favorable,[6] with $\Delta H = -210 \pm 6$ kcal/mol for the overall reaction $2N_3 \rightarrow 3N_2$. Indeed this could account, in part, for the explosion and detonation decomposition of azide crystals. It is tentatively suggested that the nature of the intermediate X is N_6. The structure of N_6 could be either extended or cyclic. The following points could be used in support of a cyclic structure, similar to that of the benzene ring: (a) the nitrogen atom is isoelectronic with the –CH– radical, and this endows it with similar physical properties of molecular symmetry and structure; (b) the absorption maximum of N_6 is close to the first absorption band of benzene[7] (λ_{max} ~255 nm and ϵ ~200 M^{-1} cm^{-1}); (c) the electrolysis of aqueous solutions of $^{14}N^{15}N^{14}N$ gave[8] no $^{15}N_2$ but $^{14}N_2 + 2\,^{14}N^{15}N$. An extended structure for N_6 could be related to 1,3,5-hexatriene, which has absorption maxima[9] at 251, 244, 241, and 234 nm and ϵ ~6000 M^{-1} cm^{-1}. It is interesting to note that the gas-phase photolysis[9] of 1,3,5-hexatriene produces benzene and other cyclic products. The exothermicity of reaction 3 could induce the cyclization of the intermediate N_6.

Alternatively, the decay of $N_3\cdot$ could give rise to

$$2N_3 \xrightarrow{k_a} N_6 \xrightarrow{k_b} N_2 + N_4$$

If the intermediate X is N_4, the kinetics require that $k_b \gg k_a$. Further work is in progress to elucidate the nature and structure of the 242-nm absorption band.

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A Correlation between Negative Charge on Nitrogen and the Reactivity of Aromatic Nitrenes

Sir:

The chemistry of organic nitrenes has received considerable attention in recent years,[1] because of their potential in synthesis. While carbonyl nitrenes[2] and sulfonyl nitrenes[3] insert into CH bonds, add to double bonds, and abstract hydrogen very efficiently from suitable substrates, the aromatic nitrenes appear to be less reactive and their common precursors, aromatic azides and nitroxides, have often been disappointing in preparative applications.

We have recently measured the hydrogen abstraction rates of a few simple aromatic nitrenes in hydrocarbons and alcohols.[4] The rate constants are remarkably low for diradical species (typical values for hydrogen abstraction from ethanol are on the order of 10^2 l. mol^{-1} sec^{-1}). A similar conclusion can be drawn from the high selectivity of hydrogen abstraction by phenylnitrene.[5] Abstraction yields from primary, secondary, and tertiary CH bonds are in the ratio 1 : 10 : 100.

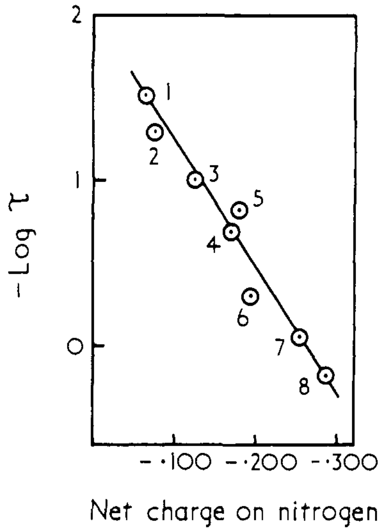
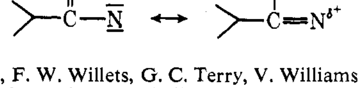


Figure 1. The lifetimes (τ, sec) of some aromatic triplet nitrenes in a polystyrene matrix as a function of the net negative charge on nitrogen: 1, 4-nitrenoacetophenone; 2, 3-nitrenoquinoline; 3, phenylnitrene; 4, dinitrenobiphenyl; 5, mesitylnitrene; 6, 1-nitrenonaphthalene; 7, 1-nitrenoanthracene; 8, 4-*N*-morpholinophenylnitrene.

This low reactivity of an electron-deficient molecular fragment is unexpected. We believe it is due to the negative charge which appears on nitrogen when connected to an aromatic system. To test this hypothesis we have measured the lifetimes of a group of aromatic triplet nitrenes in polystyrene matrices. In the solid medium nitrene recombination and attack upon azide by nitrene are eliminated. The lifetime of the nitrene in the matrix is then a measure of the rate of hydrogen abstraction.[4] It can be seen from Figure 1 that the logarithm of the lifetime correlates quite well with negative charge on nitrogen as calculated by the Hückel molecular orbital method.

Thus, the aromatic nitrenes appear to be in the paradoxical situation of an electron-seeking reagent which is repelled by sites of high electron density. One can now understand why carbonyl nitrenes, sulfonyl nitrenes, and indeed carbenes, are so much more reactive. The carbene function does not attract electrons from the aromatic system; in the carbonyl nitrenes the negative charge is removed from the reaction site to oxygen. The same applies to the sulfonyl nitrene.



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