# Cyclopropylcarbinyl, Cyclobutyl, and Allylcarbinyl Cations from Anodic Oxidations of the Carboxylic Acids

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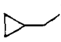
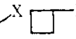
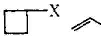
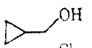
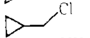
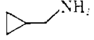
**Abstract:** Anodic oxidations of cyclopropaneacetic, cyclobutanecarboxylic, and allylacetic acids produce the corresponding carbonium ions. These carbonium ions undergo substantial, but not complete, equilibration prior to being trapped as the alcohols or esters; the olefinic products are derived from less equilibrated intermediates.

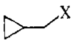
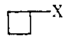
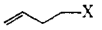
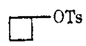
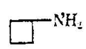
A great deal of attention has been given to the cyclopropylcarbinyl, the cyclobutyl, and the allylcarbinyl cations.[1-3] In solvolysis each of these cations gives the same mixture of products (Tables I–III). Even in deamination cyclopropylcarbinylamine and cyclobutylamine give product mixtures which are nearly identical with each other and with the solvolysis product mixtures (Tables I and II). Allylcarbinylamine on deamination gives about the same *ratio* of cyclopropylcarbinyl to cyclobutyl products as do solvolysis and deamination of the isomers. However, a larger amount of allylcarbinyl and rearranged allyl products are also produced (Table III).

**Table I.** Substitution Products of the Cyclopropylcarbinyl System

| Reaction | Products, % | | | Ref |
|---|---|---|---|---|
| |  |  |  | |
|  + HBr (aq) $\longrightarrow$ | 60 | 30 | 10 | *a* |
|  + 50% aq EtOH $\longrightarrow$ | 48 | 48 | 4 | *a*, *b* |
|  + HONO $\xrightarrow{\text{aqueous}}$ | 56 | 40 | 4 | *c* |

[a] J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.*, **73**, 2509 (1951). [b] M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960). [c] E. Renk and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 878 (1961).

**Table II.** Substitution Products of the Cyclobutyl System

| Reaction | Products, % | | | Ref |
|---|---|---|---|---|
| |  |  |  | |
|  + $HCO_2H$ $\xrightarrow{\overset{+}{Na}\overset{-}{O}CHO}$ | 45 ± 5 | 45 ± 5 | 10 ± 5 | *a* |
|  + HONO $\xrightarrow{\text{aqueous}}$ | 52 | 45 | 4 | *b* |

[a] K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 3773 (1964). [b] See Table I, footnote *c*.

We have studied the anodic oxidations of cyclopropaneacetic, cyclobutanecarboxylic, and allylacetic acids. There is evidence that this reaction, related to the Kolbe electrosynthesis, is a source of carbonium ions.[4] In other alkyl systems the carbonium ions produced by anodic oxidation have been shown to have much in common with carbonium ions produced by deamination or deoxideation.[5] The over-all reaction proceeds this way.

$$RCO_2^- \xrightarrow{-2e^-} R^+ + CO_2$$

## Results and Discussion

The three acids were studied as their potassium salts, 1 *M* in aqueous solution. Except where indicated, platinum electrodes were used and the electrolysis cell was cooled to keep the temperature in the range of 20–30°. Because some of the current is used to convert water to hydrogen and oxygen, and because this tendency increases with increasing pH, current yields are not significant and are omitted from the tables. Unless otherwise noted, the alcoholic products listed comprise more than 90% of the liquid products (alcohols and esters). The portion of the product that was not identified was that eluted before the alcohols by glpc and may have been formed by fragmentation of the cations. Tables IV–VI give the data on the substitution products from the anodic oxidations of the three isomeric acids.

At or near neutrality, each of the acids gives products and product distributions very similar to its opposite number in deamination. This is true for alcohols; comparative data are not available for the esters but from solvolysis it appears that in these cationic systems, better nucleophiles tend to give more of the cyclopropylcarbinyl substitution product. Thus treatment of cyclopropylcarbinol with hydrobromic acid gives more cyclopropylcarbinyl product than does solvolysis of cyclopropyl chloride with aqueous ethanol.[6,7] This trend is also seen here.

One departure from the similarity with deamination is that cyclopropaneacetic acid at pH 8 gives somewhat more allylcarbinyl product than does the deamination of cyclopropylcarbinylamine. This may not be significant; cyclopropylcarbinyl radical, the supposed intermediate in the anodic oxidation,[4] is known to rearrang

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(1) The subject has been reviewed by M. Hanack and H.-J. Schneider, *Angew. Chem. Int. Ed. Engl.*, **6**, 666 (1967).

(2) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 272.

(3) M. Vogel and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 2262 (1967).

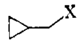
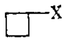
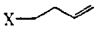
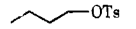
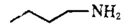
(4) P. H. Reichenbacher, M. D. Morris, and P. S. Skell, *ibid.*, **90**, 3432 (1968); P. S. Skell and P. H. Reichenbacher, *ibid.*, **90**, 3436 (1968).

(5) J. T. Keating and P. S. Skell in "Carbonium Ions," Vol. 2, G. A. Olah and P. von R. Schleyer, Ed., Interscience Publishers, New York, N. Y., 1968, in press. For results pertinent to the system at hand: E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanova, Jr., and E. T. Kaiser, *J. Amer. Chem. Soc.*, **82**, 2645 (1960).

(6) See Table I, footnote *a*.

(7) See Table I, footnote *b*.

Table III, Substitution Products of the Allylcarbinyl System

| | Products, % | | | |
|---|---|---|---|---|
| Reaction |  |  |  | Ref |
|  + $HCO_2H$ $\xrightarrow{\text{Na}\overset{+}{}\overset{-}{\text{O}}\text{CHO}}$ | 45 ± 5 | 45 ± 5 | 10 ± 5 | *b* |
|  + HONO $\xrightarrow{\text{aqueous}}$ | 16 | 14 | 42[a] | *c* |

[a] The rest of the product is methylallyl and crotyl derivatives, the result of 1,2-hydride shift and some allyl rearrangement. [b] See Table II, footnote *a*. [c] See Table I, footnote *c*.

Table IV. Electrolysis Products of Cyclopropaneacetic Acid (Alcohols and Esters)

| | pH | | | | |
|---|---|---|---|---|---|
| | 8–9<br>Run 1 | 8<br>Run 2 | 11<br>Run 3 | 14<br>Run 4 | 14<br>Run 5 |
| Alcohols | | | | | |
| Cyclopropylcarbinyl, % | 55.2 | 55.4 | 52.7 | 67.8 | 65.5 |
| Cyclobutyl, % | 27.3 | 36.8 | 23.8 | 16.0 | 21.6 |
| Allylcarbinyl, % | 17.5 | 7.9 | 23.5 | 16.3 | 12.9 |
| Esters | | | | | |
| Cyclopropylcarbinyl, % | 72.0 | | 67.7 | 63 | 63 |
| Cyclobutyl, % | 19.4 | | 20.8 | 23 | 27 |
| Allylcarbinyl, % | 8.7 | | 11.4 | 14 | 10 |
| Alcohol/ester | 75/25 | | 70/30 | 99/1[a] | 93/7[a] |
| Mmoles of liquid[b] | 2.5 | 1–2 | 26 | 16 | 18 |

[a] Pyrolytic graphite electrodes were used. Very little ester was formed. [b] Estimated from the weight of neutral liquid products; to be compared with the mmoles of gaseous product from this system, Table VII.

to allylcarbinyl radical.[8–12] Further oxidation of this radical would give allylcarbinyl cation and this would raise the amount of allylcarbinyl product.

The differences in the three systems appear as the basicity increases. For cyclopropaneacetic acid, increasing the base concentration results in an increase in the percentage of cyclopropylcarbinyl product. This may be due to faster trapping of the first-formed carbonium ion—the shorter lifetime of the cation means less time for rearrangement. It may also be due to the aforementioned effect of better nucleophiles. This base effect is marked in the alcohols but not in the esters, and affects the allylcarbinyl product very little.

Cyclobutanecarboxylic acid is uniform in its behavior over the range from pH 7 to 6 *M* potassium hydroxide. The principal change is the formation of some allyl alcohols and some unidentified material. The relative amounts of cyclopropylcarbinyl, cyclobutyl, and allylbinyl products are little changed.

For allylacetic acid, reproducibility is not good but it is clear that at pH 14 the amount of cyclopropylcarbinyl product increases at the expense of allylcarbinyl; the cyclobutyl product is almost unaffected by the basicity change.

Although the substitution products from the three acids at pH 7 are quite similar to one another and to the products of deamination, the elimination products show considerable dependence on the acid from which they derive. No comparison with deamination is possible because elimination products are not reported for reaction in aqueous solution. Table VII gives the results for the three acids. The elimination product can have two sources, the radical disproportionation and the cation elimination.

$$2C_4H_7\cdot \longrightarrow C_4H_8 + C_4H_6$$

$$C_4H_7^+ \longrightarrow C_4H_6 + H^+$$

To find what part of the $C_4H_6$ product arises from the cation, one subtracts the percentage of $C_4H_8$ from the percentage of $C_4H_6$. What remains is due to the carbonium ion. The analysis is deficient in that it does not allow one to determine which isomers have cationic sources.[13]

Cyclopropaneacetic acid at low pH gives little hydrocarbon that is not attributable to disproportionation of the cyclopropylcarbinyl radical, or the allylcarbinyl radical to which it is easily converted. At the graphite anode, which suppresses radical reactions, the elimination product due to cation is mostly butadiene and the fragment ethylene.[14] At pH 14 small amounts of cyclobutene and bicyclobutane are formed. All in all however, little hydrocarbon product is formed in the anodic oxidation of cyclopropaneacetic acid, and that little is largely due to reactions of the radical rather than of the cation.

Cyclobutanecarboxylic acid gives substantial amounts of hydrocarbon product, chiefly the expected cyclobutane, cyclobutene, and bicyclobutane. A good part of these last two arises from the carbonium ion. Only at 6 *M* base does lower molecular weight product appear (fragmentation). Butadiene is not a major product. The ratio of cationic elimination product to substitution product is near unity, much higher than is found in the anodic oxidation of cyclopropaneacetic acid.

The chief products of allylacetic acid are butadiene and the fragment ethylene. Fragmentation is important even at pH 7. Much of the elimination product comes from the carbonium ion. Although the figures are rough, the elimination to substitution product ratio is 0.5, less than that of cyclobutanecarboxylic acid but much more than that of cyclopropaneacetic acid.

The relation of these data to the question of the nature of the cyclopropylcarbinyl cation is deferred to a later paper, as requested by the referees.

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(8) E. Renk, P. D. Shafer, W. H. Graham, R. H. Mazur, and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 1987 (1961).

(9) L. H. Slaugh, *ibid.*, **87**, 1522 (1965).

(10) L. K. Montgomery and J. W. Matt, *ibid.*, **89**, 3050 (1967).

(11) T. A. Halgren, M. E. H. Howden, M. E. Medof, and J. D. Roberts, *ibid.*, 89, 3051 (1967).

(12) E. S. Huyser and J. O. Taliaferro, *J. Org. Chem.*, **28**, 3442 (1963); E. S. Huyser and L. R. Munson, *ibid.*, 30, 1436 (1965).

(13) Butadiene is probably partially destroyed by the oxygen produced in the anodic oxidation. This will impair the accuracy.

(14) The fragment could conceivably come from the radical, but fragmentation is well known to the chemistry of free-carbonium ions.

**Table V.** Electrolysis Products of Cyclobutanecarboxylic Acid (Alcohols and Esters)

| | pH 7<br>Run 1 | pH 7<br>Run 2 | pH 7<br>Run 3 | pH 14<br>Run 4 | pH 14<br>Run 5 | pH 14.8[a]<br>Run 6 |
|---|---|---|---|---|---|---|
| | | Alcohols | | | | |
| Cyclopropylcarbinyl, % | 48.2 | 50 | 47.5 | 56.3 | 47.5 | 46.5[b] |
| Cyclobutyl, % | 41.5 | 40 | 44.6 | 30.2 | 33.4 | 43.4 |
| Allylcarbinyl, % | 10.3 | 10 | 7.9 | 13.6 | 19.1 | 10.1 |
| | | Esters | | | | |
| Cyclopropylcarbinyl, % | 54.6 | 56.5 | 56.0 | 49.5 | | |
| Cyclobutyl, % | 34.6 | 34.2 | 33.2 | 40.1 | | |
| Allylcarbinyl, % | 10.9 | 9.3 | 10.8 | 10.3 | | |
| Alcohol/ester | 75/25 | 80/20 | 57/43 | 93/6 | | |
| Mmoles of liquid[c] | 0.9 | 11 | 1.5 | 2.5 | 4.2 | <0.2 |

[a] The solution was 6 *N* in hydroxide. [b] The listed alcohols comprised 62% of the liquid products, another, unidentified alcohol, 11.1%; crotyl alcohol and an unknown material, 12.5%, 1-buten-3-ol, 3.3%; and what may be propyl alcohol, 11.1%. [c] Estimated from the weight of neutral liquid products; to be compared with the mmoles of gaseous product from this system, Table VII.

**Table VI.** Electrolysis Products of Allylacetic Acid (Alcohols and Esters)

| | pH 7<br>Run 1 | pH 7<br>Run 2 | pH 7<br>Run 3 | pH 14<br>Run 4 | pH 14<br>Run 5 |
|---|---|---|---|---|---|
| | Alcohols | | | | |
| Cyclopropylcarbinyl, % | 15.4 | 21.8 | 17.6 | 31.2 | 41.7 |
| Cyclobutyl, % | 13.2 | 19.8 | 16.9 | 12.9 | 13.4 |
| Allylcarbinyl, % | 46.8 | 33.0 | 45.7 | 27.8 | 26.6 |
| Crotyl,[a] % | 12.1 | 3.6 | 10.2 | 2.8 | 1.2 |
| 1-Buten-3-ol,[a] % | 12.6 | 21.8 | 9.7 | 25.2 | 17.2 |
| | Esters | | | | |
| Cyclopropylcarbinyl, % | | 22.5 | 45 | Very little ester formed | |
| Cyclobutyl, % | | 16.2 | 15 | | |
| Allylcarbinyl, % | | 38.4 | 23 | | |
| Crotyl,[a] %<br>1-Buten-3-yl,[a] % | | 24.1 | 15 | | |
| Alcohol/ester | | 90/10 | 80/20 | ... | ... |
| Mmoles of liquid[b] | | ~1 | 0.3 | | <0.8 |

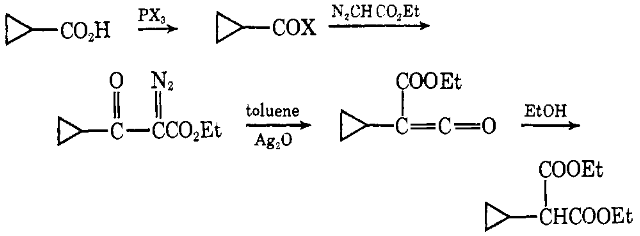
[a] These alcohols and esters were not found in the anodic oxidations of cyclopropaneacetic acid, or cyclobutanecarboxylic acid below pH 14.8. [b] Estimated from the weight of neutral liquid products; to be compared with the mmoles of gaseous product from this system, Table VII.

## Experimental Section

Standard vacuum line techniques were used for handling the volatile materials formed in the anodic oxidations. After equilibration, the product mixtures were analyzed on a gas-liquid partition chromatography unit attached to a vacuum system.

For gas-liquid partition chromatography, the following columns were used: column 30, 2,5-hexanedione, 50 ft, 30% on 45-60 Chromosorb P (this was used for gas analyses at 0° with 30 psi of helium; approximate flow rate was 70 cm$^3$/min); column 50, $\beta,\beta'$-oxydipropionitrile, 30 ft, 25% on Chromosorb P, for gas analyses at 0°, helium flow of 120 cm$^3$/min; column 79, capillary column, tris(cyanoethoxy)propane, 100 ft, 75°, argon pressure of 20 psi; column 135, Apiezon J, 10% on 50-60 Gaschrom R, 30 ft, 100°, 5 psi helium pressure; column 146, diethylene glycol adipate (28%) and phosphoric acid (2%) on 60-80 Firebrick, 180°, helium flow of 70 cm$^3$/min. Tables VIII and IX give the retention times and relative responses of the products found in this work.

**Preparation of Cyclopropaneacetic Acid.** Two synthetic methods were used. The first was that of Turnbull and Wallis.[15] Their procedure was the Arndt-Eistert reaction on cyclopropanecarboxylic acid. The method was followed without modification and the desired acid was obtained in 52% yield based on cyclopropanecarboxylic acid.



An alternative synthesis used the following scheme.[16] When the malonic acid was obtained, it could be exchanged with deuterium oxide if labeled acid were desired.[17] Decarboxylation gives cyclopropaneacetic acid. The yields for this method were low, ~20%. The purity of the acid used in the electrolyses was >98%, according to glpc analysis (column 146).

**Cyclobutanecarboxylic Acid.** This acid was obtained from the Aldrich Chemical Co., Milwaukee, Wis. Analysis on column 146 showed no detectable contaminants; purity >98%.

**Allylacetic Acid.** This acid was obtained from the Chemical Procurement Laboratories, College Point, N. Y. Analysis on column 146 showed it to be >98% pure.

**Preparation of Cyclopropylcarbinol.** Cyclopropanecarboxylic acid or methyl cyclopropanecarboxylate was reduced with lithium aluminum hydride.[18,19] The alcohol obtained was identified by comparison of its infrared spectrum and nmr spectrum with the spectra in the literature.[6,20] Analysis on column 79 showed it to be uncontaminated.

**Preparation of Cyclobutanol.** Cyclobutanone, obtained from Aldrich Chemical Co., Milwaukee, Wis., was reduced with lithium aluminum hydride. The product, analyzed on column 135, gave a trace of six peaks, one of which accounted for 80% of the mixture. The second largest peak was attributable to cyclobutanone. The infrared spectrum and nmr spectrum of the product mixture corresponded well with those published for cyclobutanol in the literature, despite the contamination.[6,21] The impurities were found to be present in the starting material.

**Preparation of Allylcarbinol.** This material was prepared by the reduction of methyl 3-butenoate with lithium aluminum hydride. Analysis on column 146 showed the alcohol to be about 80% pure, the contaminant probably is one of the methyl-substituted allyl alcohols.

**Analysis and Separation of the Electrolysis Products.** The products obtained from the three isomeric acids were analyzed on the capillary glpc with column 79. The separation was satisfactory. The retention times and relative responses of the alcohols are given in Table IX. The retention times of the esters are also given. The relative responses of the esters were not determined, but it was assumed that they would be the same as cyclopropylcarbinol. The

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(15) J. H. Turnbull and E. S. Wallis, *J. Org. Chem.*, 21, 663 (1956).

(16) L. I. Smith and S. McKenzie, *ibid.*, 15, 74 (1950).

(17) P. Holemann and K. Clusius, *Chem. Ber.*, 70, 819 (1937).

(18) R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.*, **69**, 2948 (1947).

(19) D. E. Applequist and D. E. McGreer, *ibid.*, **82**, 1965 (1960).

(20) S. E. Wiberly and S. C. Bunce, *Anal. Chem.*, **24**, 623 (1952).

(21) J. D. Roberts and C. W. Sauer, *J. Amer. Chem. Soc.*, **71**, 3925 (1949).

Table VII. Hydrocarbons from the Anodic Oxidations of Cyclopropaneacetic, Cyclobutanecarboxylic, and Allylacetic Acids

| | Cyclopropaneacetic | | | | Cyclobutanecarboxylic | | | | | Allylacetic | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2[a] | 3[b] | 4[c] | 2 | 3 | 4 | 5 | 6[d] | 3 | 4 | 5 |
| | pH | | | | pH | | | | | pH | | |
| | 8–9 | 8 | 11 | 14 | 7 | 7 | 14 | 14 | 14.8 | 7 | 14 | 14 |
| Ethylene, % | 3 | 30 | 6 | 18 | | | | | 15 | 20 | 56 | 61 |
| Acetylene, % | | | | | | | | | *e* | 2 | 14 | 2 |
| Propylene, % | | | | 6 | | | | | 17 | 6 | 13 | 8 |
| Cyclopropane, % | | | | 10 | | | | | 2 | <1 | 2 | 3 |
| 1-Butene, % | 50 | 10 | 50 | 31 | | | | | | 17 | 8 | 8 |
| 1,3-Butadiene, % | 38 | 57 | 35 | 23 | | | | | | 36 | 17 | 17 |
| Methylcyclopropane, % | 9 | 4 | 7 | 2 | | | | | | 3 | | |
| Cyclobutane, % | | | | | 23 | 30 | 8 | 15 | 0 | 3 | | |
| Cyclobutene, % | | | | 5 | 75 | 70 | 92 | 85 | 64 | 8 | | |
| Bicyclobutane, % | | | | 4 | 2 | <1 | | | 2 | | | |
| Mmoles of gas | 0.5–1.0 | 0.06 | 0.4 | 1.3 | >4.0[f] | 2.0 | 5.0 | 2.6 | 0.24 | 0.14 | 0.35 | 0.4 |
| % cation product[g] | 3 | 72 | 6 | 18 | 53 | 40 | 84 | 70 | 100 | 47 | 83 | 83 |

[a] Pyrolytic graphite electrodes were used. [b] About 2% of other gaseous materials were formed. [c] The identities of some of the lower molecular weight products are not certain. [d] The solution was 6 *M* in hydroxide. [e] There were traces of acetylene in the mixture. [f] Some of this material was lost in the work-up. [g] This value was obtained by taking all the monounsaturated $C_4$ hydrocarbons (1-butene, methylcyclopropane, cyclobutane) and doubling their total percentage to include the diunsaturated material that arose from disproportionation. All the remaining material, including the fragments, is taken to be cationic in origin.

Table VIII. Relative Molar Responses and Retention Times of Hydrocarbon Products on Glpc Columns[a]

| Formula | Compound | Response[b] | Retention time,[c] min Col 30 | Col 50 |
|---|---|---|---|---|
| $C_2H_2$ | Acetylene | . . . | 43.9 | . . . |
| $C_2H_4$ | Ethylene | 100 | 10.0 | 2.3 |
| $C_3H_6$ | Propylene | 120 | 20.8 | 3.7 |
| | Cyclopropane | 120 | 36.8 | 5.9 |
| $C_4H_6$ | 1,3-Butadiene | 146 | 111 | . . . |
| | Cyclobutene | . . . | 94.2 | 19.4[d] |
| | Bicyclobutane | . . . | . . . | 41.9[d] |
| $C_4H_8$ | 1-Butene | 147 | 49.7 | 7.8 |
| | Isobutylene | 136 | 53.5 | 8.0 |
| | *trans*-2-Butene | 136 | 62.8 | 9.6 |
| | Methylcyclopropane | . . . | 65.3 | . . . |
| | *cis*-2-Butene | 142 | 75.7 | 11.5 |
| | Cyclobutane | . . . | 79.4 | 15.2[d] |

[a] Hot wire detector, helium carrier gas. [b] Relative molar response = [(area per mole of compound)/(area per mole of ethylene)] 100. [c] All times measured from the point of injection. [d] These figures obtained at 50 $cm^3$/min helium flow, the others on the column at 120 $cm^3$/min.

Table IX. Relative Molar Responses and Retention Times of Liquid Products on Glpc Column 79[a]

| Compound | Response | Retention time,[b] min |
|---|---|---|
| Crotyl alcohol | *c* | 7 |
| Allylcarbinol | 0.82 | 9 |
| Cyclobutanol | 1.04 | 12 |
| Cyclopropylcarbinol | Unity | 14 |
| Cyclopropylcarbinyl cyclopropaneacetate | *d* | 45 |
| Cyclobutyl cyclopropaneacetate | *d* | 39 |
| Allylcarbinyl cyclopropaneacetate | *d* | 33 |

[a] Argon carrier gas, ionization detector. [b] All times measured from point of injection. [c] Taken to be the same as allylcarbinol. See footnote *d*, Table VIII. [d] Assumed to be the same as cyclopropylcarbinol. The other esters had very similar retention times.

isolation of the products was accomplished with preparative glpc using tris(cyanoethoxy)propane as the substrate. Several different columns were made up; all had the disadvantage of bleeding. After this work had been completed, Berson, *et al.*,[22] reported that this bleeding could be eliminated if, before use, a methylene chloride solution of the substrate were percolated through alumina (Woelm, basic activity grade III). Some exploratory work by R. A. Plepys of this laboratory indicated however, that this alumina treatment decreases the effectiveness of the substrate.

**Synthesis of Esters, $C_4H_7OCOC_4H_7$.** In the electrolyses the cations formed can be trapped by solvent (water in this study) or by carboxylate. Since each of the three acids under consideration yields substantial amounts of three alcohols, cyclopropylcarbinol, cyclobutanol, and allylcarbinol, it might be expected that some of the corresponding esters would be formed also. These esters were synthesized: cyclopropylcarbinyl cyclopropaneacetate, cyclobutyl cyclopropaneacetate, allylcarbinyl cyclopropaneacetate, cyclopropylcarbinyl cyclobutanecarboxylate, cyclobutyl cyclobutanecarboxylate, allylcarbinyl cyclobutanecarboxylate, cyclopropylcarbinyl allylacetate, cyclobutyl allylacetate, and allylcarbinyl allylacetate. The method was to mix, in a capillary melting point tube about 10 μl each of the appropriate acid and alcohol, and to allow the tubes to stand in a warm place for several days. Glpc analysis of the contents of the tubes on column 79 showed peaks for the alcohol, the ester, and, at great retention time, the acid. These retention times provided the only identification of the esters formed in the electrolyses.

**Bicyclobutane.** This material was not actively sought among the products of the cyclobutyl cation although under certain conditions it becomes an important product in the deamination of cyclobutylamine.[23] The presence of bicyclobutane was detected initially in the nmr spectrum of the gaseous products of the electrolysis of cyclobutanecarboxylic acid. In addition to the expected absorptions (cyclobutane at 1.96 ppm; cyclobutene, two singlets at 4.03 and 2.54 ppm in ratio 2:1),[24] two small, rather broad peaks were noted at about 0.43 and 1.4 ppm in ratio 1:2. The chemical shifts and the area ratio are correct for bicyclobutane.[25] Further support for this assignment was obtained by comparison with known retention times[26] of the products on column 50. The relative amounts of cyclobutene, cyclobutane, and bicyclobutane were the same whether determined from the nmr spectrum or from the glpc trace.

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[23] J. Bayless, L. Friedman, J. A. Smith, F. B. Cook, and H. Shechter, *ibid.*, **87**, 661 (1965).

[24] K. B. Wiberg and B. J. Nist, *ibid.*, **83**, 1226 (1961).

[25] D. M. Lemal, F. Monger, and G. W. Clark, *ibid.*, **85**, 2529 (1963).

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**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 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 basic 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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[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).

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# Reactions of Triatomic Carbon with Alcohols

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*Received September 18, 1968*

**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.

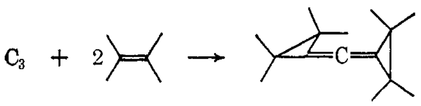
The cocondensation near −196° of chlorine (a large excess) and carbon vapor produces $CCl_4$, $C_2Cl_4$, $C_2Cl_6$, $C_3Cl_6$, and $C_3Cl_8$. The latter, hexachloropropene and octachloropropane, isolated in 2:1 ratio, are products resulting from addition of chlorine to $C_3$. The primary product could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

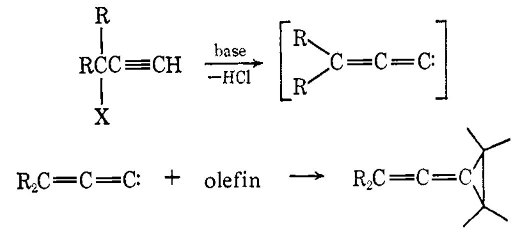
The absolute yield, although subject to some uncertainty, indicates the $C_3$ content of the carbon vapor to be between the limits 12 and 20%. The summation of the known $C_3$ products from similarly produced carbon vapor and other substrates, *vide infra*, indicate the lower limit to be the preferred 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 reported[4] 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). Hartzler[5–7] 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.





Previously[8] 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-

$$2ROH + C_3 \longrightarrow (RO)_2CHC{\equiv}CH$$

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[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.

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