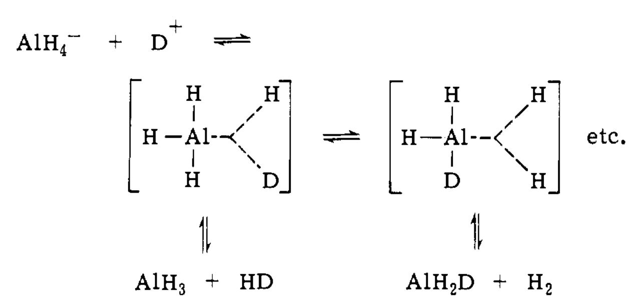
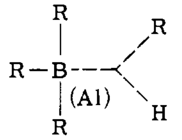


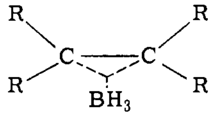
to be similar to that discussed previously for similar cleavages of trialkylboranes and involves pentacoordinated aluminum intermediates.

Conclusion

The intermediacy of BH$_5$ and AlH$_5$ is indicated by extensive hydrogen–deuterium exchange of borohydrides and aluminum hydrides in strong anhydrous acids. The species must exist as intermediates with finite lifetimes in order to explain the exchange results. Theoretical calculation (CNDO/2 method) favors the C_s symmetry structure for BH$_5$, which thus is isosteric with CH$_5^+$. Trialkylboranes (alanes) are suggested to undergo protolytic cleavage through similar pentacoordinated intermediates. Finally it should be mentioned that related pentacoordinated boron and aluminum bridged transition states were suggested[16] for the Brown hydroboration[12] and Ziegler hydroalanation[17] reactions.

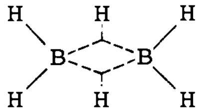


R = H or alkyl



(AlH$_3$)

Diborane itself is, of course, also a pentacoordinated boron compound in which, however, each boron is involved in forming two three-center bonds.



Experimental Section

Materials. NaBH$_4$, NaBD$_4$, LiAlH$_4$, LiAlD$_4$, (CH$_3$)$_3$B, (C$_2$H$_5$)$_3$, and (i-C$_4$H$_9$)$_3$B were obtained from Alfa Inorganics, Inc. Al(CH$_3$)$_3$ and Al(C$_2$H$_5$)$_3$ were obtained from Ethyl Corp. D$_2$SO$_4$ was obtained from Merck Sharp and Dohme of Canada, Limited. DF was prepared from the reaction of CaF$_2$ with D$_2$SO$_4$ in a bomb. LiB(CH$_3$)$_4$ was prepared from CH$_3$Li and B(CH$_3$)$_3$.[15]

General Procedure of Protolysis. (a) In a stainless steel bomb 0.02 mol of D$_2$SO$_4$ (H$_2$SO$_4$) or DF (HF) was cooled at −78°. NaBH$_4$ (NaBD$_4$) or LiAlH$_4$ (LiAlD$_4$) (0.05 mol) contained in a small test tube (extending above the level of acid) was placed in the bomb, which was then degassed and sealed. By shaking, the borohydride (or aluminum hydride) was introduced into the acid. The reaction was completed by continued shaking for 30 min. The gaseous products, H$_2$, HD, and D$_2$, were analyzed by mass spectrometry using a Consolidated Engineering Corp. Model 21-620 mass spectrometer. The results are shown in Table I.

(b) Trialkylboranes (alanes), such as trimethyl, triethyl, and triisobutyl, and LiB(CH$_3$)$_4$ were introduced into a bomb containing liquid HF at −78°. The reaction was completed in 10 min at room temperature. The product alkanes were analyzed by mass spectrometry and gas–liquid chromatography.

Acknowledgment. Support of our work by the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

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(16) G. A. Olah, *Angew. Chem.*, in press.

(17) For a review, see H. Lehmsuhl and K. Ziegler in "Houben-Weyl Methoden der Organischen Chemie," Vol. 13, 4th ed, E. Muller, Ed., Georg Thieme Verlag, Stuttgart, 1970.

Reaction of Diatomic Carbon with Alkanes and Ethers. Trapping of Alkylcarbenes by Vinylidene

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Received March 28, 1972

Abstract: Singlet-state C$_2$, produced in a carbon arc under high vacuum, reacts with alkanes and ethers, RCH$_3$, at a liquid-nitrogen cooled surface to give allenes, RCH=C=CH$_2$, as well as the acetylene previously reported from reaction with other substrates. A typical reaction proceeds through an alkylcarbene–vinylidene pair, with product formation arising from coupling of the vinylidene with the alkylcarbene.

Previous reports have shown that C$_2$ reacts with alcohols[1] and carbonyl compounds[2,3] to produce acetylene as the major product. Two electronic states of C$_2$, the singlet (X$^1\Sigma_g^+$)[4] ground state and the long-lived triplet (X$'^3\pi_u$)[4] state, have been suggested as those responsible for acetylene formation from reaction with acetone.[2,3] This paper presents data concerning the reaction of singlet C$_2$ with alkanes and ethers. While acetylene is still the major product, there occurs an apparent insertion of C$_2$ into carbon–hydrogen bonds, which is of considerable mechanistic interest.

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

(2) P. S. Skell, J. H. Plonka, and R. F. Harris, *Chem. Commun.*, 689 (1970).

(3) P. S. Skell and J. H. Plonka, *J. Amer. Chem. Soc.*, 92, 5620 (1970).

(4) E. A. Ballik and D. A. Ramsay, *Astrophys. J.*, 137, 61, 84 (1963).

Table I. Products from Reaction of C_2 with Various Substrates

Substrate	Product
$(CH_3)_3CH$	$(CH_3)_2CHCH{=}C{=}CH_2$
$CH_3CH_2CH_3$	$CH_3CH_2CH{=}C{=}CH_2$, $(CH_3)_2C{=}C{=}CH_2$ (4.8:1)
$CH_3CH_2CH_2CH_3$	$CH_3CH_2CH_2CH{=}C{=}CH_2$, $CH_3CH_2CH(CH_3){=}C{=}CH_2$ (2.5:1)
$(CH_3)_4C$	$(CH_3)_3CCH{=}C{=}CH_2$
c-C_3H_6	c-$C_3H_5{=}C{=}CH_2$
CH_3OCH_3	$CH_3OCH{=}C{=}CH_2$

Results and Discussion

C_2, which accounts for 28% by weight of the carbon vapor produced in a 16-V (ac) arc,[3,5] reacts under vacuum with isobutane at a liquid-nitrogen cooled surface to produce a 10% yield of 4-methyl-1,2-pentadiene, in addition to a 25% yield of acetylene.[6] The reaction is general with alkanes and simple ethers. Typical products are shown in Table I. All yields are 5–11%, except for reaction with methyl ether, which forms methoxyallene in 35% yield. C_2 inserts into methyl groups 2.5 times as readily as into methylene groups.

In order to confirm C_2 as the precursor of these products, reactions of propane, isobutane, and methyl ether were carried out with carbon-14-enriched carbon vapor. If the allenic products result from incorporation of C_2 into substrate, then those products should have a molar activity twice that of products known to arise from incorporation of C_1.[7] The results of the ^{14}C-enriched carbon vapor reactions, shown in Table II, require that C_2 be the precursor of the allenes formed.

Table II. Carbon-14 Content of Products from Propane, Isobutane, and Methyl Ether

Substrate	Product	Rel molecular activity[a]	Precursor
Propane	1,2-Pentadiene	2.05	C_2
	3-Methyl-1,2-butadiene	1.78	C_2
	Butane	(1.00)	C_1
	Isobutane	0.97	C_1
	1-Butene	1.10	C_1
	Isobutylene	1.05	C_1
Isobutane	4-Methyl-1,2-pentadiene	1.83	C_2
	Isopentane	(1.00)	C_1
	1,1-Dimethylcyclopropane	0.95	C_1
	3-Methyl-1-butene	1.03	C_1
Methyl ether	Methoxyallene	2.11	C_2
	Methyl vinyl ether	(1.00)	C_1
	Dimethoxymethane	0.21	

[a] (Curies/mole of sample)/(Curies/mole of standard).

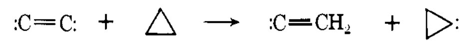
The spin state of the C_2 responsible for this reaction was determined by trapping triplet C_2 and observing the effect on product formation. Acetaldehyde has been shown[3] to be a highly effective trap for triplet C_2. When C_2 reacted with a substrate mixture containing 90% isobutane and 10% acetaldehyde, there was no significant depression of the yield of 4-methyl-1,2-pentadiene. On this basis, it was concluded that the reactive C_2 species must be a singlet.

The reaction occurs at a single carbon site since neopentane reacts to form 4,4-dimethyl-1,2-pentadiene. Thus, hydrogens on an atom adjacent to the attacked carbon atom are not required.

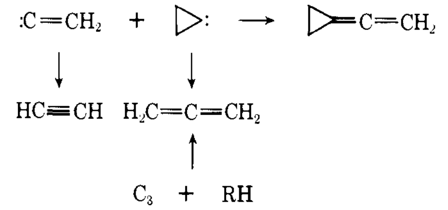
A previously reported pathway[3] in the reaction of C_2 with acetone involves the abstraction of two hydrogens from the same carbon, to produce vinylidene, which then rearranges to acetylene.

$$:C{=}C:\ \xrightarrow{\text{acetone}}\ :C{=}CH_2 \longrightarrow HC{\equiv}CH$$

One can visualize a similar process in the insertion reaction of C_2, as, for instance, with cyclopropane, in which C_2 abstracts two hydrogens producing vinylidene and cyclopropylidene



Coupling of the vinylidene and cyclopropylidene forms the enthanoallene in competition with the other known rearrangement processes of vinylidene to acetylene[3] and cyclopropylidene to allene.[8]



An alternate source of allene in this system is the abstraction of hydrogens from substrate by excited-state C_3,[9] also present in carbon vapor. Allene is produced in the reaction with cyclopropane, but the reaction of ^{14}C-enriched carbon vapor with cyclopropane, the results of which are shown in Table III, indicates that only 24% of the allene formed could have arisen from C_3. If the allene had resulted from C_3 only, its molar activity, relative to known C_1 products,[7] would have been 3.0. Thus, 76% of the allene arises from rearrangement of cyclopropylidene.

Table III. Carbon-14 Content of Products from Cyclopropane Reaction

Product	Relative molar activity	Precursor
Methylenecyclopropane	(1.00)	C_1
Cyclobutene	0.97	C_1
Allene	0.70	No more than 24% from C_3

Further evidence for carbene involvement is provided by a reaction of carbon vapor with methyl ether. The presumed intermediate, methoxycarbene, couples with

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(5) R. F. Harris, Ph.D. Thesis, The Pennsylvania State University, 1968.

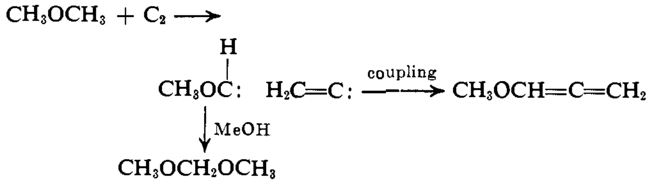
(6) Yields based on C_2 available for reaction.

(7) P. S. Skell and R. R. Engel, *J. Amer. Chem. Soc.*, **88**, 4883 (1966).

(8) L. Skattebol, *Acta Chem. Scand.*, **17**, 1683 (1963).

(9) P. S. Skell and R. F. Harris, *J. Amer. Chem. Soc.*, **91**, 699 (1969).

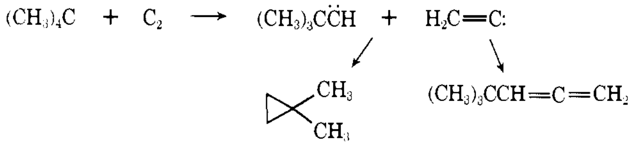
vinylidene to produce methoxyallene but can also be trapped by methanol to form dimethoxymethane in 17% yield (based on C_2).



$$CH_3OCH_3 + C_2 \longrightarrow$$
$$CH_3O\overset{H}{C}: \quad H_2C{=}C: \xrightarrow{\text{coupling}} CH_3OCH{=}C{=}CH_2$$
$$\downarrow \text{MeOH}$$
$$CH_3OCH_2OCH_3$$

The methanol which traps the methoxycarbene to form dimethoxymethane is already present in small quantities in the reaction mixture. A photolysis blank, using a heated tungsten filament as a light source, showed the methanol to be a photoproduct. Dimethoxymethane is also known to result from reaction of C_1 with methanol.[10] The apparent ambiguity regarding the origin of the dimethoxymethane was eliminated by the reaction of dimethyl ether with carbon vapor enriched with carbon-14 (Table II). If the dimethoxymethane results from reaction of C_1 with methanol, the relative molar activity would be 1.0. Since it is only 0.21, another source of dimethoxymethane is indicated. A likely source, then, is the trapping of the methoxycarbene by methanol.

Likewise, the reaction of carbon vapor with neopentane produced trace amounts of 1,1-dimethylcyclopropane, the intramolecular insertion product of *tert*-butylcarbene.



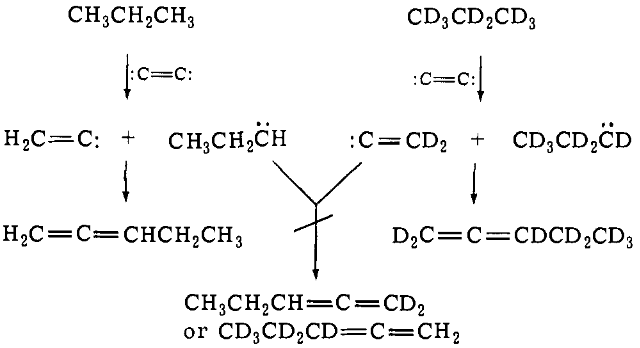
The involvement of two discrete carbenes seems likely. The intramolecular nature of this carbene coupling was examined by carrying out the reaction with a mixture of deuterated and undeuterated substrate. C_2 reacted with a mixture of propene and propane-d_8; the 1,2-pentadiene formed was analyzed for deuterium content. A similar reaction was carried out with a methyl ether and methyl ether-d_6 mixture, followed by analysis of the methoxyallene. In both cases, it was demonstrated that the products had deuterium distributions similar to those of the substrate mixtures. Figures are shown in Table IV.

Table IV. Deuterium Distribution in Substrates and Products for Propane and Methyl Ether Reactions

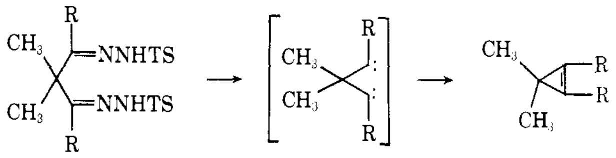
Compound	% d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
Propane substrate	59.4							7.2	33.5
1,2-Pentadiene product	50.3	4.8						11.3	33.7
Methyl ether substrate	52.0						48.0		
Methoxyallene product	59.5	6.0					40.5		

The data require that the reaction take place by attack of C_2 on a single substrate molecule and that the resulting vinylidene couple only with the same alkylcarbene with which it was formed. The reaction scheme is shown in Scheme I. The lack of any dideuterio or diprotio product eliminates the possibility that the vinylidene or alkylcarbene migrates through the cold matrix to couple with the corresponding carbene initially formed from a different substrate molecule. On this basis it seems clear that after initial attack by C_2 on substrate, the resulting species react in a predominantly intramolecular fashion. An allenyl radical intermediate, $RCH{=}C{=}\dot{C}H$, in the amount of 9–12%, can account for the monodeuterio products; the origin of such a radical is not known.

Scheme I



Little precedent exists for the trapping or coupling of simple alkylcarbenes. A recent report[11] claimed that the coupling can take place if the spatial arrangement is favorable, as in the case of 1,3-dicarbenes. The alkali-thermal decompositions of certain 1,3-ditosylhydrazones yield, among other products, small amounts of the cyclopropenes attributed to intramolecular coupling of the dicarbene intermediates. However, it is unlikely that loss of both molecules of N_2 occurs simultaneously. It is more likely that the bis diazo compound loses one nitrogen to form a monocarbene which then undergoes intramolecular cyclization accompanied by loss of the second molecule of N_2.



R = CH3, R = H

The formation of allenes by insertion of C_2 into R_2CH_2 is explained by an abstraction of two hydrogens to produce a geminate pair of carbenes which undergo cage combination.[12] The vinylidene, because of its

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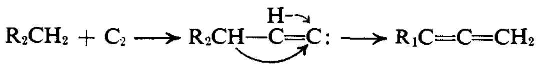
(10) P. S. Skell and R. F. Harris, *J. Amer. Chem. Soc.*, **91**, 4440 (1969).

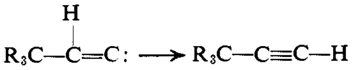
(11) K. Geibel and H. Mader, *Chem. Ber.*, **103**, 1645 (1970).

(12) A mechanism involving insertion of the kind which is well demonstrated for carbenes is difficult to adapt to this reaction and, therefore, is not considered likely because of rearrangements required to form product. This mechanism would lead one to expect as major products



$$R_2CH_2 + C_2 \longrightarrow R_2CH{-}C{=}\overset{H}{C}: \longrightarrow R_1C{=}C{=}CH_2$$

ones which are not obtained, such as $R_2CHC{\equiv}CH$ and cyclopropenes. Further insertion at a tertiary hydrogen atom should occur readily to produce

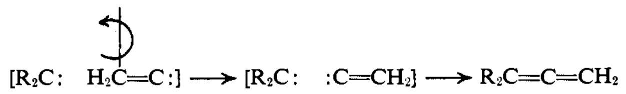


$$R_3C{-}\overset{H}{C}{=}C: \longrightarrow R_3C{-}C{\equiv}C{-}H$$

geometric positioning, must rotate 180° to couple

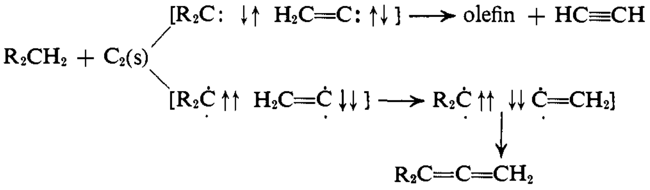
$$R_2CH_2 + :C{=}C: \longrightarrow [R_2C:\quad H_2C{=}C:] \longrightarrow R_2C{=}C{=}CH_2$$

with the alkylcarbene.



A three-way competition is open for this geminate pair of carbenes: (1) end-for-end reorientation followed by coupling to form allene, (2) escape from the cage giving the vinylidene and the alkylcarbene independent pathways which lead mainly to acetylene and alkene, respectively, and (3) the same noncoupling reactions occurring in the cage. The noncoupling pathways were demonstrated earlier.[3] In the reaction of arc-generated C_2 with acetone, 75% of the acetylene formed (a major product) resulted from 1,1-diabstraction of two hydrogen atoms by singlet C_2 to produce singlet acetylcarbene and singlet vinylidene, these rearranging to methylketene and acetylene, respectively. With all substrates the yields of acetylene are substantially greater than the yields of insertion allenes, $R_2C{=}C{=}CH_2$. Since rotation of vinylidene and combination with R_2C: must be processes with rates equal to or greater than 10^{10} sec^{-1}, it follows that the rates of the rearrangements must be slightly greater. This high rate of rearrangement of singlet alkylcarbenes has been implicit in the many failures over the years to trap these carbenes with olefins by addition or with other substrates by insertion. Indeed, the formation of $R_2C{=}C{=}CH_2$ must be counted as a unique instance of trapping a singlet R_2C: which has the capacity to rearrange (:CH_2 and :CCl_2 do not).

An interesting alternative speculation is that two competitive reaction paths are involved, one leading to singlet and the other to triplet geminate pairs. The triplet pairs are unable to rearrange and thus live sufficiently long for rotation and coupling. Spin conservation requires the geminate pair of triplets to have opposite spins in relation to each other so there is no spin restriction to their coupling.



Experimental Section

Diatomic carbon is produced simultaneously with C_1, C_3, and C_4 in the reaction system previously described.[11] The reaction procedure, used in all reactions, has also been described.[3] All arcing was done at 16 V (ac). Carbon-14 reactions were carried out as outlined earlier.[3]

Products were identified by comparison to authentic samples or by interpretation of the spectral data described below. Infrared spectra were recorded on a Beckman IR-5. Nuclear magnetic resonance spectra, in CCl_4 expressed in τ units relative to internal TMS, were recorded on a Varian A-60A spectrometer. Mass spectral analyses were carried out on an AEI-MS-902 spectrometer. Product yields were determined by gas chromatography. Peak areas were compared to those of an external standard.

Reaction with Isobutane. The reaction mixture consists of ~12 g of isobutane and 50 mg of carbon. The reaction was isolated from the pumping system, the liquid nitrogen coolant removed, and the substrate–product mixture trap-to-trap distilled from the reactor, using traps at −131 and −196°. The −196° trap contained acetylene for analysis by gas chromatography. The −131° trap contained isobutane substrate and products resulting from reaction of isobutane with C_1 or C_2. This trap material was fractionally distilled through a 33-cm packed distillation column and concentrated at atmospheric pressure until the pot residue was 1–2 g. The products were separated from the remaining isobutane by gas chromatography. The yield of 4-methyl-1,2-pentadiene was 11% based on C_2. The same yields were obtained in a small run in which the total reaction mixture was analyzed by gas chromatography without prior fractionation.

4-Methyl-1,2-pentadiene showed a characteristic allenic absorption at 5.17 μ in its infrared spectrum. The 70-eV mass spectrum exhibited a parent peak at *m/e* 82 and a (P − 15) peak at *m/e* 67. The nmr spectrum consisted of a doublet at τ 8.97 (6.0 H), a complex multiplet centered at τ 7.7 (1.1 H), and an absorption from τ 4.8 to 5.5 (2.8 H).

Reaction with *n*-Butane. The procedure was identical with that described above for reaction with isobutane. The yields were 3.5% 1,2-hexadiene and 1.5% 3-methyl-1,2-pentadiene, based on C_2.

1,2-Hexadiene absorbed at 5.13 μ in the infrared. The 70-eV mass spectrum showed a parent peak at *m/e* 82 and a (P − 15) peak at *m/e* 67. The nmr spectrum consisted of a triplet at τ 9.07 (2.9 H), a multiplet at τ 8.55 (2.0 H), a multiplet at τ 8.03 (2.1 H), and an absorption from τ 4.8 to 5.6 (2.9 H).

3-Methyl-1,2-pentadiene showed allenic absorption at 5.13 μ in the infrared. The 70-eV mass spectrum exhibited a parent peak at *m/e* 82 and a (P − 15) peak at *m/e* 67. The nmr spectrum contained a triplet at τ 8.98 (3.4 H), an absorption at τ 8.33 and a complex signal at 8.1 (total of 5.0 H for both absorptions), and an absorption at τ 5.4 (2.0 H).

Reaction with Neopentane. The entire substrate–product mixture was transferred to a vacuum work-up line, where products were separated from substrate by gas chromatography. The 4,4-dimethyl-1,2-pentadiene was produced in 9% yield based on C_2.

4,4-Dimethyl-1,2-pentadiene was identified by its allenic absorption in the infrared at 5.08 μ and by the methyl region in the nmr spectrum, which consisted of a sharp singlet at τ 8.95 resulting from the three equivalent methyl groups. The 70-eV mass spectrum exhibited a parent peak at *m/e* 96 and a (P − 15) peak at *m/e* 81.

Reaction with Cyclopropane. The work-up procedure was identical with that used for neopentane above. 1,1-Ethanoallene was formed in 5% yield based on C_2.

1,1-Ethanoallene. This product was identified by the characteristic absorption of a strained allene[13] at 4.94 μ in its infrared spectrum. The 70-eV mass spectrum exhibited a parent peak at *m/e* 66 and a (P − 1) peak at *m/e* 51.

Reaction with Propane. The reaction mixture was trap-to-trap distilled through a −131° trap into a −196° trap. Products were separated from the −131° trap by gas chromatography. The reaction produced 5% 1,2-pentadiene and 1% 3-methyl-1,2-butadiene, based on C_2.

Reaction with Methyl Ether. The entire substrate–product mixture was trap-to-trap distilled repeatedly through a −116° trap into a −196° trap. After five distillations, the −116° trap contained ~0.25 ml of material, while the −196° trap contained the bulk of excess substrate. The products in the −116° trap were separated by gas chromatography. Methoxyallene was produced in 35% yield and dimethoxymethane in 17% yield, both based on C_2.

Methoxyallene showed allenic absorption at 5.10 μ in its infrared spectrum. The mass spectrum exhibited a parent peak at *m/e* 70 and a (P − 31) peak at *m/e* 39. The nmr spectrum consisted of a singlet at τ 6.63 (2.9 H), a doublet at τ 4.56 (2.0 H), and a triplet at τ 3.33 (1.1 H).

Reaction with Propane-d_0–Propane-d_8 Mixture. Propane-d_8 was purchased from Stohler Isotopic Chemicals and was used as received. It was mixed with an equimolar quantity of propane-d_0. Since this substrate was recycled and used in several runs, it was triply distilled through a −131° trap before each reaction. Blanks showed that it contained no 1,2-pentadiene from the previous reaction. Deuterium content of the substrate mixture was determined from its 16-eV mass spectrum recorded, as were all mass spectra, on an AEI-MS-902 mass spectrometer. Since fragmentation could not be avoided, the spectrum of the propane-d_0–propane-d_8 mixture was compared to that of a propane-d_0 standard and corrected accordingly.

The substrate–product mixture from this reaction was worked up using the same procedure as that from the propane reaction

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[13] H. D. Hartzler, *J. Amer. Chem. Soc.*, **83**, 4997 (1961).

described above. The deuterium content of the 1,2-pentadiene was determined from the mass spectrum recorded at 10.2 eV, corrected by comparison to the spectrum of a 1,2-pentadiene standard.

Reaction with Methyl Ether-d_0–Methyl Ether-d_6 Mixture. Methyl ether-d_6 was prepared by a Williamson ether synthesis using methyl iodide-d_3 and methanol-d_4 obtained from Stohler Isotopic Chemicals. Mass spectral analysis at 16 eV showed the compound to be >95% d_6. This compound was then mixed with an equimolar quantity of methyl ether-d_0, and the deuterium distribution of the mixture was determined from the 16-eV mass spectrum.

The work-up procedure used for the methyl ether-d_0–methyl ether-d_6 substrate–product mixture was identical with that used in the methyl ether reaction described above. The deuterium content of the resulting methoxyallene was determined from the 16-eV mass spectrum, which was corrected for fragmentation by comparison to the spectrum of a methoxyallene standard.

Acknowledgments. We gratefully acknowledge the financial support of the Air Force Office of Scientific Research (Grant No. 1983).

Formation of Vinylidene Intermediates in the Reaction of Diatomic Carbon with Propylene

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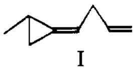
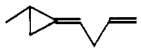
Abstract: Diatomic carbon reacts with two molecules of propylene to form 5,6-methane-1,4-heptadienes. The reaction involves a singlet state C_2 precursor and a vinylidene intermediate.

In the course of our investigations of the reactions of carbon vapor species with olefins we have found that C_2 undergoes the reactions characteristic of singlet carbenes, carbon–hydrogen bond insertion and addition to a double bond.

When carbon vapor from a low intensity carbon arc[1] was codeposited with a large excess of propylene in a vacuum at −196°, 5,5-methano-1,4-heptadienes (I and II) were isolated by gas chromatography on work-up.[2] The two geometrical isomers (I and II) accounted for ~5% of the C_2 estimated to be in the arc.[3] Some acetylene was formed. Products resulting from reaction of C_2 with a single molecule of propylene were 1-penten-4-yne (IV) in 4% yield, 2-methylbutenyne (V) in 1% yield, and 1-pentyne (VI) in 2% yield.

Both compounds I and II gave an *m/e* 108 in the 70-eV mass spectrum. The nmr spectrum of the most easily isolable isomer showed a complex olefinic absorption of four protons between τ 4.0 and 5.5, a complex absorption at τ 7.1, corresponding to two allylic hydrogens, a methyl doublet at τ 8.9 which overlaid the three ring protons absorbing between τ 7.5 and 9.2. The ring and methyl region is almost identical with the spectrum of 2,3:5,6-dimethano-3,4-heptadiene (III),[1] which has this same structural unit. The spectrum of the second geometrical isomer, though less pure, was almost identical with the first. The ir spectra


I


II


III

of I and II were identical and gave absorptions at 3.23, 3.35, 3.40, 6.1, 7.5, 7.7 and 11.0 μ. When a mixture of both isomers was hydrogenated with an atmosphere of H_2 over PtO_2,[4] *n*-octane, 3-methylheptane, and 2-methylheptane were found in the ratio of 2.2:1.0:1.0, respectively. These hydrocarbons correspond to cleavage at each of the positions on the ring.

To verify the source of the products I and II, one of the electrodes used in the arc was ^{14}C enriched[5] and the relative radioactivity per mole was compared to compound III, which has a known C_3 precursor.[1] The results are listed in Table I. Since its molar activity is $^2/_3$ that of III, I and II must have C_2 precursors.

Table I. Reaction of Propylene with Carbon-14 Enriched Carbon Vapor

Product	Rel activity/mol
I and II	1.8 2.2
III	[3.00]
IV	1.8
V	2.0
VI	1.5

Two equivalent processes can lead to I and II. If C_2 adds to the double bond of propylene in one step, the resulting vinylidene, A, must insert into the allylic carbon–hydrogen bond of a second propylene molecule (path A). On the other hand, an initial insertion would produce a different vinylidene, B, which would then add to the double bond of a second propylene molecule (path B). No products could be found which would correspond either to two insertions or two additions to the double bond. Path B would produce an intermediate with a hydrogen atom β to the carbene site. The parent vinylidene is known to rearrange to acetylene[6] but when this species is produced by the

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[1] P. S. Skell, L. D. Wescott, Jr., J.-P. Golstein, and R. R. Engel, *J. Amer. Chem. Soc.*, **87**, 2829 (1965).

[2] A 20 ft × 0.25 in. 7.5% silicone rubber (SE-30) column on 45–60 mesh Gas Chrom Z at 80° was used.

[3] R. F. Harris, Ph.D. Thesis, The Pennsylvania State University, University Park, Pa., 1968.

[4] P. R. Rylander, "Catalytic Hydrogenation Over Platinum Metals," Academic Press, New York, N. Y., 1967.

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

[6] H. Okabe and J. R. McNesby, *J. Chem. Phys.*, **36**, 601 (1962).