Purpurogallin. Part XII. The Action of Organometallic Compounds on the Tropolones.*

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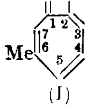
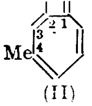
The constitutions of three isomeric methylphenyl*cyclo*heptatrienones, prepared by the action of phenyl-lithium or phenylmagnesium bromide on derivatives of 4-methyltropolone, have been determined by alkaline rearrangement to the methyldiphenylcarboxylic acids, which were identified by conversion into the corresponding methylfluorenones. The results throw considerable light on the mechanism of the reaction of organometallic compounds with tropolones, and new views are advanced to account for the reactions.

In Part XI* the action of phenylmagnesium bromide on the isomeric methyl ethers (I and II; R = OMe) and dimethylamino-compounds (I and II; R = NMe_2) was shown to give two methylphenyl*cyclo*heptatrienones, m. p. 93° and 99° respectively. By making the assumption that the Grignard reaction occurred by attack at $C_{(1)}$ (path X mechanism: see Part XI) it was suggested that the compounds of m. p. 93° and 99° were 4(?)- and 6(?)-methyl-2-phenyl*cyclo*heptatrienones (II and I; R = Ph) respectively. It was realised that the elucidation of the structures of the two methylphenyl*cyclo*heptatrienones would provide valuable information regarding the mechanism of the Grignard reaction on tropolones, and the present paper reports the results obtained in a further investigation.


(I)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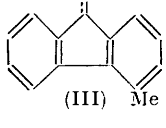
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The earlier preparations of the methylphenyl*cyclo*heptatrienones involved a tedious separation of the picrates of the isomeric methyl ethers (I and II; R = OMe) of 4-methyltropolone, and it was hoped to make the *cyclo*heptatrienones more accessible by the reaction of phenyl-lithium on the copper complex of 4-methyltropolone (cf. Doering and Mayer, *J. Amer. Chem. Soc.*, 1953, **75**, 2387). The reaction was expected to give a mixture of the isomeric *cyclo*heptatrienones (I and II; R = Ph), but to our surprise a

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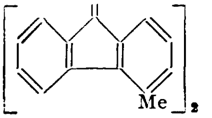
* Part XI, *J.*, 1954, 286.

homogeneous pale yellow methylphenyl*cyclo*heptatrienone, m. p. 134°, was obtained. This new isomer gave an oily hydrochloride, a 2 : 4-dinitrophenylhydrazone, m. p. 138°, and a typical *cyclo*heptatrienone ultra-violet absorption spectrum, but it differed markedly from two isomers of m. p. 93° and 99° respectively. It was therefore apparent that previous views on the reaction of organometallic compounds on tropolones were inadequate, as the two mechanisms involving attack at $C_{(1)}$ or $C_{(2)}$ (path X and path Y mechanisms : see Part XI) cannot account for the formations of these three isomers. The elucidation of their structures has proceeded along similar lines by a study of the alkali-rearrangement products of the three *cyclo*heptatrienones themselves, or of their 2-halogenated derivatives which were prepared by Doering and Mayer's method (*loc. cit.*). In the case of the methylphenyl*cyclo*heptatrienone, m. p. 93°, it was found that definite rearrangement products could not be obtained by the action of alkali. Bromination, however, yielded a pale yellow-green 2-bromo-derivative, m. p. 113°. Attempted acid hydrolysis to the corresponding methylphenyltropolone led to intractable tars which lacked the characteristic tropolone colour reactions and properties, but as in the case of other halogenated *cyclo*heptatrienones (see Seto, *Sci. Rep. Tohôku Univ.*, 1953 **37**, 377) the 2-bromo*cyclo*heptatrienone, m. p. 113°, was readily rearranged to 6-methyldiphenyl-2-carboxylic acid, m. p. 154°, by the action of ethanolic potassium hydroxide. The constitution of this acid was established by cyclisation with concentrated sulphuric acid to 4-methylfluorenone (III), which was identified by comparison with an authentic sample kindly supplied by Dr. M. Orchin (Orchin and Woolfolk, *J. Amer. Chem. Soc.*, 1945, **67**, 122) and also by Clemmensen reduction to a mixture of 4-methylfluorene and a sparingly soluble compound, probably the difluorenylidene derivative (IV). It follows from these experiments that the *cyclo*heptatrienone, m. p. 93°, is 3-methyl-2-phenyl*cyclo*heptatrienone (V).



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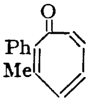

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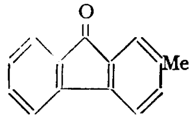
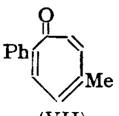


(VI)

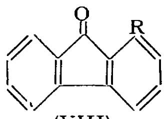
This structure (V) is also consistent with the ultra-violet absorption spectrum which differs from those of 2-phenyl*cyclo*heptatrienone (Doering and Hiskey, *ibid.*, 1952, **74**, 5688; Tsuboi, *Bull. Chem. Soc., Japan*, 1952, **25**, 369) and of its two isomers (I) and (VII) (see p. 914). The spectrum of (V) lacks the peak at 265—270 mμ, and has a maximum at 308 mμ (log ε 3·75). Thus it resembles more closely the spectra of *cyclo*heptatrienone and its homologues (Dauben and Ringold, *J. Amer. Chem. Soc.*, 1951, **73**, 896; Doering and Detert, *ibid.*, p. 876; Doering and Hiskey, *loc. cit.*; Nozoe *et al.*, *Proc. Japan Acad.*, 1951, **27**, 477), as would be expected on the assumption that steric interference by the 3-methyl group prevents the phenyl group in (V) from becoming coplanar with the seven-membered ring. As is implicit in the above explanation we regard the spectra of sterically unhindered 2-phenyl*cyclo*heptatrienones as resulting from conjugation of the two rings analogous to that of unhindered diphenyl derivatives (Braude, *Ann. Reports*, 1945, **42**, 125; Gillam and Hey, *J.*, 1939, 1170). Comparison of the spectra of 2-benzyl*cyclo*heptatrienone (Nozoe *et al.*, *Proc. Japan Acad.*, 1953, **29**, 169) and 2-phenyl*cyclo*heptatrienone is sufficient to disprove the opposite contention of Tsuboi (*loc. cit.*) who regards the spectrum of the latter substance as resulting from mere addition of the spectra of benzene and *cyclo*heptatrienone.

The constitution of the methylphenyl*cyclo*heptatrienone, m. p. 99°, was established in a similar manner. Bromination gave a 2-bromo-derivative, m. p. 110°, which was converted into 4-methyldiphenyl-2-carboxylic acid, m. p. 152°, by the action of aqueous-ethanolic potassium hydroxide. The structure of the acid was determined by cyclisation with concentrated sulphuric acid to 2-methylfluorenone (VI), which was identified by comparison of the ketone and its 2 : 4-dinitrophenylhydrazone with authentic specimens kindly supplied by Dr. O. Kruber (*Ber.*, 1932, **65**, 1382). These interconversions prove that the *cyclo*heptatrienone, m. p. 99°, is 5-methyl-2-phenyl*cyclo*heptatrienone (VII), and the conclusion is confirmed by the ultra-violet spectrum.

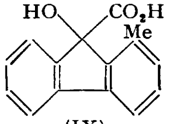
Bromination in carbon tetrachloride or acetic acid of the methylphenyl*cyclo*heptatrienone, m. p. 134°, prepared from the copper complex of 4-methyltropolone, yielded an oil, which with ethanolic potassium hydroxide gave a small yield of 3-methyldiphenyl-2-carboxylic acid, m. p. 132°, and the same acid was obtained, also in low yield, by the action of ethanolic potassium hydroxide on the unbrominated methylphenyl*cyclo*heptatrienone. On cyclisation with sulphuric acid this diphenylcarboxylic acid gave 1-methylfluorenone (VIII; R = Me), m. p. 98° (Lothrop and Goodwin, *J. Amer. Chem. Soc.*, 1943, **65**, 363; Chardonnens and Lieneit, *Helv. Chim. Acta*, 1949, **32**, 2340; Kruber and Raeithel, *Chem. Ber.*, 1954, **87**, 1469), identical with a specimen synthesised by heating 1-methylphenanthraquinone with lead oxide at 220—230° as described for other cases (Cook and Stephenson, *J.*, 1949, 845). These experiments prove that the *cyclo*heptatrienone, m. p. 134°, is 6-methyl-2-phenyl*cyclo*heptatrienone (I; R = Ph). During attempts to improve the preparation of the fluorenone (VIII; R = Me), the impure glycollic acid (IX), obtained by the action of alkali on 1-methylphenanthraquinone, was oxidised with alkaline permanganate to a mixture containing fluorenone-1-carboxylic acid (VIII; R = CO_2H) which clearly arose from further oxidation of 1-methylfluorenone or an intermediate product in its formation. A neutral ketonic compound, $C_{15}H_{10}O_4$, of unknown constitution was also obtained during the permanganate oxidation.



(VII)

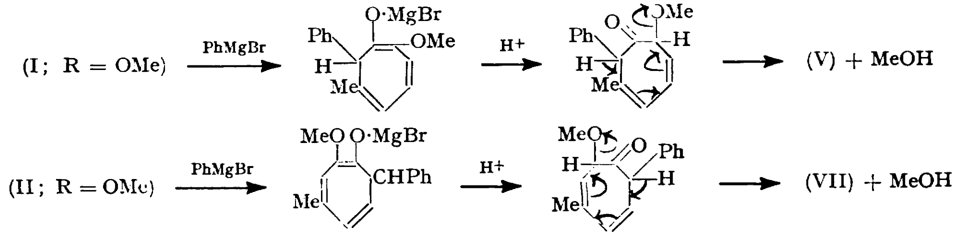


(VIII)



(IX)

In view of these results previous theories concerning the addition of organometallic compounds to tropolones must be modified. Although the product (I; R = Ph) obtained by the action of phenyl-lithium on the copper complex may be accounted for by one of the mechanisms previously advanced (path X or Y; Part XI, *loc. cit.*) it is clear that the reaction with tropolone ethers results in the attachment of the phenyl group to $C_{(7)}$, probably by 1 : 8-addition to the conjugated system,  $-\overset{\overset{O}{\|}}{C}\cdot\overset{\overset{OMe}{|}}{C}{:}CH\cdot CH{:}CH\cdot CMe{:}CH-$, as shown in the following reaction-mechanism schemes :



Nozoe *et al.* (*Proc. Japan Acad.*, 1951, **27**, 419; *Sci. Reports Tohôku Univ.*, 1953, **37**, 388) treated a mixture of hinokitiol methyl ethers with phenylmagnesium bromide and obtained one crystalline product, which on the basis of the above mechanism and the ultra-violet spectrum is probably 2-phenyl-5-*iso*propyl*cyclo*heptatrienone. Similarly the product from 3-bromo-2-methoxy*cyclo*heptatrienone (Nozoe *et al.*, *Proc. Japan Acad.*, 1952, **28**, 142) will be 6-bromo-2-phenyl*cyclo*heptatrienone.

An analogous 1 : 8-addition mechanism will also account for the results of Nozoe, Seto, and Sato (*ibid.*, 1954, **30**, 473) on the action of ammonia on 2-halogenated *cyclo*heptatrienones.

EXPERIMENTAL

*7-Bromo-3-methyl-2-phenyl*cyclo*heptatrienone.*—Bromine (0·41 g.) in carbon tetrachloride (5 c.c.) was added dropwise and with stirring during 2¼ hr. to a solution of 3-methyl-2-phenyl*cyclo*heptatrienone (V) (0·5 g.) [ultra-violet absorption in EtOH : max. at 2330 and 3080 Å (log ε 4·50, 3·75)], prepared as described in Part XI (*loc. cit.*), in carbon tetrachloride (50 c.c.) containing anhydrous sodium carbonate (0·3 g.) in suspension. After a further 7 hours' stirring, pyridine (0·45 g.) was added and the mixture refluxed for 1 hr. The pyridine hydrobromide was removed by filtration and the yellow solution was washed with dilute sulphuric acid, sodium hydrogen carbonate, and water. Evaporation of the dried carbon tetrachloride solution gave a semisolid product which crystallised from *cyclo*hexane in pale green scales (0·16 g.), m. p. 113° (Found : Br, 29·3. $C_{14}H_{11}OBr$ requires Br, 29·1%).

6-*Methyldiphenyl*-2-*carboxylic Acid*.—7-Bromo-3-methyl-2-phenyl*cyclo*heptatrienone (0·1 g.) was refluxed for 7 hr. with 10% ethanolic potassium hydroxide (5 c.c.). After 12 hr. the deep yellow solution was acidified with dilute hydrochloric acid and extracted three times with chloroform. The product was taken up in sodium hydrogen carbonate solution and recovered with chloroform; a buff-coloured solid (0·037 g.) was obtained which separated from *cyclo*hexane–light petroleum (b. p. 60—80°), or aqueous methanol, in white needles, m. p. 154° (Found : C, 78·9; H, 5·9. $C_{14}H_{12}O_2$ requires C, 79·2; H, 5·7%). 6-*Methyldiphenyl*-2-*carboxylic acid* (3 mg.), dissolved in 1% sodium hydroxide solution (0·5 c.c.), was heated on the steam-bath and 5% potassium permanganate solution was gradually added during 3 hr. until a permanent colour was obtained; the solution was clarified with sulphur dioxide and addition of concentrated hydrochloric acid (2 drops) led to the gradual separation in slender needles (1 mg.) of an acid, m. p. 270°, possibly the expected 2-phenyl*iso*phthalic acid, but the quantities available were too small for identification.

4-*Methylfluorenone* (III).—6-Methyldiphenyl-2-carboxylic acid (6 mg.) in concentrated sulphuric acid (4 drops) was warmed at 40° for 10 min. and, after decomposition with ice, the pale yellow solid (5·5 mg.) was collected. Crystallisation from ethanol yielded 4-methylfluorenone (III) in yellow needles, m. p. and mixed m. p. 88—89°, giving a red precipitate with Brady's reagent. The fluorenone (III) (8 mg.) was refluxed with amalgamated zinc (5 g.) and 5N-hydrochloric acid (15 c.c.) for 16 hr., and the product, isolated with ether, was separated by crystallisation from ethanol into the sparingly soluble *compound*, probably (IV) (4·5 mg.), m. p. 208—209°, and the more soluble 4-methylfluorene, m. p. 69—70° (Orchin and Woolfolk, *loc. cit.*, give m. p. 70—71°).

7-*Bromo*-5-*methyl*-2-*phenyl*cyclo*heptatrienone*.—5-Methyl-2-phenyl*cyclo*heptatrienone (VII) (0·5 g.) [ultra-violet absorption in EtOH : max. at 2260, 2670, and 3250 Å (log ε 4·36, 3·75, 4·03)], brominated as described for the isomer on p. 913, gave a yellow oil (0·8 g.), which after sublimation and crystallisation from *cyclo*hexane (charcoal) yielded the *bromo*cyclo*heptatrienone* as small yellow-green prisms (0·2 g.), m. p. 110° (Found : C, 60·9; H, 3·8; Br, 29·4. $C_{14}H_{11}OBr$ requires C, 61·1; H, 4·0; Br, 29·1%).

4-*Methyldiphenyl*-2-*carboxylic Acid*.—(i) 7-Bromo-5-methyl-2-phenyl*cyclo*heptatrienone (0·1 g.) was refluxed for 6 hr. with 10% ethanolic potassium hydroxide solution (5 c.c.). After 12 hr. the deep red solution was acidified with dilute sulphuric acid, and the acid was isolated with ether, taken up in sodium hydrogen carbonate solution, and recovered as a gum. The crude acid was dissolved in 2% sodium hydroxide solution, and impurities were removed by oxidation with a slight excess of 5% permanganate for 30 min. at room temperature. Clarification with sulphur dioxide and addition of concentrated hydrochloric acid precipitated the acid as a white solid (1 mg.).

(ii) 7-Bromo-5-methyl-2-phenyl*cyclo*heptatrienone (50 mg.) was refluxed for 5 hr. with a 2N-solution (5 c.c.) of potassium hydroxide in a mixture of methanol (4 vol.) and water (1 vol.). The solution was treated as above, but acidification of the sodium hydrogen carbonate solution gave the acid as a white solid (20 mg.).

Prepared by either method, 4-*methyldiphenyl*-2-*carboxylic acid* crystallised from aqueous methanol in colourless needles, m. p. 152° (Found : C, 79·6; H, 5·7%).

2-*Methylfluorenone* (VI).—The foregoing acid (7 mg.) was warmed with concentrated sulphuric acid (1 c.c.) for 10 min., and the red solution was decomposed with ice. The yellow precipitate was collected and crystallised from aqueous ethanol or light petroleum (b. p. 60—80°) in yellow needles (1 mg.), m. p. 89—90°, undepressed when mixed with an authentic specimen of 2-methylfluorenone, but a mixture with the 4-methyl isomer (III) melted at 55—60°.

6-*Methyl*-2-*phenyl*cyclo*heptatrienone* (I; R = Ph).—A solution of phenyl-lithium, prepared from lithium (2 g.) and bromobenzene (22 g.), was filtered through glass wool under nitrogen, and the copper complex (14 g.; crystallised from chloroform) of 4-methyltropolone was added in small portions. After 12 hr., ice and dilute sulphuric acid were added and the mixture was extracted with chloroform. The organic layer was washed with water, and then very dilute aqueous sodium hydroxide, dried, and evaporated under reduced pressure. The residual dark oil, after being washed several times with small amounts of ether, gave the yellow *cyclo*heptatrienone (I; R = Ph) as a yellow solid (3·5 g.) which crystallised from *cyclo*hexane in slender yellow-green needles, m. p. 133° (Found: C, 85·6, 85·6; H, 6·0, 6·2. $C_{14}H_{12}O$ requires C, 85·7; H, 6·1%). Ultra-violet absorption in EtOH: max. at 2325, 2690, and 3240 Å (log ε 4·40, 3·95, 3·93). 6-*Methyl-2-phenyl*cyclo*heptatrienone* (I; R = Ph) was readily soluble in ethanol, moderately so in benzene, and almost insoluble in light petroleum. It dissolved in concentrated hydrochloric acid from which it was recovered by dilution after refluxing for 24 hr., but the hydrochloride was precipitated as a dark viscous oil by passing hydrogen chloride through an ethereal solution of the *cyclo*heptatrienone. The 2 : 4-*dinitrophenylhydrazone*, prepared in ethanol and precipitated by addition of water, crystallised from a small volume of acetic acid in deep red needles, m. p. 138° (Found: C, 63·9; H, 4·2; N, 14·9. $C_{20}H_{16}O_4N_4$ requires C, 63·8; H, 4·3; N, 14·9%).

3-*Methyldiphenyl-2-carboxylic Acid.*—(i) The *cyclo*heptatrienone (I; R = Ph), brominated either as described on p. 913 or in aqueous acetic acid, yielded the 2-bromo-derivative as a brown tar. This tar (0·14 g.) was refluxed for 5 hr. with 10% ethanolic potassium hydroxide (10 c.c.). (ii) The *cyclo*heptatrienone (I; R = Ph) (0·5 g.) was refluxed for 1½ hr. with 8% ethanolic potassium hydroxide (25 c.c.). After dilution the red-brown solution obtained either by method (i) or by method (ii) was acidified and extracted with ether. The acid was removed in sodium hydrogen carbonate solution, recovered, and dissolved in 2% sodium hydroxide solution, and impurities were removed by oxidation with excess of cold 5% permanganate solution for 1 hr. Sulphur dioxide precipitated 3-methyldiphenyl-2-carboxylic acid which crystallised from dilute ethanol in needles, m. p. 132° (Found: C,79·0; H, 5·8%). Yields were: method (i), 2·5 mg.; method (ii), 2 mg.

1-*Methylfluorenone* (VIII; R = Me).—(i) The foregoing acid (2·5 mg.) was warmed in concentrated sulphuric acid (2 c.c.) for 15 min. on the steam-bath. The red solution was poured on ice, and the yellow solid collected. (ii) 1-Methylphenanthraquinone (0·1 g.), m. p. 192°, was thoroughly mixed with lead oxide (1 g.) and heated in a metal-bath at 220°. After 3 min., the temperature was lowered to about 150°, and the product sublimed at 8 mm. The orange sublimate (15 mg.) was dissolved in benzene and absorbed on a small column of alumina; unchanged quinone was strongly retained but elution with benzene–*cyclo*hexane (1 : 2) readily removed the fluorenone (VIII; R = Me).

Prepared by either method, 1-methylfluorenone (VIII; R = Me) separated from light petroleum (b. p. 60—80°) in bright yellow prisms, m. p. 98° (Found: C, 86·3; H, 5·5. Calc. for $C_{14}H_{10}O$: C, 86·5; H, 5·2%) (lit., m. p. 98°).

Fluorenone-1-carboxylic Acid (VIII; R = CO_2H).—Potassium permanganate was gradually added to the cooled solution obtained by refluxing 1-methylphenanthraquinone (0·08 g.) for 7 hr. with excess of 2N-sodium hydroxide. The solution was finally heated on the steam-bath for 2 hr., and a slight permanent excess of permanganate added. The orange yellow solid precipitated by sulphur dioxide was extracted with ether, taken up in sodium hydrogen carbonate solution and recovered; fluorenone-1-carboxylic acid (VIII; R = CO_2H) separated from ethanol in fibrous orange needles (25 mg.), m. p. 190—191°, undepressed on admixture with an authentic specimen kindly supplied by Dr. P. L. Pauson and prepared as described by Koelsch and Steinhauer (*J. Org. Chem.*, 1953, **18**, 1516). The oxime of the acid (VIII; R = CO_2H) had m. p. 229° [Goldschmiedt, *Monatsh.*, 1902, **23**, 886, gives m. p. 230° (decomp.)]. The neutral ethereal solution yielded a *compound*, $C_{15}H_{10}O_4$, which separated from ethanol in yellow needles (10 mg.), m. p. 130—132° (Found: C, 71·3; H, 4·0. $C_{15}H_{10}O_4$ requires C, 70·9; H, 3·9%), and gave an orange-red precipitate with Brady's reagent.

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