis set includes a set of six *d* functions (identical with the set used in the larger 6-31G* basis set[23b]) on all non-hydrogen atoms.[23c] For comparison we also performed similar calculations for *o*-benzyne (**4**)[19] and for cyclopropabenzene (**1**). The latter set of calculations have been reported recently.[4a] Restrictions imposed by the size of the molecules and the limitations of computer resources have prevented the use of the larger 6-31G* basis set *or* the inclusion of correlation energy in the calculations reported herein. As the inclusion of correlation energy is essential for a reliable calculation of singlet–triplet energy differences,[24] we have restricted our study to the singlet states of **13** and **15**. The analogy with **4**, which is generally accepted as a ground-state closed singlet,[19,25] coupled with the method of chemical generation and the reactions of **13** and **15** argue strongly for the same to apply to the isomeric cyclopropabenzynes. The calculated geometries of **1, 4, 13,** and **15** are presented in Figure 1, and the relevant total energies are provided in Table I.

The calculations show that **15** is considerably more stable than its angular isomer **13**. The calculated energy differences are 7.7 and 7.4 kcal·mol⁻¹ at the 3-21G and 3-21G* levels, respectively, and thus, the inclusion of polarization functions leads to only a small change in the energy difference. The effect of correlation energy on the **15**–**13** energy difference could not be evaluated directly, due to the relatively large size of these molecules. However, Radom et al. have shown in a very recent paper that in the related 1,3- and 1,4-benzidynes (i.e., C_6H_2 isomers) the addition of correlation energy stabilizes the 1,3-benzidynes relative to the 1,4-isomer by 5 kcal·mol⁻¹.[19j] Assuming that this correction applies also to **13** and **15**, then the best current theoretical estimate is that **15** is more stable than **13** by ca. 2.4 kcal·mol⁻¹. This stability order is fully consistent with the experimental finding that **11** gives **15** predominantly; **13** is present to an extent of ca. 2%. This product ratio (98:2) corresponds at room temperature to a 2.3 kcal·mol⁻¹ energy difference between the competing processes that lead to these products. Note that the excellent agreement between theory and experiment may be somewhat fortuitous because the observed **15:13** product ratio is determined not simply by their relative stabilities but also by the relative acidities of the protons α and β to the cyclopropene ring in pre-
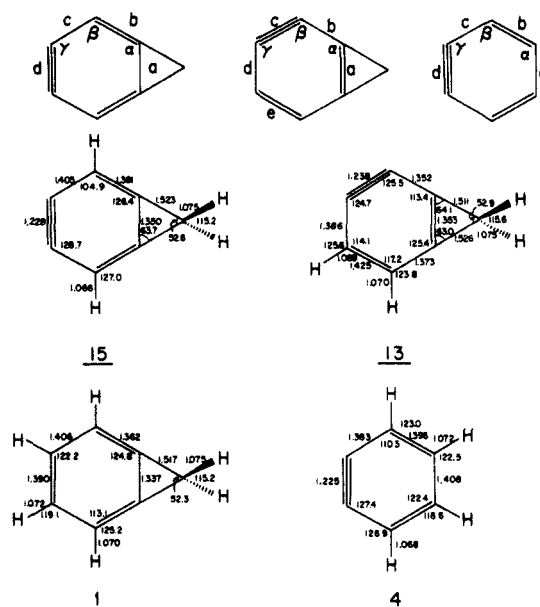
Figure 1. Geometrical parameters and 3-21G calculated geometries of cyclopropabenzene (**1**), benzyne (**4**), and *o*- and *p*-cyclopropabenzynes (**13** and **15**, respectively). C_{2v} symmetry was assumed for **1, 4,** and **15** and C_s symmetry was used for **13**.

cursor **11**. The proton α to the cyclopropene (H2) is expected to be more acidic than the β proton (H4) (see also below). This acidity difference will favor the formation of **13**.

One may ask why it is that **15** is more stable than **13**. Electronically, one might expect **13** to be favored, due to conjugation between the fused cyclopropene ring and the acetylenic in-plane π-orbital. Calculations for ethynylcyclopropane estimate[26] this preference as 1.0–1.7 kcal·mol⁻¹. Obviously, some other factor offsets the conjugative advantage of **13**. A glance at Figure 1 reveals that the geometry of **13** is much more distorted than that of **15** and that it is thus more strained. An examination of the structures of benzyne (**4**) and of cyclopropabenzene (**1**) (also provided in Figure 1) shows that the distortions present in **1** and **4** complement one another in **15** but not in **13**. Thus, the acetylenic bond length is 1.225 Å, in **4**, and the angle γ is widened to 127.4°, while β shrinks to 110.3° and α widens to 122.4° (for the notations of bond angles see Figure 1).[27] In **1** the fused C1a–C5a bond is short (1.337 Å), the angle α widens to 124.8°, β decreases to 113.1°, and γ is 122.2°.[4a] Thus, in both molecules the angles adjacent to the distorting function (α and γ in **1** and **4**, respectively) are widened but β shrinks significantly. These two angular requirements are satisfied concurrently in **15** but not in **13**. Thus, in **15** β is smaller (104.9°), while α (126.4°) and γ (128.7°) are larger than 120°, in harmony with their "natural" values in **1** and **4**. In **13**, on the other hand, the situation is entirely different. The triple bond imposes a wide β angle of 125.5° which clearly overwhelms the contrasting geometrical requirements of the fused cyclopropene ring that operate to reduce β to values well below 120°. Similarly, angle α is 113.4° in **13** which deviates significantly from its value of 124.8° in **1**. Following the strong dis-

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(26) (a) Greenberg, A.; Stevenson, T. A. *J. Am. Chem. Soc.* **1985,** *107*, 3488–3494. (b) Similarly, at 3-21G, 3-methylbenzyne is more stable than 4-methylbenzyne by 1.8 kcal·mol⁻¹. See also ref 37.

(27) Our 3-21G calculations give bond lengths which are generally shorter by 0.01–0.02 Å than the previously reported 4-31G,[19f] 6-31G,[19a] and 6-31G*[19a] calculations. The agreement for the bond angles is good.

tortions in the bond angles the bond lengths in **13** also differ from those in **15**. In particular, the triple bond of **13** is 0.01 Å longer than that of **15**, indicative of a weaker bond. Furthermore, bond b is shorter in **13** than in **15** by 0.03 Å and bond e of **13** is unusually long (1.425 Å). We conclude that the highly distorted geometry of **13** contains significant additional angle strain to raise its energy relative to that of **15**.

One may also ask whether the triple bond of **15** is more strained than in benzyne. The calculated hydrogenation energies of benzyne (eq 1) and of **15** (eq 2) show that in both molecules the triple bond is strained essentially to the same degree. Thus, at 3-21G* the hydrogenation energies of **4** and **15** differ by only 0.8 kcal·mol⁻¹. The hydrogenation of **13** is of course more exothermic than that of **15** by 7.4 kcal·mol⁻¹ (at 3-21G*, 2.4 kcal·mol⁻¹ after correction for correlation energy—see above), which reflects the higher strain involved. It should be noted that the absolute values of these hydrogenation energies are not expected to be in good agreement with experiment because eq 1–3 are not isodesmic, i.e.,

$$4 + H_2 \rightarrow C_6H_6 \quad\quad (1)$$

$$\Delta E \text{ (kcal·mol}^{-1}) = -119.4 \text{ (3-21G)}; \quad -118.1\text{(3-21G*)}$$

$$15 + H_2 \rightarrow 1 \quad\quad (2)$$

$$\Delta E \text{ (kcal·mol}^{-1}) = -118.0 \text{ (3-21G)}; \quad -117.3\text{(3-21G*)}$$

$$13 + H_2 \rightarrow 1 \quad\quad (3)$$

$$\Delta E \text{ (kcal·mol}^{-1}) = -125.7 \text{ (3-21G)}; \quad -124.7\text{(3-21G*)}$$

the types and numbers of bonds on the two sides of the equation differ.[28] However, a *comparison* of the hydrogenation energies of **4** and **15** is isodesmic and thus the calculated *relative energies* are expected to remain the same at higher levels of theory. On the basis of prior experience[4a] and on the fact that ΔE for eq 1 is −115.7 at 6-31G*//6-31G*, −94.4 at MP2/6-31G*//6-31G*,[19a] and −98 ± 5 kcal·mol⁻¹ experimentally,[29] we estimated that the calculated hydrogenation energies at 3-21G*//3-21G are too large by ca. 20 kcal·mol⁻¹. We expect the experimental hydrogenation energy of **15** to be comparable to that of benzyne, viz., 98 ± 5 kcal·mol⁻¹.

Similarly we find that the triple bond in **15** does not induce additional strain upon the fused cyclopropene ring. This is best shown by comparing the energies of hydrogenative ring cleavage of **1** (eq 4) and **15** (eq 5). As before these equations are not

$$1 + H_2 \longrightarrow C_6H_5CH_3 \quad\quad (4)$$

$$\Delta E \text{(kcal·mol}^{-1}) = -103.0 \text{ (3-21G)}; -93.5\text{(3-21G*)}$$

$$15 + H_2 \longrightarrow \text{[C}_6\text{H}_5\text{CH}_3\text{]} \quad\quad (5)$$

$$\Delta E \text{(kcal·mol}^{-1}) = -101.1 \text{ (3-21G)}$$
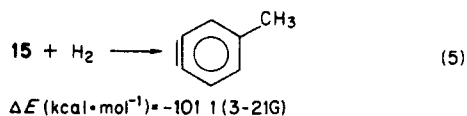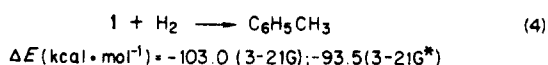
isodesmic, but a comparison between them is. We conclude in complete harmony with the discussion of the geometries presented above that in **15** there is no additional strain resulting from the "linear" fusion of a cyclopropane ring and a benzyne skeleton. This is not the case for "angular" fusion as in **13**.

The heats of formation of **15** and **13** can be estimated from the calculated energy of the isodesmic[28] (eq 6) and the known experimental heats of formation of **1**,[3,4a] C_2H_4, and C_2H_2.[30] Thus,

$$15 + C_2H_4 \rightarrow 1 + C_2H_2 \quad\quad (6)$$

$$\Delta E \text{ (kcal·mol}^{-1}) = 66.5 \text{ (3-21G)}; \quad 64.1 \text{ (3-21G*)}$$

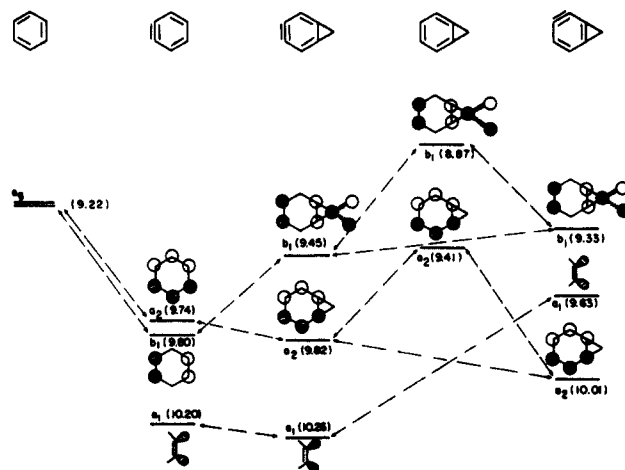at 3-21G*, $\Delta H_f°$ (**15**) = 90 + 54.3 − 12.4 + 64.1 = 196.0

Figure 2. Calculated (3-21G) ionization potentials (in eV)[32] of benzene, **1**, **4**, **13**, and **15**.

kcal·mol⁻¹.[31] Using the same procedure,[31] we calculate that $\Delta H_f°$ (**4**) = 126.5 kcal·mol⁻¹ at 3-21G*//3-21G, a value only slightly in excess of experiment (118.5 kcal·mol⁻¹).[29] By using this difference (8 kcal·mol⁻¹) as a correction factor for **15**, we estimate that $\Delta H_f°$ (**15**) = 190 ± 7 kcal·mol⁻¹. $\Delta H_f°$ (**13**) is higher by ca. 3–7 kcal·mol⁻¹. These predictions await experimental testing.

The electronic structures of **13** and **15** are also of interest. By using Koopman's theorem[32] and the 3-21G calculated orbital energies, we have correlated the energies of the three highest occupied molecular orbitals of **1**, **4**, **13** and **15** as shown in Figure 2. In the ensuing discussion we use the 3-21G values; the 3-21G* ionization potentials are generally lower by 0.2–0.3 eV.

The π-orbitals of benzene are degenerate. In benzyne this degeneracy is lifted slightly: the b_1 orbital decreases in energy due to better overlap across the shorter triple bond, and the a_2 orbital rises in energy. The b_1–a_2 splitting is 0.06 eV. Both b_1 and a_2 are pulled to lower energies (by 0.55 eV relative to benzene) by the inductive effect of the triple bond. The acetylenic in-plane π-orbital (of a_1 symmetry) lies considerably lower in energy at −10.20 eV. In a very recent study Dewar reported[33] the first photoelectron (PE) spectrum of **4** and determined these ionization potentials (in eV) as −9.24 (a_2), −9.75 (b_1), and −9.87 (π). At the MNDO level, Dewar[33] calculates (in eV) −9.57 (a_2), −9.83 (b_1), and −9.93 (π). In **15** the energy of the in-plane π-orbital (−10.26 eV) is almost unchanged relative to **4**. The benzene-type b_1 and a_2 orbitals are at −9.41 and −9.82 eV, respectively. Relative to **4** the b_1 orbital of **15** is pushed to higher energy (by 0.42 eV) by interaction with the π_{CH_2}-orbital of the external methylene group;[4a] the a_2 orbital is pulled down slightly in energy (by 0.25 eV relative to **4**), due to the inductive effect of the cyclopropene ring. The b_1–a_2 splitting in **15** and **1**[4a] is similar, but because of the triple bond these orbitals are at lower energies in **15**. Thus, the PE spectrum of **15** is predicted to be a superposition of the PE spectra of **1** and **4**. In **13** there is a further splitting of the b_1–a_2 π-pair, but the major change relative to **15** is the much higher energy of the in-plane π-orbital which appears at −9.63 eV (Figure 2). This is a further manifestation of the additional strain that is present in the acetylenic bond of **13** relative to **15** and **4**. The cyclopropene Walsh orbitals in both **13** and **15** lie much lower in energy than the π-type orbitals, i.e., at energies lower than −12.2 eV, as discussed for **1**.[4a]

Finally, a comment on the reactivities of **13** and **15** is appropriate. The reactions of **13** and **15** are highly exothermic, and the relevant transition states should thus resemble the reactants[34a]

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(28) For a general discussion, see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

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(30) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: New York, 1970.

(31) Note: This value does not include the zero-point energy of **15**, and it is not corrected for changes in $\Delta H_f°$ in going from 0 to 298 K. The values used for **1**, C_2H_4, and C_2H_2 are at 298 K and include zero-point energies.[30] The same comments apply to benzyne.

(32) Koopmans, T. *Physica* **1934**, *1*, 104–113.

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and reflect part of the 3–7 kcal·mol⁻¹ energy difference that exists between them.[34] Based on the principle of Bell et. al.,[34c] "angular" **13** is expected to be more reactive than "linear" **15**.[34] Bent alkynes, and benzynes in particular, are found to exhibit a special reactivity for nucleophiles. Recent theoretical studies[35] have attributed this increased electrophilicity of bent alkynes to their lower LUMO energy. If this hypothesis is valid, then we expect that **15** (and **13**) should be more reactive toward nucleophiles than benzyne since the calculated 3-21G π^*-energies are 2.18 and 2.39 eV for **15** (or **13**)[36] and **4**, respectively. By comparison the π^* 3-21G energy is 6.42 eV in dimethylacetylene.

A question of special interest concerns the regioselectivity of addition to unsymmetrical **13**. We expect *both* electrophiles and nucleophiles to add preferentially to the position meta to the cyclopropene ring, viz., C3 (eq 7). Thus, the addition of ENu
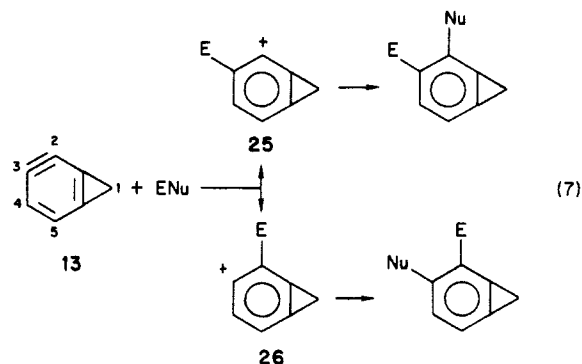
(E = electrophile; Nu = nucleophile) to **13** would give different products depending upon whether the first step of the sequence involves the incorporation of the E or Nu fragment (eq 7). This prediction is based upon the ability of a cyclopropane ring to stabilize adjacent charge when in an appropriate conformation.[37,38] For example, proton addition to C3 of **13** to give **25** (E = H) is more exothermic by 22 kcal·mol⁻¹ (3-21G*) than addition to C2 to give **26** (E = H) (eq 7).[39] Similarly, in the carbanionic analogues, the negatively charged equivalent to **25**, where E is replaced by Nu, is expected to be more stable than **26**.[37,38]

The degree of regioselectivity in such additions depends, of course, on the amount of charge that is developed in the transition state. Recent calculations[35a] have found considerable charge separation in the transition structures for the addition of water and hydroxide ion to bent alkynes. As these compounds closely model benzyne,[35a] we believe that the regioselectivity in the reactions of **13** can be significant,[40] as is observed for substituted benzynes.[25] Further experimental and theoretical studies of this interesting question are planned.

Experimental Section

Melting points were determined by using a Reichert hot stage melting point apparatus and are uncorrected. Microanalyses were performed by the Microanalytical Unit, Otago University, Dunedin, New Zealand. High-resolution mass measurements were made on an A.E.I. MS902 instrument. NMR spectra were recorded for deuteriochloroform solu-

tions with Me₄Si as the internal standard by using a Varian Assoc. FT80A instrument operating at 20.00 MHz for ¹³C and 79.56 MHz for ¹H. Infrared spectra were recorded for Nujol mulls or as thin films on a Pye Unicam SP3-100 spectrometer. All reactions were performed under oxygen-free nitrogen atmospheres.

Bromocyclopropabenzenes 11 and 12. Dehydrobromination of 1α,3α,4β,6α- and 1α,2α,3β,6α-tetrabromobicyclo[4.1.0]heptane according to the published procedure[1a] furnished **11** (53%) and **12** (48%), respectively.

Generation and Trapping of Benzynes 4, 13, 15, and 20. I. Preparation of the Complex Base. A solution of *tert*-butyl alcohol (1.2 g, 16 mmol) in THF (3 mL) was added dropwise to a stirred suspension of sodium amide (2.0 g, 50 mmol) in the same solvent (4 mL) maintained under nitrogen. The mixture was heated at 35–40 °C for 1.5 h and then cooled (ice–water bath) before immediate use.

II. Dehydrobromination and Trapping Reactions. To the cooled and stirred complex base generated as above was added a solution of the appropriate halide (3.3 mmol) in furan (8 mL). Stirring was continued for 3 h at room temperature and then the reaction quenched by pouring into ice–water (50 mL). The aqueous mixture was extracted with CH₂Cl₂ (2 × 75 mL), and the combined organic extracts were washed (H₂O, 2 × 75 mL), dried (MgSO₄), and concentrated to an oil.

(a) The oil obtained from reaction with bromobenzene (**18**) slowly solidified. Recrystallization (ether × 2) furnished 1,4-epoxy-1,4-dihydronaphthalene (**21**) (260 mg, 54%) as white neeldes: mp 55–56 °C [lit.[16] 55–56 °C]; ¹H NMR δ 5.63 (narrow m, 2 H, H1(4)); 6.85–7.24 (m, 4 H, aromatic), 6.93 (t, 2 H, *J* = 1.0 Hz, H2(3)); ¹³C NMR δ 82.2 (d, C1(4)), 120.1 (d, C5(8)), 124.9 (d, C6(7)), 143.0 (d, C2(3)), 149.2 (s, C4a(8a)).

(b) The oil obtained from reaction with bromocyclopropabenzene **12** was subjected to chromatographic separation on silica gel (light petroleum/ethyl acetate, 9:1 elution) whereupon unchanged **12** (73 mg, 13%) was eluted first and then **2,5-epoxy-2,5-dihydro-1*H*-Cyclopropa[a]-naphthalene (14)** (50 mg, 10%) as an unstable pale-yellow oil: IR ν 3000, 2940, 2860, 1680, 1398, 1280, 998, 837, 697, 640 cm⁻¹; ¹H NMR δ 3.19 (t, 2 H, *J* = 5 Hz, CH$_A$H$_{A'}$), 5.70 (t, 2 H, *J* = 1.0 Hz, H2(5)), 6.78 (d, 1 H, *J* = 6.1 Hz, H7), 6.99 (t, 2 H, *J* = 1.0 Hz, H3(4)), 7.13 (d, 1 H, *J* = 6.1 Hz, H6); ¹³C NMR δ 18.4 (t, C1), 79.9 (d, C2 or C5), 81.8 (d, C5 or C2), 109.0 (d, C7), 115.0 (s, C1a), 120.2 (d, C6), 122.5 (s, C7a), 136.0 (s, C1b), 141.5 (d, C3 or C4), 143.3 (d, C4 or C3), 151.4 (s, C5a); mass spectrum, *m/e* 156.0570 (C₁₁H₈O requires 156.0575) (M⁺·, 75%), 128.0623 (C₁₀H₈ requires 128.0625) (M⁺· – CO, 100%).

(c) The oil obtained from reaction with bromocyclopropabenzene **11** was subjected to column chromatography as for (b) above to give **3,6-epoxy-3,6-dihydro-1*H*-Cyclopropa[b]naphthalene (16)** (260 mg, 51%) (with shorter reaction times, the yield of **16** decreases and unchanged **11** (up to 29%) is returned) as an unstable pale-yellow oil: IR ν 3000, 2930, 2840, 1658, 1360, 1274, 1101, 981, 690, 641 cm⁻¹; ¹H NMR δ 3.18 (d, 1 H, *J* = 2.0 Hz, *anti*-H1), 3.22 (d, 1 H, *J* = 2.0 Hz, *syn*-H1), 5.62 (narrow m, 2 H, H3(6)), 6.97 (narrow m, 2 H, H4(5)), 7.10 (s, 2 H, H2(7)); ¹³C NMR δ 24.2, (t, C1), 82.1 (d, C3(6)), 109.6 (d, C2(7)), 124.6 (s, C1a(7a)), 143.4 (d, C4(5)), 152.0 (s, C2a(6a)); mass spectrum, *m/e* 156.0569 (C₁₁H₈O requires 156.0575) (M⁺·, 62%), 128.0623 (C₁₀H₁₀ requires 128.0625), (M⁺· – CO, 100%).

(d) Microdistillation of the oil obtained from reaction with 1-bromo-4-(methoxymethyl)benzene (**19**)[20] (synthesized from *p*-bromotoluene via 1-bromo-4-(bromomethyl)benzene) afforded **1,4-epoxy-6-(methoxymethyl)-1,4-dihydronaphthalene (17)** (383 mg, 62%) as a clear, colorless oil: IR ν 2920, 1278, 1110, 998, 853, 711 cm⁻¹; ¹H NMR δ 3.34 (s, 3 H, OCH₃), 4.37 (s, 2 H, ArCH₂O), 5.67 (s, 2 H, H1(4)), 6.84–7.22 (complex m, 3 H, aromatic), 6.97 (t, 2 H, *J* = 1.0 Hz, H2(3)); ¹³C NMR δ 58.0 (q, OCH₃), 74.7 (t, ArCH₂O), 82.2 (d, C1 or C4), 82.3 (d, C4 or C1), 119.9 (d, C5 or C8), 120.0 (d, C8 or C5), 124.4 (d, C6), 135.4 (s, C7), 143.0 (d, C2(3)), 148.7 (s, C8a), 149.8 (s, C4a). Anal. Calcd for C₁₂H₁₂O₂: C, 76.7; H, 6.5. Found: C, 76.6; H, 6.4.

Reaction of 14 and 16 with AgI-MeOH. The epoxycyclopropanaphthalenes **14** and **16** in CCl₄ (5 mL) were stirred at room temperature for 30 min with AgNO₃ (~0.3 M equiv) in dry MeOH (<100 mL). The solutions were concentrated to dryness in vacuum and extracted with ether (100 mL), and the organic layer was dried (MgSO₄) and concentrated to a pale-yellow oil. Preparative TLC (light petroleum/ether, 3:2 elution) gave a single major band from each substrate which was extracted with CH₂Cl₂ (100 mL). Concentration in vacuum afforded **17** (70% from **14**; 74% from **16**) identical in all respects with the sample recorded in II(d) above.

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(36) There is practically no difference in the LUMO energies of **13** and **15**.

(37) de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 809–826.

(38) In highly stabilized carbanions the effect of a cyclopropyl group is small,[37] but this probably does not apply to less stable carbanions. Thus, at STO-3G *c*-C₃H₅CH₂⁻ is more stable than (CH₃)₂CHCH₂⁻ by 14.3 kcal·mol⁻¹.

(39) Apeloig, Y.; Arad, D. *J. Am. Chem. Soc.* **1985**, *107*, 5285–5286.

(40) Whilst regioselectivity is observed only when the addition reactions involve a positive activation barrier, a higher regioselectivity is expected for a weak rather than strong nucleophiles.[25,35a]

The Preparation and Characterization of Radical Cation Salts Derived from Perfluorobenzene, Perfluorotoluene, and Perfluoronaphthalene

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Abstract: The salts $C_6F_6^+AsF_6^-$ (yellow), $C_6F_5CF_3^+AsF_6^-$ (lime green), and $C_{10}F_8^+AsF_6^-$ (dark green) may be prepared by electron oxidation of the appropriate perfluoro aromatic molecule with $O_2^+AsF_6^-$. Other O_2^+ salts can be similarly employed as can the more strongly oxidizing transition-metal hexafluorides, but salts of the latter are more labile than their AsF_6^- relatives. $C_6F_6^+AsF_6^-$ is a convenient electron oxidizer ($C_6F_6AsF_6 + C_{10}F_8 \rightarrow C_{10}F_8AsF_6 + C_6F_6$) since that which remains from the reaction decomposes at room temperature to volatile products ($2C_6F_6AsF_6 \rightarrow C_6F_6 + 1,4\text{-}C_6F_8 + 2AsF_5$). Magnetic susceptibilities for $C_6F_6AsF_6$ and $C_{10}F_8AsF_6$ approximate to Curie law behavior, and g values are close to free-electron values. X-ray diffraction data (single crystal) show $C_6F_6AsF_6$ to be primitive rhombohedral with $a_0 = 6.60$ (1) Å, $\alpha = 106.0$ (1)°, $V = 246.1$ Å³, $Z = 1$, probable space group $R\overline{3}$, and (powder data) $C_{10}F_8AsF_6$ to be tetragonal with $a_0 = 8.27$ (5) Å, $c_0 = 18.57$ (s) Å, $V = 1270$ Å, $Z = 4$. Salts derived from the monocyclic perfluoro aromatics are thermally unstable but can be kept below -15 °C. The perfluoronaphthalene salts are indefinitely stable at room temperatures. All hydrolyze rapidly. The products of thermal decomposition of the hexafluoroarsenates of the monocyclic cation salts parallel the products of the attack by F^-. The latter reaction products are in the molar ratios indicated by the following equations: $2C_6F_6^+ + 2F^- \rightarrow C_6F_6 + 1,4\text{-}C_6F_8$; $2C_6F_5CF_3^+ + 2F^- \rightarrow C_6F_5CF_3 + 1,3\text{-}C_6F_7CF_3$. The $1,3\text{-}C_6F_7CF_3$ isomerizes to a 1:1 mixture with $1,4\text{-}C_6F_7CF_3$ over several days in the presence of fluoro acids. Mechanisms for the formation of the dienes are discussed.

Radical cations derived from perfluoro aromatic molecules were first described by Bazhin et al.[1,2] The species were made in super acid or oleum solutions and were unambiguously characterized by ESR spectroscopy.[1-5] Such species have also been proposed as intermediates in the oxidative fluorination of aromatic molecules by high-valent metal fluorides[6] such as cobalt trifluoride, by bromine trifluoride,[7] and by xenon difluoride.[8] They have also been invoked in the electrochemical fluorination[9] of aromatic molecules in the presence of F^-. Salts of such radical cation species were unknown prior to the synthesis of $C_6F_6^+AsF_6^-$ in these laboratories.[10,11]

An earlier attempt by Jha[12] to prepare $C_6F_6^+PtF_6^-$ from C_6F_6 and PtF_6 yielded a promising orange-yellow solid at low temperatures. A similar material obtained[11] using IrF_6, decomposed well below 0 °C. Kinetically stable salts sufficiently stable to be manipulated at room temperatures were first obtained[10,11] by exploiting dioxygenyl salts as oxidizers:

$$C_6F_6 + O_2AsF_6 \rightarrow C_6F_6AsF_6 + O_2$$

$$C_6F_6 + O_2Sb_2F_{11} \rightarrow C_6F_6Sb_2F_{11} + O_2$$
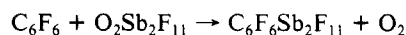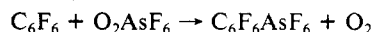
The range of salts has been extended since the preliminary report.[10] Utilization of the low-melting solvent SO_2ClF has improved yields and provided access to less thermally stable perfluoro aromatic radical cation salts. Less powerful oxidizers than O_2^+ salts are needed for the synthesis of $C_{10}F_8^+$ and polycyclic cation salts which have much higher thermal stability than their monocyclic relatives. The preparation and characterization of monocation salts derived from C_6F_6, C_6F_5 CF_3, and $C_{10}F_8$ is reported here. The preparation and some properties of the pentafluoropyridine radical cation salts have been described elsewhere.[13]

Particular attention has been given to the products of thermal decomposition of the radical cation salts and the products of F^- attack, since the sets of products are related. Salts of the single-ring aromatics are thermally unstable at room temperature but can be kept below 258 K. Their thermal decomposition gives an equimolecular mixture of the parent fluoro aromatic and a perfluorocyclohexadiene. The initial diene product is a specific isomer. This provides clean high-yield syntheses for those dienes and provides insight into the reaction mechanisms.

Results and Discussion

Composition of the Salts and Structural and Magnetic Properties. The high ionization potential of C_6F_6 ($\sim$10 eV)[14] requires

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