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Studies in the Cycloproparene Series: Reactions of Alkylidenecycloproparenes with Electrophiles*

Simon J. Buckland,[A] *Brian Halton,*[A, B] *Qiu Mei*[C] *and Peter J. Stang*[B, C]

[A] Department of Chemistry, Victoria University of Wellington, Private Bag, Wellington, New Zealand.
[B] Author to whom correspondence may be addressed.
[C] Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, U.S.A.

Abstract

The addition of an electrophile to the alkylidenecycloproparenes (2a–d) is dominated by capture at the exocyclic centre with formation of the corresponding cycloproparenyl cation, e.g. (15). Subsequent reaction with the counter ion is usually accompanied by cleavage of the three-membered ring. Thus compounds (2) give the ethanones (4) with aqueous acids whilst anhydrous acetic acid yields the vinyl acetates (5). Silver(I)-catalysed methanolysis of (2) leads to vinyl ethers (6); the alkyne (7) is formed only from (2d) which carries a vinylic proton. Brominations and bromine water additions lead to products of ring expansion (8)–(10) or ring cleavage (11)–(14) depending upon the conditions employed. These latter reactions demonstrate a delicate balance between cycloproparenylcarbinyl cation formation and cleavage of the three-membered ring.

The cycloproparenes are the most highly strained members of the *ortho*-fused series of aromatic compounds capable of isolation, and they have attracted considerable interest in recent times.[1] Of particular note has been a solution, on an *ab initio* basis, to the question of bond localization in the parent member,[2] the preparation and characterization of new members of the series,[3–7] and a growing interest in the utilization of the molecules in synthesis.[8]

The preparation of a range of alkylidenecycloproparenes, e.g. (2a–d) (Scheme 1), has been accomplished recently[5] from the parent hydrocarbons (1a,b) by way of

* For the previous part see: *Tetrahedron Lett.*, 1986, **27**, 5159.

[1] Halton, B., *Ind. Eng. Chem., Prod. Res. Dev.*, 1980, **19**, 349; *Chem. Rev.*, 1973, **73**, 113.
[2] Apeloig, Y., and Arad, D., *J. Am. Chem. Soc.*, 1986, **108**, 3241.
[3] Halton, B., Dent, B. R., Böhm, S., Officer, D. L., Schmickler, H., Schophoff, F., and Vogel, E., *J. Am. Chem. Soc.*, 1985, **107**, 7175; Dent, B. R., and Halton, B., *Tetrahedron Lett.*, 1984, **25**, 4279; *Aust. J. Chem.*, 1986, **39**, 1789.
[4] Müller, P., and Thi, H. C. N., *Chimia*, 1985, **39**, 362; Billups, W. E., Lin, L.-J., Arney, B. E., Rodin, W. A., and Casserly, E. W., *Tetrahedron Lett.*, 1984, **25**, 3935.
[5] Halton, B., Randall, C. J., and Stang, P., *J. Am. Chem. Soc.*, 1984, **106**, 6108; Halton, B., Randall, C. J., Gainsford, G. J., and Stang, P., *J. Am. Chem. Soc.*, 1986, **108**, 5949.
[6] Halton, B., Buckland, S. J., Mei, Q., and Stang, P. J., *Tetrahedron Lett.*, 1986, **27**, 5159.
[7] Apeloig, Y., Arad, D., Halton, B., and Randall, C. J., *J. Am. Chem. Soc.*, 1986, **108**, 4932; Halton, B., and Randall, C. J., *J. Am. Chem. Soc.*, 1983, **105**, 6310.
[8] Mynott, R., Neidlein, R., Schwager, H., and Wilke, G., *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 367; Vogel, E., Puttmann, W., Duchatsch, W., Schieb, T., Schmickler, H., and Lex, J., *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 720; Vogel, E., Schieb, T., Schulz, W. H., Schmidt, K., Schmickler, H., and Lex, J., *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 723; Martin, J. C., and Muchowski, J. M., *J. Org. Chem.*, 1984, **49**, 1040.

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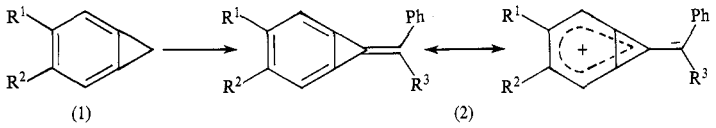
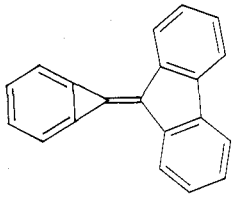


	R^1	R^2	R^3
(a)	H	H	Ph
(b)	$-(CH)_4-$		Ph
(c)	$-(CH)_4-$		Me
(d)	$-(CH)_4-$		H
(e)	H	H	H

Scheme 1

silylation and Peterson[9] olefination. These fulvenes are thermally stable, coloured, crystalline solids. An X-ray structure determination[5] of compound (1a) shows the fused three- and six-membered rings to be coplanar and to display bond length and angle deformations which are remarkably similar to those in other cycloproparenes;[10] the exocyclic double bond is normal in length (1·343 Å). Whilst many fulvenes and fulvalenes appear to exist as polyolefins, contributions from the relevant charge-separated forms are evident from spectroscopic data and dipole moment measurements.[11] The alkylidenecycloproparenes appear to be no exception;[5] the fulvalene derivative (3) (tribenzocalicene)[6] has a dipole moment of 2·6 D. In this contribution we report upon the behaviour of the novel alkylidenecycloproparenes (2a–d) towards electrophiles.



(3)

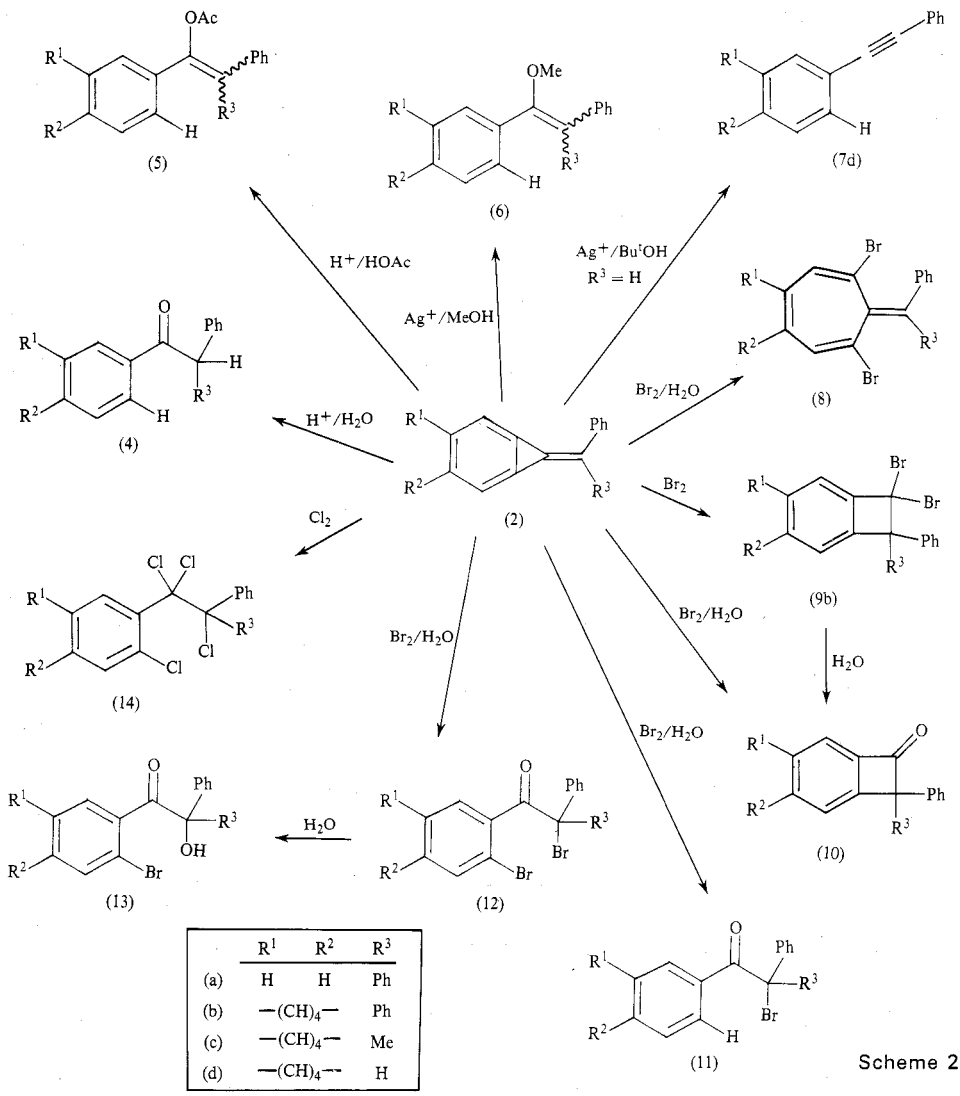
Of the ten alkylidenecycloproparenes whose syntheses have been reported[5] compounds (2a–d) were chosen as representative examples for the present study. The outcomes of the reactions of these compounds with a variety of electrophilic reagents are depicted in Scheme 2. The results are best considered in three groups, namely reactions with protic acids, reactions catalysed by silver(I), and halogenation reactions.

When compounds (2) react with acids (HCl, H_2SO_4, CF_3SO_3H), the corresponding ethanone (4) is obtained in a yield of 50–95% depending upon the particular substrate and the conditions employed (Experimental). The assignment of ethanone structure to the products follow from the i.r. and n.m.r. spectroscopic data (Experimental). The absence of cycloproparene structure in the products is clearly evident from the disappearance of the characteristic ^{13}C n.m.r. resonances[1] at *c.* 110 ppm due to the carbon atoms adjacent to the sites of ring fusion. In the absence of water the addition of acetic acid is catalysed by trifluoromethanesulfonic acid, and the alkene (5b) and an (*E*)/(*Z*) mixture of (5c) have been obtained from (2b) and (2c) respectively. With dry hydrogen chloride ethanones (4b,c) are also obtained.

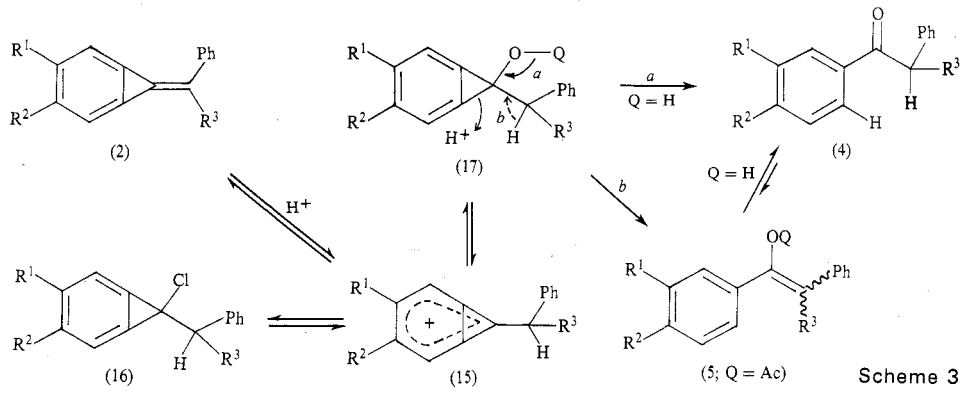
[9] Ager, D. J., *Synthesis*, 1984, 384.

[10] Allen, F. H., *Acta Crystallogr., Sect. B*, 1981, **37**, 900.

[11] Prinzbach, H., and Knothe, L., *Pure Appl. Chem.*, 1986, **58**, 25; Prinzbach, H., *Pure Appl. Chem.*, 1971, **28**, 281; Neuenschwander, M., *Pure Appl. Chem.*, 1986, **58**, 55; Prinzbach, H., and Woischnik, E., *Helv. Chim. Acta*, 1969, **52**, 2472.

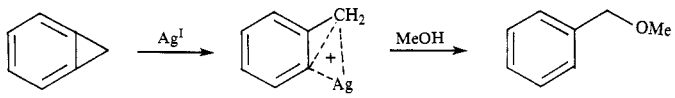


	R¹	R²	R³
(a)	H	H	Ph
(b)	—(CH)₄—		Ph
(c)	—(CH)₄—		Me
(d)	—(CH)₄—		H



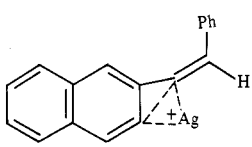
It is presumed that addition to (2b,c) affords the 1-chlorocycloproparenes (16b,c) (Scheme 3) as highly moisture-sensitive compounds[1] which do not survive the reaction conditions. Indeed in none of these experiments was any evidence found for products with the three-membered ring intact.

The results of these electrophilic additions are consistent with *protonation at the exocyclic carbon atom of (2) only*. The ensuing cycloproparenyl cation (15) (Scheme 3) is captured by water or acetic acid to give (17) which, with an oxygen substituent attached to the three-membered ring, is expected to be unstable.[1] Cleavage of cycloproparene (17; Q = H) by either path *a* or path *b* of Scheme 3 accounts for ethanone formation and follows well documented examples;[1] path *a* is blocked for (17; Q = Ac) and the product of path *b*, namely the styrene derivative (5), is isolated. It should be noted that the reactions of the diphenylmethylene derivatives (2a,b) follow the paths of Scheme 3 rather than protonating at the alternative C 1 cycloproparenyl centre to yield diphenylcarbinyl cations. This behaviour of the fulvenes (2) is thus consistent with charge separation as illustrated in Scheme 1.

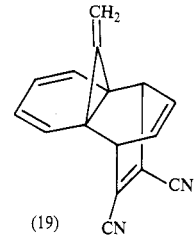


Scheme 4

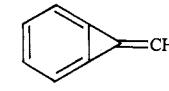
The interaction of a cycloproparene with silver(I) results in electrophilic cleavage of the three-membered ring and in methanol a methyl arenyl ether is formed (Scheme 4).[1,7,12] The alkylidenecycloproparenes (2a,b) behave in a strictly analogous manner to give the methoxystyrenes (6a)[13] and (6b) in 77% and 78% yield respectively. However, when applied to the unsymmetrical naphthalene derivative (2d) the ethyne (7d) (21%)[14] accompanies a 1:8 mixture (50%) of the (*E*)- and (*Z*)-isomers of vinyl ether (6d). These latter compounds, formed as a gum, have thus far proved to be inseparable. When the Ag^I-catalysed cleavage of (2d) is performed in t-butyl alcohol, vinyl ether formation is completely supressed and ethyne (7d) is the sole characterizable product (31%) from a multicomponent mixture. The appearance of ethyne (7d) in these latter reactions is not unexpected; proton loss from the σ-complex (18d) provides a plausible alternative reaction path. Indeed, the isolation of phenylethyne from both solution phase thermolysis and flash vacuum pyrolysis of the [10]annulene derivative (19) has been taken[15] to imply formation of the parent hydrocarbon (2e), a view with which we concur.



(18d)



(19)



(2e)

[12] Bee, L. K., Garratt, P. J., and Mansuri, M. M., *J. Am. Chem. Soc.*, 1980, **102**, 7076.
[13] Newman, M. S., and Kutner, A., *J. Am. Chem. Soc.*, 1951, **73**, 4199.
[14] Reimlinger, H., *Chem. Ind. (London)*, 1969, **37**, 1306.
[15] Klärner, F.-G., Dogan, B. M. J., Weider, R., Ginsburg, D., and Vogel, E., *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 346.

The course followed upon bromination of the alkylidenecycloproparenes (2) has proved to be less predictable as the results depicted by Scheme 2 imply. Bromination of the alkylidenecyclopropabenzene (2a)* results in a complex mixture from which no discernible products have thus far been isolated. However, with saturated bromine water the ring-expanded methylenecycloheptatriene (8a) is formed. The reaction is easy to apply but the product is obtained in only 25% yield as the sole isolable component from a multicomponent mixture. The assignment of cycloheptatriene structure to compound (8a) follows from its spectroscopic properties. The mass spectrum shows molecular ions at *m/z* 412, 414 and 416 in a ratio of 1:2:1 as expected from the addition of one mole of bromine to (2a). The ^{1}H n.m.r. spectrum displays an AB system (6·45 and 6·58 ppm) and an aromatic singlet (7·30 ppm) in a ratio of 2:5 whilst the ^{13}C n.m.r. spectrum shows only four types of methine carbon resonances in a ratio of 1:2:3:1 in the range 127·9–130·6 ppm (Experimental); compound (8a) requires such resonances in a ratio of 1:1:1:2:2 and it is presumed that a one-carbon and a two-carbon resonance are coincident. The cycloproparenes are known to provide 1,6-dihalocycloheptatrienes under free radical conditions,[16] but it would seem that the alkylidene derivative (2a) does not fit this pattern since (8a) is not formed from reaction with *N*-bromosuccinimide.

The reaction of the diphenylmethylenecyclopropabenzene (2a) with dilute bromine water takes a different course from its saturated counterpart discussed above. A carbonyl containing (1765 cm^{-1}) halogen-free colourless crystalline solid is obtained in 91% yield. The compound is identified as the oxocyclobutabenzene (bicyclo[4.2.0]octa-1,3,5-trien-7-one) (10a). Whilst the ^{1}H n.m.r. spectrum is uninformative (aromatic protons only), the ^{13}C n.m.r. spectrum shows a carbonyl (189·7 ppm) and an alicyclic (aliphatic) quaternary resonance (81·1 ppm) which was assigned to the $>CPh_2$ moiety. In addition, the carbon atoms at the ring junction (formally C 1 and C 6) resonate downfield relative to the substrate at 146·6 and 158·5 ppm respectively as expected for such a compound.[17] The molecular ion at *m/z* 270 ($C_{20}H_{14}O$ is the base peak of the mass spectrum and $(M-CHO)^+$ is the major fragment ion.

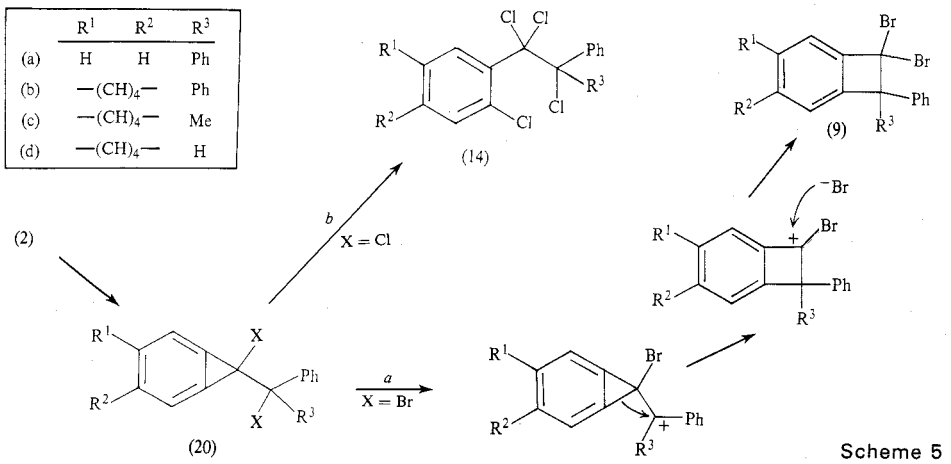
Unlike (2a) the diphenylmethylenecyclopropanaphthalene (2b) affords a dibromo addition product from reaction with bromine even in the presence of an excess of the reagent. The product, which is moisture-sensitive, is identified as the ring-expanded dibromodiphenylcyclobuta[*b*]naphthalene (9b) (70%). The structure of the compound follows from its spectroscopic properties and from hydrolysis to the oxocyclobutarene (10b) (see below). The ^{13}C n.m.r. spectrum displays distinct quaternary resonances for *gem*-dibromo and *gem*-diphenyl carbon centres at 66·4 and 77·6 ppm respectively and also for the four quaternary naphthalenyl carbons. There are no shielded (*c.*

* Fusion nomenclature requires compound (2a) to be named as 7-diphenylmethylenebicyclo-[4.1.0]hepta-1,3,5-triene whereas (2b) is correctly named 1-diphenylmethylene-1*H*-cyclopropa[*b*]naphthalene. The non-systematic family name of cyclopropabenzene is retained for clarity in the ensuing discussion, but systematic nomenclature is followed in the Experimental section.

[16] Okazaki, R., O-oka, M., Tokitoh, N., and Inamoto, N., *J. Org. Chem.*, 1985, **50**, 180; Okazaki, R., O-oka, M., Tokitoh, N., Shishido, Y., and Inamoto, N., *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 799.

[17] Thummel, R. P., and Nutakul, W., *J. Org. Chem.*, 1978, **43**, 3170; Kametani, T., Kajiwara, M., Takahashi, T., and Fukumoto, K., *Tetrahedron*, 1975, **31**, 949; Olah, G. A., and Liang, G., *J. Am. Chem. Soc.*, 1977, **99**, 6045.

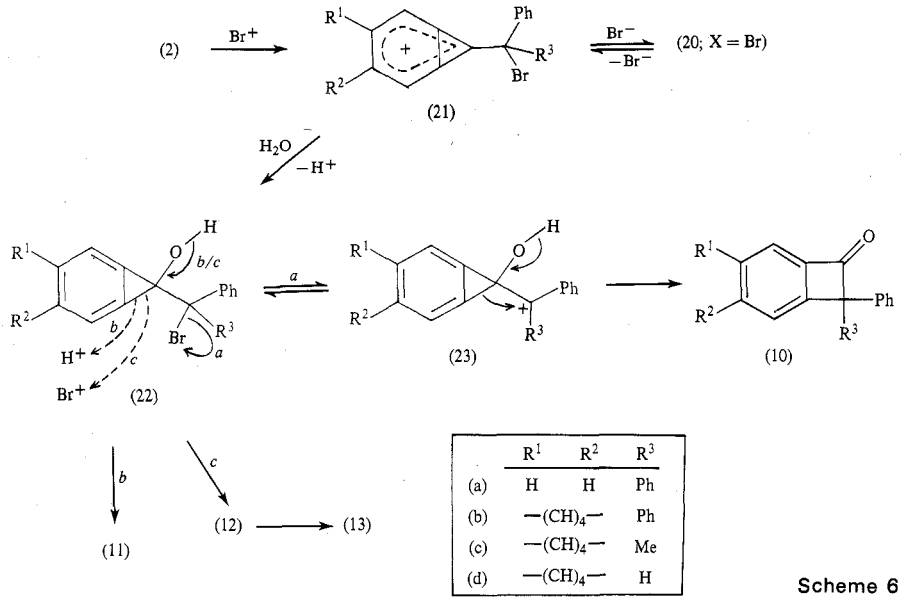
110 ppm) methine resonances and a cyclopropanarene structure is excluded. Molecular ions are not recorded in the mass spectrum even at low ionizing potentials, but $(M-Br)^+$ (*m/z* 383, 385) and $(M-Br_2)^{+\bullet}$ (*m/z* 304) are observed. The bromination of (2b) to give (9b) is uncomplicated and even in an n.m.r. experiment the ^1H spectrum of (9b) only is obtained immediately after the addition of bromine. The most plausible pathway from (2b) to (9b) involves electrophilic bromination of the polar exocyclic double bond to give dihalide (20b) (Scheme 5). Ionization at the diphenylmethyl centre of this compound triggers ring expansion, and capture of the nucleophile completes the sequence (path *a*, Scheme 5). Chlorination of (2b) does not give rise to the dichloro analogue of (9b), but provides the ring-opened tetrachloride (14b) instead in 65% yield. It seems likely that dichloride (20b; X = Cl) is formed and that this adds a second molecule of chlorine across the strained σ-bond (path *b*, Scheme 5) by analogy with other cyclopropanarenes.[1] We take the difference in behaviour towards bromine and chlorine to reflect the different rates of ionization of the diphenylmethyl halides (20b; X = Br, Cl).



Scheme 5

As was noted above the dibromocyclobutarene (9b) is sensitive to water. For example, column chromatography of (9b) leads to a halogen-free, carbonyl-containing (1756 cm^{-1}) product (61%) identified as the oxocyclobutarene (10b) from its spectroscopic properties (Experimental) and by comparison with those of its lower homologue (10a). The same compound is also formed (75%) when (2b) is treated with dilute bromine water. However, when the phenylmethylenecyclopropanaphthalene (2d) is allowed to react with dilute bromine water under the same set of reaction conditions, the three-membered ring is cleaved and the bromoethanones (11d) and (12d) are isolated in yields of 47 and 23% respectively. On the other hand, compound (2d) affords the α,o-dibromo ketone (12d) as the major product of reaction (67%) with saturated bromine water or with bromine and subsequent hydrolysis. The identity of the α-bromoethanone (11d) is established by comparison with an authentic sample prepared from 1-(naphthalen-2-yl)-2-phenylethanone and that of the α,o-dibromide (12d) from its spectroscopic properties. Molecular ions at *m/z* 402, 404 and 406 (1:2:0·9) confirm the presence of two bromine atoms in this latter compound and the carbonyl group is evident from the infrared absorption at

1715 cm^{-1}. The ^1H n.m.r. spectrum displays a one-proton singlet at 6·31 ppm for the benzylic proton and the carbon atom at this centre appears at 53·5 ppm in the ^{13}C n.m.r. spectrum. Moreover, eight distinct aromatic methine carbon resonances are present and these correspond (integration) to the 11 non-equivalent centres required by (12d); four of the five aromatic quaternary signals necessary for (12d) are observed. With saturated bromine water the diphenylmethylenecyclopropa[*b*]naphthalene (2b) provides the *o*-bromo-α-hydroxy ketone (13b) and the ring-expanded cyclobutanone (10b) in almost equal proportions. The former compound is presumed to result from hydrolysis of initially formed α,*o*-dibromide (12b) which with a diphenylmethyl centre ionizes much more readily than its monophenyl homologue (12d). This difference in behaviour of (2b) towards saturated bromine water compared with homologue (2a) undoubtedly reflects the additional energy which would be needed to lose aromaticity in both rings of (2b) to give rise to fulvene (8b).



	R^1	R^2	R^3
(a)	H	H	Ph
(b)	—$(CH)_4$—		Ph
(c)	—$(CH)_4$—		Me
(d)	—$(CH)_4$—		H

Scheme 6

The formation of the 1-oxocyclobutarenes (10a,b) and the ethanones (11d)/(12d) and (13b) is readily explicable and demonstrates a delicate balance between cycloproparenylcarbinyl cation formation and cleavage of the three-membered ring as illustrated in Scheme 6. Electrophilic addition of Br^+ to (2) provides the α-bromo cycloproparenyl cation (21) which is captured by water to give the unstable[1] alcohol (22) after proton loss. Compounds (22) have an α-bromo substituent in the side chain and for (22a,b) ionization to the stabilized tertiary cycloproparenyldiphenylmethyl cation (23a,b) is favourable. Cyclopropylcarbinyl–cyclobutyl ring expansion is well known[18] and applied to cations (23a,b) (path *a*, Scheme 6) accounts for the facile formation of the ring-expanded ketones (10a,b). By comparison with (23a,b) the cycloproparenyl phenyl cation (23d) derives less stabilization and appears not to be formed. Instead, proton loss from (22d) triggers cleavage of the three-membered

[18] See e.g., Halton, B., 'Three-membered Rings' in 'Alicyclic Chemistry' (Ed. A. McKervey) Vol. 6, p. 76 (The Chemical Society: London 1978).

ring and capture of electrophile by the aromatic nucleus to give (11d) (H^+ addition; path *b*) and/or (12d) (Br^+ addition; path *c*) dependent upon the reaction conditions. Competition between paths *a* and *c* of Scheme 6 accounts for the formation of both (10b) and (13b) from the reaction of (2b) with saturated bromine water.

Our interest in the novel fulvenes (2) continues. Their behaviour with nucleophiles, towards oxidation, and under cycloaddition conditions will form the subjects of future publications.

Experimental

Microanalyses were performed by Professor A. D. Campbell and associates, Otago University, Dunedin. Infrared spectra were recorded for Nujol mulls or thin films unless specified otherwise on a Pye–Unicam SP3-300, a Perkin–Elmer 298 or 1000 FT–IR spectrophotometer. Ultraviolet spectra were determined as described earlier.[3] N.m.r. spectra were recorded on Varian Associates EM390, FT80A or XL300 instruments for (D)chloroform solutions and with Me_4Si as internal standard. Low-resolution mass spectra were recorded on a Micromass 12F or a Hewlett–Packard 5995 instrument. Compounds (5b), (8a), (10a), (13b) and (14b) recorded herein slowly decomposed prior to the acquisition of microanalytical data; acceptable accurate mass measurements (A.E.I. MS902 or Micromass 7070 instruments) have been recorded. Preparative t.l.c. plates were coated (0·75 mm thick) with Merck Kieselgel GF254.

Reactions of the Alkylidenecycloproparenes (2) with Acids

(a) 1,2,2-Triphenylethanone (4a)

To a stirred solution of 7-diphenylmethylenebicyclo[4.1.0]hepta-1,3,5-triene (2a)[5] (51 mg, 0·2 mmol) in methanol/dichloromethane (28 cm^3, 4:1) was added hydrochloric acid (2 M, 1 cm^3, 2·0 mmol). After 24 h at room temperature, an additional aliquot of acid was added and the solution was stirred for a similar period. The excess of acid was neutralized (solid sodium bicarbonate), and the solution concentrated to a slurry which was partitioned between dichloromethane and water (100 cm^3, 1:1). The separated aqueous phase was washed with dichloromethane (50 cm^3) and the combined organic solution washed (water, 2×50 cm^3), dried ($MgSO_4$) and concentrated in vacuum, the residue was flash-chromatographed over silica (dichloromethane/light petroleum, 3:2) to give 1,2,2-triphenylethanone (4a) (52 mg, 95%) as colourless needles, m.p. 135–135·5° (lit.[19] 135–136°). ν_{max} 1680, 1215, 750, 705, 693, 625 cm^{-1}. ^1H n.m.r. δ 6·02, s, Ph_2CH; 7·18–7·48, m, 3H; 7·26, s, 10H; 7·93–8·05, m, 2H. ^{13}C δ 59·6, Ph_2CH; 127·2, 128·7(5), 129·0, 129·3, 133·0, all aromatic CH; 137·2, q, *ipso*-**Ph**CO; 139·3, q, *ipso*-$\mathbf{Ph_2}CH$; 198·2, CO. *m/z* 272 (3%, M), 167 (23, M − PhCO), 165 (14, M − PhCO − 2H), 105 (100, PhCO), 77 (18).

(b) 1-(Naphthalen-2-yl)-2,2-diphenylethanone (4b)

(i) To a solution of 1-diphenylmethylene-1*H*-cyclopropa[*b*]naphthalene (2b)[5] (122 mg, 0·4 mmol) in acetonitrile/water (20 cm^3, 5:1) at 50° was added trifluoromethanesulfonic acid (1 cm^3) in acetonitrile (3 cm^3). The solution was stirred at 50° for 45 h, cooled, diluted with water (30 cm^3) and extracted with dichloromethane (3×30 cm^3). The combined organic extracts were washed with saturated sodium bicarbonate (50 cm^3), water (2×50 cm^3), dried ($MgSO_4$), concentrated in vacuum and the product chromatographed over silica (dichloromethane/hexane, 1:1) to afford colourless crystals proposed as *1-(naphthalen-2-yl)-2,2-diphenylethanone* (4b) (106 mg, 82%), m.p. 103–104° (Found: $M^{+\bullet}$ 322·1359. $C_{24}H_{18}O$ requires $M^{+\bullet}$ 322·1357). ν_{max} (KBr) 3052, 3020, 1658, 1622, 1592, 1490, 1449, 1349, 1274, 1206, 1190, 1170, 1118, 906, 858, 820, 766, 754, 744, 732, 714, 698, 638, 618 cm^{-1}. ^1H n.m.r. δ 6·3, s, Ph_2CH; 7·42, s, 10H; 7·60–8·34, m, 6H; 8·68, bs, 1H. ^{13}C δ 59·4, Ph_2CH, 124·6, 126·7, 127·1, 128·4, 128·5,

[19] Beilstein, F. K., 'Handbuch der Organischen Chemie' Vol. 7, p. 522 (Springer-Verlag: Berlin 1918).

128·7, 129·2, 129·7, 130·7, all aromatic CH; 132·4, 134·1, 135·5, all q; 139·2, q; *ipso*-Ph_2CH; 198·1, CO. *m/z* (17 eV) 322 (0·9%, M), 167 (0·5, Ph_2CH). 156 (12), 155 (100, $C_{10}H_7CO$).

(ii) To a solution of (2b) as above but in dry dichloromethane (20 cm^3) was bubbled dry hydrogen chloride for 40 h. Concentration in vacuum and column chromatography as in (i) above gave ethanone (4b) (65 mg, 50%), m.p., m.m.p. 103–104°. It is presumed that 1-chloro-1-(chlorodiphenylmethyl)-1 *H*-cyclopropa[*b*]naphthalene is the primary product of reaction and that this is hydroysed upon chromatography [cf. halide (9b) below].

(c) 1-(Naphthalen-2-yl)-2-phenylpropanone (4c)

1-Phenylethylidene-1 *H*-cyclopropa[*b*]naphthalene (2c)[5] (54 mg, 0·22 mmol) was allowed to react with dry hydrogen chloride as described in (b)(ii) above. After chromatography colourless crystals proposed as *1-(naphthalen-2-yl)-2-phenylpropanone* (4c) (41 mg, 70%) were obtained, m.p. 82–83° (Found: $M^{+\bullet}$ 260·1189. $C_{19}H_{16}O$ requires $M^{+\bullet}$ 260·1200). ν_{max} (KBr) 3050, 3020, 2978, 2922, 1662, 1618, 1594, 1434, 1352, 1252, 1186, 1164, 1124, 1013, 972, 959, 950, 932, 914, 822, 789, 748, 734, 692 cm^{-1}. ^1H n.m.r. δ 1·59, d, *J* 7·0 Hz, CH_3; 4·85, q, *J* 7·0 Hz, CH; 7·15–8·05, complex m, 11H; 8·48, s, 1H. ^{13}C δ 19·5, CH_3; 47·9, CH; 124·6, 126·6, 126·9, 127·7, 128·3, 128·4, 129·6, 130·4, all CH; 127·8, 129·0, each 2×CH; 132·5, 133·8, 135·4, 141·6, all q; 200·3, CO. *m/z* 260 (2·5%, M), 155 (100, $C_{10}H_7CO$), 127 (42, $C_{10}H_7$), 105 (4·1, $PhCHCH_3$), 77 (10, Ph).

(d) 1-(Naphthalen-2-yl)-2-phenylethanone (4d)

(i) To a solution of 1-phenylmethylene-1 *H*-cyclopropa[*b*]naphthalene (2d)[5] (25 mg, 0·11 mmol) in acetonitrile was added sulfuric acid (3·6 M, 1 cm^3) and after 24 h at room temperature workup as in (*a*) (above) afforded 1-(naphthalen-2-yl)-2-phenylethanone (4d) (22 mg, 80%) as a colourless crystalline solid, m.p. 97–98° (lit.[20] 99–99·5°). ν_{max} 1685, 1504, 1330, 1190, 1178, 1130, 1039, 838, 832, 756, 730, 708 cm^{-1}. ^1H n.m.r. δ 4·39, s, CH_2; 7·30, s, 5H; 7·48–7·66, m, 2H; 7·79–8·01, m, 4H; 8·52, bs, 1H. ^{13}C n.m.r. 45·6, CH_2; 124·4, 126·8(5), 127·8, 128·7, 129·5, 130·5(5), aromatic C–H; 132·7, 134·3, 124·8(5), 135·7, all q; 197·5, CO. *m/z* 246 (4%, M), 156 (13), 155 (100, $C_{10}H_7CO$), 127 (56, $C_{10}H_7$), 77 (8, Ph).

(ii) The reaction of compound (2d) with conc. HCl in the manner described in (i) above gave ethanone (4d) (74%), m.p., m.m.p. 97–98·5°.

(e) 1-(Naphthalen-2-yl)-2,2-diphenylethenyl Acetate (5b)

To a solution of 1-diphenylmethylene-1 *H*-cyclopropa[*b*]naphthalene (2b) (122 mg, 0·4 mmol) in glacial acetic acid (10 cm^3) containing acetic anhydride (5 drops) was added trifluoromethanesulfonic acid (5 drops). After 2 days at 40°, water (40 cm^3) and hexane (40 cm^3) were added, the organic phase was separated and the aqueous extracted with hexane (3×15 cm^3). The combined organic extracts were washed with saturated sodium bicarbonate (2×50 cm^3), water (2×50 cm^3), dried ($MgSO_4$) and concentrated in vacuum to a yellow solid. Column chromatography (silica; dichloromethane/hexane 1 : 1) furnished *1-(naphthalen-2-yl)-2,2-diphenylethenyl acetate* (5b) (102 mg, 70%) as a yellow crystalline solid, m.p. 136–137° (Found: $M^{+\bullet}$ 364·1451. $C_{26}H_{20}O_2$ requires $M^{+\bullet}$ 364·1462. ν_{max} (KBr) 3058, 1759, 1597, 1504, 1493, 1443, 1368, 1276, 1211, 1174, 1129, 1053, 862, 819, 774, 752, 701, 656 cm^{-1}. ^1H n.m.r. δ 2·00, s, CH_3; 7·10–7·44, m, 16H; 7·78, s, 1H. ^{13}C δ 20·9, CH_3; 125·9, 126·3, 126·7, 127·1, 127·2, 127·3, 127·4, 127·5, 127·8, 127·9, 128·0, 128·9, 130·7, aromatic CH; 132·2, 132·6, 132·8, 133·3, 139·4, 140·0, 143·6, all q; 169·7, CO. *m/z* 364 (11%, M), 323 (25), 322 (100, $M-CH_2CO$), 215 (19·4), 167 (6), 166 (23), 165 (28), 155 (49), 131 (16·5), 127 (34), 119 (17), 105 (6), 77 (6).

(f) (E/Z)*-1-(Naphthalen-2-yl)-2-phenylprop-1-enyl Acetate (5c)*

1-Phenylethylidene-1 *H*-cyclopropa[*b*]naphthalene (2c) (27 mg, 0·11 mmol) was allowed to react with acetic acid as described in (*e*) above. Workup provided a solid proposed as an (*E*/*Z*) mixture of 1-(naphthalen-2-yl)-2-phenylprop-1-enyl acetate (5c) (10 mg, 30%). ^1H n.m.r. δ 1·72, s, 2·8H; 2·24, s, 3H; 7·2–8·0, m, 12H. ν_{max} 1735, 1628, 1594, 1205, 1016, 740, 692 cm^{-1}.

[20] Ruggli, P., and Reinert, M., *Helv. Chim. Acta*, 1926, **9**, 67.

m/z 302 (1·0%, M), 260 (34, M − CH_2CO), 259 (25, M − CH_3CO), 245 (44, M − C_3H_5O), 244 (79, M − CH_2CO_2), 243 (58, M − CH_3CO_2), 242 (100, M − CH_3CO_2H), 155 (88, $C_{10}H_7CO$), 127 (50, $C_{10}H_7$). The major isomer is present to an extent of *c.* 93% (^{1}H n.m.r.).

Silver(I)-Catalysed Ring Cleavage of the Alkylidenecycloproparenes (2)

(a) 1-Methoxy-1,2,2-triphenylethene (6a)

To a solution of silver nitrate (17 mg, 0·1 mmol) in methanol (20 cm^3) was added a solution of 7-diphenylmethylenebicyclo[4.1.0]hepta-1,3,5-triene (2a) (51 mg, 0·2 mmol) in methanol (50 cm^3). After the mixture had been stirred in the dark for 8 h, the solvent was removed in vacuum, the residue dissolved in ether (100 cm^3), and the solution washed (water, 3×50 cm^3), dried ($MgSO_4$) and concentrated in vacuum. Preparative t.l.c. (ethyl acetate/light petroleum, 1:9) showed a band, R_F 0·6, which after extraction and treatment with activated charcoal gave colourless crystals of 1-methoxy-1,2,2-triphenylethene (6a) (44 mg, 77%), m.p. 106·5–108° (lit.[13] 108·4–109·2°). ν_{max} 1610, 1260, 1208, 1094, 1078, 1036, 1012, 792, 744, 716 cm^{-1}. ^{1}H n.m.r. δ 3·46, s, CH_3O; 6·96–7·11, m, 5H; 7·18, s, 5H; 7·28, s, 5H. ^{13}C δ 58·1, CH_3O; 125·7, C2; 126·1, 126·5, both CH; 127·9, 7×CH; 129·8, 130·3, 131·4, all 2×CH; 135·5, q; 141·2, 2×q; 153·1, C1. *m/z* 287 (22%), 286 (100, M), 271 (20, M − Me), 248 (34, M − OMe), 165 (46), 77 (8).

(b) 1-Methoxy-1-(naphthalen-2-yl)-2,2-diphenylethene (6b)

1-Diphenylmethylene-1*H*-cyclopropa[*b*]naphthalene (2b) (61 mg, 0·2 mmol) in methanol (80 cm^3) was allowed to react with silver nitrate (170 mg, 1·0 mmol) in methanol (20 cm^3) over 4 h at room temperature as described in (*a*) above. Flash chromatography (dichloromethane/light petroleum, 1:2) gave a colourless solid. Recrystallization (light petroleum) afforded *1-methoxy-1-(naphthalen-2-yl)-2,2-diphenylethene* (6b) (52 mg, 78%) as colourless crystals, m.p. 138–139·5° (Found: C, 89·1; H, 6·0. $C_{25}H_{20}O$ requires C, 89·2; H, 6·0%). ν_{max} 1607, 1590, 1274, 1262, 1230, 1202, 1190, 1082, 1068, 1012, 866, 833, 773, 757, 705 cm^{-1}. ^{1}H n.m.r. δ 3·49, s, CH_3O; 7·00, s, 5H; 7·16–7·73, m, 12H. ^{13}C δ 58·4, CH_3O; 126·0(5), 126·2, 126·3, 126·6, 127·4, 127·6, 127·8, 128·0, 128·2, 129·8, 131·5, aromatic CH; 133·0, 141·3, both 2×q; 133·1, q; 153·0, C1. *m/z* 337 (28%), 336 (100, M), 321 (14, M − Me), 293 (35, M − COMe), 215 (75, M − MeCO − C_6H_6), 165 (37, $C_{13}H_9$), 127 (42, $C_{10}H_7$), 77 (23, Ph).

(c) (E/Z)-1-Methoxy-1-(naphthalen-2-yl)-2-phenylethene (6d) and 1-(Naphthalen-2-yl)-2-phenylethyne (7d)

(i) The reaction of 1-phenylmethylene-1*H*-cyclopropa[*b*]naphthalene (2d) (46 mg, 0·2 mmol) with methanolic silver nitrate as described in (*a*) above gave [in order of elution from flash chromatography (dichloromethane/light petroleum, 1:4)]:

1-(Naphthalen-2-yl)-2-phenylethyne (7d) (10 mg, 21%) as a colourless crystalline solid, m.p. 115–116° (lit.[14] 117°). ν_{max} 1603, 1278, 1080, 977, 961, 927, 918, 878, 836, 767, 757, 702 cm^{-1}. ^{1}H n.m.r. δ 7·23–7·62, m, 8H; 7·72–7·87, m, 3H; 8·04, s, 1H. ^{13}C n.m.r. δ 89·9, q, C1/C2; 120·5, q, (Np)C–C≡; 123·5, q, (Ph)C–C≡; 126·7, 127·8, 128·0, 128·4, 131·5, 131·7(5), aromatic CH; 133·0, 133·2, both q. *m/z* 229 (20%), 228 (100, M), 114 (10).

(E/Z)-*1-Methoxy-1-(naphthalen-2-yl)-2-phenylethene* (6d) (26 mg, 50%) as a pale yellow oil (Found: C, 87·4; H, 6·4. $C_{19}H_{16}O$ requires C, 87·6; H, 6·2%). The *E*/*Z* ratio is assigned as 1:8 from integration of the vinyl and the methoxyl proton resonances. ^{1}H n.m.r. δ (*Z*)-isomer 3·84, s, CH_3O; 5·92, s, CH=C; 7·0–7·9, m, aromatic; (*E*)-isomer, 3·68, s, CH_3O; 6·25, s, CH=C; 7·0–7·9, m, aromatic. ^{13}C δ (*Z*)-isomer 55·7, MeO; 102·5, C2; 125·4, 126·0, 126·4, 127·2, 127·6, 128·1, 128·4, 129·1, aromatic CH; 133·4, 133·9, 137·0, all q; 157·3, C1; (*E*)-isomer 58·2, CH_3O; 113·4, C2. *m/z* 261 (22%), 260 (100, M), 229 (19, M − OMe), 217 (43, M − COMe), 215 (46, M − COMe − 2H), 202 (36), 127 (20, $C_{10}H_7$).

(ii) The reaction of compound (2d) (46 mg, 0·2 mmol) with Ag^I in t-butyl alcohol following the procedure described above gave a multicomponent mixture. Preparative t.l.c. (dichloromethane/light petroleum, 1:4) gave a band (R_F 0·44) which upon extraction afforded alkyne (7d) (14 mg, 31%), m.p., m.m.p. 115–116°.

Reactions of the Alkylidenecycloproparenes (2) with Bromine Water

(a) Reactions with 7-Diphenylmethylenebicyclo[4.1.0]hepta-1,3,5-triene (2a)

(i) To a solution of (2a) (51 mg, 0·2 mmol) in tetrahydrofuran (25 cm^3) was added dropwise saturated bromine water (*c.* 0·22 mol dm^{-3}, 2·5 cm^3). After 40 min at room temperature the solvent was removed in vacuum, water (10 cm^3) added to the residue and the mixture extracted with dichloromethane (2×30 cm^3). The combined organic phases were washed with aqueous sodium metabisulfite (30 cm^3), water (3×30 cm^3), dried ($MgSO_4$) and concentrated in vacuum. The residue was flash-chromatographed (dichloromethane/light petroleum, 1 : 3) to give *1,6-dibromo-7-diphenylmethylenecyclohepta-1,3,5-triene* (8a) (21 mg, 25%) as colourless crystals, m.p. 139–141° (Found: $M^{+\bullet}$ 411·9463. $C_{20}H_{14}{}^{79}Br_2$ requires $M^{+\bullet}$ 411·9462). ν_{max} 1600, 1590, 1321, 1158, 1084, 1040, 996, 950, 935, 775, 760, 748, 711, 681, 675, 612 cm^{-1}. ^1H n.m.r. δ 6·45, 6·58, br AB, *J* 2·8 Hz, H2/H5 and H3/H4, 7·30, s, 10H. ^{13}C δ 108·6, q, C1/C6; 127·9, C2(3)/C5(4); 128·1, 4×CH; 128·8, 6×CH; 130·5(5), C3(2)/C4(5); 139·2, *ipso*-$\mathbf{Ph}_2$C=. λ_{max} (MeCN) 304 (log ε 3·82), 262sh (4·34), 256 (4·41), 252sh (4·38), 226 nm (4·42). *m/z* 416, 414, 412 (1·9, 3·8, 1·9%, M), 335, 333 (7·3, 7·9, M−Br), 334, 332 (8·7, 8·1, M−Br−H), 255 (20), 254 (100, M−Br_2), 253 (69, M−Br−HBr), 252 (57, M−2HBr).

(ii) To a solution of (2a) in tetrahydrofuran (thf) as above was added dropwise dilute bromine water (3×10^{-2} mol dm^{-3}, 6·7 cm^3). After 6, 12 and 18 h additional thf (20 cm^3) and a further aliquot of bromine water were added and the solution was stirred at room temperature for a total of 30 h. The solution was extracted with light petroleum (3×50 cm^3). The combined organic extracts were washed with aqueous sodium metabisulfite (50 cm^3), water (2×50 cm^3), dried ($MgSO_4$) and concentrated in vacuum. Preparative t.l.c. (dichloromethane/light petroleum, 1 : 1) resulted in a band (R_F 0·36) which when extracted gave *8,8-diphenylbicyclo[4.2.0]octa-1,3,5-trien-7-one* (10a) (49 mg, 91%) as a colourless crystalline solid, m.p. 104–105° (Found: $M^{+\bullet}$ 270·1040. $C_{20}H_{14}O$ requires $M^{+\bullet}$ 270·1045). ν_{max} 1765, 1587, 1335, 1280, 1178, 1154, 1139, 1100, 1085, 1040, 985, 890, 848, 782, 760, 709, 690, 644 cm^{-1}. ^1H n.m.r. δ 7·08–7·97, m, 14H; ^{13}C δ 81·0(5), CPh_2; 122·1, 124·1, 129·9, 136·1, all CH; 127·1, 6×CH; 128·6, 4×CH; 141·5, *ipso*-$\mathbf{Ph}_2$C; 146·6, 158·3, both q, C1/C6; 189·7, CO. *m/z* 271 (22%), 270 (100, M), 269 (20), 242 (10, M−CO), 241 (39, M−HCO), 240 (11, M−CO−2H), 239 (32, M−HCO−2H).

(b) Reactions with 1-Diphenylmethylene-1H-cyclopropa[b]naphthalene (2b)

(i) To a solution of (2b) (61 mg, 0·2 mmol) in thf (50 cm^3) was added saturated bromine water (2·5 cm^3) as described in (*a*)(i) above. Preparative t.l.c. (dichloromethane/light petroleum, 1 : 1) resulted in two major fluorescent bands A and B.

Band A (R_F 0·30) yielded *2,2-diphenylcyclobuta[b]naphthalen-1(2H)-one* (10b) (28 mg, 44%) as colourless crystals (from hexane), m.p. 168–169° (Found: C, 89·7; H, 4·8. $C_{24}H_{16}O$ requires C, 90·0; H, 5·0%). ν_{max} (KBr) 3046, 3020, 1756, 1612, 1586, 1484, 1440, 1260, 1138, 1108, 1072, 1066, 1022, 918, 898, 882, 792, 754, 722, 708, 696, 680 cm^{-1}. λ_{max} (EtOH) 306 (log ε 3·92), 296sh (3·85), 243 nm (4·61). ^1H n.m.r. δ 7·17–7·68, m, 12H; 7·87–7·99, m, 3H; 8·18, bs, 1H. ^{13}C δ 81·4, CPh_2; 122·1, 122·3, 126·5, 128·9, 130·9, all CH; 127·1, 6×CH; 128·6, 5×CH; 134·4, 138·4, 144·6, 151·3, all q; 141·5, q, *ipso*-$\mathbf{Ph}_2$C=; 191·8, CO. *m/z* 321 (26%), 320 (100, M), 319 (22, M−1), 291 (33, M−HCO), 290 (14, M−CO−2H), 289 (38, M−HCO−2H), 243 (16, M−Ph), 215 (14, M−PhCO).

Band B (R_F 0·15) afforded colourless rods (hexane) of *2,2-diphenyl-2-hydroxy-1-[2-(3-bromonaphthalenyl)]ethanone* (13b) (36 mg, 43%), m.p. 163·5–164° [Found: *m/z* 336·1142 and 232·9601. $C_{24}H_{17}BrO_2-HBr$ requires 336·1150 and $C_{24}H_{17}BrO_2-Ph_2C(OH)$ requires 232·9602(5)]. ν_{max} 3543, 1699, 1145, 1061, 969, 877, 760, 728, 703 cm^{-1}. ^1H n.m.r. δ 4·03, OH; 7·10, 1H; 7·31–7·67, m, 14H; 8·02, s, 1H. ^{13}C δ 86·3, Ph_2COH; 116·7, CBr; 126·8, 127·0(5), 131·9, all CH; 128·2, 5×CH; 128·4, 8×CH; 130·7, 134·4, 137·5, all q; 140·9(5), q, *ipso*-$\mathbf{Ph}_2$C; 203·8, CO. *m/z* 235, 233 (5·9, 5·6% M−Ph_2COH); 207, 205 (3·8, 4·0; $C_{10}H_6Br$); 184 (14) 183 (100; Ph_2COH); 105 (81, PhCO); 77 (54, Ph).

(ii) To a solution of (2b) (61 mg, 0·2 mmol) in thf (50 cm^3) was added dilute bromine water and the reaction performed as in (*a*)(ii) above. Workup followed by flash chromatography (dichloromethane/light petroleum, 1 : 1) gave after recrystallization (hexane) the cyclobuta[*b*]naphthalenone (10b) (48 mg, 75%), m.p., m.m.p. 168–169°.

(c) Reactions with 1-Phenylmethylene-1H-cyclopropa[b]naphthalene (2d)

(i) Alkylidenecycloproparene (2d) (46 mg, 0·2 mmol) was treated with saturated bromine water as described in (*a*)(i) above. Flash chromatography (dichloromethane/light petroleum, 1 : 1) yielded *2-bromo-1-(3-bromonaphthalen-2-yl)-2-phenylethanone* (12d) (54 mg, 67%) as colourless crystals (hexane), m.p. 112–113° (Found: C, 53·7; H, 3·0; Br, 39·5. $C_{18}H_{12}Br_2O$ requires C, 53·5; H, 3·0; Br, 39·5%). ν_{max} 1706, 1623, 1582, 1136, 1053, 960, 905, 897, 887, 805, 770, 760, 728, 697, 632 cm^{-1}). ^1H n.m.r. δ 6·31, s, CHBr; 7·24–7·82, m, 10H; 8·06, s, H 1. ^{13}C δ 53·5, CHBr; 115·1, CBr; 126·9, 127·4, 128·8, 128·9, 129·3, 129·7, 130·1, 132·4, aromatic CH; 131·2, 135·0, 136·7, all q; 194·6, CO. *m/z* 406, 404, 402 (0·9, 1·9, 0·9%; M); 235, 233 (100, 99; M − PhCHBr); 215 (20; M − 2Br − CHO); 126 (27; $C_{10}H_6$).

(ii) Treatment of (2d) with dilute bromine water as in (*a*)(ii) above. Preparative t.l.c. (dichloromethane/light pretroleum, 1 : 1) showed two fluorescent bands A and B.

Band A (R_F 0·55) gave the dibromoethanone (12d) (19 mg, 23%), m.p., m.m.p. 110–111°, identical to the sample from (i) above.

Band B (R_F 0·45) furnished 2-bromo-1-(naphthalen-2-yl)-2-phenylethanone (11d) (30 mg, 46%) as colourless crystals, m.p. 109·5–111° (lit.[20] 111–111·5°). ν_{max} 1690, 1628, 1280, 1188, 1133, 925, 826, 803, 758, 707, 689 cm^{-1}. ^1H n.m.r. δ 6·53, s, CHBr; 7·21–8·08, m, 11H; 8·49, bs, 1H. ^{13}C δ 51·0, CHBr; 124·5, 127·0, 127·8, 128·7, 128·9, 129·0, 129·1, 129·2, 129·7, 130·9, aromatic CH; 131·7, 132·5, 135·8, 136·1, all q; 191·1, CO. *m/z* 326, 324 (3, 3%; M); 156 (12), 155 (100; M − PhCHBr); 127 (41, $C_{10}H_7$).

Reactions of the Alkylidenecycloproparenes (2) with Halogens

(a) Reaction of (2a) with Bromine

Treatment of the diphenylmethylenecycloproparene (2a) with molecular bromine under a variety of conditions failed to provide characterisable material.

(b) Reaction of (2b) with Bromine

To a precooled (−25°) solution of 1-diphenylmethylene-1*H*-cyclopropa[*b*]naphthalene (2b) (122 mg, 0·4 mmol) in dry dichloromethane (10 cm^3) was added slowly bromine (64 mg, 0·4 mmol) in the same solvent (3 cm^3). The mixture was warmed to room temperature over 1 h and concentrated in vacuum to a pale brown solid which was crystallized from dichloromethane to afford *1,1-dibromo-2,2-diphenyl-1,2-dihydrocyclobuta[b]naphthalene* (9b) (130 mg, 70%) as colourless crystals, m.p. 149–150° (dec.) (Found: C, 61·3; H, 3·5; Br, 33·7. $C_{24}H_{16}Br_2$ requires C, 62·1; H, 3·4; Br, 34·5%).* ν_{max} (KBr) 3050, 3022, 1598, 1490, 1440, 1328, 1258, 1236, 1128, 1084, 1070, 1060, 1030, 998, 936, 902, 878, 820, 745, 695, 668, 750, 612 cm^{-1}. λ_{max} (pentane) 327 (log ε 3·55), 288 (4·09), 237 nm (4·98). ^1H n.m.r. δ 7·15–7·32, m, 6H; 7·35–8·05, m, 6H; 8·25–8·42, br s, 4H. ^{13}C δ 66·4, CBr_2; 77·6, CPh_2; 121·1, 123·7, 126·3, 126·8, 128·7, all CH; 127·6, 6×CH; 129·1, 5×CH; 134·9, 136·2, 139·8, 147·1, all q; 141·1, *ipso*-$\mathbf{Ph_2}$C. *m/z* 385, 383 (16, 18%; M − Br); 305 (39), 304 (100; M − Br_2); 303 (42, M − Br_2 − H); 302 (42; M − Br_2 − 2H).

Column chromatography dichloromethane/hexane, 1 : 1) of the crude reaction product from above resulted in hydrolysis of the dibromide to give 2,2-diphenylcyclobuta[*b*]naphthalene-1(2*H*)-one (10b) (63 mg, 61%) identical to the samples recorded above, m.p., m.m.p. 168–169°.

(c) Reaction of (2b) with Chlorine

Through a stirred and pre-cooled (−25°) solution of 1-diphenylmethylene-1*H*-cyclopropa[*b*]naphthalene (2b) (122 mg, 0·4 mmol) in dry dichloromethane (20 cm^3) was bubbled pre-dried chlorine gas for 30 min. The pale yellow solution was warmed to room temperature over 1 h, concentrated to dryness in vacuum and the resultant solid chromatographed (dichloromethane/hexane, 1 : 1) to give *2-chloro-3-(2,2-diphenyl-1,1,2-trichloroethyl)naphthalene* (14b) (115 mg, 65%) as colourless crystals (from hexane), m.p. 85–86° (dec.) (Found: $M^{+\bullet}$ 445·9779, 443·9809. $C_{24}H_{16}{}^{37}Cl^{35}Cl_3$ and $C_{24}H_{16}{}^{35}Cl_4$ require $M^{+\bullet}$ 445·9818, 443·9849).

* The susceptibility of this compound to hydrolysis has prevented the acquisition of more accurate microanalytical data.

ν_{max} (KBr) 3044, 3020, 1590, 1484, 1432, 1258, 1238, 1128, 1080, 1020, 992, 938, 908, 882, 840, 778, 758, 738, 700, 660, 610 cm^{-1}. ^1H n.m.r. δ 7·25–7·65, m, 12H; 7·85–8·15, m, 4H. ^{13}C δ 77·9, Ph_2CCl; 91·0, CCl_2; 120·5, 124·0, 126·3, 126·9, 128·7, 129·1, all CH; 127·5, 2×CH; 127·7, 3×CH; 129·2, 5×CH; 134·8, 136·3, 140·9, 145·2, all q; 140·4, *ipso*-$\mathbf{Ph_2C}$. *m/z* (17 eV) 448, 446, 444 (4, 10, 17%; M); 413, 411, 409 (9, 24, 25; M − Cl); 412, 410, 408 (24, 76, 86; M − HCl).

(d) Reaction of (2d) with Bromine

To a solution of 1-phenylmethylene-1*H*-cyclopropa[*b*]naphthalene (2d) (46 mg, 0·2 mmol) in dry tetrahydrofuran (25 cm^3) was added bromine (160 mg, 1·0 mmol). After the mixture had been stirred for 15 min at room temperature, water (7·2 mg, 0·4 mmol) in the same solvent (1 cm^3) was added and the stirring continued for 5 min. Water (10 cm^3) was added, and the solution was extracted with dichloromethane (2×30 cm^3). The combined organic extracts were washed with aqueous sodium metabisulfite (30 cm^3), water (3×30 cm^3), dried ($MgSO_4$) and concentrated in vacuum to an oil. Flash chromatography (dichloromethane/light petroleum, 1 : 1) afforded dibromoethanone (12d) (55 mg, 68%) as colourless crystals (hexane), m.p., m.m.p. 112–113°, and bromoethanone (11d) (11 mg, 17%), m.p., m.m.p. 110–111° (lit.[20] 111–111·5°).

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