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DEOXYGENATION OF CYCLOPROPANECARBOXALDEHYDE AND CYCLOPROPYLMETHYLKETONE

CYCLOPROPYL AND CYCLOPROPYLMETHYLCARBENE

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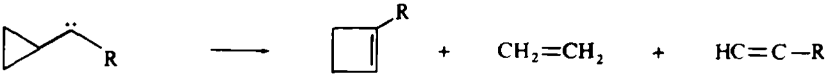
Abstract Cyclopropyl and cyclopropylmethylcarbene have been generated by cocondensation of the corresponding carbonyl compound with atomic carbon at a liquid nitrogen cooled surface. While these carbenes generated from cleavage of the corresponding diazocompounds are known to undergo minor fragmentation, the deoxygenative carbenes containing cyclopropyl rings bound to the divalent carbon exhibit fragmentation as a major route to product. Evidence is presented indicating that fragmentation of cyclopropylcarbenes may involve further energy-rich intermediates of sufficient longevity to influence eventual product formation. It is suggested that vibrationally excited intermediates may have sufficient lifetime in the condensed phase to account for the observed reactions.

SINCE THE initial observation that the tosylhydrazones of cyclopropanecarboxaldehyde and cyclopropylmethylketones undergo rearrangement to cyclobutenes and fragment to ethylene and acetylenes when treated with base in aprotic media, it has



been clear that cyclopropylcarbenes exhibit behavior not normally observed in other alkyl analogs. Recently, it has been reported[2] that dicyclopropylcarbene has a sufficient lifetime in aprotic media to undergo dimerization to tetracyclopropylethylene; this suggests that cyclopropyl substituents may stabilize carbene centers since

simple alkyl carbenes undergo intramolecular product formation more rapidly than intermolecular reaction.

Detailed mechanistic studies of the cyclopropylcarbene system are lacking. However, an investigation of the pressure dependence of the gas phase decomposition of *trans*-2,3-dimethylcyclopropyldiazomethane[3] led to the postulate that cyclopropylcarbene multiplicity determined the nature of the fragmentation reaction

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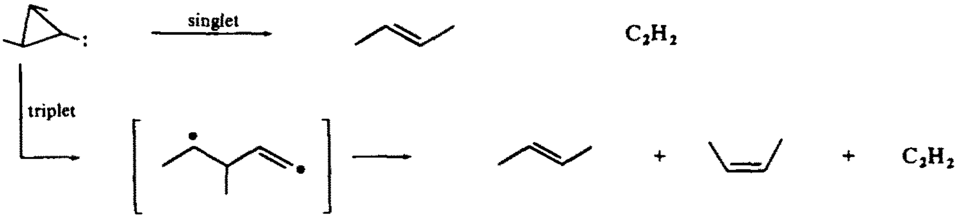
While fragmentation was proposed from both the singlet and triplet states, the singlet state was thought to decompose in a concerted manner while the triplet state process involved diradical intermediates.*



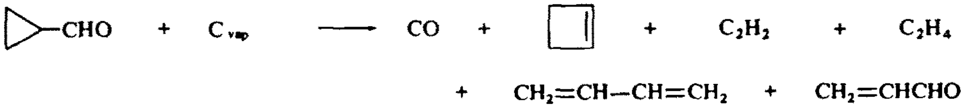
In previous studies of deoxygenation by atomic carbon it has been shown that ketones and aldehydes may be converted to singlet carbenes and carbon monoxide by singlet, metastable, atomic carbon.[4] This paper reports the chemistry of cyclopropylcarbenes generated by the deoxygenation process.

$$R_1R_2C{=}O + :C: \rightarrow CO + R_1R_2C{\downarrow\uparrow}$$

RESULTS AND DISCUSSION

A. *Deoxygenation of cyclopropanecarboxaldehyde*

When cyclopropanecarboxaldehyde and carbon vapor are cocondensed on a liquid N_2 cooled surface, carbon monoxide, cyclobutene, acetylene and ethylene are the major products along with small amounts of butadiene and acrolein. Acetylene is always a major product of the codeposition of carbon vapor with carbonyl compounds, being formed from C_2 molecules, which comprise ~28 weight % of the carbon vapor under our reaction conditions.[5] However, the yield of acetylene from cyclopropanecarboxaldehyde and carbon vapor is 166% (based on the amount of C_2 available for reaction), indicating that other sources of acetylene are involved. The simultaneous presence of a large amount of ethylene suggested that the fragmentation of the cyclopropylcarbene from deoxygenation was one pathway leading to acetylene (Path 1). The presence of acrolein in the product mixture implied that carbon atom insertion into a carbon-hydrogen bond of the cyclopropane ring gave a cyclopropylcarbene capable of fragmentation (Path 2). Since these two paths may complete with acetylene formation from C_2 (Path 3), it was necessary to examine the reaction of cyclopropanecarboxaldehyde with carbon-14 enriched carbon vapor to determine the relative importance of each of the three pathways. Table 1 gives the



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* Diradical intermediates have recently been postulated in the intramolecular reactions of cyclopropylcarbenes in bullvalene like systems, M. Jones, Jr., S. D. Reich and L. T. Scott, *J. Am. Chem. Soc.* **92**, 3118 (1970)

yields of the above mentioned products and their relative molar radioactivities vs carbon monoxide.

Summary of Acetylene Forming Reactions from Cyclopropanecarboxaldehyde

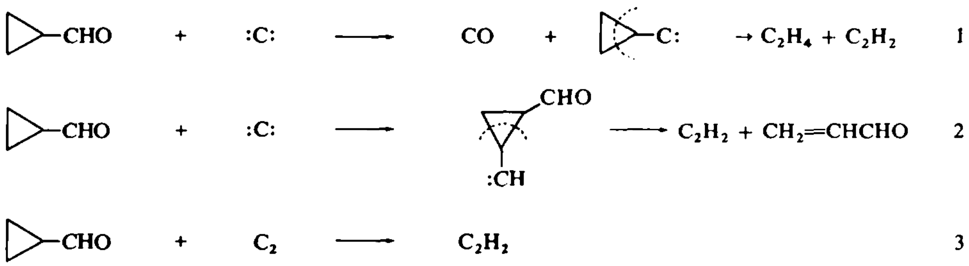


TABLE 1. CYCLOPROPANECARBOXALDEHYDE PLUS CARBON-14

Product	Yield[a] (mole %)	Rel. molar radioact.[b]
carbon monoxide	47	[1·00]
cyclobutene	19	0·1
butadiene	2	0·1
acetylene	166	1·08
ethylene	80	0·13
acrolein	5	[c]

[a] Yields of CO, C_4H_8's and acrolein are based on C_1 (~40 weight % of carbon vapor) and the C_2H_2 and C_2H_4 yields are based on C_2 (~ 28 weight % of carbon vapor)

[b] $(\text{curies/mole})_{\text{sample}}/(\text{curies/mole})_{\text{CO}}$

[c] not determined

Carbon monoxide was used as a radioactivity standard since it is produced in the deoxygenation stop and contains one carbon atom from the vapor.[4] The possibility that substantial unlabeled carbon monoxide arises from the decarbonylation of the

aldehyde substrate may be excluded by observing that the cyclopropane:carbon monoxide ratio is 0·02 in this system. This was compensated for by dividing the carbon monoxide radioactivity by 0·98 prior to normalizing the radioactivity data.

The relative molar activity of the acetylene (1·08) is related to the three acetylene forming pathways by the following equation, with the subscripts referring to reactions

$$\text{rel. molar radio act. } C_2H_2 = \frac{2[C_2H_2]_3 + [C_2H_2]_2}{[C_2H_2]_1 + [C_2H_2]_2 + [C_2H_2]_3}$$

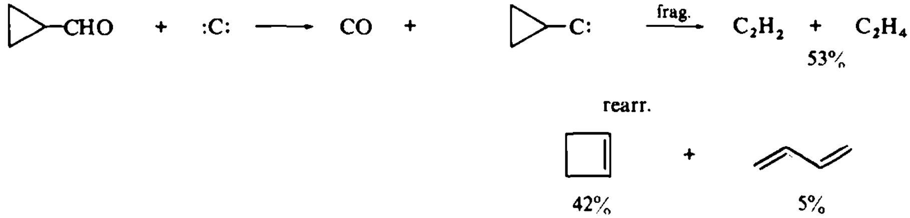
1, 2, and 3 above. The value of $[C_2H_2]_1$ was set equal to the amount of unlabeled ethylene, since, in the cyclopropylcarbene[1,6] fragmentation (Path 1), no carbon-14 would end up in the acetylene or in the ethylene (the radioactive ethylene present is derived from C_2).[7] The value of $[C_2H_2]_2$ (Path 2) was set equal to the acrolein produced; this acetylene contains one carbon-14 atom. Given the relative molar radioactivity of the total acetylene sample, the value of $[C_2H_2]_3$ (the acetylene produced from C_2 (Path 3)) may be computed from the fact that it must contain two carbon-14 atoms from the vapor. On an absolute basis, $[C_2H_2]_1 = 0{\cdot}130$ mmol and $[C_2H_2]_2 = 0{\cdot}029$ mmol; this requires that $[C_2H_2]_3$ have a value of 0·180 mmol. Using this break-down, the origins of the products are summarized in Table 2. The corrected yields support the reaction scheme: the yield of carbon monoxide (47% of the C_1) balances with the sum of the species produced by the oxygen abstraction, $[C_2H_2]_2$ + cyclobutene + butadiene = 45% of the C_1, as must be the case if these are formed in the deoxygenation process. The removal of the $[C_2H_2]_1$ and $[C_2H_2]_2$ requires that 88% of the C_2 molecules present react to form acetylene.[*] The relative importance of the deoxygenatively formed products is summarized in Scheme 1.

TABLE 2. CORRECTED YIELDS FROM CYCLOPROPANECARBOXALDEHYDE

Compound	Source	Yield[a]
carbon monoxide	deox (C_1)	47
cyclobutene	deox (C_1)	19
butadiene	deox (C_1)	2
$[C_2H_2]_1 \equiv [C_2H_4]$	deox (C_1)	24
$[C_2H_2]_2 \equiv$[acrolein]	C—H insert-frag. (C_1	5
$[C_2H_2]_3$	(C_2)	88

[a] Calculated as mole % of designated precursor. See footnote a, Table 1

SCHEME 1



The predominance of fragmentation (53%) in the deoxygenative production of cyclopropylcarbene is unexpected since condensed phase reactions usually provide an effective medium for the dissipation of vibrational excitation. While the high exothermicity of the deoxygenation reaction (85 to 100 kcal/mol)[8] should provide the cyclopropylcarbene with sufficient vibrational excitation to undergo fragmentation, it would have been expected that transfer of the vibrational energy to the frozen matrix would be very rapid (approaching the vibrational frequency of contacted, neighbour molecules $> 10^{10}$ sec^{-1}). The failure to observe complete deactivation of the carbene intermediate led us to examine the possibility that the deoxygenation

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[*] This is consistent with previously examined reactions of C_2 with acetone and acetaldehyde, see ref. 5

process was occurring outside the frozen matrix in the dense vapor layer or liquid phase present on the surface of the frozen matrix.

Cyclopropanecarboxaldehyde was frozen to the walls of the reaction flask at $-196°$ and, with a pressure in the reactor of 5×10^{-6} mm Hg, 2 mg of carbon vapor were impinged on the frozen matrix. GC analysis of the frozen matrix products allowed the determination of the relative amount of each material formed (the small quantity of carbon from the electrodes did not allow reliable absolute yields to be determined). These relative amounts and their comparison with those from a continuous deposition method are presented in Table 3. The insensitivity of the product distribution to the two methods of reaction shown in Table 3 eliminates the possibility of gas or liquid phase reaction as an explanation for the dominance of the observed fragmentation. The inability of a frozen matrix to deactivate the species leading to fragmentation has also been demonstrated in the photolysis of cyclopropyldiazirine in a fluorocarbon matrix at $-196°$ where fragmentation to ethylene

TABLE 3. COMPARISON OF PRODUCT RATIOS FROM FROZEN MATRIX AND CONTINUOUS DEPOSITION

Product	rel. amount[a]	
	Frozen matrix	Continuous dep.[b]
carbon monoxide		0·80
cyclobutene	0·38	0·32
butadiene	0·01	0·03
acetylene	[1·00]	[1·00]
ethylene	0·45	0·40
acrolein		0·08

[a] (mmol product)/(mmol acetylene)
[b] computed from data in Table 1
[c] not determined

and acetylene accounts for 35% of the product mixture.[9] The difficulty of retarding cyclopropylcarbene decomposition has been observed previously in an investigation of the gas phase photolysis of cyclopropyldiazomethane.[10] In this study a 700 fold change in total pressure (N_2 dilution) had no effect on the relative amount of carbene fragmentation vs rearrangement.* The facile decomposition of the cyclopropyl ring

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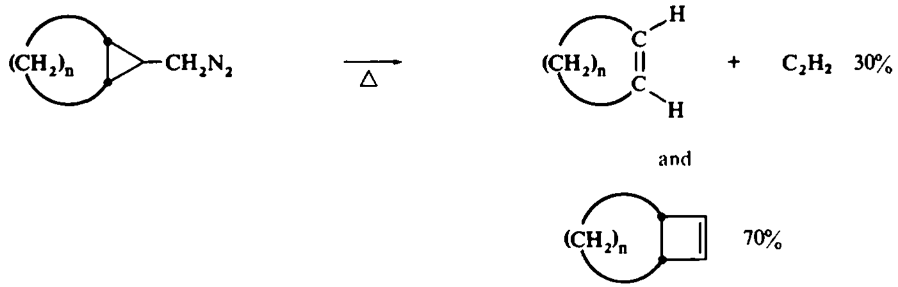
* Studies of the carbon atom plus cyclopropane reaction[6, 10] show nearly exclusive formation of ethylene and acetylene. These reactions may also involve cyclopropylcarbene, although other intermediates may be responsible (M. J. Welch and A. P. Wolf, *J. Am. Chem. Soc.* **91**, 6584 (1969)). Reactions of carbon atoms with cyclopropane under deoxygenative conditions do not exhibit the behavior of the cyclopropylcarbenes discussed in this work (P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.* **88**, 4883 (1966)); cyclopropylcarbene may not be involved in this reaction.

in frozen matrices at −196° suggests that, if excited cyclopropylcarbene is formed under these conditions, its rate of fragmentation must be competitive with the rate of energy transfer to the frozen matrix ($>10^{10}$ sec^{-1})· This short time interval would not allow the departing molecule (CO or N_2) sufficient time to difuse from the vicinity of the carbene site. Therefore when precursors of cyclopropylcarbene are endowed with sufficient energy content, as in deoxygenation and photolysis, the entire precursor adduct may fragment in an essentially concerted step. The carbene precursors which are matrix stabilized would yield cyclopropyl carbenes with life times sufficient for rearrangement to cyclobutene and butadiene.

While cyclopropylcarbene generated from the thermal cleavage of the diazo-compound still gives decomposition products, the importance of the fragmentation pathway decreases to 14% of the product mixture.[1] In fact, fragmentation is a general property of cyclopropylcarbene systems. Kirmse has examined the thermal diazo cleavage (160–170°) of the analogous bicyclo[n.1.0]alkyl structures[11] and found that for n = 3, 4, 5 the fragmentation process generally accounted for ~30% of the product mixture. It appears that the less energetic, thermal cleavage produces a greater number of cyclopropylcarbenes in a vibrationally relaxed state and, therefore, high yields of cyclobutene. The more energetic methods of decomposition discussed above give species with sufficient energy for fragmentation and the rate of energy loss to the matrix is competitive with vibrational relaxation. Therefore, in the deoxygenation of cyclopropanecarboxaldehyde, the relative amount of cyclobutene vs fragmentation is a measure of the rate at which sufficient energy is transfered to the matrix to stop the fragmentation vs the normal cyclopropylcarbene transformation.



B. *Deoxygenation of cyclopropylmethylketone*

The report that cyclopropylmethylcarbene produced from the thermal cleavage of the diazocompound gave only 3% fragmentation[1] as opposed to the 13% observed in the parent system suggested that substitution of the divalent site with an alkyl group had a stabilizing effect on the carbene. The deoxygenation of cyclopropylmethylketone was examined to see if the same stabilizing behavior would be observed under deoxygenative condition.

As in the case of cyclopropanecarboxyaldehyde deoxygenation, it was necessary to carry out a carbon-14 enriched carbon vapor reaction to isolate the reaction pathways involved. Fragmentation of the incipient carbene in this system gives ethylene and a C_3H_4 compound (path 4) while the rearrangement of the carbene gives 1-methylcyclobutene and vinylcyclopropane (path 5). The results of the carbon-14 enriched vapor reaction with cyclopropylmethyl ketone are given in Table 4.

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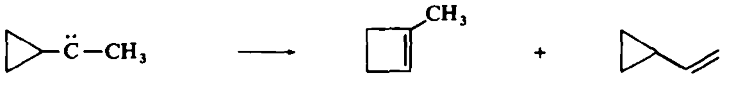

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TABLE 4. CYCLOPROPYLMETHYLKETONE PRODUCT YIELDS AND RELATIVE MOLAR RADIOACTIVITIES

Product	Yield[a]	Rel. molar radioact.[b]
carbon monoxide	38	[1·00]
ethylene	16	0·33
propyne	11	0·67
allene	4	1·49
1-methylcyclobutene	14	0·1
vinylcyclopropane	6	0·1
isoprene	trace	[c]

[a] all yields are based on C_1 see Table 1 footnote a

[b] $(\text{curies/mole})_{\text{prod.}}/(\text{curies/mole})_{\text{CO}}$

[c] insufficient quantity for analysis

Carbon monoxide was again taken as the molar radioactivity standard since it is derived from the deoxygenation reaction and contains one carbon atom from the vapor. The amount of non-radioactive ethylene, which may be computed from its relative molar radioactivity, given in Table 4, by assigning a C_2 precursor to the radioactive ethylene.[5] The amount of propyne produced in the fragmentation was also determined from its relative molar activity (Table 4) assuming the radioactive propyne came from C_3.[12] The low relative molar radioactivity of the allene (1·49) was of considerable interest since a concerted fragmentation of the methylcyclopropylcarbene would be expected to yield only propyne. The presence of nonradioactive allene suggested a more complex mechanism was involved. After the removal of radioactive pathways, ($C_3 \rightarrow$ allene + propyne; $C_2 \rightarrow$ ethylene) the overall deoxygenation processes were isolated; they are summarized in Scheme 2. The ratio of propyne: allene for the decomposition is 3·5.

The thermal decomposition of cyclopropylmethyldiazomethane in solution at 160–170°[2] yields much less fragmentation than the deoxygenation (3 vs 40%) and the 1-methylcyclobutene: vinylcyclopropane ratio is decidedly different (94 vs 2·5). No mention was made of allene being present in the product mixture.*

The experimental results are consistent with the deoxygenative cyclopropylmethylcarbene taking two different routes to product: a high energy fragmentation

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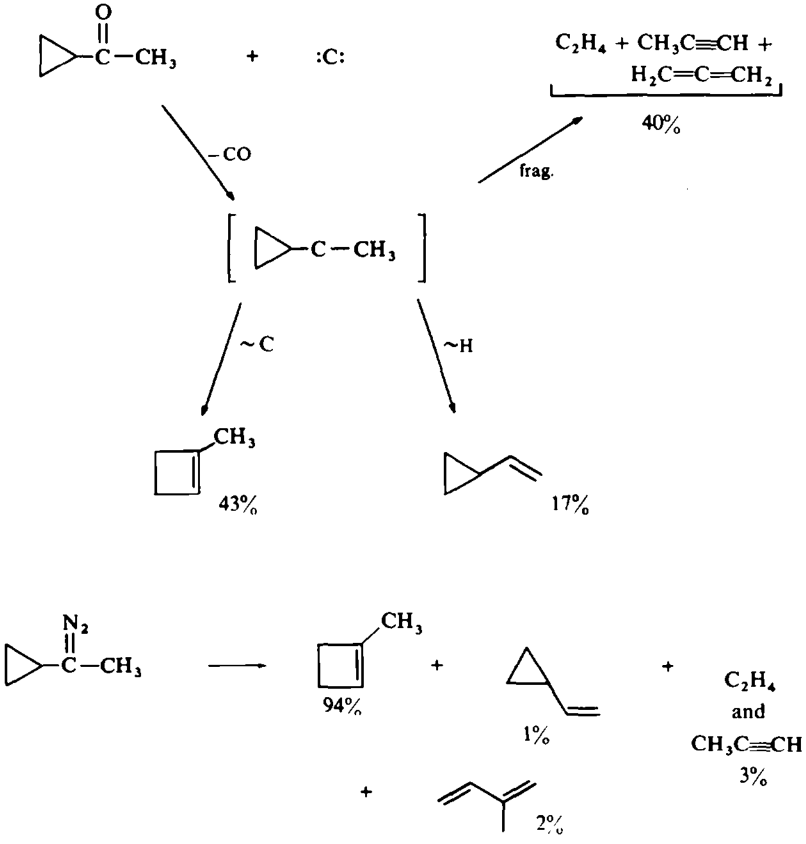
* The thermal cleavage of the diazocompound was repeated and the results are in accord with those reported in ref.[1]

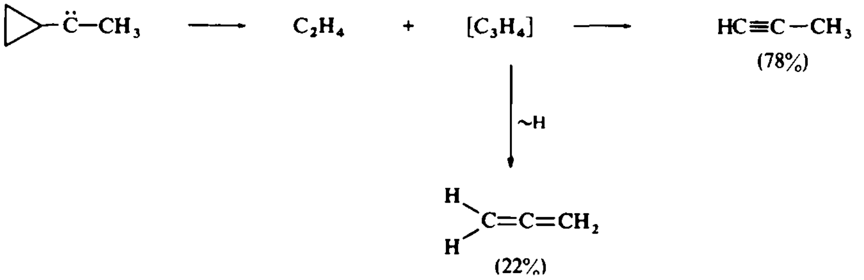
SCHEME 2



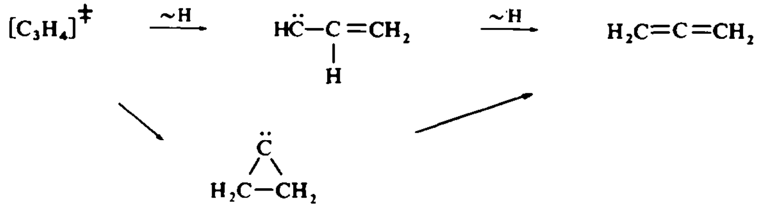
occurring competitively with relaxation of the intermediates by the frozen matrix and a lower energy pathway giving a relaxed carbene intermediate. This postulate is supported by the apparent hydrogen atom rearrangement (propyne → allene) during fragmentation (allene and propyne are not interconverted by the experimental conditions employed) and the virtual absence of isoprene, from the ring opening of a vibrationally excited cyclobutene, under deoxygenative conditions. The greater preference for hydrogen vs carbon atom migration in the carbene at low temperature may reflect a slight activation energy difference for the two processes. Although such effects were found to be unimportant in carbenes previously generated by deoxygenation,[4] a small temperature dependence on the relative migratory aptitude of carbon vs hydrogen may be present in this system (the ~350° temperature difference in the reaction media would greatly magnify any temperature dependence).

To probe the nature of allene and propyne production cyclopropyltrideuteriomethylketone was deoxygenated and the deuterium content of the ethylene, allene and propyne were examined by IR and mass spectroscopy. The recovered ethylene was found to be 93 mole % C_2H_4 by mass spectroscopy; this is in agreement with the carbon-14 vapor labeling experiment (Table 4) which showed 84 mole % of the total ethylene was derived from cyclopropyl ring fragmentation. The allene was found to be 63 mole % C_3HD_3 by mass spectroscopy (carbon-14 vapor labeling showed 51% of the allene produced came from the ketone—Table 4). The propyne was found to be 80% C_3HD_3 by mass spectroscopy. The IR spectrum of the propyne-d_3 showed only $\equiv$C—H bands and CD_3 bands and matched a literature spectrum of CD_3—C$\equiv$CH.[13] This result indicates that during the fragmentation of the ring an intermediate which may effect 1,3-hydrogen transfer in an intramolecular manner (propyne → allene transformation) must exist. Such a process would be formulated as depicted in Scheme 3.

SCHEME 3

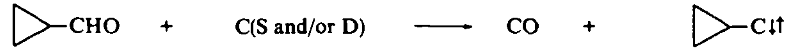


The nature of the C_3H_4 species responsible for hydrogen atom transfer is uncertain. Allene and propyne have long been known to equilibrate: ΔH difference is only 0·81 kcal/M[14] and the interconversions have *Ea*'s of ~55 kcal/M.[15] As mentioned earlier, deoxygenation is a sufficiently exothermic process (85–100 kcal/M)[4] to induce such an isomerization. When one also considers that a singlet carbon atom brings an additional 1–2 eV of electronic energy to the system it is difficult to draw conclusions concerning the multiplicity of the C_3H_4 species as low lying singlet and triplet states are available.[16] Two structures derived from the C_3H_4 can account for the 1,3-hydrogen atom transfer:

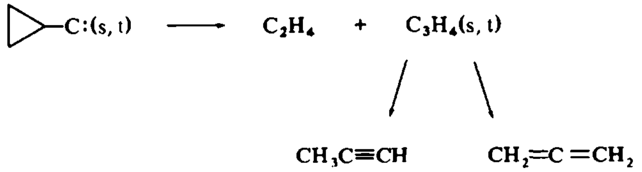


Consecutive hydrogen migrations involving vinyl carbene or three membered ring formation to yield cyclopropylidene followed by collapse to allene.[17] The vinyl carbene route is the most likely since hydrogen transfer in carbenes is generally much faster then cyclopropane formation.[4]

As mentioned in the introduction, intermediates have been previously postulated[3] in cyclopropylcarbene reactions and their presence has been attributed to a triplet multiplicity. The results presented in this work indicate that intermediates are involved in the formation of the alkyne products from the decomposition of cyclopropylmethylcarbene. It is unclear what spin multiplicities are involved in this process. The initial deoxygenative carbene is present in a singlet state.[4] If electronic



interconversion to a lower triplet state occurred, the isomerizations would then occur from a triplet C_3H_4 rather than singlet C_3H_4 molecule. Both species should possess sufficient energy to accomplish the observed isomerization. However, if vinyl carbene is a subsequent intermediate, the singlet pathway seems most reasonable as triplet vinyl carbene would produce propene by hydrogen abstration.



It appears that cyclopropyl substituents in alkyl carbenes are sensitive probes for the presence of excess energy since, in other alkyl carbenes, it has not been possible to observe the corresponding fragmentation.[18]

$$\cdot R—CH_2—CH_2—\ddot{C}—H \rightarrow RCH_3 + C_2H_2$$

This is attributable to decreased vibration degrees of freedom imposed on the three membered ring system which results in a lower activation energy for decomposition.

EXPERIMENTAL

The reaction system

The high vacuum system employed in these studies has been described in detail.[19] The general experimental procedure followed is outlined below. All reactions were run in this manner unless specified otherwise.

General reaction procedure: (a) the reaction system was pumped down to a pressure of 5×10^{-6} mm Hg. (b) the graphite electrodes were degassed by resistive heating at ~1400° for 10 to 20 min. (c) the reactive substrate was degassed at liquid nitrogen temperature at least twice. (d) the degassed substrate was added to the reaction flask in the vapor phase at a rate of 0·5 to 1·0 g/min. (e) during addition of substrate, carbon vapor was also deposited at the walls of the liquid N_2 cooled reaction vessel at the rate of 1 to 2 mg/min (during this process the pressure inside the reactor did not exceed 1×10^{-4} mm Hg). (f) after sufficient carbon had been deposited (30 to 60 mg) the material in the reactor was transferred to a vacuum line for trap to trap distillation and further workup procedure.

Blank reactions were carried out according to the general reaction procedure with the exception that carbon was not vaporized during the addition of the substrate. None of the reported products were present in the blanks.

Solid matrix reactions at −196° were run by precondensing the reactive substrate on the walls of the reaction flask and then striking the arc for ~5 sec. This technique ensured that there could not be gas phase collisions between carbon atoms and reactive substrate.

In the reactions where it was necessary to isolate noncondensable gases, pumping of the reaction system was effected by silica gel adsorbant held at − 196°. The gases trapped in this manner were transferred to an injection coil for analysis by GC using a Toepler pump. In this technique, the pumping speed is greatly reduced and arcing may only be carried out for 10 to 15 sec before the pressure rises above 1×10^{-3} mm Hg. At this point arcing must be discontinued until the pressure again falls under 1×10^{-4} mm Hg.

Product identification

Product isolation was carried out by trap to trap distillation followed by GC. Yields were determined by use of internal standards. The isolated products were identified by comparison of their retention times and IR and mass spectra with those of authentic samples or existing literature data.

Carbon-14 experiments

Procedure for these reactions is identical with the general method except that the upper electrode is replaced with a carbon-14 enriched graphite rod ($\frac{1}{2}$ in. long × $\frac{1}{8}$ in. diameter; 3·4 mCi/rod). These rods were purchased from the United Kingdom Atomic Energy Authority.

The activity measurements were carried out with an ionization chamber (Cary No. 5010) using a critically damped vibrating reed electrometer (Cary No. 31) according to a literature procedure.[20] By attaching the radioactivity counting instrument to the exit of a gas chromatograph and simultaneously monitoring the quantity of each material entering the ionization chamber the molar radioactivity of each eluting component could be determined. The ionization chamber was calibrated using a commercial toluene standard (New England Nuclear) with an activity of $4{\cdot}65 \times 10^5$ dpm/ml.

Deuterium analysis

Deuterium content of the materials reported in this work was determined by low voltage mass spectroscopy under conditions where P-1 peaks were not observed.[21] The conditions required for elimination of the P-1 peak were determined before each analysis using undeuterated samples of the same compound. These reference spectra were also used to make P-1 corrections for the sample spectra: data were collected by measuring peak heights. Spectra were run on Nuclide G-12-90 and Picker MS-902 mass spectrometers.

Materials employed

Cyclopropanecarboxaldehyde. This was prepared by the Cerric ammonium nitrate oxidation of cyclopropylmethanol (Aldrich) according to a literature procedure.[22]

Cyclopropyltrideuteromethylketone. This was prepared by refluxing 20 g (0·24 mol) of cyclopropylmethylketone (Aldrich) and 200 g (10 mol) of D_2O with KOH pellets for five hr. The solution was cooled, saturated with NaCl and extracted 4 × with 25 ml portions of CH_2Cl_2. The combined extracts were dried ($MgSO_3$) and removal of CH_2Cl_2 followed by distillation gave 13 g (0·15 mol) of the desired cyclopropyltrideuteromethylketone. The deuterium incorporation at the methy group was 92% by NMR and mass spectroscopy. No deuterium incorporation was observed elsewhere in the molecule.

Acknowledgement—We gratefully acknowledge the financial support of the Air Force Office of Scientific Research.

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