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SELECTIVE IMIDOYLNITRENES

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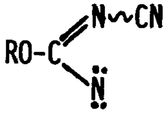
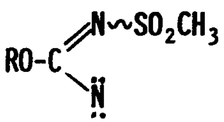
Summary : Two new imidoylnitrenes and alkoxycarbonylnitrene form a sequence of reactivities : Only ROCO-N attacks C-H bonds, it and RO-C(=NCN)-N convert benzene to azepines. Benzene is not attacked by RO-C(=NSO$_2$CH$_3$)-N, but all three nitrenes react with olefins, alcohols, etc.

The reactivities of singlet nitrenes, N-Z, cover a wide spectrum from the highly reactive phosphorylnitrenes (1) to the sluggish dialkylaminonitrenes (2,3). However, intermolecular nitrene reactions have only occasionally been used in synthesis. Some nitrenes have been seldom used because of difficulties in handling their precursors [e.g. NC-N$_3$ (4)]. For others, convenient precursors are available, such as α-elimination precursors for alkoxycarbonylnitrene (5). This nitrene, however, lacks selectivity and C-H insertion accompanies the reactions with other functional groups. For example, the reaction of ethoxycarbonylnitrene with cyclohexene gave a 56% yield of the aziridine, along with a 15% yield of a mixture of three C-H insertion products (6). To be synthetically useful, nitrenes should be easily generated and should have good selectivities. For making aziridines one would want nitrenes which do not attack C-H bonds but which react in good yields with C=C double bonds.

We report here two such nitrenes, alkoxy-N(cyano)-carbimidoylnitrene and alkoxy-N(methanesulfonyl)-carbimidoylnitrene, 1 and 2, respectively. The nitrenes are generated in situ from

1a R = CH$_3$
1b R = C$_2$H$_5$





2a R = CH$_3$
2b R = C$_2$H$_5$

the corresponding azides, **3** and **4**, by photolysis (300 nm) or thermolysis (80°), with or without solvents. The azides **3** and **4**, in turn, are easily obtained from the readily available 5-alkoxytetrazoles (7) by treatment with cyanogen bromide or methanesulfonyl chloride, respectively (8). No C-H insertion products were ever detected when **1** or **2** were generated. With olefins, aziridine yields were 70 - 85% (isolated pure) or 78 - 100% (formed, determined by nmr in the crude reaction mixture), form **1a**, **1b**, **2a**, and **2b**, except that the aziridine from **1b** and cyclohexene was somewhat unstable and was isolated pure in only 53% yield.

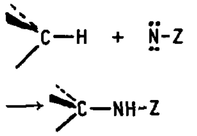
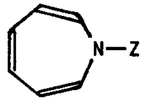
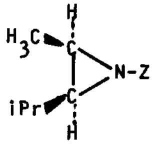
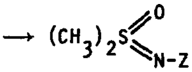
Importantly, **1** and **2** produced aziridines stereospecifically and in good yields even at low olefin concentrations. A 0.5 mole% solution of *cis*-4-methyl-2-pentene in dichloromethane and **2b** gave the *cis*-aziridine in 72% isolated yield, and the nitrene **1b** gave a 68% isolated yield of the corresponding *cis*-aziridine when generated in a 0.1 mole% *cis*-4-methyl-2-pentene solution in dichloromethane. In neither case were the corresponding *trans* aziridines detected (although we have in hand both *trans* aziridines and thus know their nmr spectra). These results indicate long-lived singlet stated for the nitrenes **1** and **2**.

We use here as an example for the virtues of the new nitrenes the clean aziridine formation. The reactions of **1** and **2** with alcohols are similarly clean, and result in addition of the nitrenes to the oxygen, followed by a proton shift, to give alkoxyamine derivatives Z-NH-OR from Z-N and HO-R. Table I shows the reactions of **1**, **2**, and of ethoxycarbonylnitrene with C-H bonds, benzene, olefins, alcohols, and dimethyl sulfoxide. (The reaction course with dimethyl sulfoxide is different for ethoxycarbonylnitrene, deoxygenation is observed instead of addition).

The intermediacy of nitrenes in our reactions may be assumed for several reasons : 1) The analogy with ethoxycarbonylnitrene reactions; 2) The stereospecificity, combined with high yields, of the aziridine formation. Such a result would not be expected from the photolytic or thermal decomposition of intermediate triazolines (9); 3) The reaction with alcohols, which demands a nitrene intermediate.

The azides **3** and **4** are stable in the refrigerator, but decompose when left at room temperature for weeks. Their preparation and properties are being reported (8). All new compounds gave good (± 0.3%) elemental analyses for C, H, and N. Their structures were confirmed by nmr, ir, and mass spectrometry. No evidence for E - Z isomerism was found in any of the compunds, but low temperature nmr studies have not yet been done. We assume rapid E - Z isomerization

TABLE I : INTERMOLECULAR REACTIONS OF THREE NITRENES. ISOLATED PRODUCT YIELDS.

Reactions and Products	Nitrenes $\ddot{N}{-}Z$		
	$Z = -COOC_2H_5$	$Z = -C(=NCN){-}OC_2H_5$	$Z = -C(=NSO_2CH_3){-}OC_2H_5$
	often 50%	NO REACTION	NO REACTION
Benzene + $\ddot{N}{-}Z$ → 	70%	60%	NO REACTION
cis-4-Methyl-2-pentene + $\ddot{N}{-}Z$ → 	58% *cis* + 9% *trans*	85% *cis* no *trans*	93% *cis* no *trans* (*trans* olefin → 92% *trans* aziridine, no *cis*)
$H_3C{-}OH + \ddot{N}{-}Z$ → $H_3C{-}O{-}NH{-}Z$	44% $H_3C{-}O{-}NHCOOC_2H_5$ + 13% $H_5C_2{-}O{-}NCO$ (as $H_5C_2O{-}NH{-}COCH_3$)	77% (no $H_5C_2O{-}N{=}C{=}N{-}CN$).	74% (with t-BuOH → $tBuO{-}NH{-}C(=NSO_2CH_3){-}OC_2H_5$ 59% by photlysis, 60% by thermolysis)
$(CH_3)_2SO + \ddot{N}{-}Z$ →  $(CH_3)_2S(=O)(=N{-}Z)$	(deoxygenation of the $(CH_3)_2SO$ is observed).	73%	59%

at room temperature.

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