

Replacement Reactions of 1,1-Dichloro-2,5-diphenylcyclopropabenzene with Organometallic Reagents

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The replacement of the chloro-substituents of 1,1-dichloro-2,5-diphenylcyclopropabenzene (1) can be effected by various organometallic reagents. The products of reaction with Grignard and organolithium reagents and with lithium aluminium hydride have been characterised. Although the *gem*-diethyl derivative (8) is the only isolated product in which the ring system is retained, spectroscopic evidence is presented which supports the involvement of 1,1-disubstituted cyclopropabenzene in all the reactions. With methylmagnesium iodide, the cyclopropabenzene (1) suffers the equivalent of Grignard reduction to afford the unanticipated fluorene (25).

THE majority of the routes available for cyclopropabenzene synthesis yield products which are not susceptible to changes in the substitution pattern without destruction of the ring system.¹ A major objective in effecting a convenient and high yield synthesis of *gem*-dichlorocyclopropabenzene (1)² was to determine if other, less readily accessible, members of the series could be obtained by reactions involving exchange of the halogen atoms. Such exchange has indeed proved possible and, during the course of our studies, Müller has described syntheses of compounds (2)³ and (3)⁴ from (1). We now report the results of exchange reactions of the cyclopropabenzene (1) with various organometallic reagents.

Recent reinvestigations⁵ concerning the addition of secondary diazo-compounds to quinone derivatives, *e.g.* (10), have led to a reidentification of the products as 7,7-disubstituted bicycloheptenes, *e.g.* (11), and not *gem*-diaryl cyclopropa-arenes, *e.g.* (4), as originally suggested.⁶ This, coupled with the report that photolysis of a 3*H*-indazole (12) gives a fluorene (13) as opposed to the cyclopropabenzene (5), led to an investigation of the behaviour of (1) with phenylmagnesium bromide in an attempt to produce an isolable *gem*-diaryl cyclopropabenzene.

Treatment of compound (1) with an excess of phenylmagnesium bromide resulted in a brown halogen-free oil which exhibited the typical¹ cyclopropa-arene medium intensity i.r. band at 1670 cm⁻¹ and showed only aromatic resonances in the ¹H n.m.r. spectrum. These data are fully compatible with the production of 1,1,2,5-

¹ B. Halton, *Chem. Rev.*, 1973, **73**, 113.

² B. Halton, P. J. Milsom, and A. D. Woolhouse, preceding paper.

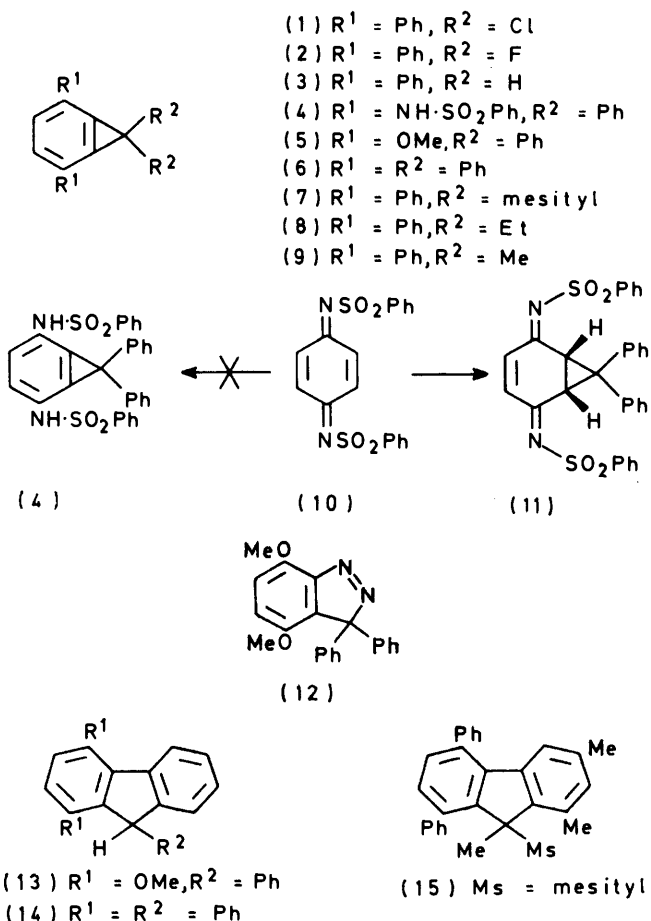
³ P. Müller, *J.C.S. Chem. Comm.*, 1973, 895.

⁴ P. Müller, *Helv. Chim. Acta*, 1974, **57**, 704.

⁵ 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.

⁶ A. Mustafa and M. Kamal, *J. Amer. Chem. Soc.*, 1953, **75**, 2939.

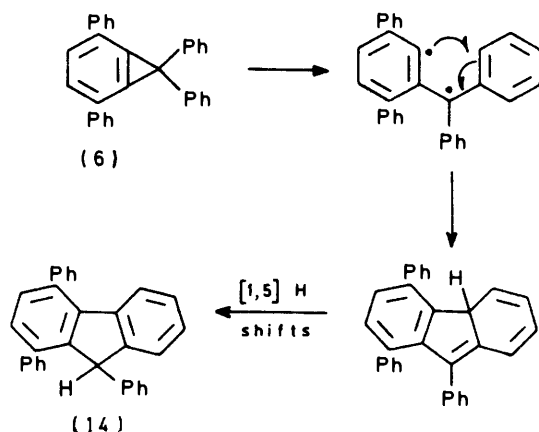
tetraphenylcyclopropabenzene (6). However, all attempts at purification resulted in the generation of an



isomeric compound which exhibits a one-proton singlet (δ 5.18) and a twenty-one proton multiplet (δ 6.8–7.5) in the n.m.r. spectrum and lacks cyclopropabenzene i.r.

absorption. This compound has been identified as 1,4,9-triphenylfluorene (14) principally from its spectroscopic data; the C-9 benzylic proton of the fluorene (13) resonates at δ 5.03,⁷ and that of 9-phenylfluorene at δ 5.05.⁸

The formation of the fluorene (14) (Scheme 1) is reminiscent of the thermal⁹ and photochemical¹⁰ rearrangements of tetra-arylcyclopropenes to 1,2,3-triarylindenes and is complete within minutes at 60 °C, as demonstrated by the appearance of the n.m.r. signal of the C-9 proton. Thus the rearrangement of (6) proceeds readily at a temperature *ca.* 100 °C lower than that required for the tetraphenylcyclopropene-triphenylindene conversion,⁹ a result consistent with the high (*ca.* 286 kJ mol⁻¹) strain energy of the cyclopropabenzene



SCHEME 1

ring system.¹¹ A minor (2%) product isolated from the reaction of the cyclopropabenzene (1) with phenylmagnesium bromide may be a dimer of (6) having lost the elements of biphenyl (C₅₀H₃₄; *M*⁺ 634), but its structure remains unknown. The reaction between (1) and phenyl-lithium paralleled that described above, although the yield of the fluorene (14) was reduced.

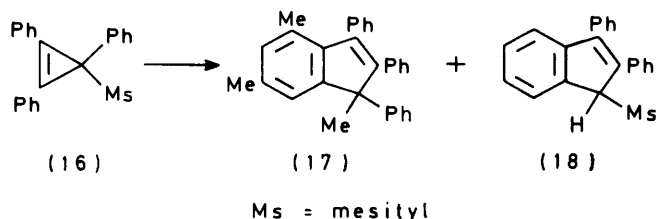
Blocking the *ortho*-positions of the aryl function in the Grignard reagent was expected to result in a simplified product distribution. However, the reaction between the cyclopropabenzene (1) and an excess of mesitylmagnesium bromide proved complex, and only after mild thermolysis (100 °C) was it possible to separate the product mixture. The single compound thus far obtained (36%) has analytical data consistent with the formal replacement of both chloro-substituents of (1) by mesityl groups, but it is not compound (7). From the presence of five non-equivalent methyl n.m.r. signals the product is tentatively identified as 9-mesityl-1,3,9-trimethyl-5,8-diphenylfluorene (15), in which rotation of the mesityl ring is restricted, by analogy with the rearrangement of (16) to (17) and (18).⁹

⁷ H. A. Staab and J. Ipaktschi, *Chem. Ber.*, 1968, **101**, 1457.
⁸ K. D. Bartles, D. W. Jones, and P. M. G. Bavin, *J. Chem. Soc. (B)*, 1971, 388.

⁹ M. A. Battiste, B. Halton, and R. H. Grubbs, *Chem. Comm.*, 1967, 907.

¹⁰ B. Halton, M. Kulig, M. A. Battiste, J. Perreten, D. M. Gibson, and G. W. Griffin, *J. Amer. Chem. Soc.*, 1971, **93**, 2327.

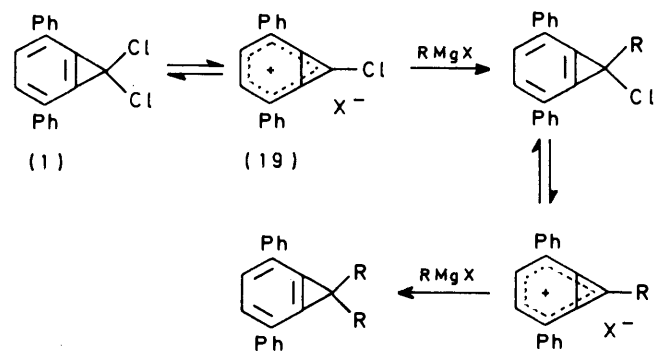
Replacement of both halogen atoms of compound (1) by the alkyl groups of aliphatic Grignard reagents has also been effected. With ethylmagnesium bromide a



SCHEME 2

single product is obtained (85%), the structure of which is established as (8) from the 1685 cm⁻¹ i.r. absorption and the magnetic equivalence¹² of the ethyl groups, and has been confirmed by X-ray methods.¹³ The formation of (8) [and (6) and (7) above] from the cyclopropabenzene (1) is best regarded as an S_N1 process with nucleophilic attack of the carbanionic centre of the Grignard reagent on the known¹⁴ cyclopropabenzylum ion (19) (Scheme 2).

The cyclopropabenzene (8) is stable when pure, but mild thermolysis (or purification by chromatographic methods) results in quantitative rearrangement to the styrene (20), thought to be the sterically more favoured *E*-isomer. Rearrangement of *gem*-dialkylcyclopropabenzene to styrenes *via* a five-membered transition state (Scheme 3) is to be expected from the known rearrangement of 1-methoxy-1-methylcyclopropabenzene to α -methoxystyrene at room temperature.¹⁵ The rearrangement of (8) provided no evidence for hydrogen transfer



occurring through a six-membered transition state to give an arylcyclopropane (Scheme 3). Although thermolysis of cyclopropabenzene¹⁶ and some of its derivatives¹⁵ in the presence of buta-1,3-diene leads to pro-

¹¹ W. E. Billups, W. Y. Chow, K. H. Leavell, E. S. Lewis, J. L. Margrave, R. L. Sass, J. J. Shieh, and J. L. Wood, *J. Amer. Chem. Soc.*, 1973, **95**, 7878.

¹² R. Anet and F. A. L. Anet, *J. Amer. Chem. Soc.*, 1964, **86**, 525.

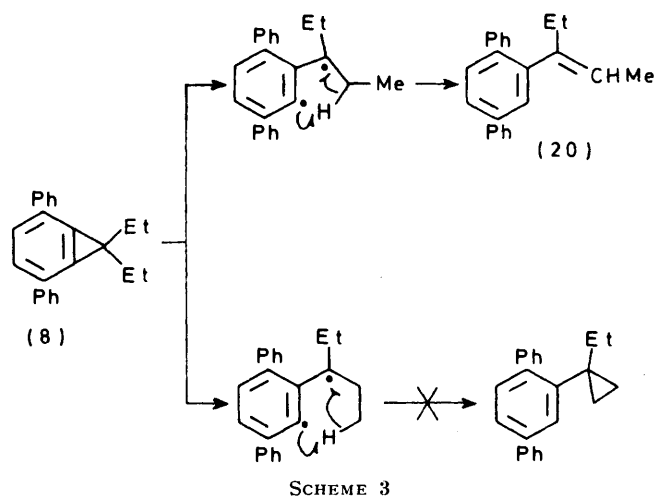
¹³ E. Carsten-Oeser and B. Müller, personal communication.

¹⁴ B. Halton, H. M. Hügel, D. P. Kelly, P. Müller, and U. Burger, *J.C.S. Perkin II*, 1976, 258.

¹⁵ G. L. Closs, K. R. Kaplan, and V. I. Bendall, *J. Amer. Chem. Soc.*, 1967, **89**, 3376.

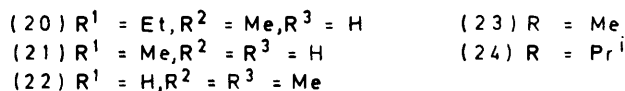
¹⁶ E. Vogel, personal communication.

ducts of radical trapping, analogous experiments with (8) have been singularly unsuccessful; in every case the



styrene (20) was obtained as the sole characterised product.

The formation of the *gem*-dimethylcyclopropabenzene (9) can be inferred from the spectral characteristics and thermal behaviour of the product mixture derived from compound (1) and methylmagnesium iodide. However, as with (6), the isolation of (9) proved impossible; the α -methylstyrene (21) was isolated, but only as the minor product (18%). The major product (45%) derived from (1) is a $C_{20}H_{16}$ species resulting from replacement of the chlorine atoms by the elements of methane—in effect the product of a Grignard reduction by methylmagnesium iodide. The compound has been identified as 9-methyl-2-phenylfluorene (25) from spectral data

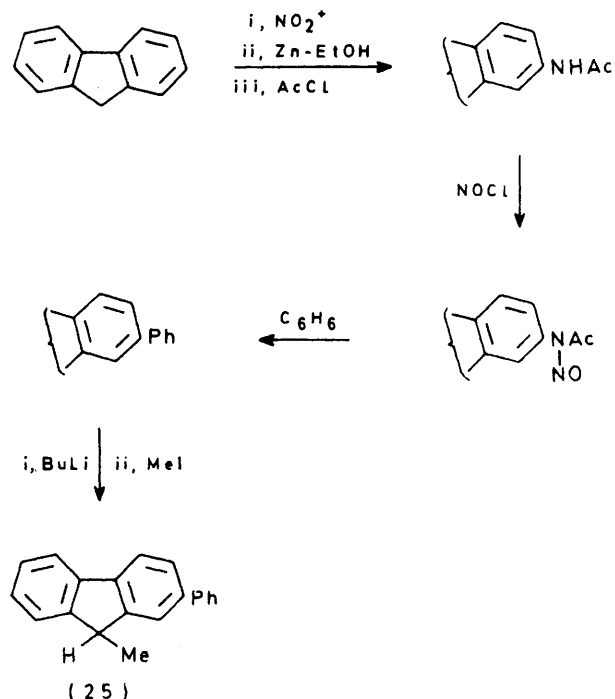


and by independent synthesis from fluorene (Scheme 4). The origin of the fluorene (25), which is isomeric with monomethylcyclopropabenzene (23), is not clear. Although it is well established that Grignard reagents can effect reductions in many circumstances, such a process by methylmagnesium iodide appears unprecedented. However, should (23) be formed, plausible routes from it to (25) can be written. The reaction of compound (1) with methyl-lithium gives a severely discoloured product mixture from which styrene (21) has been isolated (24%). No evidence was obtained for the fluorene (25); the more complex mixture could well result from carbenoid formation.

On increasing the steric requirements of the Grignard

reagent Grignard reduction was effected as anticipated. Thus with isopropylmagnesium bromide, compound (1) afforded the $\beta\beta$ -dimethylstyrene (22). The lack of evidence for the presence of the isopropylcyclopropabenzene (24) is not surprising in view of the behaviour of compounds (6)–(9). No characterised products were obtained from reaction of compound (1) with *t*-butyl Grignard reagents.

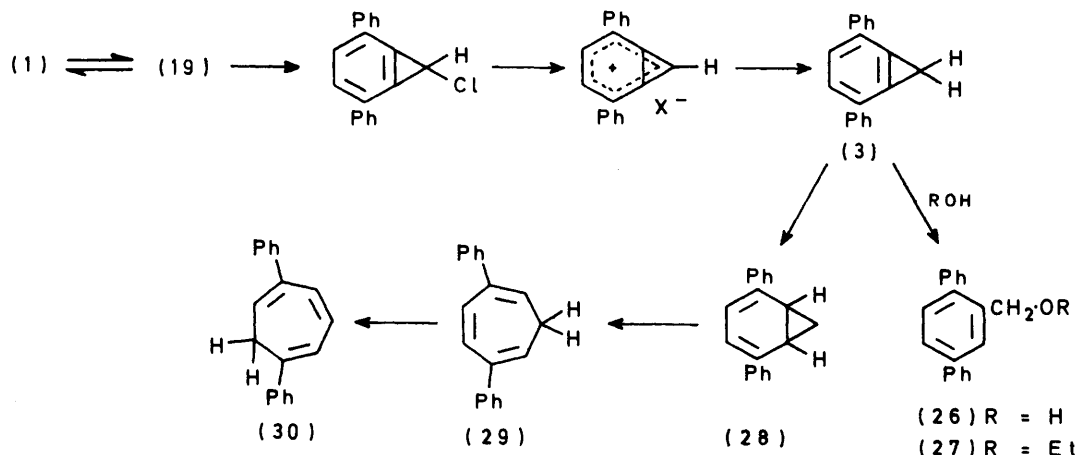
Attempts to effect mono-replacement in (1) by controlling the molar ratio of the reactants led only to bis-replacement in reduced yield. For example, equimolar quantities of (1) and ethylmagnesium bromide gave the



product (8) in 46% yield; unchanged (1) (47%) was characterised by conversion into methyl 2,5-diphenylbenzoate.²

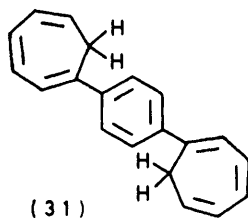
Although the formation of the cyclopropabenzene (3) from (1) has been effected with aluminium hydride,⁴ Müller reports that reduction of (1) by lithium aluminium hydride resulted only in uncharacterised decomposition products.⁴ In our hands, treatment of (1) with a slight excess of this latter reagent results in a homogeneous syrup which has the spectral characteristics of (3) but which suffers ring cleavage to give the alcohol (26) on preparative t.l.c. With an excess of lithium aluminium hydride, compound (3), characterised by conversion into the ether (27) with ethanol (64%), and the cycloheptatriene (30) (34%) are produced. The structure of (30) follows from spectral data. In particular, a two-proton doublet (J 7.4 Hz) centred at δ 2.82 is fully consistent with structure (30) and excludes the alternative (29) for which a triplet would be expected. Furthermore, the chemical shift of this doublet is in excellent agreement

with that for (31) (2.80).¹⁷ The facility with which compound (3) suffers cleavage of the three-membered ring to give (27) is markedly greater than that of cyclopropabenzene and cyclopropa[*b*]naphthalene,¹⁸ a feature ascribable only to the electronic effects of the pendant phenyl rings. The production of (30) (Scheme 5) is presumed to proceed *via* norcaradiene (28), with the final step involving [1,5] hydrogen migration to place a phenyl group in full conjugation with the triene system. The appearance of the cycloheptatriene parallels the formation of a cycloheptane from a cyclopropabenzene on catalytic hydrogenation.¹⁹



SCHEME 5

Thus replacement of the halogeno-substituent of the cyclopropabenzene (1) can be brought about readily. However, the reactivity of the resultant cyclopropabenzene plays a dominant role in determining the nature of the product isolated.



EXPERIMENTAL

For general details see preceding paper.

Treatment of 1,1-Dichloro-2,5-diphenylcyclopropabenzene (1) with Grignard Reagents.—To an ethereal solution of the appropriate Grignard reagent (2.5–4.0 mol. equiv.; prepared in the usual manner) under nitrogen, and externally cooled in a solid CO₂-acetone bath, was added slowly, with stirring, a solution of compound (1) (0.62 g, 2.0 mmol) in dry benzene (15 cm³) containing ether (7 cm³) over *ca.* 4 h. The solution was then allowed to warm to room temperature, diluted with benzene (50 cm³), washed with saturated ammonium chloride solution (10 cm³) and water (2 × 15 cm³), and dried (MgSO₄). Concentration, under vacuum, afforded a dark halogen-free oil:

¹⁷ R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, 1966, **88**, 3527.

¹⁸ A. R. Browne and B. Halton, *Tetrahedron*, in the press.

(i) **Phenylmagnesium bromide.** The orange-brown oil showed only aromatic n.m.r. signals and exhibited a prominent i.r. band at 1 670 cm⁻¹, as required for structure (6). Attempts at fractional crystallisation of the product resulted in rearrangement. Chromatography over basic alumina [benzene-light petroleum (1:4)] gave two products. Fraction (i) (150 cm³) was recrystallised from hexane to give biphenyl (0.15 g), m.p. 69–70° (lit.,²⁰ 70°). Fraction (ii) (100 cm³) was recrystallised from benzene-light petroleum (1:3) to give 1,4,9-triphenylfluorene (14) (43%) as pale yellow needles, m.p. 165–166° (Found: C, 94.5; H, 5.75. C₃₁H₂₃ requires C, 94.35; H, 5.65%); ν_{\max} . 1 600, 1 080, 1 025, 835, 800, 780, 775, 765, 750, and 700

cm⁻¹; δ 5.18 (1 H, s), 6.80–7.21 (16 H, m), and 7.45br (5 H, s); λ_{\max} . (cyclohexane) 233 (log ϵ 4.45) and 2.58 nm (4.33).

The column was stripped (methanol-acetone, 1:1) and the semi-solid obtained subjected to preparative t.l.c. (benzene). The sole fluorescent species (R_F 0.5) was extracted with chloroform. Recrystallisation from hexane gave pale yellow prisms (1.5%), m.p. 206–208° (Found: C, 94.55; H, 5.4. C₅₀H₃₄ requires C, 94.65; H, 5.35%); M^+ 634.

Repetition of the reaction, at various temperatures (<0 °C) gave a dark brown product in each instance, the spectral properties of which were consistent with formation of (6). The n.m.r. spectrum consistently displayed only complex aromatic resonances, and the infrared spectrum exhibited the characteristic absorption at 1 675 cm⁻¹. By warming a solution of the crude product in the n.m.r. probe, it was possible to observe the appearance of the fluorene proton signal at δ 5.18, and at 60 °C the isomerisation was complete after several minutes.

(ii) **Mesitylmagnesium bromide.** The dark orange oil (98%) was shown by t.l.c. to consist of two prominent fluorescent species. The n.m.r. spectrum exhibited eight discrete methyl signals. Trituration with benzene-light petroleum (1:2) followed by filtration afforded a brown microcrystalline solid, which showed no cyclopropabenzene i.r. absorption at *ca.* 1 670 cm⁻¹. Preparative t.l.c. (light

¹⁹ E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Letters*, 1965, 3625.

²⁰ 'Handbook of Chemistry and Physics,' 48th edn., ed. R. C. Weast, The Chemical Rubber Co., Cleveland, Ohio, 1968.

petroleum) gave two bands (R_F 0.25 and 0.30), which were extracted with chloroform (100 cm³). Recrystallisation of each fraction from benzene–light petroleum (1 : 1) gave identical pale yellow needles (m.p. 194–198°) (i.r. and n.m.r. spectra). The combined samples were recrystallised from the same solvent to give the same product, tentatively identified as 9-mesityl-1,3,9-trimethyl-5,8-diphenylfluorene (15) (36%), m.p. 196–198° (Found: C, 92.65; H, 7.3%; M^+ , 478.264 719. $C_{37}H_{34}$ requires C, 92.85; H, 7.15; M , 478.266 038); ν_{\max} , 1 605, 1 465, 1 080, 1 015, 900, 890, 850, 835, 755, and 695 cm⁻¹; δ 1.06 (3 H, s), 1.32 (3 H, s), 1.90 (3 H, s), 2.03 (3 H, s), 2.12 (3 H, s), 6.81br (5 H, s), 6.90–7.15 (2 H, m), 6.98 (2 H, s), and 7.39 (7 H, s); λ_{\max} (EtOH) 279 (log ϵ 4.51) and 258 nm (4.31).

(iii) *Ethylmagnesium bromide*. The orange oil crystallised slowly. Two low-temperature recrystallisations from pentane yielded 1,1-diethyl-2,5-diphenylcyclopropabenzene (8) (61%) as prisms, m.p. 120–121° (Found: C, 92.65; H, 7.7. $C_{23}H_{22}$ requires C, 92.55; H, 7.45%); ν_{\max} (KBr) 3 020, 2 950, 1 685, 1 475, 1 390, 1 085, 1 010, 830, 770, 705, 700, and 655 cm⁻¹; δ 0.58 (6 H, t, J 7.8 Hz), 2.16 (4 H, q, J 7.8 Hz), 7.24–7.51 (6 H, m), 7.55 (2 H, s), and 7.58–7.96 (4 H, m); λ_{\max} (cyclohexane) 291 (log ϵ 4.38), 298sh (4.30) and 320sh nm (4.01); m/e 298, (M^+ 20%) and 269 [(M – Et)⁺, 100%].

(iv) *Methylmagnesium iodide*. The black immobile oil, shown by t.l.c. to consist of two major and *ca.* ten minor components, exhibited a 1 670 cm⁻¹ i.r. band consistent with the formation of (9); the vinylic resonance of (21) (below) was absent from the n.m.r. spectrum. Attempts at fractional crystallisation of the products were unsuccessful. Preparative t.l.c. (two elutions with light petroleum) afforded two u.v. active bands, A and B (R_F 0.4 and 0.6). Band A afforded 9-methyl-2-phenylfluorene (25) (45%) as waxy needles, m.p. 104–105° (from dry ethanol) (Found: C, 93.65; H, 6.35. $C_{20}H_{16}$ requires C, 93.7; H, 6.3%); ν_{\max} , 1 450, 1 405, 1 250, 1 175, 1 070, 1 005, 890, 815, 750, 740, 720, and 690 cm⁻¹; δ 1.51 (3 H, d, J 7.2 Hz), 3.93 (1 H, q, J 7.2 Hz), and 7.15–7.86 (12 H, m); λ_{\max} (cyclohexane) 289 (log ϵ 4.37) and 309 nm (4.30); m/e 256 (M^+ ; 100%) and 241 [(M – Me)⁺, 79%].

Band B gave a colourless oil which crystallised on cooling at –20 °C. Recrystallisation twice from ethanol afforded α -methyl-2,5-diphenylstyrene (21) (18%) as shiny needles m.p. 64–65° (Found: C, 93.1; H, 6.85. $C_{21}H_{18}$ requires C, 93.3; H, 6.7%); ν_{\max} , 1 595, 1 085, 1 010, 900, 855, 850, 790, 770, and 700 cm⁻¹; δ 1.69 (3 H, d, J *ca.* 1 Hz), 5.09br (2 H, m), and 7.20–7.77 (13 H, m); λ_{\max} (EtOH) 241sh (log ϵ 4.26) and 267 nm (4.39); m/e 270 (M^+ ; 86%), and 255 [(M – Me)⁺, 100%].

(v) *Isopropylmagnesium bromide*. The black oil was subjected to preparative t.l.c. (light petroleum). The only fluorescent species (R_F 0.6) was extracted with chloroform (100 cm³) and concentrated to an oil which solidified. Two recrystallisations from dry ethanol afforded $\beta\beta$ -dimethyl-2,5-diphenylstyrene (22) (18%) as needles, m.p. 78–79° (Found: C, 92.8; H, 7.2. $C_{22}H_{20}$ requires C, 92.9; H, 7.05%); ν_{\max} , 1 600, 1 455, 1 080, 1 020, 1 005, 900, 830, 755, and 695 cm⁻¹; δ 1.75 (3 H, s), 1.79br (3 H, s), 6.15br (1 H, s), and 7.30–7.85 (13 H, m); λ_{\max} (cyclohexane) 250 (log ϵ 4.47) and 268sh nm (4.39).

Multicoloured bands (R_F 0.5–0.1) were removed and extracted with chloroform. Concentration gave a black oil. Thorough reinvestigation by t.l.c. showed that the remaining bands could not be effectively separated.

Thermolysis of 1,1-Diethyl-2,5-diphenylcyclopropabenzene (8).—(i) *In the absence of buta-1,3-diene*. A solution of compound (8) (0.41 g, 1.4 mmol) in dry benzene (10 cm³) was heated at 80 °C in a sealed tube for 8 h. The cooled solution was concentrated to a homogeneous oil, which crystallised. Recrystallisation from ethanol and from hexane yielded (*E*)- α -ethyl- β -methyl-2,5-diphenylstyrene (20) (0.39 g, 95%) as shiny needles, m.p. 104–105° (Found: C, 92.35; H, 7.75. $C_{23}H_{22}$ requires C, 92.55; H, 7.45%); ν_{\max} , 1 600, 1 465, 1 080, 1 025, 1 005, 900, 845, 830, 755, and 690 cm⁻¹; δ 0.79 (3 H, t, J 7.2 Hz), 1.71 (3 H, d, J 6.7 Hz), 1.80 (2 H, q, J 7.2 Hz), 5.60 (1 H, q, J 6.7 Hz), and 7.30–7.62 (13 H, m); λ_{\max} (cyclohexane) 253sh (log ϵ 4.36) and 270 nm (4.43); m/e 298 (M^+ , 21%) and 269 [(M – Et)⁺, 100%].

(ii) *In the presence of buta-1,3-diene*. The cyclopropabenzene (8) (0.48 g, 1.6 mmol) was dissolved in dry benzene (20 cm³) contained in a glass tube and cooled in liquid nitrogen while buta-1,3-diene (*ca.* 6 cm³) was added. The tube was sealed and heated in an oil bath at 75–80 °C for 96 h, after which the cooled solution was concentrated to a semi-solid (2.9 g). Chromatography over silica gel (300 g) (hexane), afforded an unidentified syrup (2.3 g), presumed to be butadiene polymers. Prolonged elution did not yield a chromatographically recognisable product; as a result, the column was stripped with methanol–acetone (1 : 1) and the concentrated eluate subjected to preparative t.l.c. (benzene–petroleum, 1 : 2). The only prominent fluorescent band (R_F 0.3) was extracted with chloroform (100 cm³) and the extract concentrated to a solid, which was recrystallised from ethanol to give (*E*)- α -ethyl- β -methyl-2,5-diphenylstyrene (20) (0.42 g, 88%) as needles, m.p. and mixed m.p. 104–105°. I.r. and n.m.r. spectra were identical with those recorded above.

From both reactions (i) and (ii), i.r. spectra of the crude products showed the complete absence of the 'aromatic double bond' absorption at 1 685 cm⁻¹. Chromatography of (8) also effected quantitative isomerisation to (20).

9-Methyl-2-phenylfluorene (25).—Nitrosyl chloride (*ca.* 7 cm³) in dry glacial acetic acid (10 cm³) containing acetic anhydride (6 cm³) was added dropwise with stirring to an externally cooled (*ca.* 8 °C) solution of 2-acetamidofluorene (4.20 g, 0.019 mol) [prepared from 2-aminofluorene²¹ by standard procedures; m.p. 187° (lit.,²⁰ 187–188°)] in glacial acetic acid (20 cm³) and acetic anhydride (12 cm³), containing finely ground fused sodium acetate (3.0 g) and phosphorus pentoxide (0.2 g). The addition was complete after 30 min and the solution was stirred for a further 10 min before being poured onto ice (100 g). The green precipitate was filtered off, washed with cold water (50 cm³), and dried by suction before being dissolved in benzene (800 cm³); the solution was washed with aqueous sodium hydroxide (1M; 50 cm³), dried, and kept over a mixture of anhydrous magnesium sulphate (10 g) and anhydrous sodium carbonate (7 g) for 40 h at room temperature, with occasional stirring. The resulting black solution was filtered and concentrated to a semi-solid, which was shown by t.l.c. (benzene–petroleum, 1 : 1) to consist of a single mobile component (R_F 0.6). The crude black material was chromatographed over neutral alumina (150 g) (benzene–petroleum, 1 : 2); the fluorescent blue component was collected in the first eluate (300 cm³). Concentration afforded a solid which was recrystallised from heptane and from ethanol to give 2-phenylfluorene (0.68 g, 15%) as

²¹ W. E. Kuhn, *Org. Synth.*, Coll. Vol. II, 1943, p. 447.

shiny plates, m.p. 192—193° (lit.,²² 193—194°), ν_{\max} . 1 450, 1 410, 945, 875, 820, 750, 735, and 690 cm^{-1} .

2-Phenylfluorene (0.21 g, 0.9 mmol) dissolved in dry benzene (6 cm^3) and dry ether (5 cm^3) was cooled and added dropwise to a stirred solution of butyl-lithium in hexane (15%; 1.2 cm^3 , ca. 2.4 mmol) under nitrogen. After the addition (1 h), the solution was stirred vigorously for 2 h, then dry methyl iodide (3.5 g, 24.6 mmol) was added dropwise. The red colour was immediately discharged with precipitation of a white crystalline solid. The solution was stirred for 15 min, diluted with benzene (40 cm^3), and treated with hydrochloric acid (1M; 4 cm^3). The organic extract was separated, washed with water (2 \times 10 cm^3), and dried (MgSO_4 ; 3 g). Concentration afforded a pale yellow oil, which solidified on cooling. Recrystallisation from dry ethanol yielded 9-methyl-2-phenylfluorene (25) (0.17 g, 76%) as waxy needles, m.p. 103—105° (Found: C, 93.6; H, 6.4. $\text{C}_{20}\text{H}_{16}$ requires C, 93.7; H, 6.3%). Spectral data were in complete accord with those recorded for compound (25) derived from (1) and methylmagnesium iodide. A mixed m.p. showed no depression.

Treatment of 1,1-Dichloro-2,5-diphenylcyclopropabenzene (1) with Lithium Aluminium Hydride.—(i) A solution of compound (1) (0.13 g, 0.42 mmol) in dry benzene (10 cm^3) was added dropwise, over 30 min, to a stirred suspension of lithium aluminium hydride (0.010 g, 0.27 mmol) in dry ether (30 cm^3). The solution was maintained at 30 °C for 8 h, diluted with benzene (40 cm^3), and treated with a trace of water. The organic solution was separated, washed with water (2 \times 10 cm^3), and dried (MgSO_4 ; 2 g). Concentration afforded an oil (ν_{\max} . 1 670 cm^{-1}) which resisted recrystallisation. Preparative t.l.c. (chloroform) led to an intense blue fluorescent species (R_F 0.8) which was extracted with benzene (100 cm^3); the extract was concentrated to a pale yellow, waxy solid. Recrystallisation from light petroleum gave 1-hydroxymethyl-2,5-diphenylbenzene (26) (0.09 g, 89%) as fine needles, m.p. 90° (Found: C, 87.55; H, 6.15. $\text{C}_{19}\text{H}_{16}\text{O}$ requires C, 87.6; H, 6.25%); ν_{\max} . 3 300, 1 180, 1 015, 1 000, 900, 835, 760, and 695 cm^{-1} ;

δ 4.37 (s, OH), 4.65 (2 H, s), and 7.24—7.80 (13 H, m); λ_{\max} . (EtOH) 277 nm (log ϵ 4.43).

(ii) A solution of compound (1) (0.25 g, 0.80 mmol) in dry benzene (10 cm^3) was treated with a large excess of lithium aluminium hydride and maintained at 0 °C for 10 h. The product was worked up as described above to give a yellow immobile gum, which was pumped at 60 °C for several minutes, before being taken up in dry ethanol and heated over a steam-bath for 30 min. T.l.c. (benzene-petroleum, 1 : 9) revealed the presence of two species, A and B (R_F 0.2 and 0.6). Concentration of the solution afforded a yellow oil, which was subjected to preparative t.l.c. (same solvent); the two bands were each extracted with chloroform (100 cm^3). Band A gave 1-ethoxymethyl-2,5-diphenylbenzene (27) (0.15 g, 64%) as a yellow oil (Found: C, 87.6; H, 6.85. $\text{C}_{21}\text{H}_{20}\text{O}$ requires C, 87.5; H, 7.0%); ν_{\max} . 1 600, 1 495, 1 455, 1 360, 1 185, 1 095, 1 080, 1 005, 835, 760, and 695 cm^{-1} ; δ 1.18 (3 H, t, J 7.0 Hz), 3.46 (2 H, q, J 7.0 Hz), 4.43 (2 H, s), and 7.25—7.84 (13 H, m); λ_{\max} . (hexane) 317 nm (log ϵ 4.07). Band B afforded a pale yellow oil which solidified immediately on cooling. Recrystallisation from light petroleum gave 1,5-diphenylcyclohepta-1,3,5-triene (30) (0.07 g, 34%) as pale yellow needles, m.p. 73—74° (Found: C, 93.05; H, 6.9. $\text{C}_{18}\text{H}_{16}$ requires C, 93.4; H, 6.6%); ν_{\max} . 1 595, 1 495, 1 450, 1 080, 835, 830, 795, 760, 740, and 690 cm^{-1} ; δ 2.82 (2 H, d, J 7.4 Hz), 5.51 (1 H, t, J 6.2 Hz), 5.68 (1 H, t, J 7.4 Hz), 6.55 (1 H, d, J 6.2 Hz), 7.02 (1 H, d, J 6.2 Hz), and 7.10—7.58 (10 H, m); λ_{\max} . (hexane) 317 nm (log ϵ 4.73).

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²² N. G. Sidorova and G. Kh. Tyshchuk, *Zhur. obshchei Khim.*, 1958, **23**, 2030 (*Chem. Abs.*, 1959, **53**, 2179g).