Formation of Enol Ethers by Alkylation of Ketones

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THE alkylation of ketone anions has long been a subject of interest.[1] As far as we are aware, the only observed products from the ambident anions of weakly acidic ketones like cyclohexanone and acetophenone are the α-alkylated ketones; formation of enol ethers by alkylation at the oxygen atom has not been observed. In two recent studies the reactive trialkyloxonium salts were used as alkylating agents: Kabachnik[2] found some oxygen alkylation of highly acidic ketones (acetylacetone, ethyl acetoacetate) in diethyl ether and House,[3] according to a footnote, suspected *O*-alkylation of 1-decalone when using 1,2-dimethoxyethane (DMC) as a solvent.

These reports prompt us to communicate briefly some of our results. We have found that with triethyl oxonium fluoroborate in aprotic polar solvents *O*-alkylation not only occurs (DMC), but may even be the major reaction [in dimethyl sulphoxide (DMSO) and dimethyl formamide (DMF)]. The same applies when a dialkyl sulphate is used as the alkylating agent.

The table contains results obtained at room temperature by adding to an approximately 0·5 molar solution of Me_3COK in DMSO or DMC first one equivalent of ketone and then one equivalent of dimethyl sulphate.

TABLE

Ketone	Cyclohexanone	Cyclohexanone	Acetophenone	Acetylacetone	Ethyl acetoacetate
Solvent	DMC	DMSO	DMSO	DMSO	DMSO
Products					
Unconverted	32%	11	16	13	0
Enol ether	24	71	68·5	71	75
Other products*	44	18	15·5	16	25

* *C*-Alkylation and poly *O*- and *C*-alkylation products.

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[1] J. M. Conia, *Rec. Chem. Progr.*, 1963, **24**, 43.

[2] T. A. Mastryukova, A. E. Shipov, V. V. Abalyaeva, E. E. Kugucheva, and M. I. Kabachnik, *Doklady Akad. Nauk S.S.S.R.*, 1965, **164**, 340.

[3] H. O. House and B. M. Trost, *J. Org. Chem.*, 1965, **30**, 2502, footnote to Table IV.