

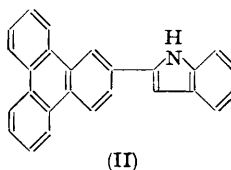
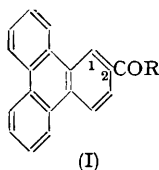
194. Friedel-Crafts Reactions of Triphenylene.

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In the Friedel-Crafts reactions triphenylene is substituted at the 2-position. Some new derivatives of triphenylene have thus been prepared.

TRIPHENYLENE is unique among tetracyclic aromatic hydrocarbons in its high degree of symmetry, on account of which there can be only two sites of monosubstitution, positions 1 and 2, as in the case of naphthalene. The reactivity of triphenylene has rarely been investigated, and the constitution of most of the products obtained is still unknown. Sulphonation (Schmelzer, D.R.-P. 654,283/1937) was stated to give triphenylene-2-sulphonic acid, converted by alkaline fusion into 2-hydroxytriphenylene (Schmelzer and Schnabel, D.R.-P. 654,715/1937); bromination yielded a mixture of a mono- and a di-bromotriphenylene of undetermined constitution (Schuster and Broich, D.R.-P. 650,058/1937), and nitration gave a trinitrotriphenylene (Mannich, *Ber.*, 1907, **40**, 162). The only Friedel-Crafts reaction studied hitherto was that of oxalyl chloride, which resulted in a triphenylenecarboxylic acid (Cook, Hewett, and Hieger, *J.*, 1933, 395).

In the present work, Friedel-Crafts reactions of triphenylene with acetyl and propionyl chloride, and with succinic anhydride, are reported. Acetylation, with aluminium chloride in carbon disulphide solution, gave a good yield of a monoketone, which was 2-acetyltriphenylene (I; R = Me), as it could be converted into the known 2-methyltriphenylene (Fieser and Joshel, *J. Amer. Chem. Soc.*, 1939, **61**, 2960; Rapson, *J.*, 1941, 15) by a Willgerodt-Kindler reaction and decarboxylation of the triphenylenylacetic acid obtained. Sodium hypobromite oxidation of 2-acetyltriphenylene yielded an acid, identical with Cook, Hewett, and Hieger's acid, which must therefore have been triphenylene-2-carboxylic acid. Wolff-Kishner reduction of the same ketone (Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2478) readily gave 2-ethyltriphenylene; Fischer indolisation of 2-acetyltriphenylene phenylhydrazone resulted in 2-2'-indolyltriphenylene (II).



Other Friedel-Crafts reactions were also studied: propionylation yielded 2-propionyltriphenylene (I; R = Et), from which 2-*n*-propyltriphenylene was prepared by reduction; succinoylation also gave a single reaction product, γ -keto- γ -2-triphenylenylbutyric acid, which was readily reduced to γ -2-triphenylenylbutyric acid. The orientations are assumed by analogy.

The preferential attack of the 2-position in the molecule of triphenylene is probably due to the fact that position 1 is subject to a strong steric hindrance; this accounts for the resistance of 1-methoxytriphenylene to dealkylating agents (Rapson, *J.*, 1941, 15).

No triphenylene derivative has yet been found to be carcinogenic (cf. Shear, *J. Nat. Cancer Inst.*, 1941, **2**, 241, 251), and the two homologues of triphenylene described in this work are similarly inactive.

EXPERIMENTAL

Acetylation of Triphenylene.—To a solution of triphenylene (10 g.) and acetyl chloride (60 c.c.) in dry carbon disulphide (200 c.c.), finely powdered aluminium chloride (10 g.) was added in small portions; the mixture was kept overnight at room temperature, then refluxed for 1 hour on the water bath. The mixture was poured into dilute hydrochloric acid, the organic layer washed with aqueous sodium hydroxide, then with water, and dried (Na_2SO_4), the solvent removed, and the residue distilled *in vacuo* (b. p. 310—315°/15 mm.) and recrystallised from

carbon tetrachloride. *2-Acetyltriphenylene* (6 g.) formed colourless needles, m. p. 152° (Found : C, 88·8; H, 5·5. $C_{20}H_{14}O$ requires C, 88·9; H, 5·2%). The *oxime* formed colourless needles, m. p. 202°, from ethanol (Found : C, 84·0; H, 5·3. $C_{20}H_{15}ON$ requires C, 84·2; H, 5·3%), and the *2:4-dinitrophenylhydrazone* orange needles, m. p. >325°, from acetic acid (Found: N, 12·1. $C_{26}H_{18}O_4N_4$ requires N, 12·4%). No isomer could be detected in the mother-liquors from crystallisation of 2-acetyltriphenylene.

When the latter was refluxed with sulphur and morpholine for 12 hours, the morpholide hydrolysed with sodium hydroxide, and the calcium salt of the crude triphenylene-2-acetic acid was dry-distilled, 2-methyltriphenylene, m. p. 105° (from ethanol) (picrate, m. p. 193°), was obtained (Fieser and Joshel, *loc. cit.*, gave m. p. 104—105° for this hydrocarbon, and m. p. 192·5—193° for its picrate).

Triphenylene-2-carboxylic Acid.—This acid (0·4 g.), obtained from sodium hypobromite and 2-acetyltriphenylene (0·5 g.) in dioxan, crystallised as colourless prisms, m. p. 326°, from ethanol (Found : C, 88·5; H, 4·5. Calc. for $C_{19}H_{12}O_2$: C, 83·8; H, 4·4%); it was identical with a sample prepared from triphenylene and oxalyl chloride (Cook *et al.*, *loc. cit.*).

2-Ethyltriphenylene.—A mixture of 2-acetyltriphenylene (2 g.), diethylene glycol (15 c.c.), and 85% hydrazine hydrate (5 g.) was heated at 100° for 5 minutes; after addition of potassium hydroxide (5 g.), the mixture was heated with removal of water, then refluxed for 4 more hours. After dilution with water, the hydrocarbon was taken up in benzene, and vacuum-distilled (b. p. 280—282°/16 mm.); *2-ethyltriphenylene* (1 g.) formed colourless needles, m. p. 90°, from ethanol (Found : C, 93·8; H, 6·4. $C_{20}H_{16}$ requires C, 93·7; H, 6·3%); its picrate crystallised as orange-yellow prisms, m. p. 144°, from ethanol (Found : N, 8·5. $C_{26}H_{19}O_7N_3$ requires N, 8·7%).

2-2'-Indolyl triphenylene (II).—A mixture of 2-acetyltriphenylene (1 g.) and phenylhydrazine (1 g.) was heated at 120° until evolution of water ceased; the crude phenylhydrazone obtained was heated with finely powdered fused zinc chloride (1 g.) at *ca.* 200° until a vigorous reaction set in. The product was treated with aqueous acetic acid and benzene, the benzene layer washed with dilute hydrochloric acid then with water, and dried (Na_2SO_4), and the solvent removed; *2-2'-indolyltriphenylene* crystallised as pale yellow prisms, m. p. 225°, from benzene (Found : C, 91·1; H, 5·2. $C_{26}H_{17}N$ requires C, 91·0; H, 5·0%); it formed a violet-brown picrate, m. p. 227—228° (decomp.), from ethanol.

2-Propionyltriphenylene.—This ketone (5·8 g.), obtained from triphenylene (7 g.), propionyl chloride (50 c.c.), and aluminium chloride (10 g.) in carbon disulphide (200 c.c.) as for the lower homologue, was recrystallised from carbon tetrachloride, then from ethanol, and formed colourless needles, m. p. 123° (Found : C, 88·5; H, 5·5. $C_{21}H_{16}O$ requires C, 88·7; H, 5·6%).

2-n-Propyltriphenylene.—Prepared from the foregoing ketone (4·5 g.), hydrazine hydrate (5 g.), and potassium hydroxide (5 g.) in diethylene glycol (70 c.c.) as for the lower homologue, *2-n-propyltriphenylene* was purified by vacuum-distillation (b. p. 212—214°/0·5 mm.), and crystallised as colourless needles (2·3 g.), m. p. 78°, from ethanol (Found : C, 93·2; H, 6·9. $C_{21}H_{18}$ requires C, 93·3; H, 6·7%); its picrate formed yellow needles, m. p. 147—148°, from ethanol.

γ-Keto-γ-2-triphenylenylbutyric Acid.—To a solution of triphenylene (15 g.) and succinic anhydride (7 g.) in anhydrous nitrobenzene (200 c.c.), finely powdered aluminium chloride (15 g.) was added in small portions. The deep green mixture was kept for 4 days at room temperature, then decomposed with water, and the nitrobenzene steam-distilled. The solid residue was crystallised, first from chlorobenzene, then from ethanol, giving colourless prisms (12 g.), m. p. 224° (Found : C, 80·2; H, 5·2. $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9%) of the *acid*; its sodium salt was sparingly soluble in water.

γ-2-Triphenylenylbutyric Acid.—The foregoing acid (10 g.) was reduced in the usual way with hydrazine hydrate (10 g.) and potassium hydroxide (9 g.) in diethylene glycol (150 c.c.); the *acid* obtained on dilution with water and acidification with hydrochloric acid crystallised as colourless prisms (8·5 g.), m. p. 168°, from benzene (Found : C, 84·0; H, 5·9. $C_{22}H_{18}O_2$ requires C, 84·1; H, 5·7%). Cyclisation of this acid will be reported elsewhere.

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