

DEHYDROTROPOLONES: A BENZYNE-TYPE INTERMEDIATE IN
THE REACTIONS OF HALOTROPOLONES WITH ALKOXIDES (1)

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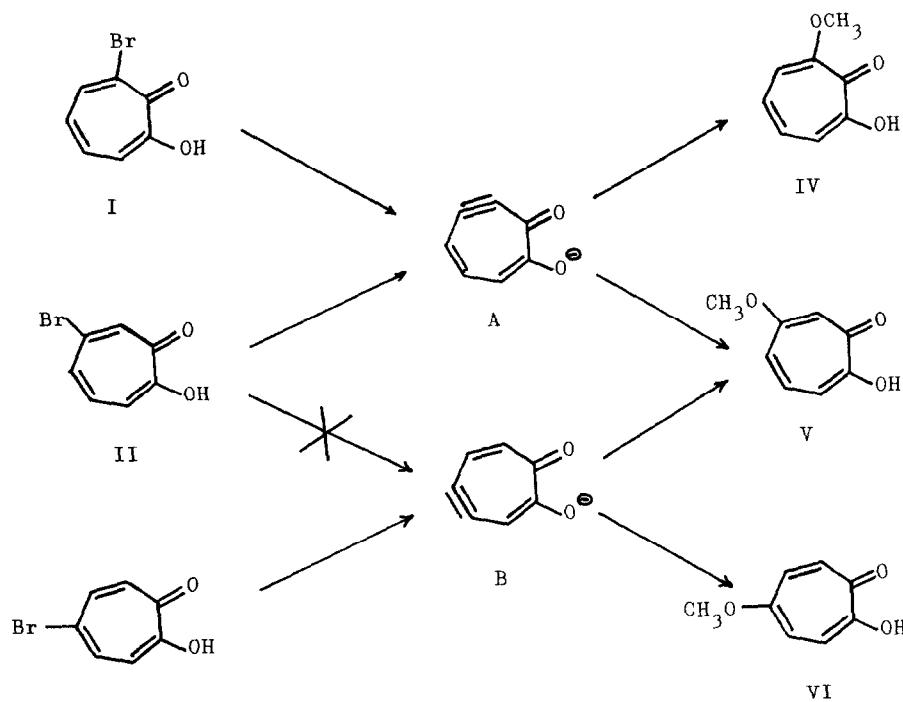
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A number of reports have been published on the benzyne and related dehydro-intermediates of aromatic compounds (3). However, no definite example of such an intermediate of non-benzenoid aromatic compounds has ever been reported, except that it has only been presumed that hydrolysis of 3-bromotropolone with aqueous alkali to 4-hydroxytropolone and some related cine-substitution (4) of 3-halo-tropolone proceed by way of the dehydro-intermediate, "tropolonyne" (5).

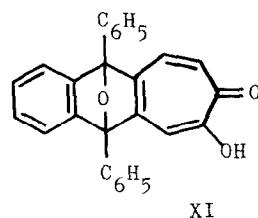
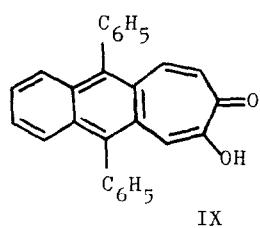
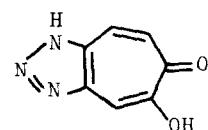
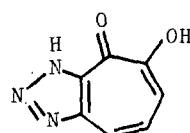
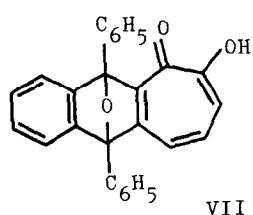
This communication will describe the formation of dehydrotropolones which must be participating as the reactive intermediate in the reaction of some halotropolones with alkoxide.

When a solution of 3-bromotropolone (I) (6) in dimethyl sulfoxide was heated with sodium methoxide at 80°C, an almost 1:1 mixture (7) of 3-methoxytropolone (IV) (5a) and 4-methoxytropolone (V) (5a) was obtained in 96% yield. A similar treatment of 4-bromotropolone (II) (8) also gave the same mixture of IV and V in 94% yield, whereas 5-bromotropolone (III) (9) gave an almost 1:1 mixture of V and 5-methoxytropolone (VI) (10) in 97% yield. These findings have let us to presume that the reactions proceed by way of the dehydrotropolone-intermediates (A and B) as shown in Scheme 1.

This presumption was confirmed on trapping the intermediates with diphenyl-isobenzofuran (11) and with sodium azide (12). Thus, a solution of I in dimethyl sulfoxide was heated with potassium tert.-butoxide in the presence of diphenyl-isobenzofuran, affording an adduct (VII), mp 220-221.5°C (Found: C, 83.02; H, 4.88%), in 47% yield; ir (KBr): 3305 cm^{-1} , 1613, 1145; uv (MeOH): λ_{max} 237 nm (log ε 4.38), 285 (4.15), 355 (3.86), 371 (385); nmr (CDCl_3): a complex of



Scheme 1



aromatic hydrogens only, δ 6.8-8.0 ppm; mass spectrum: m/e 390 (M^+), 374, 357, 346. A similar treatment of II also gave the same adduct (VII) in 32% yield. When heated with potassium tert.-butoxide in the presence of sodium azide, both I and II gave triazolo[5,4-c]tropolone (VIII) (13), mp 250°C (Found: C, 51.84; H, 3.15; N, 25.90%), in respective 62 and 29% yields; ir (KBr): 3195 cm^{-1} , 1618, 1558, 801; uv (MeOH): λ_{max} 222 nm (log ϵ 4.38), 247 (4.26), 310 (3.79); nmr (CDCl_3): a complex of aromatic hydrogens only, δ 7.1-7.8 ppm. On the other hand, the treatment of III with potassium tert.-butoxide in the presence of diphenyl-isobenzofuran gave a naphtotropolone (IX), mp 223-224°C (Found: C, 85.87; H, 4.90%), in 44% yield; ir (KBr): 3378 cm^{-1} , 1631, 1616, 899; uv (MeOH): λ_{max} 312 nm (log ϵ 4.78), 387 (3.61); nmr (CDCl_3): δ 6.81 ppm (1H, d, J 13.5 Hz), 7.91 (1H, d, J 13.5 Hz), 7.2-7.7 (15H, m); mass spectrum: m/e 374 (M^+), 357, 346, and the treatment of III in the presence of sodium azide gave triazolo[4,4-d]tropolone (X) (13), mp 275°C (decomp) (14), in 82% yield; ir (KBr): 3509 cm^{-1} , 3226, 2800, 1613; uv (MeOH): λ_{max} 229 nm (log ϵ 4.52), 259 (4.12), 269 (4.04), 345 (4.04); nmr (CDCl_3): δ 7.10 ppm (1H, d, J 12 Hz), 7.44 (1H, s), 8.08 (1H, d, 12 Hz).

The formation of the naphtotropolone (IX) is thought to be resulted in deoxygenation of the adduct (XI) which must be produced primarily, but could not be isolated. The adducts (VII and XI) must be formed on the Diels-Alder-type addition of A and B, respectively, with diphenylisobenzofuran, and the triazolo-tropolones (VIII and X) must be formed on the 1,3-dipolar cyclo-addition of A and B, respectively, with azide. The evidence presented above indicates apparently the formation of 3,4-dehydrotropolone (A) (15) from both I and II, and 4,5-dehydrotropolone (B) from III, as the reaction intermediates, by the elimination of hydrogen bromide on the treatment with alkoxide. 4-Bromotropolone (II) would be expected to give rise to both the intermediates (A and B), but only the former was formed. This could be explained in terms of differences in acidity of the hydrogens at the 3- and 5-positions of tropolone; the inductive effect of the carbonyl group affects the hydrogen at the 3-position to be more acidic.

A kinetic study of these reactions shows that the reactivity is in order of 4-bromo- (II) > 3-bromo- (I) > 5-bromotropolone (III).

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15. In a midcourse of this study, it has been informed by Nozoe that Tochtermann has also confirmed the formation of 3,4-dehydrotropolone (A) on the reaction of I with potassium tert.-butoxide, in the presence of sodium azide or diphenylisobenzofuran, in dimethylformamide; W. Tochtermann, Doctor Thesis (1966). Acknowledgements are made to Professor Tetsuo Nozoe for his kind information and to Dr. W. Tochtermann for his kind offer of the unpublished data.