109. *Tropolones. Part IV.* The Preparation of αβ-Benzotropolone.*

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Direct dehydrogenation of benzo*cyclo*heptene-3 : 4-dione (I) with palladium–charcoal gives a small yield of αβ-benzotropolone (III; X = H). A better method consists of the bromination of (I) and hydrogenolysis of the resulting α′-bromo-αβ-benzotropolone. Some properties of αβ-benzotropolone are recorded.

The first rational synthesis of a tropolone was reported by Cook and Somerville (*Nature*, 1949, **163**, 410) who described the direct dehydrogenation of benzo*cyclo*heptene-3 : 4-dione (I) to αβ-benzotropolone. Since then the intensity of the investigations on the monocyclic tropolones has led to neglect of this benzo-derivative, although the method used for its preparation has meanwhile been fruitfully employed by other investigators to obtain derivatives of the parent compound, *e.g.*, purpurogallin (Caunt, Crow, Haworth, and Vodoz, *J.*, 1950, 1631; 1951, 1313; Barltrop, Johnson, and Meakins, *J.*, 1951, 181). For the sake of completeness, therefore, the present communication describes in detail the

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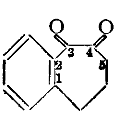
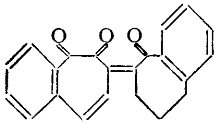
* Part III, *J.*, 1951, 2244.

original preparation of αβ-benzotropolone, together with a much superior modification, and records some properties of the product.

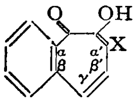
Dehydrogenation of the dione (I) in boiling trichlorobenzene in the presence of palladium–charcoal gave a small yield (16%) of the desired αβ-benzotropolone (III; X = H). In addition a higher-melting by-product was obtained which was not a tropolone. The analytical results for this compound suggest that its constitution may be represented by (II) derived by an aldol-like condensation between two molecules of the dione (I) and subsequent partial dehydrogenation. The paucity of the yield in this procedure encouraged an alternative approach, and the success of the bromination–dehydrobromination reaction for the preparation of tropolone itself (Part I, *J.*, 1951, 503) suggested its application in this case. When the dione (I) was treated in acetic acid with 2 mols. of bromine and allowed to stand at room temperature a fair yield (49%) of very pure α′-bromo-αβ-benzotropolone (III; X = Br) crystallised from the reaction mixture. In some preparations two by-products were encountered. The first, obtained in minute yield, consisted of benzotropolone itself; the other, from its general chemical characteristics and analytical data, was almost certainly 5-bromobenzo*cyclo*heptene-3 : 4-dione. Bromobenzotropolone readily formed a sodium salt but the insolubility of the latter rendered it unsuitable for hydrogenolysis by the procedure described for tropolone (Part I). It was found, however, that hydrogenolysis proceeded smoothly in ethanolic solution containing an excess of triethylamine to give a good yield (68%) of pure αβ-benzotropolone. The overall yield (34%) from this two-step procedure shows the marked advantage over the direct dehydrogenation method.



(I)



(II)



(III)

αβ-Benzotropolone possessed all the properties now familiar for this class of compound (Cook and Loudon, *Quart. Reviews*, 1951, **5**, 99). It was devoid of carbonyl reactivity, gave a red ferric colour, and a chloroform-soluble copper salt, coupled with diazonium salts, and dissolved in caustic alkali solutions; unlike tropolone, however, it was insoluble in sodium hydrogen carbonate solution and this lower acidity is reflected in its higher p*K* value (*ca.* 9·5; a more precise value could not be obtained because of the insolubility of the compound). A solid 3 : 5-dinitrobenzoate and sub-picrate were obtained but the acetate was a liquid. Even in the presence of methanol ethereal diazomethane reacted only very sluggishly with αβ-benzotropolone, to give a small yield of oily methyl ether with recovery of most of the starting material. Methylation with methyl toluene-*p*-sulphonate yielded an oil; on treatment with alcoholic 2 : 4-dinitrophenylhydrazine sulphate this product gave a red, solid derivative the analysis of which was compatible with the formulation of the compound as the 2 : 4-dinitrophenylhydrazone of αβ-benzotropolone methyl ether.

The skeletal structure of αβ-benzotropolone was proved by catalytic hydrogenation to a mixture of *cis*- and *trans*-benzo*cyclo*heptene-3 : 4-diols, oxidative fission of which gave the known γ-*o*-carboxyphenylbutyric acid. In a manner exactly analogous to that obtaining in the case of tropolone itself, αβ-benzotropolone underwent degradative fission on being treated with alkaline hydrogen peroxide, to yield *o*-carboxycinnamic acid. It is noteworthy that the aromatisation of colchiceine to *N*-acetylcolchinol by this reagent (cf. Part I) has not yet been paralleled by any other tropolone derivative. On being fused with potassium hydroxide αβ-benzotropolone behaved typically, to give a good yield of α-naphthoic acid.

Treatment of αβ-benzotropolone in acetic acid with 1 mol. of bromine gave a good yield of a monobromo-derivative which proved to be identical with the bromo-αβ-benzotropolone obtained by the bromination of the dione (I). Its constitution was not rigidly established but by analogy it is almost certainly the α′-bromo-compound (III; X = Br) (cf. Part III, *J.*, 1951, 2244). Further bromination of this product readily gave dibromo-αβ-benzotropolone, most probably the α′γ-derivative.

βγ-Benzotropolone, the position isomer of the compound described above, has been prepared by a Thiele-type condensation between *o*-phthalaldehyde and acetol (Tarbell, Scott, and Kemp, *J. Amer. Chem. Soc.*, 1950, **72**, 379) and the properties of this substance, insofar as they have been examined, resemble to a considerable degree those of the αβ-isomer. In particular it is noteworthy that a 2 : 4-dinitrophenylhydrazone was obtained from the phenyl ether.

Since this work was completed, Nozoe, Kitahara, and Andô (*Proc. Japan Acad.*, 1951, **27**, 107) have briefly reported some substitution products of αβ-benzotropolone. Their results are partly at variance with ours. In particular, they claim that αβ-benzotropolone is converted by diazomethane into its methyl ether, m. p. 82·5—83·5°, to which they ascribe the erroneous formula $C_{12}H_{11}O_2$. Our own results suggest that this is essentially unchanged benzotropolone (see above).

EXPERIMENTAL

*Benzo*cyclo*heptene*-3 : 4-*dione* (I).—A solution of selenium dioxide (10·5 g.) in ethanol (80 c.c.) was added dropwise during 4 hours to a boiling solution of benzo*cyclo*hepten-3-one (15 g.) (prepared by Plattner's method, *Helv. Chim. Acta*, 1944, **27**, 804) in ethanol (30 c.c.) and heating was continued for a further 2 hours. The cooled, filtered solution was evaporated to dryness and the residual oil fractionated under reduced pressure; after a small fore-run of unchanged starting material (0·6 g.), benzo*cyclo*heptene-3 : 4-dione (13 g.) was obtained as a yellow oil, b. p. 128—132°/0·4 mm., solidifying on long storage to yellow prisms, m. p. 45—49°. The *mono*-2 : 4-*dinitrophenylhydrazone* crystallised from *n*-butanol in yellow needles, m. p. 232—234° (Found: C, 57·5; H, 3·95; N, 15·8. $C_{17}H_{14}O_5N_4$ requires C, 57·6; H, 3·95; N, 15·8%). The dione did not form a quinoxaline on treatment with alcoholic *o*-phenylenediamine.

Fission of the dione with alkaline peroxide in the cold produced a high yield of γ-*o*-carboxyphenylbutyric acid, crystallising from water and benzene–light petroleum in needles, m. p. 138—139° (Found: C, 64·0; H, 6·3. Calc. for $C_{11}H_{12}O_4$: C, 63·5; H, 5·8%) (Hückel and Goth, *Ber.*, 1924, **57**, 1289, give m. p. 139—140°).

α′-*Bromo*-αβ-*benzotropolone* (III; X = Br).—To a stirred solution of benzo*cyclo*heptene-3 : 4-dione (10 g.) in glacial acetic acid (10 c.c.) was added slowly a solution of bromine (19·8 g., 2 mols.) in glacial acetic acid (20 c.c.), and the resulting solution set aside for 4 days at room temperature. The separated crystalline mass was filtered off, and the mother-liquors were diluted with acetic acid (10 c.c.) and heated to 60° for 3 hours, whereby a further small crop of crystals was obtained. The combined product was crystallised from glacial acetic acid; α′-*bromo*-αβ-*benzotropolone* (7 g., 49%) formed stout yellow prisms, m. p. 143—144° (Found: C, 52·5; H, 2·9; Br, 31·85. $C_{11}H_7O_2Br$ requires C, 52·6; H, 2·8; Br, 31·8%). The compound gave a deep red ferric reaction, a green amorphous copper salt, a bright yellow, sparingly soluble sodium salt, and a maroon precipitate with toluene-*p*-diazonium chloride. Treatment with ethereal diazomethane gave the *methyl ether*, m. p. 84—85° (Nozoe *et al.*, *loc. cit.*, give 65—68°), crystallising in colourless, feathery needles from light petroleum (b. p. 60—80°) (Found: C, 54·3; H, 3·4. $C_{12}H_9O_2Br$ requires C, 54·35; H, 3·4%).

In one experiment a small quantity of crystalline by-product was obtained which crystallised from *cyclo*hexane in colourless plates, m. p. 92—94° (Found: C, 52·15; H, 3·55; Br, 31·55. $C_{11}H_9O_2Br$ requires C, 52·15; H, 3·55; Br, 31·6%). The compound reacted readily with pyridine and dimethylamine, to give tars and gave a yellow precipitate on treatment with aqueous 2 : 4-dinitrophenylhydrazine hydrochloride. These data indicate the compound to be 5-*bromo*-*benzo*cyclo*heptene*-3 : 4-*dione*.

αβ-*Benzotropolone* (III; X = H).—(*a*) A solution of the dione (I) (3·2 g.) in 1 : 2 : 4-trichlorobenzene (20 c.c.) was heated under reflux under nitrogen with palladium–charcoal (2 g.; 10%) for 8 hours. Acidic impurities were removed from the filtered solution by washing it with sodium hydrogen carbonate solution, and the organic layer was then shaken with potassium hydroxide solution. An insoluble, crystalline precipitate formed was filtered off and crystallised from glacial acetic acid, to give pale yellow prisms, m. p. 270—271° (Found: C, 80·5; H, 5·05. $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9%). This condensation *product* (II) gave a bright orange colour with concentrated sulphuric acid but no ferric colouration.

The bright yellow aqueous alkaline extract was acidified and extracted with ether. Drying and evaporation gave a gummy residue which was extracted with boiling *cyclo*hexane; evaporation of the extract to crystallising point gave *αβ-benzotropolone* (0·5 g.) as pale yellow needles, m. p. 85—86°, subliming at 65—70°/0·05 mm. [Found : C, 76·5; H, 4·65%; *M* (Rast), 186. $C_{11}H_8O_2$ requires C, 76·7; H, 4·7%; *M*, 172]. Microhydrogenation with palladium in glacial acetic acid gave |= 3·1; with platinic oxide |= 7·3 were revealed. Light absorption in ethanol: $\lambda_{max.}$ in mμ (log ε); 237 (4·45), 260 (4·35), 343 (3·9). $\lambda_{infl.}$ in mμ (log ε); 268 (4·26), 332 (3·85). A plateau was exhibited at 373—388 mμ (3·83). The compound gave a blood-red ferric colour, a resinous crimson precipitate with toluene-*p*-diazonium chloride and an olive-green copper salt crystallising in needles, m. p. 249—250°, from chloroform; it dissolved in concentrated hydrochloric acid, to give a bright yellow solution from which it could be recovered unchanged by dilution with water. The 3 : 5-*dinitrobenzoate*, prepared in poor yield by the usual procedure, crystallised in colourless plates, m. p. 174—175°, from ethanol or benzene–light petroleum (Found : C, 59·05; H, 3·0. $C_{18}H_{10}O_7N_2$ requires C, 59·0; H, 2·75%). The *sub-picrate*, m. p. 63—64°, crystallised from ethanol in orange prisms [Found : C, 58·7; H, 3·55; N, 7·35. $(C_{11}H_8O_2)_2,C_6H_3O_7N_3$ requires C, 58·65; H, 3·3; N, 7·35%].

With hot acetic anhydride αβ-benzotropolone formed the oily acetate, readily hydrolysable to the parent compound by dilute sodium hydroxide. Treatment with ethereal diazomethane resulted in no perceptible nitrogen evolution and even after 24 hours in the presence of methanol much unchanged αβ-benzotropolone was recovered. Methylation with methyl toluene-*p*-sulphonate (1 mol.) in aqueous alcoholic sodium hydroxide gave an oil which solidified at −15° but remelted at 0°. On being heated with alcoholic 2 : 4-dinitrophenylhydrazine sulphate this ether yielded a 2 : 4-*dinitrophenylhydrazone* crystallising from ethyl acetate in small red prisms, m. p. 242—243° (Found : C, 58·4; H, 3·7; N, 15·3. $C_{18}H_{14}O_5N_4$ requires C, 59·0; H, 3·85; N, 15·3%).

(*b*) A solution of bromobenzotropolone (5·8 g.) and triethylamine (6 c.c.) in ethanol (50 c.c.) was shaken under hydrogen at room temperature and pressure in the presence of palladium–charcoal (10%; 500 mg.). Absorption slackened after the smooth uptake of 1 mol. of hydrogen. Removal of the catalyst and solvent left a residue which was made distinctly acid by the addition of dilute sulphuric acid. The resulting solid was filtered off, dried, and purified by sublimation; crystallisation from *cyclo*hexane gave αβ-benzotropolone, m. p. 85—86° (2·75 g., 68%).

Hydrogenation of αβ-Benzotropolone.—A solution of benzotropolone (50 mg.) in ethanol (20 c.c.) was shaken with hydrogen in the presence of platinic oxide (5 mg.) until 3 mols. of hydrogen were absorbed. Removal of catalyst and solvent, followed by trituration of the residue with *cyclo*hexane, gave a pale yellow solid (40 mg.) which was purified by crystallisation from light petroleum and then water. The resulting mixture of *cis*- and *trans*-benzo*cyclo*heptene-3 : 4-diol crystallised in white prisms, m. p. 110—123° (Found : C, 74·3; H, 7·85. Calc. for $C_{11}H_{14}O_2$: C, 74·15; H, 7·9%); it gave a yellow-green colour with potassium tetramethylosmate. Oxidation of the diol with excess of warm potassium hypobromite solution gave, after acidification, γ-*o*-carboxyphenylbutyric acid, m. p. and mixed m. p. 136—138°.

Oxidation of αβ-Benzotropolone.—A solution of benzotropolone (200 mg.) in hot sodium hydroxide solution (5 c.c.; 0·5N) was cooled and the resulting deep yellow suspension of sodium salt treated with hydrogen peroxide (0·3 c.c.; 30%). After 36 hours a colourless solution was formed; acidification and extraction with ether yielded a colourless solid (60 mg.), crystallising from aqueous acetic acid in prisms, m. p. 186—188°, remelting after solidification at 146—148°. These m. p. were unchanged on admixture with authentic *o*-carboxycinnamic acid which is transformed at its m. p. into the lactone of β-hydroxy-β-*o*-carboxyphenylpropionic acid (phthalideacetic acid) (Titley, *J.*, 1928, 2576).

Bromination of αβ-Benzotropolone.—A solution of benzotropolone (100 mg.) in glacial acetic acid (5 c.c.) was treated dropwise with bromine (100 mg., 1·1 mols.) in acetic acid (0·5 c.c.). A yellow oil separated, which redissolved with evolution of hydrogen bromide when the solution was warmed. Evaporation to dryness followed by crystallisation of the residue from acetic acid gave α′-bromobenzotropolone (III; X = Br) (90 mg.), m. p. 143—145° alone or admixed with the bromination product of benzo*cyclo*heptene-3 : 4-dione (Nozoe *et al.*, *loc. cit.*, give 148—149°).

A solution of bromobenzotropolone (100 mg.) in acetic acid (5 c.c.) was similarly treated with bromine (200 mg.) in acetic acid (1 c.c.) and the solution heated under reflux for 30 minutes. Evaporation and crystallisation of the residue from acetic acid gave *α′γ-dibromobenzotropolone* (120 mg.) in silky, yellow needles, m. p. 119—121° (Found : C, 40·0; H, 1·95. $C_{11}H_6O_2Br_2$ requires C, 40·0; H, 1·85%).

α-Naphthoic Acid.—αβ-Benzotropolone (26 mg.) was treated with potassium hydroxide solution (80%; 1 c.c.), and the mixture heated to 180—185° at which temperature it was kept for 30 minutes. The cooled melt was dissolved in water and then acidified, and the voluminous precipitate (20 mg.) crystallised from aqueous alcohol, to give α-naphthoic acid, m. p. 156—160° (m. p. 159—161° on admixture with an authentic specimen of m. p. 160—162°).

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