

## 755. *Purpurogallin. Part IX.\* The Structure of the Isomeric O-Methyl Ethers of $\beta$ -Methyltropolone.*

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The methoxyl group of  $\beta$ -methyltropolone methyl ether-A or -B is readily replaced by the amino-, anilino-, or hydrazino-group, and the properties of these derivatives are described. The Stevens-McFadyen decomposition reaction has been applied to the hydrazino-derivatives-A and -B, and the products have been reduced to 3- and 4-methylcycloheptanone, respectively. Consequently the -A and the -B series are assigned structures (I) and (II), respectively.

IN Part IV of this series (*J.*, 1951, 561) attention was drawn to the existence of isomeric forms of the *O*-acyl and the *O*-alkyl derivatives of a number of tropolones. Two  $\beta$ -methyltropolone methyl ethers, m. p. 97° and m. p. 46°, were described and referred to as the methyl ethers -A and -B, respectively, the suffix A being ascribed arbitrarily to the higher-melting and less soluble ether until methods for determining the structure were developed.

Fernholz (*Chem. Ber.*, 1951, 84, 110) observed that benzene or chloroform solutions of perbenzoic acid oxidised the aromatic nucleus of certain phenolic ethers, including the dimethoxy- and trimethoxy-compounds colchicine and colchicine; the reactions have usually been followed by uptake of per-acid, but the products of the reaction were rarely determined. It was thought that perbenzoic acid might attack *O*-tetramethylpurpurogallin with the formation of a derivative of tropolone of known structure, but preliminary experiments showed that tropolone derivatives were not produced, and the reaction was not investigated further.

Although it has not been possible to replace the hydroxyl group of  $\beta$ -methyltropolone by chlorine, it was observed that  $\beta$ -methyltropolone methyl ethers-A and -B reacted with ammonia in sealed tubes to give the 2-aminomethylcycloheptatrienones-A and -B, m. p. 112° and 123°, respectively; during the course of these experiments Doering and Knox (*J. Amer. Chem. Soc.*, 1951, 73, 828) have described the preparation of 2-aminocycloheptatrienone from tropolone methyl ether. The reaction resembles the conversion of esters into amides and the products, like amides, were readily hydrolysed to  $\beta$ -methyltropolone by warming them with alkalis. The 2-amino-methylcycloheptatrienones formed *N*-acetyl derivatives, and stable hydrochlorides and sulphates, and a bright red azo-dye was precipitated when *p*-chlorobenzenediazonium chloride was added to alkaline solutions of the amino-tropolones. The amino-methylcycloheptatrienones reacted vigorously with nitrous acid at 0° without the formation of diazonium compounds; the nature of the products is under investigation. The 2-anilino-methylcycloheptatrienones-A and -B, m. p. 121° and m. p. 99°, respectively, were obtained either by heating the corresponding methyl ethers with methanolic aniline at 90°, or by refluxing the corresponding 2-amino-methylcycloheptatrienones with aniline. The methoxyl group of  $\beta$ -methyltropolone methyl ethers-A and -B may also be replaced by the hydrazino-grouping yielding the crystalline 2-hydrazino-methylcycloheptatrienones-A and -B, m. p. 124° and m. p. 135° respectively; the former was converted by the action of nitrous acid into 2-amino-methylcycloheptatrienone-A, m. p. 112°, described above. The 2-hydrazino-methylcycloheptatrienones-A and -B gave crystalline benzenesulphonyl derivatives, m. p. 199° and m. p. 188°, respectively, which, in the presence of sodium carbonate, undergo the Stevens-McFadyen (*J.*, 1936, 584) decomposition, and yield 3- and 4-methylcycloheptatrienone, respectively. These non-ketonic, basic substances (compare Dauben and Ringold; Doering and Detert, *J. Amer. Chem. Soc.*, 1951, 73, 876) were oils, which gave, on catalytic reduction, 3- and 4-methylcycloheptanone, respectively (Adamson and Kenner, *J.*, 1939, 181), which were identified by comparison of the semicarbazones, m. p. 179–180° and m. p. 158–160°, respectively, with authentic samples kindly supplied by Mlle. Tchoubar (Tchoubar, *Bull. Soc. chim.*, 1949, 16, 164). It follows from the above series of reactions that  $\beta$ -methyltropolone methyl ethers-A and -B are 2-methoxy-6- (I; R = OMe) and 2-methoxy-4-methylcycloheptatrienone (II; R = OMe), respectively, and dipole-moments measurements of the two methyl ethers, made by Dr. L. E. Sutton and Mr. M. F. Saxby at Oxford (personal communication from Dr. Sutton), support the constitutions now advanced. The structures of 2-amino- and 2-anilino-methylcycloheptatrienones-A,

\* Part VIII, *J.*, 1951, 2067.

prepared from (I; R = OMe), are therefore fixed as (I; R = NH<sub>2</sub>) and (I; R = NPh), and those of the B-isomers, prepared from (II; R = OMe), as (II; R = NH<sub>2</sub>) and (II; R = NPh), respectively.



The reactions mentioned above are fully consistent with the representation of the tropolone structure as a trivinyl analogue of a carboxylic acid, but the structures now assigned to the two methyl ethers of  $\beta$ -methyltropolone do not give a very ready explanation of the comparatively easy oxidation to the corresponding aldehyde (see Part IV, *loc. cit.*) or of the hygroscopic nature of the ether (II; R = OMe). The former may be related to the greater hyperconjugation associated with the extended conjugation of (II; R = OMe).

#### EXPERIMENTAL.

*2-Amino-6-methylcycloheptatrienone* (I; R = NH<sub>2</sub>).—2-Methoxy-6-methylcycloheptatrienone (I; R = OMe) (0.6 g., m. p. 96–97°) and methyl alcohol (5 c.c.), saturated with ammonia at room temperature, were heated in a sealed tube for 65 hours at 80°. The dark red solution was evaporated and the residue crystallised from water (charcoal) or cyclohexane; pale brown elongated prisms (0.4 g.), m. p. 111–112° (Found: C, 71.2; H, 6.9; N, 10.3. C<sub>8</sub>H<sub>9</sub>ON requires C, 71.1; H, 6.7; N, 10.4%). readily soluble in alcohol, moderately so in ether, and insoluble in light petroleum (b. p. 40–60°), were obtained, which gave a dark green ferric test in ethyl alcohol. The amine (I; R = NH<sub>2</sub>) was hydrolysed to  $\beta$ -methyltropolone by boiling it with 6*N*-sodium hydroxide solution (50 parts) for 20 hours.

*p*-Chlorobenzenediazonium chloride, prepared from *p*-chloroaniline (0.1 g.), *N*-hydrochloric acid (2 c.c.), and sodium nitrite (0.05 g.) in water (0.5 c.c.), was added to a suspension of the amine (I; R = NH<sub>2</sub>) (0.1 g.) in 1.5*N*-sodium hydroxide (9 c.c.); after 6 hours the bright red precipitate was collected, suspended in water and acidified with dilute hydrochloric acid. The red azo dye was collected, dried, and crystallised from cyclohexane. The hydrochloride separated from concentrated hydrochloric acid in elongated prisms, m. p. 248° (decomp.) (Found: N, 8.3. C<sub>8</sub>H<sub>9</sub>ONCl requires N, 8.1%). The sulphate crystallised from 40% sulphuric acid in small prisms, m. p. 204° (Found: N, 6.2. C<sub>8</sub>H<sub>11</sub>O<sub>2</sub>NS requires N, 6.0%). The picrate, prepared in aqueous solution, crystallised from aqueous ethyl alcohol in yellow elongated prisms, m. p. 197–198° (decomp.) (Found: C, 46.1; H, 3.5; N, 15.6. C<sub>8</sub>H<sub>9</sub>O<sub>2</sub>N<sub>2</sub> requires C, 46.2; H, 3.3; N, 15.4%).

*2-Acetamido-6-methylcycloheptatrienone* (I; R = NHAc), prepared by warming the amine (I; R = NH<sub>2</sub>) with acetic anhydride at 100° for 40 minutes, crystallised from water in elongated prisms, m. p. 115–116° (Found: C, 68.1; H, 6.4; N, 7.9. C<sub>10</sub>H<sub>11</sub>O<sub>2</sub>N requires C, 67.8; H, 6.3; N, 7.9%). Hydrolysis to the amine (I; R = NH<sub>2</sub>) was brought about by refluxing it for 20 minutes with 70% sulphuric acid (20 parts).

*2-Amino-4-methylcycloheptatrienone* (II; R = NH<sub>2</sub>).—This compound prepared as described above in the case of the isomer, separated from water or cyclohexane in light brown prisms, m. p. 123° (Found: C, 70.9; H, 6.9; N, 10.5%), which gave a dark green ferric test. Hydrolysis to  $\beta$ -methyltropolone was effected by heating it with 6*N*-sodium hydroxide. The hydrochloride, separated from concentrated hydrochloric acid in long prisms, m. p. 241° (decomp.) (Found: N, 8.2%), and the picrate crystallised from aqueous ethyl alcohol in yellow elongated prisms, m. p. 172–173° (decomp.) (Found: C, 46.0; H, 3.4%).

*2-Acetamido-4-methylcycloheptatrienone* (II; R = NHAc) crystallised from cyclohexane in elongated prisms, m. p. 114–115° (Found: C, 67.9; H, 6.5; N, 8.0%).

*2-Anilino-6-methylcycloheptatrienone* (I; R = NPh).—This was prepared from 2-amino-6-methylcycloheptatrienone (*a*) by refluxing it with aniline (20 parts) for 2 days or (*b*) by heating (I; R = OMe) with aniline (1.5 parts) and methyl alcohol (10 volumes) for 70 hours in a sealed tube at 80°; the anilino-compound crystallised from methyl alcohol in yellow elongated prisms, m. p. 121–122° (Found: C, 79.6; H, 6.3; N, 6.4. C<sub>14</sub>H<sub>13</sub>ON requires C, 79.6; H, 6.2; N, 6.6%).

*2-Anilino-4-methylcycloheptatrienone* (II; R = NPh).—When prepared as in method (*b*) described above, this anilino-compound separated from methyl alcohol or cyclohexane in yellow elongated prisms, m. p. 98–99° (Found: C, 79.5; H, 6.3; N, 6.5%).

*2-Hydrazino-6-methylcycloheptatrienone* (I; R = NH·NH<sub>2</sub>).—To a solution of 2-methoxy-6-methylcycloheptatrienone (I; R = OMe) (2 g.) in water (2 c.c.) was added 90% hydrazine hydrate (1.5 g.), and the mixture was warmed on the water-bath for 5 minutes. After cooling, the yellow crystalline precipitate was collected, and gave, after two crystallisations from water, 2-hydrazino-6-methylcycloheptatrienone (I; R = NH·NH<sub>2</sub>) as yellow needles (1.5 g.), m. p. 124° (Found: C, 63.7; H, 6.6; N, 18.6. C<sub>8</sub>H<sub>10</sub>ON<sub>2</sub> requires C, 64.0; H, 6.7; N, 18.6%). Dilution of the aqueous mother-liquors with water and extraction with ether yielded a further quantity (0.6 g.) of the hydrazide. The benzylidene derivative of (I; R = NH·NH<sub>2</sub>) was prepared by warming (I; R = NH·NH<sub>2</sub>) with excess of benzaldehyde; the mixture was cooled and diluted with light petroleum (b. p. 60–80°), and the yellow solid

was collected and crystallised from ethanol, giving yellow needles, m. p. 186° (Found: C, 75.4; H, 6.0; N, 11.9).  $C_{15}H_{14}ON_2$  requires C, 75.6; H, 6.0; N, 11.8%. The *benzenesulphonyl* derivative (I; R = NH·NH·SO<sub>2</sub>Ph) was obtained when benzenesulphonyl chloride (1.9 c.c.) was added slowly to a well-stirred solution of the hydrazino-derivative (I; R = NH·NH<sub>2</sub>) (2.2 g.) in pyridine (30 c.c.), cooled in an ice-salt bath. After  $\frac{1}{2}$  hour, the solution was poured into a mixture of ice (100 g.) and concentrated hydrochloric acid (40 c.c.), and the resulting orange solid was collected and washed with a small quantity of dilute hydrochloric acid, and then with water. Several crystallisations from alcohol (charcoal) gave pale buff-coloured needles, m. p. 199° (decomp.), of the benzenesulphonyl derivative (I; R = NH·NH·SO<sub>2</sub>Ph) (2.8 g.) (Found: C, 58.2; H, 5.0; N, 9.6).  $C_{14}H_{14}O_2N_2S$  requires C, 57.9; H, 4.9; N, 9.7%.

*2-Hydrazino-4-methylcycloheptatrienone* (II; R = NH·NH<sub>2</sub>).—When prepared in a similar manner from 2-methoxy-4-methylcycloheptatrienone (II; R = OMe) the *hydrazino*-compound (II; R = NH·NH<sub>2</sub>) crystallised from water in yellow needles, m. p. 134—135° (Found: C, 64.3; H, 6.9; N, 18.6%). The *benzenesulphonyl* derivative (II; R = NH·NH·SO<sub>2</sub>Ph), prepared from (II; R = NH·NH<sub>2</sub>) (3.1 g.) in exactly the same way as the isomer, crystallised from ethanol (charcoal) in buff-coloured needles, m. p. 188° (decomp.) (Found: C, 58.3; H, 4.6; N, 10.2%).

*Degradation of 2-Benzenesulphonhydrazido-6-methylcycloheptatrienone* (I; R = NH·NH·SO<sub>2</sub>Ph).—To a solution of (I; R = NH·NH·SO<sub>2</sub>Ph) (m. p. 124°) (1.0 g.) in ethylene glycol (25 c.c.), heated in an oil-bath to 140°, was added anhydrous sodium carbonate (2 g.). Heating was continued for 5 minutes after the vigorous evolution of gas had subsided, and the dark brown mixture was cooled, diluted with water, and extracted with chloroform. The chloroform solution was washed with water and extracted three times with 4*N*-hydrochloric acid (30 c.c.), and, after being washed with chloroform, the acid extract was neutralised with sodium hydrogen carbonate, and the oil isolated with ether. The product showed no ketonic properties, gave no colour with ferric chloride, and did not yield a picrate with an aqueous solution of picric acid.

The oil (0.2 g.) was shaken in ethanolic solution with hydrogen over a 10% palladium-charcoal catalyst until there was no further absorption; 97 c.c. (2.6 mols.) of hydrogen were absorbed. The filtered solution gave a sweet-smelling oil, which yielded 3-methylcycloheptanone semicarbazone, m. p. 179—180° after several crystallisations from ethyl acetate (Found: C, 58.6; H, 9.5; N, 23.1. Calc. for  $C_8H_{11}ON_3$ : C, 59.0; H, 9.4; N, 23.0%). This melting point was not depressed on admixture of the compound with an authentic specimen, m. p. 180—181°.

*Degradation of 2-Benzenesulphonhydrazido-4-methylcycloheptatrienone* (II; R = NH·NH·SO<sub>2</sub>Ph).—(II; R = NH·NH·SO<sub>2</sub>Ph) was hydrolysed under exactly similar conditions, and the acid-soluble fraction of the products was hydrogenated over a palladium catalyst, giving a neutral oil from which 4-methylcycloheptanone semicarbazone was prepared. After several crystallisations from ethyl acetate this had m. p. 158—160° (Found: C, 59.1; H, 9.7; N, 23.3%), undepressed on admixture of the specimen with an authentic specimen, m. p. 157—158°.

*Action of Nitrous Acid on 2-Hydrazino-6-methylcycloheptatrienone* (I; R = NH·NH<sub>2</sub>).—To a solution of (I; R = NH·NH<sub>2</sub>) (0.7 g.) in *N*/2-hydrochloric acid (12 c.c.), cooled in an ice-bath, was added a cold solution of sodium nitrite (0.32 g.). The resulting pale cream precipitate was collected and dissolved in absolute ethanol; the solvent was removed on a water-bath, giving a pale brown gum. To this was added 2*N*-sodium hydroxide (10 c.c.), and after being warmed for 2 minutes the mixture was cooled and extracted with ether. Evaporation of the extract yielded a dark brown viscous oil which was extracted several times with boiling *cyclohexane*, from which, on concentration and cooling were obtained pale yellow leaflets, m. p. 112° (0.3 g.), of 2-amino-6-methylcycloheptatrienone (I; R = NH<sub>2</sub>) (Found: C, 71.3; H, 6.9; N, 10.3%) which gave no depression in melting point when mixed with a specimen prepared as described on p. 3428.

Acidification of the alkaline mother-liquors from the ether extraction, and isolation with ether yielded a small quantity of a yellow solid, which crystallised from aqueous methanol in yellow needles, m. p. 145°. This contained nitrogen (Found: N, 23.4%), was soluble in dilute hydrochloric acid, insoluble in sodium hydrogen carbonate solution, and gave no ferric colour, but was not obtained in sufficient quantity for identification.

Our thanks are due to the Department of Scientific and Industrial Research for maintenance allowances to two of us and to Imperial Chemical Industries Limited for a grant towards the expenses of this investigation.

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[Received, August 18th, 1951.]