500 mg. of IV. A deep red color developed immediately and the solution was heated at 100° for 36 hr. On cooling, the solution was poured into water, acidified with dilute hydrochloric acid, and the precipitated solid was filtered and dried *in vacuo*. Crystallization from light petroleum–ethyl acetate gave 450 mg. of yellow prisms (90%), m.p. 126–127°, alone or mixed with authentic IV.

(2) To a solution of sodium ethoxide in dry ethanol (from 20 mg. of sodium in 10 cc. of ethanol) was added 300 mg. of IV with the formation of a deep green solution. The mixture was refluxed for 24 hr., cooled, and poured into water, acidified with dilute hydrochloric acid, and the precipitated solid filtered and dried *in vacuo*. Crystallization from light petroleum–ethyl acetate gave 275 mg. of yellow prisms (91%), m.p. 126–127°, alone or mixed with authentic IV.

2-Acetyl-3,6-dihydroxy-4,5-benzcyclohept-4-ene-1-one (III). A mixture of 2.68 g. of *o*-phthalaldehyde (0.01 mole) and 2 g. of acetylacetone was heated to 50° on a water bath, 6 drops of diethylamine was added, and the resulting mixture was allowed to stand at room temperature or 24 hr. The resulting clear yellow gum was shaken with 15 cc. of benzene, which caused separation of a colorless crystalline solid, which was filtered and dried. Crystallization from benzene gave colorless prisms of the aldol III (3.83 g., 85%), m.p. 116–117°. $\lambda_{max}^{C_2H_5OH}$ 265 mμ (log ϵ 2.49) 272 mμ (log ϵ 2.45).

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.7; H, 6.2. Found: C, 67.2; H, 5.8.

Acid-catalyzed dehydration of III. A crystal of *p*-toluenesulfonic acid was added to 1 g. of the aldol III dissolved in 50 cc. of benzene and the mixture was heated in a Dean-Starck apparatus for 1 hr. (Any attempt at washing the organic phase with dilute sodium hydroxide resulted in most of the organic product passing into the alkaline phase.) The solvent was evaporated and the residue dissolved in 30 cc. of ethanol, a mixture of 1 g. of hydroxylamine hydrochloride and 1 g. of sodium carbonate in 5 cc. of water was added and the solution was refluxed for 1 hr. On cooling, the mixture was poured into water, and the precipitated solid filtered and dried. Crystallization of the *oxime* from aqueous ethanol gave 150 mg. of XV (15%), m.p. 119–120°. $\lambda_{max}^{C_2H_5OH}$ 222 mμ (log ϵ 3.54).

Anal. Calcd. for $C_{13}H_{13}NO_3$: C, 67.5; H, 5.9; N, 6.1. Found: C, 67.2; H, 5.7; N, 6.5.

Dehydration of III *to compounds* XVI–XVIII of the aldol III (1.5 g.) was effected with benzene and *p*-toluene sulfonic acid. Distillation of the resulting oil through a short path Vigreux column gave three fractions. (1) A pale yellow oil, b.p. 90°/1.6 mm. (2) A viscous deep yellow oil, b.p. 159–162°/1.0 mm. (3) A thick colorless oil, b.p. 188–190°/1.0 mm.

Fraction (1). Crystallization of the oil from light petroleum ether (b.p. 40–60°) gave pale yellow needles of *2-acetyl-6-hydroxy-4,5-benzcyclohept-2-ene-1-one* (XVII) (185 mg., 11%) m.p. 52–53°. $\lambda_{max}^{C_2H_5OH}$ 253 mμ (log ϵ 3.90). γ_{max}^{KBr} 1689 cm.$^{-1}$ (S) (α,β-unsaturated ketone).

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.2; H, 5.6. Found: C, 71.9; H, 5.8.

The *bi-2,4dinitrophenylhydrazone* was prepared by standard procedure, and formed orange prisms form chloroform-ethanol, m.p. 195–197°.

Anal. Calcd. for $C_{25}H_{20}N_8O_9$: C, 50.9; H, 4.4; N, 19.5. Found: C, 50.6; H, 4.2; N, 19.1.

Fraction (2). Crystallization of the oil from light petroleum (b.p. 40–60)-ether gave yellow prisms of XVIII (440 mg. 26%) m.p. 79–80°. $\lambda_{max}^{C_2H_5OH}$ 239 mμ (log ϵ 3.98) 281 mμ (log ϵ 3.97) 285 mμ (log ϵ 3.96). γ_{max}^{KBr} 3390 (m) (—OH group) 3058 (m) (H bonded hydroxyl group) 1695 (v.s.) (carbonyl of acetyl group) 1653 (S) 1613 cm.$^{-1}$ (s) (C=C stretching).

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.2; H, 5.6. Found: C, 72.6; H, 5.3.

Fraction (3). The oil crystallized from light petroleum-ether to give white needles of *2-acetyl-4,5-benztropone* (XVI) (120 mg., 6.8%), m.p. 89–90°. $\lambda_{max}^{C_2H_5OH}$ 235 mμ (log ϵ 4.4) 275 mμ (log ϵ 4.6). γ_{max}^{KBr} 1681 (s) (carbonyl of acetyl group) 1613 (s) (carbonyl of seven-membered aromatic ring) 1575 (s) 1550 cm.$^{-1}$ (s) (C=C stretching of aromatic seven-membered ring).

Anal. Calcd. for $C_{13}H_{10}O_2$: C, 78.8; H, 5.1. Found: C, 78.9; H, 5.2.

The *monophenylhydrazone* of XVI was prepared by standard procedure, and formed prisms from aqueous ethanol, m.p. 111–112°.

Anal. Calcd. for $C_{19}H_{16}N_2O$: C, 79.1; H, 5.6; N, 9 7. Found: C, 78.8; H, 5.4; N, 9.6.

Diels-Alder adduct XIX. A mixture of 240 mg. of XVIII and 70 mg. of maleic anhydride was dissolved in dry xylene (5 cc.), and refluxed for 5 hr. The crystalline material which separated on cooling (80 mg.) was crystallized from benzene–ethyl acetate to give colorless needles of the adduct XIX, (2.4%), m.p. 268–270°. $\lambda_{max}^{C_2H_5OH}$ 237–238 mμ (log ϵ 4.73), 286 mμ (log ϵ 4.19). γ_{max}^{KBr} 1835 (s) 1818 (s) 1770 (s) (carbonyl of anhydride group) 1610 (s) 1600 cm.$^{-1}$ (s) (aromatic C=C stretching).

Anal. Calcd. for $C_{17}H_{12}O_5$: C, 68.9; H, 4.1. Found: C, 69.2; H, 4.1

LONDON, W.1., ENGLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND BIOLOGY, THE POLYTECHNIC]

Condensation of *o*-Phthalaldehyde with Ketones. II

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Condensation of *o*-phthalaldehyde with appropriate ketones has led to the formation of benzotropolones and these products have been investigated by chemical and spectroscopic methods. Metal complexes of certain benztropolones have also been prepared. Some bromobenztropones and benztropolone-*O*-methyl ethers have been synthesized and certain of their reactions studied.

The condensation of *o*-phthalaldehyde with ketones of the type R—CH_2CO—CH_2R' (where R' = C_6H_5, —CO—CH_3, and R = H) leads to the formation of troponoid systems.[2] The 4,5-benztropolone *O*-methyl ether(II) was prepared by Tarbell

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and Bill[3] by condensation of *o*-phthalaldehyde with 1-methoxypropan-2-one. We used 3-methoxy-1-phenylpropan-2-one and obtained 2-phenyl-4,5-benztropolone *O*-methyl ether I in good yield.

Compound I formed no ketonic derivative with 2,4-dinitrophenylhydrazine, hydroxylamine, or hydrazine, whereas the 4,5-benztropolone ether(II) prepared by Tarbell, *et al.* is reported to form an oxime and 2,4-dinitrophenylhydrazone. Attempted bromination of I led to the recovery of starting material and this tropolone ether underwent decomposition under nitration conditions. In our hands 2-phenyl-4,5-benztropolone *O*-methyl ether I proved to be indifferent to substitution reactions involving replacement in the seven-membered ring, and stable to attempted benzilic acid rearrangement with alkali. The ultraviolet spectrum of compound I shows λ_{max} 246 mμ, 248 mμ (log ε 4.73, 4.19), 284 mμ, 287 mμ (log ε 4.58), which is very similar to that of 4,5-benztropolone.[3,4]

The 2-phenyl-4,5-benztropolone *O*-methyl ether (I) was readily demethylated by 46% hydrobromic acid in acetic acid to 2-phenyl-4,5-benztropolone III. This tropolone III was devoid of ketonic properties but dissolved easily in aqueous alkali to form a yellow union. A deep green-black color was obtained when an ethanolic solution of III was treated with ferric chloride in ethanol. On nitration of the tropolone III with nitric acid dissolved in acetic acid, decomposition occurred and no pure products could be isolated. The tropolone proved to be indifferent to bromination using bromine in carbon tetrachloride. Benzilic acid rearrangement of the tropolone III to a naphthalenic acid could not be effected even on long heating with ethanolic potassium hydroxide, presumably due to the stability of the tropolone anion.

The infrared spectrum of 2-phenyl-4,5-benztropolone showed a medium band at 3226 and 1634 cm.$^{-1}$ and strong absorption at 1629 and 1562 cm.$^{-1}$ Tarbell[3] quotes values of 1615, 1553 and 1260 cm.$^{-1}$ as bands characteristic of monocyclic tropolones, and benztropolones[6] all show strong absorption at 1615 and 1260 cm.$^{-1}$ The band usually associated with carbonyl stretching in monocyclic tropolones is at 1610 cm.$^{-1}$ Nichols and Tarbell[5] ascribe the band at 1610 cm.$^{-1}$ to be carbonyl stretching of benztropolones. We ascribe the band at 1629 cm.$^{-1}$ to the carbonyl frequency of the tropolone III, and the carbonyl absorption of the tropolone ether I to the peak at 1605 cm.$^{-1}$ Peaks at 1634, 1587, and 1562 cm.$^{-1}$ have been reported by other workers (*cf.* ref. 4) and are ascribed to the C=C stretching of the seven-membered aromatic ring. The absorption at 1587 cm.$^{-1}$ shown by the benztropolone ether I is assigned to the C=C stretching of the tropolone ring, as are the 1634 and 1562 cm.$^{-1}$ bands of the tropolone III. The hydroxyl stretching band of 4,5-benztropolone prepared by Tarbell is at 3226 cm.$^{-1}$ a fact which confirms our own findings for the tropolone III the hydroxyl band of which lies at 3226 cm.$^{-1}$ This hydroxyl band is absent from the 2-phenyl-4,5-benztropolone *O*-methyl ether (I), and this is also reported by Tarbell, as the 4,5-benztropolone ether II showed no absorption in this region.

The tropolone III formed a yellow copper complex (IV), when treated with a saturated solution of ethanolic cupric acetate. In the infrared this copper complex showed two carbonyl bands at 1595 and 1590 cm.$^{-1}$, both bands associated with the carbonyl stretching of copper complexes of tropolones.[7] A complex was obtained when III was treated with nickel acetate in ethanol; analysis of the product indicated the formulation $C_{17}H_{18}O_6$ Ni-$^1/_2$-H_2O (V). This might possibly be a *dsp*^{2} type complex (tropolone Ni $(H_2O)_3$)OH.

Bromination of the tropolone III was effected in glacial acetic acid to form 6-bromo-2-phenyl-4,5-benztropolone (VI); the ultraviolet spectrum of the bromotropolone showed λ_{max} 256 mμ, 292 mμ (log ε 4.4, 4.5). The infrared spectrum of this product showed absorption at 3145 cm.$^{-1}$ This band is assigned to the hydroxyl stretching mode of the tropolone, and the band at 1600 cm.$^{-1}$ is ascribed to the carbonyl frequency. The bromotropolone (VI) formed a copper complex (VII) and the infrared spectrum of the complex showed a carbonyl band at 1585 cm.$^{-1}$, a peak associated with the carbonyl stretching of copper complexes of tropolones.[7] Treatment of the bromobenztropolone VI with ethereal diazomethane afforded 6-bromo-2-phenyl-4,5-benztropolone *O*-methyl ether (XII).

The product obtained on hydrolysis of the bromobenztropolone (VI) with ethanolic potassium hydroxide was a colorless crystalline solid, elemental analysis of which indicated the formula $C_{17}H_{12}O_4$ (X). This material exhibited two maxima in the ultraviolet region λ_{max} 278 mμ, 295 mμ (log ε 3.8, 3.9), and the infrared spectrum showed two medium bands at 3559 and 3534 cm.$^{-1}$ (free hydroxyl stretching mode) and two strong bands at 3390 and 3030 cm.$^{-1}$ (ascribed to a hydrogen-bonded hydroxyl group) and a strong carbonyl peak at 1695 cm.$^{-1}$ The compound X gave no coloration with ferric chloride, and dissolved slowly in aqueous alkali to form a pale yellow solution.

These results indicated that the expected benzilic acid rearrangement of VI to 3-carboxy-4-hydroxy-2-

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(3) D. S. Tarbell and J. C. Bill, *J. Amer. Chem. Soc.*, **74**, 1234 (1952).

(4) Tarbell, *et al.*, Ultraviolet spectra for 4,5-benzotropolone and 4,5-benzotropolone *O*-methyl ether: λ_{max} 238 mμ, 240 mμ, 275 mμ, 278 mμ.

(5) Nicholls and Tarbell, *J. Am. Chem. Soc.* **74**, 4935 (1952).

(6) G. P. Scott and D. S. Tarbell, *J. Am. Chem. Soc.*, **72**, 240 (1950).

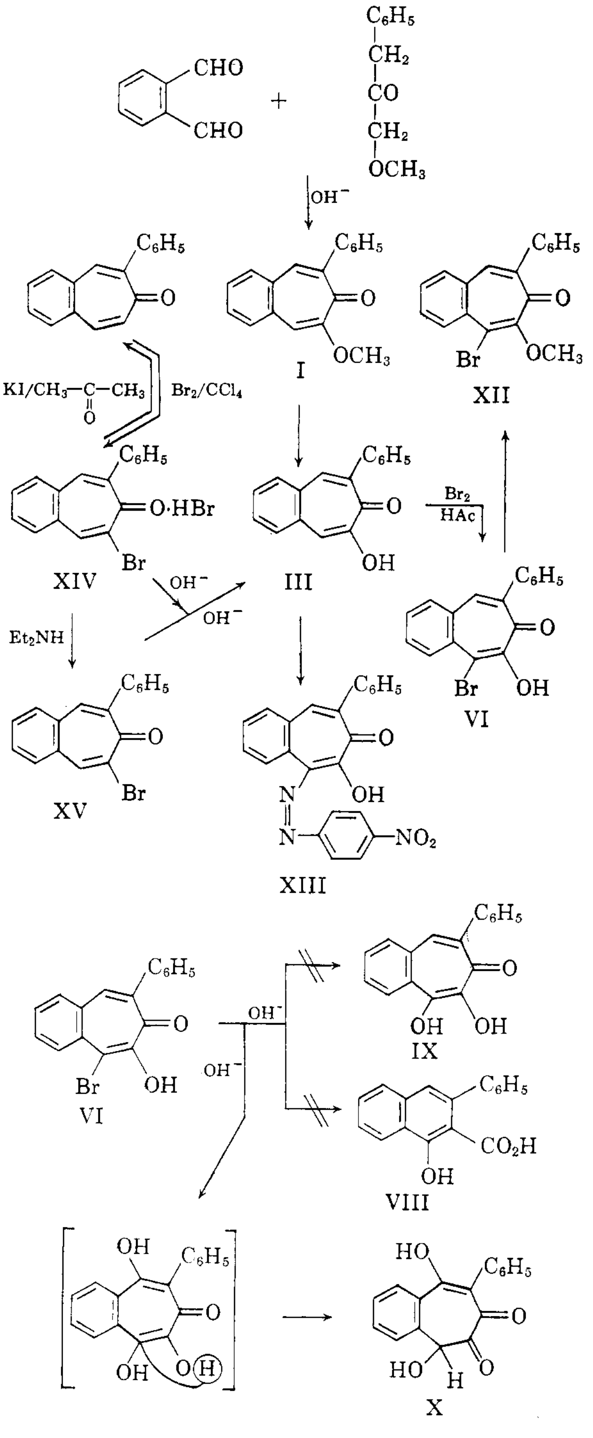
(7) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen & Co., Publishers, London, 1956, p. 130.

phenylnaphthalene (VIII) had not occurred. Furthermore, the evidence suggested that there was no formation of the precursor of VIII, namely 6-hydroxy-2-phenyl-4,5-benztropolone (IX). Neither the ultraviolet nor infrared spectra of the product X support evidence for a 4,5-benztropolone or naphthalenic structure. The analytical data for compound X shows the presence of an extra oxygen atom in the molecule, presumably due either to oxidation or nuclear hydroxylation. As compound X failed to give a color with ferric chloride and dissolved very slowly in alkali, the presence of phenolic hydroxyl or carboxylic acid groups in the molecule is doubtful.

A possible explanation to account for the physical and chemical properties of X is considered in the following way. It is proposed that during the hydrolysis of the bromobenztropolone VI, nuclear hydroxylation of the tropolone ring occurs. The only position activated and available for substitution in the tropolone ring is C-3; hence, if hydroxylation occurs at this center, then the intermediate product is 3,6-dihydroxy-2-phenyl-4,5-benztropolone (XI), which by shift of an H atom from C-7 to C-6 gives the dihydroxy diketone structure; this structure would fit the spectral results obtained for compound X. In the ultraviolet region the spectral requirements for the product X is a stilbene band at 295 mμ, and in the infrared region a free hydroxyl group (3600 cm.$^{-1}$), and hydrogen-bonded hydroxyl group (3390 cm.$^{-1}$) and an α-diketone band at 1700 cm.$^{-1}$ Hence as a possible structure, compound X is formulated as 3,6-dihydroxy-2-phenyl-4,5-benzcyclohept-2-ene-1,7-dione.

Coupling reactions between 2-phenyl-4,5-benztropolone III and diazotized amines were attempted, but no pure products were obtained using benzenediazonium chloride, as reported by earlier workers (*cf.* ref. 2). On coupling the tropolone III with *p*-nitrobenzenediazonium chloride at *p*H 6.5, a deep red crystalline azo compound (XIII), 6-(*p*-nitrobenzene-azo)-2-phenyl-4,5-benztropolone, was obtained.

A synthesis of the tropolone III could also be effected from 2-phenyl-4,5-benztropone.[8] When this tropone was brominated in carbon tetrachloride a yellow crystalline solid $C_{17}H_{12}OBr_2H_2O{}^1/_2$ (XIV) was obtained. This material evolved hydrogen bromide on standing in air and was fairly soluble in water; it gave an immediate precipitate with ethanolic silver nitrate. The ultraviolet spectrum of XIV was complex, showing fine structure from 240 mμ–340 mμ, and the infrared spectrum showed a broad hydroxyl band at 3413–3378 cm.$^{-1}$, strong carbonyl band at 1653 cm.$^{-1}$ and a C—Br stretching band at 598–595 cm.$^{-1}$ The infrared data shows that at least one bromine atom is attached to the aromatic nucleus (absorption at 595 cm.$^{-1}$), while the silver nitrate reaction and the instability of the compound in air indicates that the second bromine atom is labile. On heating XIV for a few minutes with potassium iodide in acetone, 2-phenyl-4,5-benztropone was obtained, showing that the seven membered ring system had not been ruptured during bromination. On reaction of XIV with ethanolic potassium hydroxide the only product obtained was the tropolone III; therefore one bromine atom is located at C-7 in the tropone ring.



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(8) W. Davey and H. Gottfried, Reported by condensation of *o*-phthalaldehyde and 1-phenylpropan-2-one. See Part I of this series.

The labile bromine atom was confirmed by refluxing XIV in ethanol with diethylamine. A crystalline material containing one bromine atom less was obtained ($C_{17}H_{11}OBr$, XV), showing that the organic base had caused dehydrobromination. Hydrolysis of the monobromo compound XV with ethanolic potassium hydroxide furnished 2-phenyl-4,5-benztropolone III which was characterized as its copper complex, showing an identical infrared spectrum with authentic material. Consequently the monobromo compound contains a bromine atom attached to C-7 in the tropone ring. The ultraviolet spectrum of XV showed λ_{max} 246 mμ, 286 mμ (log ε 4.4, 4.6), which is very similar to 2-phenyl-4,5-benztropone[9]; there is a slight bathochromic shift from the parent tropone (10 mμ) due to the effect of the bromine atom adjacent to the keto group of the seven-membered ring. The infrared spectrum of XV showed a strong carbonyl band at 1600 cm.$^{-1}$, and two medium C═C stretching bands at 1575 and 1538 cm.$^{-1}$, both bands associated with aromatic seven-membered ring systems, and these infrared absorptions are very similar to those of the parent 2-phenyl-4,5-benztropone.[10] On this basis, XV is formulated as 7-bromo-2-phenyl-4,5-benztropone and compound XIV as its hydrobromide salt.

EXPERIMENTAL

Melting points are uncorrected. Ultraviolet spectra were measured in 96% ethanol using a Unicam SP500 spectrophotometer. Infrared spectra were measured in potassium bromide disks using a Grubb-Parsons double beam spectrophotometer.

3-Methoxy-1-phenylpropan-2-one. This compound was prepared according to the procedure of M. Darmon.[11] The product was obtained as a colorless oil, b.p. 73–74°/0.4 mm. n_D^{19} 1.5171.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.1; H, 7.4. Found: C, 73.1; H, 7.2.

2-Phenyl-4,5-benztropolone-O-methyl ether (I). To a mixture of 1.34 g. of *o*-phthaldialdehyde (0.01 mole) and 1.64 g. g. of 3-methoxy-1-phenylpropan-2-one dissolved in 25 cc. of of ethanol, saturated ethanolic potassium hydroxide was added dropwise until a permanent red color was obtained. The mixture was allowed to stand overnight and the crystalline material which separated was filtered off and dried *in vacuo* to give 2.2 g. of product (83%), m.p. 156–157°. Repeated crystallization from ethanol gave *2-phenyl-4,5-benztropolone-O-methyl ether* as pale yellow prisms, m.p. 159–160°. $\lambda_{max}^{C_2H_5OH}$ 246 mμ (log ε 4.52) 248 mμ (log ε 4.53), 284 mμ (log ε 4.58), 287 mμ (log ε 4.58). γ_{max}^{KBr} 1605 (S) (carbonyl stretching of seven-membered aromatic ring), 1587 (S) 1538 (m) (aromatic C═C stretching of seven-membered aromatic ring) 1242 (S) (C═O stretching of O-methyl ether), 1130 cm.$^{-1}$ (S) (C—O stretching of methyl ether).

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.4; H, 5.4. Found: C, 82.6; H, 5.1.

No ketonic derivatives could be prepared by standard procedures for the formation of oxime, 2,4-dinitrophenylhydrazone, or semicarbazone.

2-Phenyl-4,5-benztropolone (III). A mixture of 3.00 g. of the tropolone methyl ether (I) and 40 cc. of 46% hydrobromic acid dissolved in 10 cc. of glacial acetic acid was heated under reflux for 6 hr., cooled, and poured into crushed ice, when a yellow crystalline solid separated. The product was filtered off and dried, and then dissolved in 50 cc. of ether and filtered from any unchanged starting material, and the solvent was evaporated. Crystallization of the residue from light petroleum gave 2-phenyl-4,5-benztropolone (III) as yellow needles, m.p. 91.5–92.5° (1.67 g., 59%). $\lambda_{max}^{C_2H_5OH}$ 250 mμ (log ε 4.5), 287 mμ (log ε 4.6). γ_{max}^{KBr} 3226 (W) (—OH stretching of tropolone) 1634 (m) (C═C stretching of seven-membered aromatic system), 1629 (S) (C═O of tropolone system), 1562 (S) 1536 cm.$^{-1}$ (S) (bands associated with C═C stretching of benztropolones).

Anal. Calcd. for $C_{17}H_{12}O_2$: C, 82.2; H, 4.9. Found: C, 82.1; H, 4.7.

Reactions. An ethanolic solution of the tropolone gave an immediate green-black color with ethanolic ferric chloride. The tropolone dissolves rapidly in aqueous 4% sodium hydroxide to give a yellow solution. The tropolone (300 mg.) was dissolved in 2 cc. of glacial acetic acid and 1 cc. of concd. nitric acid (*d.* 1.42) was added, and the mixture was shaken for 1 hr. at room temperature. Attempted isolation of the product yielded only tars. Bromination of the tropolone was attempted by addition of bromine in carbon tetrachloride. Any attempt at isolation of a product led to complete decomposition. The tropolone was indifferent in reaction towards ketonic reagents; refluxing ethanolic solutions of the tropolone with aqueous solutions of hydroxylamine or hydrazine hydrate led to the recovery of the starting material.

Attempted rearrangement of III. To 500 mg. of the tropolone dissolved in 5 cc. of ethanol, was added 3 cc. of 70% potassium hydroxide and the mixture was refluxed for 10 hr., cooled, poured into water, and acidified with 4% hydrochloric acid when a yellow solid separated, which was filtered and dried *in vacuo*. Crystallization from light petroleum gave yellow needles (480 mg., 96%), m.p. 91.5–92.5°, and an undepressed mixed melting point with authentic 2-phenyl-4,5-benztropolone.

Copper complex (IV). To 150 mg. of the tropolone in ethanol was added a saturated ethanolic solution of cupric acetate, followed by immediate precipitation of a yellow solid, which was filtered and dried *in vacuo*. Crystallization from benzene-ethanol gave 130 mg. (44%) of the copper complex of the tropolone IV, m.p. 317–319° dec. γ_{max}^{KBr} 1595 (S) 1590 cm.$^{-1}$ (S) (bands associated with carbonyl stretching of the copper complexes of tropolones).

Anal. Calcd. for $C_{34}H_{22}O_4Cu$: C, 73.2; H, 3.8. Found: C, 73.4; H, 3.8.

Nickel complex (V). A saturated solution of nickel acetate in ethanol was added dropwise to a solution of 200 mg. of the tropolone in ethanol, until the green color of nickel acetate was permanent. Concentration of the solution to half volume caused separation of a yellow solid, which was filtered and dried *in vacuo*. Crystallization from ethanol afforded the nickel complex V (80 mg. 25%), as a yellow microcrystalline solid, m.p. 368–369° dec.

Anal. Calcd. for $C_{17}H_{18}O_6Ni\ ^1/_2\ H_2O$: C, 52.9; H, 5.0; Ni, 15.2. Found: C, 52.5; H, 5.0; Ni, 15.6.

6-Bromo-2-phenyl-4,5-benztropolone (VI). A mixture of 1.45 g. of the tropolone in 30 cc. of glacial acetic acid and 0.3 cc. (0.93 g.) of bromine (1 mole) was heated under reflux for 3 hr. until no more hydrogen bromide was evolved. The clear green solution was poured into 200 cc. of water and the precipitated yellow solid was filtered off and dried *in vacuo*. Crystallization from ethanol gave flat pale yellow needles of the bromotropolone VI (1.25 g., 41%), m.p. 124–125°. $\lambda_{max}^{C_2H_5OH}$ 256 mμ (log ε 4.46) 292 mμ (log ε 4.20). γ_{max}^{KBr} 3145 (m) (—OH group) 1600 cm.$^{-1}$ (S) (carbonyl band of tropolone).

Anal. Calcd. for $C_{17}H_{11}O_2Br$: C, 62.2; H, 3.3; Br, 24.4. Found: C, 61.9; H, 3.3; Br, 24.3.

The bromotropolone gave an immediate green-brown

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[9] The ultraviolet spectrum of 2-phenyl-4,5-benztropone shows maxima at 238 mμ, 277 mμ.

[10] The corresponding bands in 2-phenyl-4,5-benztropone are at 1626, 1613, 1587 cm.$^{-1}$

[11] M. Darmon, *Compt. rend.*, **197**, 1328–9 (1933).

color with ethanolic ferric chloride. The copper complex (VII) of 6-bromo-2-phenyl-4,5-benztropolone was prepared by adding a saturated ethanolic solution of cupric acetate to the bromotropolone in ethanol. Crystallization of the precipitated material from chloroform yielded the copper complex as a deep yellow microcrystalline solid, m.p. 249–250° dec. $\gamma_{\max}^{\mathrm{KBr}}$ 1585 cm.$^{-1}$ (m) (carbonyl stretching band of copper complex of tropolones).

Anal. Calcd. for $C_{34}H_{20}O_4Br_2Cu$: C, 57.1; H, 2.8; Br, 22.3. Found: C, 56.8; H, 3.1; Br, 21.9.

6-Bromo-2-phenyl-4,5-benztropolone O-methyl ether (XII). An ethereal solution of 1.5 g. of the bromotropolone VI, was treated at 0° for 1 hr. with an ethereal solution of diazomethane. Evaporation of the solvent and crystallization of the residue from ethanol gave yellow plates of the bromotropolone ether (1.4 g., 89%), m.p. 129–130°.

Anal. Calcd. for $C_{18}H_{13}O_2Br$: C, 63.4; H, 3.9; C, 63.2. Found: C, 63.2; H, 4.0.

3,6-Dihydroxy-2-phenyl-4,5-benzcyclohept-2-ene-1,7-dione (X) *from* VI. To 850 mg. of the bromotropolone VI dissolved in 20 cc. of ethanol was added 2 cc. of 50% potassium hydroxide and the mixture was refluxed for 5 hr. The reaction mixture was poured into 100 cc. of water, acidified with dilute sulfuric acid, and extracted with ether (3 × 25 cc.), the ethereal extract was dried magnesium sulfate and evaporated. Crystallization of the residue from ethyl acetate–light petroleum gave X (450 mg., 62%), as colorless needles, m.p. 186–187°; $\lambda_{\max}^{C_2H_5OH}$ 278 mμ (log ϵ 3.83), 295 mμ (log ϵ 3.93). $\gamma_{\max}^{\mathrm{KBr}}$ 3559 (W) 3534 (W) (—OH stretching) 3390 (S) 3030 (S) (H bonded —OH group) 1695 (V.S.) (carbonyl stretching of α-diketone), 1105 cm.$^{-1}$ (S) (—OH deformation of secondary alcohol).

Anal. Calcd. for $C_{17}H_{12}O_4$: C, 72.9; H, 4.3. Found: C, 72.5; H, 4.4.

Compound XI gave no coloration with ethanolic ferric chloride, and dissolved slowly in 4% sodium hydroxide to form a pale yellow solution.

6-(p-Nitrobenzene-azo)-2-phenyl-4,5-benztropolone (XIII). A solution of 150 mg. of the tropolone III in 50% aqueous acetic acid, was brought to *p*H 5 by the addition of 1 g. of sodium acetate, and the mixture was chilled in ice. *p*-Nitroaniline (200 mg.) was dissolved in 10 cc. of 7% hydrochloric acid and diazotized at 0°, by the addition of 350 mg. of sodium nitrite in 5 cc. of water. The coupling reaction with the tropolone was effected by rapid addition of the diazonium salt at 0°, and adjusting the *p*H to 6.5 by addition of 8% sodium hydroxide. On standing a deep red solid separated, which was filtered off and dried *in vacuo.* Crystallization from acetone gave deep red needles of the azo compound (XIII, 69%), m.p. 229–230° (120 mg.).

Anal. Calcd. for $C_{23}H_{15}O_4N_3$: C, 69.5; H, 3.8; N, 10.6. Found: C, 69.4; H, 4.0; N, 10.2.

7-Bromo-2-phenyl-4,5-benztropone hydrobromide (XIV). A solution of 530 mg. of 2-phenyl-4,5-benztropone in carbon tetrachloride was brominated with bromine in carbon tetrachloride until the evolution of hydrogen bromide ceased and a permanent red color of excess bromine was obtained (the bromination was carried out at 40° during 1 hr.). Evaporation of the solvent and crystallization of the residue from light petroleum–ethyl acetate gave yellow plates of the hydrobromide salt (XIV) (450 mg., 61%), m.p. 123–124°. $\lambda_{\max}^{C_2H_5OH}$ 228 mμ (log ϵ 4.28), 231 mμ (log ϵ 4.27), 240 mμ (log ϵ 4.31), 244 mμ (log ϵ 4.33), 246 mμ (log ϵ 4.33), 253 mμ (log ϵ 4.30), 326 mμ (log ϵ 4.05), 329 mμ (log ϵ 4.07), 331 mμ, 336 mμ, 339 mμ (all log ϵ 4.07), 342 mμ (log ϵ 4.06) $\gamma_{\max}^{\mathrm{KBr}}$ 3413–3378 (broad) (hydroxyl stretching band), 1653 (S) (carbonyl stretching), 1600 (m) 1562 (m) (C=C stretching bands associated with seven-membered aromatic ring) 598–595 cm.$^{-1}$ (S) (C—Br stretching).

Anal. Calcd. for $C_{17}H_{12}OBr_2$ $^1/_2/H_2O$: C, 50.9; H, 3.3; Br, 39.9. Found: C, 51.2; H, 3.2; Br, 40.2.

The compound is unstable and decomposes on storage and evolves hydrogen bromide on standing in air. An ethanolic solution of XIV gives an immediate precipitate with ethanolic silver nitrate.

Reaction of XIV *with potassium iodide in acetone.* On addition of 2 cc. of 50% potassium iodide solution to 500 mg. of the hydrobromide salt (XIV) dissolved in 5 cc. of acetone, iodine was immediately liberated. The mixture was heated under reflux for 10 min. and then chilled in ice, and diluted with 50 cc. of water, when a dark tar separated. The tarry material was filtered off and suspended in 100 cc. of water, and on addition of 10 cc. of 8% sodium hydroxide, the dark-colored material dissolved, leaving a pale yellow solid, which was filtered off and dried *in vacuo.* Crystallization of the material from light petroleum–ethyl acetate gave 60 mg. (17%) of pale yellow needles, m.p. 142–143°, undepressed on admixture with authentic 2-phenyl-4,5-benztropone.

Alkaline hydrolysis of XIV. To a solution of 450 mg. of the hydrobromide in 10 cc. of ethanol was added 500 mg. of potassium hydroxide in 3 cc. of water and the mixture was heated under reflux for 2 hr., cooled, and poured into 50 cc. of water, and extracted with ether (3 × 25 cc.). The aqueous fraction was acidified with dilute sulfuric acid; the precipitated solid was extracted with ether, the organic layer washed with water until neutral, dried magnesium sulfate, and evaporated. Crystallization of the residue from light petroleum gave 145 mg. (42%) of yellow needles, m.p. 90–91°. A mixed melting point with authentic 2-phenyl-4,5-benztropolone showed no depression.

7-Bromo-2-phenyl-4,5-benztropone (XV). A mixture of 1.2 g. of the hydrobromide salt (XIV) and 10 cc. of diethylamine was dissolved in 20 cc. of ethanol and the mixture heated for 2 hr. On cooling in ice 1.05 g. of pale yellow crystalline material separated, which was filtered off and dried *in vacuo.* Crystallization from ethanol gave pale yellow prisms of *7-bromo-2-phenyl-4,5-benztropone,* m.p. 140.5–11.5° (850 mg., 83%). $\lambda_{\max}^{C_2H_5OH}$ 246 mμ (log ϵ 4.43) 286 mμ (log ϵ 4.59). $\gamma_{\max}^{\mathrm{HBr}}$ 1600 (S) (carbonyl stretching of seven-membered aromatic ketonic rings), 1575 (m) 1538 cm.$^{-1}$ (m) (bands associated with C=C stretching of tropones).

Anal. Calcd. for $C_{17}H_{11}OBr$: C, 65.6; H, 3.6; Br, 25.7. Found: C, 65.3; H, 3.6; Br, 25.4.

Alkaline hydrolysis of XV. A solution of 50% potassium hydroxide (3 cc.) was added to 800 mg. of the bromotropone XV, dissolved in 10 cc. of ethanol, and the mixture refluxed for 6 hr. On cooling, the mixture was poured into 25 cc. of water, and extracted with ether. The aqueous phase was acidified with dilute sulfuric acid, and extracted with ether (3 × 10 cc.), and the ethereal layer was washed to neutrality with water, dried magnesium sulfate and evaporated. Crystallization of the residue from light petroleum gave 240 mg. (38%) of yellow needles, m.p. 91–92°, which showed no depression on admixture with authentic 2-phenyl-4,5-benztropolone (III). This was confirmed by preparation of the copper complex from material obtained in this reaction, the infrared spectrum of which was superimposable on that of the authentic copper complex IV.

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