Formation of Enamines by Alkylation of Imines

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THE ambident anions of ketones and imines,[1,2] bearing the negative charge both on a carbon and on a heteroatom, are generally considered to be alkylated exclusively at the carbon atom. Recently[3] we reported that in aprotic dipolar solvents, reactive alkylating reagents alkylate the anions of ketones at the heteroatom.

Now we have found that reactive alkylating reagents cause extensive *N*-alkylation with formation of enamines. Since imines are less acidic than ketones, only strong bases such as sodium hydride or sodium amide effect complete ionization.

The Table contains results obtained by the addition, with ice cooling, of one equivalent of alkylating reagent to an approximately 1M-solution of the imine anion.

TABLE

Solvent	Diethylcellosolve			Hexamethylphosphoric triamide					
Base	Sodium hydride			Sodium amide					
Imine	Acetophenone anil			*N*-Ethylcyclohexanone imine			*N*-Ethyl diethyl ketone imine		
Alkylating agent	Et_3OBF_4	Et_2SO_4	EtI	Et_3OBF_4	Me_2SO_4	EtI	Et_3OBF_4	Me_2SO_4	EtI
Products									
Unconverted	8	9	5	29	11	15	26	17	20
Enamine	88	49	5	53	75	17	29	57	~0
C-Alkyl product	4	42	90	18	10	56	42	26	71
Polyalkyl product	—	—	—	—	4	12	3	~0	9

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[2] J. Szmuszkovicz, *Adv. Org. Chem.*, 1963, **4**, 1.
[3] G. J. Heiszwolf and H. Kloosterziel, *Chem. Comm.*, 1966, 51.