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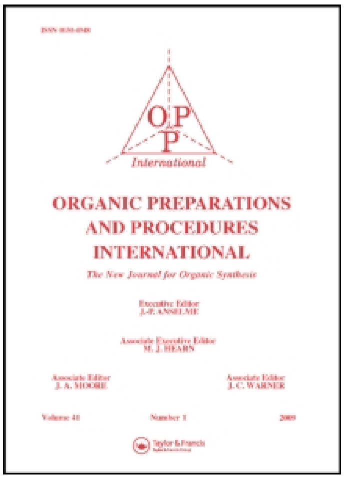

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O-METHYLATION OF TROPOLONE

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O-Methylation of Tropolone

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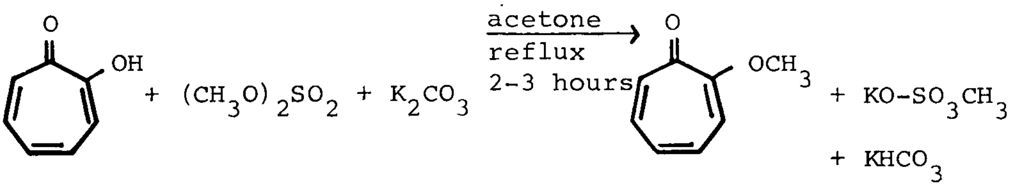
Alkyl ethers of tropolone have been shown to be intermediates of considerable synthetic utility.[1] A variety of procedures employing acidic or basic catalysis[2a,b,c] have been reported for the preparation of these compounds from tropolone. The product yield and purity is, however, considerably less than the essentially quantitative conversion achieved with diazomethane under neutral conditions. This fact is not surprising, since the lability of these vinylogous β-diketo enol ethers is well-known.[1]

We wish to report a facile and high yield synthesis of 2-methoxytropone which obviates the use of diazomethane and thus is ideally suited for large scale preparations. The conversion of tropolone into its methyl ether is accomplished by simply refluxing with the appropriate amount of dimethyl sulfate in acetone in the presence of potassium carbonate. Although this simple procedure has been used often in the phenolic series, it has not been rigorously explored with tropolones.[3] Since tropolone has been regarded as an "extended acid" and conversion of tropolone into its methyl ether thus corresponds to an esterification reaction, this method is an extension of the work of Pailer and Bergthaller[4] who have shown that esterification of carboxylic acids occurs in high yield under similar conditions.[5]



Experimental

Tropolone (4.9 g., 0.040 mole) was dissolved in 75 ml. of dry acetone in a 250 ml. round bottom flask fitted with a reflux condenser and drying tube; anhydrous potassium carbonate (5.5 g., 0.040 mole) was added followed directly by dimethyl sulfate* (5.05 g., 0.040 mole) in one portion. The yellow reaction mixture was heated at reflux for two to three hours when conversion was shown to be complete by thin layer chromatography (silica gel eluted with 5% methanol in benzene). The cooled reaction mixture was filtered, and the solvent was removed under reduced pressure to give 5.2 g. (96%) of a viscous pale yellow syrup which on prolonged standing could be induced to crystallize to give a beige solid, m. 39-40.5°. Without further purification the 2-methoxytropone was homogeneous by TLC and was identical

(IR, NMR) to a sample prepared by reaction with diazomethane.

* Use of one equivalent (0.020 mole) of reagent resulted in only 50% conversion.

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2. a. W. von E. Doering, L. H. Knox, J. Am. Chem. Soc., 73, 828 (1951).

   b. R. M. Horowitz, G. E. Ullyot, ibid, 74, 587 (1952).

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3. cf. 2c.: Alkylation of 4,5-benzotropolone with excess dimethylsulfate and potassium hydroxide in ethanol led to a reported yield of only ca. 22% of methyl ether.

4. M. Pailer, P. Bergthaller, Monatsh., 99, 103 (1968).

5. P. K. Kadaba, Synthesis, 316 (1971). Reports an effective procedure for esterification of carboxylic acids with boron trifluoride etherate as catalyst. This method fails completely in the case of tropolone.

NOTE ADDED IN PROOF: After submission of this paper to Organic Preparations and Procedures International, a communication appeared [(J. Grundy, B. G. James, and G. Pattenden, Tetrahedron Letters, 757 (1972)] which dealt with the esterification of hindered carboxylic acids using similar conditions to those reported by us and by Pailer and Bergthaller.[4]

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