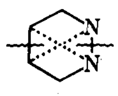
in dimethylformamide at 100° produced a single, crystalline dichlorodifluoropyridazine (**8**) in high yield:[10] mp 50–52°; uv (cyclohexane) λ_{max} (ϵ) 228 (8650), 263 (2340), 305 nm (177); ir (KBr) λ_{max} 6.49, 8.58, 8.68, 10.35, 11.52 μ; nmr 81.3 ppm;[11] mass spectrum *m/e* 184, 156, 125, 121, 106. Selective dehalogenation of **8** was accomplished with hydrogen over 10% palladium-on-charcoal in ether containing triethylamine, and the resulting difluoropyridazine was found to be identical with the authentic 3,6 isomer (prepared from its dichloro analog by heating with potassium fluoride). Irradiation of **8** in Freon 114 at 254 nm gave a single dichlorodifluoropyrazine: mp 80–82°; uv (cyclohexane) λ_{max} (ϵ) 224 (11,000), 252 (1300), 297 nm (10,600); nmr 81.0 ppm;[11] mass spectrum *m/e* 184, 149, 78. Reductive dechlorination in the manner described yielded a difluoropyrazine, purified by vapor chromatography: uv (cyclohexane) highly structured band centered at 272 nm (4550); ir (neat) λ_{max} 6.81, 7.40, 8.00, 8.56, 9.79, 11.14, 13.10 μ; mass spectrum *m/e* 116, 89, 44. This difluoropyrazine was very clearly different in its infrared, ultraviolet, and mass spectra from authentic samples of the 2,3 and 2,6 isomers which had been synthesized from their known dichloro counterparts[12] (again using potassium fluoride at elevated temperatures).

On the basis of this and other[13] evidence, the photoproduct can be assigned structure **9** with confidence; hence the results of our double-labeling experiment are in accord with those of Musgrave's group. Since the significance of the present experiment is not subject to the doubts surrounding its earlier counterpart, the diazaprismane mechanism can be eliminated from consideration.

The bond-making and -breaking processes (see **10**) revealed by the labeling experiments are not accommodated by "conventional" pathways for phototransposition of benzenoid rings.[6] Quantum yield measurements at different wavelengths have indicated that rearrangement requires only $n \rightarrow \pi^*$, not the higher energy $\pi \rightarrow \pi^*$ excitation.[14] Sensitization and quenching studies, though not yet definitive, suggest that rearrangement originates in the n,π^* singlet state. Interestingly, bonding and antibonding interactions in the occupied π^* level **11** of this state[15] match neatly the requirements summarized in **10**. Although the timing of bond-making and -breaking events remains a matter for speculation, the fact that rearrangement proceeds even at 77°K without detectable accumulation of an intermediate reveals that no step requiring significant activation intervenes along the pathway.



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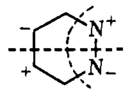

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[10] Selective displacement of the 4- and 5-fluorines by other nucleophiles has been accomplished by Chambers (ref 7a).

[11] ^{19}F chemical shifts are in parts per million upfield from solvent trichlorofluoromethane.

[12] A. A. Miller, U. S. Patent 2,573,268 (1951); *Chem. Abstr.*, 46, 7594*c* (1952); K. H. Collins, U. S. Patent 3,291,802 (1966); *Chem. Abstr.*, 66, 95086*g* (1967); French Patent 1,457,963 (1966); *Chem. Abstr.*, 68, 2917*g* (1968).

[13] The photoproduct from **8** was not identical with 2,6-dichloro-3,5-difluoropyrazine: C. G. Allison, R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, *J. Chem. Soc. C*, 1023 (1970). Moreover, its ^{19}F resonance appeared at too low field for the 2,3-dichloro-5,6-difluoro structure, as judged from the spectra of model compounds.

[14] This finding contrasts sharply with the requirement for $\pi \rightarrow \pi^*$ excitation in the rearrangement of pyrazine and methyl-substituted pyrazines (ref 4a).

[15] Here the most naïve representation of the lowest n,π^* singlet state is assumed.

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Interception of Hydrogen Cyanide Precursor(s) in the Reaction of Active Nitrogen with Alcohols in Aqueous Solution

Sir:

The literature records very few reports[1,2] of the reactions of active nitrogen in aqueous solution. We initiated investigation of such reactions with organic solutes in order to determine whether a solvent which itself appears to be only slightly reactive[3] to active nitrogen could serve as a moderator and inhibit the deep-seated degradation, largely to HCN, which is characteristic[4] of the reactions of organic substrates with active nitrogen in gaseous and condensed phases. The work communicated here has been largely devoted to investigation of products formed by the reaction of active nitrogen with 10^{-2}–10 *M* aqueous methanol and the effect of approximately 10^{-2} *M* tetranitromethane (TNM) on these products. Under the conditions employed, the concentrations of substrate and scavenger did not change significantly during an experiment. More limited data have also been obtained for the analogous reactions of ethyl, isopropyl, and *tert*-butyl alcohols. These studies show that HCN is an important product formed from all the alcohols but that its yield is suppressed below its threshold of detection by tetranitromethane. The extensive data obtained with methanol[5] lead to the conclusion that *TNM acts by intercepting a precursor of HCN.* A mechanism based

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[1] P. Harteck and E. Roeder, *Z. Phys. Chem., Abt. A*, 178, 389 (1937).

[2] N. N. Lichtin, S. E. Juknis, R. Melucci, and L. Backenroth, *Chem. Commun.*, 283 (1967).

[3] I. M. Campbell and B. A. Thrush, *Trans. Faraday Soc.*, 64, 1275 (1968), conclude that $N_2(A^3\Sigma_u^+)$ is responsible for slight decomposition of water vapor. See also S. V. Vadlamudy and C. A. Winkler, *Can. J. Chem.*, 45, 2463 (1967).

[4] See A. N. Wright and C. A. Winkler, "Active Nitrogen," Academic Press, New York, N. Y., 1968, pp 412–467.

[5] HCN is the only carbonaceous product observed in the gas-phase reaction of methanol; see M. J. Sole and P. A. Gartaganis, *Can. J. Chem.*, 41, 1097 (1963).

on determination of yields of a number of products from methanol and their dependence on reaction conditions postulates that the intercepted species is the product of an insertion reaction.[6]

That N(^{4}S) does not attack water significantly is indicated by rates of formation of NH_2OH and "total nitroxyl" ($NO_2 + N_2O + NH_2OH$) which are not more than 0.01 and 0.1%, respectively, of the flow rate of N(^{4}S). That TNM is not attacked by active nitrogen itself is suggested by the fact that its rate of reduction to nitroform[7] when present in saturated aqueous solution (~5 mM) in the absence of alcohols is only 2% of the flow rate of N(^{4}S). The same ratio of rate of formation of Fe(III) to flow rate of N(^{4}S) is observed in the reaction of Fe(II) in 0.8 N H_2SO_4.[8] Both these reactions appear to involve attack by H atoms[7,9] produced in the decomposition of water vapor by $N_2(A^3\Sigma_u^+)$[3]. The inference that N(^{4}S) does not react with TNM is supported by the observation that the variation of the rate of production of HCN from methanol with change in concentration of methanol is paralleled by the variation in the rate of production of ethylene glycol, the principal product which replaces it in the presence of TNM. The precursor of HCN which is scavenged by TNM cannot be a free CH_2OH radical since this would be oxidized rapidly[7a] to formaldehyde. In the absence of TNM, ethylene glycol is a minor product. The increase in its limiting rate of production in the presence of TNM, corrected for direct oxidation of methanol to ethylene glycol by TNM, is equal within experimental error to the limiting rate of formation of HCN in the absence of TNM.

Active nitrogen was generated in a fast flow system[10] by irradiation with 2450-MHz microwaves. Its flow rate as determined by NO titration[11] at a point 1 cm above the water was 50×10^{-2} μmol sec^{-1}. The reaction flask was immersed in a bath maintained at 9 ± 1°. Yields of nitroform were determined by taking ϵ of its anion at 350 nm to be 1.48×10^4 M^{-1} cm^{-1}.[7b] Formaldehyde,[12] ethylene glycol,[13] and HCN[14] were determined by standard methods. Reaction times were 5 min. Yields of various products, expressed below in units of 10^{-2} μmol sec^{-1}, were constant at concentrations of methanol from 1 to 10 M and diminished gradually at lower concentrations, whether or not TNM was present. In the plateau region, yields from CH_3OH in the absence of TNM were: HCN, 20; CH_2O, 8; $(CH_2OH)_2$, 2. Under identical conditions, except that saturation with TNM was maintained, the yields were: HCN, <0.2; CH_2O, 11; $(CH_2OH)_2$, 30; $HC(NO_2)_3$, 8.5. Under the latter conditions, except that the discharge was not used, so that active nitrogen was absent, yields due to oxidation of CH_3OH by TNM were: CH_2O, <0.5; $(CH_2OH)_2$, 6; $HC(NO_2)_3$, 0.6. Yields of HCN from 2 M solutions of C_2H_5OH, $(CH_3)_2CHOH$, and $(CH_3)_3COH$ were, respectively, 20, 14, and 7. No HCN was detectable from such solutions when saturated with TNM and yields of nitroform were 22 from isopropyl alcohol and 18 from *tert*-butyl alcohol. That 2 M concentrations correspond to plateau conditions was established for the latter two alcohols.[15]

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[6] This analysis will be presented in the full report of this work.

[7] For the background of this experiment see (a) K. D. Asmus, A. Henglein, M. Ebert, and J. P. Keene, *Ber. Bunsenges. Phys. Chem.*, 68, 657 (1964); (b) B. H. J. Bielski and A. O. Allen, *J. Phys. Chem.*, 71, 4544 (1967); (c) J. Rabani, W. A. Mulac, and M. S. Matheson, *ibid.*, 69, 53 (1965).

[8] Unpublished work by J. A. Goldberg in this laboratory.

[9] In the case of reaction with Fe(II) the yield of Fe(III) responds to variation of acid concentration in the same way as has been reported for oxidation of Fe(II) by H atoms; see G. Czapski and G. Stein, *J. Phys. Chem.*, 63, 850 (1959).

[10] See A. Fujino, S. Lundsted, and N. N. Lichtin, *J. Amer. Chem. Soc.*, 88, 775 (1966), for a description of apparatus and procedures. In the present work the gas stream was introduced about 1 cm below the surface of the well-stirred solution.

[11] P. Harteck, G. Mannella, and R. R. Reeves, *J. Chem. Phys.*, **29**, 608 (1958).

[12] C. E. Bricker and H. R. Johnson, *Ind. Eng. Chem., Anal. Ed.*, 17, 400 (1945).

[13] N. N. Lichtin, *J. Phys. Chem.*, 63, 1449 (1959).

[14] J. M. Kruse and M. J. Mellon, *Anal. Chem.*, **25**, 446 (1953).

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Novel Intramolecular Aryl Migrations from Carbon to Silicon by a Free-Radical Mechanism. Migration *vs.* Cyclization[1]

Sir:

Although migration of the phenyl group is the major reaction pathway in carbon-centered radicals, no example of rearrangement of radicals involving silicon or the other group IVb elements has been reported. Nelson, Angelotti, and Weyenberg[2] found that the phenyl groups in benzyldimethylsilyl radicals did not undergo 1,2 shifts. Wilt, Kolewa, and Kraemer[3] have recently disclosed that no migration of phenyl groups takes place in the intermediate triphenylsilylmethyl radical produced from triphenylsilylacetaldehyde at 150°. Thus, phenyl groups do not seem to undergo 1,2 shifts either to or from silicon. Also, in the case of silyl radicals derived from hydrosilanes of general formula $ArCH_2YCH_2SiMe_2H$ ($Y = CH_2$ or $SiMe_2$), no migration of the phenyl group took place, only the cyclization product being obtained.[4]

In this communication, the first example of phenyl migration to a silicon-centered radical is reported.[5] A mixture of (4-phenylbutyl)dimethylsilane [**1a**, bp 117° (20 mm); n^{20}D 1.4929; $d^{20}{}_4$ 0.8727] and di-*tert*-butyl peroxide (DTBP) in a molar ratio of 1:0.343 was placed in a sealed tube with degassing, and allowed to react in a constant-temperature bath kept at 135.0° for 15 hr. From a combination of nmr and ir spectra and vpc retention times the rearrangement product, *n*-butyldimethylphenylsilane [**2a**, bp 106° (19 mm); n^{20}D 1.4925; $d^{20}{}_4$ 0.8733], and the cyclization product, 1,1-dimethyl-2,3-benzo-1-silacyclohept-2-ene [**3a**, nmr (CCl_4) τ 9.65 (s, 4 H), 9.10–9.35 (m, 2 H), 8.10–8.50 (m, 4 H), 7.00–7.35 (m, 2 H), 2.45–2.90 (m, 4 H)],

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[1] Silyl Radicals. VII. For part VI, see H. Sakurai and M. Yamagata, *Chem. Commun.*, 1144 (1970).

[2] L. E. Nelson, N. G. Angelotti, and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **85**, 2662 (1963).

[3] J. W. Wilt, O. Kolewa, and J. F. Kraemer, *ibid.*, **91**, 2624 (1969).

[4] H. Sakurai, A. Hosomi, and M. Kumada, *Tetrahedron Lett.*, 1757 (1969).

[5] Thermal phenyl migrations in certain ω-phenylalkylsilanes in vapor phase have been reported recently although the mechanistic details remain uncertain: H. Sakurai, A. Hosomi, and M. Kumada, *Chem. Commun.*, 521 (1969).