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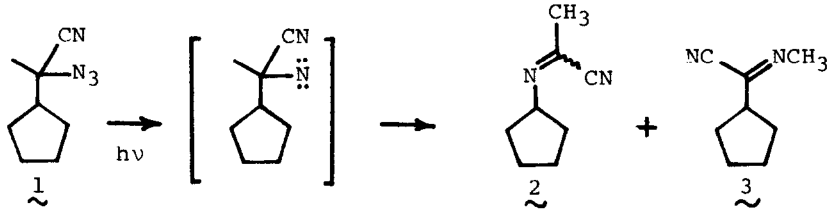
THE PHOTOLYSIS OF α-AZIDONITRILES

Anthony D. Barone and David S. Watt*

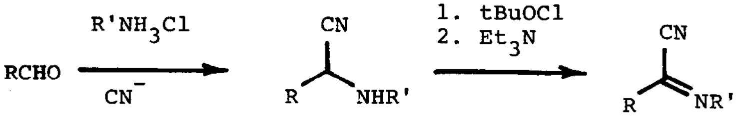
Department of Chemistry, University of Colorado, Boulder, Colorado 80309

The photolytic generation of nitrenes from alkyl azides leads to a variety of products derived from intramolecular and intermolecular processes.[1] Among the latter processes, hydrogen abstraction from solvent has been encountered fairly frequently. We were interested in examining the photolysis of tertiary α-azidonitrile systems where intramolecular hydrogen transfer might compete effectively with the major intramolecular process, 1,2-alkyl group migration. We wish to report that we have realized this objective in the photolysis of an α-azidonitrile imbedded in a steroid system.

As a model for the steroid system, we examined the photolysis of the α-azidonitrile **1** prepared from cyclopentyl methyl ketone.[2] Irradiation in hexane (0.5 M) through a Pyrex filter for 24 hr using a 450 W high-pressure Hanovia lamp resulted in two major products in a 1:1.2 ratio. The dimunition of the azide absorption in the infrared spectrum of **1** and the appearance of an imine absorption at 6.12 μ and weak nitrile absorption at 4.52 μ suggested that either the methyl or the cyclopentyl moieties had migrated to the nitrene center.[3]



The propensity of the photoproduct to hydrolyze during preparative silica gel chromatography led us to separate **2** and **3** by vapor phase chromatography (2 m 5% FS-1265 on 60/80 mesh Diatoport S at 90°). In addition to the spectral data which supported these assignments,[4] we independently synthesized **2** and **3** *via* the Strecker synthesis[5] followed by chlorination/dehydrochlorination.[6]



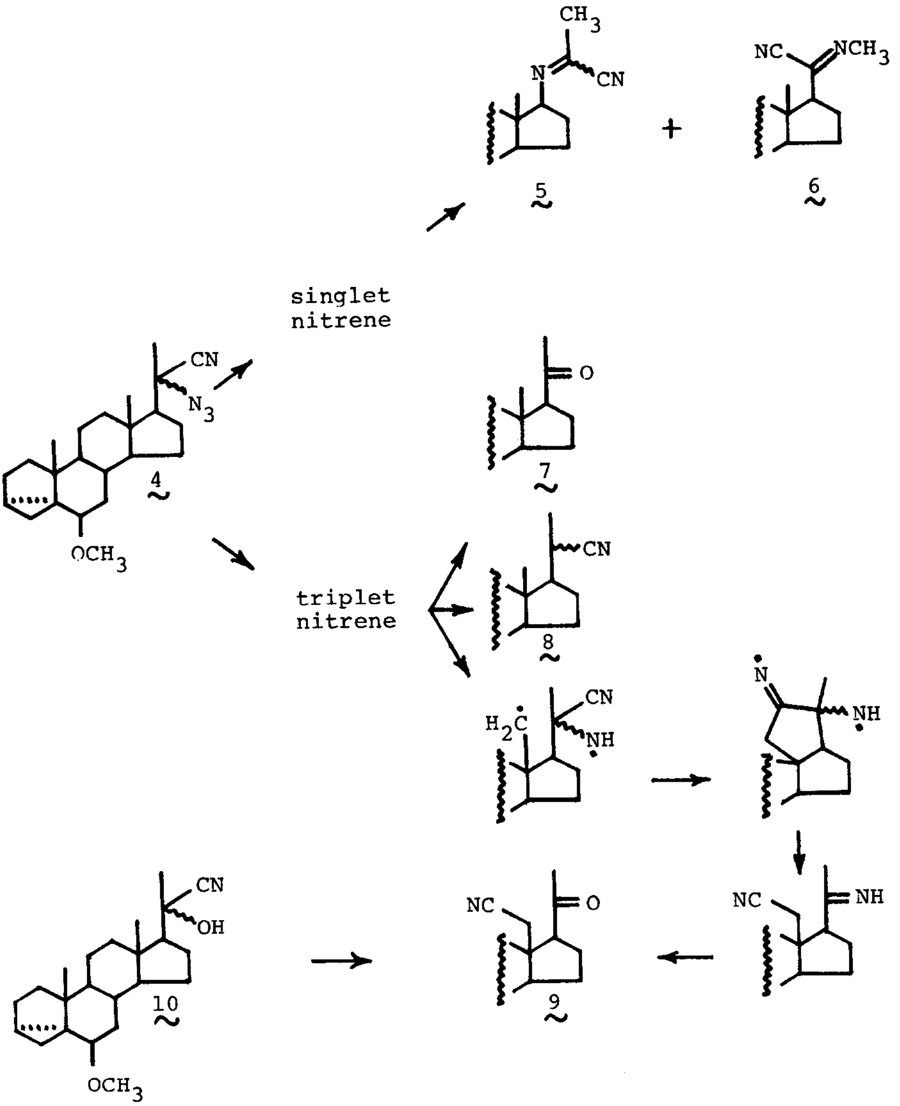
2 R = CH_3, R' = c-C_5H_9
3 R = c-C_5H_9, R' = CH_3

Turning to the steroid system, we next examined the photolysis of 20-azido-20-carbonitrile-6β-methoxy-3α,5α-cyclopregnane[2] (**4**) (λ_{max} 284 nm (ε 21) in ethanol) under conditions identical to those employed in the photolysis of **1** and isolated the cyanoimines **5** and **6** as the principal reaction products. Careful scrutiny of other minor reaction products failed to disclose any of the long-sought[7b-h] but ill-starred[7a] pyrrolidine insertion product. In agreement with a literature report on the photolysis of α-azidocarboxylic acids,[7c] we assumed that the cyanoimines **5** and **6** were derived from the singlet nitrene which underwent rapid 1,2-alkyl group migrations.

In changing the solvent from hexane to acetone, we noted that the photolysis of **4** led to no cyanoimines but rather led to three different products. The two minor constituents were identified as 6β-methoxy-3α,5α-cyclopregnan-20-one[8] (**7**) and 20-carbonitrile-6β-methoxy-3α,5α-cyclopregnane (**8**) as a mixture of diastereomers. The identity of the latter product was established by an independent synthesis from 20-carbonitrile-3β-hydroxypregn-5-ene.[9] The major and most interesting product was 18-carbonitrile-6β-methoxy-3α,5α-cyclopregnan-20-one[10] (**9**) which involved a migration of a nitrile group from C-20 to C-18. The structure of this curious product was confirmed by an independent synthesis of **9** employing the iodide-lead tetraacetate oxidation[11] of the cyanohydrin **10**.

To the tenuous extent that product studies are indicative of mechanism, we would account for the differences in product distribution in the hexane _versus_ acetone photolyses by postulating that the former involves the singlet and the latter involves the triplet state of the nitrene. In the latter case, hydrogen transfer from C-18 to the nitrene center, intramolecular cyano group migration[11] and imine hydrolysis would account for the appearance of **9** as shown in Scheme 1. The other reaction product, the saturated nitrile **8**, may derive from direct loss of the azide[12] or possibly the decomposition of the azo compound derived from the precedented dimerization[7f,g] of two nitrene centers.[13]

Scheme 1


CH3
N
CN
NC
NCH3
+
5
6
singlet nitrene
CN
N3
4
OCH3
O
7
triplet nitrene
CN
8
H2C
CN
NH
N
NH
NC
NH
NC
O
9
CN
OH
10
OCH3

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4. All compounds had infrared, nmr and mass spectral data in accord with assigned structures. New compounds (where thermally stable) gave satisfactory elemental analyses.

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10. ir ($CHCl_3$) 4.46 (C≡N) and 5.86 μ (C=O); nmr ($CDCl_3$) 1.02 (s, 3, C-19 angular CH_3), 2.27 (s, 3, $COCH_3$) and 3.30 (s, 3, OCH_3); mass spectrum (70 eV) m/e (rel. intensity) 355 (43), 340 (66) and 300 (100); mp 162-163°; Anal. Calcd. for $C_{23}H_{33}NO_2$: C, 77.70, H, 9.36. Found: C, 77.67; H, 9.39.

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