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A NEW REACTION OF CYCLOHEPTATRIENONES : ALKYL-OXYGEN BOND FISSION OF 2-METHOXYTROPONE

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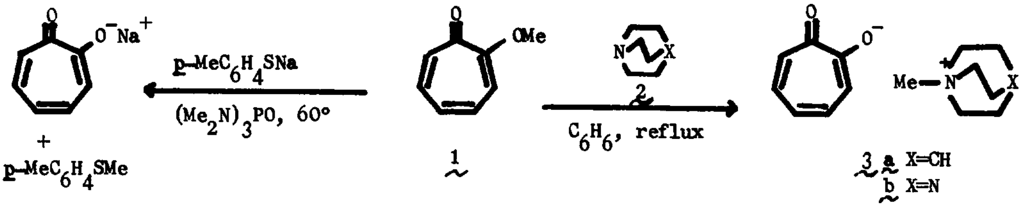
Despite the extreme variety of reaction patterns found for cycloheptatrienones with either electrophilic or nucleophilic reagents[3] (ring substituents having good anionic or neutral stability may be replaced by a variety of nucleophiles without rearrangement[4] or with concomitant rearrangement, where the seven-membered ring is either preserved[5] or contracted to a benzenoid one,[6] or may be directly attacked[7]), no method is available to perform the simple fission of the alkyl-oxygen bond of alkyl ethers of α-tropolones. Notably, both alkaline (with 2-methoxytropone[8]) and acid (with colchicine[9]) hydrolyses lead to C_{sp^2}-O bond fission instead. Moreover, the methoxy group is replaced by protic amines as easily as a halogen.[4]

We report that 2-methoxytropone (**1**) can be cleanly demethylated by a tertiary amine in benzene or by a mercaptide in hexamethylphosphoric triamide. Thus, anhydrous[4b] **1**, 0.1 M, and a 4-fold molar excess of quinuclidine (**2**, X=CH) were refluxed in dry benzene under N_2 for 80 hr. Removal of some tars and cooling to room temperature gave a precipitate of the hygroscopic **3a**, mp 258°,[10] in 35% yield. Concentration of the mother liquor raised the yield to 60%. With triethylenediamine (**2**, X=N), under otherwise identical conditions, the reaction is slower. After five days the extremely hygroscopic **3b**,[11] was isolated, by the same technique used for **3a**, in 25% overall yield and the uv spectrum of the mother liquor showed that ca. 50% of **1** was unreacted.



1, 0.15 M, reacts slowly with p-tolylmercaptide in $(Me_2N)_3PO$ at room temperature whereas on the raising of the temperature to 60°, 75% of sodium tropolonate and p-tolyl methyl thioether[12] were obtained in 1.5 hr. On the contrary, when the solvent was anhydrous ethanol, all the 2-methoxytropone disappeared but, besides much tars, only 15% of p-tolyl methyl thioether (glpc), 50% of tropolone (uv), and traces of 2-p-tolylthiotropone[13] (tlc) could be detected. Similar results were obtained with either sodium thiophenoxide or sodium ethylmercaptide.

With sodium ethylmercaptide in ethylmercaptane no tars formed but, although tropolone proved to be stable under the conditions used, only complex high molecular weight compounds (so far not characterized) were found.

These results sharply contrast with related ones by Nozoe who reported clean replacement of the methoxy group by SR(Ar) in similar cases.[14]

Besides its obvious practical usefulness, demethylation of 1 by tertiary amines gives strong support to the mechanism involving intramolecular catalysis as suggested[4b] for the replacement of the methoxy group by protic amines. Moreover, dealkylation of 1 by mercaptides suggests that the order of replaceability of substituents on the tropone nucleus by anionic nucleophiles should be drastically different from that found[4] for protic amines as nucleophiles. A study of this point would be worthwhile.

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REFERENCES

(1) Post-doctoral Fellow.

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(3)(a)D. Lloyd,''Carbocyclic Non-Benzenoid Aromatic Compounds'', Elsevier, Amsterdam, 1966; (b)T. Nozoe,''Non-Benzenoid Aromatic Compounds'', D. Ginsburg, ed., Interscience, N.Y., 1959.

(4) (a) F. Pietra, M. Giocasta, and F. Del Cima, Tetrahedron Lett., 5097 (1969); (b) F. Pietra and F. Del Cima, J.Chem.Soc.(B), 2224 (1971).

(5) (a) G. Biggi, F. Del Cima, and F. Pietra, J.C.S.PerkinII, 1424 (1972); G. Biggi, F. Del Cima, and F. Pietra, J.Amer.Chem.Soc., 94, 4700 (1972).

(6) G. Biggi, F. Del Cima, and F. Pietra, Chem.Commun., 1627 (1971).

(7) F. Pietra, G. Biggi, and F. Del Cima, J.Chem.Soc.(C), 3626 (1971).

(8) K. Bowden and M.J. Price, J.Chem.Soc.(B), 1784 (1971).

(9) T.J. Fitzgerald, PhD thesis, Ohio State University, 1965.

(10) Structure 3a is supported by analytical (found: C,72.1;H,8.4;N,5.7. $C_{15}H_{21}NO_2$ requires C,72.8;H, 8.5;N,5.7),^{1}Hnmr (in D_2O; int. lock H_2O; δ (rel. to Me_4Si) 1.3-2.0 (7H, complex), 2.6 (3H,s), 2.8-3.4 (6H, complex), 6.4-7.4 (5H, complex), ir (ν_{max} [KBr pellet] 3430s broad, 2950w, 1610m, 1510s, 1410s, 1280s, 1250sh), and uv data (the uv spectrum is identical with that of sodium tropolonate,[3b] and, on acidification, changes into that of tropolone[3b]).

(11) Structure 3b is supported by the ^{1}Hnmr spectrum (in D_2O; int. lock H_2O; (rel. to Me_4Si) 2.9 (3H,s), 3.2 br (12H), 6.4-7.4 (5H, complex).

(12) J. Gasparic, M. Vecera, and J. Jurecek, Chem.Listy, 52, 1720 (1958).

(13) T. Nozoe, M. Sato, and K. Matsui, Proc.Japan Acad., 28, 407 (1952).

(14) Reference 3b, p 420.