

Formation of Methyl Ethers from Photoaddition of Methanol to Phenyl-substituted Butadienes

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Irradiation of four phenyl- and diphenyl-butadienes in methanol produces allyl, homoallyl, cyclobutyl, and cyclopropylmethyl ethers. The products are comparable with the products of photoaddition to alkyl-dienes. Mechanistic implications are considered.

IRRADIATION of a wide variety of acyclic and *s-trans*-alicyclic conjugated dienes in hydroxylic solvents results

¹ P. G. Gassman and W. E. Hymans, *Tetrahedron*, 1968, **24**, 4437; *Chem. Comm.*, 1965, 795; W. G. Dauben and F. G. Willey, *Tetrahedron Letters*, 1962, 893; W. G. Dauben and J. A. Ross, *J. Amer. Chem. Soc.*, 1959, **81**, 6521; W. G. Dauben and W. A. Spitzer, *ibid.*, 1968, **90**, 802; G. Just and V. di Tullio, *Canad. J. Chem.*, 1964, **42**, 2153; G. Just and C. C. Leznoff, *ibid.*, p. 79; C. C. Leznoff and G. Just, *ibid.*, pp. 2801, 2919; G. Just and C. Pace-Asciak, *Tetrahedron*, 1966, **22**, 1063, 1069; T. N. Huckerby, N. A. J. Rogers and, A. Sattar, *Tetrahedron Letters*, 1967, 1113; J. C. Sircar and G. S. Fisher, *ibid.*, 1968, 5811; *J. Org. Chem.* 1969, **34**, 404; *Chem. and Ind.*, 1970, 26; J. Pusset and R. Beugelmans, *Tetrahedron Letters*, 1967, 3249.

in photoaddition¹⁻⁵ to give ethers, alcohols, or esters, but the effect of aryl substitution has not been reported. However, cyclobutene formation, a typical reaction of acyclic and *s-cis*-alicyclic dienes, has been reported in

² J. H. Smith, *Diss. Abs. (B)*, 1968, **28**, 4033.

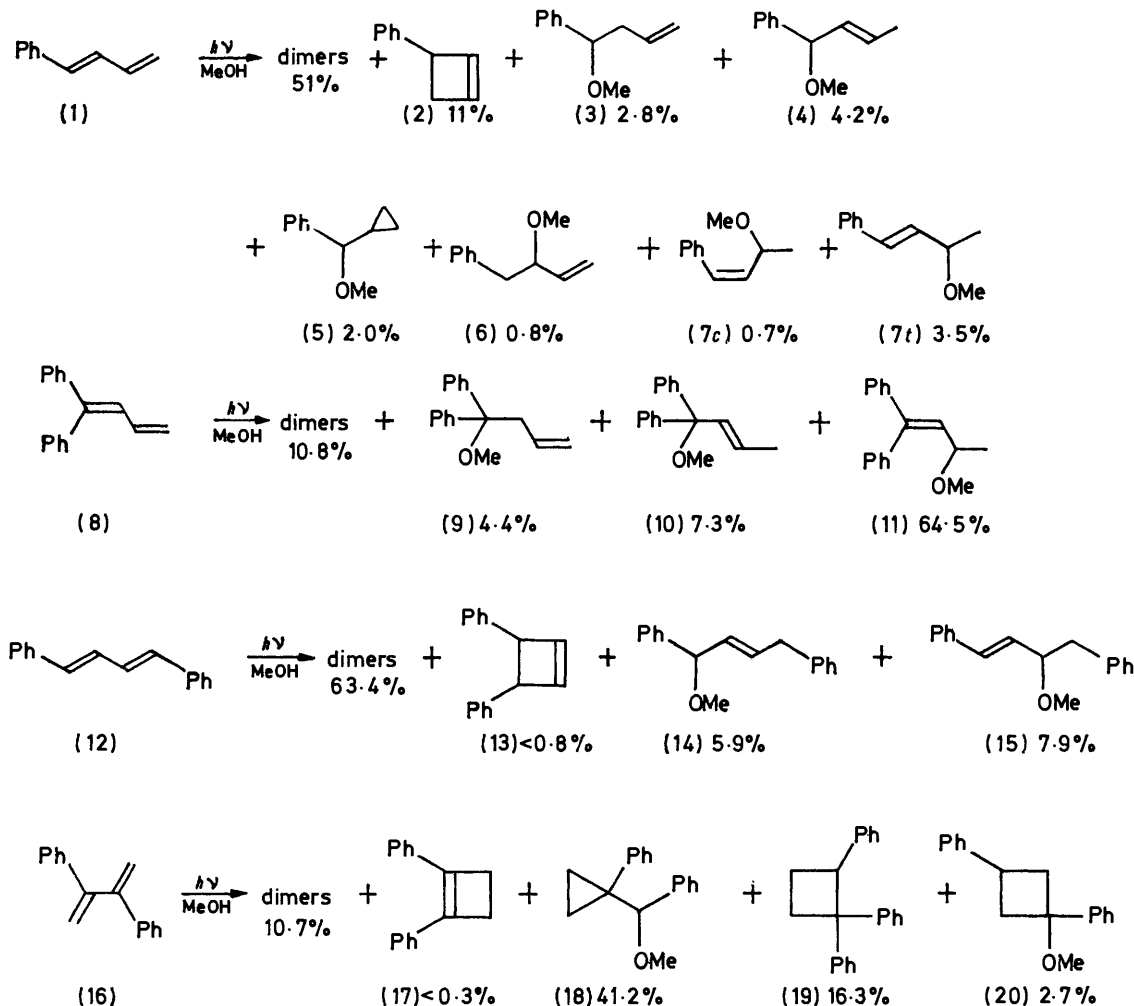
³ W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, 1964, **9**, 539; G. Bauslaugh, G. Just, and E. Lee-Ruff, *Canad. J. Chem.*, 1966, **44**, 2837.

⁴ J. A. Barltrop and H. E. Browning, *Chem. Comm.*, 1968, 1481.

⁵ P. J. Baldry, J. A. Barltrop, and H. E. Browning, in preparation.

the irradiation of phenyl-substituted cycloheptadienes,^{6,7} 1-phenylbuta-1,3-diene,⁷ and 2,3-diphenylbutadiene,⁸ and phenyl-substituted cyclohexa-1,3-dienes undergo photochemical ring opening and formation of bicyclo[3.1.0]hex-2-enes^{2,9} analogous to the photo-

substituted butadienes have considerable potential for mechanistic study, and the investigation reported here was carried out to compare the photochemistry of phenyl-substituted dienes with that of the aliphatic analogues.



SCHEME 1

chemical reactions of aliphatic cyclohexadienes.¹⁰ These similarities suggest that the excited states of phenyl-substituted butadienes are similar to those of aliphatic butadienes. However, a photocyclisation of 1,4-diarylbutadienes to give naphthalene derivatives has also been observed.¹¹ This reaction is analogous to the photocyclisation of stilbenes to phenanthrenes, and has no parallel in aliphatic diene photochemistry. Aryl-

RESULTS

The irradiation products of 1-phenylbutadiene (1), 1,1-diphenylbutadiene (8), 1,4-diphenylbutadiene (12), and 2,3-diphenylbutadiene (16) are shown in Scheme 1. Compounds (3)—(5), (7t), (9), and (15) were identified by comparison of their i.r., n.m.r., and mass spectra with those of synthetic

⁶ P. Courtot, *Ann. Chim. (France)* (13th series), 1963, **8**, 197; J. Rigaudy and P. Courtot, *Tetrahedron Letters*, 1961, 95; T. Toda, M. Nitta, and T. Mukai, *ibid.*, 1969, 4401.

⁷ M. Pomerantz and G. W. Gruber, *J. Amer. Chem. Soc.*, 1971, **93**, 6615.

⁸ E. H. White and J. P. Anhalt, *Tetrahedron Letters*, 1965, 3937.

⁹ G. R. Evanega, W. Bergmann, and J. English, jun., *J. Org. Chem.*, 1962, **27**, 13; P. Courtot and O. Le Goff-Hays, *Bull. Soc. chim. France*, 1968, 3401; P. Courtot and R. Rumin, *Tetrahedron Letters*, 1968, 1091 (correction No. 30, 1968); 1970, 1849; *Bull. Soc. chim. France*, 1969, 3665.

¹⁰ P. de Mayo and S. T. Reid, *Quart. Rev.*, 1961, **15**, 393; G. S. Hammond and N. J. Turro, *Science*, 1963, **142**, 1541; O. L. Chapman, *Adv. Photochem.*, 1963, **1**, 323; K. J. Crowley, *Acta Cient. Venez.*, *Suppl.*, 1967, **18**, 318 (*Chem. Abs.*, 1968, **69**, 76066w); M. Mousseron, *Adv. Photochem.*, 1966, **4**, 195; B. Lythgoe, *Proc. Chem. Soc.*, 1959, 141; D. H. R. Barton, *Helv. Chim. Acta*, 1959, **42**, 2604.

¹¹ H. Stobbe, *Ber.*, 1907, **40**, 3372; F. G. Baddar, L. S. El-Assal, and M. Gindy, *J. Chem. Soc.*, 1948, 1270; G. J. Fonken, *Chem. and Ind.*, 1962, 1327; R. Srinivasan and J. C. Powers, jun., *J. Chem. Phys.*, 1963, **39**, 580; C. C. Leznoff and R. J. Hayward, *Canad. J. Chem.*, 1970, **48**, 1842; R. J. Hayward and C. C. Leznoff, *Tetrahedron*, 1971, **27**, 2085; R. J. Hayward, A. C. Hopkinson and C. C. Leznoff, *ibid.*, 1972, **28**, 439; A. Santiago and R. S. Becker, *J. Amer. Chem. Soc.*, 1968, **90**, 3654.

material. Compound (2) was identified by its 100 MHz n.m.r. spectrum: τ (CCl₄) 2.77 (5 H, s), 3.72 (2 H, s), 5.99 (1 H, d, J 4 Hz), 6.96 (1 H, dd, J 4 and 13.5 Hz), and 7.63 (1 H, d, J 13.5 Hz), in agreement with the spectrum reported.¹² Cyclobutenes (13) and (17) were not positively identified; upper limits were obtained from the n.m.r. absorption at τ 7.29 in the photoproduct mixture from (16) [(17) is reported⁹ to absorb at τ 7.32] and from the largest absorption in the region τ 3–5 in the n.m.r. of the hydrocarbon mixture from (12). The remaining compounds were identified from the following data: (6) τ 2.87 (5 H, s), 4.1–4.5 (1 H, m), 4.89 (1 H, d, J 11 Hz), 4.93 (1 H, d, J 17.5 Hz), 6.4–6.7 (1 H, q, J 6.6 Hz), 6.81 (3 H, s), and 7.26 (2 H, m); (7c) τ 2.76 (5 H, s), 3.45 (1 H, d, J 12 Hz), 4.48 (1 H, dd, J 12 and 8.6 Hz), 5.80 (1 H, dq, J 8.6 and 6 Hz), 6.88 (3 H, s), and 8.74 (3 H, d, J 6 Hz); (10) τ 2.6–3.1 (10 H, m), 3.97 (1 H, d, J 15 Hz), 4.59 (1 H, m), 6.93 (3 H, s), and 8.25 (3 H, d, J 6.4 Hz), ν_{\max} 2 830, 1 670, 1 602, 1 494, 1 078, 980, 757, and 703 cm⁻¹; (11) τ 2.6–3.0 (10 H, m), 4.09 (1 H, d, J 9.1 Hz), 6.26 (1 H, m), 6.89 (3 H, s), and 8.78 (3 H, d, J 6.5 Hz), ν_{\max} 2 810, 1 630, 1 597, 1 576, 1 489, 1 109, 1 082, 833, 760, and 700 cm⁻¹ (Found: C, 85.85; H, 7.5. Calc. for C₁₇H₁₈O: C, 85.65; H, 7.6%); (14) τ 2.77 (5 H, s), 2.87 (5 H, s), 4.21 (1 H, m), 4.48 (1 H, dd, J 15.4, and 6 Hz), 5.47 (1 H, d, J 6 Hz), 6.67 (2 H, d, J 5.9 Hz), and 6.78 (3 H, s), ν_{\max} 2 820, 1 663, 1 600, 1 583, 1 491, 1 100, 972, 750, and 706 cm⁻¹; (18) τ 2.6–3.2 (10 H, m), 6.03 (1 H, s), 6.83 (3 H, s), and 8.7–9.1 and 9.1–9.4 (4 H, symmetrical A₂B₂ pattern), ν_{\max} 2 800, 1 597, 1 577, 1 485, 1 087, 1 019, 757, 712, and 694 cm⁻¹ (Found: C, 85.45; H, 7.55. Calc. for C₁₇H₁₈O: C, 85.65; H, 7.6%), m/e 238 (100%, M⁺), 210 (18), 206 (36), 205 (20), 191 (15), 180 (11), 121 (100), 115 (11), 91 (25), and 77 (14); (19) τ 2.94, 3.0–3.15, and 3.2–3.4 (10 H, m), 6.20 (1 H, t), 7.09 (3 H, s), 7.2–7.5 (1 H, m), and 7.6–8.2 (3 H, m), ν_{\max} 1 604, 1 584, 1 494, 1 238, 1 229, 1 109, 911, 778, and 705 cm⁻¹ (Found: C, 86.05; H, 7.8. Calc. for C₁₇H₁₈O: C, 85.65; H, 7.6%), m/e 238 (3%, M⁺), 210 (7), 134 (100), 133 (87), 121 (15), 104 (45), 103 (22), 91 (26), and 77 (31); (20) τ 2.75 (5 H, s), 2.87 (5 H, m), 6.23 (1 H, m), 6.7–7.4 (2 H, m), 7.04 (3 H, s), and 7.4–7.9 (2 H, m), ν_{\max} 1 605, 1 495, 1 240, 1 120, 914, 756, and 703 cm⁻¹, m/e 238 (7%, M⁺), 206 (24), 191 (15), 178 (12), 165 (9), 149 (19), 134 (83), 133 (100), 128 (12), 121 (25), 115 (25), 105 (62), 104 (50), 103 (37), 91 (95), and 77 (75).

Dimers of 1-phenylbutadiene (1) and 1,4-diphenylbutadiene (12) were identified by mass spectra: m/e 280 and 412, respectively, being twice the molecular weights of the corresponding dienes. I.r. spectra showed aromatic, saturated, and unsaturated hydrocarbon absorption, and n.m.r. spectra typically showed τ 2.7–2.9, 3.5–5.5, and 6–9, broad ragged peaks, sometimes with sharp peaks superimposed. T.l.c. showed a continuous streak from R_F 0 to slightly lower than that of the diene, and g.l.c. of the dimers from 1-phenylbutadiene showed 31 peaks. Figures in Scheme 1 for dimer yields are distillation residue plus unidentified hydrocarbon in the distillate, and may include monomeric material. In all irradiations, some insoluble polymeric material was obtained as a film on the inside of the reactor. This was impossible to weigh accurately, but probably accounts for the lack of material balance.

No addition products were obtained from the thermal reaction of 1-phenylbutadiene or 1,4-diphenylbutadiene with acidic methanol (*ca.* 0.02M-H₂SO₄), even after several weeks.

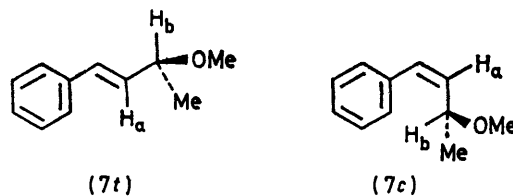
The synthetic ethers (3)–(5) and (7t), when irradiated,

were not interconverted. Ethers (3) and (5) slowly disappeared; ethers (4) and (7) disappeared more quickly. No volatile products were obtained from (3), (4), or (5); a single product was produced by (7) in 20% yield, but had a g.l.c. retention time different from those of all isolated photoproducts of the diene (1).

DISCUSSION

Structures of Photoproducts.—The structures of the products (2)–(5), (7t), (9), and (15) are proved by comparison of spectra with those of synthetic material. Of the remaining products, compound (6) has low-field signals for three protons in the n.m.r. spectrum; the position and coupling constants of the two resonating at τ 4.89 and 4.93 are characteristic of a vinyl group. The region τ 6.0–7.5, especially the seven-line multiplet at τ 7.0–7.5, is identical with the same region of the n.m.r. spectrum of compound (15), and implies the presence of the partial structure =CH-CH(OMe)-CH₂Ar in (6). Combining these two pieces of evidence with the phenyl absorption at τ 2.87 leads to the structure shown.

The n.m.r. spectrum of (7c) differs from that of (7t) only in the position of the olefinic proton signals [τ 3.45 and 4.48 instead of τ 3.55 and 4.00 in (7t)] and the CHOMe signal (τ 5.80 instead of 6.22), and in the coupling constant between the olefinic protons (12 instead of 16 Hz). These differences are easily explained if the two compounds differ in geometry about the double bond. The coupling constants of 12 and 16 Hz are typical of *cis*- and *trans*-olefinic protons, respectively. The relatively large shifts of H_a and H_b (τ 4.48 and 5.80) can be attributed to the deshielding effect of the benzene ring when these protons are forced close to it, and in the same plane. Thus H_a in (7t) and H_b in (7c) are shifted to low field.



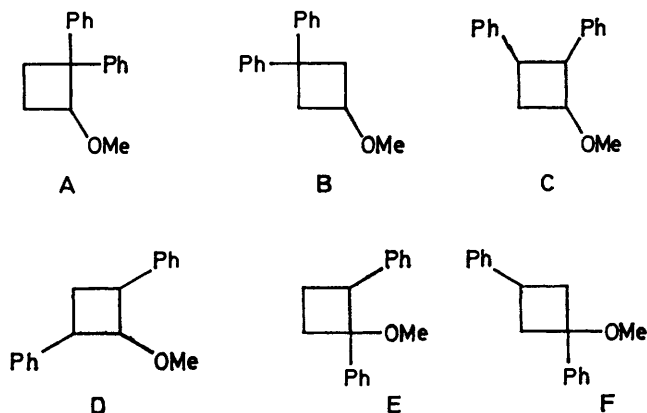
Compounds (10) and (14) were identified by the similarity of their spectra to those of the monophenyl compound (4), and (11) was identified, by the similarity of its spectra to those of the monophenyl compounds (7c) and (7t).

The product (18) is shown to have the formula C₁₇H₁₈O by microanalysis and mass spectrum; the lack of unsaturation, the i.r. absorption at 1 019 cm⁻¹, and the n.m.r. signals at τ 8.7–9.4 show that the compound is a cyclopropane derivative. The symmetrical A₂B₂ pattern in the n.m.r. and the loss of 28 mass units in the mass spectrum show that the cyclopropane is 1,1-disubstituted, and the presence of two non-equivalent phenyl groups and the singlet at τ 6.03 can be explained only by the structure shown.

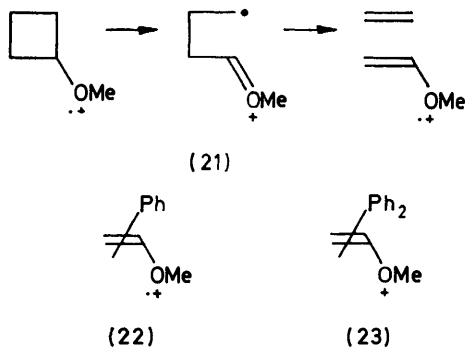
Compounds (19) and (20) have similar spectra. Microanalysis and the mass spectrum of (19) show the formula

¹² M. Pomerantz, R. N. Wilke, G. W. Gruber, and U. Roy, *J. Amer. Chem. Soc.*, 1972, **94**, 2752.

to be $C_{17}H_{18}O$, and the similarity between the spectra of (19) and (20) suggests that (20) is also $C_{17}H_{18}O$. Neither compound has $C=C$ or $=CH$ absorption in the i.r. nor $=CH$ or cyclopropane absorption in the n.m.r. The i.r. spectra show absorption at 911, 1 229, and 1 238 (19), and 914 and 1 240 (20) cm^{-1} ; absorptions at 925–910, 1 225, and 1 235 cm^{-1} have been found to be characteristic of the cyclobutane ring,¹³ and the n.m.r. absorptions at τ 7–8 are consistent with this. Since the n.m.r. absorptions at τ 6.20 (19) and 6.23 (20) could arise from either a CHAr of a CHOMe group, and both compounds show two phenyl groups in the n.m.r., structures A–F are possible.



Dauben, Smith, and Saltiel¹⁴ have shown that cyclobutyl ethers break down in the mass spectrometer as shown in Scheme 2. Both (19) and (20) have strong



SCHEME 2

peaks at m/e 134, corresponding to cleavage to (22) which cannot occur in A or B. The ether (19) also shows a peak at m/e 210, corresponding to cleavage to (23) which can only occur in A or E. The ether (19) must therefore be E.

The fragmentation of the cyclobutane ring in the mass spectrometer will be assisted by the presence of a phenyl group at the radical centre in (21), so that C should break down preferentially to stilbene, and the peak at m/e 134

should be weak [as the m/e 210 peak in the spectrum of (19) is]. Compound F also has no phenyl group to stabilise the radical centre of (21) in forming the m/e 134 fragment, but it has no competing cleavage of this type, so it should still have a reasonably intense m/e 134 peak. Structure D should give rise to a more intense m/e 134 peak. The intensity of this peak in the mass spectrum of (20) is more in agreement with structure F. Other features favouring this structure are: (i) the different resonance frequencies of the phenyl groups in the n.m.r., (ii) the presence of a peak at m/e 121, corresponding to the ion $(PhCH=OMe)^+$, which implies that the structural feature $PhC-OMe$ is present in (20). We consider, therefore, that the most likely structure of product (20) is F.

Mechanisms of Product Formation.—It is instructive to compare the results presented in Scheme 1 with typical results for the irradiation of acyclic methyl-substituted butadienes,^{4,5} in view of the similarities and differences between other photochemical reactions of aryl- and alkyl-substituted dienes. The essential features of the photochemistry are quite similar: alkyl-dienes form cyclobutenes in some cases, and photoaddition produces allyl, homoallyl, cyclopropylmethyl, and cyclobutyl ethers, and these are the types of product observed in our irradiations of phenyl-substituted dienes. The products of alkyl-diene photolysis can be rationalised by a mechanism involving an intermediate bicyclobutane,^{2,3,5,14,15} and it will be shown later that this is possible for the products of phenyl-diene photolysis. However, some differences are observed. The high yield of dimers from the dienes (1) and (12) is in contrast to the results of irradiations of aliphatic dienes, in which dimers are formed only on triplet sensitisation, or in concentrated solution. Dimers from the diene (1) were not quenched by ferrocene (triplet energy 42 kcal mol⁻¹) and had a different g.l.c. trace from the dimers formed on triplet sensitisation.¹⁶ Since the singlet lifetime of 1,4-diphenylbutadiene (12) is only 0.8 ns,¹⁷ however, the reaction of excited singlet diene with ground-state diene is unlikely to produce such a high yield of dimers at 10⁻²M-concentration. It is possible that excimers are intermediates in the dimerisation, though there is no other evidence for the existence of excimers from the diene (1) or (12). The fluorescence spectra of (1) and (12) show no excimer emission at high concentrations, and the combination of high extinction coefficient and the 'inner filter effect' prevented us from observing whether self-quenching was occurring. The lower yields of dimers from compounds (8) and (16) are consistent with an excimer mechanism since these dienes must be non-planar.

Suitably substituted aliphatic dienes normally form cyclobutenes on irradiation. 1-Phenylbutadiene (1) was found to form the corresponding cyclobutene, but no cyclobutenes were obtained from the diphenylbutadienes.

¹⁶ P. J. Baldry, J. A. Barltrop, and P. W. Wharton, in preparation.

¹⁷ J. B. Birks and D. J. Dyson, *Proc. Roy. Soc.*, 1960, *A*, 275, 135.

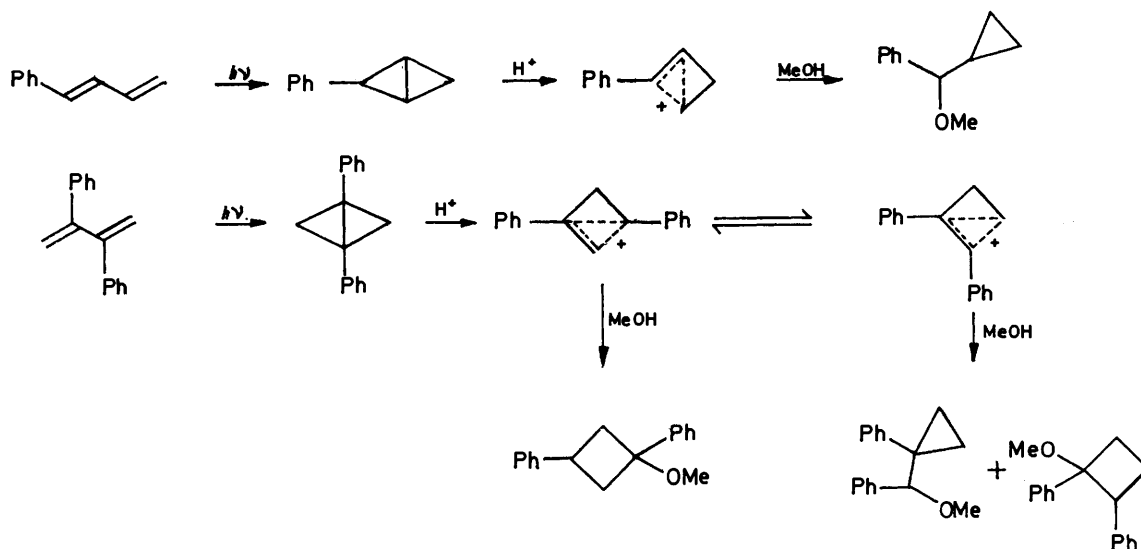
¹³ K. A. Zirvi and C. H. Jarboe, *J. Chem. Soc. (B)*, 1971, 1603, H. E. Ulery and J. R. McClenon, *Tetrahedron*, 1963, **19**, 749.

¹⁴ W. G. Dauben, J. H. Smith, and J. Saltiel, *J. Org. Chem.*, 1969, **34**, 261.

¹⁵ K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, 1970, **92**, 571.

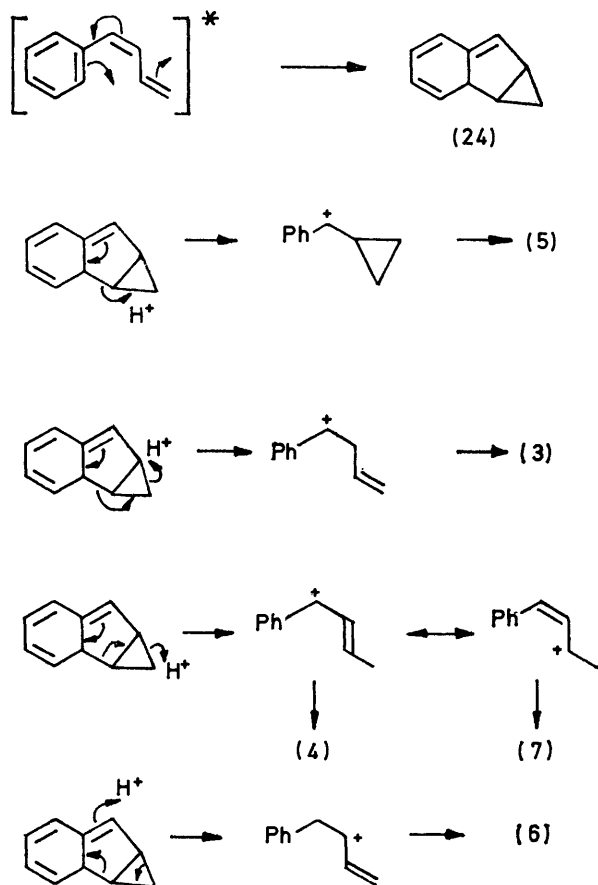
3,4-Diphenylcyclobutene (13) is reported to be unstable at room temperature,¹⁸ and 1,1-diphenylbutadiene (8) would not be expected to form a cyclobutene, since the

to form a cyclobutene, both by analogy with 2,3-dimethylbutadiene, which produces only the cyclobutene when irradiated in methanol,^{4,5} and in view of the report⁸



SCHEME 3

s-cis-conformation would be severely sterically hindered. However, 2,3-diphenylbutadiene (16) would be expected



SCHEME 4

that irradiation of (16) in inert solvents produces the cyclobutene (17). Comparison of our conditions with those of White and Anhalt⁸ shows two possible reasons for the difference: first our irradiations were complete in a much shorter time, indicating that reactions producing (18)—(20) are faster than those producing cyclobutene, and secondly for our irradiations we used an unfiltered mercury arc, whereas White and Anhalt used light at 254 nm. The cyclobutene (17) is not photostable, and has strong absorption at 297 nm,⁸ where the diene does not absorb, and it is likely that any cyclobutene formed in our irradiation was further photolysed.

The cyclopropylmethyl, cyclobutyl, and homoallyl ethers from alkylbutadienes have been shown to arise from a bicyclobutane mechanism.^{2,3,5,14,15} Such a mechanism can account for the cyclopropylmethyl and cyclobutyl products in our irradiations, as shown in Scheme 3. However, a second mechanism can account for all the products observed from 1-phenylbutadiene: this makes use of the benzene ring in an interconversion of the type hexatriene \rightarrow bicyclohexene. Such a mechanism cannot apply to 2,3-diphenylbutadiene, however, which probably reacts by the same mechanism as aliphatic dienes. A solution of 1-phenylbutadiene (1) irradiated in benzene gives the cyclopropylmethyl ether (5) when methanol is added,¹⁹ so that a long-lived intermediate is involved in the formation of (5). However, this intermediate is probably not (24), as this can give the other products as well.

The mechanism of the formation of the allyl and homoallyl ethers (Scheme 5) will be discussed in a future publication.¹⁹ Of particular interest is the nature of the

¹⁸ J. I. Brauman and W. C. Archie, jun., *Tetrahedron*, 1971, **27**, 1275.

¹⁹ P. J. Baldry, in preparation.

excited state responsible for the reaction, since there is some dispute about the nature of the lowest singlet state of polyenes.²⁰

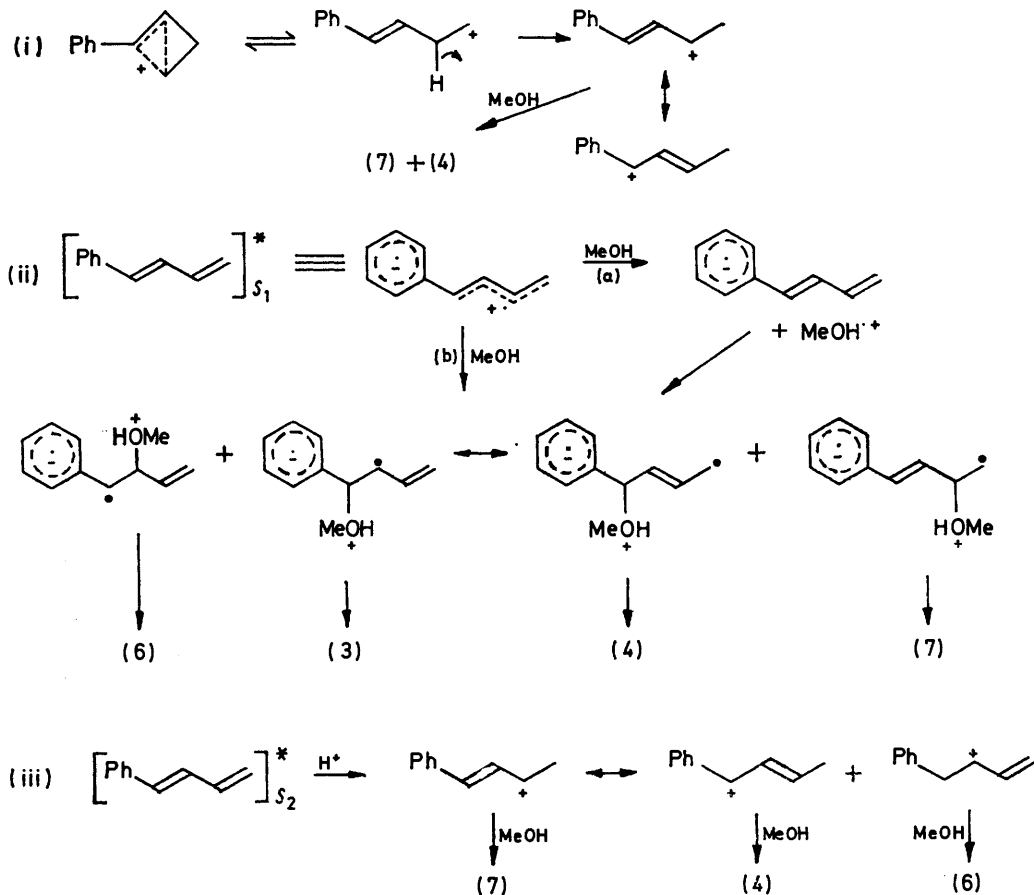
EXPERIMENTAL

I.r. spectra were recorded with a Unicam SP 1000, u.v. spectra with a Unicam SP 800, n.m.r. spectra with Perkin-Elmer R10 (60 MHz) or R14 (100 MHz), and mass spectra with an A.E.I. MS9 or Varian CH7 spectrometer. Micro-analysis was carried out by Dr. F. B. Strauss, Oxford.

1,1-Diphenylbuta-1,3-diene²² (8) had b.p. 98–104° at 0.1 mmHg (lit.,²² 93–94° at 0.3 mmHg), and was purified by chromatography on alumina, with petrol as eluant, and recrystallisation from ethanol; m.p. 35–35.5° (lit.,²² 38–39°).

1,4-Diphenylbuta-1,3-diene (12) (Koch-Light) was recrystallised from cyclohexane.

2,3-Diphenylbutane-2,3-diol.—Acetophenone (30 g, 0.25 mol) in propan-2-ol (250 ml), containing acetic acid, was irradiated for 40 h with a 450 W medium-pressure mercury



SCHEME 5

For analytical g.l.c. a 5 ft \times $\frac{3}{16}$ in glass column packed with 2% fluorosilicone oil FS 1265 on Embacel was used. For column chromatography Laporte type H alumina deactivated to activity III with 4% water was employed; 'petrol' refers to light petroleum (b.p. 40–60°) freshly distilled from P_2O_5 .

1-Phenylbuta-1,3-diene²¹ (1) had b.p. 100–110° at 20 mmHg, n_D^{20} 1.6090 (lit.,²¹ 86° at 11 mmHg, n_D^{20} 1.6086–1.6090), ν_{max} (film) 3 080, 3 060, 3 030, 1 678, 1 632, 1 600, 1 490, 1 448, 1 002, 948, 902, 754, and 697 cm^{-1} , τ (CCl_4) 2.72 (5 H, s), 3.1–3.9 (3 H, m), and 4.5–5.0 (2 H, m), λ_{max} (cyclohexane) 206 (ϵ 12 000), 209 (13 000), 219 (10 600), 225 (8 000), 233 (7 000), 274 (22 300), 280 (23 400), and 306 nm (5 000).

1,1-Diphenylbut-3-en-1-ol²² had b.p. 142–146° at 0.3 mmHg (lit.,²² 126–128° at 1 mmHg).

²⁰ See P. J. Baldry and J. A. Barltrop (in preparation) for a fuller discussion and further references.

arc, filtered through Pyrex. Evaporation, and recrystallisation of the residue from ethanol gave the diol (12.4 g, 41%), ν_{max} (film) 3 450, 3 090, 3 060, 3 030, 2 990, 2 940, 1 694, 1 599, 1 490, 1 444, 1 373, 1 202, 1 144, 1 068, 1 027, 762, and 706 cm^{-1} .

2,3-Diphenylbutadiene (16). 2,3-Diphenylbutane-2,3-diol (12.1 g, 0.05 mol) was mixed with a trace of *N*-phenyl-2-naphthylamine, and was warmed with acetyl chloride (36 ml) until the diol had dissolved. When the mixture had cooled, the acetyl chloride was evaporated off and the residue was mixed with sodium carbonate solution and extracted with chloroform. The extracts were dried (K_2CO_3) and evaporated and the product was chromatographed twice on alumina, with petrol as eluant. Recrystallisation from petrol gave the diene (2.2 g, 21%), m.p. 53–54° (lit.,²³ 47–48°), ν_{max} (KBr) 3 090, 3 060, 3 040, 1 609,

²¹ O. Grummitt and E. I. Becker, *Org. Synth.*, 1950, **30**, 75.

²² J. J. Eisch and G. R. Husk, *J. Org. Chem.*, 1966, **31**, 589.

907, 780, 759, and 710 cm^{-1} , τ (CCl_4) 2.5—2.9 (10 H, m), 4.52 (2 H, d, J 1.4 Hz), and 4.73 (2 H, d, J 1.4 Hz), λ_{max} (cyclohexane) end absorption 200—226 (ϵ_{200} 40 600) and 242.5 nm (17 600), m/e 206 (100%, M^+).

1-Phenylbut-3-en-1-ol. Benzaldehyde (10.6 g, 0.1 mol) in ether was added to allylmagnesium chloride (from 0.15 mol of allyl chloride). After 1 h, the mixture was added to 4M-ammonium chloride (75 ml) and the ether layer was dried (K_2CO_3) and evaporated to an oil, which was distilled to give the alcohol (13.3 g, 90%), b.p. 116—121° at 15 mmHg (Found: C, 81.05; H, 8.15. Calc. for $\text{C}_{10}\text{H}_{12}\text{O}$: C, 81.05; H, 8.15%), ν_{max} (film) 3 400, 3 070, 3 030, 1 638, 1 050, 1 030, 990, 918, 760, and 704 cm^{-1} , τ (CCl_4) 2.80 (5 H, s), 3.9—4.7 (1 H, m), 4.90, 5.0—5.2 (2 H, m), 5.45 (1 H, t, J 6 Hz), 7.18 (1 H, s), and 7.64 (2 H, t, J 6.4 Hz).

4-Methoxy-4-phenylbut-1-ene (3).—Sodium hydride (50% dispersion in oil; 2.4 g, 0.05 mol), washed with pentane, was suspended in dry dimethylformamide (DMF) (10 ml) and 1-phenylbut-3-en-1-ol (3.7 g, 25 mmol) in dry DMF was added with stirring. When reaction had ceased, methyl iodide was added until the dark-brown solution became pale yellow. After the excess of sodium hydride had been destroyed with methanol, water was added, the mixture was extracted with petrol, and the extracts were washed, dried (K_2CO_3), and evaporated to an oil, which was chromatographed on alumina, with 2% ether-petrol as eluant, to give the ether (3.68 g, 91%), n_D^{21} 1.5030 (Found: C, 81.7; H, 8.9. $\text{C}_{11}\text{H}_{14}\text{O}$ requires C, 81.45; H, 8.7%), ν_{max} (film) 3 070, 3 030, 2 820, 1 643, 1 106, 1 002, 980, 921, 762, and 708 cm^{-1} , τ (CCl_4) 2.83 (5 H, s), 4.0—4.7 (1 H, m), 4.98 (1 H, s), 5.21 (1 H, s), 5.99 (1 H, t, J 6.5 Hz), 6.88 (3 H, s), and 7.2—7.8 (2 H, m), m/e 162 (1%, M^+), 121 (100), 91 (21), and 77 (27), λ_{max} (MeOH) 249 (ϵ 146), 252 (186), 254 (194), 260 (171), 264 (172), 267 (95), and 272 nm (38).

1-Phenylbut-2-en-1-ol²⁴ had b.p. 118—124° at 15 mmHg (lit.,²⁴ 125° at 18 mmHg).

1-Methoxy-1-phenylbut-2-ene (4).—Sodium hydride and methyl iodide in DMF were used as described above to convert 1-phenylbut-2-en-1-ol into the methyl ether (84%), $n_D^{20.5}$ 1.5098 (Found: C, 81.7; H, 8.65. $\text{C}_{11}\text{H}_{14}\text{O}$ requires C, 81.45; H, 8.7%), ν_{max} 3 060, 3 030, 2 820, 1 674, 1 102, 971, 760, and 706 cm^{-1} , τ (CCl_4) 2.81 (5 H, s), 4.2—4.6 (2 H, m), 5.56 (1 H, d, J 5 Hz), 6.80 (3 H, s), and 8.31 (3 H, d, J 5 Hz), m/e 162 (87%, M^+), 147 (100), 131 (58), 115 (64), 91 (84), and 77 (57), λ_{max} (MeOH) 248 (ϵ 173), 252 (218), 258 (255), and 264 nm (206).

Cyclopropyl phenyl ketone²⁵ had b.p. 118—120° at 15 mmHg (lit.,²⁵ 109—110° at 10 mmHg).

Cyclopropylphenylmethanol. Cyclopropyl phenyl ketone was reduced with lithium aluminium hydride in ether to give the alcohol (77%), ν_{max} 3 460, 3 080, 3 030, 3 000, 1 027, 950, 924, 837, 740, and 704 cm^{-1} , τ (CCl_4) 2.69 (5 H, s), 6.14 (1 H, d, J 7.2 Hz), 7.01 (1 H, s), 8.5—9.3 (1 H, m), and 9.3—9.9 (4 H, m).

Cyclopropylphenylmethyl methyl ether (5).—Cyclopropylphenylmethanol (1.13 g, 7.6 mmol) in methanol (10 ml) containing sulphuric acid (0.2 ml) was left for 1 h, then was diluted with water and extracted with petrol. The extracts were dried (K_2CO_3) and evaporated and the product was chromatographed on alumina, with 2% ether-petrol as eluant, to give the methyl ether (1.25 g, 100%), n_D^{20} 1.5121 (lit.,²⁶ n_D^{25} 1.5098) (Found: C, 81.45; H, 8.7. Calc. for

$\text{C}_{11}\text{H}_{14}\text{O}$: 81.45; H, 8.7%), ν_{max} (film) 3 080, 3 010, 2 820, 1 095, 1 022, 870, 840, 752, and 705 cm^{-1} , τ (CCl_4) 2.82 (5 H, s), 6.45 (1 H, d, J 6.6 Hz), 6.87 (3 H, s), 8.5—9.3 (1 H, m), and 9.3—10.0 (4 H, m), m/e 162 (2%, M^+), 134 (100), 121 (91), 104 (92), 91 (93), and 77 (85), λ_{max} (MeOH) 247 (ϵ 118), 252 (163), 258 (196), and 264 (147) nm.

Cinnamaldehyde Dimethyl Acetal.—Cinnamaldehyde (13.2 g, 0.1 mol) and trimethyl orthoformate (16 g, 0.15 mol) in methanol (50 ml) were heated under reflux for 40 min. Dilution with water and extraction with petrol gave the crude acetal, ν_{max} (film) 3 080, 3 050, 3 020, 2 830, 1 660, 1 195, 1 137, 1 060, 973, 757, and 703 cm^{-1} , τ (CCl_4) 2.74 (5 H, s), 3.35 (1 H, d, J 16.5 Hz), 4.00 (1 H, dd, J 16.5 and 4 Hz), 5.11 (1 H, d, J 4 Hz), and 6.74 (6 H, s). This compound was used without further purification.

trans-3-Methoxy-1-phenylbut-1-ene (7t).—Cinnamaldehyde dimethyl acetal (4.5 g, 25 mmol) was mixed with acetyl chloride (2.4 g, 30 mmol) and left for 1 week. The excess of acetyl chloride was evaporated off, the residue was diluted with ether, and ethereal methylmagnesium iodide (0.1 mol) was added with stirring. After 4 h, the mixture was poured into 4M-ammonium chloride (20 ml), and the ether layer was dried (K_2CO_3) and evaporated. The residue was chromatographed on alumina, with petrol and 5% ether-petrol as eluants, to give 3-methoxy-1-phenylbut-1-ene (0.81 g, 20%) (Found: C, 81.25; H, 8.85. $\text{C}_{11}\text{H}_{14}\text{O}$ requires C, 81.45; H, 8.7%), ν_{max} (film) 3 100, 3 080, 3 040, 2 840, 1 660, 1 116, 1 088, 972, 753, and 701 cm^{-1} , τ (CCl_4) 2.74 (5 H, s), 3.55 (1 H, d, J 16 Hz), 4.00 (1 H, dd, J 16 and 7 Hz), 6.22 (1 H, quintet, J 7 and 6 Hz), 6.78 (3 H, s), and 8.74 (3 H, d, J 6 Hz), m/e 162 (57%, M^+), 147 (100), 131 (52), 115 (81), 91 (68), and 43 (68), λ_{max} (hexane) 204 (ϵ 18 900), 215 (11 300), 250 (16 500), 274 (1 200), 283 (920), and 292 nm (630). The same compound was formed in 87% yield from the reaction of 1-phenylbut-2-en-1-ol with acidic methanol.

4-Methoxy-4,4-diphenylbut-1-ene (9).—1,1-Diphenylbut-3-en-1-ol was dissolved in acidic methanol (1% H_2SO_4 v/v). After 11 h the solution was diluted with water and extracted with petrol, and the extracts were washed, dried (K_2CO_3), and evaporated to give the methyl ether (90%), pure by g.l.c. and t.l.c., ν_{max} (film) 3 060, 3 020, 2 820, 1 642, 1 082, 1 036, 1 005, 992, 921, 783, 760, 731, and 709 cm^{-1} , τ (CCl_4) 2.6—3.0 (10 H, s), 4.0—4.8 (1 H, m), 5.09 and 5.12 (2 H, overlapping doublets, J 11.5 and 15.5 Hz, respectively), and 6.95 (5 H, overlapping s and m).

3-Methoxy-1,4-diphenylbut-1-ene (15).—Cinnamaldehyde dimethyl acetal (4.5 g, 25 mmol) and acetyl chloride (2.4 g, 30 mmol) were mixed and left for 3 days. The mixture was evaporated, the residue was dissolved in ether and ethereal benzylmagnesium bromide [from benzyl bromide (75 mmol) and magnesium (0.2 g atom)] was added. After stirring for 3 h, the mixture was poured into 4M-ammonium chloride (20 ml), and the ether layer was dried (K_2CO_3) and evaporated. The residue was chromatographed twice on alumina, with 10% ether-petrol (first column) and 5% ether-petrol (second column) as eluants, to give 3-methoxy-1,4-diphenylbut-1-ene (0.77 g, 13%), n_D^{20} 1.5784, ν_{max} (film) 3 080, 3 060, 3 020, 2 820, 1 663, 1 105, 973, 751, and 706 cm^{-1} , τ (CCl_4) 2.81 (5 H, s), 2.86 (5 H, s), 3.63 (1 H, d, J 15.5 Hz), 4.04 (1 H, dd, J 15.5 and 6.5 Hz), 6.19 (1 H, q, J 6.5 Hz), 6.80 (3 H, s), and 7.17 (2 H, m), m/e 238 (0.3%, M^+), 147 (100), 115 (34), and 91 (29).

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Irradiation Procedure.—The diene (10 mmol) in methanol (250 ml) was irradiated in an immersion reactor with a Hanovia 450 W lamp, the solution being deoxygenated by passing oxygen-free nitrogen for 30 min before and during irradiation. A quartz filter was used, except for the irradiation of 1,4-diphenylbutadiene (12) in which a Pyrex filter was used. Irradiation was carried out until 80–90% of the diene had been consumed, then the solution was evaporated to an oil which was chromatographed on alumina (100–150 g), with petrol, 2% ether–petrol, and 5% ether–petrol as eluants. Fractions were analysed by t.l.c., g.l.c.,

and n.m.r., i.r., and mass spectra, the yields of products being calculated from the weight of each fraction and its composition as estimated by n.m.r. The photoproduct mixtures from 1-phenylbutadiene and 1,4-diphenylbutadiene were also bulb-distilled to separate monomeric and dimeric components; the distillate in these cases was chromatographed as above.

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