708. *Aromatic Hydrocarbons. Part LXI.* Pentaphene.*

By E. Clar and D. G. Stewart.

Pentaphene (IX) has been synthesised, the dispiran (V) being used as an intermediate.

It has been claimed (Weisz and Korczyn, *Monatsh.*, 1924, **45**, 207; Weisz and Müller, *ibid.*, 1934, **65**, 481) that the two products of different melting point obtained from the reaction of *o*-tolylmagnesium bromide with phthalic anhydride have the phthalide constitution. The higher-melting (m. p. 176°) has now been synthesised by oxidation of tri-*o*-tolylcarbinol with dilute nitric acid, and is without doubt di-*o*-tolylphthalide (II). We have found, however, that the second product (m. p. 128—131°) is a mixture of the phthalide (II) and 1 : 2-di-*o*-toluoylbenzene (I). The tendency for the formation of the latter is so pronounced that even the reaction of *as*-phthaloyl chloride with *o*-tolylmagnesium bromide yields mostly the diketone (I) and only a little phthalide (II). Mono-*o*-tolylphthalide and 2-*o*-toluoylbenzoic acid were obtained as by-products, both of which gave benzophenone-2 : 2′-dicarboxylic anhydride on oxidation with alkaline potassium permanganate solution.

The structure of (I) was proved by its condensation with hydrazine hydrate to give 1 : 4-di-*o*-tolylphthalazine (III). The reaction also served for isolation of the pure phthalide (II), as the azine remained in the alcoholic solution, while the phthalide crystallised out unchanged. A good qualitative test for the presence of the diketone (I) is reduction by zinc in acetic acid,

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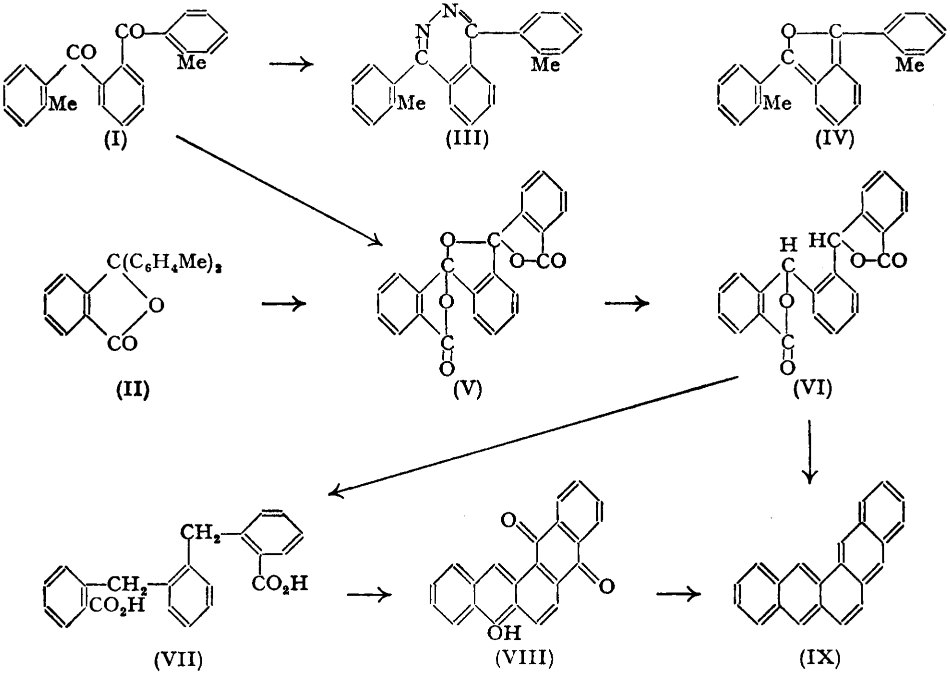
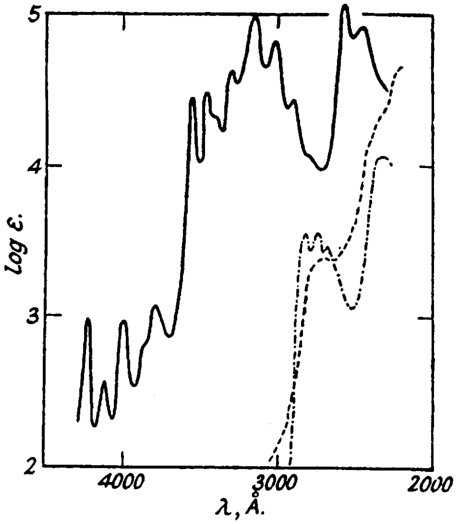
* Part LX, *Nature*, 1950, **166**, 1075.

which yields a yellow, blue-fluorescent solution of the *iso*benzofuran (IV). The interesting properties of the corresponding diphenyl compound were studied in detail by Guyot and Catel (*Compt. rend.*, 1905, **140**, 1349; *Bull. Soc. chim.*, 1906, **35**, 1124).

The pure diketone (I) melted at 146°; when mixed with an equal amount of the pure phthalide (II), it melted at 125—128°, which corresponds with the m. p. of Weisz and Korczyn's second alleged phthalide (*loc. cit.*).





Absorption spectra.

———— *Pentaphene in alcohol. Band maxima* (*in* Å) : 4235, 4120, 3990, 3790; 3560, 3450, 3290; 3145, 3020, 2895; 2575, 2450.

— · — · — o-*Di*-(3-*phthalidyl*)*benzene* (VI) *in alcohol. Band maxima* (*in* Å) : 2820, 2750, 2680; 2350.

- - - - - - *Disodium salt of* 1 : 2-*di*-o-*carboxybenzylbenzene* (VII) *in water. Band maximum at* 2700 Å.

The diketone (I) was oxidised with dilute nitric acid under pressure, or alternatively in two stages, *viz.*, first with dilute nitric acid solution and then with alkaline potassium permanganate solution, to a dicarboxylic acid which crystallised from acetic acid as the dispiran (V). Similar oxidations of the phthalide (II) gave, owing to rearrangement, good yields of (V) with only a minor proportion of what is believed to be the unrearranged dicarboxylic acid derived from (II). As the latter was soluble in acetic acid or acetic anhydride, pure (V) was readily obtained by oxidation, as described above, of the mixture of (I) and (II) resulting from the Grignard reaction of phthalic anhydride with *o*-tolylmagnesium bromide and crystallisation from acetic acid.

It is noteworthy that the melting point of the compound (V) corresponds exactly with that of Weisz and Korczyn's alleged triphenylmethane-2 : 2′ : 2″-tricarboxylic acid (*loc. cit.*) and that the melting points of their methyl esters are also very similar.

The dispiran (V) was reduced quantitatively by zinc dust and dilute sodium hydroxide solution to the double phthalide (VI). Further reduction with hydriodic acid and red phosphorus gave the acid (VII) and also, owing to a simultaneous ring closure, pentaphene (IX). Ring closure of the acid (VII) with concentrated sulphuric acid gave the reddish-brown 8-hydroxypentaphene-5 : 14-quinone (VIII). When (VII) and (VIII) were submitted to zinc-dust fusion (Clar, *Ber.*, 1939, **72**, 1645) pentaphene (IX) was obtained. This preparation of pentaphene is simpler and more efficient than the earlier synthesis (Clar and John, *Ber.*, 1931, **64**, 981) which involves a laborious separation from the accompanying dihydropentacene.

The absorption spectrum (see figure) shows the purity of the pentaphene obtained. The absorption spectra of (VI) and (VII), which are of the simple benzene type, are also reproduced.

EXPERIMENTAL.

(All m. p.s are uncorrected and were taken in evacuated capillaries. Microanalyses are by Miss R. H. Kennaway.)

Reaction of Phthalic Anhydride with o-*Tolylmagnesium Bromide.*—Procedure was as described by Weisz and Korczyn (*loc. cit.*). An 80% yield of colourless crystals of (I) and (II) (m. p. 126—130°) was obtained.

Tri-o-*tolylcarbinol.*—*o*-Toluoyl chloride (65 g.) in anhydrous ether (50 c.c.) was slowly added to a solution of *o*-tolyl-lithium prepared from *o*-bromotoluene (207·5 g.) and " atomised " lithium (16·8 g.). After decomposition of the mixture with dilute hydrochloric acid, the ethereal layer was concentrated and diluted with light petroleum. The crystals (110 g.) were recrystallised from light petroleum and yielded colourless needles (m. p. 105°) and a by-product (8%) (m. p. 240—242°). The carbinol dissolved readily in concentrated sulphuric acid to give an orange solution. The properties of the carbinol agree with those described for a sample prepared by a different method (cf. Faber and Nauta, *Rec. Trav. chim.*, 1942, **61**, 469; Theilacker and Ewald, *Naturwiss.*, 1943, **31**, 302).

Di-o-*tolylphthalide* (II).—The carbinol (75 g.) mixed with nitrobenzene (30 c.c.) was boiled in 20% nitric acid (1500 c.c.) for 16 hours, fumes of nitrogen oxides being evolved. After distillation of the nitrobenzene, the light yellow solid obtained was extracted thoroughly with boiling dilute sodium hydroxide solution to remove over-oxidised material, washed well with water, and crystallised first from glacial acetic acid and then from ethanol, to give colourless plates (68 g.), m. p. 174° (Found: C, 83·7; H, 5·5. Calc. for $C_{22}H_{18}O_2$: C, 84·0; H, 5·8%). The phthalide gave an orange-red solution in concentrated sulphuric acid which changed first to orange, then to pale yellow. The m. p. compares with that of the higher-melting phthalide (m. p. 176°) reported by Weisz and Müller (*loc. cit.*).

Reaction of as-*Phthaloyl Chloride with* o-*Tolylmagnesium Bromide.*—*o*-Tolylmagnesium bromide, prepared from *o*-bromotoluene (140 g.) and magnesium (21 g.) in ether (350 c.c.), was added to *as*-phthaloyl chloride (70 g.) in benzene (300 c.c.). After the usual decomposition and separation of the aqueous layer, concentration of the organic layer gave colourless crystals (12·5 g.) of o-*tolylphthalide* (m. p. 262°) (Found: C, 79·6; H, 5·4. $C_{15}H_{12}O_2$ requires C, 80·3; H, 5·4%), which gave a colourless solution in concentrated sulphuric acid. The mother-liquors, after extraction with dilute sodium hydroxide solution (10%) to remove 2-*o*-toluoylbenzoic acid (20 g.), were steam-distilled, and the resulting solid was crystallised from acetic acid to give colourless crystals, m. p. 125—129° (73 g.). Further crystallisation, first from benzene and then from ethanol, gave the pure 1 : 2-*di*-o-*toluoylbenzene* (I), m. p. 146° (76% of mixture) (Found: C, 83·8; H, 5·5. $C_{22}H_{18}O_2$ requires C, 84·0; H, 5·8%), which gave a pale yellow solution in concentrated sulphuric acid. Hot acetic acid and zinc dust yield a yellow solution of (IV) which shows a strong blue fluorescence. Both by-products, *o*-tolylphthalide and 2-*o*-toluoylbenzoic acid, on oxidation with alkaline potassium permanganate solution and recrystallisation from concentrated nitric acid gave colourless crystals, m. p. 212°, which gave a mixed m. p. of 212° with an authentic sample of benzophenone-2 : 2′-dicarboxylic acid anhydride.

1 : 4-*Di*-o-*tolylphthalazine* (III).—The mixture (m. p. 125—129°) (1 g.) was dissolved in ethanol (15 c.c.), hydrazine hydrate (100%) (0·18 c.c.) added, and the solution refluxed for 1 hour. Concentration yielded colourless plates, m. p. 174° (0·2 g.), which gave a mixed m. p. of 174° with an authentic sample of di-*o*-tolylphthalide (II). Dilution of the mother-liquors with water gave a white precipitate (0·75 g.) which, on crystallisation from ethanol, yielded colourless crystals, m. p. 162—163°, of 1 : 4-*di*-o-*tolylphthalazine* (III) (Found: N, 9·0. $C_{22}H_{18}N_2$ requires N, 9·0%). This gave a colourless solution in concentrated sulphuric acid.

Oxidation of 1 : 2-*Di*-o-*toluoylbenzene* (I) *and Di*-o-*tolylphthalide* (II).—(a) *With dilute nitric acid solution at* 210°. The diketone (I) (1 g.) was heated under pressure with 20% nitric acid at 210° for 10 hours. The solid obtained crystallised from acetic anhydride, to give colourless needles of (V), m. p. 302—303° (yield, theoretical).

(b) The phthalide (II) gave in the same way 60% of (V), m. p. 302—303°, and from the mother-liquor 35% of syrupy unrearranged dicarboxylic acid derived from (II); it did not crystallise and gave on heating with concentrated sulphuric acid and copper powder the blue condensation product described by Weiz and Korczyn (*loc. cit.*).

(c) *With dilute nitric acid solution, followed by alkaline potassium permanganate solution.* The diketone (I) (15 g.), mixed with nitrobenzene (6 c.c.), was boiled for 48 hours with 20% nitric acid (250 c.c.). After distillation of the nitrobenzene, the solid obtained was dissolved in dilute sodium hydroxide solution, and powdered potassium permanganate added till its colour persisted for 15 minutes. The filtrate was acidified and the precipitate crystallised from acetic anhydride (15 g.; m. p. 302—303°).

(d) A similar treatment of (II) yielded 75% of (V), m. p. 302—303°, and 20% of unrearranged dicarboxylic acid.

Oxidation of Mixture of (I) *and* (II).—Both methods of oxidation described above were applied to the mixture (m. p. 125—129°) of (I) and (II). Colourless needles, m. p. 302—303°, were obtained in both cases after crystallisation from acetic acid and acetic anhydride, the yields being 87% and 82%, respectively. The products (m. p. 302—303°) from the above oxidations, all proved to be *dihydro*iso*benzofuran*-1 : 3-*bis*spiro-(3-*phthalide*) (V), which sublimed in long colourless needles (Found: C, 74·2, 74·3; H, 3·5, 3·2. $C_{22}H_{12}O_5$ requires C, 74·2; H, 3·4%). The dispiran dissolved slowly in concentrated sulphuric acid to give a colourless solution which on being heated changed to dark green. 1 : 3-*Di*-(o-*carbomethoxyphenyl*)-1 : 3-*dihydro*iso*benzofuran*, prepared by refluxing (V) in methanol saturated with dry hydrogen chloride, crystallised from benzene in colourless needles or rods, m. p. 160° (Found: C, 71·6; H, 4·4. $C_{24}H_{18}O_6$ requires C, 71·6; H, 4·5%), which gave a colourless solution in concentrated sulphuric acid.

o-*Di*-(3-*phthalidyl*)*benzene* (VI).—The dispiran (V) was dissolved in boiling sodium hydroxide solution (15%) (200 c.c.), and zinc dust (20 g.) added during 2 hours. The initial yellow colour changed to a deep red, which persisted for 10 minutes. After 3 hours, the hot solution was filtered directly into concentrated hydrochloric acid, and the white precipitate crystallised from acetic acid. Colourless needles, m. p. 211—212°, of the *dilactone* (VI) (Found: C, 77·1; H, 4·3. $C_{22}H_{14}O_4$ requires C, 77·2; H, 4·1%) were obtained, which gave a colourless solution in concentrated sulphuric acid. The yield was theoretical.

1 : 2-*Di*-(o-*carboxybenzyl*)*benzene* (VII).—The dilactone (VI) (13 g.), red phosphorus (6 g.), and hydriodic acid (55%) (60 c.c.) were covered with xylene (60 c.c.), and after being refluxed for 36 hours, the mixture was filtered. The solid obtained was extracted with xylene and then with hot sodium hydroxide solution. The aqueous layer from the filtrate was extracted with xylene, and the combined xylene fractions then extracted with hot sodium hydroxide solution. The alkaline solutions obtained were acidified hot with concentrated hydrochloric acid, and the precipitate crystallised from acetic acid, to give colourless needles (10 g., 76%), m. p. 242—243°, of the *acid* (VII) (Found: C, 76·2; H, 5·2. $C_{22}H_{18}O_4$ requires C, 76·3; H, 5·2%).

8-*Hydroxypentaphene*-5 : 14-*quinone* (VIII).—The acid (VII) (3 g.) was dissolved in concentrated sulphuric acid (30 c.c.), and heated to 120° for 10 minutes. The initial pale yellow colour changed to reddish-brown and then to dark green. The cold solution was poured into water, and the reddish-brown precipitate obtained was recrystallised from nitrobenzene and sublimed in a vacuum. Dark red needles (2·6 g.), m. p. 349—351°, of 8-*hydroxypentaphene*-5 : 14-*quinone* (VIII) (Found: C, 80·9; H, 3·5. $C_{22}H_{12}O_3$ requires C, 81·5; H, 3·7%) were obtained which gave with alkaline sodium dithionite (hydrosulphite) solution a reddish-brown vat which lightens on storage.

Pentaphene (IX).—(a) *From the dilactone* (VI). In the preparation of the acid (VII), the xylene fractions, after extraction with dilute sodium hydroxide solution, were concentrated, and pale yellow needles (2 g.) crystallised, m. p. 255—257° alone or mixed with an authentic sample of pentaphene (Found: C, 94·3; H, 5·4. Calc. for $C_{22}H_{14}$: C, 94·9; H, 5·1%).

(b) *From* (VII) *or* (VIII) *by the zinc-dust melt.* The compound (VII) or (VIII) (1 part) was finely ground with zinc dust (1·2 parts) and sodium chloride (1·2 parts), and moist zinc chloride (7 parts) added. The temperature was raised with constant stirring to 300° during 15 minutes. The cold melt was decomposed with dilute acetic acid; the resulting solid was filtered off, dried, and sublimed in a vacuum. Crystallisation of the sublimate from xylene gave yellow needles, m. p. 255—256°, unchanged on admixture with pentaphene. The pentaphene was further purified by chromatography (alumina), benzene being used as eluant. The clear yellow, blue-fluorescent eluate gave on concentration pale yellow plates (m. p. 256—257°) which were insoluble in concentrated sulphuric acid.

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