Rearrangement of an α-Halogenoamides to Carbamates by Alkoxides

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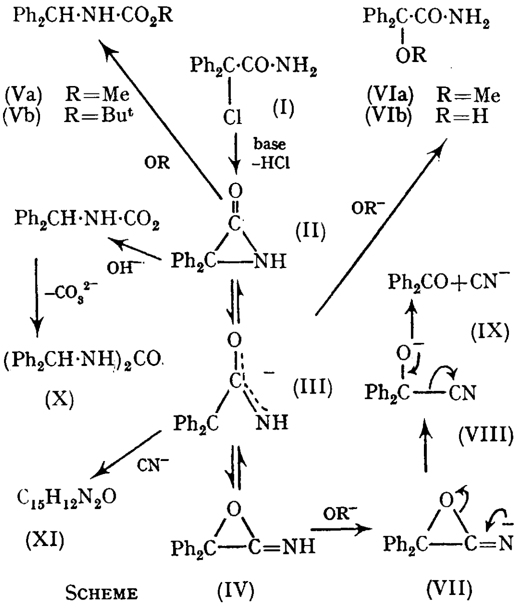
WE have previously shown that amines provoke rearrangement of α-chloro-αα-diphenylacetamide (I) into *N*-diphenylmethyl ureas.[1] We now report a new rearrangement of (I) into the *N*-diphenyl methyl carbamates (Va) and (Vb) by use of a methanolic solution of potassium hydroxide or metal alkoxides in the parent alcohols. When (I) (10 mmoles) is stirred with potassium hydroxide (30 mmoles) in methanol (30 ml.) at 20°, the rearranged product [(Va), m.p. 141—143°]† is obtained in 53% yield. If instead of potassium hydroxide, sodium methoxide is applied, the yield of (Va) drops to 40%. The yield of [(Vb), m.p. 120·5—121·5]† from the reaction of (I) with an equimolar amount of potassium t-butoxide was strikingly low (7%). In every case the reaction gives rise to formation of benzophenone (IX), substitution products [(VIa), m.p. 149°[2] and VIb] and an urea derivative [(X), m.p. 275°]† in variable yields (see Table).

The reaction of (I) with equimolar amount of Bu^{t}OK in Bu^{t}OH yielded, (Vb), (VIb), (IX), (X), and small amounts (4%) of an unidentified nitrile (XI) [m.p. 155·5—157·5° i.r. (KBr): 3370, 3300, 3140, 2250 (C≡N), 1700 (C=O) and 1630 cm.$^{-1}$], which analyzed as $C_{15}H_{12}N_2O$.

The data presented here can reasonably be explained in terms of an α-lactam intermediate (II). Whereas (V) conceivably derives from an attack of an alkoxide anion on the carbonyl of a



SCHEME

Reactions of (I)[a] *with alkoxides at* 20°

Base	Solvent[b]	Products (%) (IX)	(Va)	(Vb)	(VIa)	(VIb)	(X)	(XI)	
KOH[c]	MeOH	20	53	—	15	—	—	—	
MeONa[c]	,,	30	40	—	16	—	—	—	
MeONa[c,d]	,,	20	40	—	30	—	—	—	
KOH[c]	Bu^{t}OH	45	—	—	—	4	—	—	(45%)[e]
Bu^{t}OK[f]	,,	31	—	7	—	32	4	4	
Bu^{t}OK[c]	,,	86	—	—	—	3	2	—	

[a] 10 mmoles; [b] 30 ml.; [c] 30 mmoles; [d] At −36°; [e] benzilic acid; [f] 10 mmoles (an equimolar amount).

† Identified by comparing with authentic sample, prepared from benzhydryl isocyanate.

true α-lactam form (II), the formation of (VI) probably involves the zwitterionic form (III). Benzophenone presumably results from base-catalyzed fragmentation of the oxiran form: (IV) → (VII) → (VIII) → (IX)[3] (see Scheme).

Whereas the reaction of 1-t-butyl-3,3-diphenylaziridinone with potassium t-butoxide reportedly[4] leads to diphenylmethyl-t-butylamine, that of 1-t-3-phenylaziridinone produces t-butyl *N*-t-butylphenylglycinate and not a carbamic acid derivative.[5]

Our work shows that carbamic acid derivatives can be obtained from (I), and that in this case, methoxide is significantly a much more desired reagent for this rearrangement than the commonly used t-butoxide.

The yield of benzophenone depends principally on the amount and nature of the reagent and only slightly on temperature. The fragmentation to benzophenone appears to be a base-induced rather than a thermolytic reaction.[6]

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