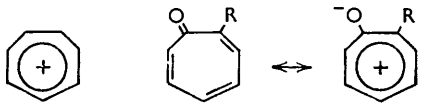
720. *Tropolones. Part X.* Synthesis and Properties of 2,3-Benzotropone.*

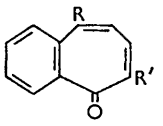
By G. L. Buchanan and D. R. Lockhart.

A practicable route to 2,3-benzotropone is described; the properties and reactions of this substance indicate that it behaves rather as a conjugated dienone than as an aromatic compound.

The widely accepted view [1] that tropolone, as a derivative of the tropylium ion (I), owes its aromatic character largely to the participation of tropylium structures in the resonance picture (II), is supported by *X*-ray,[2] electron-diffraction,[3] and dipole moment [4] measurements. Although it has been stated [5] that tropone (III) is also aromatic, we know of no compelling chemical evidence which supports this opinion and the work which we now describe contradicts it.



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



	R	R′
(IV)	OH	H
(V)	H	H
(VI)	H	OH

Our object was, first, to find a practicable synthesis of a tropone, and then to examine its properties for evidence of aromaticity. For this, we selected the known [6] 2,3-benzotropone (V). Although the benzene nucleus will modify the properties of the tropone ring,

* Part IX, *J.*, 1956, 2620.

[1] Schaeppi, Schmid, Heilbronner, and Eschenmoser, *Helv. Chim. Acta*, 1955, **38**, 1874; Doering and Knox, *J. Amer. Chem. Soc.*, 1952, **74**, 5683; Baker and McOmie, " Progress in Organic Chemistry," ed. J. W. Cook, Butterworths, London, 1955, Vol. III, p. 44; Nozoe, " Progress in the Chemistry of Organic Natural Products," Springer, Vienna, 1956, Vol. XIII, p. 235.

[2] Robertson, *J.*, 1951, 1222.

[3] Kimura and Kubo, *Bull. Chem. Soc. Japan*, 1953, **26**, 250.

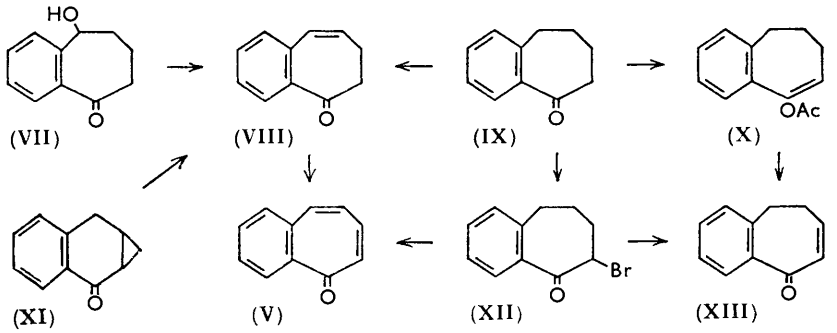
[4] Kurita, Nozoe, and Kubo, *ibid.*, 1951, **24**, 10; Di Giacomo and Smyth, *J. Amer. Chem. Soc.*, 1952, **74**, 4411.

[5] *Ann. Reports*, 1956, **53**, 149; Baker and Ollis, *Quart. Rev.*, 1957, **11**, 15; Heusner, *Angew. Chem.*, 1958, **70**, 643; Nozoe, *Experientia*, Suppl. 7, 1957, 313.

[6] Rennhard, Di Modica, Simon, Heilbronner, and Eschenmoser, *Helv. Chim. Acta*, 1957, **40**, 257.

we shall compare this ketone with its hydroxy-derivatives [7,8] (IV) and (VI), in both of which the aromatic character is similarly diminished but certainly not extinguished.

The original synthesis [6] of 2,3-benzotropone is tedious, and we have developed a superior route from the ketone (IX). First we prepared 2,3-benzocyclohepta-2,6-dienone (XIII) [ν(C=O) 1660 cm.$^{-1}$] by dehydrobromination of the α-bromo-ketone (XII) and by the action of *N*-bromosuccinimide on the enol acetate (X). However, it rapidly resinified,



and was therefore unsuitable for further work. In contrast, the isomeric ketone (VIII) is stable. Julia [9] obtained this by base-catalysed rearrangement of the cyclopropyl ketone (XI) and established the presence, but not the position, of an ethylenic group by reduction to 2,3-benzocyclohept-2-enone. We obtained the same unsaturated ketone by dehydration of the known keto-alcohol [10] (VII) by boric acid or, more conveniently, by bromination of 2,3-benzocyclohept-2-enone followed by dehydrobromination: these transformations establish the position of the double bond. We are grateful to Dr. Julia for supplying details of his work in advance of publication. The unsaturated ketone (VIII) is readily oxidised to 2,3-benzotropone by selenium dioxide, and was identified by comparison of its 2,4-dinitrophenylhydrazone and picrate with authentic samples kindly supplied by Dr. Eschenmoser.[6] Alternatively, when Julia's ketone (VIII) is brominated, the product spontaneously eliminates hydrogen bromide, at the temperature of the reaction, affording 2,3-benzotropone. This avoids the disadvantages of the selenium dioxide reaction, and represents a feasible route to the tropone. We have found it more convenient, however, to brominate the α-bromo-ketone (XII) in the benzyl position by *N*-bromosuccinimide and to dehydrobrominate the product by means of base. This procedure, which was independently employed by Elad and Ginsburg [11] on a related ketone, afforded 2,3-benzotropone from 2,3-benzocyclohept-2-enone in 65% (overall) yield, as a pale yellow oil which could be stored unchanged at 0°.

In common with other tropones, 2,3-benzotropone forms a 2,4-dinitrophenylhydrazone under normal conditions. Nevertheless, the carbonyl group is not completely normal. There are only three infrared carbonyl bands, at 1642, 1612, and 1590 cm.$^{-1}$; and although it is not possible to allocate the carbonyl stretching frequency with certainty,[6] even the highest figure is abnormally low. 2,3-Benzotropone also behaves as a base, forming a crystalline picrate and hydrobromide, and dissolves in concentrated sulphuric acid, producing the yellow tropylium cation (XIV), and it can be regenerated by diluting the acid solution with water; even after 10 minutes' boiling in concentrated sulphuric acid, 2,3-benzotropone is recovered on addition of water. Its ultraviolet absorption spectrum, and that of the tropylium ion (XIV), are shown in Figs. 1 and 2. 2,3-Benzotropone consumes exactly 2 mols. of bromine without evolution of hydrogen bromide; during the addition

[7] Buchanan, *J.*, 1954, 1060.
[8] Cook, Gibb, Raphael, and Somerville, *J.*, 1952, 603.
[9] Julia, *Compt. rend.*, 1955, **241**, 882.
[10] Buchanan and Sutherland, *J.*, 1956, 2620.
[11] Elad and Ginsburg, *J.*, 1957, 1286.

of the first mol., an orange complex is precipitated; from this, benzotropone is regenerated by water or methanol. On addition of the second mol. of bromine, the complex redissolves and removing the solvent then affords the tetrabromide (XV) [ν(C=O) 1700 cm.$^{-1}$: no C=C band above 1590 cm.$^{-1}$] which is stable at room temperature but loses hydrogen bromide at *ca.* 100° or on treatment with a base, affording a dibromotropone A, whose structure is largely revealed by the following facts. On oxidation it affords phthalic acid, showing that the bromine atoms are outside the benzene ring and excluding a (tricyclic) cyclopropane structure (such compounds resist [10] oxidative degradation). Compound A is

FIG. 1. *In ethanol.*

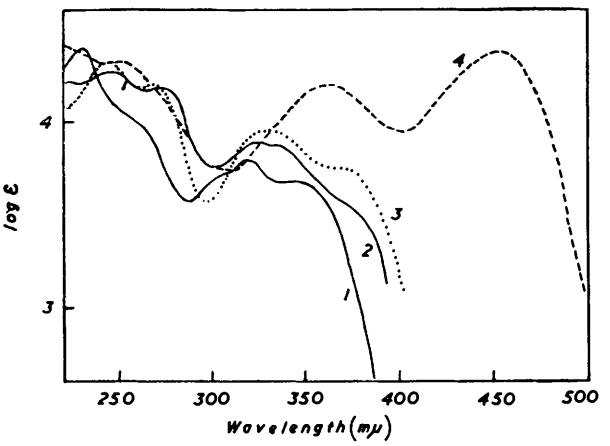
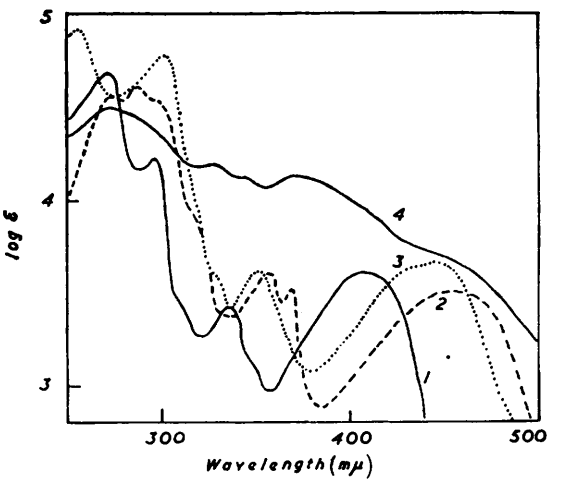


FIG. 2. *In* 15M-*sulphuric acid.*



Absorption spectra of (1) 2,3-*benzotropone* (V), (2) 5,7-*dibromo-* (XVI), (3) 4,7-*dibromo-* (XIX), *and* (4) 5,7-*dinitro*-2,3-*benzotropone* (XX).

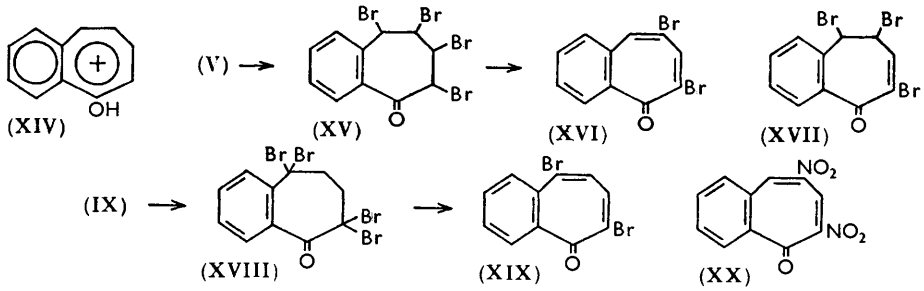
therefore most plausibly formulated as a benzotropone bearing two bromine substituents in the seven-membered ring. Like 2,3-benzotropone, it dissolves in concentrated sulphuric acid, and is reprecipitated on the addition of water, and survives treatment with *boiling* concentrated sulphuric acid, properties which are well-nigh diagnostic of the tropone ring system. Its ultraviolet spectrum (Fig. 1) is closely similar to that of 2,3-benzotropone, and in sulphuric acid the spectrum (Fig. 2) shows the same displacements and intensifications of bands as does that of 2,3-benzotropone.

If the tetrabromide is treated with one mol. of sodium hydroxide in ethanol, the comparatively stable tribromo-compound (XVII) [ν(C=O) 1665 cm.$^{-1}$] is produced, and this

must be heated to 100—120°, or treated with excess of base, before it is converted into the (same) dibromotropone. This defines the position of the ethylenic bond in compound (XVII) and excludes alternative cyclopropane structures; a structure in which the halogen atoms are vicinal may be dismissed as mechanistically improbable. When 2,3-benzotropone is treated with liquid bromine without temperature control, the product is a mixture of the tribromide (XVII) and the dibromotropone A, and the latter is the sole product of reaction between Julia's ketone (VIII) and excess of liquid bromine at 100°. It is thus clear that the ostensibly aromatic seven-membered ring in 2,3-benzotropone is sufficiently unsaturated to add two mols. of bromine, and it is noteworthy that the conjugation may be restored step-wise. It is particularly remarkable that the tribromo-intermediate (XVII) is stable, when the elimination of only a molecule of hydrogen bromide would render the molecule " aromatic."

It has been reported [12] that 2,3-benzocyclohept-2-enone (IX) with liquid bromine gives a solid product. The product, we find, is a dibromotropone B, isomeric with substance A described above. The compound B also yields phthalic acid on oxidation, and is stable in boiling concentrated sulphuric acid whence it is reprecipitated by water. Its ultraviolet spectra in ethanol and in sulphuric acid (Figs. 1 and 2) point to a close relation with isomer A and with 2,3-benzotropone; we therefore regard them both as dibromobenzotropones. It is significant that both A and B show carbonyl absorption in the infrared at $\nmid$1634 cm.$^{-1}$, although neither reacts with 2,4-dinitrophenylhydrazine under the standard conditions. Inertness of the carbonyl is characteristic of the α-substituted tropones (*e.g.*, α-bromotropones), and is some indication that one of the bromine atoms is adjacent to the carbonyl group. In the case of the dibromotropone A at least, this is consistent with its derivation from Julia's ketone (VIII), and from the tribromo-compound (XVII) whose structure has been independently argued. The position of the second bromine atom is less certain, but we visualise the formation of the two dibromotropones by the schemes, (V) ⟶ (XV) ⟶ (XVI), and (IX) ⟶ (XVIII) ⟶ (XIX), and suggest the tentative structures (XVI) and (XIX) for compounds A and B respectively. Several unsuccessful attempts were made to bring about base-catalysed ring contractions of the dibromotropones to substituted naphthoic acids: in mild conditions, starting material was recovered; more forcing conditions led to considerable decomposition.

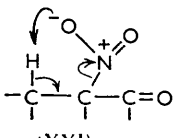
Although 2,3-benzotropone can be recovered in high yield from solution in concentrated hydrochloric or sulphuric acid, it reacts at room temperature with concentrated nitric



acid, or even with 50% aqueous nitric acid, affording a dinitro-derivative in good yield. This product does not react with 2,4-dinitrophenylhydrazine under standard conditions. Oxidation degrades it to phthalic acid, and the nitro-groups are therefore in the seven-membered ring. That the nitration product is a nitro-compound rather than a nitrite is indicated by the very intense bands at 1525 and 1332 cm.$^{-1}$ in the infrared spectrum [13]

[12] Kipping and Junter, *J.*, 1901, **79**, 602.
[13] Bellamy, " Infrared Spectra of Complex Molecules," Methuen, London, 1958, p. 227 *et seq.*

and by the failure of the diphenylamine–sulphuric acid colour reaction.[14] The oxidation evidence, the low $\nu(NO_2)$, and the absence of saturated C–H absorption in the infrared spectrum (potassium chloride disc) point to a tropone structure. Like the other tropones described above, the dinitro-compound dissolves in concentrated sulphuric acid, and is reprecipitated on dilution with water. The ultraviolet spectrum of its ethanol solution (Fig. 1) is related only in general shape to that of 2,3-benzotropone, but in that of its sulphuric acid solution (Fig. 2) no relation can be seen. Catalytic reduction of the dinitrotropone in neutral solution stopped after the uptake of only 3—4 mols. of hydrogen, but in acid solution the theoretical amount (9 mols.) was smoothly and rapidly absorbed; this behaviour is typical of nitro-olefins.[15] The product of the neutral reduction was 2,3-benzocyclohept-2-enone (IX), showing that the ring system remained intact during nitration. The benzocycloheptenone presumably arises by reduction of the diene system, elimination of nitrous acid or its equivalent, and reduction of the resulting tropone. In this case, as in the spontaneous decomposition of 1,2-dinitroalkanes,[16] the driving force is probably the achievement of conjugation (XXI). The product of the acid reduction was a water-soluble syrup, which consumed periodate but could not be further characterised. It seems unlikely that the dinitro-compound is formed by an electrophilic substitution and we regard it as an addition–elimination reaction of N_2O_4, this being produced by mutual oxidation–reduction of tropone and nitric acid. When 2,3-benzotropone is treated at 0° with a solution of dinitrogen tetroxide in carbon disulphide, an unstable intermediate can be isolated. This product spontaneously evolves dinitrogen tetroxide at room temperature, affording the same dinitro-compound in quantitative yield. By analogy with the bromine addition–elimination reaction of benzotropone, we suggest structure (XX) for the product. The dinitrotropone dissolves in aqueous alkali or sodium carbonate solution, and its ultraviolet absorption is thereby radically changed. The solubility in alkali must be ascribed to hydration of the conjugated C=C group, and consequent formation of a substituted nitrocycloalkane. Acidification of the alkaline solution afforded no identifiable product.



(XXI)

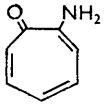
If tropones, as aromatic compounds, undergo nuclear substitutions these ought to be of a nucleophilic character; accordingly, some attempts were made to bring about amination by sodamide or hydrazine, and hydroxylation by alkali. In each instance, the tropone was either recovered or destroyed, according to the severity of the reaction conditions.

The chemistry of 2,3-benzotropone, as explored by Eschenmoser and by ourselves, provides little evidence of aromaticity in the seven-membered ring. Indeed, if we except its remarkable stability to boiling concentrated sulphuric acid—and this is in fact a property of a tropylium ion *per se*, the neutral molecule may be fairly accurately described as a conjugated dienone. In contrast to this, αβ-benzotropolone (VI) shows distinctly aromatic qualities,[8,17] and the isomeric hydroxytropone (IV) is likewise aromatic rather than olefinic.[7,10] Indeed, the remarkable influence exerted by a nuclear hydroxyl group on the character of the seven-membered ring has yet to receive a satisfactory explanation.

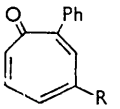
Substantially the same conclusions can be drawn from the chemistry of tropone [5,18] (III), tropolone [19] (II), and the isomeric hydroxytropones.[20] Indeed, the case for aromaticity in tropones, in terms of chemical evidence, rests entirely on amination by hydrazine or hydroxylamine. Thus tropone (III) gives the amino-derivative (XXII), and

[14] Feigl, " Spot Tests," Elsevier, Amsterdam, 1956, p. 168.
[15] Levy and Rose, *Quart. Rev.*, 1948, **1**, 385.
[16] *Idem, ibid.*, p. 382.
[17] Nozoe, Kitahara, and Ando, *Proc. Japan Acad.*, 1951, **27**, 107.
[18] Nozoe, Mukai, and Takase, *Sci. Reports Tôhoku Univ.*, 1956, **39**, 164.
[19] Pauson, *Chem. Rev.*, 1955, **55**, 9.
[20] Nozoe, Mukai, Ikegami, and Toda, *Chem. and Ind.*, 1955, 66; Coffey and Johnson, *J.*, 1958, 1741; Johns, Johnson, and Tisler, *J.*, 1954, 4605.

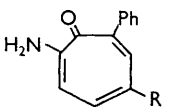
the phenyltropone (XXIII) yields [21] the amino-derivative (XXIV); in the latter case at least, cold liquid ammonia suffices to bring about the same transformation.[21] These reactions have been interpreted [21] as nucleophilic substitutions, involving a hydride-transfer step (XXVII), and the amination by ammonia presumably requires hydride-extrusion. In view of the demonstrated dienone character of tropones, it is reasonable to



(XXII)

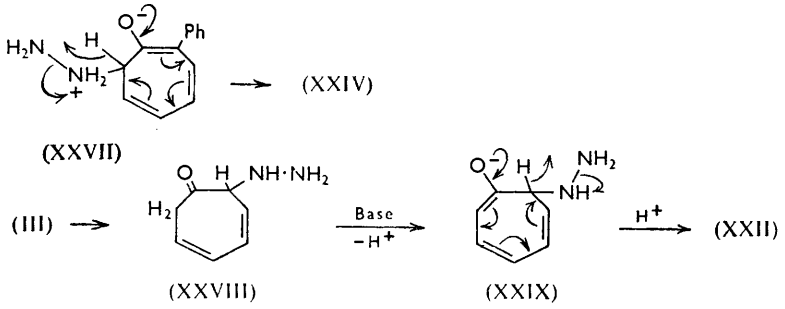


(XXIII) R = H
(XXV) R = Br



(XXIV) R = H
(XXVI) R = Br

consider an addition mechanism, *e.g.*, (III) ⟶ (XXVIII) ⟶ (XXIX) ⟶ (XXII), which utilises an essentially identical intermediate (XXIX). Such a mechanism explains adequately the reactions cited above, and explains *more* satisfactorily the remarkable



amination of the bromotropone (XXV) to (XXVI), in which the bromine atom resists nucleophilic displacement.[22] Its validity is open to dispute, but so also, we believe, is the aromatic character of tropones.

Experimental

Ultraviolet absorption spectra were measured on a Unicam S.P. 500 spectrophotometer and infrared spectra on a model 13 Perkin–Elmer double-beam instrument.

2,3-Benzocyclohepta-2,6-dienone (XIII).—(*a*) 7-Bromo-2,3-benzocyclohept-2-enone [23] (XII), b. p. 106—108°/0·05 mm. (Found: Br, 33·5. Calc. for $C_{11}H_{11}OBr$: Br, 33·65%) (2·4 g.), was heated at 170° for 1 hr. with collidine (15 ml.), cooled, treated with 6N-hydrochloric acid (50 ml.), and extracted with ether. The ethereal solution was washed with water, dried, and concentrated. The resulting pale yellow oil [ν(C=O) 1660 cm.$^{-1}$: liquid film] polymerised on storage or attempted distillation, but yielded a crimson 2,4-dinitrophenylhydrazone, which was chromatographed in benzene on alumina and, crystallised from acetic acid, had m. p. 218° (lit.,[9,23] 219°).

The bromo-ketone (XII) (2·4 g.) and 2,4-dinitrophenylhydrazine (2 g.) in acetic acid (20 ml.) containing a trace of hydrochloric acid were heated under reflux for 5 min. All solvent was then removed *in vacuo*, and the residue was chromatographed as described above, yielding the same 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 218°.

(*b*) 2,3-Benzocyclohept-2-enone (10 g.), isopropenyl acetate (50 ml.), and a few crystals of toluene-*p*-sulphonic acid were heated so that acetone slowly distilled off through a 6 inch vacuum-jacketed fractionating column. After 2 hr., no more acetone came over, and the solution was cooled, benzene (50 ml.) and 2N-sodium carbonate solution (30 ml.) were added, and the organic

[21] Nozoe, Mukai, Minigishi, and Fujisawa, *Sci. Reports Tôhoku Univ.*, 1953, **37**, 388.
[22] *Idem, ibid.*, 1954, **38**, 141.
[23] Ramirez and Kirby, *J. Amer. Chem. Soc.*, 1953, **75**, 6026.

layer was washed with water, dried, and concentrated in a vacuum. 3-*Acetoxy*-1,2-*benzocyclohepta*-1,3-*diene* (X) distilled at 90—92°/0·1 mm. and had m. p. 54° (from low-boiling light petroleum) (Found: C, 77·1; H, 6·8. $C_{13}H_{14}O_2$ requires C, 77·2; H, 6·9%), ν(C=O) 1765 cm.$^{-1}$ (in CCl_4). The enol-acetate (1·5 g.) in dry chloroform (10 ml.) and carbon tetrachloride (10 ml.) was refluxed for 1 hr. with *N*-bromosuccinimide (1·37 g.) and a trace of dibenzoyl peroxide. The solution was then cooled, washed thrice with water (20 ml.), dried, and concentrated. The oily product [ν(C=O) 1660 cm.$^{-1}$] which resinified on storage or attempted distillation, afforded a crimson 2,4-dinitrophenylhydrazone identical (m. p. and mixed m. p.) with that described above.

2,3-*Benzocyclohepta*-2,4-*dienone* (VIII).—(*a*) Anhydrous t-pentyl alcohol (2 ml.) and dry benzene (18 ml.) were boiled with sodium wire (0·8 g.) for 16 hr. To the resulting solution was added 1,2,3,4-tetrahydro-1-oxo-2,3-cyclopropanonaphthalene [10] (XI) (2 g.), and heating was continued for a further 6 hr. After cooling of the solution, excess of 6N-hydrochloric acid was added, and the organic layer was separated, washed with water, dried, and distilled, affording the dienone (VIII) (60%), b. p. 146—150°/15 mm. (lit.,[9] 145°/13 mm.), $\lambda_{max.}$ (log ε) 235 (4·74), 259 (3·81), 318 (3·29), ν(C=O) 1680 cm.$^{-1}$ (film). It gave a 2,4-dinitrophenylhydazone, m. p. 217° (from acetic acid) (lit.,[9] 224°) (Found: C, 60·6; H, 4·4; N, 16·4. Calc. for $C_{17}H_{14}O_4N_4$: C, 60·5; H, 4·2; N, 16·6%).

(*b*) 4-Hydroxy-2,3-benzocyclohept-2-enone (VII) (0·75 g.) was heated for 30 min. at 160° with boric acid (1 g.) and finally distilled from the melt at 200° (bath)/15 mm. The product was identified as the enone (VIII) by comparison of infrared spectra, and afforded the 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 217°.

(*c*) 2,3-Benzosuberenone (IX) (20 g.) in dry carbon tetrachloride (100 ml.) was heated under reflux for 1 hr. with *N*-bromosuccinimide (25 g.) and a trace of dibenzoyl peroxide. The resulting solution was washed with water (3 × 100 ml.) and concentrated *in vacuo*. The oily product was then heated at 100° for 2 hr. with collidine (50 ml.). Solid material was removed, chloroform (50 ml.) was added, and the solution repeatedly extracted with 6N-hydrochloric acid, washed with water until the washings were neutral, dried, and concentrated. The product (30%), b. p. 146°/15 mm., was identified as the unsaturated ketone (VIII) from its infrared spectrum.

2,3-*Benzotropone* (V).—(*a*) Julia's ketone (VIII) (1 g.) in t-butyl alcohol (20 ml.) and acetic acid (3 ml.) was heated under reflux for 3 hr. with selenium dioxide (0·8 g.), cooled, and filtered. The filtrate was dissolved in ether (50 ml.) and extracted with concentrated hydrochloric acid (2 × 5 ml.). The deep yellow solution of the tropylium salt was diluted with water (10 ml.), and the resulting emulsion was extracted with chloroform (3 × 10 ml.). This extract yielded 2,3-benzotropone (300 mg.), b. p. 140°/0·1 mm., $\nu_{max.}$ (liquid film) 3510 w, 3030 m, 16040 s, 1610 s, 1588 s, 1550 s, a number of sharp bands in the finger-print region, and 3 broad, strong C–H deformation bands at 800, 770, and 710 cm.$^{-1}$. The 3510 cm.$^{-1}$ band can only be due to water, but could not be removed by distillation. The benzotropone afforded a picrate, m. p. 115—117° (from chloroform), and a magenta-coloured 2,4-dinitrophenylhydrazone, m. p. 226—228° (from acetic acid), both identical with authentic samples (m. p. and mixed m. p.), and a hydrobromide, m. p. 89° (from ethyl acetate) (Found: C, 51·4; H, 4·3; Br, 31·5. $C_{11}H_9OBr$ requires C, 51·8; H, 4·3; Br, 31·2%). A few mg. of the tropone were added to concentrated sulphuric acid and boiled for 10 min. The solution darkened, but cooling and addition of water precipitated an oil which gave a 2,4-dinitrophenylhydrazone identical (m. p. and mixed m. p.) with that derived from 2,3-benzotropone.

(*b*) *N*-Bromosuccinimide (1·7 g.) and a trace of dibenzoyl peroxide were added to 2,3-benzocyclohepta-2,4-dienone (VIII) (1·56 g.) in dry " AnalaR " carbon tetrachloride (15 ml.), and the mixture was boiled under reflux. Hydrogen bromide was evolved copiously. After 2 hr., the mixture was washed with water, dried, and concentrated under a vacuum to an oil. The infrared spectrum of this product indicated that it was incompletely dehydrobrominated. It was heated at 100° for 1 hr. with collidine (5 g.), then diluted with chloroform, and the collidine was removed by washing with 6N-hydrochloric acid. Finally, the tropone was extracted by means of concentrated hydrochloric acid, and isolated in the manner described above (yield 1·02 g.).

(*c*) The α-bromo-ketone (XII) (13·6 g.), triply distilled before use, was heated in dry carbon tetrachloride (100 ml.) with recrystallised *N*-bromosuccinimide (11 g.) and dibenzoyl peroxide (50 mg.). The mixture was heated for 3 hr., cooled, washed with water, and dried. When

concentrated this yielded crude 4,7-*dibromo*-2,3-*benzocyclohept*-2-*enone*, which was heated for 3 hr. at 100° with collidine (150 ml.), and then briefly at the b. p. After cooling, collidine hydrobromide was filtered off, the filtrate was diluted with chloroform, and the solution was washed with 6N-hydrochloric acid until all collidine had been removed. The tropone was then isolated as described above (yield 5·6 g., 63%). It was possible to purify the crude 4,7-*dibromo*-2,3-*benzocyclohept*-2-*enone* by distillation at 135—145°/0·003 mm. (with considerable decomposition). The distillate solidified when rubbed with carbon tetrachloride, and crystallised from ethyl acetate; it had m. p. 80° (Found: C, 41·4; H, 3·3; Br, 50·4. $C_{11}H_{10}OBr_2$ requires C, 41·5; H, 3·1; Br, 50·3%). It was stable for *ca.* 3 months at 0°, but at room temperature slowly evolved hydrogen bromide and was converted in 3 months into 2,3-benzotropone hydrobromide (m. p. and mixed m. p. 89°). Like authentic benzotropone hydrobromide, it was decomposed by water to the parent tropone, and yielded 2,3-benzotropone 2,4-dinitrophenylhydrazone (m. p. and mixed m. p.) when treated directly with 2,4-dinitrophenylhydrazine under standard conditions.

Bromination of 2,3-*Benzotropone*.—(*a*) The tropone (V) (100 mg.) was treated with bromine (5 drops). When the initial evolution of hydrogen bromide had subsided, the solution was warmed to complete the reaction. Excess of bromine was then removed under a vacuum; the gummy residue solidified on being rubbed with methanol, yielding 5,7-*dibromo*-2,3-*benzotropone*, m. p. 169° (from ethyl acetate) (Found: C, 42·0; H, 2·3; Br, 50·6. $C_{11}H_6OBr_2$ requires C, 42·0; H, 1·9; Br, 50·95%). Evaporation of the mother-liquors afforded 4,5,7-*tribromo*-2,3-*benzocyclohepta*-2,6-*dienone* (XVII), m. p. 156° (decomp.) (from ether–pentane) (Found: C, 33·3; H, 1·65. $C_{11}H_7OBr_3$ requires C, 33·2; H, 1·8%), ν(C=O) (Nujol) 1665 cm.$^{-1}$. The substance gave a positive Lassaigne test for bromine, and at its m. p. lost hydrogen bromide, affording the dibromotropone (XVI) described above (m. p. and mixed m. p. 165°).

(*b*) The tropone (600 mg.) in carbon tetrachloride (1 ml.) was treated with bromine (1·25 g.) in carbon tetrachloride (12 ml.), a red crystalline complex separating; this solid redissolved rapidly on warming, or more slowly when the remainder of the bromine solution was added. At no time was any hydrogen bromide evolved. The solvent was removed *in vacuo* at below 30°, leaving a gum which solidified when triturated with methanol–ether. The colourless 4,5,6,7-*tetrabromo*-2,3-*benzocyclohept*-2-*enone* (XV), crystallised from ethyl acetate–pentane at −30°, had m. p. 123° (Found: C, 28·1; H, 1·55; Br, 67·0. $C_{11}H_8OBr_4$ requires C, 27·9; H, 1·7; Br, 67·1%), ν(C=O) 1700 cm.$^{-1}$.

The red complex dissolved in methanol with loss of colour, and this solution yielded 2,3-benzotropone 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 226°.

When the tetrabromide (XV) was heated at 130° for 5 min., hydrogen bromide was evolved, and the product was identified by m. p. and mixed m. p. and by its infrared spectrum as the dibromotropone (XVI). The same transformation was effected by adding 5N-sodium hydroxide (5 drops) to the tetrabromide (20 mg.) in methanol (2 ml.), the product crystallising.

When the tetrabromide (470 mg.) in ethanol (2 ml.) was heated on the steam-bath for 1 hr. with 0·1N-sodium hydroxide (10 ml., 1 mol.), there separated on cooling 4,5,7-tribromo-2,3-benzocyclohepta-2,6-dienone (XVII), m. p. and mixed m. p. 152°.

Bromination of Julia's Ketone.—The ketone (100 mg.) was treated with bromine (5 g.) and left at room temperature for 28 days. Excess of bromine was then removed under a vacuum, and the residual gum was heated at 100° for 8 hr. This produced a semisolid material which was triturated with ethyl acetate and crystallised from acetic acid; it then had m. p. 166°, undepressed on admixture with 5,7-dibromo-2,3-benzotropone.

Bromination of Benzosuberenone.—(*a*) The ketone (1 g.) was treated dropwise with bromine until the colour persisted, and thereafter a further 3 g. of bromine was added. The mixture was set aside for 3 days at room temperature, and finally warmed on the steam-bath till the evolution of hydrogen bromide ceased. The gummy residue was titrated with methanol, and the pale yellow 4,7-*dibromo*-2,3-*benzotropone* (XIX) crystallised from acetic acid, then having m. p. 220° (120 mg.) (Found: C, 41·8; H, 2·3; Br, 50·6. $C_{11}H_6OBr_2$ requires C, 42·0; H, 1·9; Br, 50·95%).

When a few mg. of either of the dibromotropones was boiled in concentrated sulphuric acid for *ca.* 5 min., the solution darkened, but the starting material was recovered on addition of water. It was also recovered from solution in concentrated sulphuric acid after about 4 months at room temperature.

Oxidation of the Dibromobenzotropones.—The dibromo-compound (100 mg.) was heated on

the steam-bath with potassium permanganate (1 g.) and potassium hydroxide (0·5 g.) in water (10 ml.). After 3 hr. sodium hydrogen sulphite was added to discharge the colour, the solution was filtered, and the filtrate was acidified with 6N-hydrochloric acid and extracted with ether. This afforded a gum which, when heated briefly with acetic anhydride and sublimed at 140—160°/15 mm., had m. p. 130°, undepressed on admixture with phthalic anhydride.

Nitration of 2,3-Benzotropone.—(*a*) The tropone (130 mg.) was added to concentrated sulphuric acid (4 ml.) and nitric acid (1 ml.), and the solution was kept at room temperature for 24 hr. During the first 10 min. the colour changed from yellow to deep magenta, and nitrous fumes were evolved. After 24 hr. the solution (which was once more yellow) was poured on ice. *5,7-Dinitro-2,3-benzotropone*, collected by filtration, washed with water, and crystallised from acetic acid, had m. p. 165° (120 mg.) (Found: C, 53·5; H, 2·6; N, 11·2. $C_{11}H_6O_5N_2$ requires C, 53·7; H, 2·4; N, 11·4%), $\lambda_{max.}$ (log ε) (in 0·1N-NaOH), 220 (4·4), 346 (4·23), 460 (3·32), $\lambda_{min.}$ (log ε) 280 (3·78), 410 (3·26).

The dinitro-compound (45 mg.) was heated on the steam-bath for 2 hr. with 6N-nitric acid (3 ml.), and the mixture was then filtered. Evaporation of the filtrate *in vacuo* gave a small amount of solid which was sublimed, giving needles of phthalic anhydride, m. p. and mixed m. p. 130°.

(*b*) The tropone (0·5 g.) was added to " AnalaR " concentrated nitric acid (15 ml.). The resulting solution slowly evolved brown fumes and deposited crystals. After 5 hr. the latter were filtered off, washed with water, and crystallised from acetic acid; it had m. p. 165° (0·65 g.).

The same product was obtained by using 50% aqueous nitric acid or nitric acid in acetic acid, and in each case nitrous fumes were given off.

(*c*) Dinitrogen tetroxide (prepared by heating a 4 : 1 mixture of " silver sand " and lead nitrate) in a stream of dry nitrogen was passed through a solution of 2,3-benzotropone (100 mg.) in dry carbon disulphide (15 ml.), until the colour changed from yellow to brown and globules of oil began to separate. The solvent was removed at <30° under a vacuum, leaving a brown pasty solid (270 mg.) which decomposed on being ground in Nujol or kept for 15 min. at room temperature. In both cases brown fumes were evolved, and the colour changed to yellow. The product, crystallised from ethyl acetate, had m. p. 164° (212 mg., 96%). It was identical (mixed m. p. and infrared spectrum) with the product above.

Reductions.—(*a*) The dinitro-compound (100 mg.) in acetic acid (25 ml.) was reduced in the presence of platinum (from 100 mg. of platinum oxide). After 1 hr., *ca.* 32 ml. of hydrogen (3·5 mols.) had been absorbed and no further uptake took place. Catalyst and solvent were removed, leaving a pale yellow oil (53 mg.) which was identified as 2,3-benzocyclohept-2-enone (IX) by comparison of infrared spectra and by the identity of the 2,4-dinitrophenylhydrazones.

(*b*) The dinitro-compound (100 mg.) in acetic acid (30 ml.) containing concentrated sulphuric acid (2 ml.) was hydrogenated in presence of platinum (from 110 mg. of platinum oxide). Absorption of hydrogen had practically ceased after 1 hr. when 92 ml. (*ca.* 9 mol.) of hydrogen had been consumed. Catalyst was removed, and the solution was basified with 2N-sodium hydroxide. Continuous ether-extraction failed to isolate any material. The aqueous solution consumed periodate, and after 3 hr. at room temperature with excess of sodium metaperiodate it was extracted with ether. This afforded a trace of oil, from which no solid could be obtained.

In an essentially identical experiment, dry ethanol saturated with hydrogen chloride was used as solvent. Reduction was even more rapid, being complete in 30 min. After removal of catalyst and solvent, there remained a syrup, which was heated under reflux in acetic acid saturated with hydrogen chloride, in an attempt to bring about a hydramine fission.[24] No pure product could be isolated.

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[24] Rabe and Schneider, *Annalen*, 1909, **365**, 377.