A New Synthesis of Benzo[2,3]tropones and Related Bicyclic Systems

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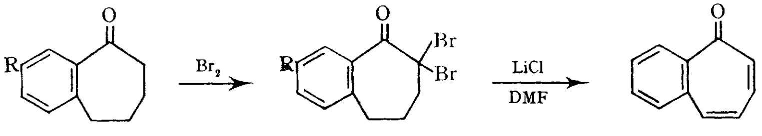
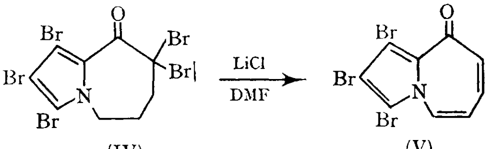
THE usual syntheses of benzo[2,3]tropones proceed from benzosuberanone (Ia) by bromination and dehydrobromination sequences,[1,2] giving in the most favourable case a 59% yield of the parent compound (IIIa).[2] We have reported[3] a synthesis of an indoloazepinone in which the key stage was the elimination of two molecules of hydrogen bromide from a suitable αα-dibromo-ketone. We

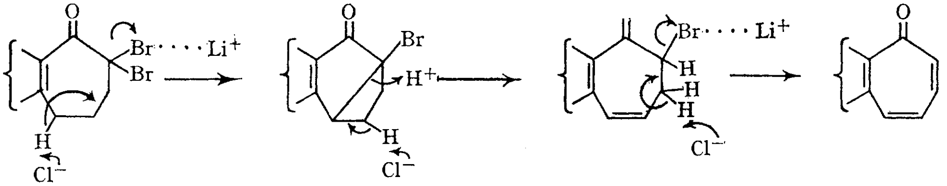


(I) (II) (III)

a, R=H; b, R=NO$_2$; c, R=NHAc



(IV) (V)



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have now shown that this reaction offers a simple, high-yield route to benzo[2,3]tropones and related systems.

Benzosuberanone (Ia) can be brominated by bromine (2 mol.) in carbon tetrachloride to give the dibromo-ketone (IIa), m.p. 42—44° (98%). Similar bromination of the nitro-derivative (Ib)[4] gave the dibromo-ketone (IIb), m.p. 110° (95%). The acetamidobenzosuberanone (Ic)[4] was brominated with phenyltrimethylammonium perbromide to avoid nuclear bromination, giving the dibromo-ketone (IIc), m.p. 136—138° (87%). All three dibromo-ketones were dehydrobrominated by LiCl in boiling dimethylformamide (DMF) (1 hr.) to give the corresponding benzo[2,3]tropones (IIIa) (92%),[2] (IIIb), m.p. 169—172° (76%), and (IIIc), m.p. 213—215° (95%). Thus this synthesis can be used for the production of benzo[2,3]tropones carrying electron-withdrawing or electron-donating substituents in the benzene ring. We have also applied this route to the production of the pyrrolo-[1,2-*a*]azepinone (V), m.p. 187—189°, from the corresponding pentabromo-ketone (IV), m.p. 151—155°; the yield of the dehydrobromination step is 79%.

We suggest the following scheme for the elimination reaction.

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