General Synthesis of Tropolone Ethers

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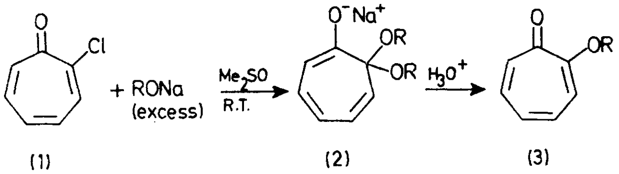
Summary Reaction of 2-chlorotropone with an excess of an alkoxide in dimethyl sulphoxide gives the *gem*-dialkoxy adduct (**2**) which on neutralization affords 2-alkoxytropone, failure only occurring for very bulky alkoxides.

It has proven difficult so far to synthesize tropolone ethers because of rearrangement to benzenoid compounds under the basic conditions of nucleophilic substitutions in protic solvents.[1] Alternative methods, which avoid generation of the tropone nucleus under alkaline conditions, lack generality and are often troublesome resulting in low yields.[1]

Because of interest in tropolone ethers,[2] we synthesised them by making use of the known σ-adducts between tropolone ethers and alkoxides in dipolar aprotic solvents.[3] We found that when 2-chlorotropone (**1**) (*ca.* 10^{-3} M) is allowed to react with a *ca.* threefold excess of an alkoxide in dimethyl sulphoxide benzenoid rearrangements are suppressed, tropolone ethers being locked as *gem*-σ-adducts (**2**)



Scheme. R = Et, Pr^i, Ph, or cyclohexyl.

from which the ethers (**3**) can be regenerated conveniently by neutralization (Scheme). After addition of water, tropolone ethers were extracted with Et_2O and purified by thick layer chromatography (SiO_2).

Using 2·5 M sodium alkoxides in absolute alcohol we thus prepared (**3**, R = Et)† [oil, picrate (hygroscopic) m.p. 103—105 °C] and (**3**, R = Pr^i)† [oil, picrate (hygroscopic) m.p. 85—88 °C] in *ca.* 50% yield each.‡

To avoid dilution with hydroxylic solvents, other less soluble alkoxides were prepared in tetrahydrofuran. Thus, we obtained (**3**, R = Ph) [m.p. 49—50 °C (lit.[4] 43—45 °C)] and (**3**, R = cyclohexyl)† [oil, picrate (hygroscopic) m.p. 116—117 °C] in 70 and *ca.* 30% yields, respectively.‡

Experiments with 3,5,7-trideuteriocycloheptatrienones showed the absence of rearrangements,[5] the alkoxy group taking the place vacated by chlorine.

So far the above method has failed only in the case of 2-t-butoxytropone which could not be obtained from the reaction of (**1**) with potassium t-butoxide either in Me_2SO or in hexamethylphosphoric triamide. Presumably formation of the adduct (**2**, R = Bu^t), for which there was no u.v. spectroscopic evidence, is hindered by the bulky Bu^t groups.

This method extends the concept of displacing an equilibrium by the locking of a reaction product by a second, reversible reaction as in Claisen condensation or Michael addition[6] reported recently.

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† Structures of all new compounds are supported by satisfactory elemental analyses and by the ^1H n.m.r. and mass spectra.

‡ No effort was made to optimize yields.

[1] F. Pietra, *Chem. Rev.*, **1973**, **73**, **345**, **347**, and **352**.
[2] *E.g.*, see G. Sunagawa and J. Nakazawa, Jap. P. 12,624, July 4, 1964; *Chem. Abs.*, **1964**, **61**, **16021f**.
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[5] G. Biggi, F. Del Cima, and F. Pietra, *J. Amer. Chem. Soc.*, **1972**, **94**, **4700**.
[6] B. M. Trost and R. A. Kunz, *J. Amer. Chem. Soc.*, **1975**, **97**, **7152**.