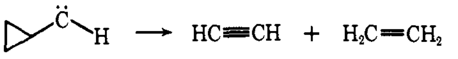
Fragmentation Reactions of Three-Membered Rings Induced by Carbon Atoms

Jon Villaume and P. S. Skell*

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received August 26, 1971*

Abstract: Carbon atoms produced in a low-intensity carbon arc under high vacuum react, upon cocondensation at a liquid N_2 cooled surface, with aziridine to form an adduct which decomposes to ethylene and HCN. With *cis*-2,3-dimethylaziridine, 2-butene is produced which is only 48% cis. Either *cis*- or *trans*-2,3-dimethylcyclopropylcarbene, produced by C_1 insertion into the unsubstituted C–H bond of the ring, fragments to acetylene and both *cis*- and *trans*-2-butene. When the carbene is produced by deoxygenation of *cis*-2,3-dimethylcyclopropanecarboxaldehyde by C_1, both isomers of 2-butene are again produced. The loss of stereochemical identity is attributed to the ability of the initial adduct with C_1, which is formed in a highly exothermic reaction, to circumvent a concerted pathway to decomposition.

Carbon atoms have been used to produce a number of unique intermediates, which makes possible the study of the fragmentation reaction of three-membered rings. Cyclopropylcarbene has been produced by insertion of energetic carbon-11 atoms[1] into a carbon–hydrogen bond of cyclopropane. Carbon atoms produced in a low-intensity carbon arc may form the same species, either by insertion into a carbon–hydrogen bond of cyclopropane[2] or by deoxygenation of cyclopropanecarboxaldehyde,[3] when substrate and carbon atoms are codeposited on a liquid N_2 cooled surface. Ethylene and acetylene are both observed from these reactions, presumably by fragmentation of a cyclopropylcarbene intermediate (eq 1). The behavior is


(1)

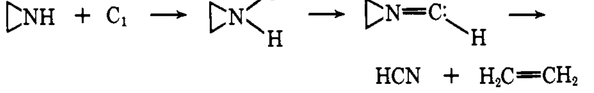
similar to cyclopropylcarbene produced by thermal decomposition of the sodium salt of cyclopropanecarboxaldehyde tosylhydrazone.[4]

Likewise, carbon atoms have been found to deoxygenate epoxides[5] and to remove sulfur from episulfides,[6] forming CO and CS, respectively, and an olefin which does not retain the stereochemical identity of the starting material on fragmentation. If the breaking of two bonds of the three-membered ring occurred simultaneously to produce a small molecule and an olefin, the latter is predicted by Woodward–Hoffmann[7] theory to be formed in a stereospecific disrotatory process.

Therefore, we have extended the investigation to aziridines and studied the stereospecificity of fragmentation and rearrangement of cyclopropylcarbene, formed in carbon atom reactions.

Results

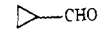
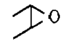
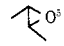
Aziridine and *cis*-2,3-Dimethylaziridine. Codeposition of carbon arc vapor and aziridine (eq 2) produced


(2)

HCN which accounts for 16% of the carbon atoms estimated to be in the arc and ethylene amounting to 18%. The ethylene is known to be formed from C_2 in small amounts in most reactions,[8] but HCN can reasonably be expected to have come only from decomposition of an ylide type adduct of C_1 with aziridine.

To study the stereochemistry of the fragmentation *cis*-2,3-dimethylaziridine was synthesized. No isomeric trans aziridine could be detected by nmr. The codeposition with carbon arc vapor produced HCN, *cis*- and *trans*-2-butene, and small amounts of both 1-butene and 1,3-butadiene. The yields of olefins and HCN each amounted to 9% of the available C_1 (see Table I). In analogy to the ring expansion of cyclo-

Table I. Stereospecificity of Three-Membered Ring Fragmentation Induced by Arc Produced Carbon Atoms

	2-Butene yield[a]	Relative amount of 2-butene		Small molecule yield (%)
		Cis	Trans	
	8	48	52	HCN (9)[a]
	4	43	57	HC≡CH (14)[b]
	4	8	92	HC≡CH (17)[b]
	10	64	36	HC≡CH (22)[b]
		82	14	CS
	53	39	61	CO
	58	58	42	CO

[a] Yield of 2-butenes and HCN based on estimated C_1 present; see footnote 14. [b] C_2 is also a precursor to acetylene. The separation into yields from C_1 and C_2 cannot be made with the available data.

---

(1) (a) C. MacKay and R. Wolfgang, *J. Amer. Chem. Soc.*, **83**, 2399 (1961); (b) P. Shevlin and A. Wolf, *ibid.*, **88**, 4735 (1966).

(2) P. S. Skell, F. A. Fagone, and J. H. Plonka, unpublished results. Previous reports (P. S. Skell and R. R. Engel, *J. Amer. Chem. Soc.*, **87**, 4663 (1965); **88**, 4883 (1966)) indicating that there was no acetylene formed with cyclopropane or other saturated hydrocarbons have proved incorrect upon reinvestigation.

(3) J. H. Plonka and P. S. Skell, submitted for publication.

(4) L. Friedman and H. Schechter, *J. Amer. Chem. Soc.*, **82**, 1002 (1960).

(5) J. H. Plonka and P. S. Skell, *J. Chem. Soc. D*, 1108 (1970).

(6) K. J. Klabunde and P. S. Skell, *J. Amer. Chem. Soc.*, **93**, 3807 (1971).

(7) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(8) P. S. Skell and R. F. Harris, *J. Amer. Chem. Soc.*, **88**, 5933 (1966).

propylcarbene[4] some of the intermediate may have ring expanded to the cyclic imine, but this possibility was not pursued.

When carbon atoms are generated in the arc they take ~10^{-5} sec to reach the walls of the flask; only the ground state ^3P and metastable singlet species (^1D and ^1S) are long lived enough to reach the reaction zone[9] and be implicated in the reaction. The participation of the metastable singlet states in reaction with other substrates has been demonstrated.[10,11] Unlike the arc, carbon atoms generated by vaporization from a thermally heated rod are formed only in the ground-state ^3P.[12] When carbon vapor, produced in this manner, was codeposited with *cis*-2,3-dimethylaziridine the yield of HCN was ~3% of the estimated C_1.[13] Therefore, it is possible that the ^3P participates to some extent in the arc vaporized C_1 reaction.[14]

cis- **and** *trans*-**1,2-Dimethylcyclopropane.** Carbon arc vapor was codeposited with both *cis*- and *trans*-1,2-dimethylcyclopropane. Acetylene and 2-butene are produced by the fragmentation of 2,3-dimethylcyclopropylcarbene, formed by insertion of a carbon atom into the carbon–hydrogen bond at the unsubstituted position of the ring. Insertion into the other ring C–H bonds is observed but is not relevant. Acetylene also comes from a C_2 precursor in most reactions,[8] but yields vary widely from substrate to substrate. The yield of this compound is ambiguous to that extent, but 2-butenes can be expected only from the decomposition of dimethylcyclopropylcarbene. This olefin is not produced in a stereospecific fragmentation (Table I); there is some memory effect. A portion of the carbene must also have undergone ring expansion to dimethylcyclobutene[4] but this fraction was not analyzed.

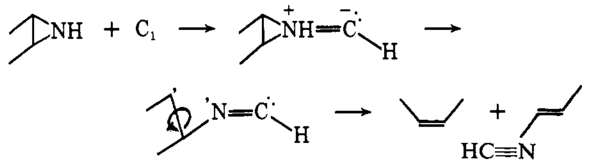
When thermally vaporized carbon was used a small amount of 2-butene (~2% of C_1) was formed and therefore, the triplet state of carbon may take a small part in the arc reaction.

cis-**2,3-Dimethylcyclopropanecarboxaldehyde.** Aldehydes and ketones are deoxygenated by carbon atoms generated in the low intensity arc, forming CO and a carbene. This process has been shown to involve only metastable singlet states of C_1, using two independent criteria.[10,15] When 2,3-dimethylcyclopropanecarboxaldehyde (a mixture of both exo and endo isomers with greater than 97% cis methyl groups) was codeposited with carbon vapor from the arc, *cis*-2,3-dimethylcyclopropylcarbene was produced by the deoxygenation process. The fragmentation of this carbene produced acetylene and 2-butene with some loss of stereochemistry of the starting material (Table I). The acetylene yield could not be correlated with 2-butene because acetylene also comes from a C_2 precursor.[8] The ring expansion reaction of dimethylcyclopropylcarbene to 3,4-dimethylcyclobutene (yield 3%, based on C_1) was also studied and showed a similar loss of stereochemistry: cis, 70%, trans, 30%.

Discussion

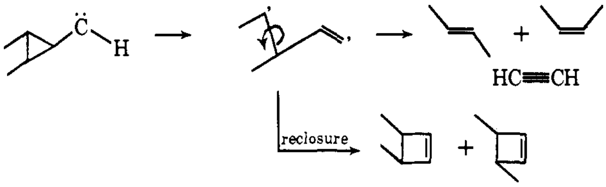
Several features are common to these three-membered ring fragmentation reactions. The initial reaction with a carbon atom produces an adduct in a highly exothermic reaction, and they are initiated, mainly, by carbon atoms in the singlet state, when a low intensity carbon arc is used as the source.

Since the carbon atoms from the arc react with *cis*-2,3-dimethylaziridine to give HCN and 2-butene (eq 3), of which only 48% has retained the cis configuration of the starting material, fragmentation cannot be concerted, although this is an allowed process for three-membered rings.[7] Instead, the initial adduct with C_1 must decompose stepwise, through a diradical intermediate. The initial insertion reaction is highly exothermic and possibly this surplus of energy is retained so that the higher activation energy reaction leading to the breaking of one bond at a time and the lower activation energy concerted process can occur. A small amount may be triplet induced but would not be great enough to alter the conclusions. This is essentially the same process postulated for the nonstereospecific deoxygenations of *cis*- and *trans*-2-butene oxide to 2-butene and CO (accounting for 58% of the C_1),[5] the energy being provided by initial complex formation of carbon with the oxygen on the ring.



(3)

When dimethylcyclopropylcarbene is produced by insertion into the appropriate ring C–H bonds of the cyclopropane there is loss of stereochemical identity in fragmentation with a strong preference for the trans isomer. There may be some contamination by the triplet state of carbon in the above method of production, but when *cis*-2,3-dimethylcyclopropylcarbene is produced by deoxygenation of the corresponding aldehyde only a metastable singlet state is involved. By spin conservation the carbene is generated in the singlet state. Both methods generate the cyclopropylcarbene in highly exothermic reactions. The deoxygenation process is exothermic by 85–100 kcal.[16] The cyclopropylcarbenes from both methods of production decompose nonstereospecifically, so that a ring bond must break to produce a diradical. This species is free to rotate, washing out the stereochemical uniqueness. Fragmentation and reclosure both occur (eq 4). Since the carbene produced by deoxygenation



(4)

---

[9] P. S. Skell, L. Wescott, Jr., J. P. Goldstein, and R. R. Engel, *J. Amer. Chem. Soc.*, **87**, 2829 (1965).

[10] P. S. Skell and J. H. Plonka, *ibid.*, **92**, 836 (1970).

[11] P. S. Skell, J. E. Villaume, J. H. Plonka, and F. A. Fagone, *ibid.*, **93**, 2699 (1971).

[12] W. A. Chupka and M. G. Inghram, *J. Chem. Phys.*, **21**, 371 (1953).

[13] W. A. Chupka and M. G. Inghram, *ibid.*, **21**, 1313 (1953).

[14] In experiments employing arcs the accounting of products yields minimum values for the arc composition: 1% C_4, 15% C_3, 30% C_2, 40% ^1D and ^1S states of C_1, and 1% ^3P state of C_1. If all unaccounted for material was assumed to be the ^3P state of C_1, a maximum of 22% of the C_1 could be triplet.

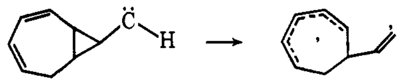
[15] P. S. Skell and J. H. Plonka, *J. Amer. Chem. Soc.*, **92**, 2160 (1970).

[16] P. S. Skell, J. H. Plonka, and R. R. Engel, *ibid.*, **89**, 1748 (1967).

(and most of that formed by C–H insertion) is generated in the singlet state, nonconcerted ring opening must be competing with the lower activation energy concerted pathway. Therefore, substantial vibrational energy from the formation step is confined long enough for ring opening, despite the presence of near-neighbor molecules which could drain off this energy. Although solid matrices are usually considered excellent media for energy relaxation, a competing ring opening appears to be general for C_1 induced fragmentations.

Wolf and Guarino[17] have shown that the same dimethylcyclopropylcarbene, produced by photolysis of the corresponding diazo compound at low pressure, rearranges and fragments stereospecifically so the concerted reaction predominates when the carbene possesses little internal energy. When an atmosphere of N_2 was added to the diazo compound, both fragmentation and rearrangement became nonstereospecific, because, the authors suggest, the carbene is collisionally deactivated and falls to the triplet ground state. This is an alternative, though less appealing, explanation for the nonstereospecificity in our dimethylcyclopropylcarbene decompositions.

Jones, *et al.*,[18] have produced a cyclopropylcarbene by the thermolysis of the lithium and sodium salts of bicyclo[5.1.0]octa-2,4-diene-8-carboxaldehyde tosylhydrazone. This method produces a singlet carbene, yet the products are best explained by proposing ring opening and then fragmentation or reclosure at various positions on the ring. The difference between the dimethylcyclopropylcarbene and the above species is the stabilization of one electron in the ring opened diradical by allylic conjugation, which suggests that ring opening may not have a very much higher E_a than the concerted process, for this bicyclic carbene.



(5)

Experimental Section

The reaction system used in this study has been described in a previous publication.[9] The changes which were necessary for the thermal vaporization of graphite have also been described before.[19]

Products were analyzed by gas chromatography. Acetylene, the butenes, and 1,3-butadiene were analyzed on a 50 ft × 0.25 in. diameter column packed with 30% 2,5-hexanedione on 45–60 mesh Chromosorb P at 0°. The HCN was chromatographed on a 20 ft × 0.25 in. diameter column packed with 6.5% SE 30 on 60–80 mesh Gas Chrom Z at room temperature.

***cis*-2,3-Dimethylaziridine.** *cis*-2,3-Epoxybutane[20,21] was made from *cis*-2-butene. The epoxide was converted, in three steps, to the aziridine.[22]

To determine HCN, the crude carbon atom reaction mixture was stirred with alcoholic NaOH for 24 hr. All volatile material was pumped off and the residue was acidified with concentrated H_2SO_4. The HCN was collected in a −196° trap under vacuum.

***cis*- and *trans*-1,2-Dimethylcyclopropane.** Both *cis*- and *trans*-2-butene were converted into the corresponding 1,1-dibromo-2,3-dimethylcyclopropane[23] stereospecifically. The dibromide was reduced with Na in NH_3[24] to the cyclopropane. Each isomer was free of the other geometrical isomer (<2% by gas chromatography).

***cis*-2,3-Dimethylcyclopropanecarboxaldehyde.** The ethyl ester of *cis*-2,3-dimethylcyclopropanecarboxylic acid was made by decomposing ethyl diazoacetate in *cis*-2-butene, in the presence of CuCl.[25,26] At this point the ester was less than 2% contaminated by the cis isomer (gas chromatography). The ester was reduced to the alcohol with $LiAlH_4$,[27] which was reoxidized to the aldehyde with CrO_3.[28]

***cis*- and *trans*-3,4-Dimethylcyclobutene.** *cis*-3,4-Dimethylcyclobutene was synthesized by the photolysis of *trans,trans*-2,4-hexadiene.[29,30] A mixture of both cis and trans isomers was the gift of Dr. R. Winter.

Acknowledgment. The financial support of the Air Force Office of Scientific Research is acknowledged with gratitude (No. 1983).

---

(17) A. Guarino and A. P. Wolf, *Tetrahedron Lett.*, 655 (1969).

(18) M. Jones, Jr., S. D. Reich, and L. T. Scott, *J. Amer. Chem. Soc.*, **92**, 3118 (1970).

(19) P. S. Skell and R. F. Harris, *ibid.*, **91**, 699 (1969).

(20) S. Winstein and H. J. Lucas, *ibid.*, **61**, 1580 (1939).

(21) C. E. Wilson and H. J. Lucas, *ibid.*, **58**, 2396 (1936).

(22) F. H. Dickey, W. Fickett, and H. J. Lucas, *ibid.*, **74**, 944 (1952).

(23) W. R. Moore and W. R. Moser, *ibid.*, **92**, 5473 (1970).

(24) H. S. Skovronek, Ph.D. Thesis, The Pennsylvania State University, University Park, Pa., 1961.

(25) N. E. Searle, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 424.

(26) T. C. Neil, Ph.D. Thesis, The Pennsylvania State University, University Park, Pa., 1959, p 83.

(27) R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.*, **69**, 1197 (1947).

(28) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *ibid.*, **75**, 427 (1953).

(29) R. Srinivasan, *ibid.*, **90**, 4498 (1968).

(30) R. Srinivasan, *ibid.*, **85**, 4045 (1963).