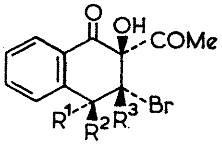
A Novel Synthesis of Benztropolones: the Expansion of a Six-membered Carbocyclic Ring under Reducing Conditions

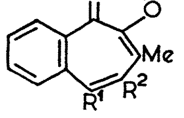
By G. READ* and V. M. RUIZ

(*Department of Chemistry, University of Exeter, Exeter*)

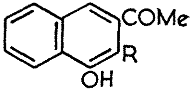
OUR work on the stereospecific elaboration of quinone epoxide systems[1] has led us to examine the action of zinc in acetic acid on the triketo-bromohydrins, (Ia) and (Ib), and the hydroxy-diketobromohydrin, (Ic). With this reagent, at about 15°, both types of bromohydrin undergo smooth transformation to the new benztropolones, (IIa), (IIb), and (IIc) respectively, in yields of from 55 to 70%. The only other products detected in the cases of (Ia) and (Ib) are the corresponding isomeric quinols (IIIa) and (IIIb). The quinol (IIIb) is also the principal by-product in the formation of (IIc). The structures of the benztropolones follow



	R^1	R^2	R^3
(Ia)	O		H
(Ib)	O		Me
(Ic)	H	OH	Me



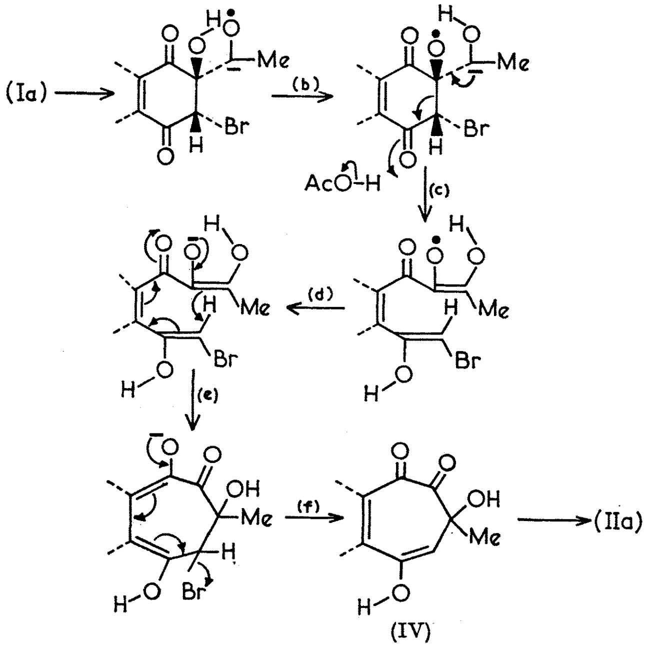
	R^1	R^2
(IIa)	OH	H
(IIb)	OH	Me
(IIc)	H	Me



(IIIa) R = H
(IIIb) R = Me

from their analyses, pK_a values, and spectroscopic properties (u.v., i.r., n.m.r., and mass spec.). The compounds have also been converted into the corresponding acetates.

Several alternative electronic pathways may be written to account for these transformations, which probably take place on the metal surface. However, we believe that the most reasonable is the one illustrated in the Scheme below, or a close variant, since this satisfactorily accounts for the expansion in both types of bromohydrin.



SCHEME

Using the conversion of (Ia) into (IIa) as an example, a one-electron reduction of the acetyl group[2] is envisaged as the first step, (a), which is followed by a hydrogen migration, (b), and a ring-opening step, (c). Steps (b) and (c) may take place in the reverse order, for this would not alter the essential course of the process. This reductive opening of the 1,4-diketone system parallels closely that suggested for the opening of cyclohexane-1,4-dione under Clemmensen conditions[3] but in this case the preferential attack appears to take place at the aliphatic rather than the aromatic keto-group.[3,4] The second one-electron reduction, (d), leads to the ring closure, (e), by a series of two-electron shifts. However, a one-electron reduction at the aryl carbonyl group, rather than the oxygen radical, followed by a series of one-electron shifts could be involved and would lead to the same intermediate. The oxy-anion formed in this process loses bromide ion, (f), to give the α-ketol, (IV), which is readily transformed to (IIa) under the conditions of the reaction, by the loss of the α-hydroxy-group. The only modification to this route, required to account for the conversion of (Ic) into (IIc), is at the ring-opening step, (c). This becomes a fragmentation process,[5] leading to the loss of the hydroxy-group as an anion and the generation of an olefinic bond instead of an enol.

We thank the British Council for a research fellowship (to V.M.R.).

(*Received, May* 21*st,* 1969; *Com.* 721.)

---

[1] A. Rashid and G. Read, *J. Chem. Soc.* (*C*), in the press.
[2] B. J. McClelland, *Chem. Rev.*, 1964, **64**, 301.
[3] J. G. St. C. Buchanan and B. R. Davis, *J. Chem. Soc.* (*C*), 1967, 1340.
[4] N. J. Cusack and B. R. Davis, *J. Org. Chem.*, 1965, **30**, 2062.
[5] C. A. Grob and P. W. Schiess, *Angew. Chem. Internat. Edn*, 1967, **6**, 1.