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DIPHENYLDIAZOALLENE AND DIPHENYLALLENYL DIAZOTATE (1,2,3)

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Of all of the methods that have been developed to synthesize diazoalkanes (and alkyl diazotates) since the pioneering work of Curtius nearly 90 years ago, (5) not one would be expected to be feasible for the generation of diazoallenes (or allenyl diazotates). Although the anticipated difficulties vary in their specifics, one of the most common problems is the instability of the functional group that is to become the diazo moiety when it is in conjugation with the allenyl group. For example, one of the most widely used methods of synthesizing diazoalkanes entails reaction of base with an N-nitrosoamine derivative. (5,6) Although there is no obvious *a priori* reason to exclude this as a method to synthesize diazoallenes, the necessary allenyl amine precursor (2) would most certainly tautomerize to its more stable imine form before nitrosation could be attempted. (7)

At this time, we would like to report the results of our attempts to generate diphenyldiazoallene. To circumvent the imine-enamine problem (*vide supra*), the plan was to generate the allene moiety *after* nitrosating the amine function.

Our approach is outlined in the Scheme. Our results to date indicate that the plan is probably successful up to the point of the allenyl diazotate 4. However, at this point only a small fraction of the diazotate loses hydroxide and nitrogen to give carbene 5. The major portion of the diazotate apparently cyclicizes to give an oxadiazole which opens to give diphenyldiazopropanone 8. *,†,‡

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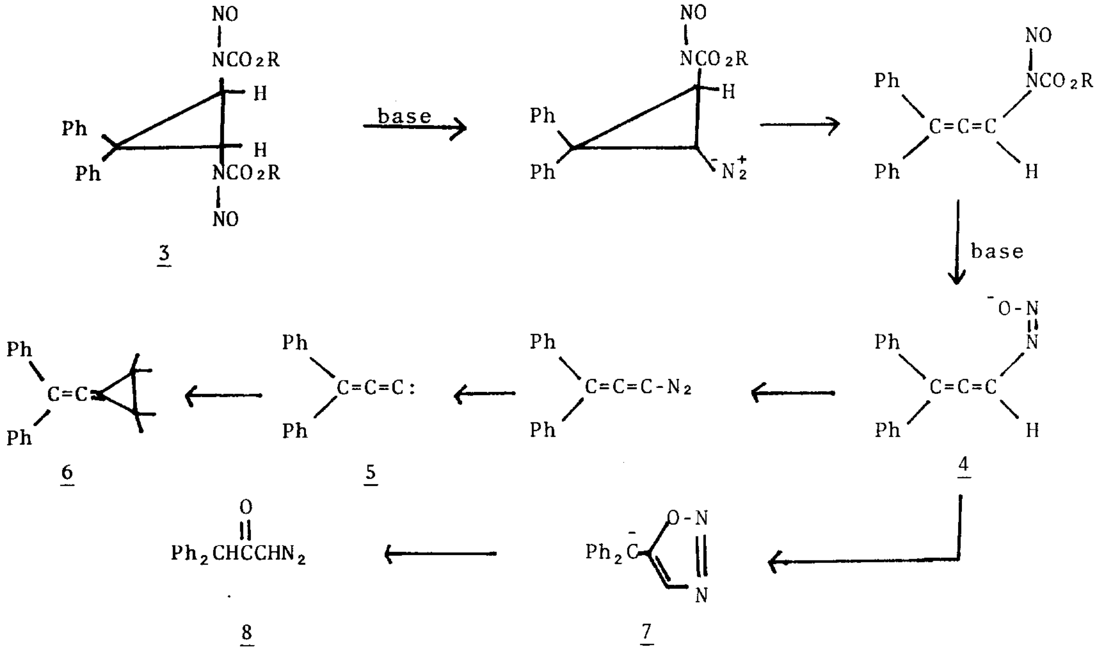
[*] The facility of this interesting ring closure probably results from a combination of the ideal geometrical relationship between the diazotate and the double bond as well as a stabilizing effect of the aromatic rings.

[†] The yield of diazopropanone varied with reaction conditions from as low as a few percent‡ to nearly 70% in concentrated sodium methoxide in methanol. It was identified by independent synthesis.

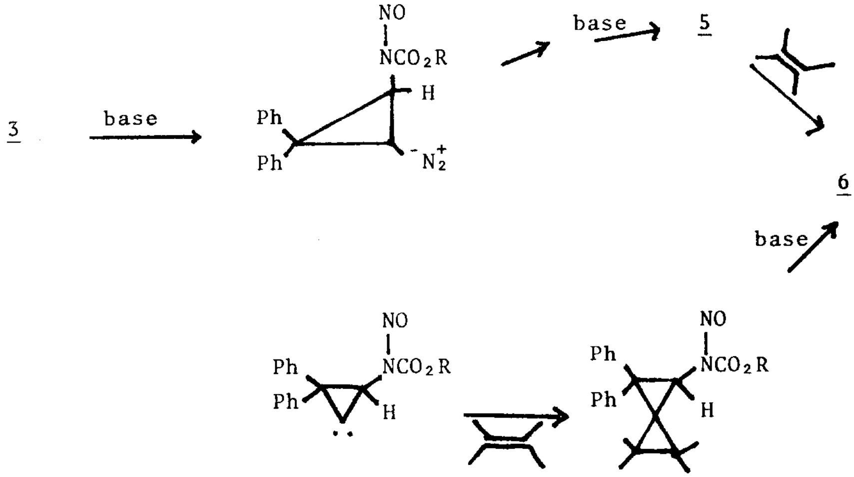
† Under selected conditions of solvent and base concentration, the cyclopropane ring was found to cleave between the two nitrogen functions. This rather remarkable opening will be discussed in detail in another manuscript.



3,3-Diphenyl-1,2-trans-bis(urethano)cyclopropane was synthesized by conventional methods (10) from the cyclopropane dicarboxylic acid via the bis-acid chloride, -acid azide, and -isocynate. (11) Nitrosation was accomplished with N_2O_4 in ether. (12)

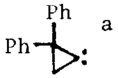
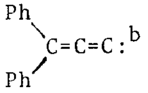
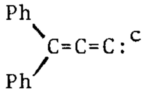
Treatment of the nitrosourethan 3 with sodium methoxide in tetramethylethylene at 0° gave the desired carbene-olefin adduct 6 (13) albeit in disappointingly low yields (on the order of 1%).

Although the yield was low, formation of 6 under these conditions (low temperature) from an alkene substituted with electron donating groups constitutes strong evidence for a carbene intermediate. However, in this system more than one carbene could ultimately lead to the same product. An alternative path involving a cyclopropylidene instead of an allenylidene is shown below. To distinguish between these possibilities, an attempt was made to characterize the intermediate by measuring its relative rates of addition to olefins.



It has been found that whereas the addition of 2,2-diphenylcyclopropylidene to olefins is abnormally sensitive to steric bulk on the olefin, (15) the addition of dimethylallenylidene is not. (16) For this reason the relative rates of addition to olefins of diphenylallenylidene (generated from the reaction of diphenylethynylcarbinyl acetate with base by the method of Hartzler (14)) were determined and compared with those of the carbene intermediate involved in the base induced decomposition of 3. The results (Table I) leave little doubt that the reactive intermediate which adds to the olefin in the latter system is the allenylidene and not the cyclopropylidene. (17)

Table I. Competition Studies of Carbene Addition to Olefins

Carbene	Relative rates of addition to Tetramethylethylene	Cyclohexene	1-Hexene
 [a]	0.33	1.0	0.18 (1-butene)
 $(Ph)_2C=C=C:$ [b]	8.0±1.5	1.0	0.70±0.18
 $(Ph)_2C=C=C:$ [c]	9.0±0.4	1.0	0.61±0.01

[a] Reference 15. [b] Generated from the reaction of base with the nitrosourethan 3. [c] Generated from diphenylethynylcarbinyl acetate by the method of Hartzler (ref. 14).

References

1. Support of this research by the National Science Foundation is gratefully acknowledged.
2. Presented in part to the 1970 Meeting-in-Miniature of the Florida Section of the American Chemical Society.
3. Abstracted from the doctoral dissertation of Dewey J. Northington, University of Florida, 1970.
4. University of Florida Arts and Sciences Fellow, 1968-1969.
5. Cf. H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N.Y., 1961.
6. P. A. S. Smith, "Open-Chain Nitrogen Compounds," W. A. Benjamin, Inc., New York, N.Y., 1966.
7. While the imine-enamine problem also plagues synthetic approaches to diazoalkenes (with the exception of cases in which the enamine is the more stable tautomer [8]), Newman[9] has recently published a very clever and apparently general method to generate diazoalkenes which avoids the imine-enamine problem by nitrosating the amine function before the double bond is formed.
8. Cf. D. Y. Curtin, J. A. Kampmeir, and B. R. O'Connor, *J. Am. Chem. Soc.*, 87, 863 (1965).
9. M. S. Newman and T. B. Patrick, *J. Am. Chem. Soc.*, 91, 6461 (1969); and M. S. Newman and A. O. M. Okorodudu, *J. Org. Chem.*, 34, 1220 (1969).
10. For example, see J. M. Walbrick, J. W. Wilson, Jr., and W. M. Jones, *J. Am. Chem. Soc.*, 90, 2895 (1968).
11. Satisfactory elemental analyses for all new compounds were obtained with the exception of the bis-N-nitrosourethan due to its thermal instability.
12. E. H. White and C. A. Aufdermarsh, Jr., *J. Am. Chem. Soc.*, 83, 1174, 1179 (1961).
13. Identity was established by comparison of glpc retention times on several columns and the ir spectrum with a sample from independent synthesis.[14]
14. H. D. Hartzler, *J. Am. Chem. Soc.*, 83, 4990 (1961).
15. W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *J. Am. Chem. Soc.*, 85, 2754 (1963).
16. (a) H. D. Hartzler, *J. Am. Chem. Soc.*, 83, 4997 (1961); and (b) H. D. Hartzler, *J. Org. Chem.*, 29, 1311 (1964).
17. The close correspondence between the reactivity of diphenylallenylidene generated by Hartzler's elimination reaction [14] and diphenylallenylidene arising from the diazoallene 2 supports the conclusion that the elimination reaction gives a free carbene rather than a carbenoid.[16b]