Dehydrohalogenation of Some Tetrahalogenobicyclo[4.1.0]hept-3-enes. Formation and Decomposition of 1,1-Dihalogenocyclopropabenzenes [1]

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Of the tetrahalogenobicyclo[4.1.0]hept-3-enes (2)—(7) only the tetrachloro-2,5-diphenyl derivative (3) yields an isolable *gem*-dihalogenocyclopropabenzene (10) on dehydrochlorination. The formation of esters and orthoesters from compounds (2) and (4)—(6) is explicable in terms of the cyclopropabenzenes (9) and (11)—(13) as intermediates. The decomposition of (10) in protic media has been studied and is believed to proceed *via* a cyclopropabenzenylium ion (30).

DESPITE continued interest in cyclopropabenzene chemistry,[2] little attention had been given to derivatives bearing halogeno-substituents at the 1-position until our preliminary account of the synthesis of 1,1-dichloro-2,5-diphenylcyclopropabenzene (10).[1] This and other *gem*-dihalogeno-species appeared to be of particular interest as precursors of other less accessible members of the series; in this connection compound (10) has recently been converted into hydrocarbon,[3] difluoro-,[4] and dialkyl and diaryl [5] derivatives, and also into the corresponding 6π C_7 σ-bridged ion (30).[6] We report here the results of studies on the dehydrohalogenation of the bicycloheptenes (2)—(7) together with aspects of the chemistry of the cyclopropabenzene (10).

Potentially the most useful route to *gem*-dihalogenocyclopropabenzenes appeared to be by dehydrohalogenation of bicyclo[4.1.0]hept-3-enes, *e.g.* (2)—(7), since these compounds are relatively easy to obtain by [4 + 2] cycloaddition of dienes with perhalogenocyclopropenes.[7] This method, applied to compound (1), gave the only previously reported halogenocyclopropabenzene (8).[8]

The 1,6,7,7-tetrahalogenobicyclo[4.1.0]hept-3-enes (2)—(7) were synthesised in moderate yields from *trans*,-*trans*-butadienes and perhalogenocyclopropenes [9] by the method of Law and Tobey.[7] These authors have shown that compounds (1) and (2), formed initially in the *endo*-configuration (A), predominantly adopt the ring-flip conformation depicted in (B), in which the interaction between the π-electrons and the *endo*-halogen atom at C-7 is minimised. In compounds (3)—(7), however, R^1 and R^2 are bulky, and conformation (B) appears the least likely because of severe steric interaction of R^1 and R^2 with the *syn*-halogen atom at C-7. The ^1H n.m.r. spectra of compounds (3)—(7) show $J_{2,3}$ and $J_{4,5}$ to be insensitive to temperature and to lie in the range 2.0—3.5 Hz. Although these data support conformation (A) with a dihedral angle between H-2 and H-3 of *ca.* 105°, the effect of sp^2 hybridisation at C-3 (and C-4) cannot be estimated with certainty.[10] Consequently these assignments, which appear reasonable on steric grounds, are not definitive.

The dehydrohalogenation of each of compounds (2)—(7) has been examined under a variety of conditions. Vogel [11] found that treatment of (2) with potassium hydroxide in triethylene glycol at temperatures up to 180 °C did not lead to aromatisation, although these same conditions afford (8) from both (1) and its 1,6-dichloro-analogue, a result with which we concur. However, the reaction of (2) with t-butoxide in tetrahydrofuran results in precipitation of inorganic halide and formation of a complex mixture of organic products from which t-butyl benzoate (20) was isolated in 16% yield. The elimination of hydrogen halide from compounds (3)—(7) also occurs with this same base–solvent combination. With (3), the cyclopropabenzene (10) was obtained in almost quantitative yield. The structure (10) was established from spectral data and confirmed by *X*-ray analysis.[12] The i.r. spectrum exhibits the typical [2] cyclopropa-arene medium intensity band at 1 680 cm^{-1} and the ^1H n.m.r. spectrum † shows a six- and a four-proton multiplet in the ranges δ 7.30—7.50 and 7.70—7.88, respectively, with the symmetry of the molecule exemplified by a two-proton singlet at δ 7.70 for the C-3 and C-4 protons.

In contrast to the behaviour of (3), the tetrabromo-adduct (4) gave rise to a highly coloured and complex mixture under the same conditions. By performing the reaction at −78 °C with a slow (30 h) addition of base, dehydrohalogenation proceeded smoothly, as judged by deposition of potassium bromide, and a black halogen-free oil was obtained from which the ester (22) (19%) was isolated. The product was characterised by hydrolysis to 2,5-diphenylbenzoic acid (25).[14] The behaviour of the unsymmetrical bicycloheptene (5) paralleled that of (4), giving rise to a single ester (26) (48%), identified

† The cyclopropabenzene (10) decomposes in chloroform solution, as evidenced by significant changes in the ^1H n.m.r. spectrum even after 10 min.[13]

[1] Preliminary communication, B. Halton and P. J. Milsom, *Chem. Comm.*, 1971, 814.
[2] For a review, see B. Halton, *Chem. Rev.*, 1973, **73**, 113.
[3] P. Müller, *Helv. Chim. Acta*, 1974, **57**, 704.
[4] P. Müller, *J.C.S. Chem. Comm.*, 1973, 895.
[5] B. Halton, A. D. Woolhouse, and P. J. Milsom, following paper.
[6] B. Halton, H. M. Hügel, D. P. Kelly, P. Müller, and U. Burger, *J.C.S. Perkin II*, 1976, 258.
[7] D. C. F. Law and S. W. Tobey, *J. Amer. Chem. Soc.*, 1968, **90**, 2376.
[8] E. Vogel, S. Korte, W. Grimme, and H. Günther, *Angew. Chem. Internat. Edn.*, 1968, **7**, 289.
[9] S. W. Tobey and R. West, *J. Amer. Chem. Soc.*, 1966, **88**, 2481.
[10] See, for example, L. M. Jackman and S. Sternhell, 'Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, Oxford, 1969, p. 284.
[11] E. Vogel, personal communication.
[12] B. Halton, T. J. McLellan, and W. T. Robinson, *Acta Cryst.*, 1976, **B32**, 1889.
[13] B. Halton, H. M. Hügel, and D. P. Kelly, unpublished observations.
[14] G. R. Ames and W. Davey, *J. Chem. Soc.*, 1957, 3480.

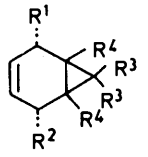
by hydrolysis to 2-methyl-5-phenylbenzoic acid (27).[15] Analogous treatment of (6) and (7) resulted in uncharacterised tars.

The formation of the t-butyl esters (20), (22), and (26) from (2), (4), and (5) respectively, is explicable in terms of initial formation of the cyclopropabenzenes (9), (11), and (12), which decompose as illustrated for (10) in the Scheme. Support for this hypothesis stems from the behaviour of the isolable cyclopropabenzene (10) in alkoxide–alcohol systems. Treatment of (10) with sodium methoxide in methanol results in rapid and quantitative conversion into the orthoester (16), which on acid-catalysed hydrolysis affords the carboxylate ester (23). In like manner (17) [and (24)] can be obtained from (10), although the stability of the orthoester (17) is less than that of (16). With potassium t-butoxide in t-butyl alcohol, the orthoester analogue of (16) and (17) is not isolable, and the t-butyl carboxylate (22) is obtained on work-up, but in low (40%) yield [*cf* (20), (22), and (26)]. Solvolysis of (10) generates a proton which, in the absence of base, is available to catalyse decomposition of the orthoester; under these conditions only carboxylate esters are obtained. We regard the formation of (16) and (17) from (10) as proceeding *via* the cyclopropabenzenylium ion (30) and the acetal (31) (Scheme), the former being known to afford the acid (25) with moisture by way of the cyclopropenone.[16]

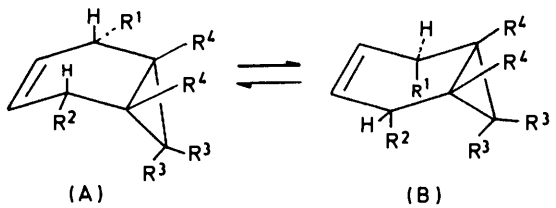
Further evidence for the involvement of the *gem*-dibromocyclopropabenzene (11) in the dehydrobrominations of (4) comes from the behaviour of (4) with sodium alkoxide in alcohol. Under these conditions both (3) and (4) give rise to the same orthoesters, (16) and (17) (in almost quantitative yield), as can be obtained from (10). The bicycloheptene (6), which gave only uncharacterised products with t-butoxide–t-butyl alcohol, affords the ester (28) (40%) with methoxide–methanol *via* the orthoester (19), whereas (7) gives rise to an as yet uncharacterised product, $C_{21}H_{17}Cl_3O_2$ (30%), corresponding to replacement of one chlorine atom of (6) by MeO.

The results of the elimination reactions undergone by (2) and the *syn*-dehydrohalogenations of (3)—(7) clearly do not provide a viable route to *gem*-dihalogenocyclopropabenzenes. However, although (10) is the only such species isolated, even under aprotic conditions, the products derived from (2) and (4)—(6) are best explained by the intervention of the desired compounds (9) and (11)—(13); only (7) has not provided products explicable in this way. The enhanced product yields from bicycloheptenes with electron-withdrawing substituents at C-2 and C-5 are perhaps indicative of *E*lcb character in the elimination process.

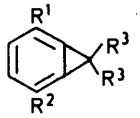
Of the products derived from the elimination reactions,



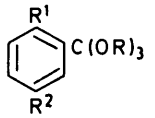
(1) $R^1=R^2=H$, $R^3=F$, $R^4=Br$
(2) $R^1=R^2=H$, $R^3=R^4=Cl$
(3) $R^1=R^2=Ph$, $R^3=R^4=Cl$
(4) $R^1=R^2=Ph$, $R^3=R^4=Br$
(5) $R^1=Me$, $R^2=Ph$, $R^3=R^4=Cl$
(6) $R^1=COPh$, $R^2=Ph$, $R^3=R^4=Br$
(7) $R^1=COPh$, $R^2=Ph$, $R^3=R^4=Cl$



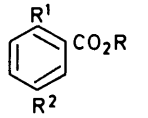
(A) (B)



(8) $R^1=R^2=H$, $R^3=F$
(9) $R^1=R^2=H$, $R^3=Cl$
(10) $R^1=R^2=Ph$, $R^3=Cl$
(11) $R^1=R^2=Ph$, $R^3=Br$
(12) $R^1=Me$, $R^2=Ph$, $R^3=Cl$
(13) $R^1=COPh$, $R^2=Ph$, $R^3=Br$
(14) $R^1=COPh$, $R^2=Ph$, $R^3=Cl$



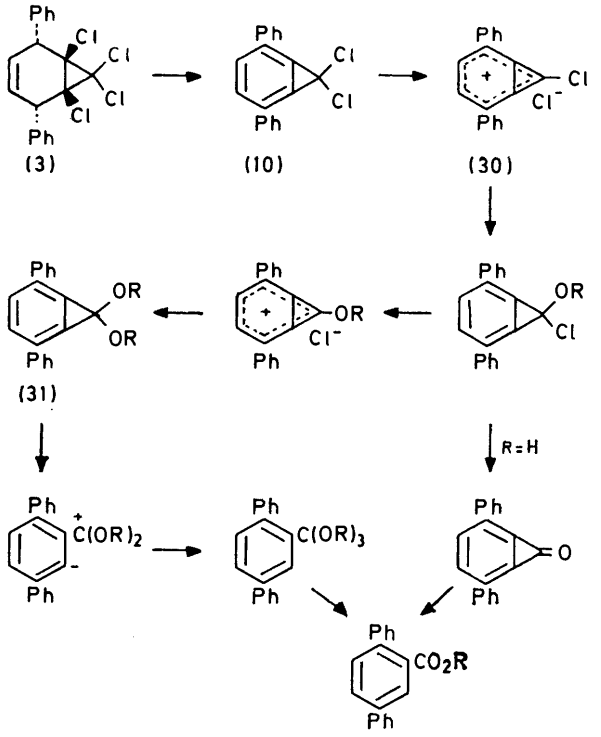
(15) $R=Me$, $R^1=R^2=H$
(16) $R=Me$, $R^1=R^2=Ph$
(17) $R=Et$, $R^1=R^2=Ph$
(18) $R=R^1=Me$, $R^2=Ph$
(19) $R=Me$, $R^1=Ph$, $R^2=COPh$



(20) $R=Bu^t$, $R^1=R^2=H$
(21) $R=R^1=R^2=H$
(22) $R=Bu^t$, $R^1=R^2=Ph$
(23) $R=Me$, $R^1=R^2=Ph$
(24) $R=Et$, $R^1=R^2=Ph$
(25) $R=H$, $R^1=R^2=Ph$
(26) $R=Bu^t$, $R^1=Me$, $R^2=Ph$
(27) $R=H$, $R^1=Me$, $R^2=Ph$
(28) $R=Me$, $R^1=Ph$, $R^2=COPh$
(29) $R=Me$, $R^1=COPh$, $R^2=Ph$

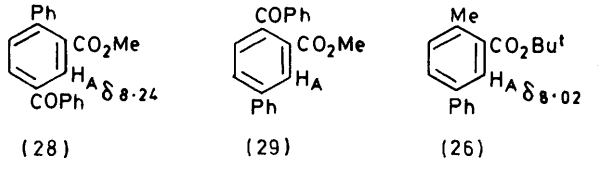
[15] V. Georgian and J. Lepe M, *J. Org. Chem.*, 1964, **29**, 40.
[16] B. Halton, A. D. Woolhouse, H. M. Hügel, and D. P. Kelly, *J.C.S. Chem. Comm.*, 1974, 247.

(26) and (28) deserve further comment. The identity of (28) as methyl 5-benzoyl-2-phenylbenzoate and not the

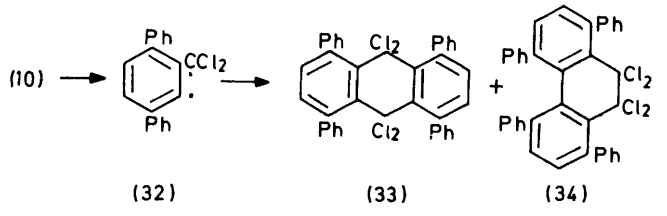


SCHEME

2-benzoyl-5-phenyl isomer (29) is based on comparison of the chemical shift of the C-6 proton (H_A) with that of the C-6 proton of unambiguously identified (26). Only



in (28), with an adjacent benzoyl function, can the observed 0.22 p.p.m. deshielding of H_A relative to that in (26) be explained. Furthermore, the formation of (26) and (28) is consistent with ring opening of the acetals [equivalent to (31); Scheme] being controlled by inductive stabilisation of developing carbanionic character.[17]



Despite the rapid decomposition of (10) in alcoholic media, the crystalline material may be stored for long periods without change, but on mild thermolysis (refluxing benzene) two distinct, and sparingly soluble, dimeric species are produced. From ^1H and ^{13}C n.m.r. data structures (33) and (34), which might be expected from head-to-tail and head-to-head dimerisation of the diradical (32), are unequivocally eliminated. The structures of the dimeric products are the subject of continuing investigation.[13]

EXPERIMENTAL

Microanalyses were performed by Professor A. D. Campbell and his associates, Otago University, Dunedin. I.r. spectra were recorded for Nujol mulls or thin films with a Unicam SP 200 or SP 1000 spectrophotometer unless otherwise stated, and u.v. spectra with a Shimadzu UV 200 instrument. N.m.r. spectra were recorded for solutions in deuteriochloroform (tetramethylsilane as internal standard) with a Hitachi–Perkin-Elmer R20 instrument operating at 34 °C, and mass spectra with an A.E.I. MS902 instrument. Merck Kieselgel GF254 was used for t.l.c., and preparative plates (1 m × 20 cm) were made to a thickness of 0.75 mm.

The Bicycloheptenes (2)—(7).—A solution of the appropriate *trans,trans*-butadiene (0.026 mol) and tetrahalogenocyclopropene (0.028 mol) in dry benzene (40 cm^3) was heated in a sealed tube at the temperature and for the period indicated below. The solution was concentrated in vacuum and the product isolated by recrystallisation: 1,6,7,7-tetrachlorobicyclo[4.1.0]hept-3-ene (2) (68%; 100 °C, 15 h) as needles (from pentane), m.p. 50—51° (lit.,[7] 50—51°); 1,6,7,7-*tetrachloro*-2,5-*diphenylbicyclo*[4.1.0]-*hept*-3-*ene* (3) (76%; 130 °C, 18 h) as needles [from benzene–light petroleum (1 : 1)], m.p. 174—175° (Found: C, 59.6; H, 3.8; Cl, 36.5. $C_{19}H_{14}Cl_4$ requires C, 59.4; H, 3.65; Cl, 36.9%); δ 4.09 (2 H, d, $J_{2,3} = J_{5,4} = 2.0$ Hz), 5.66 (2 H, d, $J_{3,2} = J_{4,5} = 2.0$ Hz), and 7.31br (10 H, s); $\nu_{max.}$ 1 600, 1 500, 1 285, 1 125, 1 075, 1 030, 990, 955, 885, 840, 770, 735, and 700 cm^{-1}; 1,6,7,7-*tetrabromo*-2,5-*diphenylbicyclo*[4.1.0]*hept*-3-*ene* (4) (74%; 112 °C, 18 h) as prisms [from benzene–light petroleum (2 : 1)], m.p. 163—165° (Found: C, 40.8: H, 2.5; Br, 56.35. $C_{19}H_{14}Br_4$ requires C, 40.6; H, 2.5; Br, 56.9%); δ 4.04 (2 H, d, $J_{2,3} = J_{5,4} = 2.0$ Hz,), 5.69 (2 H. d, $J_{3,2} = J_{4,5} = 2.0$ Hz), and 7.27br (10 H, s); $\nu_{max.}$ 1 600, 1 495, 1 280, 1 095, 1 025, 930, 865, 765, 715, and 695 cm^{-1}; 1,6,7,7-*tetrachloro*-2-*methyl*-5-*phenylbicyclo*[4.1.0]*hept*-3-*ene* (5) (53%; 130 °C, 25 h) as prisms [from benzene–light petroleum (2 : 1)], m.p. 133—134° (Found: C, 52.05; H, 3.75; Cl, 43.5. $C_{14}H_{12}Cl_4$ requires C, 52.2; H, 3.75; Cl, 44.05%); δ 1.52 (3 H, d, J 7.5 Hz), 3.01 (1 H, m, $J_{2,8}$ 7.5, $J_{2,3}$ 3.0 Hz), 3.96 (1 H, m, $J_{5,4}$ *ca.* 3.0 Hz), 5.25 (2 H, m, $J_{3,2} \sim J_{4,5} \sim 3$ Hz), and 7.21br (5 H, s); $\nu_{max.}$ 1 605, 1 500, 1 480. 1 300 1 150, 1 090, 1 080, 1 050, 1 040, 905, 885, 850, 835, 780, 750, and 705 cm^{-1}; 2-*benzoyl*-1,6,7,7-*tetrabromo*-5-*phenylbicyclo*[4.1.0]-*hept*-3-*ene* (6) (31%; 100 °C, 48 h) as fine needles [from benzene–light petroleum (1 : 1)], m.p. 209—211° (Found: C, 40.6; H, 2.65; Br, 53.95. $C_{20}H_{14}Br_4O$ requires C, 40.7; H, 2.4; Br, 54.2%); δ 4.10 (1 H, t, $J_{5,4}$ 3.5 Hz), 5.09 (1 H, t, $J_{2,3}$ 3.5 Hz), 5.70 (2 H, m, $J_{3,2} \sim J_{4,5} \sim 3.5$ Hz), 7.11—7.83 (8 H, m), and 7.81—8.03 (2 H, m); $\nu_{max.}$ 1 690, 1 600, 1 345, 1 230, 1 200, 1 175, 1 105, 990, 985, 910, 860, 790, 760, 705, 695, and 660 cm^{-1}; 2-*benzoyl*-1,6,7,7-*tetrachloro*-5-*phenylbicyclo*[4.1.0]*hept*-3-*ene* (7) (51%; 130 °C, 30 h) as needles [from benzene–light petroleum (1 : 1)], m.p. 195—196° (Found: C, 58.35; H, 3.5; Cl, 33.9. $C_{20}H_{14}Cl_4O$

[17] R. W. Hoffmann, 'Dehydrobenzene and Cycloalkynes,' Academic Press, New York, 1967, p. 135.

requires C, 58.25; H, 3.4; Cl, 34.45%); δ 4.02 (1 H, t, $J_{5,4}$ 3.5 Hz), 5.01 (1 H, t, $J_{2,3}$ 3.5 Hz), 5.65 (2 H, m, $J_{3,2} = J_{4,5} = 3.5$ Hz), 7.16—7.70 (8 H, m), and 7.88—8.11 (2 H, m); $\nu_{max.}$ 1 690, 1 600, 1 340, 1 260, 1 210, 1 175, 1 130, 990, 875, 835, 790, 765, 725, and 695 cm^{-1}.

Dehydrohalogenations of Compounds (2)—(7) *with Potassium t-Butoxide in Tetrahydrofuran.*—(i) To a stirred solution of 1,6,7,7-tetrachloro-2,5-diphenylbicyclo[4.1.0]hept-3-ene (3) (10.0 g, 0.026 mol) in dry tetrahydrofuran (THF) (40 cm^3), externally cooled in a salt–ice bath (−15 °C), was slowly added over 4 h a solution of potassium t-butoxide (6.9 g, 0.061 mol) in dry THF (70 cm^3). During the addition the solution became murky (KCl) and bright yellow. After this time the mixture was warmed to ambient temperature and concentrated in vacuum at 25 °C to a pale yellow solid, which was extracted with benzene (6 × 40 cm^3). The extract was washed with water (2 × 20 cm^3), saturated sodium chloride solution (20 cm^3), dried ($MgSO_4$; 15 g), and concentrated to a yellow crystalline mass. Recrystallisation from dry carbon tetrachloride afforded 1,1-*dichloro*-2,5-*diphenylcyclopropabenzene* (10) (5.9 g, 73%) as needles. Concentration of the mother liquors gave a further 1.4 g (91% *in toto*) of (10), m.p. 135—136° (decomp.) (Found: M^+, 310.032 415. $C_{19}H_{12}{}^{35}Cl_2$ requires M 310.031 600); δ 7.30—7.50 (6 H, m), 7.70 (2 H, s), and 7.70—7.88 (4 H, m); $\nu_{max.}$ (KBr) 1 680, 1 485, 1 410, 1 130, 1 080, 975, 755, and 705 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 316 nm (log ε 4.67).

(ii) Potassium t-butoxide (2.5—3 mol. equiv.) in THF (20 cm^3) was slowly added to a stirred solution the bicycloheptene (2) or (4)—(7) in THF (20 cm^3) over a period and at a temperature as specified below. After warming to ambient temperature and extraction, as described above, the product mixture was subjected to preparative t.l.c.

(*a*) The base was added to the solution of (2) in THF at −75 °C over 7 h. Preparative t.l.c. [benzene–light petroleum (1 : 2)] gave a band (R_F 0.4—0.7) which was rechromatographed (benzene). The only u.v. active band (R_F 0.8) was extracted with chloroform to give t-butyl benzoate (20) as a mobile liquid (16%). Base-catalysed hydrolysis afforded benzoic acid (21), m.p. and mixed m.p. 120—121°.

(*b*) The base was added to the solution of (4) in THF at −75 °C over 30 h and, after a difficult work-up, preparative t.l.c. (light petroleum) afforded one band (R_F 0.5). Extraction with chloroform gave *t-butyl* 2,5-*diphenylbenzoate* (22) as a pale yellow immobile gum (19%); δ 1.28 (9 H, s), 7.25—7.67 (12 H, m), and 8.00 (1 H, d, J_m 2.1 Hz); $\nu_{max.}$ 2 950, 1 710, 1 495, 1 400, 1 380, 1 315, 1 265, 1 155, 770, and 695 cm^{-1}. Alkaline hydrolysis gave 2,5-diphenylbenzoic acid (25), m.p. 177—179° (lit.,[14] 178—179°) (Found: C, 83.45; H, 5.15. Calc. for $C_{19}H_{14}O_2$: C, 83.2; H, 5.15%).

(*c*) The base was added to the solution of (5) in THF at −20 °C over 5 h. Preparative t.l.c. (benzene) afforded one band (R_F 0.6) which was extracted with chloroform to give *t-butyl* 2-*methyl*-5-*phenylbenzoate* (26) as a gum (48%); δ 1.60 (9 H, s), 2.59 (3 H, s), 7.20—7.66 (7 H, m), and 8.02 (1 H, d, J_m 2.0 Hz), $\nu_{max.}$ 1 705, 1 490, 1 440, 1 409, 1 386, 1 305, 1 250, 1 090, 915, 905, 820, 755, and 695 cm^{-1}. Alkaline hydrolysis gave 2-methyl-5-phenylbenzoic acid (27) (68%), m.p. 210—211° (lit.,[15] 211—212°).

(*d*) The reactions of (6) and (7) led to uncharacterised tars at temperatures from −70 to 25 °C.

Dehydrochlorinations of Compounds (2)—(7) *with Alkoxide–Alcohol.*—In a typical reaction sodium alkoxide (2.5—3.0 mol. equiv.) in alcohol (25 cm^3) was added slowly with stirring to a solution of the bicycloheptene in benzene (20 cm^3) containing alcohol (10 cm^3). The resultant solution was concentrated in vacuum and worked up as described for (10) above.

(i) Reactions of (3) and (4) with sodium methoxide in methanol at temperatures from −15 to 50 °C gave a dark orange solid. Recrystallisation from light petroleum afforded *trimethyl* 2,5-*diphenylorthobenzoate* (16) [95% from (3) and 89% from (4)], m.p. 102—104° (Found: C, 79.1; H, 6.8. $C_{22}H_{22}O_3$ requires C, 79.0; H, 6.65%); δ 3.00 (9 H, s), 7.15—7.62 (12 H, m), and 7.83 (1 H, d, J_m 2.0 Hz); $\nu_{max.}$ 1 595, 1 480, 1 445, 1 305, 1 215, 1 160—995, 990, 840, 760, and 695 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 261 nm (log ε 4.20); *m/e* 303 (base) and 334 (M^+; 11%). Acid-catalysed hydrolysis gave *methyl* 2,5-*diphenylbenzoate* (23) (96%), δ 3.52 (3 H, s), 7.25—7.70 (12 H, m), and 7.93 (1 H, d, J_m 2.0 Hz), which in turn gave 2,5-diphenylbenzoic acid (25) (89%) on alkaline hydrolysis, identical with the sample described above.

With sodium ethoxide in ethanol (3) and (4) afforded *triethyl* 2,5-*diphenylorthobenzoate* (17) [88% from (3); 94% from (4)] as an unstable pale yellow oil; δ 0.97 (9 H, t, J 7.2 Hz), 3.28 (6 H, q, J 7.2 Hz), 7.15—7.67 (12 H, m), and 7.87 (1 H, d, J_m 2.2 Hz); $\nu_{max.}$ 3 010, 2 920, 2 850, 1 600, 1 485, 1 445, 1 395, 1 305, 1 215, 1 130, 1 115, 1 100—1 005, 905, 835, 775, 695, and 685 cm^{-1}. Attempted purification of the oil either by bulb-to-bulb distillation or by preparative t.l.c. resulted in *ethyl* 2,5-*diphenylbenzoate* (24), δ 0.98 (3 H, t, J 7.5 Hz), 4.10 (2 H, q, J 7.5 Hz), 7.31—7.79 (12 H, m), and 8.01 (1 H, d, J_m 2.0 Hz), which was also produced by acidic hydrolysis of (17). Alkaline hydrolysis of (24) gave the acid (25).

(ii) Sodium methoxide addition to a chilled THF solution of (6) over 4 h, stirring for a further 1 h, and work-up as already described gave a black halogen-free oil, the ^1H n.m.r. spectrum of which provided evidence for the presence of the orthoester (19) (s, δ 3.03). Attempted purification by preparative t.l.c. (benzene) gave one u.v.-active band (R_F 0.3) which on extraction afforded an off-white solid. Recrystallisation gave *methyl* 5-*benzoyl*-2-*phenylbenzoate* (28) as needles (40%), m.p. 111—113° (Found: C, 79.5; H, 5.35. $C_{21}H_{16}O_3$ requires C, 79.75; H, 5.1%); δ 3.62 (3 H, s), 7.37 (5 H, s), 7.50—8.02 (7 H, m), and 8.24 (1 H, d, J_m 2.1 Hz); $\nu_{max.}$ 1 720, 1 665, 1 470, 1 405, 1 310, 1 250, 1 100, 1 055, 845, 760, and 700 cm^{-1}; $\lambda_{max.}$ (EtOH) 309 nm (log ε 4.29).

(iii) Reactions of (7) with sodium methoxide at various temperatures did not precipitate inorganic halide. Work-up as described above gave a dark orange halogen-containing oil containing at least seven species. ^1H N.m.r. data provided no evidence for the presence of the orthoester (19) or the ester (28). Preparative t.l.c. (benzene) led to a single u.v. active species which was extracted and recrystallised (benzene–light petroleum, 1 : 1) to give prisms of unidentified material (30%), m.p. 130°, *m/e* 406/408/ and 410 (Found: C, 62.1; H, 4.2; Cl, 26.0. Calc. for $C_{21}H_{17}Cl_3O_2$: C, 61,85; H, 4.2; Cl, 26.1%).

(iv) Reactions of sodium methoxide in methanol with (2) led to uncharacterised product under various conditions. With (5), reactions proceeded only above −40 °C, but the product mixture has, as yet, proved inseparable.

Decomposition of 1,1-*Dichloro*-2,5-*diphenylcyclopropabenzene* (10) *in Protic Media.*—To a solution of (10) (0.18 g, 0.6 mmol) in benzene (10 cm^3) was added an excess of base in alcohol (5 cm^3). Work-up afforded [with methoxide (or triethylamine) in methanol] trimethyl 2,5-diphenylor-

thobenzoate (16) (94%); (with ethoxide–ethanol) triethyl 2,5-diphenylorthobenzoate (17) (96%); or (with t-butoxide–t-butyl alcohol) t-butyl 2,5-diphenylbenzoate (22) (40%). In the absence of base the orthoesters are not isolable; the corresponding carboxylate esters are produced. With moist acetone 2,5-diphenylbenzoic acid (25) (96%) was obtained.

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