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X-RAY CRYSTAL STRUCTURE OF 1,1-DIMETHYL-1-PHENACYLHYDRAZINIUM BROMIDE. EVIDENCE FOR INTRAMOLECULAR HYDROGEN BONDING

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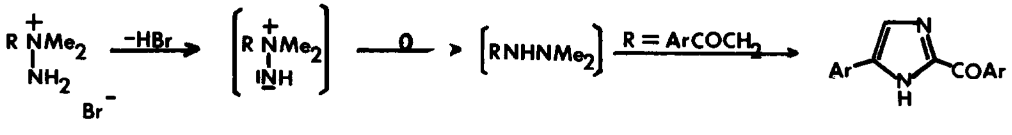
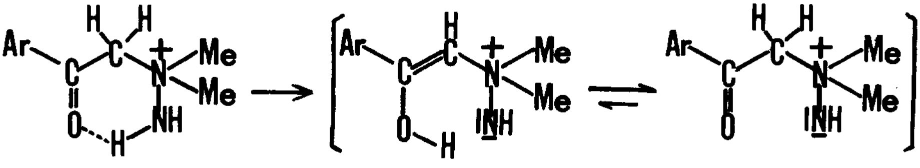
The Stevens and related rearrangements[1] have been a subject of great current interest particularly with respect to the mechanisms for these anionic migrations. The N to N migration of aminimines (e.g. II → III) known as the Wawzonek rearrangement,[2] has been investigated in our laboratories.[3] The conversion of 1,1-dimethyl-1-phenacylhydrazinium bromide (Ib, R = $PhCOCH_2$) to 2-benzoyl-4-(5-)phenylimidazole (IVb, Ar=Ph) in n-propanol at reflux[3] is to be contrasted with the strongly basic conditions required to cause the rearrangement of Ia (200°, solid potassium hydroxide[4]).



I II III IV

a) R = $PhCH_2$ b) R = $PhCOCH_2$

The Wawzonek rearrangement proceeds via the corresponding aminimines (II) and the generation of IIb from Ib under the remarkably mild conditions just described, led to the suggestion[3a] that intramolecular hydrogen bonding in



these salts (Ib) might facilitate the formation of the intermediate aminimines (IIb) as shown above. This view seems to be supported by the position of the carbonyl stretching frequency of 1,1-dimethyl-1-phenacylhydrazinium bromide(Ib, R = $PhCOCH_2$) at 1650 cm^{-1} compared to that of phenacylpyridinium bromide at 1675 cm^{-1}. The recent discovery that this rearrangement can proceed under milder conditions still, namely by photolysis in methanol[3c] or upon overnight stirring in dimethyl sulfoxide at room temperature,[3d] prompted us to determine the crystal X-ray structure of 1,1-dimethyl-1-phenacylhydrazinium bromide.

Single crystals of 1,1-dimethyl-1-phenacylhydrazinium bromide suitable for X-ray analysis were obtained by slow evaporation of a dilute methanolic solution. Its nmr spectrum in deuterium oxide containing a few drops of hydrochloric acid exhibited aromatic absorptions centered at $\delta 8.30$ (5H) and two singlets at $\delta 5.8$ (2H, CH_2) and 4.05 (6H, CH_3).

Crystal data: monoclinic, space group $P2_1$, Z = 2, a = 6.984(4), b = 5.748(5), c = 14.332(10); β = 92.71(5). X-ray intensity data were collected on a Syntex $P2_1$ four circle automated diffractometer using Cu-Kα radiation. Frequent examination of three standard reflections indicated that the salt, though susceptible to photolytic rearrangement in solution, did not decompose during the data collection. The structure was solved by standard heavy-atom Patterson and Fourier techniques. Least-squares refinement using anisotropic thermal parameters for all non-hydrogen atoms resulted in an R-factor of 0.05 for the 1125 independent reflections with $I > 3\sigma(I)$.

Although appearing at electron density levels close to background, all hydrogen atoms were located in reasonable positions in difference maps.. However, their coordinates as found were not sufficiently accurate to warrant inclusion in structure factor calculations. Since some of the hydrogen atom parameters did not refine smoothly, no hydrogen atoms were included in the final refinement.

The final coordinates (Table I) define a molecule having the bond lengths and conformation shown in Fig. 1. N2 was distinguished from C9 and C10 by its higher electron density, shorter bond length to N1, and the location of the hydrogen atoms in reasonable positions for C9, C10, and N2, in particular, between N2 and O. The intramolecular N•••O bond distance of 2.89 Å is within

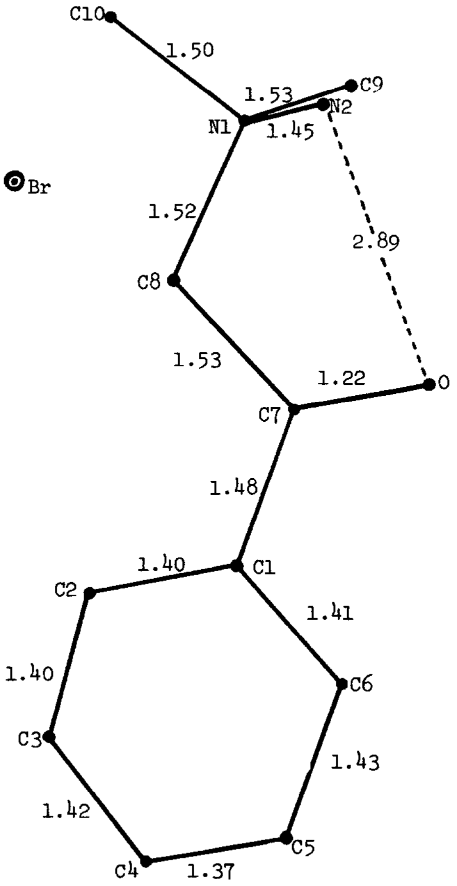


Fig. 1

View of the molecule down the a axis

the range for N-H•••O bonds compiled by Donohue,[5] who stresses the rather loose geometrical constraints on their formation.

Table I

Atomic Coordinates and Estimated Standard Deviations

Atom	x	y	z
Br^-	0.2976 (1)	0.0	0.17079 (7)
C1	0.776 (1)	0.342 (2)	0.4073 (7)
C2	0.699 (1)	0.120 (2)	0.4242 (7)
C3	0.667 (1)	0.055 (2)	0.5167 (8)
C4	0.717 (1)	0.207 (3)	0.5903 (8)
C5	0.795 (1)	0.423 (2)	0.5743 (8)
C6	0.824 (1)	0.499 (4)	0.4802 (6)
C7	0.806 (2)	0.428 (2)	0.3123 (9)
O	0.839 (2)	0.632 (2)	0.2958 (7)
C8	0.790 (2)	0.248 (2)	0.2329 (7)
N1	0.805 (1)	0.351 (2)	0.1353 (6)
N2	0.987 (1)	0.469 (3)	0.1229 (6)
C9	0.643 (2)	0. 521 (4)	0.1125 (8)
C10	0.798 (2)	0.149 (3)	0.0683 (7)

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