Tetrahedron Letters No. 26, pp 2167 - 2170, 1975. Pergamon Press. Printed in Great Britain.

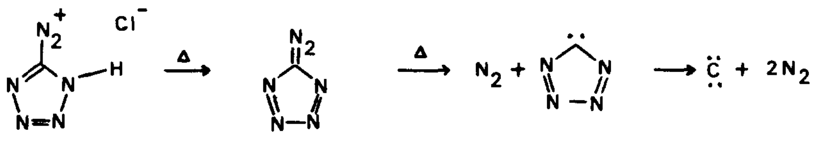
THE STEREOCHEMISTRY OF DEOXYGENATION OF EPOXIDES BY CHEMICALLY GENERATED CARBON ATOMS

Richard H. Parker and Philip B. Shevlin*

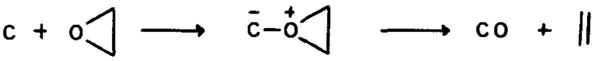
Department of Chemistry, Auburn University, Auburn, Alabama 36830

(Received in USA 5 May 1975; received in UK for publication 13 May 1975)

We have shown that atomic carbon is produced in the thermal decomposition of 5-tetrazoyl diazonium chloride (1).[1,2] Carbon atoms, produced in the pyrolysis


1

of 1, deoxygenate ethylene oxide to yield carbon monoxide and ethylene.[1] A similar reaction has been reported for atomic carbon generated in a carbon arc.[3] The ylid 2 has been proposed as an intermediate in the deoxygenation of epoxides by carbon atoms.[4]


2

We now report a study of the stereochemistry of the deoxygenation of cis and trans-2-butene oxide (3a and 3b) by these chemically generated carbon atoms. The thermal decomposition (120°) of 1 in an atmosphere of either 3a or 3b produces carbon monoxide and cis and trans-2-butene (4a and 4b) with considerable stereospecificity. The relative amounts of 4a and 4b produced in these reactions are given in the table.[5] None of the other isomeric butenes could be detected in any of the experiments. The low product yields are undoubtedly the result of competing reactions of carbon such as dimerization and reaction with 1.

Table. Stereochemistry and yields of the 2-Butenes Produced in the Deoxygenation of 3a and 3b by Chemically Generated Carbon atoms.[a,b]

Reactant	%4A	%4b	mmol 4a $\times 10^4$	mmol 4b $\times 10^4$
20 mm 3a	88	12	5.4	.7
80 mm 3a	84	15	5.0	1.0
120 mm 3a	83	17	5.1	1.1
120 mm 3a + 5% O_2	81	19	3.1	.8
20 mm 3a + 150 mm Ar	83	17	4.0	.8
20 mm 3a + 250 mm Ar	83	17	3.6	.7
3a at -196°	100	0	c	c
120 mm 3b	2	98	5.2	c

[a] In each experiment, ~1 mmol of 1 was decomposed to produce .38 mmol N_2. [b] Values are the average of multiple runs with standard deviations of 5%. [c] Absolute yields were not determined in these experiments.

A consideration of the spin state of the reacting carbon atom indicates that involvement of triplet carbon would result in the production of triplet 2-butene and subsequent nonstereospecific alkene formation. In order to test whether the small amount of nonstereospecificity results from reaction of triplet carbon atoms, we have carried out the deoxygenation of 2a in the presence of 5% oxygen. Since there is no increase in stereospecificity (table) in the presence of this effective scavenger of triplet carbon,[6] we conclude that $C(^3P)$ is not the reactive species in this system. It is probable that the reactive state of carbon in this and other reactions[7] of chemically generated carbon is the first excited singlet $(C(^1D)$. It is unlikely that there is sufficient energy for the production of $C(^1S)$.

An attempt was made to degrade the reacting carbon atoms to their ^3P ground state with added argon. A small amount of deactivation may occur as evidenced by a slight decrease in yield under these conditions (table). However, the unchanged stereochemistry in the presence of argon (table) indicates that $C(^3P)$ does not deoxygenate the epoxide. Moreover, the yield in the presence of argon suggests that carbon (^1D) reacts with epoxide considerably more rapidly than it is degraded to its ground state. This finding is consistant with the flash photolysis studies of Husain and Kirsch[8] who observe that the rate constant for the disappearance of $C(^1D)$ is far greater in the presence of organic substrates than in argon.

The high stereospecificity for the deoxygenation observed here is in contrast with the nonstereospecific deoxygenation of 3a and 3b by arc generated carbon at -196°. For example, deoxygenation of 3a codeposited on a liquid nitrogen cooled surface with arc generated carbon, is reported to yield 4a and 4b in a 1.3:1 ratio.[4] This is far less stereospecific than the 7:1 ratio reported here.

In order to assess the effect of the different reaction conditions employed in the arc system and in the present study, an apparatus was constructed which allows carbon atoms produced in pyrolysis of 1 to impinge upon a layer of epoxide coated on a surface at -196°. The table shows that, under these conditions, the deoxygenation of 3a is completely stereospecific. The high stereospecificity that we observe in the condensed phase can be attributed to a stabilization by the matrix which prevents isomerization of either vibrationally excited ylid (2) or excited butenes.

The reactions of arc generated carbon are thought to involve appreciable amounts of $C(^1S)$.[9] It may be that this high energy species, which is not formed in the present study, is responsible for the nonstereospecific deoxygenation observed in the arc system.

Acknowledgement. Financial support by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the Research Corporation is gratefully acknowledged.

References and Footnotes

1. P. B. Shevlin, J. Amer. Chem. Soc., 94, 1379 (1972).
2. S. Kammula and P. B. Shevlin, ibid., 95, 4441 (1973).
3. J. H. Plonka and P. S. Skell, J. Chem. Soc. D., 1108 (1970).
4. P. S. Skell, K. J. Klabunde, J. H. Plonka, J. S. Roberts and D. L. Williams-Smith, J. Amer. Chem. Soc., 95, 1547 (1973).
5. Product ratios were determined by gas chromatography on a 20' dimethylsulfolane column at 25°. The structures of the butenes were confirmed by ir spectroscopy.
6. F. Martinotti, M. J. Welch, and A. P. Wolf, J. Chem. Soc. D, 115 (1968).
7. S. Kammula and P. B. Shevlin, J. Amer. Chem. Soc., 96, 7830 (1974).
8. D. Husain and L. J. Kirsch, Trans. Faraday Soc., 67, 2886 (1971); 67, 3166 (1971).
9. P. S. Skell, Accounts Chem. Res., 6, 97 (1973).