The Monosubstitution of Triphenylene.

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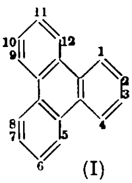
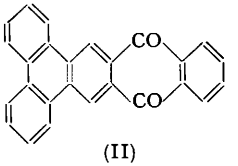
The orientations of the products obtained by mononitrating and by monobrominating triphenylene have been established, and the results are discussed in the light of the predicted reactivity of the triphenylene molecule.

The symmetry of the triphenylene molecule (I) limits the number of its isomeric monosubstituted derivatives to two, those with substituents at $C_{(1)}$ or $C_{(2)}$, and the former of these atoms is predicted to be slightly the more reactive. Thus, Dewar (*J. Amer. Chem. Soc.*, 1952, **74**, 3358) gives localisation energies of $2{\cdot}02\beta$ and $2{\cdot}12\beta$ for $C_{(1)}$ and $C_{(2)}$, respectively, and the mobile bond orders calculated by Coulson, Berthier, Greenwood, and Pullman (*Compt. rend.*, 1948, **226**, 1906) lead to free valencies of 0·439 and 0·405 for the same atoms, respectively. The simple method, which assumes the stability of the transition state to be proportional to the number of classical ionic structures written with a charge on the carbon in question, gives 23 such structures with a charge on $C_{(1)}$, and 22 with a charge on $C_{(2)}$, again predicting slightly greater reactivity for $C_{(1)}$. But $C_{(1)}$ is subjected to considerable steric hindrance from the hydrogen atom at position 12, and the effect of this factor on the course of substitution was therefore examined. The situation is analogous to that obtaining in naphthalene, where, however, the steric factor is much smaller, and the difference in reactivity between $C_{(1)}$ and $C_{(2)}$ is much greater.



(I)



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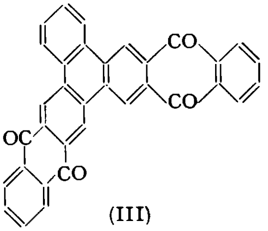

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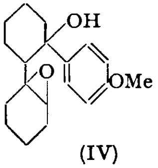

(IV)

Phthalic anhydride and triphenylene in the presence of aluminium chloride give 2-*o*-carboxybenzoyltriphenylene, and this acid cyclises only at the less hindered 3-position to give the quinone (II) (Clar, *Ber.*, 1948, **81**, 68). The condensation of one molecule of the hydrocarbon with two of phthalic anhydride yields a mixture of two, or all, of the isomeric 2 : 6-, 2 : 7-, and 2 : 11-di-*o*-carboxybenzoyltriphenylenes, and this mixture also cyclises only at the less hindered positions since a single diquinone (III) is formed (Clar, *J.*, 1949, 2440). Similarly, acetyl chloride gives 2-acetyltriphenylene (Buu-Hoï and Jacquignon, *J.*, 1953, 941), oxalyl chloride gives triphenylene-2-carboxylic acid (Cook and Hewitt, *J.*, 1933, 404; Buu-Hoï *et al.*, *loc. cit.*), and carbamoyl chloride gives triphenylene-2-carboxyamide (I.G. Farbenind. A.-G., F.P. 797,072/1936).

It is also claimed that suphonation takes place at position 2 (Schmelzer, D.R.-P. 654,283/1937). This is now established by comparing the hydroxy-compound obtained from the sulphonic acid by caustic fusion (Schuster, Broich, and Schmelzer, D.R.-P. 623,651/1936), with synthetic material obtained from 2-(1 : 2-epoxy*cyclo*hexyl)-1-*p*-methoxyphenyl*cyclo*hexan-1-ol (IV) by cyclisation and demethylation with a mixture of acetic and hydrobromic acid, followed by dehydrogenation with palladised charcoal. This method of synthesising triphenylene derivatives is an improvement of Rapson's method (*J.*, 1941, 15), and its applications will be discussed in a later paper.

The course of sulphonation and acylation reactions is, however, particularly sensitive to steric factors, and nitration and bromination of triphenylene were therefore examined. Trinitration of triphenylene has been described by Mannich (*Ber.*, 1907, **40**, 162), and it is difficult to restrict the reaction to mononitration, but by heating the hydrocarbon in acetic anhydride with the theoretical amount of nitric acid, 27% and 23% yields of 1- and 2-nitrotriphenylene, respectively, have now been obtained. No appreciable amount of dinitrophenylene was formed, but oxidation of the starting material occurred. These yields are consistent with the predicted reactivities of $C_{(1)}$ and $C_{(2)}$, and they contrast with the exclusively 2-substitution occurring in the reactions previously reported.

The bromination of triphenylene by one mol. of bromine in carbon disulphide containing iron has been described by Schuster and Broich (D.R.-P. 650,058/1937); the product is now shown to be a mixture of bromo- and dibromo-triphenylene, from which 2-bromotriphenylene, m. p. 128—132°, was obtained chromatographically in 56% yield; the pure compound has m. p. 132—133°. No 1-bromotriphenylene could be isolated, but complete resolution of the product into its components was not achieved, and a synthetic mixture of 1- and 2-bromotriphenylene containing 10% of the former could not be separated. It is clear, however, that 1-bromotriphenylene, if formed at all, is formed in much smaller amounts than the 2-isomer. This is attributed to steric hindrance of $C_{(1)}$, coupled with the larger effective size of the bromine atom.

To establish the orientation of the nitro- and bromo-triphenylenes, 2-aminotriphenylene was prepared from the 2-acetyl compound through the intermediate stages of carboxylic acid, carbonyl chloride, and azide. By use of nitrobenzene as a solvent in the preparation of 2-acetyltriphenylene, instead of the excess of acetyl chloride used by Buu-Hoï *et al.* (*loc. cit.*), the yield was improved from 50% to 88·5%, and the yield of amine amounted to 39% (on triphenylene). Attempts to convert triphenylene-2-carboxyamide into the amine by means of aqueous sodium hypobromite failed because of the insolubility of the amide, but methanolic sodium hypobromite gave methyl *N*-2-triphenylenylcarbamate which was hydrolysed subsequently to the amine, the yield amounting to only 8% (on amide). Conversion of 2-aminotriphenylene into the 2-hydroxy-compound by means of the diazo-reaction confirmed the orientation given to 2-acetyltriphenylene previously (*idem, loc. cit.*). The orientations of 1- and 2-nitrotriphenylene were then established by reducing them to the corresponding amines, which yielded 1- and 2-bromotriphenylene by the diazo-reaction.

EXPERIMENTAL

2-*Hydroxytriphenylene*.—(*a*) A mixture of 2-*cyclo*hex-1′-enyl-1-*p*-methoxyphenyl*cyclo*hexan-1-ol (6 g.; cf. Rapson, *loc. cit.*) in ether (50 c.c.) and monoperphthalic acid (4·6 g.) in ether (65 c.c.) was kept at 0° for 16 hr., then washed with aqueous sodium hydrogen carbonate and dried (Na_2SO_4), and the ether removed. The residual pale yellow, viscous liquid (6·3 g.) was dissolved in boiling acetic acid (63 c.c.), hydrobromic acid (34% w/v; 44 c.c.) was added, the mixture was refluxed for 24 hr., cooled, and diluted with water, and the product extracted with benzene. The benzene solution was washed with sodium hydrogen carbonate and dried (Na_2SO_4), the benzene was removed, and then the residue (5·4 g.) was heated with palladised charcoal (30% Pd; 0·54 g.) in a stream of nitrogen for 4 hr. at 300°. The product was sublimed at 200—220° (bath)/10^{-2} mm., the sublimate was extracted with a solution of potassium hydroxide in aqueous methanol, the extract was acidified, and the resulting precipitate was crystallised from chlorobenzene, giving 2-hydroxytriphenylene as white needles, m. p. 215—217°. Rapson (*loc. cit.*) gives m. p. 213—215°; Schuster *et al.* (*loc. cit.*) give m. p. 216—219°.

(*b*) Sodium triphenylene-2-sulphonate was prepared from triphenylene (70% yield) and converted into crude 2-hydroxytriphenylene (72% yield), m. p. 198—200°, by the processes of Schmelzer and of Schuster *et al.* (*locc. cit.*), respectively. Sublimation of this product, followed by two crystallisations from chlorobenzene, gave pure 2-hydroxytriphenylene (27% on sulphonic acid), m. p. 221°, mixed m. p. with material from (*a*) 217—219° (Found : 87·6; H, 5·1. Calc. for $C_{18}H_{12}O$: C, 88·5; H, 5·0%). Under ultraviolet light it showed a blue fluorescence which became bright apple-green on addition of alkali. The *picrate* formed orange needles (from ethanol), m. p. 224—225° (decomp.) (Found: N, 9·0. $C_{24}H_{15}O_8N_3$ requires N, 8·9%). Methyl sulphate and sodium hydroxide gave the methyl ether, m. p. 119° (from light petroleum) (Found : C, 88·8; H, 5·4. Calc. for $C_{19}H_{14}O$: C, 88·4; H, 5·5%). Rapson (*loc. cit.*) gives m. p. 97—98°. The acetyl derivative had m. p. 130°; Rapson (*loc. cit.*) gives m. p. 129°.

(*c*) By boiling an aqueous suspension of triphenylene-2-diazonium chloride until it no longer coupled with R-salt, and then subliming the dried product and thrice crystallising the picrate of the sublimate from ethanol, 2-hydroxytriphenylene picrate was obtained, m. p. and mixed m. p. 220—223° (Found : N, 8·6%).

2-*Acetyltriphenylene*.—Acetyl chloride (1·75 g.) was added at 0° to a solution of triphenylene (5·0 g.) in nitrobenzene (40 c.c.) containing aluminium chloride (3·5 g.). The mixture was kept at room temperature for 20 hr., and at 40° for a further 4 hr., and then poured into dilute hydrochloric acid at 0°. The nitrobenzene was removed by steam-distillation, and the dried product was sublimed at 160—180° (bath)/10^{-2} mm. Crystallisation of the sublimate from acetic acid gave 2-acetyltriphenylene (5·25 g.), m. p. 150—152°, recrystallisation from ethanol raising this m. p. to 152—153°. Buu-Hoï *et al.* (*loc. cit.*) give m. p. 152°.

Triphenylene-2-carboxylic Acid.—Oxidation of 2-acetyltriphenylene (10 g.) in dioxan (180 c.c.) at 60° for 1 hr. with a solution of bromine (24 g.) in water (180 c.c.) containing sodium hydroxide (24 g.) gave the acid (8·3 g.), m. p. 336—338° (from pentyl alcohol) (Found : C, 83·6; H, 4·6. Calc. for $C_{19}H_{12}O_2$: C, 83·8; H, 4·4%). Buu-Hoï *et al.* (*loc. cit.*), and Cook *et al.* (*loc. cit.*), give m. p. 325—326°. Diazomethane in ether and the acid in dioxan gave the methyl ester, m. p. 171—172° (from ethanol) (Found : C, 83·7; H, 5·1. Calc. for $C_{20}H_{14}O_2$: C, 83·9; H, 4·9%). Cook *et al.* (*loc. cit.*), give m. p. 122—124°. Thionyl chloride, purified by distillation from quinoline, converted the acid into the pale yellow *acid chloride* (90% yield), m. p. 130—131° (from light petroleum) (Found: Cl, 12·3. $C_{19}H_{11}OCl$ requires Cl, 12·2%). Concentrated aqueous ammonia converted the chloride almost quantitatively into the *amide*, m. p. 292—293° (from pyridine) (Found : C, 83·5; H, 5·2; N, 5·3. $C_{19}H_{13}ON$ requires C, 84·2; H, 4·8; N, 5·2%). By addition of sodium azide (0·5 g.) in water (2·0 c.c.) to the acid chloride (1·8 g.) in dioxan (20 c.c.) at 0°, followed, after 15 min., by the addition of water (25 c.c.), the *azide* (1·8 g.) was obtained (m. p. 135°). Decomposition of this material (0·30 g.) in toluene gave nitrogen (22·4 c.c.); the azide requires 22·6 c.c.

Benzyl alcohol and the acid azide gave *benzyl* N-2-*triphenylenylcarbamate*, m. p. 169—170° (from light petroleum) (Found : N, 3·6. $C_{26}H_{19}O_2N$ requires N, 3·7%), which failed to give 2-aminotriphenylene when heated at 140° with acetic and concentrated hydrochloric acid.

1- *and* 2-*Nitrotriphenylene*.—Nitric acid (70% w/w; 1·67 c.c.) was added during 45 min. to triphenylene (6·0 g.) in acetic anhydride (330 c.c.) at 60°, and the mixture was kept at 60° for a further 4 hr. Decomposition of the anhydride with an excess of water at room temperature yielded a brown solid which was dissolved in benzene. This solution was washed with aqueous sodium hydrogen carbonate, dried (Na_2SO_4), and chromatographed on alumina (265 × 40 mm.) with benzene as eluant, giving : F_1, triphenylene (0·23 g.); F_2, clean yellow gum (5·68 g.); F_3, dark-brown gum (0·23 g.). Chromatography of F_2 in benzene on alumina (650 × 27 mm.) gave two well-defined yellow bands, the lower of which yielded 1-*nitrotriphenylene* (1·96 g.), m. p. 165—168·5°, raised by crystallisation from acetic acid to m. p. 168·5—169·5° (Found : N, 5·2. $C_{18}H_{11}O_2N$ requires N, 5·1%). The upper band yielded 2-*nitrotriphenylene* (1·63 g.), m. p. 163—165°, raised by crystallisation from acetic acid to m. p. 165·5—166° (Found : N, 5·3%).

2-*Aminotriphenylene*.—(*a*) A mixture of 2-azidotriphenylene (3·5 g.), concentrated hydrochloric acid (100 c.c.), and acetic acid (100 c.c.) was refluxed for 7 hr., and then basified with ammonia. The dried precipitate was sublimed at 170—180° (bath)/10^{-2} mm., the sublimate was repeatedly extracted with boiling, dilute hydrochloric acid, and the resulting solution was basified with ammonia, giving 2-*aminotriphenylene* (1·74 g.), m. p. 140—140·5° (from ethanol) (Found : C, 88·8; H, 5·4; N, 5·6. $C_{18}H_{13}N$ requires C, 88·9; H, 5·4; N, 5·8%). The N-*acetyl* derivative formed needles, m. p. 257—258° (from acetic acid, and ethanol, successively) (Found : C, 84·0; H, 5·0; N, 4·9. $C_{20}H_{15}ON$ requires C, 84·2; H, 5·3; N, 4·9%).

(*b*) Bromine (0·30 g.) was added to triphenylene-2-carboxyamide (0·9 g.) in methanol (30 c.c.) containing sodium methoxide (0·40 g.), and the mixture was kept at 50° for 15 min., cooled, and acidified with acetic acid, and the methanol was removed by distillation. The residue, twice crystallised from light petroleum (b. p. 80—100°), yielded pale yellow *methyl* N-2-*triphenylenylcarbamate* (0·35 g.), m. p. 188—189° (Found : C, 79·4; H, 5·0; N, 4·8. $C_{20}H_{15}O_2N$ requires C, 79·8; H, 5·0; N, 4·7%). A mixture of this urethane (0·40 g.), concentrated hydrochloric acid (20 c.c.), and acetic acid (10 c.c.) was refluxed for 24 hr., basified with ammonia, and worked up as described in (*a*), giving 2-aminotriphenylene (0·07 g.).

1-*Aminotriphenylene*.—Hydrogen chloride was passed for 2·5 hr. into a boiling mixture of acetic acid (28·5 c.c.) and concentrated hydrochloric acid (1·5 c.c.) containing granulated tin (3·5 g.) and 1-nitrotriphenylene (1·96 g.). The mixture was then basified and extracted with ether, the ether was dried (Na_2SO_4), and hydrogen chloride was passed in. The precipitate was basified, removed in ether, and sublimed at 170—180° (bath)/10^{-2} mm., yielding 1-*aminotriphenylene* (0·94 g.), m. p. 96—101°, raised to m. p. 103—104° by crystallisation from ethanol (Found : N, 5·4%).

2-*Bromotriphenylene*.—(*a*) A solution of 2-aminotriphenylene (0·25 g.) in acetic acid (2·0 c.c.) was poured into 20% hydrobromic acid (5 c.c.), thus precipitating the amine hydrobromide which was diazotised at 0° by addition of sodium nitrite (0·070 g.) in water (2 c.c.). The diazonium salt separated, and the resulting paste was added to cuprous bromide (1·2 g.) in 40% hydrobromic acid (6 c.c.), and then the mixture was boiled for 30 min. The dried product was sublimed at 160—180° (bath)/10^{-2} mm., and, after passage in light petroleum through a short alumina column, followed by crystallisation from light petroleum, gave 2-*bromotriphenylene* (0·10 g.), m. p. 131—132° (Found : C, 70·1; H, 3·5; Br, 26·1. $C_{18}H_{11}Br$ requires C, 70·4; H, 3·6; Br, 26·0%).

(*b*) Bromine (1·40 g.) was added at 20° to a stirred solution of triphenylene (2·00 g.) in carbon disulphide (88 c.c.) contained iron powder (0·09 g.). Stirring was continued for 72 hr., at the end of which the mixture was filtered, the filtrate was washed with aqueous sodium hydrosulphite (dithionite), and then with water, and dried (Na_2SO_4), and the carbon disulphide was removed. The residue was chromatographed on alumina (460 × 27 mm.) with light petroleum (b. p. 60—80°) as eluant, and the first 3220 c.c. of eluate yielded 2- bromotriphenylene (1·49 g.), m. p. 128—132°, raised to m. p. 132—133° by crystallisation from acetone. The mixed m. p. with material from (*a*) was 131—133°. Subsequent eluates gave residues with bromine contents increasing to a maximum of 39%, and no pure compound was isolated from them. Elution with light petroleum–benzene gave inferior separation.

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