Rearrangement of 1,1-Dimethyl-1-phenacylhydrazinium Bromide

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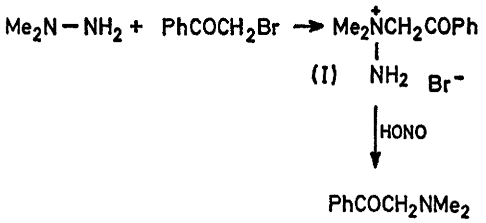
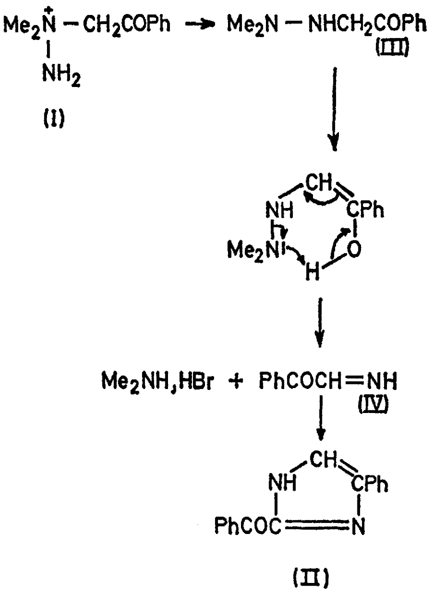
Summary 1,1-Dimethyl-1-phenacylhydrazinium bromide decomposes in n-pentyl alcohol under reflux to form dimethylamine hydrobromide (100%) and 2-benzoyl-4-phenylimidazole (65%) *via* initial rearrangement to 1,1-dimethyl-2-phenacylhydrazine followed by disproportionation of the latter; possible mechanisms for these transformations are discussed.

Much attention has recently been focussed on the mechanism of the Stevens and related rearrangements.[1] Aminimides have been shown to undergo similar transpositions (N to N) and evidence for the participation of radical intermediates in these reactions has been presented.[2] Recent studies have described the base-induced rearrangement of *NN*-dimethyl-*N*-alkylhydrazinium salts[3] to the corresponding 1,1,2-trisubstituted hydrazines. We now report the remarkably smooth rearrangement of 1,1-dimethyl-1-phenacylhydrazinium bromide (I).



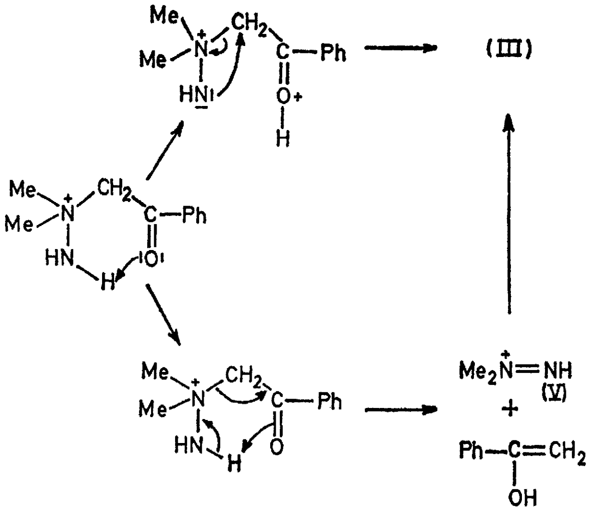
The reaction of phenacyl bromide with 1·5 equiv of 1,1-dimethylhydrazine in ethanol gave a quantitative yield of a colourless solid, soluble in water, m.p. 125—126° (decomp.). An analytical sample obtained by crystallization from acetonitrile, gave a correct elemental analysis for $C_{10}H_{15}N_2OBr$. A combination of spectral and chemical data unequivocally established the structure of this compound as (I).



Scheme 1

When a solution of (I) in n-pentyl alcohol was heated under reflux for 3 h, a smooth decomposition occurred. Evaporation of the solvent left a solid residue which was washed with hot benzene. The very hygroscopic, benzene insoluble solid, identified as dimethylamine hydrobromide was obtained in quantitative yield. Evaporation of the benzene solution gave a 65% yield of (II) as pale yellow leaflets (from ligroin), m.p. 198—199°, whose structure was established by elemental analysis, spectral data, and comparison with an authentic sample.[4]

The formation of (II) and of dimethylamine hydrobromide can best be rationalized in terms of an N to N migration of the phenacyl group to give 1,1-dimethyl-2-phenacylhydrazine (III). Decomposition of (III) into dimethylamine (as the hydrobromide salt) and phenylglyoxaldimine (IV), followed by dehydrative self-condensation of the latter accounts for the products isolated (see Scheme 1). The fragmentation of (III) into dimethylamine and (IV) finds strong support in the work of Hauptmann *et al.*[5] who reported the formation of phenylglyoxal hydrazone from the action of excess of hydrazine on phenacyl bromide.



Scheme 2

The formation of III) from (I) can be formally regarded as a Stevens type rearrangement (N to N). However, in contrast to the strong base catalysis of the previously reported examples,[3] (I) underwent rearrangement under relatively mild thermolysis and in the absence of base.† This dramatic effect can only be ascribed to the presence of the phenacyl substituent whose carbonyl group is ideally located to abstract the "acidic" proton of the pendant amino-group *via* a six-membered cyclic transition state‡ to give a protonated aminimine. Although the formation of (III) can be viewed as a simple 1,2-migration at this point, we suggest an alternative mechanism involving an initial fragmentation (either from the aminimine or by a continuous process reminiscent of the ester pyrolysis or the Chugaev reaction) to 1,1-dimethyldiazenium ion (V)[6] and the enol form of acetophenone. Recombination of these two fragments in an "aza-Mannich" type reaction would then lead to (III) (see Scheme 2). This type of addition of (V) to styrene has been reported by Urry and his group.[6]

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† In pyridine under reflux as solvent, a 73% yield of (II) was obtained in 1 h.

‡ This process would be even more favoured if (I) already exists in this conformation.

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