Organic and Biological Chemistry

Reactions of Carbon Vapor. I. Reactions of Triatomic Carbon with Olefins

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A major component of carbon vapor is C_3. The chemical properties of this substance were studied at $-196°$ in additions to olefins, the products being bisethanoallenes. Relative rates show C_3 to be a nonselective dicarbene for olefin additions and yet it does not show insertion properties. In a paraffin hydrocarbon matrix at $-196°$, C_3 is stable. This variety of C_3 adds stereospecifically to cis- and trans-2-butenes, confirming the conclusion from spectroscopic analysis of the Swings bands that the ground state is singlet. Nonstereospecificity is observed with simultaneous deposition at $-196°$ of C_3 and the 2-butenes, indicative of a hitherto unobserved triplet state C_3; limits of 10^{-1} to 10^{-5} sec.$^{-1}$ have been placed on the half-life for decay of this triplet state to a singlet state.

Introduction

The carbon arc, a rather poorly understood phenomenon, was first reported by Sir Humphrey Davey around the turn of the eighteenth century during the course of some of his experiments with electricity. Although fundamental knowledge of the processes occurring in the arc is rather meager, the carbon arc itself has found many useful applications, especially as a high-intensity light and heat source.

In the present work the carbon arc is used as a source of carbon vapor, produced as a result of the high temperature attained by the arc. Temperatures of the order of 6000°K. have been reported by MacPherson for the arc stream,[2] while much lower temperatures are found at the electrode surface, due to the sublimation of graphite. Chaney, Hamister, and Glass have estimated the maximum brightness temperature of the positive electrode of a low-intensity d.c. arc to be about 3800°K.[3]

The composition of carbon vapor from sources other than a carbon arc has received considerable attention, principally as a result of the controversy over the heat of sublimation of graphite. Early workers in this field had assumed (a) that the vapor was atomic, disregarding the possibility of molecular species, and (b) that the vaporization coefficient was unity.[4] These workers generally used a heated graphite surface as the source of carbon.

Later, when the possibility of molecular species in the vapor was considered, Knudsen cells were employed, in which it was assumed that equilibrium conditions prevailed.

The most reliable measurements of the equilibrium composition of carbon vapor are probably the mass spectrometric experiments of Drowart, Burns, DeMaria, and Inghram in which the vapor effusing from a heated Knudsen cell was ionized and subjected to mass spectrometric analysis.[5] These experiments confirmed the existence of the polyatomic species, which had first been reported by Chupka and Inghram,[6] and also estimated that at the sublimation point (4100°K.) the relative abundances of C, C_2, C_3, C_4, and C_5 are 1, 2.8, 4.5, 0.35, and 0.5, respectively. At 2500°K. the composition of the vapor is 60% C_3, 30% C, and 10% C_2, when the total pressure (estimated by the equations of Thorn and Winslow[7]) is 6×10^{-4} mm.

The absorption spectrum of C_3 in an inert gas matrix at 4°K. has been reported by Weltner, Walsh, and Angell.[8] The matrix was prepared by simultaneous deposition of carbon vapor and inert gas.

Pitzer and Clementi have reported semiempirical molecular orbital calculations capable of describing the properties of carbon vapor. They conclude that linear polyatomic molecules are the important species and that species containing odd numbers of carbons have closed shell structures and lower energies than even species. From calculations of the partial pressures of C_5 and C_7 it was predicted that C_5 should be the most abundant species in the saturated vapor at 2000°K. with C_7 becoming comparably abundant in the region from 2500 to 3000°K. However, more recent calculations[9a,b] have modified this to predict C_3 as the most abundant species (64%) even at 4000°K. with larger species contributing significantly only at temperatures well in excess of this.

The spectrum of molecular C_3 (Swings bands) was first correctly identified by Douglas[10] in studies of the spectrum of a discharge in hydrogen or deuterium using carbon electrodes.[10,11] It was originally thought by

(1) The bulk of this work is taken from the thesis presented by L. D. W. as partial requirement for the Ph.D. degree, 1963; J. P. G. and R. R. E. participated in the paraffin matrix portion of the research.

(2) H. G. MacPherson, J. Appl. Physiol., 13, 97 (1942).

(3) N. K. Chaney, V. C. Hamister, and S. W. Glass, Trans. Electrochem. Soc., 67, 107 (1935).

(4) For a review of this subject to 1950 see H. D. Springall, Research (London), 3, 260 (1950).

(5) J. Drowart, R. P. Burns, G. DeMaria, and M. G. Inghram, J. Chem. Phys., 31, 1131 (1959).

(6) W. A. Chupka and M. G. Inghram, J. Phys. Chem., 59, 100 (1955).

(7) R. J. Thorn and G. H. Winslow, J. Chem. Phys., 26, 186 (1957).

(8) W. Weltner, Jr., P. N. Walsh, and C. L. Angell, ibid., 40, 1299 (1964).

(9) (a) K. S. Pitzer and E. Clementi, J. Am. Chem. Soc., 81, 4447 (1959); (b) K. S. Pitzer and S. J. Strickler, private communication.

(10) A. E. Douglas, Astrophys. J., 114, 466 (1951).

(11) K. Clusius and A. E. Douglas, Can. J. Phys., 32, 319 (1954).

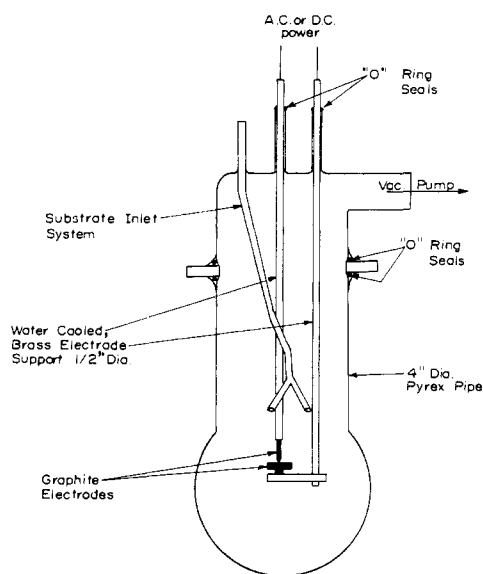Figure 1. Reaction chamber.

Herzberg[12] that the Swings bands were due to CH_2 and much of the intervening literature mentions them as being due to such a species. From Douglas' analysis however, it is now known that the Swings bands are due to a C_3 molecule which is linear and symmetrical in both upper and lower states and that the bond distance in the lower state is 1.28 Å.

There are a number of reported sources of C_3. It has been recognized from the spectra of comets and stars by its well-known 4050 Å. Swings bands.[13] It has been produced in the laboratory by discharges in methane,[14] the explosive combustion of acetylene,[15] the flash photolysis of diazomethane,[16] the flash photolysis of diacetylene,[17] the oxyacetylene flame[18, 19] and the carbon tube furnace.[20] However, until the present work the chemical properties have remained uninvestigated.[21]

The use of olefins as reactive reagents for trapping C_3 has numerous analogies in studies of the chemical properties of carbenes. The linear C_3 molecule, it could be anticipated, would react with two molecules of olefin to produce bisethanoallenes, hitherto unknown compounds. Bisethanoallenes have two cyclopropane rings lying in orthogonal planes, so that when viewed
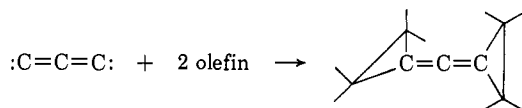
along the long axis of the molecule the planes of the rings are represented by orthogonal lines and the substituents lie above and below these lines.

(12) G. Herzberg, *Astrophys. J.*, **96**, 314 (1942).
(13) For a review of this subject see B. Rosen and P. Swings, *Ann. Astrophys.*, **16**, 82 (1953).
(14) See ref. 12.
(15) R. G. Norrish, G. Porter, and B. A. Thrush, *Proc. Roy. Soc.* (London), **A216**, 165 (1953).
(16) L. Gausset, G. Herzberg, A. Lagerqvist, and B. Rosen, *Discussions Faraday Soc.*, **35**, 113 (1963).
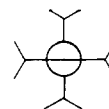(17) J. H. Callomon and D. A. Ramsay, *Can. J. Phys.*, **35**, 129 (1957).
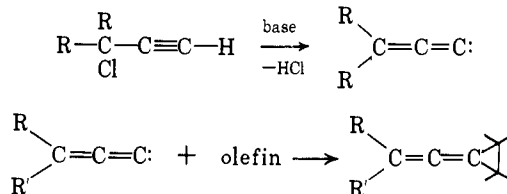(18) G. V. Marr and R. W. Nicholls, *ibid.*, **33**, 394 (1955).
(19) G. V. Marr, *ibid.*, **35**, 1265 (1957).
(20) W. R. S. Garton, *Proc. Phys. Soc.* (London), **A66**, 848 (1953).
(21) Preliminary communication: P. S. Skell and L. D. Wescott, Jr., *J. Am. Chem. Soc.*, **85**, 1023 (1963).

Close relatives of the bisethanoallenes are the mono-ethanoallenes reported by Hartzler,[22] obtained by addition reactions of vinylidene carbenes to olefins.

These monoethanoallenes have an absorption band at 4.95 μ, characteristic of strained allenes (unstrained allenes, 5.10 μ), which proved to be useful in identifying bisethanoallenes.

Apparatus and Procedure

The reaction system consisted of a 4-in. diameter Pyrex pipe flask fastened to a 2-in. diameter high-capacity, high-vacuum system. The system was capable of pumping at the rate of 80 l./sec. at the pressures employed.

Leading into the flask through two water-cooled Tru-Bore stirrer bearings were the electrodes for the carbon arc. Also leading into the flask was a tube through which the gaseous substrates were admitted (Figure 1). In a typical run the system was evacuated, the flask was immersed in liquid nitrogen, the olefin flow was started, and the arc was struck.

The vacuums employed in these studies were 10^{-4} mm. or less so that the carbon vapor produced would have to travel one mean free path or less to the walls of the chamber (5 cm.) thus eliminating gas phase reactions. The failure to observe any significant olefin decomposition products was considered evidence that little or none of the olefin came into contact with the hot zone or was photolyzed. Exception to this is the case of 1,3-butadiene in which 4-vinylcyclohexene (butadiene photodimer) was produced.

Results and Discussion

A. Reaction of C_3 with Isobutene. The reaction of C_3 with isobutene yielded a *single* product, 1,1,1',1'-tetramethylbisethanoallene, in about 40% yield (*Anal.* Calcd: C, 89.12; H, 10.88. Found: C, 89.06; H, 11.00). Although the crude product generally contained many other components, the total of which constituted about 25% of the crude, it was possible to choose conditions whereby these products were eliminated. Some of these products have been shown to arise from reactions of C_1 and C_2. The yields were calculated by weighing the graphite electrodes before and after the reaction, assuming that all of the loss in weight was due to C_3 vaporized and basing the calculation on the bisethanoallene derivative produced. This method gives a minimum yield since some of the weight loss was due to vaporization of other species as well as mechanical attrition resulting in detachment of small pieces of carbon during the experiments.

(22) H. D. Hartzler, *ibid.*, **83**, 4990 (1961).

Stereochemical considerations permit the prediction that there are no isomers of 1,1,1',1'-tetramethylbis-ethanoallene (I).

$$C_3 + 2 \quad \rightarrow$$

I
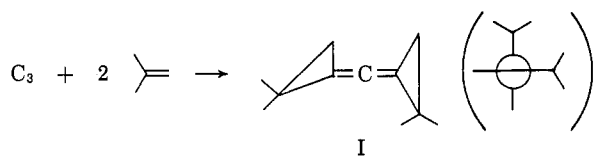
Infrared analysis of the pure 1,1,1',1'-tetramethylbis-ethanoallene (purified by gas chromatography) showed a strong absorption at 4.90 μ similar to the ethano-allenes of Hartzler. Mass spectrometry confirmed the composition with a parent peak at 148 mass units, and the n.m.r. spectrum comprised two singlet absorptions, one at τ 8.72 (CH_3) and one at 8.67 (ring hydrogens) with relative intensities of 3:1, respectively.

B. Reaction of C_3 with Propylene. The reaction of C_3 with propylene yielded a bisethanoallene product (20% yield) which could be collected as a single component from the gas chromatograph using a packed column. However, when this component was analyzed further by capillary gas chromatography it was shown to consist of three components in the ratio of 1:2:1. The assumption of random stepwise addition of C_3 to propylene, predicts that the ratio of diastereoisomeric

$$C_3 + \quad \rightarrow \quad :C=C$$

$$:C=C \quad + \quad \rightarrow \quad C$$
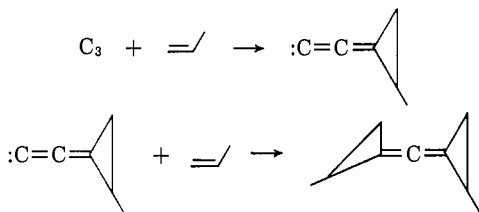
forms of 1,1'-dimethylbisethanoallene should be 1:2:1. From the illustration, showing all possible configurations, it can be seen that a, d, e, and h constitute one diastereoisomer, b and g a second, and

a   b   c   d

e   f   g   h
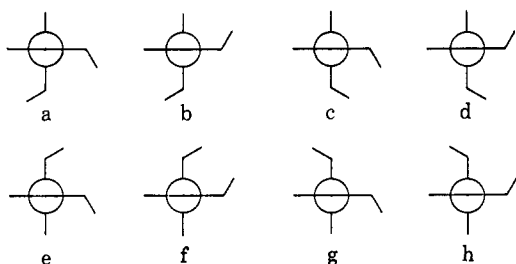
c and f a third. Since the second molecule of olefin adds at a site far removed from the cyclopropane nucleus, no steric interaction is expected; hence, one can assign to the most abundant diastereoisomer structure III. The remaining two isomers have not been distinguished from one another.

II   III   IV
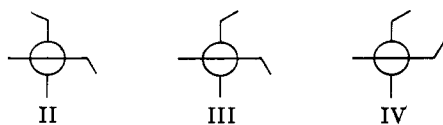
Infrared analysis of the mixture of diastereoisomeric forms of 1,1'-dimethylbisethanoallene shows a strong absorption at 4.89 μ; the mass spectrum shows a parent peak at 120 mass units.

Additional support for the 1,1'-dimethylbisethano-allene structure was obtained by subjecting a sample to catalytic hydrogenation over a palladium-on-charcoal catalyst. Unfortunately ring hydrogenolysis occurs readily in ethanoallene systems,[22] but the products are in accord with the assigned structures.

$$C=C=C \quad + \quad H_2 \quad \xrightarrow[0°]{Pd-C}$$
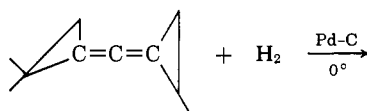
1. 2,6-dimethylheptane (78%)
2. 2-methyloctane (19%)
3. *n*-nonane (3%)

C. Reaction of C_3 with 1-Butene. The reaction of C_3 with 1-butene yielded the expected 1,1'-diethylbis-ethanoallenes (*Anal.* Calcd: C, 89.12; H, 10.88. Found: C, 89.34; H, 10.72) which could be separated by packed column gas chromatography into the three diastereoisomeric forms predicted by the same arguments as in the preceding section. These three isomers had identical infrared spectra with the characteristic absorption at 4.87 μ.

Mass spectrometric analysis unexpectedly did not show a parent peak at 148 mass units as predicted but rather showed a weak group of peaks in the 130–134 mass unit range as the heaviest masses observed as well as a moderately strong peak of mass 119. Apparently this molecule is not as stable as other bis-ethanoallenes in the mass spectrometer and suffers loss of methyl and ethyl groups.

D. Reaction of C_3 with 1,3-Butadiene. The reaction of C_3 with 1,3-butadiene yielded a product (10% yield) which could be collected as a single component from the gas chromatograph using a packed column. However, as in the case of the reaction of C_3 with propylene, when this component was analyzed by capillary gas chromatography it was shown to consist of three components in ratio 1:2:1. The same stereochemical arguments as were used to describe the reaction of C_3 with propylene can be used to rationalize this observation.

Infrared analysis of the mixture of diastereoisomers showed an absorption at 4.87 (strained allene) and another at 6.10 μ (normal carbon–carbon double bond). Mass spectrometric analysis showed a parent peak of 144 mass units as expected. Combustion analysis also supported the 1,1'-diethenylbisethanoallene structure (*Anal.* Calcd.: C, 91.61; H, 8.39. Found: C, 91.52; H, 8.91).

E. Singlet and Triplet C_3. Reactions with cis- and trans-2-Butenes. From the reaction of C_3 with *cis*-2-butene bisethanoallenes are obtained in 19% yield. This is a mixture which is separable by gas chromatography into two components, VII and X; see Table I.

Bisethanoallenes are obtained from *trans*-2-butene in 18% yield, a mixture separable into three components, VIII, XI, and X; see Table I.

There is no isomerization of unreacted olefin in these experiments, or any crossing over of bisethanoallene products except for X. Products X from both reactions were identical in mixed gas chromatography and infrared.

There are only four diastereoisomeric 1,2,1',2'-tetra-methylbisethanoallenes, one with all methyl pairs *cis*,

Table I. C_3 Reactions with the 2-Butenes

Product	M.p., °C.	Infrared, μ	Parent peak	Relative yields, %	
				cis-2-Butene	trans-2-Butene
VII	35	4.88, 4.92	148	93	0
VIII and IX	45	4.90	148	0	47
	93	4.90	148	0	47
X	Liq.	4.90	148	7	6

two with all methyl pairs *trans*, and one with one methyl pair *cis* and the other *trans*. This and other data (*vide infra*) are compelling for the following assignments; no distinguishing features are apparent for the unique assignments of VIII and IX.

VII   VIII and IX   X
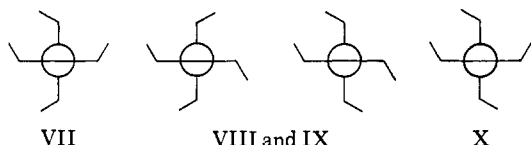
The source of X was elucidated by a time-delay technique, employing the knowledge that C_3 does not react with paraffin hydrocarbons at $-196°$, and, if present in low concentration, is stable for periods in excess of 2 hr. A film of neopentane was deposited on the clean glass wall of the reaction system. Brief arcing (~ 10 sec.) deposited less than a monomolecular film of carbon molecules. Addition of the 2-butenes to the system at time intervals between 9 sec. and 2 hr. produced bisethanonallenes: VII from *cis*-2-butene and VIII and IX in 1:1 ratio from *trans*-2-butene; *X was not a reaction product*.

Simultaneous deposition of C_3 and a 2-butene produced mixtures as summarized in Table I, X being the only crossover product in all experiments. The ratio of X to the stereospecific products is a function of the arc voltage (*vide infra*).

Product X results from the interaction of an excited C_3 with olefins, the unexcited C_3 producing VII or (VIII and IX), depending on the choice of olefin. The precursors in these two reaction modes are assigned to singlet and triplet forms of C_3.

The exclusive formation of VII from *cis*-2-butene and the stable form of C_3 is the resultant of two successive stereospecific addition reactions; VIII and IX from *trans*-2-butene also indicate the additions are stereospecific in both steps. These observations are rationalized if the stable form of C_3 is in a singlet state,[23] a conclusion consistent with the analyses of spectra[10,11] and theoretical calculations.[9a] Singlet forms of bivalent carbon bond simultaneously to both atoms of an olefinic linkage, freezing into the resultant cyclopropane the stereochemical relations of the substituents on the double bond: *cis*-dimethylcyclopropanes from *cis*-2-butene and *trans*-dimethylcyclopropanes from *trans*-2-butene.[23]

The metastable form of C_3 reacts with either *cis*- or *trans*-2-butene to form X, a substance having *cis* methyl groups in one ring and *trans* methyls in the other. Thus, starting with either olefin, X results from one stereospecific addition and one nonstereospecific addition. These observations are rationalized

(23) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, 78, 4496 (1956); P. S. Skell and A. Y. Garner, *ibid.*, 78, 5430 (1956); R. C. Woodworth and P. S. Skell, *ibid.*, 81, 3383 (1959).
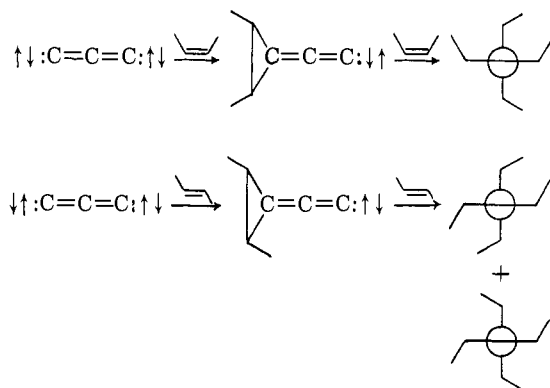
with the postulate that the metastable C_3 is in a triplet state,[23] an hypothesis consistent with theoretical predictions.[9a,24] The first addition is stereospecific, leading to a diradical intermediate: A from *cis*-2-butene and B from *trans*-2-butene. The second step is nonstereospecific,[25] leading to triplet diradical intermediates which suffer equilibration by rotation about the single bond prior to ring closure; this second cyclopropane forming step leads indiscriminately to products with *cis* or *trans* methyl groups regardless of structure of the 2-butene precursor.

The same yield of X is obtained from either *cis*- or *trans*-2-butene (constant arcing conditions) despite their origin from intermediates A and B, respectively. This observation suggests that the probabilities are the same for *cis* and *trans* ring closures. Since only half of A or B is converted to X, it follows that the measure of the amount of metastable C_3 reaching the wall is obtained by doubling the yield of X.[26] The manner in

$$\frac{C_3(\text{triplet})}{C_3(\text{singlet}) + C_3(\text{triplet})} = \frac{2X}{VII + X} \text{ or } \frac{2X}{VIII + IX + X}$$

(24) Analysis of C_3 spectra have indicated a linear singlet ground state, $^1\Sigma_g$, C–C distance 1.28 Å., and an excited $^1\pi_u$ state; the transition probability is high. No report of spectra attributable to triplet states has been made. Pitzer and Clementi[9a] have calculated that triple states $^3\Delta_u$, $^3\Sigma_u^+$, $^3\pi_u$, and $^3\pi_u^-$ lie 40, 42, 54, and 62 kcal. above the ground state, respectively. Some of these states would be metastable with respect to one another and to the ground state. Unfortunately there is no experimental corroboration and perhaps an uncertainty as large as 20 kcal. in these estimations; there seems to be little doubt that metastable triplets should exist.

(25) The reverse order of additions for the triplet is rejected on energetic grounds since that would involve an intermediate C less stable than A by approximately 60 kcal. However, if C is the primary inter-

C   A
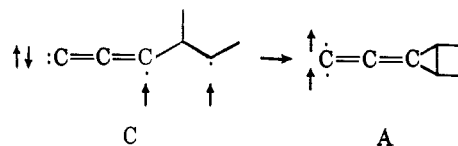
mediate, stereospecific ring closure to A would be required to explain the absence of VIII and IX in *cis*-2-butene reaction mixtures; this is feasible since there is no spin restrictions on this C → A process.

(26) $C_3(\text{triplet})/C_3(\text{singlet}) = 2X/(VII - X)$ or $2X/(VIII + IX - X)$.

A

VII   and   X

B

VII and IX   X
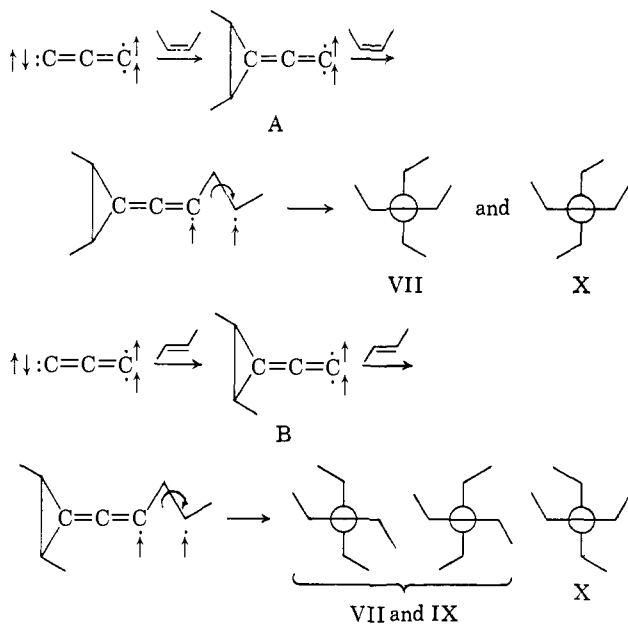
which the per cent $C_3(t)$ varies with arc voltage is summarized in Table II.

Table II. Per Cent $C_3(t)$ in Arc Plasma

Arc voltage, a.c.	$C_3(t)$, %
11	14
12	21
13	28
14	60

In work which will be described elsewhere (R. R. E.) it has been demonstrated that pure thermal vaporization of carbon produces C_3 free of triplet. Thus triplet C_3 is produced in the arc by electron bombardment of C_3 in the plasma. During the flight to the walls ($\sim 10^{-5}$ sec.) decay of upper states via optically allowed transitions occur ($t_{1/2} \sim 10^{-8}$ sec.), so that arrivals are vibrationally excited singlet ground state ($^1\Sigma_g^+$) and metastable triplets. It is probable that excess vibrational energy is dissipated to the lattice with vibration frequencies (10^{13} sec.$^{-1}$), so that the chemical properties observed are those of the lowest triplet states and the ground state.

The forbidden optical transitions between the metastable triplets and ground state have not been observed so that radiative lifetimes are not known. Since the triplets survive the free flight to the wall, $t_{1/2} \geq 10^{-5}$ sec. In the shortest time-delay experiments (9 sec.) product X is not present. From the sensitivity of detection by gas chromatography, a lower limit for the half-life in a neopentane matrix is obtained ($t_{1/2} \leq 0.1$ sec.). There is no evidence to indicate that radiative lifetimes would be altered by paraffin matrix, or that nonradiative decay would occur in this unreactive medium. Nonetheless these brackets of 10^{-5} sec. $\leq t_{1/2} \leq 10^{-1}$ sec. must be accepted with caution.

F. Reaction of C_3 with Other Substrates. In the case of the reaction of C_3 with ethylene a crude product (6% yield) was isolated which showed an absorption at 4.88 μ in the infrared. However, attempts to purify this material by gas chromatography always resulted in

decomposition as noted by the disappearance of the 4.88-μ band in the eluted material.

Tetrafluoroethylene was treated with C_3 in the usual manner to yield a crude product (1%) which showed an absorption in the infrared at 4.92 μ.

Reaction of styrene with C_3 yielded a tarry crude material which showed an absorption in the infrared at 4.88 μ. Purification of this tar was unsuccessful.

Tetramethylethylene was treated with C_3 in the usual manner to yield a crude material absorbing at 4.95 μ in the infrared. Purification of this product was not attempted.

Reaction of C_3 with vinyl chloride yielded a crude material with an infrared absorption at 4.89 μ, but attempts to purify this product by gas chromatography always resulted in the disappearance of this band in the eluted materials.

No significant products were noted when reactions were attempted between C_3 and n-butane, methyl chloride, propyne, acrylonitrile, benzene, or hydrogen cyanide.

G. Relative Reactivity of Some Olefins toward Singlet C_3. The relative rate constants for the reaction of C_3 with various olefins were determined by running competitive reactions using the same experimental techniques of simultaneous deposition (14% C_3 triplet). In the competitive reactions it was always possible to isolate and identify by infrared spectra, mass spectra, and isomer number the C_3 products resulting from reaction with both olefins, one at each end of the C_3 systems, e.g.

$C_3 + $ $\longrightarrow$

and
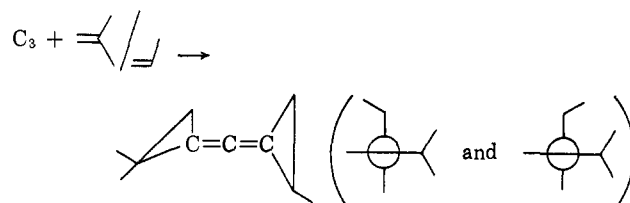
Correction factors, relating peak area on the gas chromatograms to moles of sample, were determined for two mixtures of bisethanoallenes but the error introduced by using peak areas directly was found to be within the margin of reproducibility of the areas for the same peaks for the same mixture on successive chromatograms; hence peak areas were used directly in calculating relative rate constants.

The system can be described by the following diagram (Figure 2) where A and B are the competing olefins.
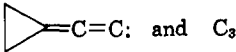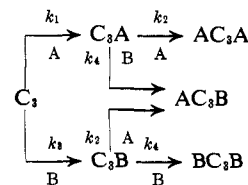
Figure 2. Competitive reaction paths.

With a steady-state approximation it is possible to derive the following three equations.

Table III. Relative Rates for Some Carbene Additions to Olefins

	$\triangleright$=C=C: and C$_3$	R$_2$C=C=C^a	CCl$_2$^{b}	CBr$_2$^{c}
RR'C=CH$_2$	1.00^d	1.00^f	1.00^d	1.00^d
cis-RCH=CHR'	0.45 (0.49, 0.54)^d		0.22	
trans-RCH=CHR'	0.26 (0.34, 0.45)^d		0.24	
RCH=CH$_2$	0.51 (0.60, 0.72)^e; 0.42 (0.43, 0.44)^f	0.05^g	0.02^g	0.07^g
1,3-Butadiene	0.16 (0.15, 0.08)			0.51
Cyclohexene		0.20	0.12	0.41

^{a} See ref. 27. ^{b} See ref. 28. ^{c} See ref. 29. ^{d} R = R' = CH$_3$. ^{e} R = C$_2$H$_5$. ^{f} R = CH$_3$. ^{g} R = C$_4$H$_9$.

$$\frac{k_3 k_4}{k_1 k_2} = \frac{[A]^2[BC_3B]}{[B]^2[AC_3A]} \tag{a}$$

$$\frac{k_1 k_2}{k_2 k_3 + k_1 k_4} = \frac{[B][AC_3A]}{[A][AC_3B]} \tag{b}$$

$$\frac{k_3 k_4}{k_2 k_3 + k_1 k_4} = \frac{[A][BC_3B]}{[B][AC_3B]} \tag{c}$$

If one makes the assumption that C$_3$ shows the same selectivity toward A and B as do AC$_3$ and BC$_3$, then the relation $k_1/k_3 = k_2/k_4$ make these three equations tractable. If all values of k are related to $k_1 = 1.00$ for isobutene, these equations become

$$k_3{}^2 = \frac{[A]^2[BC_3B]}{[B]^2[AC_3A]} \tag{1}$$

$$\frac{1}{2k_3} = \frac{[B][AC_3A]}{[A][AC_3B]} \tag{2}$$

$$\frac{k_3}{2} = \frac{[A][BC_3B]}{[B][AC_3B]} \tag{3}$$

The assumption derives from the proposition that electronic and steric effects are not transmitted from C-1 to C-3 of the two systems shown in Figure 3; C-2 provides "insulation" for electronic interactions.
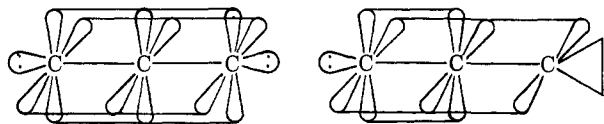

Figure 3. Reactive intermediates.

Table III lists the values of k_3. Since the concentration of BC$_3$B was generally the least accurately known quantity (it corresponded to the smallest peak on the gas chromatogram), values of k_3 calculated from eq. 2 were considered to be the most reliable. The figures in parentheses were calculated from expressions 1 and 3, respectively.

Singlet C$_3$ is a nonselective reagent, the differences between rates of additions to olefins being too small to justify any electronic interpretation. It is particularly noteworthy that free C$_3$ and c-C$_3$H$_4$=C=C: at −196° are nonselective and the closely related substance R$_2$C=C=C: is a selective electrophilic carbene at 200–300° higher temperatures. Clearly, Hartzler's

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(28) W. Von E. Doering and W. A. Henderson, Jr., ibid., **80**, 5274 (1958).
(29) P. S. Skell and A. Y. Garner, ibid., **78**, 5430 (1956).

R$_2$C=C=C: cannot be a free carbene; it is complexed to the Lewis bases of the medium in which it is generated.

The relative reactivities toward olefins of triplet C$_3$ and
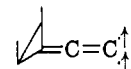
are strikingly different from those of the singlet species; this work will be presented elsewhere.

Experimental

Most reactions were run with a continuous addition of substrate while generating carbon vapor in the carbon arc (11 v. a.c. at 100 amp.).

Approximately 0.1 to 0.2 g. of carbon was consumed per hour in each experiment and approximately a 1000-fold excess of olefin was used to minimize reaction of C$_3$ with itself and with product. Pressures in the system measured with a hot filament ionization gauge. Generally about 30–40% of the carbon vaporized was isolated as products in experiments with reactive olefins.

After the reaction was completed the product was isolated by trap-to-trap distillation under high vacuum, collecting the product in a trap appropriately cooled so that the unreacted olefin would pass through and the product remain behind. Since the differences in the boiling points between products and substrates was usually of the order of 200°, a clean separation from the substrate was easily obtained.

The graphite rods used in these experiments were high-purity spectroscopic grade, obtained from Ultra Carbon Co.

The olefins (Phillips pure grade) were satisfactory after passing through a drying tube. The purity of the hydrocarbons was checked for the presence of high-boiling impurities which might contaminate the products.

The thermal stability was checked by recording the infrared spectrum neat, before and after chromatographing on a column at the highest temperatures used for analytical or preparative work (100°). In all cases, except that of unsubstituted ethanoallene, the spectrum was unchanged, indicating stability at these conditions, provided an inert support such as Gas Chrom S or Gas Chrom Z^{30} was employed. If firebrick was used no allenic materials were eluted; instead unidentified substances were isolated which showed acetylenic character (infrared).

(30) A deactivated diatomaceous earth available from Applied Science Laboratories, State College, Pa.

In experiments employing cis-2-butene the olefin was checked before and after the reaction for the presence of the trans isomer; none was found.

The hydrogenation of 1,1'-dimethylbisethanoallene was carried out in ether solvent at 0° in the vacuum line using a 500-mm. partial pressure of hydrogen and a 5% palladium-on-charcoal catalyst. The uptake of hydrogen could not be determined accurately in the system, but subsequent gas chromatographic separation of the products and mass spectral analysis on the individual components showed them to be 2,6-dimethylheptane and 2-methyloctane. The third component expected, n-nonane was identified by retention time only.

Free-Radical Addition of Trimethyltin Hydride to Allenes[1]

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The azobisisobutyronitrile-catalyzed addition of trimethyltin hydride to allene, 1,2-butadiene, 2,3-pentadiene, 2-methyl-2,3-pentadiene, and 3-methyl-1,2-butadiene has been studied. Structures and configurations of all of the adducts have been assigned on the basis of infrared and n.m.r. spectroscopy, degradation, or comparison with authentic samples prepared by other methods. Information regarding the direction of addition and stereochemistry thus obtained is discussed in terms of the probable mechanism and the roles of electronic and steric factors on the individual steps of the over-all reaction.

The addition of free radicals to allenes has been the subject of several investigations, results of which have not yet provided a clear understanding of the factors which determine the direction of addition. For example, Haszeldine and co-workers[4] have shown that the highly electrophilic trifluoromethyl radical attacks the terminal position of allene exclusively, indicating an intermediate vinylic radical. On the other hand, addition of hydrogen bromide gives products resulting from attack at the central carbon by the electrophilic bromine atom suggesting an intermediate allylic radical.[5,6] The addition of thiyl radicals occurs preferentially, but not exclusively, at the terminal carbon atom on allene.[7-9] Methyl substitution in-

creases the tendency for central carbon attack which amounts to 12.8, 48.2, and 100% for attack by the ethylthiyl radical on allene, 1,2-butadiene, and 3-methyl-1,2-butadiene, respectively.[8] It has been argued, on the basis of relative reactivities of allenes and substituted allenes, that the relatively nucleophilic methyl radical attacks the central carbon of allenes.[10,11]

It has been shown that the addition of organotin hydrides to olefins is catalyzed by free-radical sources such as azobisisobutyronitrile (AIBN) and benzyl hyponitrite.[12] The organotin radical (Sn = R_3Sn) presumably initiates the addition reaction chain (eq. 1 and 2).[13] We undertook to examine the prod-

$$Sn\cdot + RCH{=}CH_2 \longrightarrow RCHCH_2Sn \qquad (1)$$
$$RCHCH_2Sn + SnH \longrightarrow RCH_2CH_2Sn + Sn\cdot \qquad (2)$$

ucts of addition of trimethyltin hydride to allene and four methyl-substituted allenes in order to ascertain the pattern of addition, with respect to both direction of addition and stereochemistry of products, as a function of allene structure.

Results

The addition reactions, catalyzed by AIBN, were carried under similar conditions. In each case an excess of allene was used and the reaction mixtures were heated at 100 ± 5° for 9 hr. to ensure complete reaction. The products were first analyzed by gas–liquid chromatography (g.l.c.) to determine relative amounts of isomeric adducts, and the total yield of adducts was subsequently determined by isolation. In no case was there any indication of higher boiling products which would result from the addition of 2 moles of hydride to 1 mole of allene. Individual adducts were

(1) (a) Supported in part by the U. S. Army Research Office (Durham) and by the National Science Foundation. Purchase of the nuclear magnetic spectrometer used in this work was also made possible by a grant from the Foundation. (b) Presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 9, 1965, Abstracts p. 48P. (c) Taken from the Ph.D. Dissertation of R. H. Fish, University of New Hampshire, Feb. 1965.

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