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AZULENES AND RELATED SUBSTANCES—XIV

SYNTHESIS OF SOME BENZOTROPYLIUM SALTS AND BENZOTROPONES*†

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Abstract—In connection with the synthesis of system I, preparation of certain benzotropylium salts and benzotropones has been investigated. Action of NBS on benzocycloheptatriene yielded 1,2-benzo-1,3,5-cycloheptatrien-7-yl-N-succinimide, a ready substrate for benzotropylium ion generation. Selenium dioxide oxidation of benzocycloheptatriene yielded both 2,3-benzotropone and 4,5-benzotropone. Similar oxidation of 4'-methoxy-1,2-benzo-1,3,5-cycloheptatriene furnished all three possible methoxybenzotropones.

THE WORK DESCRIBED in the present communication was primarily undertaken with a view to synthesizing system I.‡ However, we were anticipated in this by Proctor

I

et al.[1-3] In as much as our work has led to some novel and useful procedures for the preparation of certain benzotropylium salts and benzotropones, we wish to place it on record.

Benzocycloheptatrienes

A number of methods are currently available[4] for the preparation of tropone and tropylium salts from cycloheptatriene. It was planned to extend some of these methods to the required benzotropones and benzotropylium salts. For this purpose the synthesis of suitable benzocycloheptatrienes was first undertaken.

Though several methods[5-7] for the preparation of 1,2-benzocycloheptatriene (II/IV) are on record, it appeared desirable to investigate its preparation by simple allylic bromination-dehydrobromination of benzosuberene (III).[8] Benzosuberene readily reacted with one mole of N-bromosuccinimide (NBS) in refluxing CCl_4 to

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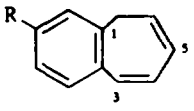
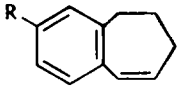
† Abstracted from the Ph.D thesis (Poona University, 1966) of K. C. Srivastava

‡ Molecular orbital calculations (LCAO method) of this system have been carried out by Prof. K. P. Sinha and these indicate a delocalization energy of 2·05 β.

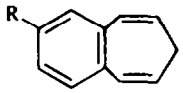
give an unstable bromo derivative,* which after usual work-up gave a product (85–90%), shown by GLC to consist of unreacted benzosuberene (10–15%) and a new compound (85–90%). A similar product resulted when the crude bromination product was first treated with $AgNO_3$ in DMSO.[9] The new compound was isolated by prep. GLC and readily characterized (m.p. -8 to $-7°$; λ_{max}^{EtOH} 274·5 nm, log ε 3·90; IR) as II, by comparison with the reported[5] data; its NMR spectrum is also in full agreement with structure II. None of the isomeric benzocycloheptatriene (IV)[5] was formed.



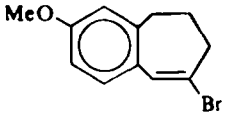
II: R = H
V: R = OMe



III: R = H
VI: R = OMe



IV: R = H
VII: R = OMe



VIII

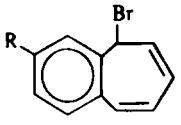
Next, the preparation of 4′-methoxy-benzocycloheptatriene (V/VII) was investigated. 7-Methoxybenzosuberone[10] was prepared by the polyphosphoric acid cyclization† of δ-(*m*-methoxyphenyl)-valeric acid.[10] The ketone was reduced (LAH) and the resulting alcohol dehydrated with *p*-TsOH in C_6H_6 to furnish the required olefin (VI) in over 94% yield. This on interaction with NBS led to a product which after distillation showed at least nine components (GLC) of which four (c Nos. 4, 5, 7 and 8 with RRT of 1, 1·1, 3·2 and 3·7 and, amounting to 21, 50, 7 and 18% respectively) predominated. Of these components 4, 5 and 8 could be obtained pure by chromatography over $AgNO_3$-silica gel. Component 4 was identified as the unreacted olefin (VI) while the major product (component 5), from its spectral data (λ_{max}^{EtOH} 220, 288 nm with log ε 4·66 and 4·33 respectively. NMR: benzylic allylic C$\underline{H}_2$, 2H doublet centred at $\delta = 2{\cdot}97$, $J = 6{\cdot}5$ Hz; OC$\underline{H}_3$, 3H singlet at $\delta = 3{\cdot}73$: olefinic and aromatic protons, complex 7H multiplet located between $\delta = 5{\cdot}43$–$7{\cdot}27$) was recognized as the desired 4′-methoxybenzocycloheptatriene (V). The third product (component 8) $C_{12}H_{13}OBr$) shows λ_{max}^{EtOH} 268 nm (log ε 4·1) and its bromine atom is unreactive (no precipitate with alc. $AgNO_3$; recovered unchanged from distillation with quinoline) and hence is considered to be VIII. Formation of this vinyl bromo compound in the NBS reaction is readily rationalized and similar examples are known.[11]

* It appears that the bromo derivative readily loses HBr during solvent removal, so that the product obtained after work-up is essentially the elimination product

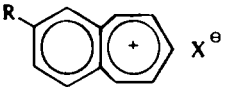
† During this cyclization it was found that demothoxylation (to give unsubstituted benzosuberone) took place to the extent of ~10%)

Benzotropylium salts

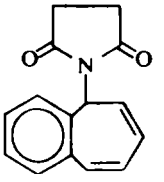
Action of NBS on the above two benzocycloheptatrienes was investigated with the hope of obtaining the covalent bromo derivatives (IX, X), as these on interaction with $AgClO_4$ in $MeNO_2$ should conceivably give the corresponding benzotropylium salts (XI, XII).[12] In practice, 1,2-benzo-1,3,5-cycloheptatriene (II) on exposure to one mole equivalent of NBS in refluxing CCl_4 yielded in 22% yield a crystalline compound analyzing for $C_{15}H_{13}O_2N$, as the only identifiable product. From its elemental analysis and spectral data [λ_{max}^{EtOH} 272 nm, log ε 3·84. IR in Nujol: C=O 1710, 1770 (weak) cm^{-1} characteristic of N-substituted succinimides[13]] this product is assigned structure XIII. A similar product has been reported from the reaction of cycloheptatriene and NBS.[13] We now find that compound XIII is an excellent, stable precursor for benzotropylium salts (XI). Thus, the succinimide derivative (XIII) on



IX: R = H
X: R = OMe



XI: R = H
XII: R = OMe



XIII

treatment with $HClO_4$ in AcOH readily furnished benzotropylium perchlorate (XI, $X^- = ClO_4^-$)[14] as a yellow crystalline salt in ~60% yield.

Reaction of 4'-methoxy-1,2-benzo-1,3,5-cycloheptatriene (V) with NBS, on the other hand, failed to give any succinimide derivative corresponding to XIII, but instead yielded an unstable bromide, presumably X. Treatment of the crude bromide with $AgClO_4$ in $MeNO_2$ furnished in only low yield a microcrystalline brown solid, recognized from its IR spectrum [in Nujol: the spectrum is superimposable on that of the fluoroborate, described below, except for the strong absorptions due to different anions—at 1100 cm^{-1} (ClO_4^-),[14] at 1070 cm^{-1} (BF_4^-)[15]] as 4'-methoxybenzotropylium perchlorate (XII; $X^- = ClO_4^-$).

Both benzotropylium and 4'-methoxybenzotropylium fluoroborate could be more conveniently obtained by hydride exchange between the appropriate benzocycloheptatriene (II or V) and triphenylmethyl fluoroborate; this procedure is patterned after the earlier work of Dauben *et al.*[16] on the synthesis of tropylium salts.

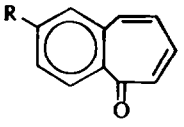
Benzotropones

It has been reported[17,18] that SeO_2 oxidation of cycloheptatriene gives tropone in 30–40% yield. Since we had already standardized the preparation of methoxybenzocycloheptatriene (V), extension of the SeO_2 oxidation procedure to this substrate, appeared to be the method of choice for preparing methoxybenzotropone, required in connection with our projected synthesis of I.

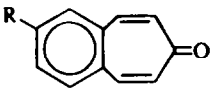
As a preliminary, SeO_2 oxidation of benzocycloheptatriene (II) was investigated. This reaction, as expected, yielded both 2,3-benzotropone[14] (XIV: 13%) and 4,5-

benzotropone[19,20] (XVI; 27%), which were identified by comparison with the data reported in the literature.

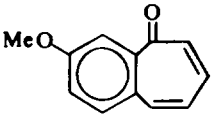
Reaction of 4'-methoxy-benzocycloheptatriene (V) with SeO_2 proved quite complex resulting in the formation of at least six compounds. By systematic chromatography four of these (A, B, C, D, in order of decreasing R_f) could be obtained pure in 0·2, 10, 1·6 and 20% yield respectively. Compound A (m.p. 82–83°, $C_{12}H_{10}O_2$) is assigned



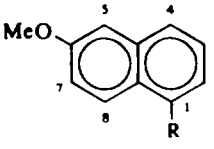
XIV: R = H
XV: R = OMe



XVI: R = H
XVII: R = OMe



XVIII



XIX: R = CHO
XX: R = COOH

structure XIX in view of its spectral characteristics: λ_{max}^{EtOH} 308 (log ε 4·21), 244 nm (log ε 4·78), (*cf.* α-naphthaldehyde $\lambda_{max}^{heptane}$ 329, 310, 248, 243, 224, 211 nm);[22] IR (KBr), C=O 1690 cm^{-1}; NMR (CCl_4), $OC\underline{H}_3$ (3H, s, 3·8 ppm), C_5—H (1H, d, 6·98 ppm, J = 2 Hz), C_7—H (1H, dd, 7·15 ppm, J_o = 9·5 Hz, J_m = 2 Hz), C_8—H (1H, d, 9·05 ppm, J = 9·5 Hz; this proton is deshielded by virtue of its being in the peri-position to the aldehyde function), C_2, C_3, C_4-protons (3H, ABC-type, 9-line multiplet located between 7·33–7·83 ppm), C$\underline{H}$O (1H, s, 10·16 ppm). This aldehyde was further characterized by its Ag_2O oxidation to the corresponding carboxylic acid (XX). The other three compounds (B, C, D) have been identified as the methoxy-benzotropones XVIII, XV and XVII respectively. These structures rest on their spectral characteristics (Table 1); the characterization of each of these isomers was made possible by an analysis of their NMR spectra and this is briefly discussed below. Both in the SeO_2 oxidation of benzocycloheptatriene (II) and the 4'-methoxy-benzocycloheptatriene (V), the major tropone resulted from oxidation at C_5 (cyclo-heptatriene numbering), being the less hindered position. Naphthaldehyde (XIX), evidently results from a rearrangement during the SeO_2 oxidation.[23]

Table 1 summarizes the NMR spectral data of these benzotropones. All three 2,3-benzotropones (XIV, XV, XVIII) have a 1H signal in the ~7·6–8 ppm region, assignable to the benzene-ring proton that is at the peri-position (6'-carbon) to the carbonyl, this deshielding arising due to the anisotropy of the carbonyl group.[24]

TABLE 1. SPECTRAL CHARACTERISTICS OF SOME BENZOTROPONES

Compound / Absorption	4'-Methoxy-2,3-benzotropone XV	5'-Methoxy-2,3-benzotropone XVIII	4'-Methoxy-4,5-benzotropone XVII
λ_{max}^{EtOH} nm (log ε)	229 (4·27) 273 (4·30) 325 (3·58) 350 (3·40)	232 (4·46) 248 (4·47) 318 (3·98) 330 (3·94) 370 (3·80)	237 (4·61) 272·5 (4·70) 322 (4·07) 340 (4·00)
IR (KBr):			
C=O (cm^{-1})	1580	1600	1600
C=C (cm^{-1})	1610 1645	1645 1660	1625 1650
NMR:	6H, complex pattern at 6·1–7·1 ppm); C_6'—H, d, 8·1 ppm, J = 8 Hz OCH_3, s, 3·74 ppm	6H, complex pattern at 6·1–7·36 ppm; C_6'—H, d, 7·63 ppm, J = 3 Hz OCH_3, s, 3·81 ppm	7H, complex pattern at 6·1–7·3 ppm; OCH_3, s, 3·71 ppm

This signal is absent from the NMR spectra of the 4,5-benzotropones (XVI, XVII) and hence serves to differentiate between the two classes, which are otherwise hard to distinguish on the basis of UV and IR data. The splitting pattern of this signal (Table 1) uniquely differentiates between 4'-methoxy-2,3-benzotropone (XV; *ortho*-coupled, J = 8 Hz) and 5'-methoxy-2,3-benzotropone (XVIII; *meta*-coupled, J = 3 Hz).

EXPERIMENTAL

For general remarks see Part XIII of this series.[25] Analytical GLC was carried out on an "Aerograph" model A-350-B using 150 cm × 5 mm column packed with 20% diethyleneglycol polysuccinate on Chromosorb W (60–80 mesh), using H_2 as carrier gas. For preparative GLC a 6' × 1" column with the same stationary phase was used on a Perkin-Elmer Vapour Fractometer (Model 154-D), using N_2 as the carrier gas.

TLC was carried out with silica gel containing 15% plaster of Paris, unless specified to the contrary: visualization was carried out by spraying with conc. H_2SO_4, followed by heating at 100–110° for 10–15 min. $AgNO_3$-silica gel was prepared according to a previously reported procedure.[26]

1,2-*Benzo*-1,3,5-*cycloheptatriene* (II). Benzosuberene[8] (4·32 g, 0·03 M), NBS (freshly crystallised, 5·06 g, 0·03 M), benzoyl peroxide (20 mg) and dry CCl_4 (30 ml) were mixed and refluxed (N_2) over an electric tungsten lamp. After 1 hr, the product was cooled, filtered to remove succinimide and, the filtrate washed with 5% $NaHCO_3$ aq (10 ml) and then with H_2O (20 ml) and dried. Solvent was removed and product thus obtained was distilled to give a colourless liquid (3·83 g), b.p. 78–80°/2 mm, n_D^{30} 1·6; GLC (temp 160°) showed it to consist of benzosuberene (~ 15%) and the required II. Pure II was isolated from this by prep. GLC: b.p. 59°/1 mm, m.p. − 8 to − 7°, n_D^{30} 1·6050 (Lit.[5]: m.p. − 8 to − 7°). IR (liq. film): 1481, 1444, 1423, 942, 882, 816, 793, 772, 748, 720, 692 cm^{-1}. NMR (CCl_4): benzylic allylic CH_2 (2H, d, 2·96 ppm, J = 6 Hz), olefinic protons (3H complex multiplet located between 5·4–6·55 ppm; 1H signal overlapped by aromatic protons ~6·9 ppm, aromatic protons (4H multiplet located between 6·9–7·3 ppm). (Found: C, 92·70; H, 6·90. $C_{11}H_{10}$ requires: C, 92·91; H, 7·09%).

In a variation of the above method, the product after removal of CCl_4 was dissolved in DMSO (2 ml) and a soln of $AgNO_3$ (5·2 g) in the same solvent (12 ml) was added. There was immediate precipitation of

AgBr. After keeping aside in the dark, at room temperature for 1 hr, the mixture was worked up (filtration of AgBr, dilution with water and extraction with pet. ether) to give a product essentially identical with the one obtained by the earlier method.

4'-Methoxy-1,2-benzo-1,3,5-cycloheptatriene (V): *7-Methoxybenzosuberone.*[10] To polyphosphoric acid (from 18 g P_2O_5 and 9 ml 85% orthophosphoric acid)[27] at 85-90°, *δ-(m*-methoxyphenyl)-valeric acid[10] (2·7 g) was added and the mixture stirred at this temp for 45 min. After the usual work-up the product was distilled to give two fractions: (i) b.p. 80-85°/1 mm, 0·26 g and, (ii) b.p. 110-120°/1 mm, m.p. 56-58°, 1·97 g. Fraction (i) was identified as benzosuberone. Fraction (ii) was recrystallised from cyclohexane and had m.p. 58-59° and was the required 7-methoxybenzosuberone (Lit.[10] m.p. 59-60°): λ_{max}^{EtOH} 223 (log ε 4·19), 271·5 nm (log ε 4·22): IR (Nujol): C=O 1667 cm^{-1}.

7-Methoxybenzosuberol. The above ketone (2·63 g, 0·014 M) in dry ether (20 ml) was reduced with a slurry of LAH (0·23 g, 0·006 M) in ether (20 ml) in the usual manner (room temp, 15 hr) and worked up with H_2SO_4 aq (15%, 15 ml). The crude product was recrystallised from EtOH to give silky needles (2·64 g), m.p. 91-93°. (Found: C, 75·03: H, 8·59. $C_{12}H_{16}O_2$ requires: C, 74·97: H, 8·39%).

7-Methoxybenzosuberene (VI).* The above alcohol (1·2 g, 0·006 M), *p*-TsOH (0·1 g) and C_6H_6 (50 ml) were refluxed with azeotropic removal of water (15 min). Finally, some C_6H_6 (20 ml) was distilled off, the residue cooled, diluted with pet. ether (20 ml) and passed through a column of silica gel (II; 10 cm × 1·5 cm), which was washed with pet. ether (300 ml). From the combined eluterates, the solvent was flashed off and the residue distilled to give VI (1·03 g), b.p. 81-82°/1 mm, n_D^{30} 1·5860. λ_{max}^{EtOH} 260 nm (log ε 4·36). IR (smear): 1616, 1513, 1269, 1122, 1042, 820 cm^{-1}. NMR (CCl_4): C_4—$C\underline{H}_2$ (2H, m, 1·98 ppm), C_3—$C\underline{H}_2$ (2H, m, 2·35 ppm), C_5—$C\underline{H}_2$ (2H, m, 2·77 ppm), $OC\underline{H}_3$ (3H, S, 3·7 ppm), C_1—$\underline{H}$ (1H, two triplets centered at 5·6 ppm, J_1 = 13 Hz, J_2 = 4·5 Hz), C_2—$\underline{H}$ (1H, two triplets centered at 6·25 ppm, J = 13 Hz, J_2 = 1·5 Hz), aromatic protons (3H, complex multiplet located between 6·43-7·05 ppm). (Found: C, 82·93: H, 8·23. $C_{12}H_{14}O$ requires: C, 82·72: H, 8·10%).

4'-Methoxy-1,2-benzo-1,3,5-cycloheptatriene (V). 7-Methoxybenzosuberene (0·57 g, 0·003 M), NBS (0·57 g, 0·003 M; freshly crystallised), benzoyl peroxide (10 mg) and CCl_4 (30 ml) were mixed and refluxed over an electric lamp, while a slow stream of dry N_2 was being continuously bubbled through the mixture. All NBS appeared to have reacted after two hr, when the mixture was worked up in the usual manner (see II) to furnish a pale yellow oil (0·55 g). GLC (temp 200°, gas 100 ml/min) of this material showed at least nine components with the following RRT and relative percentage: (1) (0·30, 1%), (2) (0·37, 1%), (3) (0·75, 0·5%), (4) (1·0, 21%), (5) (1·1, 50%), (6) (2·7, 0·75%), (7) (3·2, 7%), (8) (3·7, 18%), (9) (4·8, 0·75%). This material (0·45 g) was chromatographed on 15% $AgNO_3$-silica gel (25 cm × 1 cm) with GLC monitoring:

Frac. 1:	pet. ether	20 ml × 3	21 mg, rejected
Frac. 2:	pet. ether	20 ml × 7	32 mg, pure 8
Frac. 3:	pet. ether	20 ml × 5	52 mg, 7 with some 8
Frac. 4:	25% C_6H_6 in pet. ether	20 ml × 5	25 mg, 8 with some 7
Frac. 5:	40% C_6H_6 in pet. ether	20 ml × 4	75 mg, pure 4 (VI)
Frac. 6:	40% C_6H_6 in pet. ether	20 ml × 2	34 mg, mixture of 4 and 5
Frac. 7:	50% C_6H_6 in pet. ether	20 ml × 7	155 mg, pure 5, crystalline solid
Frac. 8:	C_6H_6	20 ml × 6	33 mg, essentially 5

Frac. 7 was distilled to give the required cycloheptatriene (V): b.p. 110° (bath)/1 mm, m.p. 45-45·5°. IR (Nujol): 1600, 1460, 1452, 1320, 1250, 1160, 1098, 1030, 867, 830, 782, 693 cm^{-1}. (Found: C, 83·62: H, 6·95. $C_{12}H_{12}O$ requires: C, 83·69: H, 7·02%).

Frac. 2 was distilled to give *4'-methoxy-1,2-benzo-4-bromo-1,3-cycloheptadiene* (VIII): b.p. 180° (bath)/0·8 mm. IR (Liq.): 1615, 1580, 1515, 1478, 1440, 1315, 1260, 1165, 1130, 1058, 1045, 892, 855 cm^{-1}. (Found: C, 57·42: H, 5·20: Br, 31·86. $C_{12}H_{13}OBr$ requires: C, 56·93: H, 5·14: Br, 31·62%).

1,2-Benzo-1,3,5-cycloheptatriene-7-yl-N-succinimide (XIII). Benzocycloheptatriene (0·571 g, 0·005 M), NBS (0·89 g, 0·005 M, freshly crystallized), benzoyl peroxide (10 mg) and CCl_4 (10 ml) were mixed and refluxed (N_2) over an electric lamp for 24 hr. The mixture was filtered hot to remove succinimide (0·365 g) and the filtrate left aside at 0° for 15 hr. The buff-coloured solid, which had separated, was collected (0·2 g, m.p. 160-170°) and repeatedly crystallized from EtOAc to furnish crystals, m.p. 185-187°. (Found: C, 75·20: H, 5·50: N, 5·53. $C_{15}H_{13}O_2N$ requires: C, 75·31: H, 5·44: N, 5·85%).

* This procedure is patterned after that described for benzosuberene and a related olefin[9]

Essentially the same yield of the pure product (XIII) was obtained by substituting crude benzocycloheptatriene (i e crude product from the action of NBS on benzosuberene, *vide supra*. This material contains 10% unchanged benzosuberene) in the above reaction.

Benzotropylium perchlorate (XI: $X^- = ClO_4^-$). A mixture of glacial AcOH (0·5 ml) and $HClO_4$ (60%, 0·3 ml) was added drop by drop to the above benzocycloheptatrienyl succinimide (XIII: 0·1 g) and the resulting clear deep yellow solution diluted with dry ether (20 ml) and then thoroughly cooled in ice. The canary yellow microcrystalline solid was collected by filtration, and recrystallized from AcOH-dry ether to give the perchlorate as yellow needles (100 mg), m.p. turns black on heating (150–160°) without melting: the salt is quite hygroscopic. $\lambda_{max}^{60\%\ H_2SO_4\ aq}$ nm (log ε): 233 (4·30), 280 (4·80), 335 (3·46), 425 (3·27). IR (Nujol): 1600, 1580, 1520, 1458, 1368, 1260, 1085 and 801 cm^{-1}. NMR ($F_3C.COOH$): Complex overlapping multiplets located between 8·53–10·2 ppm.

4'-Methoxybenzotropylium perchlorate (XII: $X^- = ClO_4^-$). A mixture of 4'-methoxybenzocycloheptatriene (V: 0·11 g), NBS (0·11 g), benzoyl peroxide (10 mg) and CCl_4 (25 ml) was refluxed (N_2) till succinimide started floating (2·5 hr). Succinimide was filtered, the filtrated freed of solvent at room temp under suction to give an oil. This was taken up in $MeNO_2$ (8 ml), cooled and treated with a soln of $AgClO_4$ (0·124 g) in $MeNO_2$ (1 ml). After several hr at 0°, the precipitated AgBr was filtered and the brown filtrate diluted with dry ether (~100 ml) and chilled for several hr at −10°. A brown solid (20 mg) separated, which was collected by filtration and characterised by IR (Nujol): 1610 (m), 1480 (s), 1440 (m), 1390 (s), 1320 (m), 1270 (m), 1235 (m), 1100 (v.s.), 880 (m), 845 (w), 765 (m) cm^{-1}.

Benzotropylium fluoroborate (XI: $X^- = BF_4^-$). Triphenylcarbinol (0·3 g, 0·001 M) was dissolved in Ac_2O (3 ml) by warming, cooled and treated with fluoroboric acid (48%: 0·2 ml) dropwise. To the resulting soln of triphenylmethyl fluoroborate, benzocycloheptatriene (II: 0·15 g, 0·001 M) was added in portions with cooling and mixing. The mixture was finally diluted with ether (3 ml) and the yellow microcrystalline solid, which separated, was collected by filtration and washed with dry ether (4 ml × 4): yield, 220 mg: the compound is hygroscopic and on heating turns brown at 125° and finally melts at 133–135°.

4'-Methoxybenzotropylium fluoroborate (XII: $X^- = BF_4^-$). When methoxybenzocycloheptatriene (V: 0·1 g) was treated with triphenyl methyl fluoroborate (from 0·17 g of the carbinol) as above, an orange microcrystalline solid (m.p. 153–154°, with previous blackening 140°: 0·14 g) was obtained. $\lambda_{max}^{60\%\ H_2SO_4\ aq}$ nm (log ε): 224 (4·40), 245 (4·48), 301 (4·82), 354 (3·61), 440 (3·55). IR (Nujol): 1630, 1610, 1480, 1440, 1390, 1320, 1270, 1235, 1070 (BF_4),[15] 880, 845 and 765 cm^{-1}. NMR ($F_3C.COOH$): OMe (3H, s, 4·4 ppm) aromatic protons (8H, overlapping signals located between 8·0–9·8 ppm).

SeO_2 *oxidation of benzocycloheptatriene* (II). A mixture of benzocycloheptatriene (II: 1·0 g, 0·007 M), SeO_2 (1 g, 0·009 M), KH_2PO_4 (0·3 g, 0·002 M), dioxane (8 ml) and H_2O (1·5 ml) were gently refluxed (N_2) for 15 hr. The mixture was cooled, filtered to remove precipitated Se, the filtrate diluted with H_2O (30 ml), and then extracted with CH_2Cl_2 (20 ml × 3). The extract was washed with H_2O, brine and dried. After solvent removal, a red gum (1·2 g) was obtained, which was roughly chromatographed over silica gel/IIA (15 cm × 2 cm): (i) pet. ether, 20 ml, gave 184 mg of an oil, identified as the starting material, (ii) C_6H_6, 250 ml and, 30% ether in C_6H_6, 250 ml, together gave 0·859 g of thick oil. The second fraction was distilled and the distillate (0·587 g) consisting of XIV (30%) and XVI (50%, by GLC) was separated by column chromatography over silica gel/IIA (25 cm × 1·5 cm).

Frac. 1: pet. ether	15 ml × 5	rejected
Frac. 2: C_6H_6	20 ml × 2	rejected
Frac. 3: 5% ether in C_6H_6	20 ml × 10	150 mg, essentially XIV
Frac. 4: 10% ether in C_6H_6	20 ml × 4	295 mg, essentially XVI
15% ether in C_6H_6	20 ml × 4	

2,3-*Benzotropone* (XIV). Fraction 3 was distilled to give pure XIV: pale yellow liquid, b.p. 140° (bath)/3 mm, n_D^{30} 1·6660. (Found: C, 84·14; H, 5·27. $C_{11}H_8O$ requires: C, 84·59; H, 5·16%). *Picrate*, pale yellow needles, m.p. 114–115° (Lit.[14] m.p. 115°). 2,4-*Dinitrophenylhydrazone*, deep red flakes, m.p. 228° (Lit.:[14] m.p. 228°).

4,5-*Benzotropone* (XVI). Fraction 4 (m.p. 63–64°) was recrystallized to give colourless solid, m.p. 67–68° (Lit.:[20] m.p. 66–67°). (Found: C, 84·29; H, 5·23. $C_{11}H_8O$ requires: C, 84·59; H, 5·16%). 2,4-*Dinitrophenylhydrazone*, dark red flakes, m.p. 253–254° (Lit.:[20] m.p. 256°).

SeO_2 *oxidation of 4'-methoxy-1,2-benzo-1,3,5-cycloheptatriene* (V). The cycloheptatriene V (0·5 g, 0·003 M), SeO_2 (0·65 g, 0·006 M), KH_2PO_4 (0·15 g, 0·001 M), dioxane (4 ml) and H_2O (0·8 ml) were mixed

and gently refluxed (N_2) for 6 hr. The mixture was worked up as above to furnish a reddish brown gum (0·78 g), which was chromatographed over silica gel/IIA (26 cm × 1·7 cm) with TLC monitoring (solvent: 5% EtOAc in C_6H_6):

Frac. 1:	pet. ether	20 ml × 1	74 mg, starting triene
Frac. 2:	10% C_6H_6 in pet. ether	20 ml × 3	2 mg, compound A
Frac. 3:	50% pet. ether in C_6H_6	20 ml × 5	1 mg, rejected
Frac. 4:	C_6H_6	20 ml × 6	116 mg, compound B
Frac. 5:	5% ether in C_6H_6	20 ml × 2	8 mg, mixture of B and C
Frac. 6:	5% ether in C_6H_6	20 ml × 1	10 mg, compound C
Frac. 7:	5% ether in C_6H_6	20 ml × 2	11 mg, essentially compound D
Frac. 8:	8% ether in C_6H_6	20 ml × 8	162 mg, compound D

6-Methoxy-1-naphthaldehyde (XIX). From a number of different extracts, fraction 2 was collected and recrystallised from CCl_4 to give needles, m.p. 82-83°. (Found: C, 76·86; H, 5·49. $C_{12}H_{10}O_2$ requires: C, 77·40; H, 5·41%). *Oxime*, colourless flakes from dilute EtOH, m.p. 114-115°. (Found: N, 6·80. $C_{12}H_{11}O_2N$ requires: N, 6·96%.) The *acid* (XX), was obtained by oxidation of the aldehyde (XIX: 20 mg) with Ag_2O (from 0·5 g of $AgNO_3$) in NaOH aq (10%, 5 ml) at ~ 50° (20 min), m.p. 167-168 (pet. ether).

5'-Methoxy-2,3-benzotropone (XVIII). Fraction 4, above, was distilled to furnish a pale yellow liquid, which partly solidified: b.p. 180° (bath)/1 mm. (Found: C, 76·99; H, 5·40. $C_{12}H_{10}O_2$ requires: C, 77·40; H, 5·41%).

4'-Methoxy-2,3-benzotropone (XV). Fraction 6, from a number of extracts was pooled and distilled to give a pale yellow oil, which on cooling solidified: b.p. 160° (bath)/0·5 mm. (Found: C, 77·02; H, 5·10. $C_{12}H_{10}O_2$ requires: C, 77·40; H, 5·41%).

4'-Methoxy-4,5-benzotropone (XVII). Fraction 8, above, was distilled and the distillate, b.p. 185° (bath)/0·6 mm, crystallized from pet. ether to furnish buff-coloured needles, m.p. 66-67°. (Found: C, 77·43; H, 5·64. $C_{12}H_{10}O_2$ requires: C, 77·40; H, 5·41%).

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