

UNUSUAL NITRONES

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Several review articles¹ have drawn attention to the unusual nitrones $\overset{\text{X}}{\text{C}}\text{N}(\text{Y})$ (X = Br, Y = H), $\overset{\text{X}}{\text{C}}\text{N}(\text{Y})$ (X = Cl, Y = H), and $\overset{\text{X}}{\text{C}}\text{N}(\text{Y})$ (X = H, Y = NO₂) (geometry unspecified) which are reportedly² formed by the action of an aqueous solution of hydroxylamine hydrochloride and potassium cyanate on the corresponding aldehyde, i.e. p-bromo-, p-chloro-, and m-nitrobenzaldehyde, respectively

Treatment of each of the aldehydes specified under the reported conditions yields³ material with the appropriate elemental analyses⁴ Of the possible structures which might, a priori, be written for these compounds, $\overset{\text{X}}{\text{C}}\text{N}(\text{Y})$ were apparently preferred because of the observation that each of them yielded, on treatment with cyanide ion, in aqueous solution, the corresponding urea derivative $\overset{\text{X}}{\text{C}}\text{N}(\text{Y})$ (x = Br, Y = H), $\overset{\text{X}}{\text{C}}\text{N}(\text{Y})$ (x = Cl, Y = H), and $\overset{\text{X}}{\text{C}}\text{N}(\text{Y})$ (X = H, Y = NO₂) (geometry unspecified) This reaction, apparently without precedent, presumably involves attack of cyanide ion on the oxygen of the nitrone $\overset{\text{X}}{\text{C}}\text{N}(\text{Y})$ ⁵

In accord with the structural assignment $\overset{\text{X}}{\text{C}}\text{N}(\text{Y})$ (or some similar formulation), mass spectrometric examination⁶ of $\overset{\text{X}}{\text{C}}\text{N}(\text{Y})$ produced a molecular ion, m/e 209. The base peak, m/e 166, corresponded to the molecular ion obtained from the E-oxime (E- $\overset{\text{X}}{\text{C}}\text{N}(\text{Y})$) and the remainder of the spectrum of $\overset{\text{X}}{\text{C}}\text{N}(\text{Y})$ was superimposable upon that of $\overset{\text{X}}{\text{C}}\text{N}(\text{Y})$

However, examination of the infrared spectra of the compounds Ia-c revealed that the $1170\text{-}1280\text{ cm}^{-1}$ absorption characteristic of nitrones⁷ was clearly absent a result which could possibly be attributed to the very unusual structure ascribed to them

Curiously, however, contrary to the earlier reports,² in our hands Ia-c failed to yield the urea derivative Za-c on treatment with cyanide ion under the reported (or any other) conditions. Instead, we routinely obtained high yields of oximes E-Za-c .⁸ In addition, reduction of Ia-c with diborane in tetrahydrofuran solution⁹ generated the corresponding benzylamines, *i.e.*, *p*-bromo-, *p*-chloro, and *m*-nitrobenzylamine, a result which is not in accord with Ia-c since nitrogen-oxygen but not nitrogen-carbon bond cleavage is expected under these conditions.¹⁰

On the basis of these data, we conclude that treatment of *p*-bromo-, *p*-chloro-, and *m*-nitrobenzaldehyde, respectively, with an aqueous solution of hydroxylamine hydrochloride and potassium cyanate generates the corresponding O-carbamoyl oximes Aa-c rather than the nitrones Ia-c as originally reported.

In an effort to determine the geometry about the carbon-nitrogen double bond, each oxime (E-Za-c and Z-Za-c) was treated with chlorosulfonyl isocyanate¹¹ and the resulting, unstable, carbamoyl chlorosulfonates hydrolyzed directly to Aa-c . Regardless of the geometry of the starting oxime (*E* or *Z*) the same O-carbamoyl oxime (Aa-c) was obtained - a result we attribute to isomerization catalyzed by the hydrogen chloride liberated during the course of the hydrolysis and these products were identical to those obtained in the initial reaction between aldehyde, hydroxylamine hydrochloride and potassium cyanate.

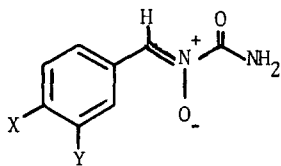
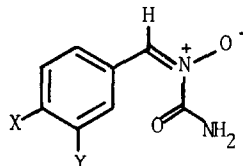
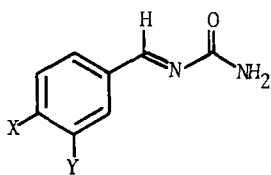
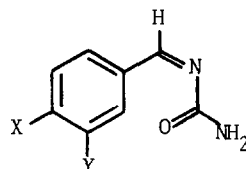
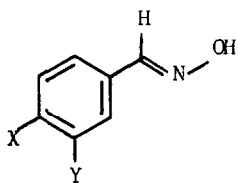
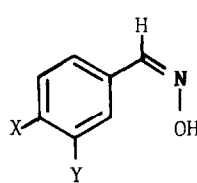
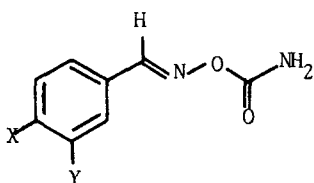
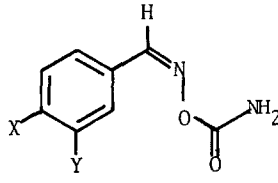
Finally, the O-carbamoyl oximes (Aa-c) were identified as possessing the *E*-configuration by X-ray crystal analysis of Aa ¹² and correlation of the pmr spectra of the analogous Ab and Ac with Aa .¹³ In all of these compounds, as with the corresponding oximes, the chemical shift of benzylic proton is down field of the aromatic protons (oximes 8.0 - 8.7 ppm, acetone- d_6 , TMS = 0.00, O-carbamoyl oximes 8.0-8.7 ppm, acetone- d_6 , TMS = 0.00) while in the *Z*-oximes, all of the benzylic proton resonances are upfield (7.3-7.6 ppm, acetone- d_6 , TMS = 0.00) of the aromatic protons.

We therefore conclude that the reported nitrones Ia-c remain unknown.

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- (2) (a) V Bellavita and N Cagnoli, Gazz Chim Ital., 69, 583 (1939), Chem Abs., 34, 1638 (1940)
(b) V Bellavita and N Cagnoli, ibid., 69, 602 (1939), Chem. Abs., 34, 1978 (1940)
- (3) Significant amounts of the corresponding E-oximes (3a-c) accompany the desired product.
- (4) Satisfactory analyses for all compounds reported have been obtained.
- (5) See reference 1(b), p 340 "If a carbonyl group is attached to the nitrogen atom, its -I effect influences the nitron system to lose the oxygen atom, thus potassium cyanide reacts with the nitron to give the deoxygenated product...and potassium cyanate "
- (6) Mass spectra were obtained on an AEI MS-9 at 70eV. We gratefully acknowledge the aid of Dr S Schrader in obtaining these spectra.
- (7) P. A S Smith and J E Robertson, J Amer Chem. Soc , 84, 1197 (1962)
- (8) The original reports² provide melting point and other analytical data for the urea derivatives The elemental analyses, as recognized by the authors, were unsatisfactory and, in the cases reported here, the melting points presented for the urea derivatives are, within experimental error, identical with those of the E-oximes
- (9) Obtained, and used as received, as a 1 M solution in THF from Ventron Corp., Beverly, Mass
- (10) See e g , H Feuer and D. M Braunstein, J. Org. Chem , 34, 1817 (1969)
- (11) R. Graf, Ber , 96, 56 (1963)
- (12) Compound 4a forms monoclinic needles, space group $P 2_1/c$, with $a = 14.39$, $b = 5.101$, $c = 12.5 \text{ \AA}$, $\beta = 99.51^\circ$, and four molecules in the unit cell. The structure was solved by Patterson and Fourier methods and full-matrix least squares refinement is in progress The crystal and molecular structure will be the subject of a future communication
- (13) See e g , L. M. Jackman and S. Sternhall, Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 2nd edit , Pergamon Press, New York, N Y , 1969, p.226

 $\underline{Z} - 1a-c$  $\underline{E} - 1a-c$  $\underline{E} - 2a-c$  $\underline{Z} - 2a-c$  $\underline{E} - 3a-c$  $\underline{Z} - 3a-c$  $\underline{E} - 4a-c$  $\underline{Z} - 4a-c$