Carbon Atom Routes to Nitrenes

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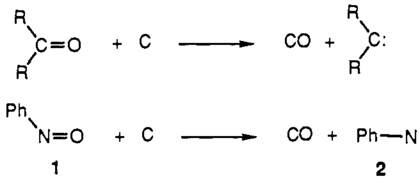
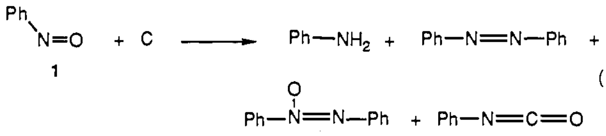
The deoxygenation of carbonyl compounds by atomic carbon is a well-established route to carbenes (eq 1).[1] We report here that the analogous deoxygenation of nitrosobenzene, **1**, generates phenylnitrene, **2**. Thus, cocondensation of atomic carbon and **1** at 77 K in a conventional carbon arc reactor[2] results in the formation of aniline, azobenzene, azoxybenzene, and phenyl isocyanate (eq 2) in the ratios shown in Table 1.[3] Aniline, azobenzene, and azoxybenzene are postulated to be products resulting from triplet phenylnitrene. Aniline results from hydrogen abstractions by triplet **2**, while azobenzene is a product of its dimerization.[4] The formation of azoxybenzene can rationalized by the fact that nitrosobenzene is an effective radical trap and has been observed to react with triplet **2** to generate azoxybenzene.[5] These results demonstrate that atomic carbon, like other oxophilic species such as trialkyl phosphites,[6] can deoxygenate **1** to produce **2**.



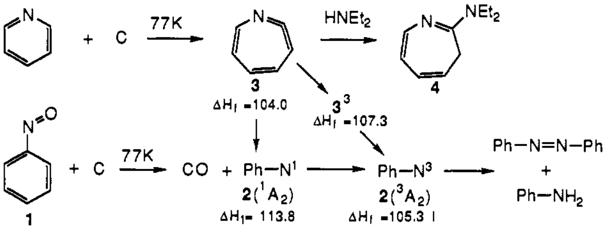
(1)



(2)

This experiment provides evidence for the intermediacy of triplet **2** in the deoxygenation of **1** by carbon atoms. However, in analogy with other deoxygenations by atomic carbon,[1a,7] we expect that the deoxygenating carbon is in the singlet state and that singlet **2** will be the initial product. Since singlet **2** is well known to undergo ring expansion to 1-azacyclohepta-1,2,4,6-tetraene (**3**), which can be effectively trapped by diethylamine,[8] we have cocondensed carbon with a 1:4.8 ratio of nitrosobenzene and diethylamine at 77 K. Product analysis revealed aniline, azobenzene, azoxybenzene, and phenyl isocyanate in the ratios shown in Table 1, but no 2-(diethylamino)-3*H*-azepine (**4**), the product expected to result from trapping of **3** with diethylamine. The absence of products due to singlet **2** can be explained by the propensity of this species to undergo intersystem crossing at low temperatures, with substantial ring expansion to 1-azacyclohepta-1,2,4,6-tetraene (**3**) occurring only at temperatures above 193 K.[9,10]

Scheme 1



In order to develop an alternative route to **3** and to determine if it could be trapped if it were produced under our reaction conditions, atomic carbon was cocondensed with a 1:2.2 ratio of pyridine and diethylamine at 77 K. That this reaction results in the formation of **3** is indicated by the fact that the (diethylamino)-azepine (**4**) is trapped (Table 1). Since aniline and azobenzene are also formed in this reaction, it seems likely that initially formed **3** can rearrange to **2**, a process which has been postulated when **3** is generated by phenyl azide photolysis.[9b,12] The fact that **3** is not trapped when nitrosobenzene is deoxygenated at 77 K indicates that the rearrangement of singlet **2** to **3** is not competitive with intersystem crossing to triplet **2** at the low temperatures of the reaction. Similar results are observed when singlet **2** is generated by photolysis of phenyl azide at low temperatures.[9,10] These reactions are summarized in Scheme 1, which also gives AM-1[13] energies in kilocalories per mole of relevant intermediates.[14]

In our search for products resulting from ring expansion of singlet **2** to **3**, nitrosobenzene was condensed with carbon at higher temperatures. Thus, cocondensation of nitrosobenzene with atomic carbon at 195 K again results in the formation of aniline, azobenzene, azoxybenzene, and phenyl isocyanate in the ratios shown in Table 1. However, when this reaction was repeated with a 1:3.8 ratio of nitrosobenzene to diethylamine in order to trap any azepines formed, a small amount of **4** was formed along with the other products, as shown in Table 1.

These results indicate that, by analogy with deoxygenation of carbonyl compounds to carbenes, carbon atom deoxygenation of nitroso compounds provides a route to nitrenes. In both cases, the high energy of atomic carbon coupled with the stability of carbon monoxide renders deoxygenation an extremely exothermic

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(2) The reactor is modeled after that described by Skell et al.: Skell, P. S.; Wescott, L. D., Jr.; Golstein, J. P.; Engel, R. R. *J. Am. Chem. Soc.* **1965**, *87*, 2829.

(3) Products were identified by GC/MS, with retention times and mass spectra compared to those of authentic samples. Relative yields are shown. In a typical run, in which 1.56 g of **1** was condensed with carbon at 77 K, a 0.44% yield of aniline was obtained based on carbon lost from the rods. However, this is very much a lower limit on yields, as much carbon is physically removed from the rods as macroscopic pieces during the arcing process.

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(9) (a) Leyva, E.; Platz, M. S. *Tetrahedron Lett.* **1985**, 2147. (b) Leyva, E.; Platz, M. S.; Persy, G.; Wirz, J. *J. Am. Chem. Soc.* **1986**, *108*, 3783. (c) Platz, M. S. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Maloney, V. M., Eds.; Plenum Press: New York, 1990; p 306 ff.

(10) Chapman and LeRoux (Chapman, O. L.; LeRoux, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 282) reported that photolysis of **1** at 8 K gives **3**. However, it has been shown that **3** results from photolytic rearrangement of triplet **2** in the low-temperature matrix.[11]

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(13) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(14) The AM-1 calculated energy difference between **2**($^1A_2$) and **2**($^3A_2$) of 8.5 kcal/mol may be compared to a recent MCSCF[15] and experimental[16] value of 18.3 kcal/mol. AM-1 places **2**($^1A_1$) 20 kcal above **2**($^1A_2$), while the MCSCF value is 38.7 kcal. It is interesting and perhaps fortuitous that the AM-1 and experimental[16b] ΔH_f values of **2**($^1A_2$) are virtually identical.

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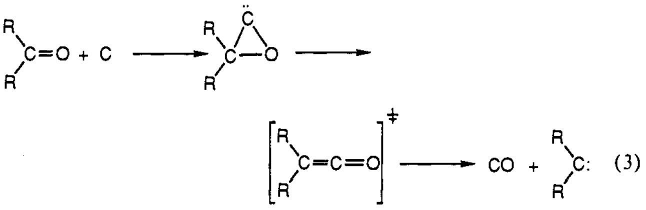
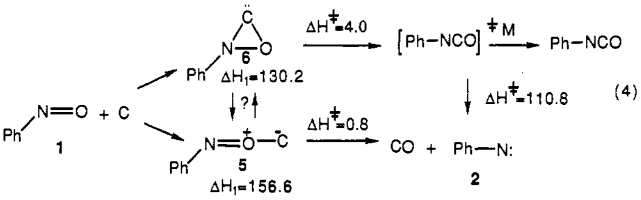
Table 1. Products in the Reaction of Atomic Carbon with Nitrosobenzene and Pyridine

reactants	*T*, K	aniline	azobenzene	azoxybenzene	phenyl isocyanate	**4**
1 + C	77	1.0	0.12	1.75	0.47	
1 + C	195	1.0	0.32	3.43	1.28	
1 + C + DEA[a]	77	1.0	0.11	5.61	2.83	
1 + C + DEA	195	1.0	0.15	3.18	3.10	0.10
pyridine + C + DEA[b]	77	1.0	0.31			0.36

[a] DEA, diethylamine. [b] The three isomeric picolines were also formed in this reaction.

process. We have proposed that deoxygenation of carbonyls by atomic carbon involves a ketene intermediate with excess energy which fragments to carbon monoxide and the corresponding carbene (eq 3), and we have trapped the ketene.[17] In the present investigation, addition of carbon to the N═O double bond would yield phenyl isocyanate with 246 kcal/mol of excess energy. It is certainly possible that this species could partially fragment to CO and **2**, with the remainder degrading to the observed phenyl isocyanate. Photolysis of aryl isocyanates has been shown to give the corresponding nitrene.[18] Alternatively, **2** and phenyl isocyanate may arise by two different pathways, with zwitterion **5** serving as a possible precursor to **2** while **6** leads to phenyl isocyanate (eq 4). A consideration of the large exothermicities involved in C atom deoxygenations along with a qualitative evaluation of the energetics of these reactions with AM-1 (in kilocalories per mole in eq 4) indicates that both pathways are viable. A detailed mechanistic interpretation of this interesting reaction awaits more sophisticated calculations, which will consider both open- and closed-shell surfaces.





A likely pathway to **2** and **3** in the reaction of C with pyridine is attack on N, followed by ring expansion to **3**, which subsequently contracts to **2**. However, the reaction is complicated by the fact the methylpyridines, possible pyridylcarbene products, are also formed, raising the possibility that carbene–nitrene interconversions may be operative under the energetic reaction conditions.[19] The elucidation of mechanisms in the pyridine reaction awaits labeling studies.

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