over magnesium sulfate and the anhydrous benzene solution was filtered. Crystalline sulfonamides were obtained by concentrating and cooling the benzene solution in an ice bath. The crystals which formed were recrystallized from ethanol. The liquid sulfonamide was distilled in vacuo after evaporation of solvent: Nisopropylbenzenesulfonamide, mp 101-102° (lit.18 mp 101.5°); N-isopropylbenzenesulfonamide, bp 162-164° (4 mm) (lit.¹⁹ bp (lit.²⁰ mp 49–50°); *N*-isopropyl-*p*-toluenesulfonamide, mp 48–50° (lit.²⁰ mp 49–50°); *N*-isopropyl-*p*-chlorobenzenesulfonamide, mp 84–86° (lit.²¹ mp 85–86°); *N*-isopropyl-*p*-nitrobenzenesulfonamide, mp 114-116° (lit.22 mp 114-115°); N-isopropyl-2,4-dinitrobenzenesulfonamide, mp 98-100°.

(18) A. Nickon and A. S. Hill, J. Amer. Chem. Soc., 86, 1152 (1964). (19) J. v. Braun, F. Jostes, and A. Wagner, Ber. Deut. Chem. Ges. B, 61, 1423 (1928).

(20) M. Sekiya and K. Oishi, J. Pharm. Soc. Jap., 73, 1017 (1953); Chem. Abstr., 48, 10663f (1954).

(21) M. Kulka, J. Amer. Chem. Soc., 72, 1215 (1950).

(22) K. N. Campbell, B. K. Campbell, and E. M. Salm, Proc. Indiana Acad, Sci., 57, 97 (1948); Chem. Abstr., 43, 4630c (1949).

N-Isopropyl-N-arenesulfonylarenesulfenamides 2-6. Butyllithium (2.8 ml of a 23% solution in hexane) was added dropwise over a period of 30 min to a well-stirred solution of 0.01 mol of the appropriate sulfonamide in 75 ml of anhydrous benzene under nitrogen. A precipitate of the lithium salt formed after about 15 min. After stirring for an additional 30 min, a solution of the appropriate sulfenyl chloride (0.01 mol) in 25 ml of dry benzene was added. The reaction mixture was stirred at room temperature for a minimum of 3 hr and then filtered. The reaction mixture can be tested for completion with starch-iodide paper. A negative test signifies completion and indicates that there is no sulfenyl chloride present. The filtrate was successively washed with water, 10% sulfuric acid, 10% sodium bicarbonate, and water, dried over anhydrous magnesium sulfate, and concentrated to ca. 50 ml in vacuo. The concentrate was cooled and the precipitate recrystallized from ethanol. Care must be taken with some of the more sensitive compounds, e.g., 2,4-dinitrobenzenesulfenyl derivatives, because alcoholysis may take place at high temperatures or upon prolonged heating. Physical properties and analytical data are given in Table IV.

Reactions of Metastable Singlet Carbon Atoms with Unsaturated Hydrocarbons

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Abstract: Carbon atoms produced in a low-intensity carbon arc under high vacuum react with olefins on their cocondensation at a liquid nitrogen cooled surface to give dienes as well as the allenes previously reported. The diene forming reaction is assigned a singlet precursor and occurs by insertion into allylic carbon-hydrogen bonds followed by hydrogen migration; the stereochemistry of the original olefinic site is essentially retained. Previous work concerning atom plus olefin systems is reevaluated in light of the present results.

Previous work using carbon atoms aged in neopentane matrices suggested³ that the metastable ¹S state was the species responsible for allene formation from olefins. Similar behavior was observed in the reaction of recoil carbon-11 with ethylene⁴ where metastable, singlet atoms were designated as the species responsible for allene formation. In both cases it was postulated



that the exothermic production of a singlet cyclopropylidene was accompanied by rapid collapse to an allene. This description of the carbon plus olefin reaction is consistent with recent theoretical results⁵ which also require a ¹S carbon atom for allene formation. The photolysis of carbon suboxide at 3000 Å with olefins⁶ gave allenes from a conversion of cyclopropylideneketene to a hot cyclopropylidene. Recoil ¹¹C is also known to react with olefinic substrates by carbonhydrogen bond insertion as well as by the carboncarbon double bond insertion pathways.^{7,8} We now report that the metastable singlet carbon atoms also react with olefins by a carbon-hydrogen insertion mechanism which leads to diene formation.

Results and Discussion

A. Ethylene. The cocondensation of carbon vapor and ethylene at a liquid nitrogen cooled surface yields allene and propyne as the major ethylene plus carbon atom (1:1) products. An ambiguity exists in this result since excited-state C_3 molecules are known to react with alcohols to give allene and propyne⁹ and similar reactions may be occurring in the ethylene system. To determine the relative importance of the C_1 and C₃ pathways to allene and propyne, an ethylene reaction with carbon-14 enriched carbon vapor was carried out. Table I gives the yields of allene and propyne and their molar activities relative to 1-pentyne, which is assigned a C_3 precursor in this system (C_2H_4 + $C_3 \rightarrow HC \equiv CCH_2CH_2CH_3)^{10}$ and therefore must have

⁽¹⁾ NASA Trainee, 1967-1970.

⁽²⁾ NIH Predoctoral Fellow, 1967-1970.

⁽³⁾ P. S. Skell and R. R. Engel, J. Amer. Chem. Soc., 89, 2912 (1967). (4) M. Marshall, C. MacKay, and R. Wolfgang, ibid., 86, 4741 (1964).

⁽⁵⁾ M. J. S. Dewar, E. Haselbach, and M. Shanshal, ibid., 92, 3505 (1970).

⁽⁶⁾ C. Willis and K. D. Bayes, ibid., 88, 3203 (1966); D. G. Williamson and K. D. Bayes, ibid., 90, 1957 (1968).

⁽⁷⁾ A. P. Wolf, Advan. Phys. Org. Chem., 2, 201 (1964).

 ⁽a) C. MacKay and R. Wolfgang, Science, 148, 899 (1965).
 (9) P. S. Skell and R. F. Harris, J. Amer. Chem. Soc., 91, 699 (1969).

⁽¹⁰⁾ The bisethanoallenes are usually the C_3 products from olefins; however, the parent bisethanoallene does not have sufficient stability to allow isolation although infrared examination of the crude reaction

Table I. Ethylene and Carbon-14

Product	Yield, ^{α} mol $\%$	Rel molar activity ^b
H ₂ C=CCH ₂	25	1.4
CH₃C≡CH	9	1.2
CH ₃ CH ₂ CH ₂ C=CH	30	[3.0]

^a C₃H₄ yields are based on the amount of C₁ present (40%) and the C_5H_8 yield is based on the amount of C_8 present (14%). See R. F. Harris, Ph.D. Thesis, The Pennsylvania State University, 1968, and P. S. Skell and J. H. Plonka, J. Amer. Chem. Soc., 92, 5620 (1970). ^b 3(curies/mole)_{samp}/(curies/mole)_{1-pentyne}.

a relative molar activity of 3.00 since it contains three carbon atoms from the arc. From the relative molar activities of allene and propyne, the amount of each material derived from reaction with C1 may be computed. The remainder, 5 and 1%, respectively, is derived from C₃. No other products attributable to the missing 70% of the C₁ were found. The further

$$H_2C = CH_2 + C_1 \longrightarrow H_2C = C = CH_2 + CH_3C = CH_2$$
$$20\% \qquad 8\%$$

olefin work presented below contrasts with the ethylene results, accounting for C_1 with the higher olefins being substantially higher. This may be due to the presence of more labile allylic hydrogens or reflect on some physical property of the matrices, or an inability to find the products.

B. Propylene. The cocondensation of propylene and carbon vapor at a liquid nitrogen cooled surface results in the formation of methylallene and butadiene as the major reaction products with smaller amounts of isomeric C_4 molecules. Table II presents the yields of

Table II. Propylene and Carbon-14

Product	Yield, mol $\%^a$	Rel molar activity ^b
CH ₃ CH=C=CH ₂	61	[1.00]
CH2=CH-CH=CH2	26	1.00
CH₃CH₂C≡CH	2	1.00
HC=C-CH=CH ₂	3	0.90
CH₃C≡C−−CH₃	1	0.92
Total C_1 recovery	93	

^a All yields based on C₁ present (see footnote a, Table I). ^b (Curies/mole)_{samp}/(curies/mole)_{methylallene}.

propylene plus atomic carbon products and their relative molar activities as determined from a reaction with carbon-14 enriched carbon vapor. In this case the methylallene was assigned a molar activity value of 1.00 for the purpose of comparing its activity with those of the other products envisioned as resulting from C₁ reactions. The close correspondence of the relative molar activities requires that all of the listed products are derived from C_1 plus propylene. While attack of atomic carbon on the π system of the propylene gives the allene, the formation of butadiene is more easily envisioned as resulting from a carbon-hydrogen bond insertion to give a singlet allylcarbene followed by hydrogen migration.¹¹ The triplet allylcarbene may



The reaction of propylene with thermally vaporized carbon atoms produced none of the above products under otherwise identical experimental conditions. Since this thermal vaporization procedure avoids the electron bombardment of gaseous species which occur in arcs (\sim 100-A currents), ground-state carbon atoms (³P) predominate. Thus it follows that the C_4 compounds from arc-generated carbon atoms are not the result of ground-state carbon atom reactions. The reaction of propylene with thermally vaporized carbon atoms does not give any isolable product.

The inability to discern reaction of propylene with ³P carbon atoms led to a reinvestigation of the previous report¹⁵ that ground-state carbon atoms reacted with olefins to give spiropentanes. After a careful search for higher boiling products, the only product isolated, whose composition was C_7H_{12} (mol wt 96; $C_1 + 2$ propylene), was present in yields less than 1% and the infrared spectrum of the separated compound showed unsaturation. It appears from the present evidence that spiropentanes are not significant products from carbon atom plus olefin reactions.

As argued earlier,³ the high conversion to allene in an olefin matrix is evidence against the intermediacy of a thermolyzed cyclopropylidene; at much higher temperatures they add to olefins yielding spiropentanes.¹⁶ Consequently, the route to methyallene includes a hot, singlet cyclopropylidene of lifetime too short for successful trapping with olefins. The metastable singlet states (1D and/or 1S) are therefore assigned as the precursors of both allene and diene formation in the propylene system.¹⁷ If a triplet cyclopropylidene were present, it would exist long enough for reaction with a second molecule of propylene.16

C. Isobutylene. The codeposition of isobutylene and carbon vapor at a liquid nitrogen cooled surface produced 1,1-dimethylallene and isoprene in 50 and

- (12) H. E. Zimmerman and J. H. Munch, *ibid.*, 90, 187 (1968).
 (13) I. Moritani, Y. Yamamoto, and S. I. Murahashi, *Tetrahedron*
- (14) P. S. Skell and J. H. Plonka, J. Amer. Chem. Soc., 92, 836 (1970).
 (15) P. S. Skell and R. R. Engel, *ibid.*, 88, 3749 (1966).

(16) W. T. Borden, Tetrahedron Lett., 447 (1967).

mixture confirms its presence initially. See L. D. Wescott, Jr., Ph.D. Thesis, The Pennsylvania State University, 1963.

⁽¹¹⁾ Allylcarbene generated from the low-temperature (-78°) photolysis of allyldiazomethane is known to give butadiene as the major reaction product: D. M. Lemal, F. Menger, and G. W. Clark, J. Amer. Chem. Soc., 85, 2529 (1963).

⁽¹⁷⁾ The results of the calculations in ref 5 suggest that the 1S state of atomic carbon is responsible for allene formation. This does not exclude the possibility that 'S carbon atoms as well as 'D atoms may participate in diene formation.



(allene:diene = 2.3) may reflect a statistical factor since isobutylene possesses twice as many labile, allylic hydrogens and thus may have more reactive collisions with the carbon atoms which are properly oriented for carbon-hydrogen bond insertion. The increase in diene yield with increasing substitution of the double bond is consistent with an allylcarbene route (singlet) to diene as opposed to an isomerization of a highly excited cyclopropylidene since increasing substitution would be expected to stabilize such a species.

Isobutylene gave a product in 2-3% yield whose molecular weight (m/e = 124) suggested it might be 1,1,1',1'-tetramethylspiropentane. However, its infrared spectrum showed bands from 5.8 to 6.2 μ and its nmr spectrum showed absorption between τ 5.3 and 5.0 indicating the presence of a double bond.

The spectra were consistent with structure 1, 1, 1-dimethyl-2-isobutenylcyclopropane. Independent synthesis of 1 confirmed the assignment. Since 1 could be a thermal decomposition product, the stability of 1, 1, 1', 1'tetramethylspiropentane was examined. It was demonstrated that an authentic sample of the spiropentane was not converted to 1 by the work-up conditions. Consequently, the spiropentane is not a product formed in excess of 1% yield. It is not possible to exclude a hot spiropentane which decomposes faster than it is stabilized, but, if 1 is the product of a hot spiropentane, this reaction path cannot account for more than 4% of the atomic carbon present.



D. *cis-* and *trans-2-Butene.* Reactions of carbon vapor with *cis-* and *trans-2-butene* were of interest with respect to the stereochemistry of diene formation. Table III presents the yields of 2,3-pentadiene and the

Table III. 2,3- and 1,3-Pentadiene from 2-Butenes plus C₁

Product	Yield ^a	
	<i>trans</i> -2- Butene	<i>cis</i> -2- Butene
2,3-Pentadiene	59	51
cis-1,3-Pentadiene	5	22
trans-1,3-Pentadiene	27	8

ⁿ Based on C₁ present (mole per cent).

isomers of 1,3-pentadiene produced from the codeposition of the indicated olefin with carbon vapor at a liquid nitrogen cooled surface. The results show that diene formation occurs with a preference for the retained geometrical disposition of the atoms about the original double bond. Since it was shown that the dienes are



stereochemically stable to the reaction conditions, the isomerization must occur prior to the final hydrogen migration giving the diene product. This implies that if the allylcarbenes are the intermediates leading to dienes, some interconversion of the stereochemistry at the olefinic site occurs prior to the hydrogen migration.



This would require that the initial vibrationally excited adduct of a carbon atom to a molecule of 2-butene undergoes geometrical isomerization prior to the transfer of a hydrogen atom to give the 1,3-pentadiene products. Since both diene products are observed, the rate of the isomerization must be within the same order of magnitude as the rate of hydrogen transfer. Since the distribution of the diene isomers is not the same from both *cis*- and *trans*-2-butene the vibrationally excited adduct cannot achieve geometric equilibration and the fact that the retained isomer predominates in both cases suggests that hydrogen transfer is the faster of the two reactions in question.

Reactions of recoil carbon-11 with cis- and trans-2butene in solid Xenon matrices also give 1,3-pentadienes with a preference for the retained isomer, cis-2-butene producing 1,3-pentadiene with a cis:trans ratio of 1.4 in a matrix of 99.7% solid Xenon, and trans-2butene giving a trans: cis ratio of 3.0 under the same conditions.¹⁸ These results are consistent with values obtained in this work, cis-2-butene giving 1,3-pentadiene with a cis: trans ratio of 2.7 and the trans-2-butene produces 1,3-pentadiene with a trans: cis ratio of 5.2. The greater preference for retained stereochemistry in the vapor-deposited carbon system probably reflects the lower energy of arc-generated carbon atoms as opposed to the recoil carbon-11 and supports the hypothesis that excited adducts are responsible for the isomerizations.

Conclusions

The results of the present investigation of arcgenerated carbon atoms and olefins indicate that allene and diene formation are the only significant reactions. The failure to observe product formation from groundstate carbon atoms and olefins is not understood at this time. We have recently suggested¹⁹ that ground-state

⁽¹⁸⁾ J. Nicholas, C. MacKay, and R. Wolfgang, Tetrahedron, 22, 2967 (1966).

⁽¹⁹⁾ P. S. Skell, J. H. Plonka, and L. S. Wood, Chem. Commun., 710 (1970).

carbon atoms react with saturated hydrocarbons to give triplet carbenes which subsequently abstract two hydrogen atoms to give the eventual methyl derivatives.

The analogus process may be observed in the case of olefins but, as in the reported examples, 19 the yields do not exceed 2-3%. This leaves the present understanding of ground-state carbon atom chemistry in an undesirable state. Efforts are continuing to characterize this species.

Despite the confusion concerning the ground states' reactions, there is no doubt that metastable singlet states are the species responsible for allene and diene formation from olefins.

Experimental Section

The reaction system employed in this study has been described previously²⁰ and the modifications required for the production of thermally vaporized carbon have also appeared.²¹

Carbon vapor enriched in carbon-14 was produced by replacing the upper arcing electrode with enriched carbon-14 (0.01 Ci/g). These electrodes were obtained from the United Kingdom Atomic Energy Authority.

Products described in this paper were isolated by gas chromatography and identified by comparison of their spectral properties with known samples.

1,1,1',1'-Tetramethylspiropentane. This compound was prepared from commercial tetramethylallene (Aldrich) by addition of dibromocarbene²² to give 1,1-dibromo-2,2-dimethyl-3-isopropyli-

(20) P. S. Skell, L. D. Wescott, Jr., J. P. Golstein, and R. R. Engel, J. Amer. Chem. Soc., 87, 2829 (1965); P. S. Skell and J. H. Plonka, ibid., 92, 5620 (1970).

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

(22) W. Rahman and H. G. Kuivila, J. Org. Chem., 31, 772 (1966).

denecyclopropane in 33% yield. The structure of this compound was verified by a comparison of its spectral properties with those reported in the literature.23 Reduction of the dibromo compound with sodium in wet methanol²⁴ gave a 32% yield of 1,1-dimethyl-2isopropylidenecyclopropane which was identified by comparison with literature spectral data.23 Repeating the procedure just described starting with 1,1-dimethyl-2-isopropylidenecyclopropane gave the desired 1,1,1',1'-tetramethylspiropentane in 10% yield based on the starting allene. The spiropentane was isolated by gas chromatography on a cyanoethylsilicone column and was characterized by its spectral properties. The infrared showed no unsaturation and the parent peak in the mass spectrum was m/e 124 with a very intense base peak at m/e 109 (P - CH₃). The nmr spectrum showed two overlapping singlets of three protons each at τ 8.90 and 8.92 and an AB pattern centered at τ 9.58 (four protons).

1,1-Dimethyl-2-isobutenylcyclopropane (1). This material was prepared by a Wolff-Kishner reduction of phorone.25 Phorone (13.8 g; 0.1 mol) (Chemical Procurement Industries) was added to a solution of 9.6 g (0.3 mol) of hydrazine hydrate (85%in water) in 100 ml of diethylene glycol and heated on a steam bath for 5 hr. Sodium hydroxide (8 g) was added and the solution was refluxed for 2 hr. Steam distillation of the reaction mixture gave a two-phase system. The organic phase was removed and dried over MgSO₄; subsequent distillation gave 5.7 g (0.046 mol) of 1, bp 128° (760 mm).

Identification was accomplished by analysis of its spectral properties; the infrared spectrum exhibited unsaturation and the nmr spectra gave a broadened doublet of one proton at τ 5.18, two singlets of three protons each at τ 8.99 and 8.90, which also covered a complex one-proton absorption, and a complex pattern of two protons centered at τ 9.65.

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(23) J. Meinwald, J. W. Wheeler, A. A. Nimetz, and J. S. Liu, ibid., 30, 1038 (1965).

(24) S. Winstein and J. Sonnenberg, J. Amer. Chem. Soc., 83, 3235 (1961).

(25) D. Todd, Org. React., 4, 378 (1948).

The Equilibria between Polyenes and Polyenyl Cations

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Abstract: The equilibria between four polyenes and their conjugate acids, polyenyl cations, have been measured as a function of sulfuric acid concentration. Although polyenyl cation stability increases with increasing conjugation, the effect is smaller than stabilizing effects associated with either hyperconjugation by methyl groups or ring closure.

Pertain polyenyl cations are stable species in strong acids, ¹⁻³ which affords the opportunity of studying their equilibria with their conjugate bases as a function of acidity. These studies were initiated (1) to assess quantitatively the effect of extending conjugation on carbonium ion stability and (2) to determine the acidity function dependence of the protonation equilibria.

Exploratory studies⁴ had shown that I, II, and III were 50 % formed from the equilibration diene(s) at the per cent H₂SO₄ shown under each structure. In all three cases, the equilibria approximately fit eq 1.4

$$H_0 = pK_a + \log [B]/[BH^+]$$
 (1)⁵

(4) N. Deno, J. Bollinger, N. Friedman, K. Hafer, J. D. Hodge, and

⁽¹⁾ N. Deno and C. U. Pittman, Jr., J. Amer. Chem. Soc., 86, 1871 (1964); N. Deno, C. U. Pittman, Jr., and J. O. Turner, ibid., 87, 2153 (1965).

⁽²⁾ T. S. Sorensen, ibid., 87, 5075 (1965); Can. J. Chem., 42, 2768, 2781 (1964); 43, 2744 (1965)

⁽³⁾ P. E. Blatz and D. L. Pippert, J. Amer. Chem. Soc., 90, 1296 (1968); Tetrahedron Lett., 1117 (1966); Chem. Commun., 176 (1968); P. E. Blatz, D. L. Pippert, and V. Balasubramaniyan, Photochem. Photobiol., 8, 309 (1968).

⁽¹⁾ I. J. Houser, J. Amer. Chem. Soc., 85, 2998 (1963). (5) Standard state for pK_a is molarity \equiv activity at pH 7. This and other aspects of eq 1 are given in L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1940, Chapter IX, and