

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: *N*-isopropylbenzenesulfonamide, mp 101–102° (lit.¹⁸ mp 101.5°); *N*-isopropylbenzenesulfonamide, bp 162–164° (4 mm) (lit.¹⁹ bp 190° (13 mm)); *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 sulfonyl 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 sulfonyl 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-dinitrobenzenesulfonyl derivatives, because alcoholysis may take place at high temperatures or upon prolonged heating. Physical properties and analytical data are given in Table IV.

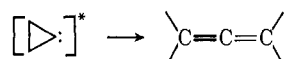
Reactions of Metastable Singlet Carbon Atoms with Unsaturated Hydrocarbons

P. S. Skell,* J. E. Villaume,¹ J. H. Plonka,² and F. A. Fagone

Contribution from the Department of Chemistry,
The Pennsylvania State University, University Park, Pennsylvania 16802.
Received April 3, 1970

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 cyclopropylidene-*ketene* to a hot cyclopropylidene. Recoil ¹¹C is also known to react with olefinic substrates by carbon-

hydrogen bond insertion as well as by the carbon-carbon 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 C₃ 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 C₁ 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 C₃ precursor in this system (C₂H₄ + C₃ → HC≡CCH₂CH₂CH₃)¹⁰ and therefore must have

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

(8) 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 C₃ products from olefins; however, the parent bisethanoallene does not have sufficient stability to allow isolation although infrared examination of the crude reaction

(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).

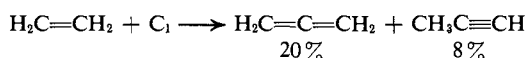
Table I. Ethylene and Carbon-14

Product	Yield, ^a mol %	Rel molar activity ^b
H ₂ C=C=CH ₂	25	1.4
CH ₃ C≡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 C₃H₈ yield is based on the amount of C₃ 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)_{amp}/(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



olefin work presented below contrasts with the ethylene results, accounting for C₁ 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 C₄ 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]
CH ₂ =CH-CH=CH ₂	26	1.00
CH ₃ CH ₂ C≡CH	2	1.00
HC≡C-CH=CH ₂	3	0.90
CH ₃ C≡C-CH ₃	1	0.92
Total C ₁ recovery	93	

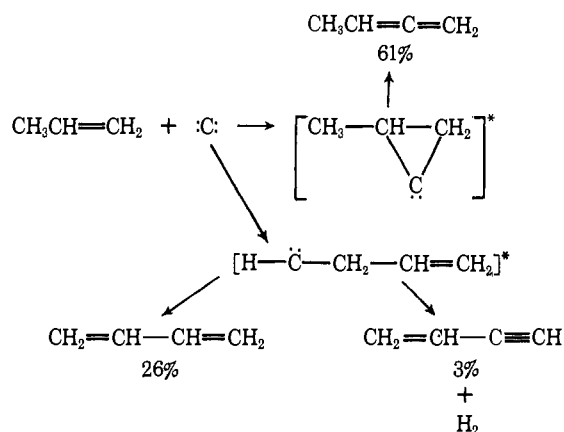
^a All yields based on C₁ present (see footnote a, Table I). ^b (Curies/mole)_{amp}/(curies/mole)_{methylallene}.

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 C₁ 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

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).

be eliminated on the basis that present evidence precludes a triplet precursor for double bond formation in carbene species.¹²⁻¹⁴



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 (~100-A currents), ground-state carbon atoms (³P) predominate. Thus it follows that the C₄ 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 spiropanes. After a careful search for higher boiling products, the only product isolated, whose composition was C₇H₁₂ (mol wt 96; C₁ + 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 spiropanes are not significant products from carbon atom plus olefin reactions.

As argued earlier,⁸ 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 spiropanes.¹⁶ Consequently, the route to methylallene 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 Lett.*, 5697, 5755 (1968).

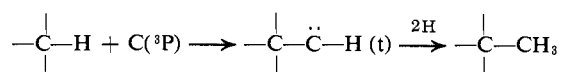
(14) P. S. Skell and J. H. Plonka, *J. Amer. Chem. Soc.*, **92**, 836 (1970).

(15) P. S. Skell and R. R. Engel, *ibid.*, **88**, 3749 (1966).

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

(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 ¹S carbon atoms as well as ¹D atoms may participate in diene formation.

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



The analogous 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-isopropyl-

(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-2-isopropylidenecyclopropane 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.

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

(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

N. C. Deno* and Philip C. Scholl

Contribution from the Department of Chemistry,
The Pennsylvania State University, University Park, Pennsylvania 16802.
Received September 12, 1970

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.

Certain 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

$$H_0 = \text{p}K_a + \log [\text{B}]/[\text{BH}^+] \quad (1)^5$$

(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. Balasubramanian, *Photochem. Photobiol.*, **8**, 309 (1968).

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