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## 9-Phenethylfluorene and its Dehydro Derivatives

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9-Phenethylfluorene, 9-phenylethylidenefluorene, β-9-fluorenylstyrene, and spiro-1-(9-fluorenyl)-2-phenylcyclopropane have been synthesised and their structure established. Certain erroneous statements about 2-(9-fluorenyl)-1,1-diphenylethene and 2-fluorenylidene-1,1-diphenylethane have been corrected and the isomerisation of these substances compared with that of 9-phenylethylidenefluorene and β-9-fluorenylstyrene and of 1,3,3- and 1,1,3-triphenylpropene.

UNCERTAINTY about 9-phenethylfluorene (I) and the corresponding unsaturated derivatives (II) and (III) led us to study the preparation and properties of these hydrocarbons. The first is described <sup>1</sup> as melting at 209-210°, but we have synthesised the hydrocarbon by interaction of phenethyl bromide with 9-lithiofluorene and have found that it melts at 38-39°. Attempts to condense 9-sodiofluorene with phenethyl bromide<sup>2</sup> gave only bifluorenyl and bifluorenylidene. 9-Phenethylfluorene was also prepared by the hydrogenation of 9-phenylethylidenefluorene (II), which resulted from the dehydration of the alcohol (IV), obtained by the action of phenethylmagnesium bromide on fluorenone. The position of the double bond in (II) was established by the similarity of the ultraviolet spectrum to that of 9ethylidenefluorene.<sup>3</sup> The isomeric  $\beta$ -9-fluorenylstyrene (III) is described <sup>4</sup> as melting at  $242-244^{\circ}$ , but we prepared it by the pyrolysis of the xanthate (V) and found that it melts at 106–107°. It is the *trans* isomer (infrared and n.m.r. spectra) as would be expected since a cis-elimination of an anti-conformer is involved. In

alkaline solution  $\beta$ -9-fluorenylstyrene (III) is rapidly isomerised to the fluorenylidene compound (II) as evidenced by change in the ultraviolet spectrum. This is not surprising since double bonds tend to conjugate with the fluorene rather than with the phenvl nucleus.<sup>3</sup>

For the synthesis of the above hydrocarbons other methods were tried. 9-Phenacylfluorene was reduced by sodium borohydride to 2-(9-fluorenyl)-1-phenylethanol (VI; R = OH), but attempts to dehydrate this were unsuccessful. With phosphorus tribromide the alcohol yielded the bromide (VI; R = Br), which with alkali underwent dehydrohalogenation to give spiro-1-(9fluorenyl)-2-phenylcyclopropane (VII). The structure of this product was confirmed by the similarity of its ultraviolet spectrum to that of fluorene, its n.m.r. spectrum, and by its preparation from the unsaturated ketone (VIII) by Wolff-Kishner reduction via the pyrazoline.5

9-Phenacylfluorene when heated with solid potassium

<sup>3</sup> D. M. W. Anderson, N. Campbell, J. T. Craig, and D. A. Crombie, J. Chem. Soc., 1960, 781.

<sup>4</sup> J. T. Craig, Thesis, Edinburgh, 1953, p. 109.
<sup>5</sup> See, e.g., S. G. Beech, J. H. Turnbull, and W. Wilson, J. Chem. Soc., 1952, 4686; G. Lardelli and O. Jeger, Helv. Chim. Acta, 1949, 32, 1817.

<sup>&</sup>lt;sup>1</sup> R. C. Fuson and F. E. Mumford, J. Org. Chem., 1952, 17,

<sup>257.</sup> <sup>2</sup> Cf. E. J. Greenhow, E. N. White, and D. McNeil, J. Chem. Soc., 1951, 2848.

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hydroxide, hydrazine hydrate, and ethylene glycol at 200° gave fluorene, but when the hydrazone was heated with dry potassium t-butoxide in toluene the spirane (VII) and the azine of 9-phenacylfluorene resulted.<sup>6</sup>

The alkaline decomposition of 9-phenacylfluorene toluene-p-sulphonhydrazone yielded no unsaturated hydrocarbon, the only products isolated being the spirane



(VII) and the azine.<sup>7</sup> The formation in this reaction of cyclopropane derivatives along with or in preference to unsaturated hydrocarbons has been observed in several instances<sup>8</sup> and it is thought to occur through the formation of intermediate carbenes followed by carbene insertion at a carbon-hydrogen bond.

To prevent the formation of cyclopropane derivatives, the 9-hydrogen atom in 9-phenacylfluorene was replaced by a cyano- or an ethoxycarbonyl group, but no advantage accrued. The cyano-compound failed to condense with toluene-p-sulphonhydrazide and reduction of the oxogroup in the ethoxycarbonyl compound (IX; R = $CO_2Et$ ) gave the lactone (X) so readily that these compounds were not further investigated.



The decarboxylation of 2-phenyl-3-(9-fluorenyl)acrylic acid would yield  $\beta$ -9-fluorenylstyrene (III) and to prepare this acid 9-formylfluorene was heated with phenylacetic acid, triethylamine, and acetic anhydride. The products were unchanged phenylacetic acid and the enol-

<sup>6</sup> M. F. Grundon, H. B. Henbest, and M. D. Scott, J. Chem.

 Soc., 1963, 1855.
<sup>7</sup> W. R. Bamford and T. S. Stevens, J. Chem. Soc., 1952, 4735; P. Clark, M. C. Whiting, G. Papenmeier, and W. Reusch, J. Org. Chem., 1962, 27, 3356; cf. A. P. Krapcho and J. Diamanti, Computer States and Stat Chem. and Ind., 1965, 847.

acetate of 9-formylfluorene.9 The enol-acetate when boiled with copper chromite in quinoline gave 9fluorenylidene-9-fluorenylmethane, which had previously been prepared by different routes.<sup>10a, b</sup>

It was of interest to compare our results with those obtained with related compounds containing a second phenyl group. 2-(9-Fluorenyl)-1,1-diphenylethene (XI) is described by Schlenk and Bergmann as a solid, m. p.

111-112°,11 but Kuhn, Neugebauer, and Fischer regarded this as the isomeric 2-fluorenylidene-1,1-diphenylethane (XII), m. p. 105-107°, identical with the hydrocarbon they prepared by a different route. We have found that the product prepared by the method of Kuhn et al., from the similarity of its ultraviolet spectrum to that of  $\beta$ -9-phenylethylidenefluorene, is in fact slightly impure 2-fluorenylidene-1,1-diphenylethane (XII), m. p. 113°, while that of Schlenk and Bergmann is a mixture of the isomers. By repeating Schlenk and Bergmann's method we obtained the fluorenyldiphenylethene (XI), m. p. 150°, whose structure was established by ultraviolet and n.m.r. spectra. It is probable that Schlenk and Bergmann, when treating an intermediate alcohol with hydrogen chloride, isolated the hydrocarbon (XI) and not a chloride as they thought and this with pyridine underwent partial isomerisation. 2-(9-Fluorenyl)-1,1diphenylethene (XI) was rapidly isomerised in ethanol containing sodium ethoxide to give an equilibrium mixture in which as before the fluorenylidene compound (XII) greatly predominated.

The isomerisation of 1,3,3-triphenylpropene (XIII)<sup>12</sup> and its isomer 1,1,3-triphenylpropene<sup>13</sup> yielded an oil

Ph₂CH•CH <b>∶</b> CHPh	Ph₂C <b>:</b> CH•CH₂Ph
(XIII)	(XIV)

from which on two occasions a solid, m. p. 40-41°, separated. Neither the oil nor the solid exhibited the trans-CH:CH band at 975 cm.<sup>-1</sup> characteristic of the infrared spectrum of (XIII), thus indicating the almost complete isomerisation to the more highly conjugated compound (XIV). This was confirmed by the n.m.r. spectrum of the oil which resembled that of 1,1,3-triphenylpropene (XIV).

## EXPERIMENTAL

Unless otherwise stated ultraviolet spectra were measured in ethanol and chromatographic separations were effected on alumina, Peter Spence, Grade H. Nuclear magnetic resonance spectra were measured for deuteriochloroform

<sup>8</sup> W. Kirmse, Angew. Chem., 1962, 74, 183; L. Friedman and

<sup>8</sup> W. Kitmse, Angew. Chem., 1902, 14, 105; L. Friedman and H. Shechter, J. Amer. Chem. Soc., 1959, 81, 5512.
<sup>9</sup> W. Wislicenus and M. Waldmüller, Ber., 1909, 42, 785.
<sup>10</sup> (a) R. Kuhn, F. A. Neugebauer, and H. Fischer, Annalen, 1962, 654, 64; (b) S. Wawzonek and E. Dufek, J. Amer. Chem. Soc., 1956, 78, 3530.
<sup>11</sup> W. Schlenk and E. Bergmann, Annalen, 1928, 463, 1, 271.
<sup>12</sup> M. Schlenk and E. Bergmann, Annalen, 1928, 463, 1, 271.

<sup>12</sup> J. H. Burckhalter and S. H. Johnson, J. Amer. Chem. Soc., 1951, **73**, 4830.

<sup>13</sup> C. F. Koelsch and P. R. Johnson, J. Org. Chem., 1941, 6, 538

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solutions by means of a Perkin-Elmer R 10 (60 Mc./sec.) spectrometer.

9-Phenethylfluorene.-Phenethyl bromide (4.5 g.) in dry ether (10 ml.) was added slowly to an ether solution (60 ml.) of 9-lithiofluorene, prepared by the action of phenyl-lithium on fluorene (4 g.) with stirring. After  $\frac{1}{2}$  hr. the solution was poured into water (50 ml.). The dried  $(Na_2SO_4)$ ether layer was evaporated to an oil which was chromatographed in light petroleum. Development with light petroleum containing an ever-increasing proportion of benzene gave first fluorene (1.3 g.), then phenethylfluorene (4.5 g.), m. p. 38-39°, which crystallised when kept for several days in contact with ethanol (Found: C, 93.5; H, 6.6.  $C_{21}H_{18}$  requires C, 93.3; H, 6.7%);  $\nu_{max.}$  695s cm.<sup>-1</sup> (Ph group); ultraviolet spectrum similar to that of fluorene,  $\lambda_{\rm max.}$  211, 230, 264, 267, 291, and 301 mµ (log  $\varepsilon$  4.68, 3.88, 4.25, 4.25, 3.76, and 3.94). It was unstable in air, giving a vellow oil, possibly a hydroperoxide, with a strong band at ν 3450 cm.<sup>-1</sup>.

9-β-Phenylethylidenefluorene.-Fluorenone (3.6 g.) in the minimum of benzene-ether (1:1 v/v) was added dropwise to the Grignard reagent prepared from phenethyl bromide (11.1 g.) and magnesium (1.5 g.) in ether (70 ml.). The mixture was boiled (7 hr.) and poured into ice-ammonium chloride. Benzene (50 ml.) was added and the organic layer steam-distilled. The resultant oil with the minimum of boiling benzene yielded on cooling fluoren-9-ol, m. p. and mixed m. p. 152-154°. The filtrate was evaporated and chromatographed in 10% ether-benzene. Development with solvent containing an ever-increasing proportion of ether until elution with ether alone was achieved gave a pale vellow band followed by a light brown band which contained fluoren-9-ol (total yield 1 g.). The yellow band gave 9-phenethylfluoren-9-ol (3.7 g.), prisms (from light petroleum, b. p. 60-80°), m. p. 59-60° (Found: C, 87.7; H, 6.9.  $C_{21}H_{18}O$  requires C, 88.1; H, 6.3%);  $\nu_{max}$  3310s cm.<sup>-1</sup> (OH); the ultraviolet spectrum,  $\lambda_{max.}$  228, 236, 276, and 307 mµ (log ɛ 4·37, 4·27, 4·09, and 3·54), was very similar to that of 9-benzylfluoren-9-ol.<sup>3</sup>

The alcohol (4.5 g.) was heated (2 hr.) in 90% formic acid (90 ml.) and water was added. Extraction with ether followed by washing with sodium hydrogen carbonate and removal of the ether gave 9- $\beta$ -phenylethylidenefluorene (4 g.), needles (from light petroleum, b. p. 60—80°), m. p. 88—90° (Found: C, 94.0; H, 5.8. C<sub>21</sub>H<sub>16</sub> requires C, 94.0; H, 6.0%);  $\lambda_{max}$  230, 248, 257, 283, 299, and 313 mµ (log  $\varepsilon$  4.64, 4.51, 4.66, 4.21, 4.11, 4.12);  $\nu_{max}$  1640 cm.<sup>-1</sup> (C:C); n.m.r. spectrum: 2 methylene protons at  $\tau$  5.88 (doublet) and 1 olefinic proton at  $\tau$  3.25 (triplet). The hydrocarbon (0.53 g.) in the minimum of ethanol with hydrogen and a palladium-charcoal catalyst yielded 9-phenethylfluorene (0.48 g.), m. p. and mixed m. p. with the substance described above, 38—39°, after purification by chromatotography and standing in ethanol for several days.

The ultraviolet spectrum of phenylethylidenefluorene was only slightly changed when a solution of the hydrocarbon in ethanolic sodium ethoxide was kept for 12 days.

2-(9-Fluorenyl)-1-phenylethanol.—Ethyl 9-phenacylfluorene-9-carboxylate,<sup>14</sup>  $\nu_{max}$  1720 (ester CO) and 1690 cm.<sup>-1</sup> (Ph·CO), was hydrolysed and decarboxylated to 9-phenacylfluorene,<sup>14</sup>  $\nu_{max}$  1690 cm.<sup>-1</sup> (ketonic CO), 4 g. of which were suspended in ethanol (20 ml.) and sodium borohydride (0.5 g.) added. Gentle warming followed by boiling ( $\frac{1}{2}$  hr.) and removal of the ethanol under reduced pressure gave a residue which was triturated with water. Extraction of the aqueous solution with ether and evaporation gave the alcohol, crystals (from light petroleum), m. p. 108—110° (lit.,<sup>15</sup> 108—109°%) (Found: C, 88·4; H, 6·5. Calc for  $C_{21}H_{18}O$ : C, 88·1; H, 6·3%);  $\nu_{max}$  3580 cm.<sup>-1</sup> (OH). The alcohol (1·43 g.) was heated ( $2\frac{1}{2}$  hr.) with formic acid (15 ml.), water was added, and the mixture extracted with ether, which on evaporation gave the *formate* of the alcohol, m. p. 104—106°, after crystallisation from benzene–light petroleum, depressed when admixed with the alcohol (Found: C, 85·4; H, 6·2.  $C_{22}H_{18}O_2$  requires C, 84·05; H, 5·8%);  $\nu_{max}$  1730 (CO ester) and 1155 cm.<sup>-1</sup> (ester COC).

β-9-Fluorenylstyrene.—Sodium hydride (0·12 g.) in 50% oil suspension was added to a stirred solution of the alcohol (1·5 g.) in anhydrous ether (20 ml.) and boiled (3 hr.). Carbon bisulphide (0·38 g.) was added and the mixture boiled (3 hr.), then addition of methyl iodide was followed by a further 3 hours' boiling. Water was added and the ether layer yielded the xanthate (1·3 g.), m. p. 88—90°, after crystallisation from light petroleum (b. p. 60—80°);  $v_{max}$ . 1060s cm.<sup>-1</sup> (CS) and 1210 cm.<sup>-1</sup> (CO). The xanthate (2·7) g.) was heated until the temperature reached 160° and crystallisation of the product from ethanol gave β-9-fluorenyl-styrene (1·8 g.), m. p. 106—107° (Found: C, 94·1; H, 5·9, C<sub>21</sub>H<sub>16</sub> requires C, 94·0; H, 6·0%);  $v_{max}$ . 980 cm.<sup>-1</sup>

(CHR:CHR' trans), and an ultraviolet spectrum similar to that of fluorene;  $\lambda_{max}$  220, 261, 294, and 304 mµ (log  $\varepsilon$  4·38, 4·53, 3·79, and 3·84); n.m.r. spectrum: one tertiary proton at  $\tau$  5·52 and olefinic protons at  $\tau$  3·25 (doublet) and 4·11 (quartet), with  $J_{AB} = 16\cdot2$  c./sec. indicative of a trans isomer, and 13 aromatic protons at  $\tau$  2·25—3·0 (multiplet).

 $\beta$ -9-Fluorenylstyrene (5.09 mg.) and sodium (0.12 g.) were each dissolved in spectroscopic ethanol (25 ml.). A mixture of 1 ml. of each solution was made up to 25 ml. by the addition of ethanol. The spectrum of this solution measured immediately was almost identical with that of 9- $\beta$ -phenylethylidenefluorene. Attempts to isolate this hydrocarbon from the alkaline solution were unsuccessful owing to polymerisation.

spiro-1-(9-Fluorenyl)-2-phenylcyclopropane.-(a) 9-Phenacylfluorene (2.8 g.) and toluene-*p*-sulphonhydrazide (1.9 g.)were boiled (1 hr.) in ethanol, which on cooling deposited the hydrazone (3 g.), m. p. 174-176° (Found: N, 6.2; S, 7.1.  $C_{28}H_{24}N_2O_2S$  requires N, 6.2; S, 7.1%),  $\nu_{max}$  3055 (NH) and 1165s cm.<sup>-1</sup> (S.O). From the filtrate the 9-phenacylfluorene-azine (0.08 g.), orange needles, m. p. 190—191°, separated (Found: C, 89.0; H, 6.0; N, 5.8. C42H32N2 requires C, 89.3; H, 5.7; N, 5.0). The hydrazone (0.95 g.) and sodium (0.05 g.) in ethylene glycol (5 ml.) were boiled (3 hr.), cooled, and water added. Extraction with ether and evaporation gave spiro-1-(9-fluorenyl)2-phenylcyclopropane (0.25 g.), m. p. 130-131° (Found: C, 93.4; H, 6.1%; M, 243.  $C_{21}H_{16}$  requires C, 94.0; H, 6.0%; M, 268) with an ultraviolet spectrum similar to that of fluorene,  $\lambda_{max}$  211, 270, 293, and 304 mµ (log  $\varepsilon$  4.77, 4.25, 3.93, and 3.93); n.m.r. spectrum: 2 CH<sub>2</sub> protons at  $\tau$  7.84 (doublet) and 1 tertiary proton at  $\tau$  6.65 (triplet). The preparation of the spirocompound is capricious and sometimes the azine is also formed or is the sole product isolated.

(b) The alcohol (VI) (2.86 g.) and freshly distilled phosphorus tribromide (1 ml.) were heated  $(1\frac{1}{2} \text{ hr.})$  and added to water. The bromide (1.5 g.), m. p. 114°, after crystallisation from ethanol, was boiled (2 hr.) in ethanol containing

<sup>15</sup> W. D. Garden and F. D. Gunstone, J. Chem. Soc., 1952, 2650.

<sup>&</sup>lt;sup>14</sup> W. Wislicenus and W. Mocker, Ber., 1913, 46, 2792.

potassium hydroxide (0.28 g.). The ethanol was distilled off and water was added to give the *spiro*-compound, m. p. and mixed m. p. with the above *spiro*-compound,  $130-131^{\circ}$ .

(c) 9-Phenacylidenefluorene (1 g.), potassium hydroxide (1 g.), hydrazine hydrate (99%, 1 ml.), and ethylene glycol (10 ml.) were heated for 1 hr. at 185° and for 1 hr. at 195—200°. Addition of water and extraction with ether yielded the *spiro*-compound, m. p. and mixed m. p. 130—131°.

Reaction of 9-Phenacylfluorene with Hydrazine Hydrate and Alkali.—9-Phenacylfluorene (1·4 g.), excess of hydrazine hydrate, potassium hydroxide (0·6 g.), and diethylene glycol (15 ml.) were heated at 200° (3 hr.). Fluorene, m. p. and mixed m. p. 115°, collected in the condenser and was also obtained from the reaction mixture, giving a total weight of 0·3 g. A control experiment without hydrazine hydrate did not yield fluorene.

9-Phenacylfluorene (1 g.), ethanol (20 ml.), and hydrazine hydrate (5 ml.), were heated (1 hr.) at 80°, more hydrazine hydrate (5 ml.) was added, and heating continued (2 hr.). Evaporation to dryness under reduced pressure gave an oil which yielded the hydrazone (0.5 g.), prisms (from ethanol), m. p. 104-105° (Found: N, 9.4. C<sub>21</sub>H<sub>18</sub>N<sub>2</sub> requires N, 9.3%). The hydrazone (0.5 g.), dry potassium t-butoxide (0.3 g.), and sulphur-free xylene (17 ml.) were boiled (4 hr.). Water was added and the aqueous layer extracted with ether. Combination of the organic extracts and evaporation gave an oil which was chromatographed in benzene-light petroleum (1:1 v/v), the proportion of benzene being increased until elution was effected by benzene alone. The first fractions from the column gave spiro-1-(9 fluorenyl)-2-phenylcyclopropane (0.15 g.), identified by m. p. and mixed m. p., and 9-phenacylfluoreneazine (0.18 g.), identified similarly.

9-Phenacylfluorene-9-carboxylic Acid Derivatives.—Ethyl 9-phenacylfluorene-9-carboxylate (1 g.) and sodium borohydride (0.23 g.) were warmed in ethanol (25 ml.) until the ester dissolved. After 4 hr. the lactone (X) separated (0.70 g.), needles (from ethanol), m. p. 179—181° (Found: C, 84.6; H, 5.8.  $C_{22}H_{16}O_2$  requires C, 84.6; H, 5.2%);  $v_{max}$ . 1765s ( $\gamma$ -lactone C:O) and 1170s cm.<sup>-1</sup> (C-O-C); n.m.r.: 1 tertiary proton at  $\tau$  3.98 (triplet) and 2 methylene protons at  $\tau$  7.05 (doublet).

Sodium (0.9 g.) in ethanol (20 ml.) was warmed with 9cyanofluorene (7.5 g.), sufficient ethanol being added to ensure complete solution. The solution was boiled (4 hr.) with phenacyl bromide (7.8 g.) and the ethanol removed under reduced pressure. Water was added and the solution extracted with benzene-ether. The organic layer yielded 9-cyano-9-phenacylfluorene (8 g.), m. p. 142—144° (Found: C, 85·1; H, 5·1; N, 4·7. C<sub>22</sub>H<sub>15</sub>NO requires C, 85·4; H, 4·9; N, 4·6%);  $\nu_{max}$  2250m (CiN) and 1680s cm.<sup>-1</sup> (CO). The ketone failed to react with 2,4-dinitrophenylhydrazine or toluene-p-sulphonylhydrazide.

9-Formylfluorene Enol-acetate.—In an attempt to prepare 3-(9-fluorenyl)-2-phenylacrylic acid, 9-formylfluorene (15 g.), phenylacetic acid (11 g.), triethylamine (8·1 g.), and acetic anhydride (24·5 g.) were heated (24 hr.) and poured into 10% hydrochloric acid. Extraction with benzene yielded the enol-acetate of 9-formylfluorene, m. p. 133° (lit.,<sup>9</sup> 132—134°) (Found: C, 81·4; H, 5·5. Calc. for  $C_{16}H_{12}O_2$ : C, 81·3; H, 5·1%);  $v_{max}$ . 1765s (C:O) and 1670s cm.<sup>-1</sup>; n.m.r.: 8 aromatic protons at  $\tau$  1·98—2·98, 3 methyl protons at  $\tau$  7.74 (singlet), and 1 olefinic proton at  $\tau$  1.77 (singlet). The compound was identical (mixed m. p.) with that obtained (62%) by heating (2 hr.) 9-formyl-fluorene, acetic anhydride, and pyridine. The enol-acetate (3.1 g.) was boiled (45 min.) with copper chromite (0.2 g.) in quinoline and the mixture poured into hydrochloric acid. Extraction with ether gave a purple oil which when chromatographed in benzene and developed with light petroleum (b. p. 60—80°) gave 9-fluorenyl-9-fluorenylidenemethane, m. p. 205—206° (lit.,<sup>106</sup> 206—208°) with an ultraviolet spectrum very similar to that reported; <sup>10a</sup> n.m.r. spectrum: 16 aromatic protons at  $\tau$  2.10—2.95, 1 tertiary proton at  $\tau$  4.16 (doublet), and 1 olefinic proton at  $\tau$  3.50 (doublet).

2-(9-Fluorenyl)-1,1-diphenylethene.— Phenylmagnesium bromide reacted with ethyl 9-fluorenylacetate to give an alcohol which in ether with hydrogen chloride gave a precipitate.<sup>11</sup> This was dissolved in ether, washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to give 2-(9-fluorenyl)-1,1-diphenylethene, m. p. 150-151°, after crystallisation from light petroleum (Found: C, 94.1; H, 5.9. C27H20 requires C, 94·2; H, 5·8%);  $\lambda_{max}$  212, 261, 291, 303 m $\mu$ (log  $\varepsilon$  4.75, 4.49, 3.83, 3.90), the spectrum being similar to that of  $\beta$ -fluorenylstyrene; n.m.r. spectrum: 18 aromatic protons at  $\tau 2.20$ —2.80, 1 olefinic proton at  $\tau 4.17$  (doublet), and 1 tertiary proton at  $\tau 5.28$  (doublet). The hydrocarbon was also obtained from the alcohol by warming with formic acid (2 hr.) or thionyl chloride (15 min.). The hydrocarbon in ethanol containing 0.16 g. of sodium per litre gave a mixture of isomers shown by its ultraviolet spectrum to be predominately 2-fluorenylidene-1,1-diphenylethane. The hydrocarbon (0.7 g.) was boiled (3 hr.) in pyridine (5 ml.) to give a mixture, m. p. 110-112°, after crystallisation from light petroleum, whose ultraviolet spectrum in ethanol was almost identical with that of the equilibrium mixture just described.

2-Fluorenylidene-1,1-diphenylethane.— The hydrocarbon <sup>10a</sup> had m. p. 113° after three crystallisations from light petroleum (Found: C, 94·1; H, 5·7. Calc. for  $C_{27}H_{20}$ : C, 94·2; H, 5·8%);  $\lambda_{max}$  223, 229, 248, 257, 277, 285, 301, and 314 mµ (log  $\varepsilon$  4·59, 4·61, 4·49, 4·64, 4·20, 4·23, 4·16, and 4·18); n.m.r. spectrum: 18 aromatic protons at  $\tau$  2·10— 2·90, 1 olefinic proton at  $\tau$  2·95 (doublet), and one tertiary proton at  $\tau$  4·12 (doublet).

Isomerisation of 1,3,3-Triphenylpropene. 1,3,3-Triphenylpropene had n.m.r. spectrum: 15 aromatic protons at  $\tau 2.55$ —2.95, 1 olefinic proton at  $\tau 3.29$  (quartet), one at  $\tau$  3.70 (doublet), and 1 tertiary proton at  $\tau$  5.15 (doublet). 1,1,3-Triphenylpropene had n.m.r. spectrum: 15 aromatic protons at  $\tau 2.57$ —2.95, 1 olefinic proton at  $\tau 3.78$  (triplet), and 2 methylene protons at  $\tau$  6.58 (doublet). Each isomer (0.5 g.) in ethanol (5 ml.) was boiled (2 hr.) with potassium hydroxide (1 g.) in ethanol (15 ml.). The ethanol was removed in vacuo, the residue dissolved in ether, washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent evaporated. The oils which resulted were shown by infrared and n.m.r. spectra to be predominately 1,1,3-triphenylpropene. In two instances a product, m. p. 40-41°, crystallised from ethanol and was found to be mainly 1,1,3-triphenylpropene.

We thank the S.R.C. for a research studentship (K. W. D.).

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[6/467 Received, April 19th, 1966]