Reaction of Diphenylmethylene with Non-conjugated Dienes

By **J. E. Fox** and **D. W. Young,** * School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

Reactions of the triplet carbene, diphenylmethylene, with the non-conjugated annular dienes, norbornadiene and cyclo-octa-1,5-diene, have been studied in the hope of achieving transannular addition which might give useful synthetic entry into bridged systems. New compounds were obtained but there was no evidence for the presence of any transannular adducts.

SKELL [1-3] has suggested that, whereas singlet carbene may add concertedly to an olefin to yield a cyclopropane, triplet carbene cannot add concertedly to an olefin with spin conservation. The singlet reaction would result in retention of the stereochemistry of the original olefin in the product cyclopropane whereas the triplet reaction would result in loss of this stereospecificity.

These suggestions have been found to be in good agreement with empirical evidence, since carbenes which have been considered to be in the singlet state, such as dihalogenocarbenes, and methylene generated by direct photolysis of diazomethane or of keten, add to olefins in solution with retention of the original olefin stereochemistry in the resultant cyclopropane. [1-5] Non-stereospecific addition has been demonstrated by methylene generated by irradiation of diazomethane

[1] P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.,* 1956, **78**, 4496, 6427.

[2] R. C. Woodworth and P. S. Skell, *J. Amer. Chem. Soc.,* 1959, **81**, 3383.

[3] P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.,* 1956, **78**, 5430.

[4] W. von E. Doering and P. LaFlamme, *J. Amer. Chem. Soc.,* 1956, **78**, 5447.

[5] B. S. Rabinovitch, E. Tschuikow-Roux, and E. W. Schlag, *J. Amer. Chem. Soc.,* 1959, **81**, 1081.

in the vapour phase in the presence of an inert gas.[6–9] There is spectroscopic evidence [10] that methylene obtained in this way is in the triplet state. Duncan and Cvetanović [11] have obtained non-stereospecific addition on photolysis of keten or diazomethane sensitised by triplet mercury (Hg 6^3P_1) and Hammond [12,13] has used the triplet sensitiser benzophenone in diazomethane photolysis and obtained non-stereospecific additions. Jones [14] and (earlier) Murahashi [15] have shown that triplet fluorenylidene reacts in a non-stereospecific manner with olefins, although Murahashi has shown that two proven triplet species in fact react stereospecifically with olefins.[16,17]

We have observed that, although there are numerous examples of the reaction of carbene with non-conjugated dienes [18–27] and with conjugated polyenes,[20,28–43] there is no reported case of transannular attack of the carbene simultaneously on more than one olefinic linkage in the case of non-conjugated systems. The carbene used with non-conjugated olefins is most likely to be in the singlet state or present as a metal complex and hence should add concertedly to one double bond. Skell [1–3] has suggested that spin multiplicity considerations would make addition of a singlet carbene to an olefin an allowed process and Hoffmann [44] has reached similar conclusions from consideration of orbital symmetry requirements.

Since we were interested in the possibility of trans-annular additions of carbenes to non-conjugated dienes for use in the synthesis of certain bridged natural products, we decided to investigate the reaction of such dienes with triplet carbenes. In view of Skell's spin multiplicity arguments, the triplet species would not add concertedly to one olefinic bond and should form an intermediate diradical which might add to a suitably placed second olefinic linkage if this reaction were competitive with the spin inversion required for cyclopropane formation.

We chose as a model carbene for this reaction diphenylmethylene, which has been shown to be a triplet by physical methods.[45–47] Diphenylmethylene generated photolytically has been shown to react with olefins non-stereospecifically,[48,49] and unlike singlet electrophilic carbenes it reacts with oxygen to form benzophenone.[50] The diene substrates we chose were norbornadiene (I) and cyclo-octa-1,5-diene. Free radical attack on norbornadiene takes place predominantly from the less hindered exo-face but there is evidence [51,52] that endo-attack will also occur. Attack from the endo-face is, obviously, required for transannular carbene addition. It has been observed that ethoxycarbonylmethylene attacks from both exo- and endo-faces of norbornadiene,[27] and concerted cycloadditions give tetracyclic transannular addition products such as (II) and (III) when norbornadiene (I) reacts with tetracyanoethylene,[53] benzyne,[54] or methylphosphonous di-

[6] F. A. L. Anet, R. F. W. Bader, and A-M. Van der Auwera, J. Amer. Chem. Soc., 1960, 82, 3217.

[7] H. M. Frey, J. Amer. Chem. Soc., 1960, 82, 5947.

[8] H. M. Frey, Proc. Roy. Soc. (A), 1959, 251, 575.

[9] R. F. W. Bader and J. G. Generosa, Canad. J. Chem., 1965, 43, 1631.

[10] G. Herzberg and J. Shoosmith, Nature, 1959, 183, 1801.

[11] F. J. Duncan and R. J. Cvetanović, J. Amer. Chem. Soc., 1962, 84, 3593.

[12] K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, J. Amer. Chem. Soc., 1961, 83, 2397.

[13] K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, J. Amer. Chem. Soc., 1962, 84, 1015.

[14] M. Jones, jun., and K. R. Rettig, J. Amer. Chem. Soc., 1965, 87, 4013, 4015.

[15] E. Funakubo, I. Moritani, T. Nagai, S. Nishida, and S. Murahashi, Tetrahedron Letters, 1963, 1069.

[16] S. Murahashi, I. Moritani, and M. Nishino, J. Amer. Chem. Soc., 1967, 89, 1257.

[17] I. Moritani, S. Murahashi, M. Nishino, Y. Yamamoto, K. Itoh, and N. Mataga, J. Amer. Chem. Soc., 1967, 89, 1259.

[18] S. Winstein and J. Sonnenberg, J. Amer. Chem. Soc., 1961, 83, 3235.

[19] G. I. Fray, J. Chem. Soc., 1963, 4284.

[20] K. Hofmann, S. F. Orochena, S. M. Sax, and G. A. Jeffrey, J. Amer. Chem. Soc., 1959, 81, 992; K. Hofmann, S. F. Orochena and C. W. Yeo, ibid., 1957, 79, 3608.

[21] E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, Tetrahedron Letters, 1963, 673; E. Vogel and H. D. Roth, Angew. Chem. Internat. Edn., 1964, 3, 228.

[22] A. J. Birch, J. M. H. Graves, and F. Stansfield, Proc. Chem. Soc., 1962, 282.

[23] A. J. Birch, J. M. H. Graves, and J. B. Siddall, J. Chem. Soc., 1963, 4234.

[24] W. Von E. Doering and A. K. Hoffmann, J. Amer. Chem. Soc., 1954, 76, 6162.

[25] S. D. Koch, R. M. Kliss, D. V. Lopiekes, and R. J. Wineman, J. Org. Chem., 1961, 26, 3122.

[26] V. Franzen, Rev. Chim. (Roumania), 1962, 7, 859.

[27] R. R. Sauers and P. E. Sonnet, Chem. and Ind., 1963, 786.

[28] W. Von E. Doering and W. R. Roth, Tetrahedron, 1963, 19, 715.

[29] W. M. Wagner, Proc. Chem. Soc., 1959, 229.

[30] D. D. Phillips, J. Amer. Chem. Soc., 1955, 77, 5179.

[31] F. Korte, K-H. Buchel, and F. F. Wiese, Annalen, 1963, 664, 114.

[32] S. Akiyoshi and T. Matsuda, J. Amer. Chem. Soc., 1955, 77, 2476.

[33] A. P. ter Borg and A. F. Bickel, Proc. Chem. Soc., 1958, 283.

[34] B. Fohlisch, Chem. Ber., 1964, 97, 88.

[35] C. Grundmann and G. Ottmann, Annalen, 1953, 582, 163.

[36] P. Weyerstahl, D. Klamann, M. Fligge, C. Finger, F. Nerdel, and J. Buddrus, Annalen, 1967, 710, 17.

[37] R. C. Woodworth and P. S. Skell, J. Amer. Chem. Soc., 1957, 79, 2542.

[38] A. Ledwith and R. M. Bell, Chem. and Ind., 1959, 459.

[39] M. Orchin and E. C. Herrick, J. Org. Chem., 1959, 24, 139.

[40] N. P. Neureiter, J. Org. Chem., 1959, 24, 2044.

[41] B. Grzybowska, J. H. Knox, and A. F. Trotman-Dickenson, J. Chem. Soc., 1961, 4402; 1962, 3826.

[42] H. M. Frey, Trans. Faraday Soc., 1962, 58, 516.

[43] V. Franzen, Chem. Ber., 1962, 95, 571.

[44] R. Hoffmann, J. Amer. Chem. Soc., 1968, 90, 1475.

[45] R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. A. Yager, J. Amer. Chem. Soc., 1962, 84, 3213.

[46] A. M. Trozzolo, R. W. Murray, and E. Wasserman, J. Amer. Chem. Soc., 1962, 84, 4990.

[47] A. M. Trozzolo, Accounts Chem. Res., 1968, 1, 329.

[48] R. M. Etter, H. S. Skovronek, and P. S. Skell, J. Amer. Chem. Soc., 1959, 81, 1008.

[49] G. L. Closs and L. E. Closs, Angew. Chem. Internat. Edn., 1962, 1, 334.

[50] W. Kirmse, L. Horner, and H. Hoffmann, Annalen, 1958, 614, 19.
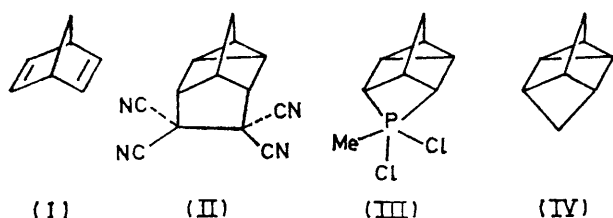
[51] D. I. Davies and L. T. Parfitt, J. Chem. Soc. (C), 1967, 2691.

[52] T. V. Van Auken and E. A. Rick, Tetrahedron Letters, 1968, 2709.

[53] A. T. Blomquist and Y. C. Meinwald, J. Amer. Chem. Soc., 1959, 81, 667.

[54] I. Tabushi, H. Yamada, Z. Yoshida, and H. Kuroda, Tetrahedron Letters, 1971, 1093.

chloride.[55] The parent tetracyclic system (IV) has been synthesised [56] by more conventional means.

(I)   (II)   (III)   (IV)

Diphenylmethylene was prepared by photolysis of diphenyldiazomethane [57] under dry nitrogen (Hanovia 125 W lamp) and was treated *in situ* with norbornadiene (I) in dry ether. The mixture was washed with acetic acid, neutralised, and worked-up to yield a crude solid which was separated into eleven components by chromatography on silicic acid.

Tetraphenylethylene [58,59] was obtained, as was 9,10-diphenylphenanthrene.[60,61] The former would result from the attack of diphenylmethylene on diphenyldiazomethane [62] and the latter by photolysis of the tetraphenylethylene in the presence of oxygen,[63] although precautions had been taken to exclude both oxygen and water. That some oxygen was in fact present was shown by the finding of benzophenone [58] among the products, an indication of the intermediacy of triplet diphenylmethylene.[50] Bisdiphenylmethyl ether (V),[64] which might arise from insertion of diphenylmethylene into diphenylmethyl alcohol, was found, and diphenylmethyl alcohol [58] itself was possibly the compound eluted last from the column. Another product, diphenylmethyl acetate, would arise from the esterification of acetic acid with diphenyldiazomethane in the work-up, and a further compound was identified as benzophenone azine [65] (VI) from its physical and spectroscopic properties. This is an expected product of the reaction of diphenylmethylene with diphenyldiazomethane.[62]

(V)   (VI)
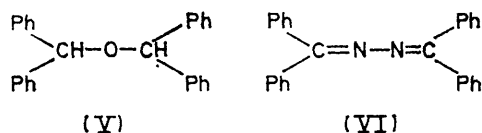
As well as the foregoing seven compounds, the reaction mixture contained four new compounds which were products of reaction between the two reagents. The first of these was a white solid, $C_{20}H_{18}$, m.p. 53—69°. The n.m.r. spectrum was consistent with structure (VII). The *exo*-geometry was assigned to the structure in view of its synthesis from the *exo*-pyrazoline (VIII), which was also a component of the reaction mixture.

The second new compound (22% of the reaction mixture) was a solid, $C_{20}H_{18}N_2$, m.p. 145·5—147°. The n.m.r. spectrum was consistent with structure (VIII), with proton H_E showing a similar chemical shift to proton H_A in the pyrazoline (IX) [66] (τ 4·93). The *exo*-configuration was assigned to the molecule in view of the equivalence of the olefinic protons H_C and the non-equivalence of the bridge protons H_A and $H_{A'}$. In the *endo*-isomer, which we also isolated from the reaction mixture, the olefinic protons are non-equivalent and the bridge protons are equivalent.

The Δ^1-pyrazoline (VIII) on pyrolysis yielded the cyclopropane (VII), thus inter-relating the two structures. Compound (VIII) could also be catalytically hydrogenated to yield the dihydro-compound (X), m.p. 116—123°. The n.m.r. spectrum of this compound, elucidated by double-irradiation experiments, was consistent with the compound being derived from (VIII), showing signals for ten aromatic protons, a one-proton quartet at τ 4·96 (H_E coupling to H_F, J_{EF} 6 Hz, and to H_D, J_{ED} 7 Hz; irradiation at H_F and H_D separately each caused collapse of the quartet to a doublet), a one-proton multiplet at τ 6·92 (H_F), and a one-proton octet at τ 7·06 (H_D). Both the H_F and H_D signals collapsed on irradiation at the frequency of H_E. A one-proton multiplet at τ 7·66 was assigned to H_B and the six protons H_A and H_C resonated as a complex multiplet between τ 8·4 and 8·8. Irradiation at the frequency of H_B simplified the H_D octet and irradiation at that of H_D simplified the H_B multiplet. The remaining coupling of H_D was probably long-range coupling with H_A. This is analogous to a long-range coupling of H-2 with the *anti*-7-proton in *exo*-2-cyanobicyclo[2,2,1]hept-5-ene [67] (XI) (J_{27} 3 Hz).

A second isomeric pyrazoline, $C_{20}H_{18}N_2$, m.p. 65—70 °C, was obtained from the reaction mixture in very low yield and this was assigned the *endo*-configuration (XII) on the basis of the n.m.r. spectrum and decoupling evidence. The n.m.r. spectrum had signals for ten aromatic protons, a one-proton quartet at τ 4·21 (H_E; J_{EF} 5·5, J_{ED} 7 Hz) which collapsed to doublets on irradiation at the frequencies of H_F and H_D, respectively, a one-proton quartet at τ 4·32 (H_C; $J_{CC'}$ 6, J_{CF} 3 Hz) which collapsed to doublets on irradiation at the frequencies of $H_{C'}$ and H_F respectively, a one-proton quartet at τ 5·25 ($H_{C'}$; $J_{CC'}$ 6, $J_{C'B}$ 3 Hz) which collapsed to doublets, on irradiation at H_C and H_B respectively, a one-proton multiplet at τ 6·4 (H_F), a one-proton

[55] M. Green, *J. Chem. Soc.*, 1965, 541.
[56] P. K. Freeman, V. N. M. Rao, and G. E. Bigham, *Chem. Comm.*, 1965, 511.
[57] L. I. Smith and K. L. Howard, *Org. Synth.*, 1955, Coll. Vol. III, p. 351.
[58] R. C. Weast (ed.), 'Handbook of Chemistry and Physics,' 45th edn., The Chemical Rubber Co., Cleveland, Ohio.
[59] G. Kortüm and G. Dreesen, *Chem. Ber.*, 1951, **84**, 182.
[60] R. C. Fuson and P. Tomboulian, *J. Amer. Chem. Soc.*, 1957, **79**, 956.
[61] C. S. Schoepfle and J. D. Ryan, *J. Amer. Chem. Soc.*, 1932, **54**, 3687.

[62] H. Staudinger and O. Kupfer, *Ber.*, 1911, **44**, 2197.
[63] See for example, F. B. Mallory, C. S. Wood, J. T. Gordon, L. C. Lindquist, and M. L. Savitz, *J. Amer. Chem. Soc.*, 1962, **84**, 4361.
[64] 'Beilstein's Handbuch der Organischen Chemie,' Springer Verlag, Berlin.
[65] E. R. Blout, V. W. Eager, and R. M. Gofstein, *J. Amer. Chem. Soc.*, 1946, **68**, 1983.
[66] S. G. Cohen and R. Zand, *J. Amer. Chem. Soc.*, 1962, **84**, 586.
[67] J. C. Davis and T. V. Van Auken, *J. Amer. Chem. Soc.*, 1965, **87**, 3900.

quartet at τ 6·71 (H$_D$; J_{DB} 4, J_{DE} 7 Hz) which collapsed to doublets on irradiation at H$_E$ and H$_B$ respectively, and a one-proton multiplet at τ 7·2 (H$_B$). The bridge

(VII) (VIII) (IX)

(X) (XI) (XII)

(XIII) (XIV)
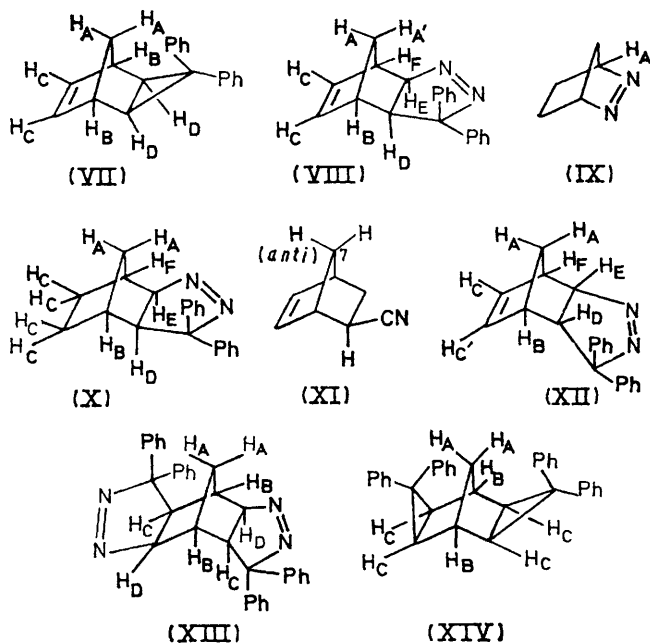
protons H$_A$ resonated as a two-proton triplet at τ 8·56. The non-equivalence of the olefinic protons H$_C$ and H$_{C'}$ and the equivalence of the bridge protons H$_A$ is consistent with assignment of the *endo*-configuration to (XII) and of the *exo*-configuration to the isomeric (VIII).

Another compound from the reaction mixture, C$_{33}$H$_{28}$N$_4$, m.p. 216—218°, was obtained in 2·6% yield. The n.m.r. spectrum was consistent with the structure (XIII) with signals for twenty aromatic protons, a two-proton doublet at τ 5·02 (H$_D$; J_{DC} 6 Hz), a two-proton doublet at τ 7·12 (H$_C$; J_{DC} 6 Hz), a two-proton singlet at τ 7·58 (H$_B$), and a two-proton singlet at τ 9·47 (H$_A$). The simplicity of the spectrum precludes all but the di-*exo*-isomer (XIII), possessing C_2 symmetry, rather than the alternative di-*exo*-isomer with the mirror plane of symmetry in which the bridgehead protons H$_B$ would not be expected to be equivalent. The asymmetric *exo,endo*-isomer would give rise to a spectrum of greater complexity and a di-*endo*-isomer would not be sterically feasible.

Pyrolysis of the dipyrazoline gave rise to compound (XIV), C$_{33}$H$_{22}$, m.p. 198—200°. The n.m.r. spectrum was very simple, with signals for twenty aromatic protons, a two-proton singlet at τ 7·18 (H$_B$), a four-proton singlet at τ 8·23 (H$_C$), and a two-proton singlet at τ 9·86 (H$_A$). The shielding of the bridge protons and the deshielding of the cyclopropyl protons lends

further support to the assignment of the di-*exo*-geometry to this series.

No products other than those already reported were observed after intensive t.l.c. examination of all fractions, and so we had failed in our endeavour to obtain transannular attack on the system. Since completion of our studies,[68] Filipescu[69] has published his work on photolysis of 9-diazofluorene in norbornadiene, both neat and in ethereal solution. He obtained the *exo*-pyrazoline (XV) and found no evidence of carbene intermediacy. In our work with diphenyldiazomethane, we find, like Filipescu, that the major product is the *exo*-1,3-dipolar adduct (VIII), but we also find smaller amounts of the *endo*-adduct (XII) and the di-*exo*-diadduct (XIII). We have also some evidence of carbene intermediates being present in our isolation of tetraphenylethylene, benzophenone azine (VI), and benzophenone itself

(XV) (XVI)
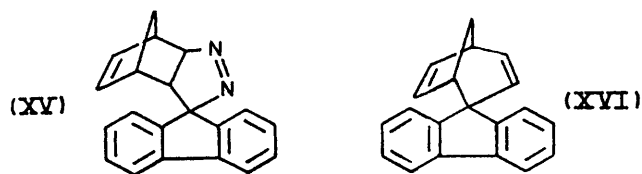
from the reaction mixture. On pyrolysis of the *exo*-pyrazoline (VIII) we obtained only the cyclopropane (VII) and none of the rearranged compound corresponding to compound (XVI) obtained by Filipescu on pyrolysis of his derivative (XV).

The reaction of diphenylmethylene with cyclo-octa-1,5-diene (XVII), where the two double bonds have no homoconjugative interaction, was then examined to see if there were any transannular products. Transannular reactions of this diene with borane[70] and with carbon monoxide in the presence of palladium catalysts[71] are known, and diphenylmethylene adducts such as (XVIII) should not be as strained as the product (XIX) of photochemical isomerisation of cyclo-octa-1,5-diene (XVII).[72,73]

Diphenyldiazomethane was photolysed under nitrogen in the presence of cyclo-octa-1,5-diene (Hanovia 125 W medium-pressure mercury lamp). Sixteen compounds were isolated from the crude mixture. As before, tetraphenylethylene, benzophenone azine, benzophenone, and diphenylmethanol were present, as also were 1,1,2,2-tetraphenylethane and tetraphenylethylene oxide.

Three further products were a solid, m.p. 50—53° (0·3% yield) and two gums (0·8 and 0·7% yields). They all had parent ions in the mass spectrum at m/e 214 (C$_{16}$H$_{22}$) and similar n.m.r. spectra, with olefinic proton signals in the τ 4·0—5·0 region, allylic protons in the τ 7·0—8·0 region and, with the exception of one of the gums, aliphatic protons in the τ 8·0—9·0 region. In all cases the ratio of olefinic to aliphatic protons was 8 : 14 and in no case was there any appreciable u.v.

[68] J. E. Fox, D.Phil. Thesis, Sussex, 1968.
[69] N. Filipescu and J. R. DeMember, *Tetrahedron*, 1968, **24**, 5181.
[70] E. F. Knights and H. C. Brown, *J. Amer. Chem. Soc.*, 1968, **90**, 5280.
[71] S. Brewis and P. R. Hughes, *Chem. Comm.*, 1966, 6.
[72] R. Srinivasan, *J. Amer. Chem. Soc.*, 1964, **86**, 3318.
[73] J. E. Baldwin and R. H. Greeley, *J. Amer. Chem. Soc.*, 1965, **87**, 4514.

absorption (apart from end-absorption). This indicates that the compounds were dimers of the cyclo-octadienyl radical with four olefinic hydrogen atoms and non-conjugated double bonds. On the basis of the number of aliphatic protons which were not allylic, the solid of m.p. 50—53 °C was assigned structure (XX); the gum eluted first structure (XXI), and the gum eluted last structure (XXII). Attempted ozonolysis and methylation studies gave no reliable information on these structures but since they were obviously not the desired transannular adducts no further structural work was done.

Three further compounds, a solid, m.p. 58—62° (2% yield) and two gums (0·43 and 2·3% yields) had parent ions in the mass spectrum at m/e 274 ($C_{21}H_{22}$). If there were to be a transannular adduct it would be

(XVII)   (XVIII)   (XIX)   (XX)

(XXI)   (XXII)

(XXIII)   (XXIV)   (XXV)
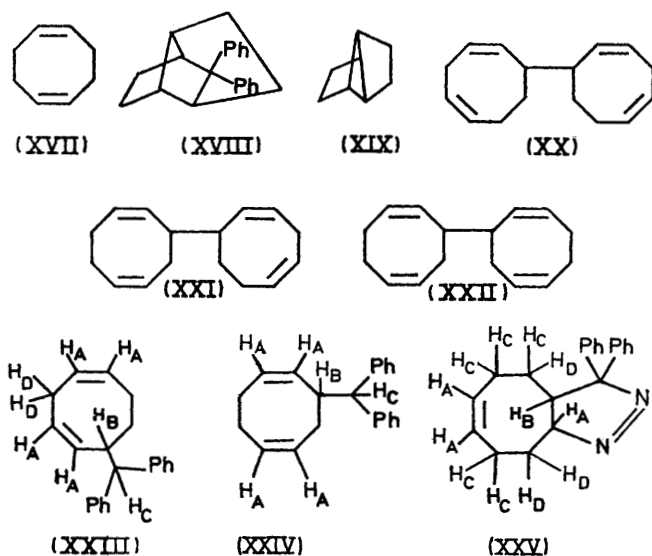
one of these. None of the products had any u.v. absorption other than aromatic and end-absorption. Each had, in the n.m.r. spectrum, signals for ten aromatic and four olefinic protons, and so we had isolated three insertion products of diphenylmethylene and a con-conjugated cyclo-octadiene. The solid of m.p. 58—62° was tentatively assigned structure (XXIII) and the gum obtained in 2·3% yield structure (XXIV), from the n.m.r. spectra.

A pyrazoline $C_{21}H_{22}N_2$ was present as an oil in 1·5% yield. The n.m.r. spectrum was consistent with the compound having structure (XXV), with signals for ten aromatic protons at τ 2·78, multiplets at τ 3·33 (1H) and 4·43 (2H) for H_A, a one-proton multiplet at τ 7·17 for H_B, and two areas of four protons each at τ 7·75 and between τ 8·0 and 9·0 which were assigned to H_C and H_D, respectively.

Three other compounds isolated had m/e 333, 184, and 290, respectively as the peaks of highest mass in their mass spectra. These were not present in sufficient amounts to allow us to assign structures, but they were evidently not the desired transannular adducts.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were determined for solutions in carbon tetrachloride (unless otherwise stated) on a Perkin-Elmer 237 instrument; u.v. spectra were measured for solutions in methanol on a Unicam SP 800 spectrophotometer; and n.m.r. spectra (solutions in CDCl$_3$) were recorded on a Varian A60A or HA100 instrument. All decoupling experiments were performed with the latter instrument. Mass spectra were recorded on an A.E.I. MS9 instrument and microanalyses were performed by Mr. B. J. Saunderson and his staff.

Photolysis of Diphenyldiazomethane in the Presence of Norbornadiene.—Benzophenone hydrazone [57] (20 g) was converted into diphenyldiazomethane [74] and photolysed without further purification with redistilled norbornadiene (40 ml) in dry diethyl ether (100 ml) under nitrogen, by use of a Hanovia water-cooled 125 W medium-pressure mercury lamp and a Pyrex filter. After 19 h the deep red solution had become yellow and more diethyl ether (100 ml) was added. The solution was washed with dilute aqueous acetic acid, followed by saturated aqueous sodium hydrogen carbonate and then water. The solution was dried (Na$_2$SO$_4$) and evaporated under reduced pressure to give a solid (22 g). A portion of this was chromatographed on silicic acid (B.D.H.; 100 g).

Elution with light petroleum (b.p. 60—80°)–benzene (1 : 1) (10 ml fractions) first yielded a mixture of products which were separated further by preparative t.l.c. [0·5 mm of silica gel (Merck GF$_{254}$); light petroleum (b.p. 60—80°)–benzene (4 : 1)].

3,3-*Diphenyltricyclo*[3,2,1,0^{2,4}]*oct-6-ene* (VII), R_F 0·6, sublimed readily at 40° and 0·05 mmHg to yield a white solid, m.p. 53—69° (Found: C, 93·0; H, 7·0. $C_{20}H_{18}$ requires C, 93·0; H, 7·0%), m/e 258 (M^+) and 167 (base peak), τ 2·8 (10H, m, aromatic), 3·52 (2H, t, H_C, J 1 Hz), 6·98 (2H, s, H_B), 8·3 (2H, s, H_D), and 9·27 (2H, q, H_A and $H_{A'}$, $J_{AA'}$ 9 Hz).

Tetraphenylethylene R_F 0·47, crystallised from light petroleum (b.p. 60—80°) as prisms, m.p. 225—227°, $\lambda_{max.}$ 238 and 305 nm, $\nu_{max.}$ 1600 cm^{-1}, m/e 332 (M^+), τ 3·01 (s) (lit.,[58] m.p. 223—224°).

9,10-*Diphenylphenanthrene*, R_F 0·42, crystallised from light petroleum (b.p. 60—80°)–benzene (1 : 1) as needles, m.p. 238°, $\lambda_{max.}$ 252, 258, and 300 nm, m/e 330, τ 3·05 (m) (lit.,[60,61] m.p. 235°, $\lambda_{max.}$ 252, 258, and 300 nm).

Bisdiphenylmethyl ether (V), R_F 0·26, crystallised from light petroleum (b.p. 60—80°); m.p. 107—108°, aromatic u.v. absorption, m/e 238, 182, and 166, τ 2·8 (20H, m) and 4·71 (2H, s) (lit.,[64] m.p. 109°).

Further elution of the silicic acid column with light petroleum (b.p. 60—80°)–benzene (1 : 1) gave benzophenone azine (VI) (4%), which crystallised as pale yellow needles, m.p. 165—165·5°, $\lambda_{max.}$ 235, 278, and 315 nm, m/e 360 and 283, τ 2·75 (m) (lit.,[65] m.p. 163—164°).

Fractions eluted after this yielded a yellow oil (0·7 g) which appeared as one spot on t.l.c. [silica gel (Merck GF$_{254}$); chloroform–benzene (1 : 9)]; m/e 226 ($C_{15}H_{14}O_2$) and 182 ($C_{13}H_{10}O$), τ 2·3 (10H, m, aromatic), 2·7 (25H, m, aromatic), 3·16 (1H, s, Ph_2CH·O), and 8·02 (3H, s, Ac). The data are best rationalised if the oil is a 2·5 : 1 mixture of benzophenone and diphenylmethyl acetate.

The fractions eluted next with the same solvent system

[74] L. F. Fieser and M. Fieser, ' Reagents for Organic Synthesis,' vol. 1, Wiley, New York, 1967, p. 338.

yielded 5,5-*diphenyl*-3,4-*diaza*-exo-*tricyclo*[5,2,1,0^{2,6}]*deca*-3,8-*diene* (VIII) (1·65 g, 22%), which crystallised from light petroleum (b.p. 60—80°), m.p. 145—147°, $\nu_{max.}$ (KBr) 1600 cm^{-1} (N=N) (Found: C, 83·8; H, 6·05; N, 9·55. C$_{20}$H$_{18}$N$_2$ requires C, 83·9; H, 6·35; N, 9·8%), m/e 258 ($M - N_2$) and 167, τ 2·6 (10H, m, aromatic), 3·72 (2H, s, H$_C$), 4·74 (1H, d, J 6, H$_E$), 6·38 (1H, s, H$_F$), 7·11 (1H, d, J 6 Hz, H$_D$), 7·72 (1H, s, H$_B$), and 8·84 and 9·26 (each 1H, d, J 9 Hz, H$_A$ and H$_{A'}$).

Further elution of the column with light petroleum (b.p. 60—80°)–benzene (1 : 1) yielded the *endo*-diazatricyclodecadiene (XII) in low yield as a solid, m.p. 65—70°, m/e 258 ($M - N_2$), τ 2·8 (10H, m, aromatic), 4·21 (1H, q, J 5·5 and 7 Hz, H$_E$), 4·32 (1H, q, J 5·5 and 3 Hz, H$_C$), 5·25 (1H, q, J 3 and 6 Hz, H$_{C'}$), 6·4br (1H, s, H$_F$), 6·71 (1H, q, J 4 and 7 Hz, H$_D$), 7·2br (1H, s, H$_B$), and 8·56 (2H, t, J 1 Hz, H$_A$).

The final fractions to be eluted with light petroleum (b.p. 60—80°)–benzene (1 : 1) yielded 5,5,11,11-*tetraphenyl*-3,4,9,10-*tetra-aza*-exo,exo-*tetracyclo*[5,5,1,0^{2,6}0^{8,12}]*trideca*-3,9-*diene* (XIII), which crystallised from light petroleum (b.p. 60—80°) and chloroform as prisms, m.p. 216—218° (Found: C, 82·0; H, 6·05; N, 10·9. C$_{33}$H$_{28}$N$_4$ requires C, 82·45; H, 5·85; N, 11·65%), m/e 424 ($M - 2N_2$), $\nu_{max.}$ (KBr) 1585 cm^{-1} (N=N), τ 2·7 (20H, m, aromatic), 5·02 (2H, d, J 6 Hz, H$_D$), 7·12 (2H, d, J 6 Hz, H$_C$), 7·58 (2H, s, H$_B$), and 9·47 (2H, s, H$_A$).

Elution of the silicic acid column with chloroform–benzene (1 : 9) gave a yellow oil in 1·1% yield, homogeneous (R_F 0·066) on t.l.c. [silica gel (Merck GF$_{254}$); chloroform–benzene (1 : 9)], $\nu_{max.}$ 3620sh (free OH) and 3400—3550 cm^{-1} (H-bonded OH), m/e 184 and 105, τ 2·73 (m, aromatic).

Pyrolysis of the Pyrazoline (VIII).—The pyrazoline (VIII) (30 mg) was heated under nitrogen in an oil-bath at 160° for 1 h. Chromatography of the crude product on preparative plates [0·75 mm silica gel (Merck GF$_{254}$); benzene–light petroleum (b.p. 60—80°) (1 : 4)] gave a white solid (20 mg), which sublimed at 110° and 0·1 mmHg to yield needles, m.p. 65—81°, spectroscopically identical with the compound assigned structure (VII) from the photolysis reaction.

Reduction of the Pyrazoline (VIII).—A solution of the pyrazoline (VIII) (23 mg) in AnalaR ethyl acetate (15 ml) was hydrogenated at 20 °C and atmospheric pressure over 10% palladium–charcoal (470 mg). After 1·97 ml of hydrogen had been absorbed, the solution was filtered through Celite and the residue was washed with ethyl acetate. The combined filtrate and washings were evaporated to dryness and the resultant oil was chromatographed on thin-layer plates [0·75 mm silica gel (Merck GF$_{254}$); benzene]. A solid (6·5 mg) obtained crystallised from aqueous ethanol to yield 5,5-diphenyl-3,4-diazatricyclo[5,2,1,0^{2,6}]dec-3-ene (X), m.p. 116—123°, m/e 260 ($M - N_2$), τ 2·4—3·0 (10H, m, aromatic), 4·96 (1H, q, J 6 and 8 Hz, H$_E$), 6·92 (1H, m, H$_F$), 7·06 (1H, oct, J 2·4 and 8 Hz, H$_D$), 7·66 (1H, m, H$_B$), and 8·4—8·8 (6H, m, H$_A$ and H$_C$).

Pyrolysis of the Pyrazoline (XIII).—The pyrazoline (XIII) (7·7 mg) was heated under nitrogen in an oil-bath at 180 °C for 4 h. The crude solid was chromatographed [0·75 mm silica gel (Merck GF$_{254}$); benzene–light petroleum (b.p. 60—80°) (1 : 4)] to yield 3,3,7,7-*tetraphenyltetracyclo*[3,3,1,0^{2,4}0^{6,8}]*nonane* (XIV) (6·3 mg, 82%) which crystallised as prisms from light petroleum (b.p. 60—80°), m.p. 198—200° (Found: C, 93·45; H, 6·65. C$_{33}$H$_{28}$ requires

C, 93·35; H, 6·65%), m/e 424, τ 2·8 (20H, m, aromatic), 7·18 (2H, s, H$_B$), 8·23 (4H, s, H$_C$), and 9·86 (2H, s, H$_A$).

Photolysis of Diphenyldiazomethane in the Presence of Cyclo-octa-1,5-diene.—Cyclo-octa-1,5-diene (Koch–Light) was fractionated from anhydrous sodium sulphate under nitrogen. A fraction of b.p. 148—149° at atmospheric pressure was shown to be 98·9% homogeneous by g.l.c. [5 ft column of 5% w/w β,β-oxydipropionitrile on Chromosorb G (100—120 mesh) at 60 °C; flow rate of 50 ml min^{-1}; nitrogen as carrier gas]. This fraction (80 ml) in diethyl ether (30 ml) with diphenyldiazomethane [prepared [74] from benzophenone hydrazone (22 g)] was irradiated for 36 h under nitrogen (Hanovia 125 W medium-pressure mercury lamp). Solid 1,1,2,2-tetraphenylethane (3·2 g) was recovered from the mixture and the organic phase was washed with dilute hydrochloric acid, saturated aqueous sodium hydrogen carbonate, and water and dried (Na$_2$SO$_4$). Removal of the solvent under reduced pressure left a solid (35·5 g), 5·8 g of which was chromatographed on a column of silica gel (250 g).

Elution with light petroleum (b.p. 60—80°) gave bi(cyclo-octa-2,5-dienyl) (XX) (13 mg), m.p. 50—53°, $\nu_{max.}$ 1650 cm^{-1} (non-conjugated olefinic), m/e 214 (C$_{16}$H$_{22}$), τ 4·0—5·0 (8H, m, olefinic) and 7—9·2 (14H, m, aliphatic protons, 10 allylic and 4 non-allylic).

Elution with benzene–light petroleum (b.p. 60—80°) (1 : 40) gave cyclo-octa-2,6-dienylcyclo-octa-2,5-diene (XXI) as a homogenous gum (53 mg), R_F 0·6 on t.l.c. [silica gel (Merck GF$_{254}$); benzene–light petroleum (b.p. 60—80°) (1 : 4)], $\nu_{max.}$ 1650 cm^{-1}, M^+ 214, τ 4·0—5·0 (8H, m, olefinic) and 7·0—9·0 (14H, m, aliphatic protons, 12 allylic and 2 non-allylic).

Elution with benzene–light petroleum (b.p. 60—80°) (1 : 20) gave bi(cyclo-octa-2,6-dienyl) (XXII) as a homogeneous gum (42 mg), R_F 0·543 on t.l.c. [silica gel (Merck GF$_{254}$); benzene–light petroleum (b.p. 60—80°) (1 : 4)], M^+ 214, $\nu_{max.}$ 1655 cm^{-1}, τ 4·47 (8H, m, olefinic) and 7·4—7·8 (14H, m, allylic).

Further elution with the same system yielded a homogeneous gum (27 mg), R_F 0·466 on t.l.c. [silica gel (Merck GF$_{254}$); benzene–light petroleum (b.p. 60—80°) (1 : 4)], M^+ 274, τ 2·7 (10H, m, aromatic), 4·38 (3·2H, m, olefinic), and 7·5—9·0 (10·3H, m).

Elution with benzene–light petroleum (b.p. 60—80°) (1 : 14) gave a compound tentatively identified as 6-diphenylmethylcyclo-octa-1,4-diene (XXIII) (129 mg), m.p. 58—62°, M^+ 274, τ 2·82 (10H, s, aromatic), 4·1—5·2 (4H, m, H$_A$), 6·33br (2H, s, H$_B$ and H$_C$), 7·37br (2H, s, H$_D$), and 7·32—9·2 (4H, m, H$_E$).

An oil (254 mg) was obtained on eluting with benzene–light petroleum (b.p. 60—80°) (1 : 9 and 1 : 5) and this was further chromatographed on 0·75 mm plates of silica gel (Merck GF$_{254}$) [with chloroform–benzene (1 : 9)]. Two compounds were obtained: (i) a solid (20 mg), m.p. 226—227 °C, identical (mixed m.p.) with tetraphenylethylene; (ii) 3-diphenylmethylcyclo-octa-1,5-diene (XXIV), a gum (132·6 mg), $\nu_{max.}$ 1950, 1880, and 1750 cm^{-1} (all weak), m/e 274 (C$_{21}$H$_{22}$), τ 2·8 (10H, m, aromatic), 4·42 (4H, m olefinic), 6·33 (d, J 5 Hz, H$_B$ and H$_C$), and 7·75 (6H, m, allylic protons).

Further elution of the silica gel column with benzene–light petroleum (b.p. 60—80°) (1 : 4) gave an oil which was separated into three compounds on preparative t.l.c. The first was tetraphenylethylene oxide, m.p. 205—208 °C, m/e 348 (C$_{26}$H$_{20}$O); only aromatic proton signals in the

n.m.r. spectrum (lit.,[64] m.p. 203°). The second compound was an oil, m/e 184 ($C_{13}H_{12}O$), and the third, an oil, had m/e 333. Neither of these was present in sufficient amounts to allow identification.

Elution of the silica gel column with benzene–light petroleum (b.p. 60—80°) (1 : 1) gave 1,1,2,2-tetraphenyl-ethane (326 mg), which crystallised from light petroleum (b.p. 60—80°) as needles, m.p. 212—214°, m/e 334 ($C_{26}H_{22}$), τ 2·85 (20H, m aromatic) and 5·22 (2H, s, doubly benzylic protons), identical with the material which had crystallised out of the reaction mixture (lit.,[58] m.p. 212·5°).

Further elution with benzene–light petroleum (b.p. 60—80°) (1 : 1) gave benzophenone azine (103 mg), which crystallised from light petroleum as needles, m.p. and mixed m.p. 163—165°. Elution with benzene gave an oil which resisted attempts at crystallisation but whose spectra were identical with those of authentic benzophenone.

Continuing elution with benzene gave a gum (86 mg) which was further chromatographed on preparative plates [0·75 mm silica gel; ethyl acetate–carbon tetrachloride (1 : 9)] to give three compounds. The first was 11,11-*di-phenyl*-9,10-*diazabicyclo*[6,3,0]*undeca*-4,9-*diene* (XXV), a gum (31 mg), $\nu_{max.}$ 1600 cm^{-1} (N=N), m/e 274 ($M - N_2$), τ 2·78 (10H, m, aromatic), 2·78 (10H, m, aromatic), 3·33 (1H, m) and 4·43 (2H, m) (H_A), 7·17 (1H, m, H_B), 7·75br (4H, m, H_C), and 8·0—9·0 (4H, m, H_C).

The second compound from the preparative plate was diphenylmethanol [75] (9 mg), which sublimed at 50° and 0·05 mmHg to give a solid, m.p. 65 °C, $\nu_{max.}$ 3620 cm^{-1} (free OH), m/e 184 ($C_{13}H_{12}O$), τ 2·65 (10H, m, aromatic), 4·13 (1H, s, $Ph_2CH\cdot O$), and 7·97 (1H, s, OH) (lit.,[58] m.p. 69 °C).

The final compound was a gum, $\nu_{max.}$ 3600—3620 cm^{-1} (free OH), m/e 290 ($C_{21}H_{22}O$), τ 2·72 (aromatic) (no other absorption).

[75] N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, 'NMR Spectra Catalog,' Varian Associates, Palo Alto, 1963, no. 607.