Tropolones. Part VIII. Synthesis and Properties of 7-Hydroxybenzo*cyclo*heptatrien-3-one.*

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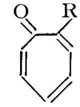
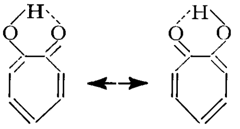
The bicyclic compound (X), named in the title, has been synthesised from benzo*cyclo*heptene-3 : 7-dione (VI), and its properties compared with those of αβ-benzotropolone.

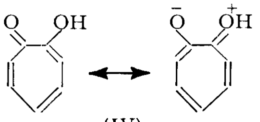
Considerations of fine structure have led to two conflicting views on the aromaticity of tropolone (I). The first was advanced by Dewar (*Nature*, 1945, **155**, 50), who originally postulated hydrogen-bonded structures (III) as the principal resonance forms, but later (*idem*, *ibid.*, p. 479) modified this in favour of the ionic resonance structures (IV). Koch (*J.*, 1951, 512) subscribed to this latter view on the basis of infra-red studies, and postulated simple prototropy to account for the symmetry of the molecule. These views agree in implicating both oxygen atoms in the fundamental resonance of the molecule. They are, however, open to the criticism (Cook and Loudon, *Quart. Reviews*, 1951, **5**, 99) that the bond between the oxygen-bearing carbon atoms is always represented as a single bond, whereas, lack of double-bond character is not substantiated by bond-length measurements (Robertson, *J.*, 1951, 1222). A second view, relating tropolone to *cyclo*heptatrienone (II), suggests that the latter is the parent substance of this new aromatic system (Buchanan, *Chem. and Ind.*, 1952, 855; Doering and Knox, *J. Amer. Chem. Soc.*, 1952, **74**, 5683). This implies major contributions from structures (V) in agreement with Nozoe's opinion (*Proc. Japan Acad.*, 1950, **26**, 30), and seems more satisfactory since it demands a regular heptagon structure, in agreement with *X*-ray data (Robertson, *loc. cit.*). It implies, however, that the second oxygen atom is not involved in the fundamental resonance of the molecule, and hence, that its position in the ring may be varied without affecting the fundamental character of the ring. It is therefore of interest to examine the properties of isomeric structures (*i.e.* *iso*tropolones) in which the oxygen atoms are not vicinal. The present communication describes the preparation and properties of 7-hydroxybenzo*cyclo*heptatrien-3-one (X), an isomer of αβ-benzotropolone (XII).



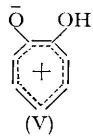
(I; R = OH)
(II; R = H)



(III)



(IV)



(V)

Preparation of the hydroxy-ketone (X) was attempted initially by the methods used in the preparation of the tropolone (XII) (Cook and Somerville, *Nature*, 1949, **163**, 410; Cook, Gibb, Raphael, and Somerville, *J.*, 1952, 603). Dehydrogenation of the dione (VI) by means of palladium–charcoal, however, failed to give an acidic product, and bromination by bromine in glacial acetic acid followed by alkali treatment yielded only dark oils. A much cleaner reaction took place with *N*-bromosuccinimide, and the bromo-derivative was readily dehydrobrominated by aqueous trimethylamine, affording a product, $C_{11}H_8O_2$, which gave a bis-2 : 4-dinitrophenylhydrazone but no picrate. It was insoluble in aqueous alkali, stable towards cold aqueous potassium permanganate, and failed to give a colour with ferric chloride. Such properties are incompatible with structure (X) (see below), and the compound is provisionally assigned the formula (VII).

To avoid ring formation during the dehydrogenation of the diketone (VI) the latter was converted by means of *iso*propenyl acetate (Hagemeyer and Hull, *Ind. Eng. Chem.*, 1949, **41**, 2920) into the bis-enol acetate (VIII), which was brominated by means of *N*-bromosuccinimide. This type of reaction produces αβ-unsaturated ketones (Gallacher, *J. Org.*

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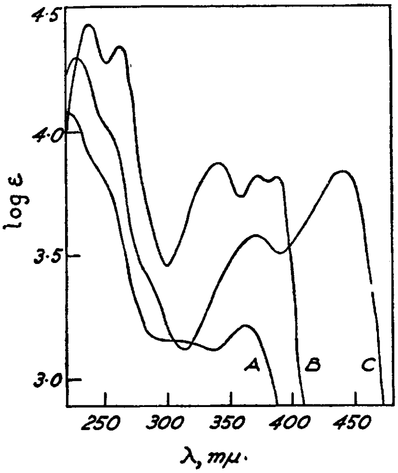
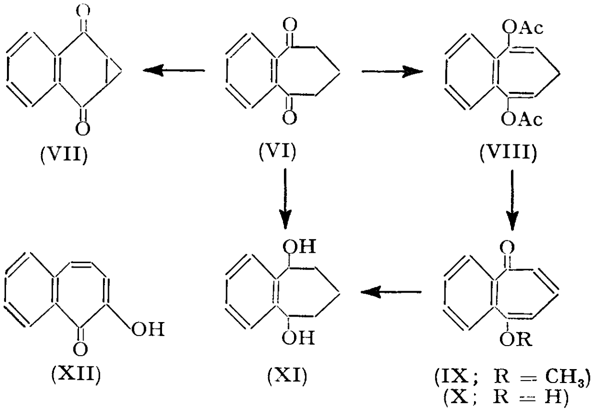
* Part VII, *J.*, 1954, 530.

Chem., 1949, **14**, 660), and the neutral oily product obtained here is presumably the acetate of (X). Alkaline hydrolysis followed by acidification gave 7-hydroxybenzo*cyclo*heptatrien-3-one (X) as a yellow solid, readily subliming *in vacuo*. It behaves as an acid (p*K* 6·40), dissolves with effervescence in sodium hydrogen carbonate solution, and rapidly decolorizes aqueous potassium permanganate. Its structure was confirmed by its reduction to the diol (XI), which can also be prepared from the diketone (VI).

The *iso*tropolone (X) resembles αβ-benzotropolone (XII) in some respects. It gives a 3 : 5-dinitrobenzoate, an oily acetate, a yellow picrate, a red-brown colour with ferric chloride, and it couples with diazotised aniline, giving a crimson dye. It also forms unstable salts with hydrochloric and perchloric acids, but in contrast to (XII) it forms a 2 : 4-dinitrophenylhydrazone, is almost insoluble in non-polar solvents, fails to form a copper complex, and is not affected by fusion with potassium hydroxide at 220°. Being more acidic than the tropolone (XII) it reacts readily with ethereal diazomethane, and the resulting methyl ether (IX) resembles tropolone methyl ether (Cook, Gibb, Raphael, and Somerville, *J.*, 1951, 503) in forming a stable hemihydrate and in being readily hydrolysed by dilute alkali. During the purification of the methyl ether (IX), a quantity of substance (VII) was isolated, and a fuller examination of this material will be reported later.

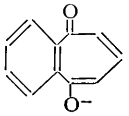


A, *7-Methoxybenzo*cyclo*heptatrien-3-one* (IX).
B, *αβ-Benzotropolone* (XII).
C, *7-Hydroxybenzo*cyclo*heptatrien-3-one* (X).
Solvent : ethanol.

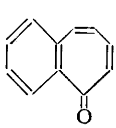


Further evidence of similarity between the *iso*tropolone (X) and αβ-benzotropolone (XII) is to be seen in their ultra-violet absorption spectra. The absorption spectrum of the methyl ether (IX) is also given in the Figure.

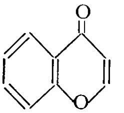
These results indicate a general similarity between the *iso*tropolone (X) and αβ-benzotropolone (XII), but they do not provide unequivocal evidence of aromatic character. The acidity, salt formation, coupling, and coloration with ferric chloride displayed by (X) may equally be the properties of a conjugated enol-ketone. The fact that (X) is a stronger acid than the tropolone (XII) is to be expected, since resonance in the anion (XIII) involves two identical canonical structures, but the appearance of ketonic properties in (X) requires further comment. It is evident that oxygenated derivatives of benzo*cyclo*heptatrien-3-one (XIV) only show ketonic properties when there is no possibility of hydrogen interaction between the two oxygen atoms. Thus both αβ- and βγ-benzotropolones are devoid of ketonic activity though their methyl ethers, and their isomer (X) gives normal ketone derivatives (Cook, Gibb, Raphael, and Somerville, *ibid.*, 1952, 603; Tarbell and Bill, *J. Amer. Chem. Soc.*, 1952, **74**, 1234). The electronic (+*E*) effect exerted by the hydroxy- or methoxy-groups has no apparent effect on the character of the carbonyl function. In the monocyclic series (II) the evidence is not complete; however, it seems to indicate that in this case the electronic (+*E*) effect of substituents is the important factor. Thus *cyclo*heptatrienone (II) gives ketonic derivatives (Doering, *Chem. Eng. News*, 1953, 2677; Nozoe, *Proc. Japan Acad.*, 1952, **28**, 477), although tropolone (I) and its methyl ether, 2-amino*cyclo*heptatrienone (XVI) (Nozoe, *Sci. Rep. Tohoku*, 1952, **36**, 126) and thiotropolone (XVII) (*idem, Proc. Japan Acad.*, 1953, **29**, 22) are all devoid of ketonic properties. Hydrogen bonding has no apparent effect on the character of the carbonyl function. This difference between the monocyclic and the benzo-series, finds a parallel in the chemistry of γ-pyrone and its benzo-derivative, chromone (XV). In the former, the electronic (+*E*) effect of the heterocyclic oxygen atom suppresses the ketonic properties of the carbonyl group, but in the latter (XV) its effect is so diminished that normal ketone derivatives are formed (Elderfield, " Heterocyclic Compounds," Wiley and Co., New York, 1951, Vol. 2, p. 254).



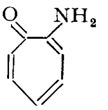
(XIII)



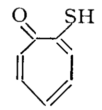
(XIV)



(XV)



(XVI)



(XVII)

EXPERIMENTAL

Benzo*cyclo*heptene-3 : 7-dione (VI) was prepared by the method of Barltrop, Johnson, and Meakins (*J.*, 1951, 181).

*Dehydrogenation of Benzo*cyclo*heptene-*3 : 7-*dione.*—(*a*) A solution of the dione (VI) (2 g.) in 1 : 2 : 4-trichlorobenzene (50 c.c.) was refluxed with palladium–charcoal (5%; 4 g.) for 12 hr. under nitrogen, and the filtered solution extracted with dilute sodium hydroxide solution. Acidification and ether extraction yielded nothing.

(*b*) The dione (VI) (1 g.) in glacial acetic acid (5 c.c.) was treated with bromine (0·95 g., 1·1 mol.) in glacial acetic acid (10 c.c.); when warmed on the steam-bath, the solution became almost colourless, hydrogen bromide was evolved, and the colour reappeared. The solution was concentrated *in vacuo*, made alkaline with sodium hydroxide solution, washed with chloroform, and acidified. This gave a dark intractable gum.

(*c*) A solution of the dione (VI) (2·6 g.) in chloroform (10 c.c.) and carbon tetrachloride (10 c.c.) was refluxed with *N*-bromosuccinimide (2·6 g.) for 15 min. under a 200-watt lamp. The solution was then washed with water and concentrated *in vacuo* to a pale yellow oil. An excess of aqueous trimethylamine was added, and the mixture warmed on the steam-bath for 5 min., and left overnight. The resulting solid *product* crystallised from dilute methanol, and was further purified by chromatography in benzene on alumina. Recrystallisation from ethanol gave plates, m. p. 130—131° (Found : C, 76·8; H, 4·8. $C_{11}H_8O_2$ requires C, 76·7; H, 4·65%). This substance, for which structure (VII) is advanced, gave no picrate, decolorised aqueous potassium permanganate solution very slowly, and was insoluble in sodium hydroxide solution. It failed to give a colour with aqueous or alcoholic ferric chloride, but yielded a *bis*-2 : 4-*dinitrophenylhydrazone* which crystallised from nitrobenzene in scarlet micro-needles, m. p. 318° (decomp.) (Found : N, 20·75. $C_{23}H_{16}O_8N_8$ requires N, 21·05%).

3 : 7-*Diacetoxybenzo*cyclo*hepta*-1 : 3 : 6-*triene* (VIII).—A solution of the dione (VI) (15 g.) and toluene-*p*-sulphonic acid (0·75 g.) in *iso*propenyl acetate (120 c.c.) was refluxed for 16 hr., and

then distilled until 80—100 c.c. had been collected. The residue was dissolved in benzene, and the solution washed with dilute sodium carbonate solution and then with water, and finally concentrated *in vacuo* to an oil. This oil was triturated with ether, the solid *diacetate* filtered off, and the filtrate re-concentrated and re-cycled. From four operations the yield was 15·5 g. The diacetate crystallised from methanol in cream rhombs, m. p. 125—126° (Found: C, 69·6; H, 5·6. $C_{15}H_{14}O_4$ requires C, 69·8; H, 5·4%).

*7-Hydroxybenzo*cyclo*heptatrien-3-one* (X).—The diacetate (VIII) (3 g.), in carbon tetrachloride (65 c.c.), was heated under reflux with *N*-bromosuccinimide (2·1 g.) and a trace of dibenzoyl peroxide, for 5 hr., under a 200-watt lamp. The solution was then washed with water and concentrated *in vacuo*. The resulting pale yellow oil was heated on the steam-bath for 30 min. with an excess of dilute sodium hydroxide solution and a few drops of ethanol. This gave a dark red solution, which was filtered and acidified. The yellow precipitate was washed, dried on a tile, and sublimed at 150—180°/10^{-4} mm., yielding 0·65 g. of the *hydroxy-ketone*, m. p. 188° (Found: C, 76·6; H, 4·8. $C_{11}H_8O_2$ requires C, 76·7; H, 4·65%). This compound was soluble in sodium hydrogen carbonate solution, and rapidly decolorised aqueous potassium permanganate. It gave a reddish-brown colour with ferric chloride in ethanol, but did not react with copper salts. Its *picrate* crystallised from dilute methanol in yellow needles, m. p. 155—158° (Found: C, 50·65; H, 3·2; N, 10·3. $C_{11}H_8O_2,C_6H_3O_7N_3$ requires C, 50·9; H, 2·7; N, 10·5%); an unstable *hydrochloride* was prepared by passing dry hydrogen chloride through a solution of the hydroxy-ketone in dry acetone; it crystallised from acetone–ether in buff needles, m. p. 150° (decomp.) (Found: C, 58·45; H, 5·1. $C_{11}H_8O_2,HCl,H_2O$ requires C, 58·2; H, 4·9%), and slowly lost hydrochloric acid. On the addition of water, it rapidly reverted to the yellow hydroxy-ketone, m. p. and mixed m. p. 186—188°. Treatment with aqueous perchloric acid gave a brown solution, from which brown needles were obtained by concentration. These decomposed violently when heated. When the hydroxy-ketone was heated with acetic anhydride, it gave an oily product, but on treatment with 3 : 5-dinitrobenzoyl chloride in dry benzene–pyridine, yielded a solid 3 : 5-*dinitrobenzoate*, m. p. 186° (Found: C, 59·3; H, 2·95; N, 7·4. $C_{18}H_{10}O_7N_2$ requires C, 59·0; H, 2·7; N, 7·65%). It also gave a *mono*-2 : 4-*dinitrophenylhydrazone*, m. p. 198° (Found: N, 15·9. $C_{17}H_{12}O_5N_4$ requires N, 15·8%), and reacted readily with ethereal diazomethane, to give an oil *methyl ether hydrate*, b. p. 170—172° (bath)/1·5 mm. (Found: C, 73·85; H, 5·9. $C_{12}H_{10}O_2,\frac{1}{2}H_2O$ requires C, 73·8; H, 5·6%). This ether was readily hydrolysed by aqueous alkali at 100° to the parent hydroxy-ketone (X), and an attempt to form the picrate of the ether gave instead the picrate, m. p. and mixed m. p. 155°, of the hydroxy-ketone. A solid by-product isolated during the purification of the ether crystallised from carbon tetrachloride in needles, m. p. 129—130° (Found: C, 76·6; H, 4·85. Calc. for $C_{11}H_8O_2$: C, 76·7; H, 4·65%). It gave no depression in mixed m. p. with the tricyclic ketone (VII). The hydroxy-ketone (X) in alkaline solution coupled with diazotised aniline, yielding a crimson dye. An electrometric titration carried out on a 30% alcoholic solution, by Dr. J. C. Speakman, indicated a p*K* value of 6·40. From this, the estimated value in water is *ca.* 6·1.

Hydrogenation.—(*a*) The dione (VI) (1 g.) in ethanol (10 c.c.) was reduced in presence of Adams's (PtO_2) catalyst (0·1 g.). Uptake was rapid until 2 mols. of hydrogen had been absorbed and slow thereafter. Concentration gave the *diol* (XI), which crystallised from aqueous alcohol in needles, m. p. 179—180° (Found: C, 74·4; H, 8·1. $C_{11}H_{14}O_2$ requires C, 74·2; H, 7·9%). The slow uptake probably represents hydrogenolysis of the diol.

(*b*) The hydroxy-ketone (X) (0·1 g.), in ethanol (5 c.c.), was hydrogenated in presence of palladium–calcium carbonate (2%; 0·75 g.). Uptake almost ceased after 3·6 mols. of hydrogen had been absorbed, and the product crystallised in needles, m. p. and mixed m. p. with (XI) 178—179°.

Alkali Fusion.—The hydroxy-ketone (X) (40 mg.) was added to a melt of potassium hydroxide (1 g.) and water (0·3 c.c.), and heated at *ca.* 220° with intermittent stirring for 30 min. After the melt had cooled water was added and the solution was filtered. Acidification yielded starting material, which was identified by mixed m. p.

Absorption Spectra.—These were determined by using a "Unicam" Spectrophotometer.

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