516. *Tropolones. Part IX.** 2 : 3-*Dihydro*-2 : 3-*methylene*-1 : 4-*naphthaquinone.*

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Synthetic and other evidence is advanced which confirms that the compound (XVII) named in the title is a dehydrogenation product of benzo*cyclo*heptene-3 : 7-dione (XII). A number of related compounds have been synthesised and studied.

IN Part VIII * of this series, which describes the synthesis of a 4-hydroxy-2 : 3-benzotropone † (II), it was found that bromination of the dione (XII) and subsequent alkali-treatment of the product (XVI) gave an isomeric substance for which the *cyclo*propane structure (XVII) was proposed. This substance was also obtained (Part VIII) from 4-hydroxy-2 : 3-benzotropone (II) *via* its methyl ether and, in view of the novelty of this rearrangement, it was desirable to establish the structure of the product firmly. This communication describes work which verifies the structure (XVII).

As previously described, the dehydrobromination product is insoluble in alkali, is stable to oxidation, and behaves as a diketone. These results have been corroborated by the preparation of a dioxime, and the recovery of the product (XVII) unchanged after attempted oxidations with alkaline permanganate, nitric acid, and chromium trioxide. In contrast, the parent diketone (XII) is readily oxidised to phthalic acid by dilute nitric acid.

Comparison of the infrared spectrum of the product (XVII) with that of the diketone (XII) (both in potassium chloride discs) revealed in the former an extra band (3040 cm.$^{-1}$), attributable to the aromatic C–H stretching frequency, or more probably, to a free $>CH_2$ in a *cyclo*propane ring.[1] It is also consistent with the formula (XVII) that whilst the diketone (XII) shows C–H stretching (2940 and 2870 cm.$^{-1}$) and C–H deformation (1456 and 1439 cm.$^{-1}$) bands typical of $>CH_2$ groups in polymethylene chains, the *cyclo*propane derivative does not absorb in these regions. The carbonyl band appears at 1680 cm.$^{-1}$, and this agrees with the value found for mesityl *cyclo*propyl ketone.[2] *cyclo*Propane derivatives are also reported [3] to absorb near 1000 cm.$^{-1}$, but although the product (XVII) shows absorption at 1000 cm.$^{-1}$ (in Nujol), the usefulness of this band is decreased by the presence of a band at 1005 cm.$^{-1}$ (in Nujol) from the diketone (XII). Sorrie and Thomson [4] have already noted this difficulty in a similar pair of compounds (XXV and XXVI) (see below). These authors also claim that comparison of the ultraviolet absorption spectra of their compounds show in the former a displacement of *ca.* 50 mμ in the position of the long-wavelength absorption band. They attribute this to conjugation of the *cyclo*propane ring with neighbouring double bonds. In comparing the ultraviolet spectra of our compounds (XII) and (XVII) (see Fig. 1) we have found only a trifling displacement (*ca.* 5 mμ) of this band; the principal difference between the two curves is the suppression of the middle peak, but this appears to be characteristic of the *cyclo*propane series (see Table 1).

An initial attempt was made to prove the constitution of the product (XVII) by treating the bis-β-keto-ester (XI) with one mol. of *N*-bromosuccinimide and dehydrobrominating the product with alkali. This yielded an alkali-insoluble product (X) and the expected similarity of this to the earlier product (XVII) is reflected in their ultraviolet spectra (see Table 1). It is also consistent with structure (X) that the infrared spectrum shows normal ketone and ester C=O bands (1694 and 1748 cm.$^{-1}$). In the bicyclic compound (XI) these are moved to 1608 and 1640 cm.$^{-1}$ by hydrogen bonding in the enol form. The tricyclic compound (X) also shows a band at 3070 cm.$^{-1}$ which is absent in the bicyclic analogue (XI), and is probably due to the *cyclo*propane $>CH_2$ group.[1] It was hoped to hydrolyse this β-keto-ester (X) under " ketonic " and " acidic " conditions, to yield

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* Part VIII, *J.*, 1954, 1060.

† In Part VIII, the 4-hydroxytropone system was termed an *iso*tropolone.

[1] Cole, *J.*, 1954, 3807.

[2] Fuson and Baumgartner, *J. Amer. Chem. Soc.*, 1948, **70**, 3255.

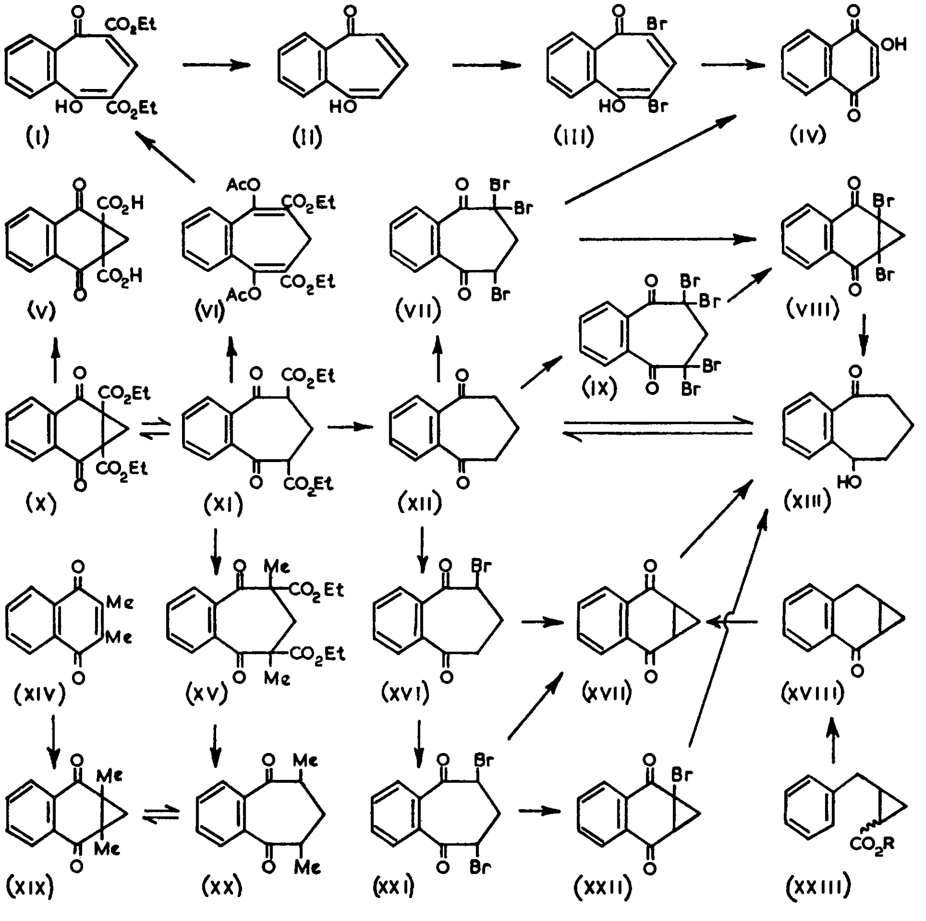
[3] Slabey, *ibid.*, 1954, **76**, 3604.

[4] Sorrie and Thomson, *J.*, 1955, 2238.

TABLE 1.

	$\lambda_{max.}$ (log ε)		
*Derivatives of benzo*cyclo*heptene-*3 : 7*-dione*			
4 : 6-Dimethyl (XX)	220 (4·38)	254 (3·89)	293 (3·30)
4 : 6-Diethoxycarbonyl-4 : 6-dimethyl (XV)	224 (4·40)	252 (3·93)	296 (3·31)
4 : 6-Diethoxycarbonyl (XI)	252 (4·56)	270 (4·37)	308 (4·08)
Derivatives of 2 : 3*-dihydro-*2 : 3*-methylene-*1 : 4*-naphthaquinone*			
2 : 3-Dicarboxylic acid (V)	227 (4·47)	305 (3·35)	
2-Bromo (XXII)	225 (4·45)	301 (3·38)	
2 : 3-Dibromo (VIII)	227 (4·46)	303 (3·36)	
2 : 3-Dimethyl (XIX)	222 (4·61)	300 (3·28)	
2 : 3-Diethoxycarbonyl (X)	227 (4·51)	304 (3·39)	

on the one hand the *cyclo*propane diketone (XVII), and on the other a mixture of phthalic acid and a *cyclo*propanedicarboxylic acid. However, " ketonic " hydrolysis gave the bis-β-keto-acid (V), and our attempts to decarboxylate it led to decomposition or returned the starting material. " Acidic " hydrolysis gave phthalic acid, but no other product could be isolated.



With the failure of this approach, it was decided to investigate the preparation of the product (XVII) by an accredited *cyclo*propane route. Kohler and Conant [5] have obtained *cyclo*propane derivatives by the action of sodium iodide in acetone on certain 1 : 3-dibromo-compounds; and when this method was applied to the crude dibromination product from

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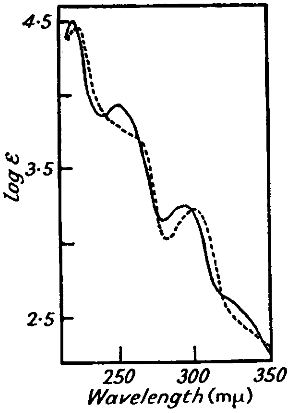
[5] Kohler and Conant, *J. Amer. Chem. Soc.*, 1917, **39**, 1404.

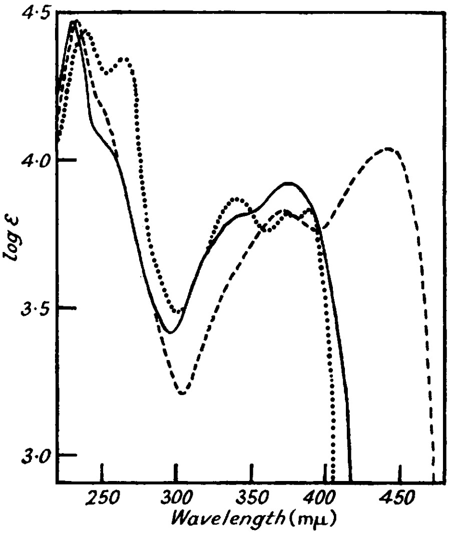
the diketone (XII), presumably (XXI), there was smooth formation of the product (XVII). The same dibromo-diketone, on treatment with aqueous trimethylamine, afforded a bromine-containing product which is formulated as (XXII) on the basis of its ultraviolet spectrum (see Table 1), and the inertness of the halogen atom to sodium acetate, sodium iodide, and sodium hydroxide (cf. Sorrie and Thomson [4] who have noted the same lack of reactivity in similar compounds). The unpurified material from tribromination of the diketone (XII), assumed to be the tribromo-diketone (VII), reacted similarly with trimethylamine to give a dibromo-product (VIII), and here again, the halogen atoms were inert and the ultraviolet spectrum was typical of this series (Table 1). It was hoped to prepare the monobromo-compound (XXII) from the tribromo-ketone (VII) by the action of sodium iodide in acetone, but the product was a mixture and no pure component could be isolated. The crude tetrabrominated ketone, presumed to be (IX), yielded the same dibromo-product on treatment with either aqueous trimethylamine or sodium iodide in acetone. The monobromo*cyclo*propane compound (XXII) afforded only a mono-oxime, and in all attempts to prepare an oxime of the dibromo-analogue (VIII) the starting material was recovered.

FIG. 1.



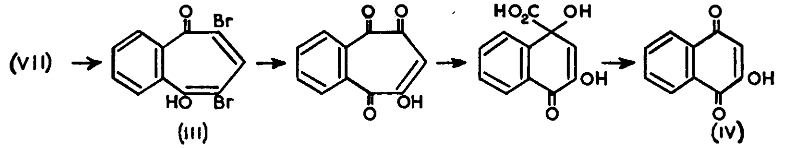
——— *Benzo*cyclo*heptene*-3 : 7-*dione* (XII).
– – – – 2 : 3-*Dihydro*-2 : 3-*methylene*-1 : 4-*naphthaquinone* (XVII).

FIG. 2.



. . . . *αβ-Benzotropolone.*
4-*Hydroxy*-2 : 3-*benzotropone* (II), ——— *in acid*,
– – – – *in alkali.*

The effect of aqueous alkali on the tribromo-diketone (VII) deserves special mention, for, although this reagent can effectively replace aqueous trimethylamine in the dehydrobromination of the monobromo-ketone (XVI) to the *cyclo*propane derivative (XVII), it hydrolyses and rearranges the tribromo-ketone (VII) to 2-hydroxy-1 : 4-naphthaquinone (IV). In considering the mechanism of this transformation, the most plausible intermediate seemed to be the dibromo-4-hydroxybenzotropone (III) :



In order to test this, the 4-hydroxybenzotropone (II) was brominated and gave a dibromo-derivative which is assigned the structure (III). That the halogen atoms are in the 7-membered ring is shown by its oxidation to phthalic acid, whilst its ultraviolet spectrum (see Table 2) agrees with its formulation as a 4-hydroxytropone. The orientation of the bromine atoms adjacent to the oxygenated carbons seems most probable in the light of Nozoe's work on 4-hydroxytropone.[6] On treatment with hot aqueous alkali or, preferably, with solid potassium hydroxide at 110° the dibromo-compound gave 2-hydroxy-1 : 4-naphthaquinone (IV). This supports not only the above mechanism, but also the orientation of the bromine atoms. Ring contraction of tropolones or 2-halogenotropones induced by alkali normally gives aromatic carboxylic acids,[7] and the ring contractions of hydroxylated tropolones are usually difficult, or even impossible to achieve; [8] it is therefore noteworthy that the above rearrangement takes the course it does, and that it proceeds under very mild conditions.

TABLE 2.

Derivative of 4-hydroxy-2 : 3-benzotropone	$\lambda_{max.}$ (log ε)	
5 : 7-Dibromo (III)	236 (4·32)	266 (4·18)
	330 (3·86)	390 (3·76)
5 : 7-Diethoxycarbonyl (I)	241 (4·45)	336 (4·11)

*cyclo*Propane derivatives are also obtained by the addition of diazomethane to double bonds, but, when diazomethane is added to naphthaquinone, the product is known to enolise and then be oxidised to the diazole (XXIV) which cannot be pyrolysed to a *cyclo*propane derivative.[9] Since this enolisation would be impossible in 2 : 3-dimethylnaphthaquinone (XIV), this substance was allowed to react with an excess of diazomethane, and the oily product was pyrolysed. This afforded a product which resisted oxidation with alkaline permanganate, showed the characteristic ultraviolet spectrum of the diketo-*cyclo*propane derivatives (see Table 1), and is accordingly formulated as (XIX). Like the dibromo-compound (VIII), it failed to give an oxime but, surprisingly, it yielded a mono-2 : 4-dinitrophenylhydrazone. The same compound was obtained from the β-keto-ester (XI) by dimethylation, hydrolysis of the product (XV) to 4 : 6-dimethylbenzo*cyclo*heptene-3 : 7-dione (XX), and cyclisation by the bromine–sodium iodide route described above. The product was not obtained pure but its 2 : 4-dinitrophenylhydrazone was shown to be identical with that derived from the compound (XIX) by a mixed m. p. determination and by comparison of the infrared spectra. The synthesis of this substance from both 6- and 7-membered-ring precursors firmly establishes its structure, and serves also to confirm the other *cyclo*propane-diketone formulæ discussed above.

Although the issue was thus beyond doubt, it was still of interest to find an alternative route to the parent compound (XVII) of the *cyclo*propane series, and this was achieved from allylbenzene. Allylbenzene was prepared by Bredereck's method,[10] when another method [11] failed. With diazoacetic ester it gave a mixture of esters (XXIII; R = Et) which was hydrolysed to a mixture of acids (XXIII; R = H). Neither of these mixtures was analysed, but the latter gave two anilides of m. p. 99—100° and 124—126°. When the mixture of acids was cyclised under Friedel–Crafts conditions, it yielded a ketone (XVIII), and a residual acid, which was characterised as its anilide, m. p. 124—126° : this derivative was identical with the higher-melting isomer described above, and no trace of the lower-melting anilide was found. It can be seen from molecular models that only in the *cis*-acid is the carboxyl group close enough to the aromatic ring to allow cyclisation; thus it follows that the higher-melting anilide has the *trans*-configuration, and the lower-melting anilide is its *cis*-isomer. Oxidation of the monoketone (XVIII) with chromium trioxide gave the diketone (XVII), identical in m. p., mixed m. p., and infrared spectrum with samples previously obtained.

With a number of *cyclo*propane derivatives now available, their degradation was studied for comparison with the recent work of Sorrie and Thomson.[4] These authors demonstrated the tricyclic structure of their product (XXV) by reduction to the 7-membered diketone

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[6] Nozoe, Mukai, Ikegami, and Toda, *Chem. and Ind.*, 1955, 66.

[7] Pauson, *Chem. Rev.*, 1955, **55**, 75.

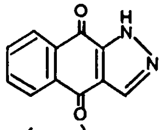
[8] *Idem, ibid.*, p. 85.

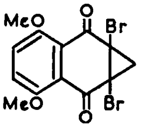
[9] Fieser and Peters, *J. Amer. Chem. Soc.*, 1931, **53**, 4080.

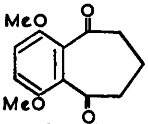
[10] Weygand, " Organic Preparations," Interscience, New York, 1945, p. 356.

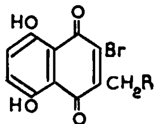
[11] Hershberg, *Helv. Chim. Acta*, 1934, **17**, 351; mentioned in *Org. Synth.*, **31**, 86.

(XXVI), and by ring opening under acid conditions to the naphthazarins (XXVII; R = Cl or Br). In contrast, reduction of our compound (XVII) by zinc dust in acetic acid, or catalytically, gave the ketol (XIII) (OH band 3410 cm.$^{-1}$; C=O band 1670 cm.$^{-1}$), which afforded a mono-2 : 4-dinitrophenylhydrazone and could be oxidised to the corresponding diketone (XII) or obtained from it by reduction. Its formulation as (XIII) rather than the dimeric pinacol is based on a molecular-weight determination. The same ketol was obtained from the monobromo- (XXII) and dibromo-*cyclo*propane diketone (VIII) by chemical reduction, but similar reduction of the dimethyl (XIX) and the diethoxycarbonyl compound (X) yielded the corresponding diketones (XX) and (XI) respectively.


(XXIV)


(XXV)


(XXVI)


(XXVII)

The preparation of the 4-hydroxytropone (II) has already been described [12] *via* the bis-enol acetate of (XII). The preparation of this enol acetate is tedious, and it has been found more convenient to use the β-keto-ester (XI), which is readily converted into its enol acetate (VI) (C=O bands 1710 and 1774 cm.$^{-1}$), and bromination of this product followed by treatment with alkali and then acid gave the diethoxycarbonyl-4-hydroxytropone (I). When the bromination product was hydrolysed more vigorously with alkali and acidified, carbon dioxide was evolved, and the product was the parent substance (II).

The ultraviolet absorption spectrum of 4-hydroxy-2 : 3-benzotropone (II) has been redetermined under acidic and basic conditions (see Fig. 2) and clearly indicates that the curve previously published [12] was in fact that of its anion. It can be seen now that, as might be expected, the true curve closely resembles that of αβ-benzotropolone. It can also be seen that in the presence of alkali, the spectrum undergoes displacements identical with those observed in the tropolone series; [13] the peak at *ca.* 230 mμ is unaffected, but those at *ca.* 320 and *ca.* 370 mμ are displaced towards the visible, and the latter in particular is intensified.

The infrared spectrum of 4-hydroxy-2 : 3-benzotropone (II) indicates strong *inter*molecular hydrogen bonding in the solid state, the O–H band appearing as a broad absorption (*ca.* 3300—2060 cm.$^{-1}$) with the band centre at 2600 cm.$^{-1}$ and the chelated carbonyl band as a very strong peak at 1470 cm.$^{-1}$. The only other band occurring in this region is at 1610 cm.$^{-1}$ (w) and is probably skeletal in origin. In solution the O–H and C=O absorptions are found at 3175 (m) and 1698 (s) cm.$^{-1}$ respectively. This intermolecular hydrogen bonding accounts for the high m. p. and insolubility of the substance. In contrast, the diester (I), in which the hydrogen bond can be *intra*molecular, is much lower-melting and dissolves readily in organic solvents.

The reactions of the 4-hydroxytropone (II) are as yet largely unexplored, but it should be noted that, as shown above, the molecule undergoes nuclear substitution. We have also found it to be unaffected by alkaline hydrogen peroxide, and these properties taken together bespeak a certain amount of aromatic character in the molecule.

EXPERIMENTAL

Ultraviolet spectra were measured in ethanol, by means of a Unicam S.P. 500 spectrophotometer, and infrared spectra by means of a Model 13 Perkin-Elmer double-beam instrument. Light petroleum used was of boiling range 60—80°.

2 : 3-*Dihydro*-2 : 3-*methylene*-1 : 4-*naphthaquinone*-2 : 3-*dicarboxylic Acid* (V).—The diester (XI) (5 g.), *N*-bromosuccinimide (2·9 g.), and a trace of benzoyl peroxide were refluxed for 15 min. in chloroform (25 ml.) and carbon tetrachloride (25 ml.). The succinimide was filtered off and the solution washed with 5N-sodium hydroxide solution (25 ml.) and with water (25 ml.).

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[12] Part VIII, Buchanan, *J.*, 1954, 1060.

[13] Doering and Knox, *J. Amer. Chem. Soc.*, 1951, **73**, 828; Cook and Loudon, *Quart. Rev.*, 1951, **5**, 99.

Concentration *in vacuo* yielded the *keto-ester* (X) (4·9 g.), m. p. 115—116° (colourless needles from ethanol) (Found : C, 64·6; H, 5·4. $C_{17}H_{16}O_2$ requires C, 64·6; H, 5·1%), $\nu_{max.}$ (in $CHCl_3$) 3070 (w), 3000 (w), 1748 (s), 1694 (s) cm.$^{-1}$.

The ester (1 g.) was refluxed for 3 min. with 5N-sodium hydroxide (4 ml.) and ethanol (1 ml.). On acidification with hydrochloric acid (*d* 1·17), colourless needles of the *monohydrate* of the *diacid* (V) separated, having m. p. 165—185° (decomp.) (from water) (Found : C, 56·2; H, 3·4. $C_{13}H_8O_6,H_2O$ requires C, 56·2; H, 3·6%). Recrystallisation from acetone–benzene and drying at 100°/1 mm. for 4 hr. gave faintly violet prisms of the anhydrous *acid*, m. p. 165—185° (decomp.) (Found : C, 60·0; H, 3·6. $C_{13}H_8O_6$ requires C, 60·0; H, 3·1%).

2 : 3-*Dihydro*-2 : 3-*methylene*-1 : 4-*naphthaquinone* (XVII).—(*a*) To the dione (XII) (1 g.) in carbon tetrachloride (1 ml.) was added a 10% solution of bromine in carbon tetrachloride (18·4 ml.; 2 mol.). The colour disappeared almost at once, and the solvent was removed *in vacuo*, leaving a yellow oil which was redissolved in acetone (25 ml.) containing sodium iodide (3 g.). After boiling for 2 hr., the solution was set aside for 3 hr. and, finally, the iodine colour was discharged by the addition of excess of aqueous sodium thiosulphate. Most of the acetone was removed *in vacuo* and the resulting solid was recrystallised from methanol. This gave the dione (XVII) (756 mg.), m. p. and mixed m. p. 128—130°, $\nu_{max.}$ (KCl disc) 3040 (m), 1680 (s), 1000 (ms), 880 (m), 870 (m) cm.$^{-1}$. It afforded a *dioxime*, m. p. 260—265° (decomp.) (from aqueous dioxan) (Found : C, 65·5; H, 5·2; N, 13·8. $C_{11}H_{10}O_2N_2$ requires C, 65·3; H, 5·0; N, 13·9%).

(*b*) The monoketone (XVIII) (85 mg.) in aqueous acetic acid (5 ml.; 80%) was refluxed for ½ hr. with chromic oxide (500 mg.). After being made strongly alkaline with 5N-sodium hydroxide the solution was extracted with ether (2 × 25 ml.), and the extract dried and concentrated. The product (63 mg.) was the dione, m. p. and mixed m. p. 128—130°, and its infrared spectrum (KCl disc) was identical with that of authentic material.

2-*Bromo*-2 : 3-*dihydro*-2 : 3-*methylene*-1 : 4-*naphthaquinone* (XXII).—The dione (XII) (50 mg.) was treated with a 10% solution of bromine in carbon tetrachloride (0·92 ml.; 2 mols.). The colour disappeared almost instantly and, after removal of the solvent *in vacuo*, the residual oil was taken up in ether (1 ml.) and shaken with 30% aqueous trimethylamine (1 ml.). When the ether was then removed by evaporation the crude *bromo-dione* (62 mg.) separated. This was filtered in benzene through neutral alumina and gave colourless prisms (from methanol), m. p. 115—116° (Found: C, 52·6; H, 3·2; Br, 31·7. $C_{11}H_9O_2Br$ requires C, 52·6; H, 2·8; Br, 31·9%), $\nu_{max.}$ (in Nujol) 1680 (s) cm.$^{-1}$. It gave a *mono-oxime*, m. p. 175—177° (decomp.) (Found : C, 49·4; H, 3·0; N, 5·2. $C_{11}H_8O_2NBr$ requires C, 49·6; H, 3·0; N, 5·3%).

2 : 3-*Dibromo*-2 : 3-*dihydro*-2 : 3-*methylene*-1 : 4-*naphthaquinone* (VIII).—(*a*) The dione (XII) (100 mg.) was treated with a 10% solution of bromine in carbon tetrachloride (2·74 ml.; 3 mols.) and left until pale yellow (*ca.* 3 hr.); the solvent was then removed *in vacuo*, and the resultant yellow oil treated with aqueous trimethylamine (2 ml.; 30%). Immediately, the *dibromo-ketone* was precipitated; it had m. p. 195° (decomp.), forming colourless prisms from acetone (Found: C, 40·1; H, 2·0; Br, 48·3. $C_{11}H_6O_2Br_2$ requires C, 40·0; H, 1·8; Br, 48·5%), $\nu_{max.}$ (in Nujol) 3070 (w), 1690 (s) cm.$^{-1}$. Attempts to prepare an oxime were unsuccessful.

(*b*) The dione (XII) (100 mg.) in a 10% solution of bromine in carbon tetrachloride (3·68 ml.; 4 mols.) was refluxed until the solution was pale red (*ca.* 5 hr.). The solvent was then removed *in vacuo*, and the resultant red oil was taken up in 75% aqueous acetone (4 ml.) containing potassium iodide (300 mg.). After ½ hr., excess of aqueous sodium thiosulphate was added and further dilution gave the dibromo-dione, m. p. 190° (decomp.), identical in infrared spectrum (Nujol) with that obtained above.

(*c*) After being kept for 5 days, a 10% solution of bromine in carbon tetrachloride (3·68 ml.; 4 mols.) containing the dione (XII) (100 mg.) was concentrated *in vacuo*. The resulting oil was shaken with 30% aqueous trimethylamine (3 ml.). Immediately a dark solid separated and this was crystallised from acetone, to give the dibromo-dione (21 mg.), m. p. and mixed m. p. 195° (decomp.).

Treatment of 4 : 4 : 6-*Tribromobenzo*cyclo*heptene*-3 : 7-*dione* (VII) *with Alkali*.—The dione (XII) (200 mg.) was set aside for 3 hr. in a 10% solution of bromine in carbon tetrachloride (5·52 ml.; 3 mols.); the solvent was then removed *in vacuo*, to give the crude tribromo-compound which was warmed on a steam-bath for 5 min. with 5N-sodium hydroxide (4 ml.). After filtering, the dark red solution was acidified with hydrochloric acid (5N), and the dark brown precipitate extracted with boiling water (3 × 1 ml.). The combined extracts deposited a red solid (17 mg.) on cooling. Sublimation at 130°/2 × 10^{-3} mm. gave 2-hydroxynaphtha-1 : 4-quinone, m. p. 190° (decomp.), identical in infrared spectrum with an authentic specimen.

5 : 7-*Dibromo*-4-*hydroxy*-2 : 3-*benzotropone* (III).—To a sublimed sample of the hydroxybenzotropone (II) (250 mg.) suspended in glacial acetic acid (15 ml.) a 10% solution of bromine in glacial acetic acid (4·65 ml.; 2 mols.) was added, and the suspension shaken until dissolution was complete and the bromine colour had disappeared (*ca.* ½ hr.), then poured into water (40 ml.). The pale yellow *dibromo-derivative* (460 mg.) separated. A sample sublimed at 120—$140^\circ/10^{-4}$ mm. had m. p. 160° (decomp.) (Found: Br, 48·1. $C_{11}H_8O_2Br_2$ requires Br, 48·2%), $\nu_{max.}$ (in Nujol) 3340 (s), 1680 (m), 1620 (s), 1590 (s), 1569 (s) cm.$^{-1}$.

The dibromo-compound was oxidised with boiling nitric acid (*d* 1·2) to phthalic acid, identified as the anhydride (m. p. and mixed m. p.).

Rearrangements. (*a*) The dibromo-compound (III) (75 mg.) was heated on the steam-bath for 15 min. with 5N-sodium hydroxide (3 ml.). The solution was then acidified and filtered, and the filtrate kept overnight. A few mg. of brown-yellow crystals separated, having m. p. *ca.* 180° (decomp.). Their infrared spectrum was identical with that of 2-hydroxynaphtha-1 : 4-quinone in almost every respect.

(*b*) A mixture of potassium hydroxide (900 mg.) and the dibromo-compound (III) (120 mg.) was heated at 110° for 10 min. After cooling, water (5 ml.) was added, and the solution acidified with hydrochloric acid (5N). Ether-extraction (2 × 20 ml.), drying, and concentration yielded a black solid which was extracted with boiling water (3 × 1 ml.). On cooling, a yellow solid (8 mg.) separated; this was sublimed at $140^\circ/10^{-3}$ mm., to give 2-hydroxynaphtha-1 : 4-quinone, m. p. 190° (decomp.), identical in infrared spectrum (Nujol) with an authentic specimen.

4 : 6-*Diethoxycarboxyl*-4 : 6-*dimethylbenzo*cyclo*heptene*-3 : 7-*dione* (XV).—The diester (XI) (5 g.) was dissolved in dry ethanol (35 ml.) containing sodium (750 mg.). After addition of methyl iodide, the solution was set aside for 24 hr., most of the solvent was distilled off, and water (200 ml.) was added. The oil which separated was taken up in ether (50 ml.), washed with 5N-sodium hydroxide solution (25 ml.), dried, and concentrated, yielding a brown solid (4·5 g.). A small portion was extracted with boiling light petroleum (charcoal) and, on cooling, colourless needles of the *dimethyl compound*, m. p. 93—94°, separated (Found: C, 65·5; H, 6·7. $C_{19}H_{22}O_6$ requires C, 65·8; H, 6·4%).

4 : 6-*Dimethylbenzo*cyclo*heptene*-3 : 7-*dione* (XX).—The crude ester (XV) (4·4 g.) was refluxed for 115 hr. with dioxan (30 ml.), water (150 ml.), and sulphuric acid (30 ml.; *d* 1·84). The cooled mixture was extracted with ethyl acetate (2 × 25 ml.), and the extract washed with 5N-sodium hydroxide (2 × 25 ml.). Drying and concentration yielded a brown solid which was extracted with boiling light petroleum (charcoal). On cooling, the *dimethyl-dione* (715 mg.) separated as colourless prisms, m. p. 93—95° (Found: C, 76·8; H, 6·7. $C_{13}H_{14}O_2$ requires C, 77·2; H, 6·9%). It gave a *dioxime*, m. p. 230° (decomp.) (Found: C, 67·2; H, 6·8; N, 11·6. $C_{13}H_{16}O_2N_2$ requires C, 67·2; H, 6·9; N, 12·0%).

2 : 3-*Dihydro*-2 : 3-*dimethyl*-2 : 3-*methylene*-1 : 4-*naphthaquinone* (XIX).—2 : 3-Dimethylnaphtha-1 : 4-quinone (5 g.), dissolved in ethereal diazomethane (from 15 g. of methyl-*N*-nitrosourea) was kept at 0° for 4 weeks, and then concentrated. The resulting red oil was heated at 200° for 4 hr. (gas evolution) and finally distilled. The fraction, b. p. 180—190° (bath)/3·5 mm., collected as a yellow wax which was extracted with boiling light petroleum (5 × 20 ml.). Evaporation gave a yellow solid which crystallised from aqueous methanol and then from light petroleum as colourless needles of the *dione*, m. p. 79—80° (Found: C, 78·1; H, 5·6. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0%), $\nu_{max.}$ (KCl disc) 3070 (w), 1675 (s) cm.$^{-1}$. It gave a *mono*-2 : 4-*dinitrophenylhydrazone*, m. p. 283° (decomp.) (from nitrobenzene) (Found: C, 59·9; H, 4·4; N, 14·7. $C_{19}H_{16}O_5N_4$ requires C, 60·0; H, 4·2; N, 14·7%), $\nu_{max.}$ (Nujol) 1675 (s) cm.$^{-1}$. Attempts to prepare an oxime were unsuccessful.

The compound was reduced by zinc dust and acetic acid by the method described below, to give the dione (XX), characterised as its oxime, identical in infrared spectrum (Nujol) with the specimen previously prepared.

(*b*) The dimethyl-dione (XV) (100 mg.) was set aside in carbon tetrachloride (5 ml.) containing bromine (160 mg.; 2 mols.) until the colour had disappeared (*ca.* 1 hr.). Removal of solvent *in vacuo* gave an oil which was taken up in acetone (20 ml.) containing sodium iodide (300 mg.). After 3 hr. the colour was discharged with aqueous sodium thiosulphate, and removal of acetone *in vacuo* gave an oil which was taken up in ether (10 ml.). Drying and concentration yielded an oil which gave a 2 : 4-dinitrophenylhydrazone, m. p. 277° (decomp.) identical [mixed m. p. and infrared spectrum (Nujol)] with that obtained from the tricyclic dione (XIX).

Ethyl 2-*Benzyl*cyclo*propanecarboxylates* (XXIII; R = Et).—To refluxing allylbenzene[10]

(20 g.) containing copper bronze (1 g.), diazoacetic ester (30 g.) was added dropwise during 2 hr. After refluxing for a further 2 hr. the dark mixture was filtered and steam-distilled until the distillate was clear (*ca.* 7 hr.). The distillate was extracted with ether (2 × 400 ml.) and, after drying and concentration, the resulting oil was distilled, giving allylbenzene (11 g.), b. p. 158—161°, and the mixture of esters (15 g.), b. p. 270—272°/754 mm., $\nu_{max.}$ (thin film) 3060 (w), 1725 (s) cm.$^{-1}$.

2-*Benzyl*cyclo*propanecarboxylic Acids* (XXIII; R = H).—The mixture of esters (XXIII; R = Et) (15 g.) was refluxed for 30 min. with sodium hydroxide (15 g.), methanol (15 ml.), and water (50 ml.). After cooling, the solution was washed with ether (30 ml.), acidified with hydrochloric acid (5N), and extracted with ether (2 × 50 ml.). On concentration this gave an oil which was distilled, the fraction, b. p. 188—190°/16 mm. (8·6 g.), being collected as the acids.

A mixture of anilides was prepared in the usual way, giving an oil which was extracted with boiling light petroleum. Upon cooling, white needles of the cis-*anilide* separated, having m. p. 99—100° (Found: C, 81·0; H, 6·9; N, 5·9. $C_{17}H_{17}ON$ requires C, 81·3; H, 6·8; N, 5·6%). The remainder of the oil was extracted with boiling light petroleum–methanol. Upon cooling, fine white needles of the trans-*anilide*, m. p. 124—126°, separated (Found: C, 81·2; H, 6·9; N, 5·7%). The ratio of *cis*/*trans*-isomers was *ca.* 10/1.

2 : 3-*Methylene*-1-*tetralone* (XVIII).—The mixture of acids (XXIII; R = H) (3·6 g.) was refluxed with thionyl chloride (5 ml.) for 15 min. and excess of reagent was removed *in vacuo*. The acid chlorides in dry ethylene dichloride (35 ml.) containing aluminium chloride (2·80 g.) were set aside for 2 hr.; the mixture was then poured on ice (50 g.) and hydrochloric acid (20 ml.; *d* 1·17). The aqueous layer was removed and extracted with ethylene dichloride (25 ml.), and the combined extracts were washed with 5N-sodium hydroxide. From the latter (alkaline) extract a crude acid was isolated by acidification, ether extraction, etc. It gave only the *trans*-anilide, m. p. and mixed m. p. 124—126°.

Concentration of the ethylene dichloride extracts yielded an oil which was distilled. The fraction, b. p. 124—127°/15 mm. (1·53 g.), was the ketone, $\nu_{max.}$ (thin film) 1675 cm.$^{-1}$, and gave a 2 : 4-*dinitrophenylhydrazone*, m. p. 226° (softens at 215°) (Found: C, 60·4; H, 3·9; N, 16·5. $C_{17}H_{14}O_4N_4$ requires C, 60·3; H, 4·1; N, 16·6%).

*Reduction of Benzo*cyclo*heptene*-3 : 7-*dione with Zinc Dust and Acetic Acid.*—The dione (XII) (53 mg.) was refluxed for 1½ hr. in glacial acetic acid (5 ml.) containing zinc dust (500 mg.). After being filtered and basified with 5N-sodium hydroxide the solution was extracted with ether (2 × 25 ml.) and concentrated to the oily ketol (XIII), $\nu_{max.}$ (thin film) 3410 (s), 1670 (s) cm.$^{-1}$ [Found: *M* (Rast), 204. Calc. for $C_{11}H_{12}O_2$: *M*, 176], which gave a 2 : 4-*dinitrophenylhydrazone*, m. p. 195° (softens at 162°) (from acetic acid) (Found: C, 57·5; H, 4·0; N, 15·6. $C_{17}H_{16}O_5N_4$ requires C, 57·3; H, 4·5; N, 15·7%), $\nu_{max.}$ (Nujol) 3485 (m) cm.$^{-1}$. The ketol also gave an *oxime*, m. p. 215—217° (from methanol) (Found: C, 69·2; H, 7·0; N, 7·5. $C_{11}H_{13}O_2N$ requires C, 69·1; H, 6·8; N, 7·3%).

The crude ketol [from 250 mg. of (XII)] was set aside overnight in 80% aqueous acetic acid (7 ml.) containing chromic oxide (500 mg.), then basified with 5N-sodium hydroxide solution, and extracted with ether (2 × 25 ml.); concentration yielded an oil which gave the *bis*-2 : 4-*dinitrophenylhydrazone*, m. p. 248—250° (decomp.) (from nitrobenzene), of the dione (XII) (Found: C, 51·5; H, 3·6; N, 21·0. $C_{23}H_{18}O_8N_8$ requires C, 51·7; H, 3·6; N, 20·9%), identical in infrared spectrum with that prepared from an authentic sample of the dione (XII).

Reduction of the Methylenenaphthaquinones with Zinc Dust and Acetic Acid.—The dione (XVII) (200 mg.), the bromo-dione (XXII) (200 mg.), and the dibromo-dione (VIII) (200 mg.) were each reduced in boiling glacial acetic acid (10 ml.) containing zinc dust (750 mg.), and the products isolated as in the previous experiment and characterised as the 2 : 4-dinitrophenylhydrazone of the ketol (XIII) [mixed m. p.s and infrared spectra (Nujol)].

Reduction of 2 : 3-*Diethoxycarbonyl*-2 : 3-*dihydro*-2 : 3-*methylene*-1 : 4-*naphthaquinone* (X) *with Zinc Dust and Acetic Acid.*—The keto-ester (X) (300 mg.) was refluxed in glacial acetic acid (10 ml.) containing zinc dust (600 mg.) for 2½ hr. Filtration and dilution gave a small quantity of a sticky solid which was dissolved in ether (5 ml.) and extracted with 5N-sodium hydroxide (3 ml.). Acidification of the extract gave a white solid, m. p. 83—85° (from light petroleum), undepressed in mixed m. p. with the ester (XI).

4 : 6-*Diethoxycarbonyl*-3 : 7-*diacetoxybenzo*cyclo*hepta*-1 : 3 : 6-*triene* (VI).—Acetyl chloride (5 ml.) was added dropwise during 10 min. with shaking and cooling to the diester (XI) (5 g.) in dry pyridine (15 ml.). Next morning the solid was filtered off and washed with dry ether (50 ml.), and the ethereal solution extracted with hydrochloric acid (4 × 50 ml.; 5N), sodium hydroxide solution (4 × 50 ml.; 5N), and water (50 ml.). Drying and concentration gave the *enol acetate*

(6·0 g.) as an oil which solidified, m. p. 91—92° (prisms from ether) (Found : C, 63·0; H, 5·5. $C_{21}H_{22}O_8$ requires C, 62·7; H, 5·5%), $\nu_{max.}$ (in CCl_4) 1774 (s), 1710 (s), 1285 (s), 1210 (s) cm.$^{-1}$.

4-*Hydroxy*-2 : 3-*benzotropone* (II).—The diacetate (VI) (3·0 g.) and *N*-bromosuccinimide (2·1 g.) in carbon tetrachloride (50 ml.) was refluxed for 1 hr. with a trace of benzoyl peroxide. Washing with water (3 × 25 ml.) and concentration *in vacuo* yielded a pale yellow oil which, on addition of 5N-sodium hydroxide (10 ml.), gave an extremely insoluble sodium salt. Acidification of a small quantity of this salt with hydrochloric acid (*d* 1·17) afforded the pale yellow *diester* (I), m. p. 74—75° (prisms from hexane) (Found : C, 64·5; H, 5·1. $C_{17}H_{16}O_6$ requires C, 64·5; H, 5·1%), $\nu_{max.}$ (in CCl_4) 2950 (w), 1710 (s), 1650 (s), 1620 (m) cm.$^{-1}$.

Hydrolysis of the remainder of the salt with 5N-sodium hydroxide (50 ml.) and ethanol (10 ml.) gave a dark brown solution, which, on acidification with hydrochloric acid (*d* 1·17), evolved carbon dioxide and gave the yellow 4-*hydroxy*-2 : 3-*benzotropane* (1·3 g.), m. p. 175—180°. A sample sublimed at 150—160°/10^{-4} mm. had m. p. 183—185° (Found : C, 76·4; H, 5·1. $C_{11}H_8O_2$ requires C, 76·7; H, 4·7%), $\nu_{max.}$ (in $CHCl_3$) : 3175 (m), 1698 (s), 1650 (s), 1593 (s), 1570 (s) cm.$^{-1}$, $\nu_{max.}$ (Nujol) : 3300—2060 (m), 1610 (w), 1540—1470 (s), 1330 (s), 1240 (s), 786 (m), 760 (s) cm.$^{-1}$.

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