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REACTION OF KETIMINE ANIONS WITH CARBONYL AND THIOCARBONYL COMPOUNDS

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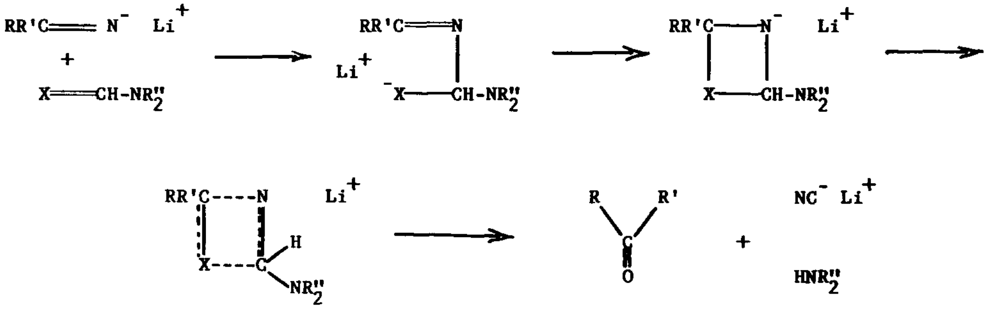
A number of chemical conversions - most notably the Wittig reaction - are best formulated as proceeding through a four-membered cyclic transition state or intermediate. We wish to report a new class of such conversions : The reaction of ketimine anions with carbonyl and thiocarbonyl compounds, and the related thermolytic decomposition of N-acylketimines. When the lithium salts of ketimines were warmed in dimethylformamide, the corresponding ketones, dimethylamine, and lithium cyanide were formed. Diethylformamide and dimethylthioformamide react analogously :



X = O or S

Nothing can be said, at this time, about the precise timing of the reaction - it might be more or be less concerted than shown above. Its scope is considerable : The dialkylformamide (or dialkylthioformamide) can be replaced by carbon disulfide or carbon dioxide. Table 1 summarizes the reaction conditions and yields for the various systems. The yields of the volatile

Table 1. Reactions of Ketimines and their Anions with Carbonyl and Thiocarbonyl Compounds

#	RR'C=N$^-$ M$^+$			Carbonyl compound	Temp.	Hours	Yields (%) of RR'C=X	of other fragments
	R	R'	M$^+$	.	°C			
1	n-C_6H_{13}	CH_3	Li	OCH-NMe$_2$	70	4	90	HNMe$_2$: 96; LiCN : 57
2	n-C_4H_9	C_6H_5	Li	OCH-NMe$_2$	80	6	33 +	Cyanohydrin : 24; HNMe$_2$:54
3	C_6H_5	C_6H_5	Li	OCH-NMe$_2$	70	3	62	not determined
4	C_6H_5	C_6H_5	Li	OCH-NEt$_2$	70	3	70	HNEt$_2$: 83
5	C_6H_5	C_6H_5	MgBr	OCH-NMe$_2$	80	3	80	HNMe$_2$: 83
6	C_6H_5	p-Br-C_6H_4	Li	OCH-NMe$_2$	70	3	50	not determined
7	C_6H_5	p-MeO-C_6H_4	Li	OCH-NMe$_2$	70	3	25	not determined
8	C_6H_5	C_6H_5	Li	SCH-NMe$_2$	25	1	52	HNMe$_2$ identified
9	C_6H_5	C_6H_5	Li	S=C=S	25	½	83	Li$^+$ NCS$^-$: 96
10	C_6H_5	C_6H_5	H	S=C=S	25	56	80	HNCS : 91
11	C_6H_5	C_6H_5 + 1 eq. Et$_3$N	H	S=C=S	25	4½	85	NCS$^-$: 81
12	C_6H_5	C_6H_5	Li	O=C=O	25	12	43	not determined

products were determined by v.p.c., the inorganic ions by volumetric methods. Base-catalysis in the reaction of CS_2 with the free imine is evident from # 9-11. An example of the reaction of CS_2 with a free imine has been reported already in 1887 (1). N-Acylketimines, $R_2C{=}N{-}CO{-}R'$, react intramolecularly : The thermolyses of N-benzoyl-benzophenoneimine (2,3) at 115°, and that of the ethanol adduct of N-acetyl-benzophenoneimine (3) at 220° gave benzophenone in about 40% yields. We are continuing the investigation of these reactions.

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References.

1 W. Fehrmann, *Berichte* **20**, 2844 (1887).

2 G. Reddelien and H. Danilof, *Berichte* **54**, 3138 (1921).

3 J.E. Banfield, G.M. Brown, F.H. Davey, W. Davies, and T.H. Ramsey, *Austral. J. Sci. Res.* **A 1**, 330 (1948).