Studies in the Cyclopropa-arene Series: Cyclopropa[*b*]naphthalenes [1]

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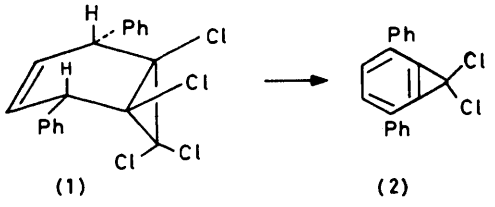
1,1,1a,7a-Tetrachloro-1a,2,7,7a-tetrahydro-2,7-diphenylcyclopropa[*b*]naphthalene (5) affords an isolable *gem*-dihalogenocyclopropa[*b*]naphthalene (7) on dehydrohalogenation, whereas the tetrabromo-analogue (6) does not. The reaction of the *gem*-dihalide (7) with a small excess of phenyl- or ethyl-magnesium bromide surprisingly results in halogen exchange and formation of *gem*-dibromocyclopropa[*b*]naphthalene (8) in high yield. Only with a large excess of Grignard reagent are the halogeno-substituents of (7) replaced by alkyl and aryl groups. Whereas the *gem*-diethyl derivative (13) is isolable, the *gem*-diphenyl compound (12) suffers ready ring cleavage, rearranging to a benzo[*b*]fluorene (18). With the *gem*-dichloride (7), methylmagnesium iodide effects the equivalent of monohalogen exchange and Grignard reduction to give a benzo[*c*]fluorene (20).

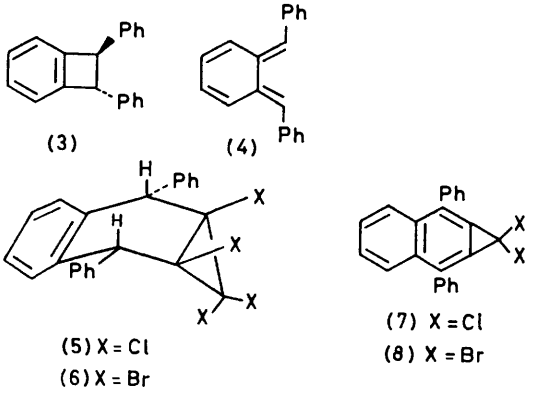
WHILE the past decade has seen significant advances in cyclopropabenzene chemistry, little attention has been given to other cyclopropa-arenes.[2] The earliest approach to this class of compounds, in which the synthesis of iminocyclopropa[*l*]phenanthrenes was claimed,[3] has been shown to be non-reproducible,[4] and compounds initially considered to be diaminocyclopropa[*b*]naphthalenes [5] have been reidentified as the isomeric di-imines.[6] More recent attempts at the synthesis of a representative cyclopropa[*b*]naphthalene have also failed.[7] In extending our studies of cyclopropabenzene chemistry to other cyclopropa-arenes, it became particularly desirable to effect convenient syntheses of appropriately functionalised cyclopropa[*b*]naphthalenes. We now report the details of the syntheses of 1,1-dichlorocyclopropa[*b*]naphthalene (7),[1] and the chemistry of this ring system which has led to the isolation of the *gem*-dibromo- and *gem*-diethyl derivatives (8) and (13).

Of the synthetic methods available for cyclopropabenzenes,[2] the dehydrohalogenation of substituted bicyclo[4.1.0]hept-3-enes appeared to be the most amenable to modification to yield cyclopropa[*b*]naphthalenes. Our studies on the dehydrohalogenation of 1,6,7,7-tetrahalogenobicyclo[4.1.0]hept-3-enes to cyclopropabenzenes have shown that the route is effective when phenyl substituents are present at the 2- and 5-positions, the reaction (1) ⟶ (2) proceeding in almost quantitative



(1) (2)

yield.[8] It thus appeared reasonable to expect the benzo-analogue (5) to give the cyclopropanaphthalene (7). Efficient syntheses of the tetrahalogenobicycloheptenes (5) and (6) have been effected from *trans*-1,2-dihydro-1,2-diphenylcyclobutabenzene (3), obtained in seven steps from phthalic anhydride in an overall yield of 15.6% (*cf.* 2.8% initially reported).[9] Mild thermolysis of (3) results in the *o*-quinodimethane (4), which has been trapped with a variety of dienophiles.[10] In the presence of tetrachloro- and tetrabromo-cyclopropene thermolysis of (3)



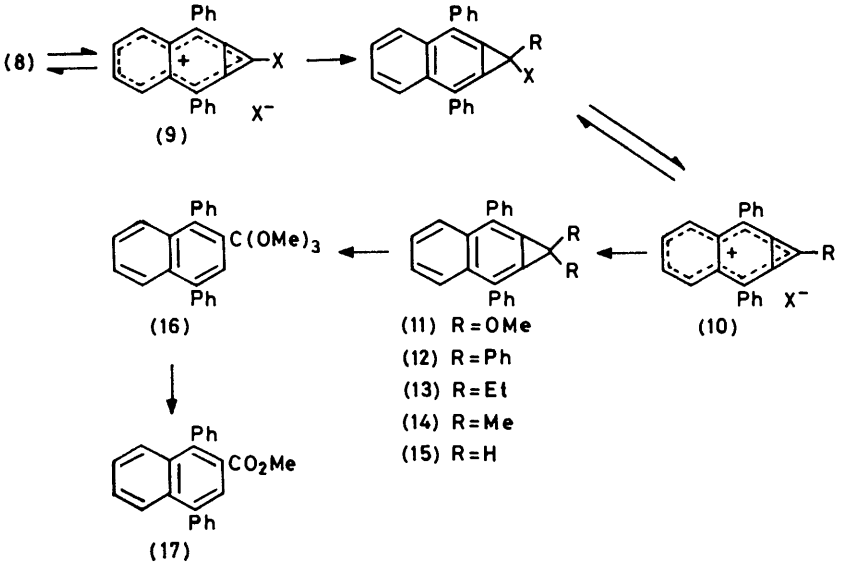
gave compounds (5) and (6), respectively, in high yields. While the configuration of these products follows from the behaviour of the quinodimethane (4) with other dienophiles and is in accord with orbital symmetry concepts,[10] the conformation of these molecules is believed to be that shown and not the ' ring-flip ' isomer in view of the severe steric compression caused in the latter by the presence of pseudoaxial phenyl substituents. These concepts have been discussed fully for the bicycloheptene (1).[8]

Dehydrochlorination of compound (5) has been effected with potassium t-butoxide in tetrahydrofuran. When the conditions found optimal for the conversion (1) ⟶ (2) were employed, formation of the *gem*-dichlorocyclopropa-[*b*]naphthalene (7) was accompanied by severe discolouration and decomposition, and the resultant yield of isolated material was only 25%.[1] However, by performing the reaction at −75 °C with a slow (6 h) addition of compound (5) to potassium t-butoxide in tetrahydrofuran,

[1] Preliminary communication, A. R. Browne and B. Halton, *J.C.S. Chem. Comm.*, 1972, 1341.
[2] For a review see B. Halton, *Chem. Rev.*, 1973, **73**, 113.
[3] S. C. De and D. N. Dutt, *J. Indian Chem. Soc.*, 1930, **7**, 537.
[4] B. Halton, S. A. R. Harrison, and C. W. Spangler, *Austral. J. Chem.*, 1975, **28**, 681.
[5] A. Mustafa and M. Kamel, *J. Amer. Chem. Soc.*, 1953, **75**, 2939.
[6] G. W. Jones, D. R. Kerur, T. Yamazaki, H. Shechter, A. D. Woolhouse, and B. Halton, *J. Org. Chem.*, 1974, **39**, 492; A. G. Pinkus and J. Tsuji, *ibid.*, p. 497.
[7] M. P. Cava and K. Narasimham, *J. Org. Chem.*, 1971, **36**, 1419; K. Geibel and J. Heindl, *Tetrahedron Letters*, 1970, 2133.
[8] B. Halton, P. J. Milsom, and A. D. Woolhouse, *J.C.S. Perkin I*, 1977, 731.
[9] L. A. Carpino, *J. Amer. Chem. Soc.*, 1962, **84**, 2196.
[10] R. Huisgen and H. Siedel, *Tetrahedron Letters*, 1964, 3381; G. Quinkert, K. Opitz, W. W. Wiersdorf, and M. Finke, *ibid.*, 1965, 3009.

the yield of (7) has been increased to 88%. The structure of (7) follows from its spectral ($\nu_{max.}$ 1 675 cm^{-1}) [2] and analytical data, and from the similarity of its behaviour to that of the cyclopropabenzene (2). Thus dissolution of (7) in methanol affords the naphthoate (17), and in the presence of an excess of added base the orthoester (16) can be isolated. The formation of (16) and (17) is best explained by nucleophilic capture of the cyclopropanaphthylium ions (9; X = Cl) and (10; R = OMe) (Scheme 1), since the former species has been generated from (7) and observed under long-lived ion conditions.[11] Such a process parallels the behaviour of the cyclopropabenzene (2) and its known ionisation to the corresponding cyclopropaphenylium ion.[12]

Attempted dehydrobromination of compound (6) has met only with partial success. Under the conditions



SCHEME 1

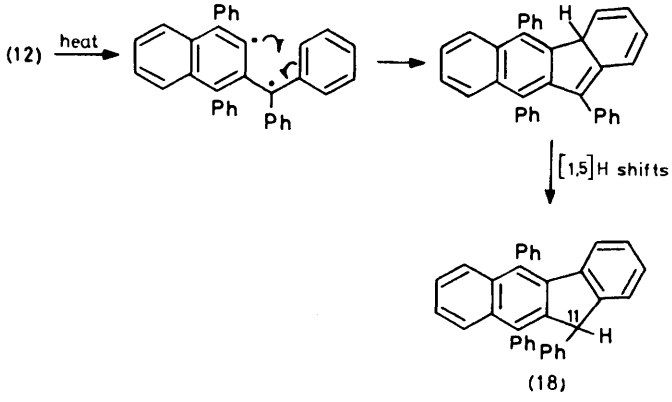
most favourable for production of the cyclopropanaphthalene (7), unchanged (6) was recovered in 65% yield. However, the remaining product mixture did display the characteristic [2] 1 675 cm^{-1} cyclopropa-arene i.r. stretching band consistent with the presence of the cyclopropanaphthalene (8), but all attempts to isolate the compound failed. Addition of methanol to the mixture led to the isolation of the naphthoate (17) (12%), which is consistent with the behaviour of compound (7) and further supports the presence of (8). Analogous studies in the cyclopropabenzene series did not provide i.r. evidence for the analogous *gem*-dibromo-compound.

Capture of the cyclopropaphenylium ion formed by ionisation of compound (2) has been effected by the nucleophilic carbon component of various organometallic species leading, ultimately, to replacement of both chlorine atoms.[13] Comparable studies with the cyclopropa[*b*]naphthalene (7) have provided some more unusual results. Treatment of (7) with a slight excess of phenylmagnesium bromide results in a product (85%) which shows a 1 675 cm^{-1} i.r. band and displays only complex aromatic signals in the ^1H n.m.r. spectrum, as expected for the *gem*-diphenyl derivative (12). However, the product is neither (12) nor unchanged (7), but the *gem*-dibromo-compound (8). The identity of (8) is supported by the spectroscopic data and further substantiated by high resolution mass measurement and the appearance of molecular ions at *m/e* 448/450/452 (1 : 2 : 1) as expected for a species containing two bromine atoms. Dissolution of (8) in methanol yields the naphthoate (17) *via* the orthoester (16) as observed for (7) (Scheme 1). A close examination of the mother-liquors from crystallisation of (8) failed to provide evidence for product resulting from replacement of the chlorine atoms of (7) by any other group. This unexpected behaviour of the bromo-Grignard reagent is not restricted to the phenyl derivative. Ethylmagnesium bromide behaves in an analogous manner affording the dibromide (8) (62%) together with the *gem*-diethylcyclopropa[*b*]naphthalene (13) (17%) (see below). The mode of formation of (8) from (7) is not clear and has no parallel in the chemistry of the cyclopropabenzene (2). While there appears to be little precedent for a halogen exchange involving Grignard reagents, such exchange in other organometallic species has been noted.[14] That the bromo-Grignard reagents behave in a manner akin to a metal halide appears unlikely, since magnesium bromide, known to effect exchange with chlorosilane derivatives,[15] has no effect on (7) under the conditions employed.

When treated with a large excess of phenylmagnesium

[11] D. P. Kelly, R. J. Spear, and B. Halton, unpublished observations.
[12] B. Halton, H. M. Hügel, D. P. Kelly, P. Müller, and U. Burger, *J.C.S. Perkin II*, 1976, 258.
[13] B. Halton, A. D. Woolhouse, and P. J. Milsom, *J.C.S. Perkin I*, 1977, 735, and references cited therein.
[14] N. F. Curtis, personal communication.
[15] U. Kruerke, *Chem. Ber.*, 1962, **95**, 174.

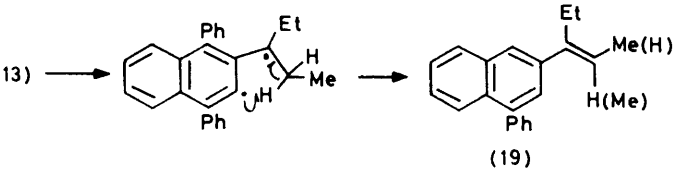
bromide, compound (7) gave rise to a halogen-free oil which exhibited a 1 675 cm^{-1} band and which showed only complex aromatic proton resonances in the ^1H n.m.r. spectrum. These data are fully consistent with the *gem*-diphenylcyclopropanaphthalene (12). All attempts to isolate (12) by fractional crystallisation failed, and



SCHEME 2

chromatographic separation led to 5,10,11-triphenylbenzo[*b*]fluorene (18) (38%). Mild thermolysis (60 °C) of the product mixture containing (12) in the cavity of an n.m.r. spectrometer led to the appearance of the H-11 signal of (18) at δ 5.10, the growth of which was complete in *ca.* 30 min. The formation of (18) from (12) (Scheme 2) parallels the behaviour of 1,1,2,5-tetraphenylcyclopropabenzene [13] and reflects the ease of ring cleavage in comparison with tetraphenylcyclopropene.[16]

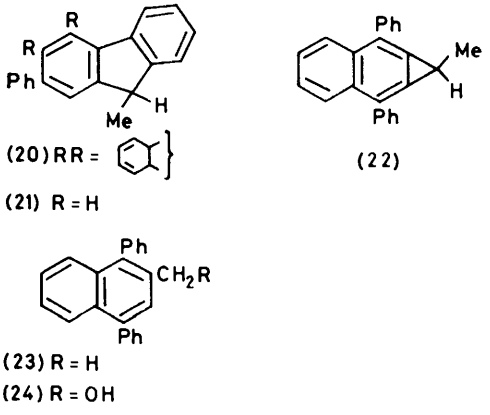
Replacement of the halogen atoms of compound (7) by ethyl groups can also be effected by employing a large excess of Grignard reagent, and in this case 1,1-diethyl-2,7-diphenylcyclopropa[*b*]naphthalene (13) is isolable in high yield. The identity of the compound has been established from its spectroscopic data and its thermal behaviour. The diagnostic 1 675 cm^{-1} i.r. band is present and the n.m.r. spectrum shows the presence of two equivalent ethyl groups. Thermolysis of (13) results in rearrangement to an inseparable mixture of the *E*- and *Z*-isomers of the styrene (19) in the ratio *ca.* 2 : 1. Cleavage of the three-membered ring of (13) to a diradical intermediate which suffers hydrogen transfer through a five-membered transition state (Scheme 3) has precedent in cyclopropabenzene chemistry.[13]



SCHEME 3

The reaction of compound (7) with an excess of methylmagnesium iodide afforded one major and a large number of minor components. The major component, isolated by preparative t.l.c., is a $C_{24}H_{18}$ species containing a CH_3·$CH<$ function and may be formulated as resulting from the replacement of both chlorine atoms of (7) by the elements of CH_4. Its identification as 7-methyl-5-phenyl-7*H*-benzo[*c*]fluorene (20) follows from its spectroscopic data and by analogy with the unequivocal formation of 9-methyl-2-phenylfluorene (21) from the cyclopropabenzene (2) under the same conditions.[13] Thus the unusual behaviour of methylmagnesium iodide with (2) is mirrored in the cyclopropa[*b*]naphthalene series, with (20) being generated by the equivalent of monohalogen exchange followed by Grignard reduction. While the route from (7) to (20) [and that from (2) to (21)] is not known, it is clear that the product is isomeric with, and perhaps formed from, the 1-methylcyclopropa[*b*]naphthalene (22). No evidence for *gem*-dimethylcyclopropa[*b*]naphthalene (14), or the styrene derived from it by ring cleavage, *cf.* (13) ⟶ (19), was obtained.

Attempts to effect dechlorination of compound (7) to the hydrocarbon (15) have met with limited success. Whereas the cyclopropabenzene (2) has been bishydrodechlorinated with aluminium hydride,[17] this same reagent has not effected the conversion of (7) into (15) in



our hands. However, treatment of (7) with lithium aluminium hydride followed by destruction of the excess of reagent with dried (but not anhydrous) magnesium sulphate leads to a mixture containing the cyclopropa[*b*]-naphthalene (15) [$\nu_{max.}$ 1 675 cm^{-1}; δ 3.44, (s, 2 H)] and the known naphthalenes (23) [18] and (24) [19] in approximately equal amounts. Chromatography afforded only (23) (30%) and (24) (63%), indicating that hydration of (15) to (24) had occurred during the separation. Further evidence supporting the relative instability of (15) stems from the ratio of crude products formed when the excess of complex metal hydride is destroyed by the addition of water. Under these conditions compounds (15), (23), and (24) are produced in the ratios *ca.* 0.5 : 1 : 1.5 [from integration of the n.m.r. singlets at δ 3.44 (15), 2.22 (23), and 4.42 (24), respectively]. The identity of (24) was

[16] M. A. Battiste, B. Halton, and R. H. Grubbs, *Chem. Comm.*, 1967, 907.

[17] P. Müller, *Helv. Chim. Acta*, 1974, **57**, 704.

[18] A. Etienne and A. Spire, *Compt. rend.*, 1950, **230**, 2030.

[19] J. Robert, *Compt. rend.*, 1946, **223**, 906.

confirmed by independent synthesis from the naphthoate (17). Variations in the molar ratio of the reactants has thus far failed to afford isolable quantities of (15); as with 2,5-diphenylcyclopropabenzene,[13] the three-membered ring of (15) is particularly prone to cleavage.

Despite the similarities in behaviour of cyclopropa[*b*]naphthalene (7) and cyclopropabenzene (2), our qualitative data on the rearrangements of compounds (12) and (13) imply that cleavage of the three-membered ring in the cyclopropa[*b*]naphthalene series proceeds less readily than in the cyclopropabenzene analogues. Quantitative studies of these processes are in progress.

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 Schimadzu UV200 instrument. N.m.r. spectra were recorded for solutions in deuteriochloroform (tetramethylsilane as internal standard) with a Hitachi–Perkin-Elmer R20 60 MHz instrument operating at 34 °C, and mass spectra with an A.E.I. MS902 spectrometer. 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.

trans-1,2-*Dihydro*-1,2-*diphenylcyclobutabenzene* (3).—This was prepared in seven steps [9] from phthalic anhydride in an overall yield of 15.6%; m.p. 93—94° (lit.,[9] 94.5—95.2°).

1,1,1a,7a-*Tetrachloro- and Tetrabromo*-1a,2,7,7a-*tetrahydro*-2,7-*diphenylcyclopropa*[b]*naphthalenes* (5) *and* (6).—A solution of *trans*-1,2-dihydro-1,2-diphenylcyclobutabenzene (3) (2.0 g, 7.8 mmol) and tetrahalogenocyclopropene [20] (15.5 mmol) in dry benzene (75 cm³) was heated under reflux for 72 h; it was then concentrated to *ca.* 20 cm³ and light petroleum was added. The precipitated solid was filtered off.

(i) Recrystallisation of the crude product from tetrachlorocyclopropene from benzene–light petroleum (1 : 2) gave the *tetrachloro-derivative* (5) (2.91 g, 86%) as needles, m.p. 171—172° (Found: C, 63.95; H, 3.8; Cl, 32.6. $C_{23}H_{16}Cl_4$ requires C, 63.6; H, 3.7; Cl, 32.65%), $\nu_{max.}$ 1 591, 1 589, 1 488, 1 078, 1 030, 878, 833, 800, 759, 750, 744, 736, 702, 687, and 672 cm^{-1}, δ 4.80 (2 H, s), 6.83 (4 H, s), 7.18 (6 H, s), and 7.38 (4 H, s).

(ii) Recrystallisation of the crude product from tetrabromocyclopropene from benzene–ethanol (1 : 2) gave the *tetrabromo-derivative* (6) (3.38 g, 71%) as needles, m.p. 178—180° (Found: C, 44.85; H, 3.0. $C_{23}H_{16}Br_4$ requires C, 45.15; H, 2.65%), $\nu_{max.}$ 1 600, 1 500, 1 112, 1 070, 1023, 768, 742, 721, and 695 cm^{-1}, δ 4.92 (2 H, s), 6.94 (4 H, s), and 7.30 (10 H, s).

1,1-*Dichloro*-2,7-*diphenylcyclopropa*[b]*naphthalene* (7).—To a stirred suspension of potassium t-butoxide (1.8 g, 16 mmol) in dry tetrahydrofuran (100 cm³), externally cooled in a solid CO_2–acetone bath (−75 °C), was added dropwise a solution of the tetrachloro-compound (5) (1.70 g, 3.9 mmol) in dry tetrahydrofuran (100 cm³). The mixture immediately became discoloured and the addition was maintained at such a rate as to minimise further discolouration. After the addition was complete (6 h), the mixture was warmed slowly to 0° C and left at this temperature overnight. Concentration at 25 °C under vacuum gave a solid which was extracted with dry benzene (150 cm³). The extract was washed quickly with water (2 × 30 cm³) and saturated sodium chloride solution (30 cm³), dried [$MgSO_4$ (25 g)], and concentrated to an orange crystalline mass. Two recrystallisations, by addition of light petroleum (2 parts) to a warm (*ca.* 40 °C) solution in benzene (1 part), gave 1,1-*dichloro*-2,7-*diphenylcyclopropa*[b]*naphthalene* (7) (1.24 g, 88%) as off-white needles, m.p. 177—179° (decomp.) (Found: M^+, 362.044 885. $C_{23}H_{14}{}^{35}Cl^{37}Cl$ requires M, 362.044 306), $\nu_{max.}$ (KBr) 3 050, 1 675, 1 583, 1 565, 1 495, 1 448, 1 358, 1 158, 1 070, 1 000, 878, 753, 714, and 695 cm^{-1}, δ 7.51—7.73 (complex m), $\lambda_{max.}$ (tetrahydrofuran) 244 (log ε 4.60), 302 (4.24), and 340 nm (4.24), *m/e* 360 (11%)/362 (8)/364 (1) and 325, (100)/327 (38) (M − Cl).

Reaction between 1,1-*Dichloro*-2,7-*diphenylcyclopropa*[b]*naphthalene* (7) *and Methanol.*—(i) *In the presence of base.* To a solution of the dichlorocyclopropa[*b*]naphthalene (7) (100 mg, 0.28 mmol) in dry benzene (20 cm³) was added a mixture of dry methanol (3 cm³) and dry triethylamine (5 cm³). The solution was left for 18 h and then concentrated to dryness. The resultant oil was dissolved in dry benzene (20 cm³), washed quickly with saturated sodium chloride solution (5 cm³), dried [$MgSO_4$ (10 g)], and concentrated to a pale yellow oil. Trituration with light petroleum and recrystallisation of the resultant solid from light petroleum gave 1,4-*diphenyl*-2-(*trimethoxymethyl*)*naphthalene* (16) (76 mg, 72%), m.p. 139—140° (Found: C, 81.25; H, 6.05. $C_{26}H_{24}O_3$ requires C, 81.2; H, 6.3%), $\nu_{max.}$ 3 060, 2 940, 1 605, 1 502, 1 446, 1 382, 1 247, 1 100, 1 078, 1 028, 808, 778, 760, 732, and 692 cm^{-1}, δ 3.08 (9 H, s), 7.26—7.69 (14 H, complex m), and 7.92 (1 H at C-3, s).

A solution of the orthoester (15) (25 mg, 0.065 mmol) in dry benzene (5 cm³) and methanol (1 cm³) was left for 1 h. Concentration to dryness and recrystallisation from dry methanol gave methyl 1,4-diphenyl-2-naphthoate (17) (27 mg, 96%), m.p. 161—162.5 (lit.,[21] 162—162.5°).

(ii) *In the absence of base.* In the absence of triethylamine, compound (7) gave the naphthoate (17) (95%) directly.

Attempted Dehydrobromination of 1,1,1a,7a-*Tetrabromo*-1a,2,7,7a-*tetrahydro*-2,7-*diphenylcyclopropa*[b]*naphthalene* (6).—To a stirred suspension of potassium t-butoxide (0.33 g, 2.95 mmol) in dry tetrahydrofuran (15 cm³), externally cooled in a solid CO_2–acetone bath (−75 °C), was added dropwise (3 h) a solution of the tetrabromo-compound (6) (0.45 g, 0.74 mmol) in dry tetrahydrofuran. The resulting yellow solution was stirred at −75 °C for a further 1 h and then at 0 °C for 2 h before being concentrated at 25 °C to dryness. The yellow solid was extracted with dry benzene (50 cm³) and the extract washed with water (20 cm³) and saturated sodium chloride solution (20 cm³), dried [$MgSO_4$ (10 g)], and concentrated *in vacuo* to a brown semi-solid. Careful fractional recrystallisation (benzene–light petroleum, 1 : 1) gave unchanged (6) (0.29 g, 65% recovery). The combined mother liquors were concentrated to a brown oil, $\nu_{max.}$ 1 675 cm^{-1}. Dissolution of this oil in benzene (10 cm³) and treatment with dry methanol (2 cm³) gave a similar brown oil, $\nu_{max.}$ 1 710 cm^{-1}. Preparative t.l.c. (elution with chloroform) and extraction of the only mobile species (R_F 0.7) with chloroform–methanol (1 : 1) gave, after recrystallisation from methanol, methyl 1,4-diphenyl-2-naphthoate (17) (30 mg, 12%), m.p. and mixed m.p. 161—163°.

[20] D. C. F. Law and S. W. Tobey, *J. Amer. Chem. Soc.*, 1968, **90**, 2376.

[21] K. R. Baucom and G. R. Butler, *J. Org. Chem.*, 1972, **37**, 1730.

Reaction between 1,1-*Dichloro*-2,7-*diphenylcyclopropa*[b]-*naphthalene* (7) *and Phenylmagnesium Bromide*.—(i) 2.5 *Molar equivalents of Grignard reagent*. To a stirred solution of phenylmagnesium bromide [from bromobenzene (0.87 g, 5.54 mmol) and magnesium (0.135 g, 5.63 mg atom)] in dry ether (50 cm³), cooled in ice–salt (−10 °C) under dry oxygen-free nitrogen, was added dropwise during 2 h a solution of the dichlorocyclopropa[*b*]naphthalene (7) (0.80 g, 2.2 mmol) in dry benzene (25 cm³). The resultant orange solution was stirred for a further 2 h at ambient temperature, diluted with benzene (50 cm³), and carefully treated with saturated aqueous ammonium chloride (10 cm³). The organic phase was washed with water (2 × 25 cm³) and dried [$MgSO_4$ (25 g)]. Concentration under vacuum gave a pale yellow solid which was twice recrystallised, by addition of light petroleum (2 parts) to a warm (*ca.* 40°) solution in benzene (1 part), to give 1,1-*dibromo*-2,7-*diphenylcyclopropa*-[b]*naphthalene* (8) (0.84 g, 85%) as pale yellow prisms, m.p. 169—171° (decomp.) (Found: M^+, 449.943 856. $C_{23}H_{14}{}^{79}Br{}^{81}Br$ requires M, 449.944 355), $\nu_{max.}$ (KBr) 3 050, 1 675, 1 588, 1 565, 1 513, 1 498, 1 428, 1 360, 1 210, 988, 770, 750, and 695 cm⁻¹, δ 7.35—7.90 (12 H, complex m) and 8.20—8.50 (2 H, complex m), $\lambda_{max.}$ (tetrahydrofuran) 242 (log ε 4.42), 303 (4.25), and 338 nm (4.21), *m/e* 448 (24%)/450 (47)/452 (23) and 369 (100)/371 (95) (M − Br).

Treatment of a solution of (8) in benzene with (i) methanol–triethylamine and (ii) methanol gave the orthoester (16) (85%) and the ester (17) (94%), respectively, as for (7).

(ii) 16 *Molar equivalents of Grignard reagent*. The reaction of the dichlorocyclopropa[*b*]naphthalene (7) with phenylmagnesium bromide was repeated as described above by addition of a solution of (7) (0.60 g, 1.66 mmol) in dry benzene (25 cm³) to a solution of phenylmagnesium bromide [from bromobenzene (4.18 g, 26.4 mmol) and magnesium (0.64 g, 26.8 mg atom)] in dry ether (50 cm³). Work-up gave a brown halogen-free oil, $\nu_{max.}$ 1 675 cm⁻¹. Efforts to isolate a crystalline sample, by trituration with cold light petroleum or by slow cooling of a light petroleum solution to −20 °C, were unsuccessful. T.l.c. (benzene–light petroleum, 1 : 7) revealed the presence of two mobile species. The crude product was subjected to preparative t.l.c. [elution with benzene–light petroleum (1 : 7)] and the two u.v.-active species (R_F 0.8 and 0.4) were extracted with chloroform (100 cm³).

Band A (R_F 0.8) gave a solid which was crystallised from light petroleum to give biphenyl (0.08 g) as fine plates, m.p. and mixed m.p. 68—70°.

Band B (R_F 0.4) gave a yellow solid which was recrystallised (benzene–ethanol, 1 : 2) to give 5,10,11-*triphenylbenzo*[b]*fluorene* (18) (0.28 g, 38%) as tiny yellow-green needles, m.p. 207—208° (Found: C, 94.75; H, 5.7. $C_{35}H_{24}$ requires C, 94.55; H, 5.45%), $\nu_{max.}$ 1 600, 1 500, 1 065, 1 022, 760, 730, 708, and 690 cm⁻¹, δ 5.10 (1 H, s) and 6.40—7.65 (23 H, complex m), $\lambda_{max.}$ (cyclohexane) 214 (log ε 4.60), 250 (4.54), 263 (4.63), 273 (4.73), 298sh (4.04), 308 (4.25), and 322 nm (4.28).

The brown halogen-free oil (above) displayed only complex aromatic proton resonances (δ 6.9—7.5), and the i.r. spectrum exhibited absorption at 1 675 cm⁻¹ consistent with tetraphenylcyclopropa[*b*]naphthalene (12). When a solution in deuteriochloroform of the crude product in the cavity of the n.m.r. spectrometer was warmed at 60 °C, the appearance, and subsequent increase in intensity, of the fluorenyl proton signal at δ 5.10 was complete after 35 min.

Lowering the temperature at which the Grignard reaction was performed had no effect on the purity of the product obtained, and in no case was it possible to purify (12) without effecting decomposition to (18).

Reaction between 1,1-*Dichloro*-2,7-*diphenylcyclopropa*[b]-*naphthalene* (7) *and Ethylmagnesium Bromide*. (i) 4 Molar equivalents of Grignard reagent. Treatment of (7) with 4 mol. equiv. of ethylmagnesium bromide as in (i) above afforded 1,1-dibromo-2,7-diphenylcyclopropa[*b*]naphthalene (8) (62%), m.p. and mixed m.p. 169—171° (decomp.). The mother liquors from recrystallisation of (8) were concentrated to a dark brown halogen-free oil which possessed spectral characteristics identical with those of the product from treatment of (7) with 20 mol. equiv. of ethylmagnesium bromide (below) and was shown by t.l.c. (benzene–light petroleum, 1 : 5) to consist of only one mobile species.

(ii) 20 *Molar equivalents of Grignard reagent*. The reaction between (7) and ethylmagnesium bromide was repeated as above with 20 mol. equiv. of Grignard reagent. Concentration of the resultant extract gave a dark brown halogen-free oil which deposited an orange solid at −20 °C overnight. The solid was recrystallised by slow cooling of a solution in light petroleum to −20 °C to give a product considered to be 1,1-diethyl-2,7-diphenylcyclopropa[*b*]naphthalene (13)* (0.44 g, 58%) as light orange crystalline masses, m.p. 118—121°, $\nu_{max.}$ 1 675, 1 590, 1 490, 1 348, 1 098, 1 069, 1 023, 961, 771, 758, 720, and 698 cm⁻¹, δ 0.61 (6 H, t, J 7.5 Hz, $CH_2{\cdot}CH_3$), 2.05 (4 H, q, J 7.5 Hz, $CH_2{\cdot}CH_3$), 7.20—7.65 (12 H, complex m), and 7.95—8.20 (2 H, m), *m/e* 348 (52%) and 319 (100) (M − Et).

Thermolysis of 1,1-*Diethyl*-2,7-*diphenylcyclopropa*[b]-*naphthalene* (13).—A solution of the *gem*-diethylcyclopropa-[*b*]napthalene (13) (0.30 g, 0.86 mmol) in benzene (50 cm³) was heated under reflux for 2 h and then concentrated to a brown oil. T.l.c. (light petroleum) revealed only one mobile species (R_F 0.6). The crude oil was subjected to preparative t.l.c. and the band at R_F 0.6 extracted with chloroform (100 cm³). Concentration of the extract yielded an oil which solidified on trituration with ethanol. Recrystallisation from the same solvent gave an inseparable mixture of (E)- and (Z)-2-(1-*ethylprop*-1-*enyl*)-1,4-*diphenylnaphthalene* (19) (0.28 g, 93%) as small needles, m.p. 121—135° (Found: C, 93.0; H, 7.05. $C_{27}H_{24}$ requires C, 93.05; H, 6.95%), $\nu_{max.}$ 1 592, 1 583, 1 177, 1 160, 1 073, 1 030, 904, 775, 766, 730, and 702 cm⁻¹, δ(*E*-isomer) 0.82 (3 H, t, J 7.5 Hz, $CH_2{\cdot}CH_3$), 1.47 (3 H, d, J 6.7 Hz, $C{=}CH{\cdot}CH_3$), 1.95 (2 H, q, J 7.5 Hz, $CH_2{\cdot}CH_3$), 5.34 (1 H, q, J 6.7 Hz, $C{=}CH{\cdot}CH_3$), and 7.10—7.96 (15 H, complex m), δ (*Z*-isomer) 0.72 (3 H, t, J 7.5 Hz, $CH_2{\cdot}CH_3$), 1.58 (3 H, d, J 6.7 Hz, $C{=}CH{\cdot}CH_3$), 1.95 (2 H, q, J 7.5 Hz, $CH_2{\cdot}CH_3$), 5.34 (1 H, q, J 6.7 Hz, $C{=}CH{\cdot}CH_3$), and 7.10—7.96 (15 H, complex m), *m/e* 348 (69%) and 319 (100) (M − Et).

Reaction of 1,1-*Dichloro*-2,7-*diphenylcyclopropa*[b]*naphthalene* (7) *with Ethereal Magnesium Bromide*.—To a stirred solution of magnesium bromide [from magnesium (0.3 g, 12 mg atom) and mercury(II) bromide (2.16 g, 6 mmol) [22]] in dry ether (60 cm³) and dry benzene (30 cm³) was added dropwise (1 h) a solution of the dichlorocyclopropa[*b*]naphthalene (7) (0.18 g, 0.5 mmol) in dry benzene (30 cm³). The solution was stirred at ambient temperature for 18 h, washed

* It has not been possible to obtain an analytically pure sample of this compound without effecting partial rearrangement to isomer (19), for which satisfactory data have been obtained.

[22] W. E. Bachmann, J. P. Horwitz, and R. J. Warzynski, *J. Amer. Chem. Soc.*, 1953, **75**, 3268.

with water (50 cm³), and dried [$MgSO_4$ (20 g)]. Concentration gave an off-white crystalline solid identified as unchanged (7) (0.17 g, 94% recovery), m.p. and mixed m.p. 168—170°.

Reaction between 1,1-*Dichloro*-2,7-*diphenylcyclopropa*[b]-*naphthalene* (7) *and Methylmagnesium Iodide:* 7-*Methyl*-5-*phenyl*-7H-*benzo*[c]*fluorene* (20)—Treatment of compound (7) with 5 mol. equiv. of methylmagnesium iodide, as for phenylmagnesium bromide (above) gave a brown oil shown by t.l.c. to consist of *ca.* eight components with only one prominent species. The mixture was subjected to preparative t.l.c. (elution twice with light petroleum) and the only prominent species (R_F 0.7) was extracted with chloroform (100 cm³) to give a pale yellow solid. Recrystallisation from hexane gave 7-*methyl*-5-*phenyl*-7H-*benzo*[c]*fluorene* (20) (0.37 g, 55%) as tiny, pale yellow needles, m.p. 159—160° (Found: C, 93.95; H, 6.15. $C_{23}H_{18}$ requires C, 93.85; H, 6.15%), $\nu_{max.}$ 1 585, 1 566, 1 488, 1 346, 1 318, 1 305, 1 105, 1 070, 1 023, 962, 771, 751, 702, and 646 cm^{-1}, δ 1.65 (3 H, d, *J* 7.5 Hz), 4.02 (1 H, q, *J* 7.5 Hz), and 7.20—7.85 (14 H, complex m), $\lambda_{max.}$ (cyclohexane) 246 (log ε 4.57), 325 (4.28), and 340 nm (4.29), *m/e* 306 (100%), 305 (53) (*M* − H), and 291 (51%) (*M* − Me).

Treatment of 1,1-*Dichloro*-2,7-*diphenylcyclopropa*[b]-*naphthalene* (7) *with Lithium Aluminium Hydride.*—A solution of the dichlorocyclopropa[*b*]naphthalene (7) (0.30 g, 0.83 mmol) in dry benzene (20 cm³) was added dropwise, over 30 min, to a stirred suspension of lithium aluminium hydride (0.25 g, 6.58 mmol) in dry ether (40 cm³). The mixture was heated under reflux for 3 h, cooled to 0 °C, and treated with dried magnesium sulphate until no further reaction was apparent. The solution was filtered and concentrated to dryness. The n.m.r. spectrum of the resultant oil showed, in addition to the resonances attributed to (23) and (24) (below), a singlet at δ 3.44 attributed to 2,7-*diphenylcyclopropa*[b]*naphthalene* (15); the ratio (15) : (23) : (24) was 1 : 1 : 1. Separation by fractional crystallisation could not be effected. Preparative t.l.c. (elution with benzene–light petroleum, 1 : 9) gave two bands.

Band A (R_F 0.6) was extracted with chloroform (100 cm³) to give an oil which solidified. Recrystallisation from ethanol gave 2-methyl-1,4-diphenylnaphthalene (23) (73 mg, 30%) as needles, m.p. 127—128° (lit.,[18] 129°), $\nu_{max.}$ 1 590, 1 065, 1 025, 883, 762, 740, and 695 cm^{-1}, δ 2.22 (3 H, s), 7.27—7.58 (14 H, m), and 7.88 (1 H at C-3, m).

Band B (R_F 0.1) was extracted with chloroform (100 cm³) to give an oil which solidified on trituration with light petroleum. Recrystallisation from benzene–light petroleum (1 : 3) gave 2-(hydroxymethyl)-1,4-diphenylnaphthalene (24) (162 mg, 63%) as needles, m.p. 121—122° (lit.,[19] 123°), identical with a sample prepared by reduction of (17) with lithium aluminium hydride; $\nu_{max.}$ 3 400, 1 600, 1 072, 1 030, 770, 740, 700, and 680 cm^{-1}, δ 1.93br (1 H, exchangeable, s), 4.42 (2 H, s), 7.00—7.50 (14 H, complex m), and 7.65—7.90 (1 H at C-3, m).

Work-up of the reaction by addition of water resulted in a crude product the n.m.r. spectrum of which indicated the presence of compounds (15), (23), and (24) in the ratio 0.5 : 1 : 1.5. Chromatography, as outlined above, led to (23) and (24) in essentially the same yields as recorded above.

We thank Dr. G. J. Wright, Canterbury University, Christchurch, for mass spectral determinations and Professor P. Müller, University of Geneva, for communicating results prior to publication. Financial assistance from Victoria University is gratefully acknowledged.

[6/1974 *Received*, 25*th October*, 1976]