

Anodic Oxidation Technique. The cell used in this work has been described.^{27,28} Some modifications were made in the electrode arrangement. The glass cylinder was omitted, and on some occasions parallel planar platinum electrodes were used. In a few of the experiments pyrolytic graphite electrodes were used. They were obtained from High Temperature Materials, Inc., Boston, Mass. After the electrolysis was complete the cell was swept with the sweep gas for at least 15 min to ensure that all of the gaseous

(27) P. H. Reichenbacher, M. Y.-C. Liu, and P. S. Skell, *J. Amer. Chem. Soc.*, **90**, 1816 (1968).

(28) P. S. Skell and P. H. Reichenbacher, *ibid.*, **90**, 2309 (1968).

products were removed from the cell. The liquid products were isolated by continuous ether extraction of the cell contents. The unreacted acid was generally recovered for reuse. On this basis the mass balance was found to be over 90% in some reactions; but, and especially in more alkaline solutions, 75–80% was more usual. Some of this may have been due to destruction of starting material by the electrode or the oxygen generated, some was Kolbe coupling product which was not sought or identified.

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Reactions of Triatomic Carbon with Alcohols

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Abstract: Ground-state C_3 reacts with alcohols by addition reactions, producing propargyl aldehyde acetals, $(RO)_2CHC\equiv CH$. Excited-state C_3 reacts with alcohols and other hydrogen-containing substrates to form C_3 hydrocarbons.

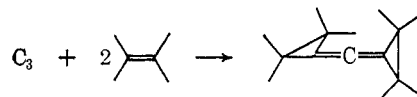
The cocondensation near -196° of chlorine (a large excess) and carbon vapor produces CCl_4 , C_2Cl_4 , C_2Cl_6 , C_3Cl_6 , and C_3Cl_8 . The latter, hexachloropropene and octachloropropene, isolated in 2:1 ratio, are products resulting from addition of chlorine to C_3 . The primary product could be C_3Cl_2 or C_3Cl_4 , but these would react further with the chlorine.²

The absolute yield, although subject to some uncertainty, indicates the C_3 content of the carbon vapor to be between the limits 12 and 20%. The summation of the known C_3 products from similarly produced carbon vapor and other substrates, *vide infra*, indicate the lower limit to be the preferred value.³ All yields of C_3 products are reported below assuming that 12% of the carbon vapor is C_3 .

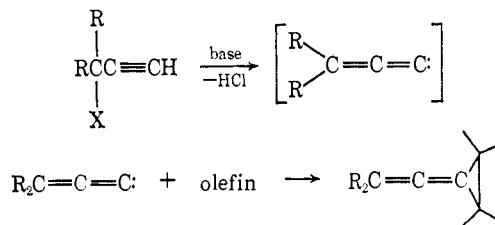
Results and Discussion

The low temperature, condensed phase reactions of C_3 and alcohols follow two major paths, addition of two molecules of alcohol to form propargyl aldehyde acetals, $(RO)_2CHC\equiv CH$, and hydrogenation of C_3 to form a variety of C_3 hydrocarbons. These observations are summarized in Table I.

There is good analogy between the chemistry of C_3 and the chemistry of vinylidene carbenes, $R_2C=C=C:$. Skell, Wescott, Golstein, and Engel reported⁴ the additions of C_3 to double bonds to form bisethanoallenes, the additions being stereospecific and electrophilic in



character for ground-state C_3 (singlet). Hartzler⁵⁻⁷ has generated $R_2C=C=C:$ by treatment of 3-halo-1-acetylenes with base; the reactions in the presence of olefins producing allenylcyclopropanes in a stereospecific and electrophilic manner.



Previously⁸ it was thought that additions of ethanol to C_3 produce 1,3-diethoxyallene because the product gave a positive Kreis test,⁹ reputed to be characteristic for malondialdehyde,^{10,11} the anticipated hydrolysis product. However, propargyl aldehyde also gives a positive Kreis test. Isolation of the pure reaction products enabled positive identification. Thus, the addi-



(1) National Institutes of Health Predoctoral Fellow, 1966–1967.

(2) Cocondensation of carbon vapor with hydrogen chloride results in the formation of 1,3-dichloroallene: R. F. Harris, Ph.D. Thesis, The Pennsylvania State University, University Park, Pa., 1968.

(3) Earlier reports of higher yields of C_3 plus olefin products have been found incorrect, due to an erroneous value for converting gas chromatography (gc) areas to absolute yields.

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

(5) H. D. Hartzler, *ibid.*, **81**, 2024 (1959).

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

(7) H. D. Hartzler, *ibid.*, **83**, 4997 (1961).

(8) L. D. Wescott, Jr., Ph.D. Thesis, The Pennsylvania State University, University Park, Pa., 1963.

(9) H. Kreis, *Chem. Ztg.*, **26**, 897 (1902).

(10) S. Patton, M. Keeney, and G. W. Kurtz, *J. Amer. Oil Chem. Soc.*, **28**, 391 (1951).

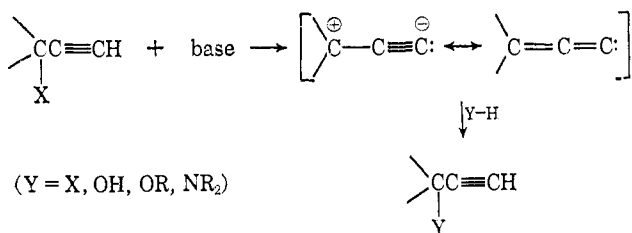
(11) P. Fleury, J. Courtois, W. Hammam, and L. Dizet, *Bull. Soc. Chim. Fr.*, 1290 (1955).

Table I. Products^a Formed from C₃ and Alcohols (wt % of total C₃)^b

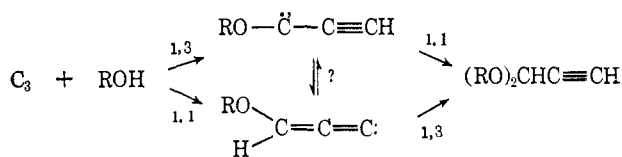
Product	Alcoholic substrate				
	Methanol	Ethanol	1-Propanol	2-Propanol	<i>t</i> -Butyl alcohol
Propane	0.58	0.90	15.1	20.0	7.0
Propene	2.3	10.8	(60.0) ^d	(104) ^d	62.5
Allene	2.8	10.8	20.0	21.6	<i>c</i>
Propyne	3.0	20.8	23.3	16.7	20.0
(RO) ₂ CHC≡CH	43	30	40	<i>c</i>	<i>c</i>

^a Some of these gases are produced, in part, by other pathways. ^b Assuming that C₃ is 12% by weight of the total carbon. ^c Do not have data. ^d For the main these are probably not derived from C₃ (*vide infra*).

tions of alcohols to C₃ are not symmetric as they are for olefins. Here too there is good analogy with the vinylidene carbenes. The 3-halo-1-acetylenes^{5-7,12-16} (and 1-haloallenes¹²) undergo substitution reactions which are initiated by bases and lead to products which are not the result of a 1,1 addition to the carbenic intermediate but a 1,3 addition. In the case of C₃ either 1,1 and/



or 1,3-addition sequences rationalize the formation of propargyl aldehyde acetals; there is no basis for choosing the order of events.



It is not possible to state definitively that 1,3-dialkoxallenes are not products of this reaction, since these substances are not available for an evaluation of the isolation procedures.

Excited-State C₃

Employing ¹⁴C-enriched graphite electrodes, it was demonstrated that all of the carbon of allene, propyne, and propene, when ethanol is employed as substrate, and allene and propyne, when methanol is employed as substrate, are derived from the electrodes (Table II); the relative molar activities are closely three times as great as for the standard which is known to derive only one carbon atom per molecule from the electrodes.

The C₃ hydrocarbons are also obtained from the re-

Table II. Relative Molar Activities of C₃ Hydrocarbons Produced by the Reaction of ¹⁴C-Enriched Vapor with Methanol and Ethanol

Product	Relative molar activities ^a	
	¹⁴ C _{vap} + ¹² CH ₃ OH	¹⁴ C _{vap} + ¹² CH ₃ ¹² CH ₂ OH
C ₁ product, CH ₂ (OR) ₂	(1.00)	(1.00)
Allene	3.00	2.92
Propyne	2.86	2.86
Propene	1.01	2.81

^a (Curies/mole)_{product} / (curies/mole)_{standard}.

action of carbon vapor with a variety of other hydrogen-containing substrates (Table III). Although it is not established (by ¹⁴C-labeling) that the C₃ molecule is the precursor in each case, it is assumed to be in most cases.¹⁷ The C₃ hydrocarbons are not formed to any appreciable extent from substrates which have only high bond dissociation energies for removal of a hydrogen atom such as water, benzene, chlorobenzene, etc.

Hydrogenation of C₃ by hydrogen-containing sub-

Table III. Summary of C₃ Hydrocarbons^a from Selected Substrates (wt % of total C₃)^b

Substrate	Propane	Propene	Allene	Propyne
Water	0.008	0.17	0.17	<i>c</i>
Methanol	0.58	2.3	2.8	3.0
Ethanol	0.90	10.8	10.8	20.8
1-Propanol	15.1	60.0	20.0	23.3
2-Propanol	20.0	104	21.6	16.7
<i>t</i> -Butyl alcohol	7.0	62.5	<i>c</i>	20.0
Chlorobenzene	<0.03	<0.03	<0.03	<0.03
Chloroform	<0.05	<0.05	<0.05	<0.05
Bromobenzene	0.10	0.17	0.17	<i>c</i>
<i>cis</i> -Dichloroethylene	<0.06	<0.06	0.06	<0.06
Vinyl chloride	<0.04	<0.04	<0.04	<0.04
Propargyl chloride	<0.03	<0.03	12.5	11.7
Allyl chloride	0.33	13.3	9.2	9.2
<i>t</i> -Butyl chloride	1.6	5.4	<i>c</i>	13.3
Allyl bromide	0.50	41.6	12.5	<i>c</i>
Ethyl chloride	0.25	4.8	4.2	<i>c</i>
Ethyl bromide	4.4	2.1	20.0	22.5
Benzene	0.14	0.58	0.83	1.08
Cyclohexane	6.1	26.6	40.0	16.7
Acetone	9.2	286	13.3	13.3
<i>cis</i> -2-Pentene	4.9	30.8	18.4	20.0
<i>n</i> -Hexane	21.6	22.5	36.6	13.3

^a Some of these gases are produced, in part, by other pathways.

^b Assuming that C₃ is 12% by weight of the total carbon. ^c Do not have data.

(12) G. F. Hennion and D. E. Maloney, *J. Amer. Chem. Soc.*, **73**, 4735 (1951).

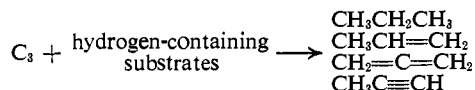
(13) G. F. Hennion and E. G. Teach, *ibid.*, **75**, 1653 (1953).

(14) G. F. Hennion and K. W. Nelson, *ibid.*, **79**, 2142 (1957).

(15) R. L. Jacobs, Abstracts of Papers, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960, p 65-P.

(16) V. J. Shiner, Jr., and J. W. Wilson, *J. Amer. Chem. Soc.*, **84**, 2402 (1962).

(17) The high yields of propene from substrates with three carbons, acetone, and propanols, are attributed to a deoxygenation process, mainly the result of reaction of C₁: P. S. Skell, J. H. Plonka, and R. R. Engel, *ibid.*, **89**, 1748 (1967).



strates is analogous to the hydrogenation of C_2 ¹⁸ and C_4 ,¹⁹ which lead to C_2 and C_4 hydrocarbons, respectively.

Formation of the C_3 hydrocarbons from a variety of partially deuterated substrates is being studied; detailed mechanistic conclusions will be discussed elsewhere.

The C_3 hydrocarbons allene and propyne result from attack of excited-state C_3 on the substrate. This was demonstrated by carrying out the reaction with carbon vapor from resistively heated carbon (no arcing) and methanol and ethanol: allene and propyne are not reaction products, virtually the sole product being the propargyl aldehyde acetal. From this experiment it follows that excited-state C_3 is the precursor of allene and propyne. Whether the excited state is one of the singlets or the previously studied triplet cannot be specified at present.

Experimental Section

The reaction system has been described.⁴ The C_3 molecules are generated, along with C_1 , C_2 , and C_4 , from a 16-V (ac) carbon arc under vacuum ($\sim 1 \times 10^{-4}$ mm). Reactions occur in condensed phase near 77°K. Products were isolated by vapor phase chromatography and the retention times and infrared and mass spectra of the C_3 hydrocarbons, hexachloropropene, and octachloropropene²⁰ were compared with those of known compounds. The

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

(19) R. F. Harris and P. S. Skell, *ibid.*, **90**, 4172 (1968).

(20) A. L. Henne and E. C. Ladd, *ibid.*, **60**, 2491 (1938).

propargyl aldehyde acetals were identified by consistent infrared and mass spectra and confirmed by nmr (Table IV).

Table IV. Nmr of 3,3-Dialkoxypropynes^a

δ	Area	Multiplicity	Assignment
$(CH_3O)_2CHC\equiv CH$			
2.41	1.00	Doublet ($J = 2$)	HC \equiv C-
3.25	6.00	Singlet	CH ₃ O-
4.95	1.00	Doublet ($J = 2$)	-OCHO-
$(CH_3CH_2O)_2CHC\equiv CH$			
1.16	6.02	Triplet ($J = 7$)	CH ₃ -
2.39 ^b	1.00	Doublet ($J = 2$)	HC \equiv C-
3.55	4.02	Multiplet	-OCH ₂ -
5.07	1.00	Doublet ($J = 2$)	-OCHO-
$(CH_3CH_2CH_2O)_2CHC\equiv CH$			
0.92	6.02	Triplet ($J = 7$)	CH ₃ -
1.55	4.00	Multiplet	-CH ₂ -
2.36	1.00	Doublet ($J = 2$)	HC \equiv C-
3.44	4.00	Multiplet	-OCH ₂ -
5.06	1.00	Doublet ($J = 2$)	-OCHO-

^a Microtubes (25 μ l). ^b Literature values: δ 2.39 in CCl_4 (M. M. Kreevoy, H. B. Charman, and D. R. Vinard, *J. Amer. Chem. Soc.*, **83**, 1978 (1961)) and δ 2.33 in CCl_4 (P. Jouve, *C. R. Acad. Sci. Paris*, **256**, 1497 (1963)).

Thermally vaporized carbon vapor was obtained by replacing the upper electrode with a thin (~ 1 mm) graphite slice and heating resistively ($\sim 2800^\circ$). Carbon vapor enriched in carbon-14 was obtained by replacing one graphite electrode with a graphite rod enriched in carbon-14 (~ 0.01 Ci/g).

Acknowledgment. The financial support of the Air Force Office of Scientific Research is gratefully acknowledged.

Stable Carbonium Ions. LXXIV.^{1a} Protonated Alkoxysilanes and Disiloxanes and Their Cleavage in Fluorosulfuric Acid-Antimony Pentafluoride Solution

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Abstract: Several alkoxysilanes and disiloxanes have been examined in the extremely strong acid system, fluorosulfuric acid-antimony pentafluoride at low temperatures by nuclear magnetic resonance spectroscopy. For trimethylmethoxysilane and hexamethyldisiloxane it was possible to directly observe the protonated species with the proton on oxygen. For the other siloxanes studied it was possible to observe the stepwise cleavage of alkoxy and alkyl groups from silicon. The mechanism of the cleavage reactions is discussed. No experimental evidence was found for the intermediacy of trivalent siliconium ion intermediates.

Alkoxysilanes undergo facile cleavage reactions in the presence of both proton and Lewis acids. Cryoscopic studies of alkoxysilanes and polysiloxanes indicate the rapid formation of silyl hydrogen sulfates at 0° in sulfuric acid.² Lewis acid adducts of moderate

stability have been isolated for the reaction of boron halides³ and aluminum halides⁴ with alkoxysilanes and disiloxanes. These complexes undergo further reaction to form halosilanes and oxy salts of boron and aluminum. Protonated intermediates have been proposed

(1) (a) Part LXXIII: G. A. Olah, M. B. Comisarow, and C. F. Kim, *J. Amer. Chem. Soc.*, in press. (b) National Science Foundation Postdoctoral Research Investigator, 1966-1967.

(2) (a) F. P. Price, *J. Amer. Chem. Soc.*, **70**, 872 (1948); (b) M. S. Newman, R. A. Craig, and A. B. Garrett, *ibid.*, **71**, 869 (1949); (c) H. H. Szmant, O. M. Devlin, and G. A. Brost, *ibid.*, **73**, 3059 (1951).

(3) (a) H. J. Emeleus and M. Onyszczuk, *J. Chem. Soc.*, 604 (1958); (b) P. A. McCusker and T. Ostdick, *J. Amer. Chem. Soc.*, **80**, 1103 (1958); (c) M. J. Frazer, W. Gerrard, and J. A. Strickson, *J. Chem. Soc.*, 4701 (1960).

(4) A. H. Cowley, F. Fairbrother, and N. Scott, *ibid.*, 717 (1959)