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REARRANGEMENTS OF HYDRAZINIUM SALTS

H.F. Hodson and D.M. Maytum,
(Wellcome Foundation Ltd., Beckenham, England)
B.R.T. Keene
(Medway and Maidstone College of Technology, Kent, England)

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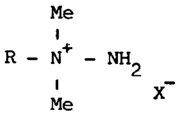
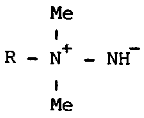
Radical pathways have been proposed for the Stevens (and related 1,2-electrophilic) rearrangements on the basis of both spectroscopic (CIDNP)[1-3] and chemical[1,4] evidence. Analogous base-catalysed rearrangements seemed likely in suitably substituted hydrazinium salts (e.g. I) and it has been reported recently that (I, R = $PhCH_2$) gives the corresponding (III) on heating with solid sodium hydroxide.[5]



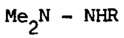
$R-\overset{Me}{\underset{Me}{N^+}}-NH_2 \quad X^-$

(I)



$R-\overset{Me}{\underset{Me}{N^+}}-NH^-$

(II)



Me_2N-NHR

(III)

Under these conditions, (I, R = p-$NO_2C_6H_4CH_2$) underwent only explosive decomposition, (ascribed to easy oxidation of the $-CH_2NH-$ link)[5], but we have found that when treated with potassamide in liquid ammonia this salt decomposes smoothly to give 4,4′-dinitrobibenzyl in fair yield, confirming a radical process in this instance at least. Other salts (some examples are given in Table 1) rearranged to the corresponding N-benzyl-N′,N′-dimethylhydrazines in acceptable yields when similarly treated: hydrazone formation[5] is minimised under these conditions.

The possibility of photochemical decomposition of the nitrogen ylides(II) has been examined. Solutions of (I, R = $PhCH_2$, m-$ClC_6H_4CH_2$ or p-$MeC_6H_4CH_2$) in aqueous sodium hydroxide (2%) were found to be stable in the dark but on irradiation (Hanovia 450W medium-pressure Hg lamp) conversion into the corresponding (III) occurred rapidly.

In neutral aqueous solution the predominant reaction is slow solvolysis: thus, after a solution of (I, R = $PhCH_2$) had been irradiated for 8 hr, benzyl alcohol (34%) was isolated, with only a trace amount (TLC) of (III, R = $PhCH_2$). Solutions of (I, R = p-$NO_2C_6H_4CH_2$) in alkali were markedly less stable even in daylight and precipitated 4,4′-dinitrobibenzyl almost instantly on irradiation: it seems likely that rapid dissociation into p-nitrobenzyl radicals provides a more plausible explanation of the violent decomposition observed previously.[5] The structures of other, minor products are being examined.

Table 1.

N-R-N,N-Dimethylhydrazinium Bromide	Yield (%) of N-R-N′,N′-Dimethylhydrazine[a]	
	Method A[b]	Method B[c]
R = $PhCH_2$	90	36
R = m-$ClC_6H_4CH_2$	-	27
R = p-$MeC_6H_4CH_2$	55	65
R = p-$NO_2C_6H_4CH_2$	0[d]	0

[a] New compounds characterised and analysed (C, H, N) as monomethiodides.

[b] KNH_2-NH_3

[c] Photochemical reaction: yields not optimised

[d] 4,4′-Dinitrobibenzyl (26%) was formed, together with small amounts of p-nitrobenzaldehyde and some tarry material.

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