The average yield of *trans*-diene (~10%) was measured on a 25 ft × 1/8 in. column packed with 25% tris(2-cyanoethoxy)propane on Chromosorb P. The quantum yield for the *cis*-to-*trans* isomerization, after being corrected for back reaction, is 0.555.[12] This method of actinometry was used to determine the amount of light impingent upon the ketone samples. The actual concentrations of ketones used absorb only 85–95% of 3130-Å radiation, so that a 5–15% correction in intensity was necessary in order to convert actual yields into quantum yields.

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The Reactions of Atomic Carbon with Alcohols

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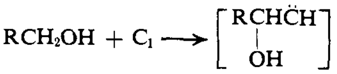
Abstract: The reactions of atomic carbon have been studied with a series of aliphatic alcohols. The reaction products have been identified and their mechanisms of reaction have been elucidated by carbon-14 and deuterium-labeling techniques. All alcohols react with C_1 to undergo deoxygenation and insertion into every OH and CH bond.

The reactions of atomic carbon with hydrocarbons,[2–4] halocarbons,[5] carbonyl compounds, and epoxides[6] have been reported; we here describe the reactions of atomic carbon with alcohols.

It could have been anticipated that carbon atoms would insert into the OH bond of alcohols to produce alkoxycarbenes; alkoxycarbenes react with alcohols by OH bond insertion;[7–10] dialkoxymethanes are major reaction products.

$$C_1 + ROH \longrightarrow [RO\ddot{C}H] \xrightarrow{ROH} (RO)_2CH_2$$

Insertion into CH bonds could also have been anticipated. Rearrangements of the expected carbene intermediates account for the observed products.



$$RCH_2OH + C_1 \longrightarrow \left[\begin{array}{c} RCH\ddot{C}H \\ | \\ OH \end{array}\right]$$

Experimental Section

The reaction system has been described.[11] Atomic carbon is produced, along with C_2, C_3, and C_4, from a 16-V (ac) carbon arc under vacuum (~1 × 10^{-4} mm). Reactions occur in condensed phase near 77°K. Products were isolated by vapor phase chromatography, and their retention times and infrared and mass spectra were compared with those of authentic compounds.

^{14}C-Enriched methanol was prepared by diluting 1.6 mg (0.1 mCi) of methanol-^{14}C to 5.0 g. ^{14}C-Enriched carbon vapor was obtained by replacing one graphite electrode with a graphite rod enriched in carbon-14 (~0.01 Ci/g). Measurements in carbon-14 experiments were carried out by passing the eluent from a gas chromatograph into an ionization chamber, thus obtaining consecutive, continuous recordings of the thermal conductivity response and the carbon-14 ionization response of each component. The integrated conductivity response was converted to a molar quantity, which was then divided into the integrated ionization response to obtain a molar activity.

Methanol-1,1,1-d_3 and ethanol-1,1,2,2,2-d_5 were obtained by distillation of the perdeuterio compounds[12] from a large excess of water (mol of H_2O:mol of ROH = 100:1).[13] Ethanol-1,1-d_2 was prepared by the lithium aluminum deuteride reduction of hexyl acetate.[14] Ethanol-2,2,2-d_3 was obtained from Merck Sharp and Dohme of Canada. The alcohols were dried by vaporization through CaH_2 at reduced pressure (~1 μ); nmr spectra confirmed the position of the deuterium label. The isotopic composition of each alcohol was determined by low-voltage mass spectrometry[15,16] on the corresponding trimethylsilyl ether derivative[17] (Table I). The deuterium analysis of each pure product was determined by low-voltage mass spectrometry.[17]

Table I. Deuterium Compositions of Alcoholic Substrates (mol %)

Deuterium content	Alcohol			
	CD_3OH	C_2D_5OH	CD_3CH_2OH	CH_3CD_2OH
d_0	1.1	0.0	3.0	5.3
d_1	0.0	0.0	0.0	0.0
d_2	1.1	6.6	1.4	94.7
d_3	97.8	0.0	95.6	
d_4		0.4		
d_5		93.0		
d_6				

Results

A. Reactions of Atomic Carbon with Methanol. The products formed by the reactions of atomic carbon with methanol are listed in Table II. These products account for 41.7% by weight of the total carbon vaporized.

B. Reactions of Atomic Carbon with ^{14}C-Enriched Methanol. The relative molar activities of the products

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[1] National Institutes of Health Predoctoral Fellow, 1966–1967.

[2] P. S. Skell and R. R. Engel, *J. Amer. Chem. Soc.*, 88, 3749 (1966).

[3] P. S. Skell and R. R. Engel, *ibid.*, 88, 4883 (1966).

[4] P. S. Skell and R. R. Engel, *ibid.*, **89**, 2912 (1967).

[5] P. S. Skell and R. F. Harris, *ibid.*, 87, 5807 (1965).

[6] P. S. Skell, J. H. Pionka, and R. R. Engel, *ibid.*, **89**, 1748 (1967).

[7] R. W. Hoffmann and H. Häuser, *Tetrahedron Lett.*, 197 (1964).

[8] H. U. Hostettler, *ibid.*, 687 (1965).

[9] R. M. McDonald and R. A. Krueger, *J. Org. Chem.*, **31**, 488 (1966).

[10] N. J. Turro and R. M. Southam, *Tetrahedron Lett.*, 545 (1967).

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

[12] Stohler Isotope Chemicals, Rutherford, N. J.

[13] A. Murray and D. L. Williams, "Organic Syntheses with Isotopes," Part II, Interscience Publishers, New York, N. Y., 1958, p 1338.

[14] Taken from the Ph.D. Thesis of Dr. P. H. Reichenbacher, The Pennsylvania State University, 1967, p 55.

[15] K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 179.

[16] G. J. Karabatos and C. E. Orzech, Jr., *J. Amer. Chem. Soc.*, 87, 4394 (1965).

[17] Reference 15, p 204.

Table II. Reaction Products of Atomic Carbon with Methanol

Compound	Wt % of total carbon
Carbon monoxide	16.8
Dimethoxymethane	17.8
Acetaldehyde[a]	6.3
Dimethyl ether	0.8

[a] Detected as acetaldehyde and as its dimethyl acetal; the latter is formed slowly at room temperature by the reaction of acetaldehyde with the methanol substrate.

formed by the reactions of atomic carbon with ^{14}C-enriched methanol are listed in Table III.

Table III. Carbon-14 Product Studies with Atomic Carbon and Methanol

Compound	Relative molar activity $^{12}C_{vap}$ + $^{14}CH_3OH$	Relative molar activity $^{14}C_{vap}$ + $^{12}CH_3OH$
CH_3OH	[1.00]	
CO	*a*	0.95
$CH_2(OCH_3)_2$	1.96	[1.00]
CH_3CHO	0.94	1.05
$CH_3CH(OCH_3)_2$	*a*	0.98
CH_3OCH_3	1.38	0.59

[a] Not determined.

C. **Reactions of ^{14}C-Enriched Carbon Vapor with Methanol.** The relative molar activities of the products formed by the reactions of ^{14}C-enriched carbon vapor with methanol are listed in Table III.

D. **Reactions of Atomic Carbon with Methanol-1,1,1-d_3.** The deuterium analysis of each product produced by the reactions of atomic carbon with methanol-1,1,1-d_3 is listed in Table IV. The mass spectrum and nmr (one peak at δ 4.44) of the dimethoxymethane so produced indicate it to be >95% $CD_3OCH_2OCD_3$. The mass and infrared spectra (strong absorption at 2070 cm^{-1} but no absorption at 2750 cm^{-1}) of the acetaldehyde so produced indicate it to be >90% CHD_2CDO.[18]

Table IV. Reaction Products from Atomic Carbon and Methanol-1,1,1-d_3

Deuterium content	Product: Acetaldehyde	Product: Dimethoxymethane	Product: Dimethyl ether
d_0			
d_1	1.4		
d_2	5.8		
d_3	92.8		4.5
d_4			23.1
d_5		4.0	41.6
d_6		96.0	30.8

E. **Reactions of Atomic Carbon with Ethanol.** The products formed by the reactions of atomic carbon with ethanol are listed in Table V. These products account for 39.9% by weight of the total carbon vaporized.

Table V. Reaction Products of Atomic Carbon with Ethanol

Compound	Wt % of total carbon
Carbon monoxide	14.3
Diethoxymethane	11.5
Propionaldehyde[a]	1.3
Acetone	8.1
Allyl alcohol	4.4
Methyl ethyl ether	0.3

[a] Detected as propionaldehyde and as its diethyl acetal; the latter was produced during the work-up.

F. **Reactions of ^{14}C-Enriched Carbon Vapor with Ethanol.** The relative molar activities of the products formed by the reactions of ^{14}C-enriched carbon vapor with ethanol are listed in Table VI.

Table VI. Carbon-14 Product Studies with Atomic Carbon and Ethanol

Compound	Relative molar activity $^{14}C_{vap}$ + $^{12}CH_3{}^{12}CH_2OH$
$CH_2(OCH_2CH_3)_2$	[1.00]
CH_3COCH_3	0.98
CH_3CH_2CHO	*a*
$CH_3CH_2CH(OCH_2CH_3)_2$	1.01
$CH_3OCH_2CH_3$	0.93

[a] Do not have data.

G. **Reactions of Atomic Carbon with Ethanol-1,1,2,2,2-d_5, Ethanol-1,1-d_2, and Ethanol-2,2,2-d_3.** The deuterium analysis of each product produced by the reactions of atomic carbon with the three partially deuterated alcohols are listed in Table VII. Acetone was worked up under conditions of minimum exchange; recovery of 100% acetone-d_6 is given for comparative purposes. The diethoxymethanes were also studied mass spectrometrically at 20 eV. Cracking patterns indicate $(C_2D_5O)_2CH_2$, $(CD_3CH_2O)_2CH_2$, and $(CH_3CD_2O)_2CH_2$ as the major products from C_2D_5OH, CD_3CH_2OH, and CH_3CD_2OH, respectively.[19]

H. **Reactions of Atomic Carbon with 1-Propanol.** The products formed by the reactions of atomic carbon with 1-propanol are listed in Table VIII. These products account for 34.6% by weight of the total carbon vaporized.

I. **Reactions of Atomic Carbon with 2-Propanol.** The products formed by the reactions of atomic carbon with 2-propanol are listed in Table IX. These products account for 34.7% by weight of the total carbon vaporized.

J. **Reactions of Atomic Carbon with *t*-Butyl Alcohol.** The products thought to result by the reactions of atomic carbon with *t*-butyl alcohol are listed in Table X. Since two of these products are formed in part by other reactions occurring simultaneously in the system, it is not possible to fix precisely the amount of carbon accounted for by C_1 products.

Discussion

A. **Carbon-14-Labeling Studies.** The two carbon-14-labeling experiments with carbon vapor and methanol clearly define C_1 as precursor to the products

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[18] The acetaldehyde was collected and separated under conditions in which exchange of the α-H is insignificant.

[19] Determined from the relative intensities of the $[RO{=}CHOR]^+$ and $[RO{=}CH_2]^+$ fragments.

Table VII. Products of Atomic Carbon with C_2D_5OH, CD_3CH_2OH, and CH_3CD_2OH

Deuterium content	Acetone[a]			Diethoxymethane			Methyl ethyl ether[b]	
	C_2D_5OH	CD_3CH_2OH	CH_3CD_2OH	C_2D_5OH	CD_3CH_2OH	CH_3CD_2OH	C_2D_5OH	CH_3CD_2OH
d_0			0.9					2.7
d_1		0.8	8.4					
d_2		7.3	90.7					44.5
d_3	1.5	91.9				4.9		40.3
d_4	8.7					95.1		12.5
d_5	89.8				3.1		3.1	
d_6					96.9		27.9	
d_7							68.5	
d_8							0.5	
d_9				6.3				
d_{10}				93.7				

[a] A sample of 100% acetone-d_6 taken through the work-up procedure analyzed 91.7% d_6 and 8.3% d_5. [b] Data with CD_3CH_2OH are not available.

Table VIII. Reaction Products of Atomic Carbon with 1-Propanol

Compound	Wt % of total carbon
Carbon monoxide	11.7
Di-*n*-propoxymethane	11.5
2-Butanone	6.7
2-Methyl-2-propen-1-ol	1.8
Crotyl alcohol	0.0[b]
3-Buten-1-ol	2.8
Butyraldehyde[a]	0.0[b]
n-Propyl methyl ether	0.1

[a] Sought after as butyraldehyde and as its di-*n*-propyl acetal. [b] Yields of 0.002% would have been at the lower limit for detection.

Table IX. Reaction Products of Atomic Carbon with 2-Propanol

Compound	Wt % of total carbon
Carbon monoxide	12.8
Diisopropoxymethane	10.6
2-Butanone	6.6
1-Buten-3-ol	4.5
Isobutyraldehyde	0.0[a]
Isopropyl methyl ether	0.2
Isobutylene oxide	0.0[a]

[a] Yields of 0.002% would have been at the lower limit for detection.

Table X. Reaction Products of Atomic Carbon with *t*-Butyl Alcohol

Compound	Wt % of total carbon[c]
Carbon monoxide	18.8
Di-*t*-butoxymethane	0.0[d]
2-Methyl-2-hydroxy-3-butene	0.0[e]
Isobutylene[a]	30.9
Ethylene[b]	6.2
Pivaldehyde	0.0[e]
t-Butyl methyl ether	0.3

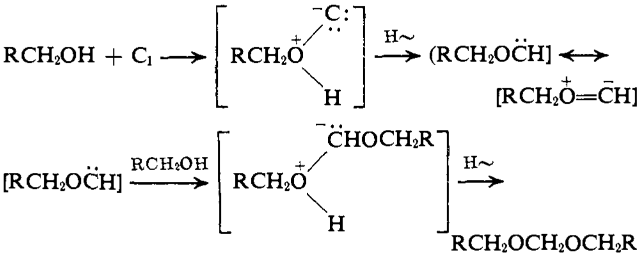
[a] Due in part to deoxygenation reactions. [b] Due in part to hydrogen abstraction by C_2. [c] Assuming a C_1 precursor only. [d] Yields of 0.1% would have been at the lower limit for detection. [e] Yields of 0.002% would have been at the lower limit for detection.

(Table III). Reaction of carbon-12 vapor with ^{14}C-enriched methanol shows that acetaldehyde and the substrate, methanol, have the same relative molar activity, indicating that one molecule of acetaldehyde is formed from one molecule of methanol. Likewise, the data indicate that one molecule of dimethoxymethane is formed from two molecules of methanol.

Reaction of ^{14}C-enriched carbon vapor with carbon-12 methanol shows (Table III) that dimethoxymethane, carbon monoxide, acetaldehyde, and 1,1-dimethoxyethane each have the same relative molar activity indicating that each contains one carbon atom per molecule derived from the carbon vapor.

A C_1 precursor is also indicated for the products formed by the reactions of ^{14}C-enriched carbon vapor with ethanol (Table VII); diethoxymethane, acetone, methyl ethyl ether, and 1,1-diethoxypropane each have the same relative molar activity.

B. The O–H Bond Insertion Reactions. Dialkoxymethanes are probably formed through oxygen ylides.



The studies employing deuterated methanol and ethanols as substrates clearly indicate that the alcohol OH group contributes the hydrogen atoms of the $-OCH_2O-$ group of the formals.

$$C_1 + 2CD_3OH \longrightarrow (CD_3O)_2CH_2$$

$$C_1 + 2C_2D_5OH \longrightarrow (C_2D_5O)_2CH_2$$

$$C_1 + 2CH_3CD_2OH \longrightarrow (CH_3CD_2O)_2CH_2$$

$$C_1 + 2CD_3CH_2OH \longrightarrow (CD_3CH_2O)_2CH_2$$

The intermediate alkoxycarbene does not undergo intramolecular ring closure to the corresponding epoxide (ethylene oxide, propylene oxide, and isobutylene oxide are not products of C_1 with methanol, ethanol, or 2-propanol, respectively). This is reasonable if one considers that the vacant orbital of the carbene will be experiencing appreciable overlap with a p orbital of oxygen and thereby making the intramolecular, electrophilic insertion a less favorable reaction on energetic grounds.

It is possible on energetic considerations that initially formed ethylene oxide (from methanol) could open to acetaldehyde.[20] This process is exothermic by 27.6 kcal/mol[21] but has a high activation energy (57.4 kcal/

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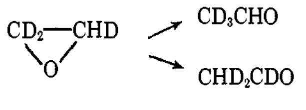
[20] M. L. Neufeld and A. T. Blades, *Can. J. Chem.*, 41, 2956 (1963).
[21] M. S. Kharasch, *J. Res. Nat. Bur. Stand.*, 2, 359 (1929).

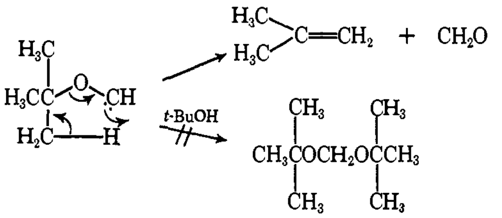
mol).[22] However, both CD_2HCDO and CD_3CHO would be expected from the experiment employing CD_3OH as substrate if ethylene oxide was an important source of acetaldehyde, whereas only CHD_2CDO is found.

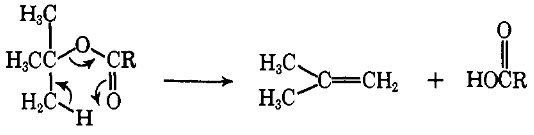


The rearrangement of alkoxycarbenes to aldehydes does not occur; CD_3CHO is not a product from substrate CD_3OH, and the corresponding aldehydes are not observed as products from the propyl alcohol or *t*-butyl alcohol substrates. The evidence has not been made conclusive in the case of ethanol, but there is no reason to suppose that a special mechanism operates solely in the case of this substrate; an alternate mechanism is proposed to explain the formation of propionaldehyde; *vide infra.*

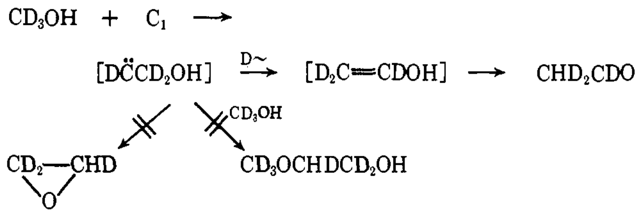
$$\mathrm{RO\ddot{C}H} \not\longrightarrow \mathrm{RCHO}$$

When *t*-butyl alcohol is employed as substrate the *t*-butoxycarbene intermediate apparently undergoes intramolecular hydrogen transfer before addition of a second alcohol molecule can occur; di-*t*-butoxymethane is not a product.[23] This is formally analogous to the intramolecular *cis* elimination of *t*-butyl carboxylic esters.[24] Detail and scope of such processes are the subjects of current investigations.



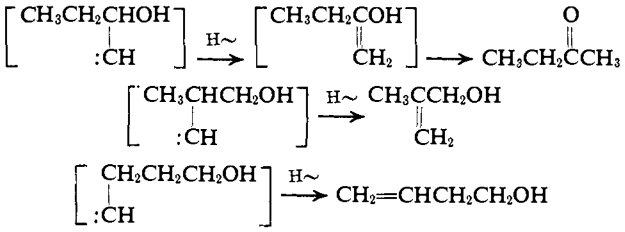


C. The C–H Bond Insertion Reactions. 1. Methanol, CD_3OH. Acetaldehyde formation is rationalized by C_1 insertion into a C–D bond of methanol. The resulting carbene then undergoes a deuterium shift to form the enol of acetaldehyde. This rearrangement must be very rapid since the intermediate carbene is trapped neither by methanol nor by intramolecular ring formation.

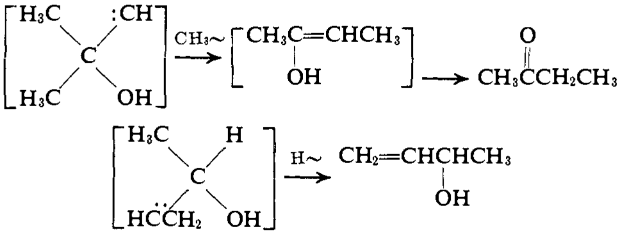


2. **Ethanol.** Acetone, propionaldehyde, and allyl alcohol formations are rationalized by α- and β-CH insertions by C_1. The formation of penta-, tri-, and dideuterioacetones from CD_3CD_2OH, CD_3CH_2OH, and CH_3CD_2OH, respectively, are in accord with this mechanism. The carbene intermediates do not cyclize by intramolecular insertion on the O–H bond; neither propylene oxide nor oxetane was present. It is not known if cyclopropanol is formed. Although pure cyclopropanol is reported to be stable in the absence of acidic or basic impurities,[25] it is easily converted to propionaldehyde and polymeric materials.[25–27] Although propionaldehyde is one of the products observed, its presence does not require the intermediacy of cyclopropanol.

3. **1-Propanol.** 2-Butanone, 2-methyl-2-propen-1-ol, and 3-buten-1-ol formations are rationalized by α-, β-, and γ-CH insertions by C_1, respectively, followed by rearrangement of a hydrogen atom from a next neighbor. Rearrangements of alkyl groups are not important reactions; if they had been, butyraldehyde and crotyl alcohol would have been detected among the products.



4. **2-Propanol.** 2-Butanone and 1-buten-3-ol formations are rationalized by α- and β-CH insertions by C_1, respectively. Insertion into the α-CH bond produces a carbene without a hydrogen atom in position for rearrangement; in this case methyl migration takes precedence over OH migration or ring closure to isobutylene oxide.



5. ***t*-Butyl Alcohol.** The carbene intermediate formed by CH insertion does not stabilize by intramolecular hydrogen migration from the β-carbon atom (2-hy-

Table XI. Position of C–H Insertion in Alcohols (Molar Ratios per Bond)

Bond ratio	Ethanol	1-Propanol	2-Propanol
α/β	2.8	3.5	8.8
β/γ		1.0	

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(22) K. H. Mueller and W. D. Walters, *J. Amer. Chem. Soc.*, **73**, 1458 (1951).

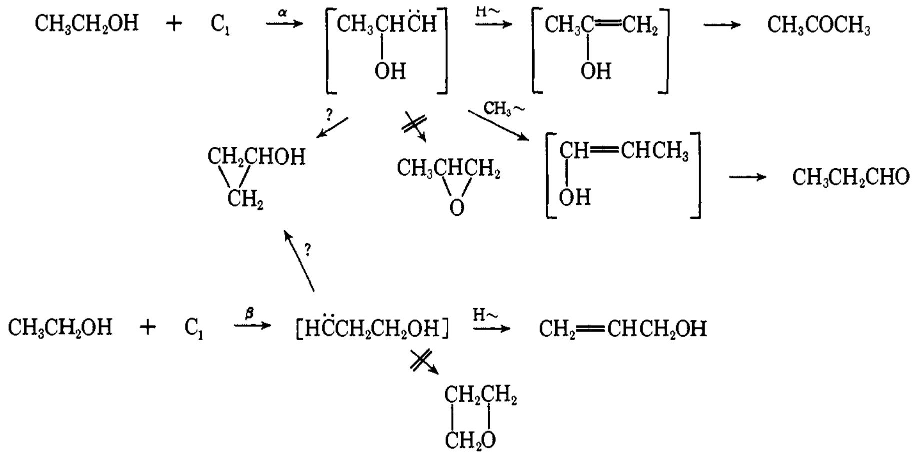
(23) An authentic sample of di-*t*-butoxymethane was prepared by the method of I. Jansson, *Suomen Kemistilehti*, **37B**, 19 (1964), and was found to be stable to the conditions of product detection.

(24) (a) G. O'Connor and H. Nace, *J. Amer. Chem. Soc.*, **75**, 2118 (1953); (b) D. Barton, A. Head, and R. Williams, *J. Chem. Soc.*, 1715 (1953).

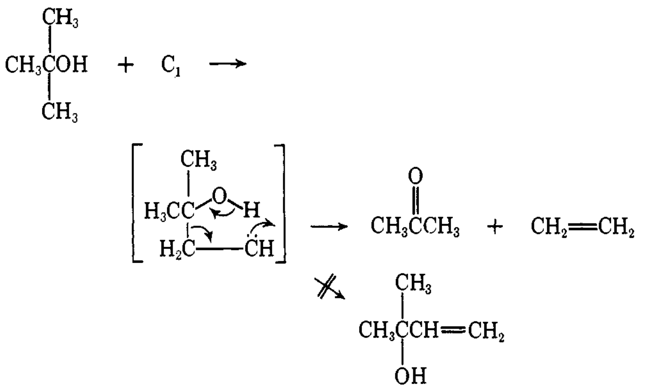
(25) C. H. DePuy and L. R. Mahoney, *J. Amer. Chem. Soc.*, **86**, 2653 (1964).

(26) C. W. Stahl and D. L. Cottle, *ibid.*, **65**, 1782 (1943).

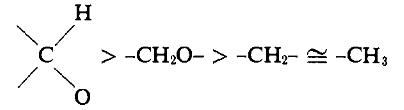
(27) C. H. DePuy, G. M. Dappen, K. L. Eilers, and R. A. Klein, *J. Org. Chem.*, **29**, 2813 (1964).



droxy-2-methyl-3-butene is not a product), but apparently stabilization occurs by the intramolecular hydrogen migration of the alcoholic hydrogen forming acetone and ethylene. Detail and scope of such processes are the subject of current investigations.



6. Summary of C–H Bond Insertion Data. Atomic carbon shows a small degree of selectivity in C–H insertion reactions (Table VI). The order of decreasing reactivity toward C–H insertion of C_1 is



One would like to compare the selectivity of C_1 in C–H insertion reactions with alcohols to the selectivity of methylene in C–H insertion reactions with alcohols. Unfortunately, this is not possible with the present state of knowledge.

D. Comparison of O–H and C–H Insertion Products. The O–H and C–H insertion products are compared in Table XII. Interestingly, although the amounts of O–H and C–H insertion products vary, their sum is nearly constant (22–25% by weight) regardless of the alcohol employed as substrate. The OH:CH ratio per bond also varies very little (5–8).

Table XII. Comparison of OH *vs.* CH Insertion Products from C_1 and Alcohols

	Methanol	Ethanol	1-Propanol	2-Propanol
OH insertion	17.8	12.8	11.5	10.6
CH insertion	6.3	12.5	11.3	11.1
Total insertion	24.1	25.3	22.8	21.7
OH:CH ratio per bond	8.5	5.1	7.1	6.7

The results indicate that C_1 is a less selective species than methylene. The ratio of OH:CH insertion (per bond) in methanol is reported to be 21.8 for methylene[28] (photolysis of diazomethane in methanol at 18°); it is 8.5 for C_1 at a much lower temperature (~77°K).

E. Deoxygenation Reactions. The process of deoxygenation of alcohols is not clear at this time. Large quantities of carbon monoxide are produced from each alcohol studied. However, a material balance of the other expected products of deoxygenation is not yet possible. Deoxygenation processes are the subject of current investigation.

F. Methyl Ether Formation. Small quantities of the corresponding methyl ethers are formed from C_1 and every alcohol studied. However, those products are always minor (<1.0% by weight of the total carbon vaporized).

^{14}C-Enriched vapor studies with ethanol (Table VI) clearly indicate that methyl ethyl ether has a C_1 precursor. Methyl ethyl ether formation from partially deuterated ethanols suggest a mechanism involving initial formation of ethoxycarbene, followed by statistical acquisition of the last two hydrogens from the medium (Table VIII). Successive hydrogen atom abstractions rather than rearrangement or reaction with neighbor nucleophiles (molecules of ethanol) suggest that this intermediate may be the triplet alkoxycarbene,

Table XIII. Methyl Ethyl Ether Formation from C_1 and CD_3CD_2OH and CH_3CD_2OH

	CD_3CD_2OH		CH_3CD_2OH	
Deuterium content	Found	Statistical abstraction from CD_3CD_2OH	Found	Statistical abstraction from CH_3CD_2OH
d_0			2.7	
d_1				
d_2			44.5	44.4
d_3			40.3	44.4
d_4			12.5	11.2
d_5	3.1	2.8		
d_6	27.9	27.8		
d_7	68.5	69.4		
d_8	0.5			

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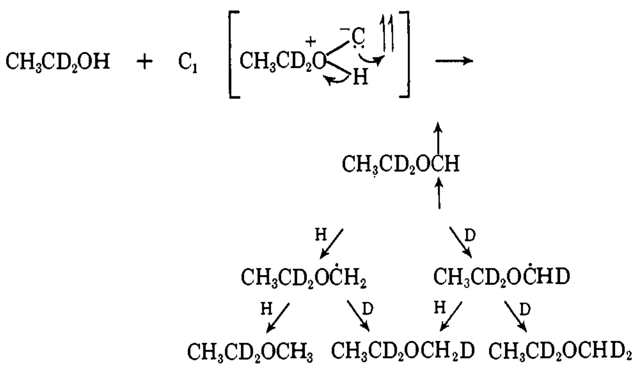
(28) J. A. Kerr, B. V. O'Grady, and A. F. Trotman-Dickenson, *J. Chem. Soc., A*, 897 (1967).

formed from ^3P carbon atoms, as illustrated for CH_3CD_2OH. However, the low degree of discrimination



for abstraction from β-CH_3 or α-CD_2, shown by the ethoxymethyl radical intermediate of this mechanism, $EtO\dot{C}H_2$, is unexpected.

Dimethyl ether formed from methanol appears to be produced by at least two pathways. A d_6 component (Table IV) is not possible if a methoxycarbene intermediate is invoked in the CD_3OH experiment. If the d_6 component is removed and the other values normalized, the values listed in Table XIV are obtained. Random abstraction by this methoxycarbene intermediate is consistent with the results, again supporting the suggestion that a triplet form of the carbene is involved.

The remainder of the dimethyl ether (30–40%) is derived exclusively from methanol by dehydration: (1) 31% of the ether from CD_3OH is CD_3OCD_3, (2) 38% of the ether from $^{14}CH_3OH$ is doubly labeled, and (3) 41% of the ether from $^{13}CH_3OH$ and ^{14}C vapor is unlabeled. Dehydration to the symmetrical ether is observed only with methanol.

Table XIV. Dimethyl Ether from C_1 and CD_3OH (d_6 Component Removed)

Deuterium content	d_6 component removed	Statistical hydrogen abstraction
d_3	6.5	6.2
d_4	33.4	37.5
d_5	60.1	56.3

G. Atomic Carbon Content of the Carbon Vapor. The C_1 products from the reactions with alcohols are summarized in Table XV. Such chemical evidence indicates that the carbon arc employed in these experiments contains a minimum of 40% by weight of atomic carbon.

Table XV. Summary of Products from the Reactions of C_1 with Alcohols[a]

Products	Methanol R = Me	Ethanol R = Et	1-Propanol R = *n*-Pr	2-Propanol R = *i*-Pr
OH insertion				
$(RO)_2CH_2$	17.8	11.5	11.5	10.6
CH insertion				
α-CH	6.3	9.4	6.7	6.6
β-CH		4.4	1.8	4.5
γ-CH			2.8	
$ROCH_3$	0.8	0.3	0.1	0.2
CO	16.8	14.3	11.7	12.8
Total	41.7	39.9	34.6	34.7

[a] Weight per cent of total carbon.

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Stereochemistry of Solvolysis of 2-Phenylethyl Sulfonate Esters. The Phenonium Ion–Equilibrating Classical Ions Problem

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Abstract: Solvolysis of diastereomerically pure $PhCHDCHDOSO_2Ar$ leads to product in which the extent of retention of diastereomeric configuration is in all cases twice the extent of label rearrangement in $PhCH_2C^*H_2OTs$. This relation, which is uniquely required by a symmetric phenonium ion, has been observed for 5, 15, 44, and 50% rearrangement attending solvolysis and 27% rearrangement attending deamination. Detailed kinetic inspection of the equilibrating classical ion scheme suggests that although it can account for the entropy spread associated with the k_s, k_Δ routes it cannot account adequately for other related observations.

The structure of 2-phenylethylcarbonium ions has been hotly contested.[2] Recent structural studies on the 2-phenylethyl carbonium ion in strongly ionizing, weakly nucleophilic solvents seem to support the phenonium ion formulation.[3] However, it can be argued that the structure of the cation generated in such an environment is at an extremum and is not representative of the structure of the cation generated under the more usual reaction conditions, *e.g.*, solvolysis and deamination. Of those criteria most often applied to the

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(2) (a) D. J. Cram, *J. Am. Chem. Soc.*, **86**, 3767 (1964); this is a general review defending the phenonium ion formulation. (b) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *ibid.*, **87**, 2137 (1965); this is a general review defending the equilibrating classical ion formulation.

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