Purpurogallin.   Part XI.   Some Further Rearrangement Reactions of the Tropolones.*

By Philip Akroyd, Robert D. Haworth, and Phillip R. Jefferies.

The reactions of β-methyltropolone methyl ethers with amines, alkoxides, lithium aluminium hydride, and Grignard reagents have been examined. Some properties of methylphenyl*cyclo*heptatrienones are described, the mechanisms of the reactions are discussed, and several examples of the conversion of tropolones into benzenoid compounds are reported.

In Part IX (*J.*, 1951, 3427) the formation of 2-amino-4- and 2-amino-6-methyl*cyclo*hepta-trienone was described. These experiments have been extended, and the methoxyl group of β-methyltropolone methyl ether-A (I; R = OMe) (see Part IX) has been replaced by the morpholino- and the dimethylamino-group. The dimethylamino-compound (I; R = NMe₂) so obtained formed a quaternary salt with methyl iodide, and a strong base on further treatment with silver oxide. Hydrogenolysis (cf. Rapoport and Williams, *J. Amer. Chem. Soc.*, 1951, **73**, 1896) in presence of Adams's catalyst ruptured the amino-linkage and gave 3-methyl*cyclo*heptanone, which was identified as its semicarbazone. The isomeric dimethylamino-compound (II; R = NMe₂) was similarly prepared from the
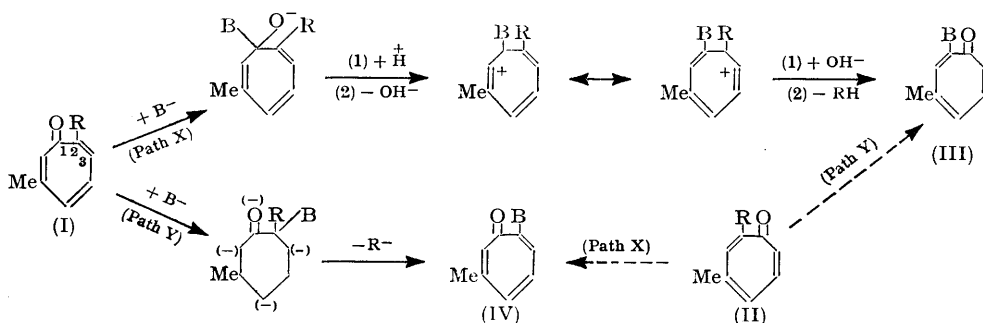
methyl ether-B, and catalytic reduction of this yielded 4-methyl*cyclo*heptanone, which was also characterized as its semicarbazone. Thus this reaction gives additional evidence that the series of substituted amino-compounds obtained from β-methyltropolone methyl ether-A and -B are represented by (I; R = NR₂) and (II; R = NR₂), respectively

* Part X, *J.*, 1952, 3705.

(see Part IX). An improved yield of 2-amino-6-methyl*cyclo*heptatrienone was obtained from the corresponding methyl ether-A by the use of liquid ammonia at room temperature (cf. Nozoe and his co-workers, *Proc. Jap. Acad. Sci.*, 1951, **27**, 556; 1952, **28**, 192; *Sci. Rep. Tohoku*, 1952, series I, **36**, 128). There are two plausible mechanisms with nucleophilic attack, namely, at the carbonyl-carbon atom, $C_{(1)}$ (path X) or at the adjacent substituted carbon atom, $C_{(2)}$ (path Y). Nozoe and his co-workers (*Proc. Jap. Acad. Sci.*, 1951, **27**, 419, 649; 1952, **28**, 85, 142, 483), Doering and Knox (*J. Amer. Chem. Soc.*, 1952, **74**, 5683), and Doering and Hiskey (*ibid.*, p. 5688) suggest that 2-substituted *cyclo*heptatrienones are produced by path Y. The orientation of the series of 2-substituted amino-methyl*cyclo*heptatrienones has been established conclusively by the Stevens–McFadyen decomposition of the hydrazino-compounds and their interconversions (Part IX) and also by the reduction of the isomeric 2-dimethylamino-compounds A and B to the 3- and 4-methyl*cyclo*heptanone, respectively, described above. But it is not established that, say, (IV; B = NH·NH₂) is derived from (I; R = OMe) by path Y, and not from (II; R = OMe) by path X. The former alternative, *i.e.*, path Y, is favoured because the predominant, but not exclusive, reaction between α-hydroxymethylene-ketones (which are structurally related to tropolones) and amines or hydroxylamine occurs at the hydroxymethylene group (path Y) (Bishop, Claisen, and Sinclair, *Annalen*, 1894, **281**, 314; Auwers, Bahr, and Frese, *ibid.*, 1925, **441**, 54; Birch and Robinson, *J.*, 1944, 501; Johnson and Shelberg, *J. Amer. Chem. Soc.*, 1945, **67**, 1745; Woodward *et al.*, *ibid.*, 1951, **73**, 2403). This mechanism is also supported by the interconversion reactions which are described below and summarised in the annexed scheme. If, as is reasonable, it is assumed that all these nucleophilic substitution reactions occur by the same mechanism, it follows that the product obtained from the methyl ether-A by a two-stage * process will be identical with that obtained by the appropriate one-stage process if path Y is involved throughout. On the other hand, if path X were operative the product of a two-stage process would differ from that obtained from the appropriate one-stage process. In the reactions studied it was found that
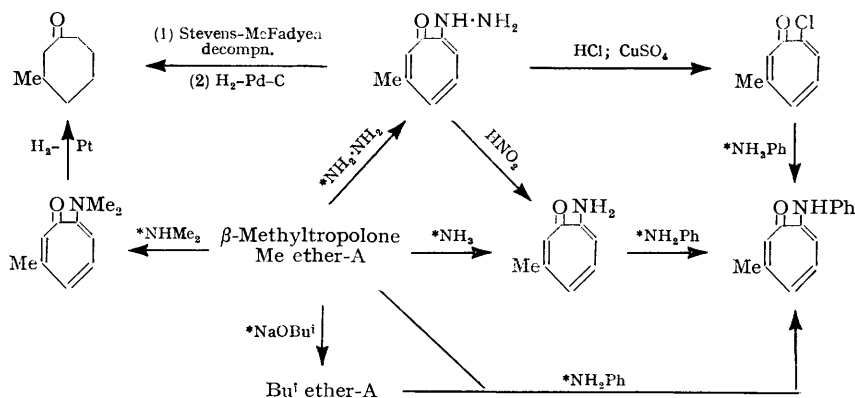
identical products were obtained from either the one- or the two-stage syntheses. Consequently, $C_{(2)}$ substitution (path Y) appears to be the correct mechanism for these reactions with amine derivatives, and the methyl ether-A, m. p. 96°, is, in fact, (I; R = Me) as was postulated in Part IX (*loc. cit.*).

Reduction of β-methyltropolone methyl ether-A and -B (I and II respectively; R = OMe) by lithium aluminium hydride has been examined. Extremely sharp-smelling lachrymatory yellow oils were produced by decomposition of the lithium complexes with dilute acid or dilute alkali, from which *m*-tolualdehyde and 3-methylbenzyl alcohol were isolated in good yield by distillation. Decomposition of the complex after a short reaction time (5 min.) yielded only the aldehyde whereas more vigorous conditions always gave a

* By a " two-stage " process is meant that two separate nucleophilic substitution reactions have been performed on the original *cyclo*heptatrienone derivative in order to obtain the required compound. Each such nucleophilic substitution is indicated by an asterisk in the reaction scheme.
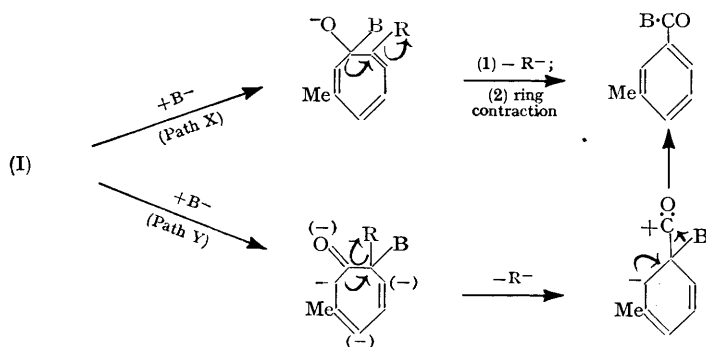
mixture of aldehyde and alcohol. When the complex from the methyl ether-A was decomposed by dilute acid after a short reaction time, 4-methyl*cyclo*heptatrienone was also obtained and identified by reduction to 4-methyl*cyclo*heptanone (see Part IX, *loc. cit.*). This *cyclo*heptatrienone was very soluble in water and sensitive to alkali (cf. Doering and Detert, *J. Amer. Chem. Soc.*, 1951, **73**, 876; Brown, *J.*, 1951, 2670; Nozoe and his co-workers, *Proc. Jap. Acad. Sci.*, 1951, **27**, 419). Since the completion of these experiments Cook, Raphael, and Scott (*J.*, 1952, 4416) have reported the isolation of benzaldehyde after lithium aluminium hydride reduction of tropolone methyl ether, and Eschenmoser and Rennhard (*Helv. Chim. Acta*, 1953, **36**, 291) have partially reduced the tetramethyl ether of purpurogallin by this reagent. Both groups of workers assume a path X attack by lithium aluminium hydride. Tropolone ethers may be regarded as cyclic divinyl analogues of the enol ethers of β-diketones. Seifert and Schinz (*ibid.*, 1951, **34**, 728), Conroy (*J. Amer. Chem. Soc.*, 1952, **74**, 3046), and Woodward and his co-workers (*ibid.*, p. 4223) showed that lithium aluminium hydride reacted with the carbonyl rather than with the ether linkage of β-diketone enol ethers, but Dreiding and Hartman (*ibid.*, 1953, **75**, 939) isolated reduction products which could only be explained by attack at both the carbonyl and the enol ether groups. The conversion of β-methyltropolone methyl ether-A (I; R = OMe) by lithium aluminium hydride into a product, which, after catalytic reduction, gave 4-methyl*cyclo*heptanone, is strong evidence that reduction with lithium aluminium hydride occurs at the carbonyl group and involves a path X mechanism.

The closely related reactions involving attack by organo-metallic compounds on the two methyl ethers and on the isomeric dimethylamino-compounds (I and II; R = NMe₂) have also been examined. Phenylmagnesium bromide reacted with the methyl ether-A forming a small amount of diphenyl-*m*-tolylmethanol, and a good yield of, probably, 4(?)-methyl-2-phenyl*cyclo*heptatrienone, m. p. 93°; more drastic Grignard attack on the isomeric methyl ether-B gave a higher yield of the same alcohol together with 6(?)-methyl-2-phenyl*cyclo*heptatrienone, m. p. 99°. Only diphenyl-*m*-tolylmethanol was isolated when the methyl ether-A was treated with phenyl-lithium. The isomeric dimethylamino-derivatives (I and II; R = NMe₂) were also converted into the methylphenyl*cyclo*hepta-trienones, m. p. 93° and 99°, respectively, by treatment with phenylmagnesium bromide. These methylphenyl*cyclo*heptatrienones were readily decomposed by bases, but they were stable towards strong acids and formed hydrochlorides in ether although stable oxonium salts were not obtained by interaction with methyl iodide. Contrary to the findings of Dauben and Ringold (*J. Amer. Chem. Soc.*, 1951, **73**, 876), they reacted with typical carbonyl reagents such as 2 : 4-dinitrophenylhydrazine and phenylhydrazine, and the compound of m. p. 93° also gave two isomeric derivatives with hydroxylamine. One of these is probably an amino-compound, not an oxime, since it gave a green ferric test and evolved ammonia when refluxed with alkali (cf. Nozoe and his co-workers, *Proc. Jap. Acad. Sci.*, 1951, **27**, 419; 1952, **28**, 287, 413, 477). The other derivative, which gave a red ferric test, was recovered unchanged after prolonged refluxing with ethanolic sodium hydroxide. Whilst these experiments were in progress, Nozoe and his co-workers (*locc. cit.*, pp. 419, 142, 287, 413) and Doering and Hiskey (*loc. cit.*) prepared 2-phenyl- and 2-alkyl-*cyclo*heptatrienones by reactions with organometallic compounds, and the Japanese workers also isolated benzenoid rearrangement products. These reactions of tropolone ethers with Grignard reagents probably proceed by path X by analogy with the lithium aluminium hydride reduction but this is not yet proven and, indeed, Doering and Hiskey and Nozoe propose a path Y mechanism. Woods (*J. Amer. Chem. Soc.*, 1947, **69**, 2549) and Woods and Tucker (*ibid.*, 1948, **70**, 2174) postulated, but did not establish, that the carbonyl group of β-diketone enol ethers reacted with Grignard reagents. The complete elucidation of the structure of the two methylphenyl*cyclo*heptatrienones, m. p. 93° and 99° respectively, obtained by the action of phenylmagnesium bromide on the two isomeric methyl ethers of β-methyltropolone would provide valuable evidence regarding the mechanism of the Grignard reaction. Work in this direction is in progress.

There are now several recorded reactions of tropolones and 2-substituted *cyclo*hepta-trienones with nucleophilic reagents, the products, usually obtained in high yield, being either substituted *cyclo*heptatrienones or benzenoid rearrangement products, the balance

between the two competing reactions frequently depending on the conditions used; in general the yield of benzenoid product is increased by the use of more drastic experimental conditions. At this stage it does not seem possible to discover whether the cogenerated benzenoid compounds occur by attack at $C_{(1)}$ or $C_{(2)}$. Doering and Knox (*loc. cit.*) and Doering and Hiskey (*loc. cit.*) favour attack at $C_{(2)}$ followed by ring rearrangement, but Nozoe and his co-workers (*e.g., Proc. Jap. Acad. Sci.*, 1951, **27**, 419, 649; 1952, **28**, 85, 142, 483) suggested that attack at the carbonyl ($C_{(1)}$) group was responsible for the production of benzenoid structures. It will be noted that paths X and Y discussed on p. 287, whilst leading to different 2-substituted *cyclo*heptatrienones (III) and (IV), give the same benzenoid derivative, as shown below. The isolation of 3-methylbenzyl alcohol from the lithium aluminium hydride reduction, and of benzenoid alcohols from the Grignard reaction, indicates bimolecular attack of these reagents on the tropolone methyl ether molecule before decomposition of the organometallic complex occurs (cf. Nozoe and his co-workers, *loc. cit.*, p. 142).

2-Amino-6-methyl*cyclo*heptatrienone (I; $R = NH_2$) reacted vigorously with nitrous acid at 0°; no diazonium compound could be detected, but 2-hydroxy-4-methylbenz-aldehyde and *m*-toluic acid were isolated. Similarly the isomeric 2-amino-4-methyl*cyclo*-

heptatrienone (II; $R = NH_2$) gave *m*-toluic acid and 2-hydroxy-6-methylbenzaldehyde. No β-methyltropolone could be detected in the products of either reaction, so that the rearrangement must proceed as shown and no hydroxyl-ion addition to the intermediate (V) occurs before ring contraction has taken place. The path P reaction here is analogous to the rearrangement undergone by α-amino-β-methyltropolone on similar treatment with nitrous acid (Part X, *loc. cit.*), but the path Q reaction is the first known example of rupture of the bond βγ to the carbonyl-carbon atom $C_{(1)}$ to give a benzenoid rearrangement product.

By a reaction comparable to alcoholysis of carboxylic acid esters, 2-*iso*butoxy-6-methyl-*cyclo*heptatrienone (I; $R = OBu^i$) was prepared from the corresponding methyl ether-A
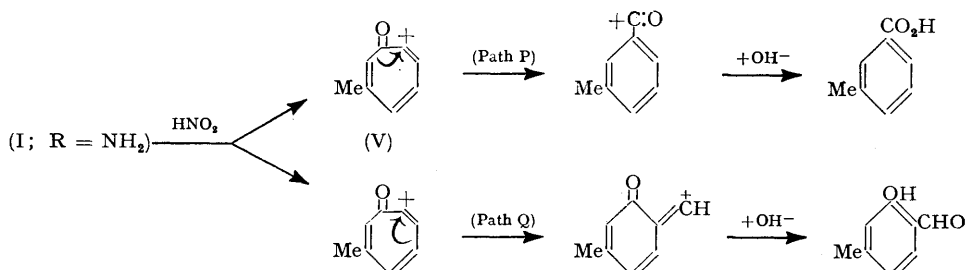

(I; $R = OMe$) and *iso*butanol containing a trace of sodium. This *iso*butyl ether, an oil, was converted into 2-anilino-6-methyl*cyclo*heptatrienone (I; $R = NHPh$) by warm aniline. When, however, the methyl ether-A was treated with methanolic sodium methoxide under more vigorous conditions, ring contraction occurred and *m*-toluic acid was isolated in poor

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yield, in contrast to the high yield reported by Doering and Knox (*J. Amer. Chem. Soc.*, 1951, **73**, 828) for the analogous rearrangement of tropolone methyl ether.

Various attempts to obtain a distillable product by the action of thionyl chloride or phosphorus trichloride on β-methyltropolone (cf. Abadir, Cook, Loudon, and Steel, *J.*, 1952, 2350) failed, but 2-chloro-6-methyl*cyclo*heptatrienone (I; R = Cl) was eventually prepared by addition of the hydrochloride of the corresponding hydrazino-compound (I; R = NH·NH₂) to boiling cupric sulphate solution (cf. Nozoe *et al.*, *loc. cit.*, p. 483). Warming this chloro-compound with aniline gave 2-anilino-6-methyl*cyclo*heptatrienone.

In Part X (*loc. cit.*) persulphate oxidation of β-methyltropolone was shown to yield γ-hydroxy-β-methyltropolone together with smaller amounts of an isomer. This isomer has now been proved to be α′-hydroxy-β-methyltropolone (VI) by catalytic reduction and subsequent oxidation with permanganate to β-methyladipic acid. Further examination of the oxidation of γ-hydroxy-β-methyltropolone has shown that it is converted by the action of hot nitrous acid into a yellow, high-melting compound $C_{16}H_{12}O_5$ which gave a ferric test and a sparingly soluble orange sodium salt, and the structure (VII) is suggested for it. Owing to the insolubility of the product, molecular-weight determinations could not be made, but acetylation gave a diacetyl derivative, $C_{20}H_{16}O_7$, which gave a negative ferric test and a Rast value supporting the bimolecular structure (VII). A similar compound was prepared by Nozoe and his colleagues (*ibid.*, 1951, **27**, 10; 1952, **28**, 488) by

(VI)   (VII)   (VIII)   (IX)
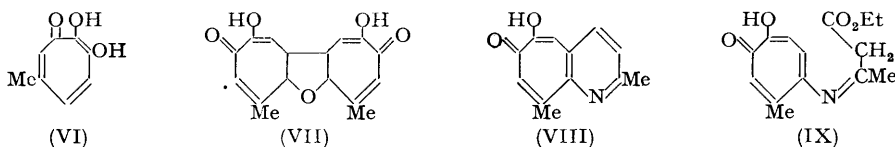
the action of hot nitrous acid on γ-amino-β-*iso*propyltropolone. Pyridinotropolones have been prepared by subjecting γ-aminotropolone to either Doebner–Miller or Skraup reactions (Attridge and Slack, *Chem. and Ind.*, 1952, 471; Cook, Loudon, and Steel, *ibid.*, p. 562), and 2 : 9-dimethylpyridino[2, 3-*d*]tropolone (VIII) has now been obtained by the action of paraldehyde or crotonaldehyde and hydrochloric acid on γ-amino-β-methyltropolone. When γ-amino-β-methyltropolone was boiled with ethyl acetoacetate, a condensation product (probably IX) was obtained in good yield, but cyclisation to a pyridinotropolone could not be brought about by sulphuric or phosphoric acid.

<center>EXPERIMENTAL</center>

*2-Amino-6-methyl*cyclo*heptatrienone* (I; R = NH₂).—An improved yield (89%) of this compound (Part IX, *J.*, 1951, 3427) was obtained by treating 2-methoxy-6-methyl*cyclo*hepta-trienone (I; R = OMe) (1·5 g.; m. p. 96°) with liquid ammonia (5 c.c.) in a sealed tube for 5 days at room temperature. The *copper* complex separated from chloroform in pale green-brown platelets, m. p. 210° (decomp.) (Found : C, 58·3; H, 5·1; Cu, 19·0. $C_{16}H_{16}O_2N_2Cu$ requires C, 57·9; H, 4·9; Cu, 19·2%).

*6-Methyl-2-morpholino*cyclo*heptatrienone* (I; R = C₄H₈ON).—The methyl ether-A (I; R = OMe) (1·0 g.; m. p. 96°) was refluxed with morpholine (10 c.c.) for 50 hr. After low-pressure removal of excess of morpholine, *6-methyl-2-morpholino*cyclo*heptatrienone* crystallized from *cyclo*hexane in pale yellow plates, m. p. 89—90° (Found : C, 70·3; H, 7·35; N, 6·7. $C_{12}H_{15}O_2N$ requires C, 70·2; H, 7·35; N, 6·8%), which did not combine with Brady's reagent in methanol.

*2-Dimethylamino-6-methyl*cyclo*heptatrienone* (I; R = NMe₂).—The methyl ether-A (I; R = OMe) (2·0 g.) and dimethylamine (4 c.c.) were kept in a sealed tube for 7 days at 20°. Distillation yielded *2-dimethylamino-6-methyl*cyclo*heptatrienone* as a pale orange viscous oil (1·8 g.), b. p. 110—113°/0·5 mm., m. p. −2° to +2°, which gave a dark green ferric test in ethanol. The *picrate* crystallized from methanol in elongated yellow prisms, m. p. 182—183° (decomp.) (Found : C, 49·6; H, 4·4; N, 14·1. $C_{16}H_{16}O_8N_4$ requires C, 49·0; H, 4·1; N, 14·3%). The *methiodide* separated from ethanol in pale yellow needles, m. p. 131—132° (decomp.) (Found : C, 43·4; H, 5·3; N, 4·8. $C_{11}H_{16}ONI$ requires C, 43·3; H, 5·3; N, 4·6%).

*2-Dimethylamino-4-methyl*cyclo*heptatrienone* (II; R = NMe₂) was prepared similarly in

90% yield from β-methyltropolone methyl ether-B (m. p. 46°), as a viscous orange oil, b. p. 130° (bath)/0·3 mm. The *picrate* crystallized from ethanol in yellow prisms, m. p. 167—168° (decomp.) (Found : C, 49·3; H, 4·3; N, 14·2%), and the *methiodide* separated from ethanol in long pale yellow prisms, m. p. 152—153° (decomp.) (Found : N, 4·6%).

Hydrogenolysis of 2-Dimethylamino-6-methylcycloheptatrienone.—No reduction took place in ethanol with a 10% palladium–charcoal catalyst. The dimethylamino-derivative (I; R = NMe₂) (1·0 g.) in glacial acetic acid (20 c.c.) was shaken with hydrogen at room temperature in the presence of platinum oxide (0·082 g.); after 15 hr., 4 mols. of hydrogen were absorbed. The product, a sweet-smelling oil, b. p. 75—80°/12 mm. (0·9 g.), gave a semicarbazone, which after crystallization from ethyl acetate had m. p. 182—183°, undepressed by admixture with 3-methyl*cyclo*heptanone semicarbazone (Part IX, *loc. cit.*).

Hydrogenolysis of 2-Dimethylamino-4-methylcycloheptatrienone.—The dimethylamino-derivative (II; R = NMe₂) was reduced similarly in acetic acid solution; 5 mols. of hydrogen were absorbed in 12 hr. The product was oxidized with chromic acid, and the saturated ketone, isolated by ether-extraction of the steam-distillate, gave a semicarbazone which crystallized from ethyl acetate in colourless prisms, m. p. 158—159° undepressed by mixture with authentic 4-methyl*cyclo*heptanone semicarbazone (Part IX).

Action of Lithium Aluminium Hydride on 2-Methoxy-6-methylcycloheptatrienone [in part with J. D. HOBSON].—(*a*) The ether-A (I; R = OMe) (1·0 g.) in ether (400 c.c.) was added to a slurry of lithium aluminium hydride (0·5 g.) in ether (50 c.c.). After occasional shaking during 40 min., the lachrymatory complex, which had a sweet odour, was decomposed by gradual addition of 2N-hydrochloric acid (100 c.c.). The ethereal layer was separated, the aqueous residue was extracted with ether (4 × 50 c.c.), and the combined ethereal solutions were dried (Na₂SO₄) and evaporated; an extremely lachrymatory oil, the bulk of which boiled at 80—100°/15 mm., was obtained. This sweet-smelling distillate contained approximately equal proportions of 3-methylbenzyl alcohol (*p*-nitrobenzoate, m. p. 88—89°; 3 : 5-dinitrobenzoate, m. p. 110—111°) and *m*-tolualdehyde (2 : 4-dinitrophenylhydrazone, m. p. 212—213°; semicarbazone, m. p. 219—221°) which were identified by comparison with authentic samples (see below).

Similar experiments were performed using the same quantities of reactants but with varying conditions :

(*b*) After 6 hr. at 20° the complex was decomposed by very slow addition of 2N-sodium hydroxide, then steam-distilled; the products, isolated with ether (4 × 50 c.c.), contained 3-methylbenzyl alcohol and *m*-tolualdehyde.

(*c*) After 5 min. at 20° the complex was decomposed by rapid addition of 2N-sodium hydroxide; the products, isolated with ether, contained much *m*-tolualdehyde but no 3-methylbenzyl alcohol.

(*d*) After 24 hr. at room temperature the complex was refluxed for 20 hr. and decomposed by very slow addition of water; the yellow oil contained approximately equal proportions of aldehyde and alcohol.

(*e*) The reaction was carried out at −2°, and after 7 min. the complex was decomposed by slow addition of 2N-hydrochloric acid. The aqueous layer was extracted with ether (2 × 80 c.c.) and then continuously extracted with ether for 75 hr.; the latter extract, after drying, yielded a pale red oil, a portion of which gave a solid hydrochloride in dry ether, and another portion, after being refluxed with dilute hydrochloric acid, gave no ferric test, thus proving the absence of starting material. The remaining oil was reduced in ethanol with a 10% palladium–charcoal catalyst; distillation of the product gave a colourless oil (0·11 g.), b. p. 74—78°/12 mm., which yielded a semicarbazone, m. p. 158—159° undepressed by admixture with authentic 4-methyl*cyclo*heptanone semicarbazone (Part IX, *loc. cit.*).

3-Methylbenzyl alcohol, b. p. 97—100°/12 mm., was obtained in 97% yield by reducing *m*-toluoyl chloride with an ethereal slurry of lithium aluminium hydride. The p-*nitrobenzoate* crystallized from light petroleum (b. p. 60—80°) in colourless prisms, m. p. 88—89° (Found : C, 66·4; H, 4·8; N, 5·3. C₁₅H₁₃O₄N requires C, 66·4; H, 4·8; N, 5·2%), and the 3 : 5-*dinitrobenzoate* separated from the same solvent in colourless prisms, m. p. 111° (Found : C, 57·1; H, 3·8. C₁₅H₁₂O₆N₂ requires C, 57·0; H, 3·8%).

m-Tolualdehyde, b. p. 72—74°/12 mm., was prepared in 75% yield by reducing *m*-toluoyl chloride in boiling xylene with hydrogen during 4 hr., with 5% palladium–barium sulphate poisoned by 1% of " quinoline-S." The 2 : 4-dinitrophenylhydrazone crystallized from acetic acid in elongated scarlet prisms, m. p. 212—213° (Bowen and Williams, *J.*, 1950, 750, give m. p. 211·5—212·5°), and the semicarbazone separated from pentan-1-ol in colourless prisms, m. p. 221—223° (G.P. 268,786 gives m. p. 223—224°).

Action of Phenylmagnesium Bromide on 2-Methoxy-6-methylcycloheptatrienone.—A solution of 2-methoxy-6-methyl*cyclo*heptatrienone (I; R = OMe) (6·0 g.) in warm benzene (200 c.c.) was slowly added to a Grignard reagent prepared from magnesium (2·3 g.) and bromobenzene (14·6 g.) in ether (80 c.c.), and after 30 min. at 30° the pale yellow solution was refluxed for 40 min., diluted with ether (500 c.c.), and decomposed by addition of a saturated solution (20 c.c.) of ammonium chloride. The red upper layer was concentrated to 100 c.c. and saturated with hydrogen chloride, and after 1 hr. the solution was decanted from the precipitated red oil and evaporated. Traces of diphenyl were removed in steam, and the remaining neutral products were taken up in ether, dried, and evaporated, and the residue was absorbed on a column of alumina; elution with light petroleum (b. p. 60—80°) gave diphenyl-*m*-tolylmethanol, m. p. 67—68° undepressed on admixture with an authentic specimen, m. p. 68—69° (Bowen and Thomas, *J.*, 1940, 1242). The precipitated dark red hydrochloride was neutralized with 2N-sodium hydroxide, and the product, isolated with ether, was absorbed on alumina, eluted with a mixture of light petroleum (b. p. 60—80°) (7 parts) and benzene (3 parts), and crystallized from *cyclo*hexane; 4(?)-*methyl-2-phenyl*cycloheptatrienone (5·1 g.) was obtained as pale buff prisms, m. p. 92—93° (Found : C, 85·5; H, 6·2. $C_{14}H_{12}O$ requires C, 85·7; H, 6·2%), which were sparingly soluble in cold water, dilute acids, or light petroleum (b. p. 60—80°), moderately soluble in warm water, 5N-hydrochloric acid, and ether, very soluble in hydroxylic organic solvents, and rapidly decomposed by bases (sodium hydroxide or methoxide) to a dark brown solution. An unstable hydrochloride, m. p. 137—139° (decomp.), was precipitated from an ethereal solution of the *cyclo*heptatrienone by hydrogen chloride, but no reaction was observed with picric acid or methyl iodide. The 2 : 4-*dinitrophenylhydrazone*, prepared in methanol, separated from ethanol or acetic acid in very dark red prisms, m. p. 171—172° (Found : C, 63·8; H, 4·2; N, 15·2. $C_{20}H_{16}O_4N_4$ requires C, 63·8; H, 4·3; N, 14·9%). 4(?)-Methyl-2-phenyl*cyclo*heptatrienone (0·5 g.), hydroxylamine hydrochloride (0·5 g.), and pyridine (3 c.c.) were heated at 100° for 4 hr., the pyridine was then evaporated, and 2N-hydrochloric acid (20 c.c.) was added. Ether-extraction (5 × 30 c.c.) left a small insoluble *compound* which crystallized from ethanol in pale yellow rhombs, m. p. 238—239° (Found : C, 79·7; H, 6·25; N, 6·6. $C_{14}H_{13}ON$ requires C, 79·6; H, 6·2; N, 6·6%), which gave a dark green ferric test. The ethereal extract yielded orange prisms, m. p. 187—188° (after crystallization from ethanol) (Found : C, 79·3; H, 6·2; N, 6·65%), which gave a red ferric test. The isomer, m. p. 238°, evolved ammonia when refluxed with ethanolic 2N-potassium hydroxide, but the compound, m. p. 187°, was recovered unchanged from prolonged refluxing with ethanolic 2N-potassium hydroxide.

*Action of Phenylmagnesium Bromide on 2-Methoxy-4-methyl*cycloheptatrienone.*—The reaction was carried out in benzene–ether solution as described above, and, after removal of the ether, the benzene solution was refluxed for 2 hr. before decomposition with ice and 2N-sulphuric acid. The diphenyl (1·8 g.) was removed in steam, and the aqueous residue was extracted with ether, and the products were absorbed on a column of alumina. Elution with light petroleum (b. p. 60—80°) gave diphenyl-*m*-tolylmethanol (0·8 g.), m. p. 67—68°, and further elution with 1 : 1 light petroleum (b. p. 60—80°)–benzene yielded 6(?)-*methyl-2-phenyl*cycloheptatrienone, which crystallized from *cyclo*hexane in pale buff prisms (2·6 g.), m. p. 98—99° (Found : C, 85·5; H, 6·1%), with properties similar to those described above for the isomer. The *phenylhydrazone* crystallized from ethanol in long orange prisms, m. p. 155—156° (Found : C, 83·7; H, 6·6; N, 9·7. $C_{20}H_{18}N_2$ requires C, 83·9; H, 6·3; N, 9·8%).

*Action of Phenylmagnesium Bromide on 2-Dimethylamino-6- and 2-Dimethylamino-4-methyl-*cycloheptatrienone.*—The dimethylamino-compound (I; R = NMe$_2$) (4·7 g.) in ether (200 c.c.) was added to phenylmagnesium bromide, prepared from magnesium (4·4 g.) and bromobenzene (28·3 g.) in ether (200 c.c.), and after refluxing for 6 hr. the solution was decomposed with ice (100 g.) and 36N-sulphuric acid. (10 c.c.). The ether was removed, diphenyl was distilled in steam, and the aqueous residue was continuously extracted with ether for 24 hr. The dried ethereal extract was absorbed on a charcoal column; elution with 1 : 1 light petroleum (b. p. 60—80°)–benzene gave 4(?)-methyl-2-phenyl*cyclo*heptatrienone (3·6 g.), m. p. 92—93° after crystallization from *cyclo*hexane.

In a similar manner, 6(?)-methyl-2-phenyl*cyclo*heptatrienone, m. p. 97—98°, was prepared from 2-dimethylamino-4-methyl*cyclo*heptatrienone (II; R = NMe$_2$).

*Action of Nitrous Acid on 2-Amino-6-methyl*cycloheptatrienone.*—Sodium nitrite (0·6 g.) in water (30 c.c.) was added to the amino-compound (I; R = NH$_2$) (1·0 g.) dissolved in water (30 c.c.) and 2N-hydrochloric acid (13 c.c.), the temperature being kept below —5°. Vigorous effervescence took place and the solution became brown, but on addition of a portion to alkaline

β-naphthol no azo-dye was produced. The remaining solution was distilled in steam; the 2-hydroxy-4-methylbenzaldehyde which separated from the first 20 c.c. of the distillate had m. p. 60—61° after crystallization from 50% ethanol and gave a semicarbazone as white platelets (from pentan-1-ol), m. p. 267—268° (Anselmino, *Ber.*, 1917, **50**, 395, gives m. p. 268°), and a 2 : 4-*dinitrophenylhydrazone*, which crystallized from glacial acetic acid in scarlet prisms, m. p. 266—267° (Found : C, 53·1; H, 4·0; N, 18·1. $C_{14}H_{12}O_5N_4$ requires C, 53·2; H, 3·8; N, 17·7%). The absence of β-methyltropolone in the steam-distillate was demonstrated by the failure of a chloroform extract to give a ferric test. The remaining steam-distillate (400 c.c.) was extracted with ether and acids were taken up in sodium hydrogen carbonate solution, recovered with ether, and crystallized from hot water (charcoal); *m*-toluic acid, m. p. 110—112°, was obtained and identified by comparison with an authentic specimen, and by preparation of the amide, m. p. 90—92°.

Action of Nitrous Acid on 2-Amino-4-methylcycloheptatrienone.—The reaction was carried out as described above, and two fractions (each 100 c.c.) of steam-distillate were collected. Fraction (1) gave 2-hydroxy-6-methylbenzaldehyde, which separated from 50% ethanol in pale yellow needles, m. p. 30—31° (Chuit and Bolsing, *Bull. Soc. chim.*, 1906, **35**, 139, give m. p. 31°); the semicarbazone crystallized from pentanol in colourless prisms, m. p. 213—214° (decomp.) (Chuit and Bolsing, *loc. cit.*, give m. p. 212—214°), and the 2 : 4-*dinitrophenylhydrazone* crystallised from acetic acid in elongated scarlet prisms, m. p. 262—263° (Found : C, 52·7; H, 3·6; N, 17·7. $C_{14}H_{12}O_5N_4$ requires C, 53·2; H, 3·8; N, 17·7%). The aldehyde was also converted into 2-hydroxy-6-methylbenzoic acid, m. p. 166—168°, by oxidation with alkaline silver oxide. Fraction (2) yielded *m*-toluic acid, but β-methyltropolone was not present in the steam-distillate.

2-iso*Butoxy*-6-*methyl*cyclo*heptatrienone* (I; R = OBu^i).—The methyl ether (I; R = OMe) (0·5 g.) was added to *iso*butanol (30 c.c.) containing a small amount (0·01 g.) of sodium. The alcohol was removed at 20 mm., and the colour of the solution changed from blue through green to brown. After dilution with ether, the solution was filtered from a small amount of solid and evaporated. Addition of methanolic picric acid to the residual red oil gave the *picrate* which crystallized from ethanol in yellow plates, m. p. 144—145° (decomp.) (Found : C, 51·0; H, 4·6; N, 10·1. $C_{18}H_{19}O_9N_3$ requires C, 51·3; H, 4·5; N, 10·0%). The ether, recovered from the picrate, was a pale yellow oil, b. p. 170°(bath)/0·5 mm., which was hydrolyzed to β-methyltropolone by hot acids or alkalis and gave 2-anilino-6-methylcycloheptatrienone, m. p. 121—122° (Part IX, *loc. cit.*), on being heated with excess of aniline at 150° for 11 hr.

Action of Sodium Methoxide on 2-Methoxy-6-methylcycloheptatrienone.—β-Methyltropolone methyl ether-A (I; R = OMe) (0·2 g.) was recovered unchanged after 80 min. in warm methanol (8 c.c.) containing sodium (0·04 g.), but 20 hr.' refluxing of the ether-A (1·0 g.) with sodium (0·2 g.) in methanol (40 c.c.) followed by evaporation gave a neutral oil converted by warm 4N-sodium hydroxide (5 c.c.) into *m*-toluic acid (0·005 g.), m. p. 108—111°.

2-*Chloro*-6-*methyl*cyclo*heptatrienone* (I; R = Cl).—2-Hydrazino-6-methylcycloheptatrienone (1·9 g.; m. p. 134—135°, not 124° as erroneously reported in Part IX, *loc. cit.*) in 10N-hydrochloric acid (5 c.c.) was added to a boiling solution of hydrated cupric sulphate (19 g.) in water (19 c.c.). After 3 min., when evolution of nitrogen had ceased, extraction with chloroform (6 × 50 c.c.) yielded an oil, b. p. 160° (bath)/0·3 mm., which solidified and crystallised from light petroleum (b. p. 60—80°) in long colourless prisms, m. p. 58—59° (Found : C, 62·3; H, 4·6; Cl, 22·5. C_8H_7OCl requires C, 62·2; H, 4·6; Cl, 22·9%). 2-Chloro-6-methylcyclohepta-trienone, which slowly decomposed, did not react with methanolic silver nitrate or 2 : 4-dinitro-phenylhydrazone, but it was converted into 2-anilino-6-methylcycloheptatrienone, m. p. 121—122°, by an excess of aniline at 140°.

Constitution of α'-Hydroxy-β-methyltropolone.—α'-Hydroxy-β-methyltropolone (0·3 g.) was shaken in alcohol (10 c.c.) with Adams's catalyst (0·028 g.) in hydrogen. Absorption ceased after 5 hr. when hydrogen uptake was 180 c.c. The non-ketonic oily product was oxidized in water (5 c.c.) containing 2N-sodium carbonate (8 c.c.) with potassium permanganate (0·8 g.). After 2 hr., the solution was acidified with 2N-sulphuric acid, reduced with sodium metabi-sulphite, and extracted with ether. The acidic portion was separated with sodium carbonate and recovered with ether as an oil which partly crystallized and gave an anilide which separated from alcohol in long plates, m. p. 199—200° alone or mixed with an authentic sample of the anilide of β-methyladipic acid.

Oxidation of γ-Hydroxy-β-methyltropolone with Nitrous Acid.—The hydroxy-compound (0·3 g.) was dissolved in boiling N-sulphuric acid (50 c.c.), and sodium nitrite (0·2 g.) in water (1 c.c.) gradually added. The brown-yellow precipitate was digested with a little hot alcohol, collected, sublimed at 290—300°/0·05 mm., and crystallized from formic acid as yellow needles,

m. p. >350° (Found : C, 67·4, 67·7; H, 4·2, 4·3. $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·3%), giving a positive ferric test in dioxan and a sparingly soluble orange sodium salt with aqueous sodium hydroxide. It did not react with boiling aniline, Brady's reagent, or sulphurous acid. The product (7 : 12-*dihydroxy-2-oxa*tricyclo[8 : 5 : 0$^{3:9}$]*pentadecane*-6 : 13-*dione*) (VII) (0·15 g.), acetic anhydride (1 c.c.), and a trace of pyridine were refluxed for 1 hr.; the *diacetate*, which separated on cooling, crystallized from acetic acid–alcohol in cream-coloured needles, m. p. 285° (decomp.) [Found : C, 64·9; H, 4·5%; *M* (Rast), 345. $C_{20}H_{16}O_7$ requires C, 65·2; H, 4·4%; *M*, 368] which regenerated the parent substance (VII) after brief warming with acid or alkali; the diacetate gave a green furan test with the Liebermann–Burckhardt reagent, but did not react with the aniline–hydrochloric acid reagent.

2 : 9-*Dimethylpyridino*[2, 3-*d*]*tropolone* (VIII).—γ-Amino-β-methyltropolone (0·3 g.), par-aldehyde (0·4 g.), and concentrated hydrochloric acid (1 c.c.) were refluxed for ½ hr. The dark mixture was diluted with water, filtered from a little amorphous material, basified with ammonia, and acidified with acetic acid. Extraction with ether (4 × 25 c.c.) and sublimation of the ethereal residue gave the *base* (0·5 g.) which separated from benzene in pale yellow needles, m. p. 192—193° (Found : C, 71·9; H, 5·7; N, 7·4. $C_{12}H_{11}O_2N$ requires C, 71·6; H, 5·5; N, 7·0%), dissolved in both acids and bases, and gave a brown ferric test. Methiodide formation was not observed in acetone.

Condensation of γ-Amino-β-methyltropolone with Ethyl Acetoacetate.—The γ-amine (0·3 g.) and ethyl acetoacetate (2 c.c.) were boiled for 2 min.; addition of a little methanol precipitated γ-(2-*ethoxycarbonyl-1-methylethylideneamino*)-β-*methyltropolone* (IX) (0·3 g.) which separated from methanol in cream-coloured prisms, m. p. 155—156° (Found : C, 61·4; H, 5·4; N, 6·3. $C_{12}H_{13}O_4N$ requires C, 61·3; H, 5·6; N, 6·0%), giving a green ferric test. Attempted cycliz-ation with concentrated sulphuric acid at 100° or 160—170°, fuming sulphuric acid (15% of SO_3) at 0°, or phosphoric acid containing 20% of phosphoric oxide at 100° gave γ-amino-β-methyltropolone.

Some Derivatives of β-*Formyltropolone* [with J. D. Hobson].—Attempts to form a phenyl-hydrazone gave a *phenylhydrazine* salt, which crystallized from benzene or aqueous methanol in red prisms, m. p. 126° (decomp.) (Found : C, 65·3; H, 5·4; N, 11·5. $C_{14}H_{14}O_3N_2$ requires C, 65·1; H, 5·4; N, 10·9%). β-Formyltropolone with *p*-toluidine in warm acetic acid gave an *azomethine* which separated from ethanol in yellow needles, m. p. 141—142° (Found : C, 75·0; H, 5·6; N, 6·0. $C_{15}H_{13}O_2N$ requires C, 75·3; H, 5·5; N, 5·9%).

β-*Methyl-γ-nitrotropolone O-Methyl Ether.*—Excess of ethereal diazomethane was added to β-methyl-γ-nitrotropolone and after 2 hr. at room temperature the precipitated *ether* was collected and crystallized from alcohol; yellow needles, m. p. 188—189° (Found : C, 55·8; H, 4·7; N, 7·3. $C_9H_9O_4N$ requires C, 55·4; H, 4·6; N, 7·2%), were obtained, which gave a negative ferric reaction and were rapidly hydrolyzed to β-methyl-γ-nitrotropolone with dilute neutral acid. Isomeric ethers could not be isolated from the mother-liquors.

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