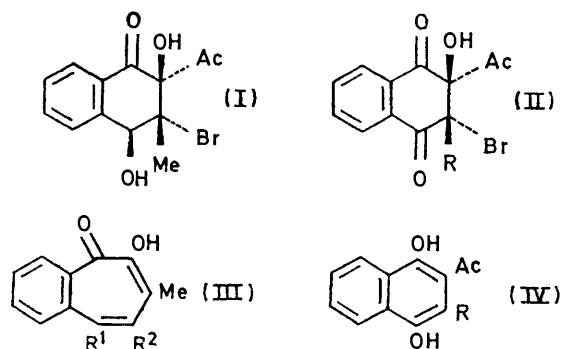


## A Novel Synthetic Route to 3,4-Benzotropolones: the Expansion of a Six-membered Carbocycle under Reducing Conditions

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6,7-Dimethyl-3,4-benzotropolone (III;  $R^1 = H$ ,  $R^2 = Me$ ) and the related 5-hydroxy-3,4-benzotropolones (III;  $R^1 = OH$ ,  $R^2 = Me$ ) and (III;  $R^1 = OH$ ,  $R^2 = H$ ) are formed in good yield when derivatives of 2-acetyl-3,4-dihydronaphthalen-1(2*H*)-one are treated with zinc in acetic acid. The reductive ring expansions are discussed in terms of cyclopropanediol intermediates.

In connection with other studies<sup>1</sup> we had occasion to examine the reduction of the bromohydrin (I) with zinc and acetic acid. We were surprised to find that the major product from this reaction was a weakly acidic compound,  $C_{13}H_{12}O_2$ , which formed a monoacetate and showed spectroscopic properties typical of a dimethyl-3,4-benzotropolone. In order to gain further insight into this novel ring expansion we examined the reactions of two other bromohydrins (II;  $R = Me$  and  $H$ ) and



obtained a dimethyl and a monomethyl 5-hydroxy-3,4-benzotropolone, respectively, in good yields. Comparison of the n.m.r. spectra of all three benzotropolones revealed the positions of the methyl groups and it is apparent that the benzotropolones (III;  $R^1 = H$ ,  $R^2 = Me$ ), (III;  $R^1 = OH$ ,  $R^2 = Me$ ), and (III;  $R^1 = OH$ ,  $R^2 = H$ ) are formed from the bromohydrins (I), (II;  $R = Me$ ), and (II;  $R = H$ ), respectively. In the first two cases the quinol (IV;  $R = Me$ ) was identified as a by-product and in the third case a small amount of the lower homologue (IV;  $R = H$ ) was formed.

The synthetic route described here is novel and, on the basis of preliminary studies,<sup>2</sup> appears to offer a general method of entry into the tropolone ring system. Many routes to tropones and tropolones have been shown to involve cyclopropane intermediates<sup>3</sup> and we believe that these are also formed in this case.† Dissolving metal

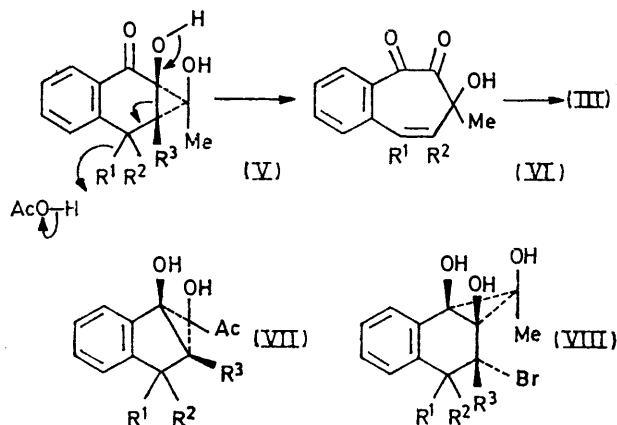
† We thank Professor L. Crombie for drawing our attention to the possibility of a cyclopropane intermediate in these reactions.

<sup>1</sup> G. Read and V. M. Ruiz, *J.C.S. Perkin I*, 1973, 235.

<sup>2</sup> G. Marin and V. M. Ruiz, unpublished results.

<sup>3</sup> T. Nozoe, in 'Non-benzenoid Aromatic Hydrocarbons,' ed. D. Ginsburg, Interscience, New York, 1959, p. 339; and *Progr. Org. Chem.*, 1961, **5**, 132; W. E. Parham, D. A. Bolon, and E. E. Schweizer, *J. Amer. Chem. Soc.*, 1961, **83**, 603; O. L. Chapman and P. Fitton, *ibid.*, 1963, **85**, 41; W. E. Parham, R. W. Soeder, J. R. Throckmorton, K. Kunel, and R. M. Dodson, *ibid.*, 1965, **87**, 321.

reductions have long been known to produce cyclopropanes from 1,3-dibromo-compounds<sup>4</sup> and recent studies have clearly established that cyclopropanediols can be formed from 1,3-diketones or 1,3-diesters under similar circumstances,<sup>5</sup> although the latter products are commonly only reaction intermediates. It has also been established<sup>2</sup> that  $\beta$ -bromo-ketones can be converted into cyclopropanols under the conditions of our experiments. We therefore consider the tricyclic derivatives (V) as probable intermediates in these reactions. The hydroxy-group at C-2 in structure (V) is the most acidic and is appropriately aligned with the carbonyl (or equatorial hydroxy-group) at C-5 for a concerted ring opening, which might be catalysed by the acetic acid present, as indicated in the Scheme. The products (VI) would be expected to lose readily the hydroxy-group of the  $\alpha$ -ketol



For (V), (VII), and (VIII)  $R^1 = OH$ ,  $R^2 = H$ ,  $R^3 = Me$ ;  $R^1R^2 = O$ ,  $R^3 = Me$ ;  $R^1R^2 = O$ ,  $R^3 = H$ .

For (VI)  $R^1 = H$ ,  $R^2 = Me$ ;  $R^1 = OH$ ,  $R^2 = Me$ ; and  $R^1 = OH$ ,  $R^2 = H$ .

system by hydrogenolysis. Two other tricyclic intermediates, (VII) and (VIII), are potentially possible, but neither can directly account for the benzotropolones obtained and no products have been isolated which might be derived from them. We suggest that their formation is prevented by steric factors, since there is considerable crowding in the alicyclic system. Alternative routes to the intermediates (VI) which do not involve

<sup>4</sup> R. G. Kelso, K. W. Greenlee, J. M. Durfer, and C. E. Boord, *J. Amer. Chem. Soc.*, 1952, **74**, 287.

<sup>5</sup> N. J. Cusack and B. R. Davis, *J. Org. Chem.*, 1965, **30**, 2062; S. A. Galton, M. Kalafer, and F. Marshall Beringer, *ibid.*, 1970, **35**, 1; F. Chen and C. Ainsworth, *J. Amer. Chem. Soc.*, 1972, **94**, 4037.

a cyclopropane ring can be envisaged, but none of these appears satisfactorily to accommodate within one mechanism conversion of substrate (I), with a benzylic hydroxy-group at C-4, and substrates (II; R = Me) and (II; R = H), with carbonyl groups at this position.

#### EXPERIMENTAL

U.v. spectra were measured for solutions in ethanol with a Hilger Ultrascan recording spectrophotometer H999 Mark II and i.r. spectra were determined for potassium bromide discs with a Hilger Infracan recording spectrophotometer H900. N.m.r. spectra were recorded with a Perkin-Elmer R10 instrument at 60 MHz and mass measurements were made with a Hitachi-Perkin-Elmer RMU-6 instrument.

*General Method.*—Zinc powder (1–5 g) was slowly added to a stirred solution of the bromohydrin (0.28–1 g) in acetic acid (10–20 cm<sup>3</sup>). The suspension was stirred for 5 min, at a temperature a little above the freezing point of the solution, and the solid residue was filtered off and washed with a little acetic acid. The washings were combined with the yellow filtrate to give a solution of the products in acetic acid.

*5-Hydroxy-6,7-dimethyl-3,4-benzotropolone.*—The solution of products obtained from treating 2-acetyl-*t*-3-bromo-2,3-dihydro-*r*-2-hydroxy-3-methyl-1,4-naphthoquinone<sup>6</sup> (1.0 g) with zinc powder was reduced in volume to *ca.* 5 cm<sup>3</sup>, diluted with chloroform (50 cm<sup>3</sup>), washed thoroughly with water, and dried. The products obtained on evaporating this solution to dryness were chromatographed on a column of silica gel (B.D.H.), in chloroform, to give *5-hydroxy-6,7-dimethyl-3,4-benzotropolone* (425 mg, 61%), m.p. 157.5–158.5° (benzene) (Found: C, 72.2; H, 5.6). C<sub>13</sub>H<sub>12</sub>O requires C, 72.2; H, 5.6%;  $\nu_{\max}$  3385 (OH str.) and 1628 cm<sup>-1</sup> (tropolone C=O str.);  $\lambda_{\max}$  232, 256sh, 325, and 350 nm (log  $\epsilon$  4.52, 4.03, 3.97, and 4.03);  $\tau$  [(CD<sub>3</sub>)<sub>2</sub>SO-D<sub>2</sub>O] 1.5–2.0 (2H, m, aryl H), 2.15–2.70 (2H, m, aryl H), 7.11 (3H, s, 6-Me), and 7.75 (3H, s, 7-Me); *m/e* 216 (*M*<sup>+</sup>) and 201 (*M*<sup>+</sup> - 15); *pK*<sub>a</sub> (H<sub>2</sub>O-Me<sub>2</sub>CO) 7.10; *R*<sub>F</sub> (PhH-CHCl<sub>3</sub>, 7:3) 0.42. Treatment of the tropolone with acetic anhydride and pyridine gave the *diacetate*, m.p. 145.5–146.5° (H<sub>2</sub>O-MeOH) (Found: C, 68.1; H, 5.4). C<sub>17</sub>H<sub>16</sub>O<sub>5</sub> requires C, 68.0; H, 5.4%;  $\nu_{\max}$  1766 and 1757 (acetoxy C=O str.) and 1700 (ketonic C=O str.);  $\lambda_{\max}$  225 and 285 nm (log  $\epsilon$  4.84 and 3.76).

Further elution of the column with chloroform gave

2-acetyl-3-methyl-1,4-naphthoquinone (254 mg, 37%), indistinguishable, in m.p. (88–89°), spectroscopic properties, and chromatographic properties, from an authentic sample.

*5-Hydroxy-7-methyl-3,4-benzotropolone.*—The acetic acid solution (9 cm<sup>3</sup>) obtained on treating 2-acetyl-*t*-3-bromo-2,3-dihydro-*r*-2-hydroxy-1,4-naphthoquinone<sup>6</sup> (0.5 g) with zinc powder, was poured into water (50 ml). This solution was treated with solid sodium carbonate to raise its pH to *ca.* 5.0, then extracted with ethyl acetate. The extract was washed, dried, and evaporated to dryness to give *5-hydroxy-7-methyl-3,4-benzotropolone* (215 mg, 64%), isolated as dark yellow crystals (from benzene), m.p. 171–172° (Found: C, 71.3; H, 4.9). C<sub>12</sub>H<sub>10</sub>O<sub>3</sub> requires C, 71.3; H, 5.0%;  $\nu_{\max}$  3250 (OH str.) and 1618 cm<sup>-1</sup> (tropolone C=O str.);  $\lambda_{\max}$  233, 255sh, 316, 356, and 370sh nm (log  $\epsilon$  4.45, 4.12, 3.89, 4.00, and 3.94);  $\tau$  [(CD<sub>3</sub>)<sub>2</sub>SO-D<sub>2</sub>O] 1.75–2.06 (2H, m, aryl H), 2.30–2.83 (2H, m, aryl H), 3.37 (1H, s, 6-H), and 7.36 (3H, s, 7-Me); *m/e* 202 (*M*<sup>+</sup>) and 187 (*M*<sup>+</sup> - 15); *pK*<sub>a</sub> (H<sub>2</sub>O-Me<sub>2</sub>CO) 7.51. The *diacetate*, m.p. 86–87°, crystallised from petroleum (b.p. 80–100°) (Found: C, 67.2; H, 4.9). C<sub>16</sub>H<sub>14</sub>O<sub>5</sub> requires C, 67.1; H, 4.9%;  $\nu_{\max}$  1774 (acetoxy C=O str.) and 1697 cm<sup>-1</sup> (ketone C=O str.);  $\lambda_{\max}$  224 and 288 nm (log  $\epsilon$  4.80 and 3.79).

*6,7-Dimethyl-3,4-benzotropolone.*—The acetic acid solution (12 cm<sup>3</sup>) obtained on treating 2-acetyl-*t*-3-bromo-3,4-dihydro-*r*-2,*c*-4-dihydroxy-3-methylnaphthalen-1(2*H*)-one<sup>1</sup> (283 mg) with zinc powder was diluted with water (250 cm<sup>3</sup>). A yellow precipitate slowly formed which was crystallised from benzene to give *6,7-dimethyl-3,4-benzotropolone* (81 mg, 45%) as yellow needles, m.p. 92–92.5° (Found: C, 78.0; H, 6.0). C<sub>13</sub>H<sub>12</sub>O<sub>2</sub> requires C, 78.0; H, 6.0%;  $\nu_{\max}$  3450w,br (OH str.) and 1632 cm<sup>-1</sup> (tropolone C=O str.);  $\lambda_{\max}$  262, 270, 297, and 375 nm (log  $\epsilon$  4.47, 4.73, 3.81, and 3.58);  $\tau$  [(CD<sub>3</sub>)<sub>2</sub>SO-D<sub>2</sub>O] 1.60–1.90 (1H, m, aryl H), 2.0–2.7 (3H, m, aryl H), 2.78 (1H, s, 5-H), 7.40 (3H, s, 6-Me), and 7.59 (3H, s, 7-Me); *m/e* 200 (*M*<sup>+</sup>) and 185 (*M*<sup>+</sup> - 15); *pK*<sub>a</sub> (H<sub>2</sub>O-Me<sub>2</sub>CO) 9.55. The *acetate* had m.p. 80–81° (Found: C, 74.2; H, 5.8). C<sub>15</sub>H<sub>14</sub>O<sub>3</sub> requires C, 74.4; H, 5.8%;  $\nu_{\max}$  1766 (acetoxy str.) and 1705 cm<sup>-1</sup> (ketone C=O str.);  $\lambda_{\max}$  223 and 282 nm (log  $\epsilon$  4.71 and 3.71).

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<sup>6</sup> G. Read and V. M. Ruiz, *J.C.S. Perkin I*, 1973, 369.