Protonated Cyclopropane Intermediates in the Reactions of Cyclopropanecarboxylic Acids

N. C. Deno, W. E. Billups, Daniel LaVietes, Philip C. Scholl, and Samuel Schneider

Contribution from the Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802. *Received November 25, 1969*

Abstract: Cyclopropanecarboxylic acids undergo ring opening in H_2SO_4. In two examples, cyclopropanecarboxylic acid and its 1-methyl derivative, running the reaction in D_2SO_4 led to deuterium scrambling in the products. This indicates protonated cyclopropane intermediates. Both compounds are characterized by the absence of opportunity for direct opening to a secondary or tertiary alkyl cation. In six other examples, such opportunity existed and the products arose *via* classical cations.

Protonated cyclopropanes are intermediates in the addition of acids,[1-3] acetyl chloride,[4] and bromine[5] to cyclopropane. They account for hydrogen scrambling in 2-butyl cation,[6] scrambling of carbon label in 1-bromopropane,[7,8] and certain acid-catalyzed rearrangements of alkanes.[9] They have been recognized for some time as important components of mass spectra.[10-14] Their structures have been examined by MO calculations.[15,16] In bicyclic systems, they have been directly observed by nmr[17] and a protonated cyclopropane structure is now favored for the much discussed norbornyl cation.[18] Finally, some of the minor products from deamination of amines, deoxideation of alcohols, electrolysis of carboxylates, and solvolyses of esters are formed *via* protonated cyclopropanes.[19]

(1) R. L. Baird and A. Aboderin, *Tetrahedron Lett.*, 235 (1963); *J. Amer. Chem. Soc.*, **86**, 252 (1964).
(2) N. Deno, D. LaVietes, J. Mockus, and P. C. Scholl, *ibid.*, **90**, 6457 (1968).
(3) C. C. Lee and L. Gruber, *ibid.*, **90**, 3775 (1968); C. C. Lee, W. K. Chwang, and K. Wan, *ibid.*, **90**, 3778 (1968); C. C. Lee, L. Gruber, and K. Wan, *Tetrahedron Lett.*, 2587 (1968).
(4) H. Hart and R. H. Schosberg, *J. Amer. Chem. Soc.*, **88**, 5030 (1966); **90**, 5189 (1968); H. Hart and O. E. Curtis, Jr., *ibid.*, **79**, 931 (1957).
(5) N. Deno and D. N. Lincoln, *ibid.*, **88**, 5357 (1966).
(6) M. Saunders and E. L. Hagen, *ibid.*, **90**, 6881 (1968); M. Saunders, E. L. Hagen, and J. Rosenfeld, *ibid.*, **90**, 6882 (1968).
(7) G. J. Karabatsos, J. L. Fry, and S. Meyerson, *Tetrahedron Lett.*, **38**, 3735 (1967).
(8) N. A. Frigerio and M. J. Shaw, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Organic Section, No. 6.
(9) D. M. Brouwer and J. M. Oelderik, *Rec. Trav. Chim.*, **87**, 723 (1968); D. M. Brouwer and J. A. Van Doorn, *ibid.*, **88**, 573 (1969); D. M. Brouwer, *ibid.*, **87**, 1435 (1968); **88**, 9 (1969).
(10) P. H. Rylander and S. Meyerson, *J. Amer. Chem. Soc.*, **78**, 5799 (1956).
(11) F. W. McLafferty, "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, p 319.
(12) H. M. Grubb and S. Meyerson, ref 11, p 518.
(13) F. Cacace, M. Caroselli, R. Cipollini, and G. Ciranni, *J. Amer. Chem. Soc.*, **90**, 2222 (1968).
(14) V. Aquilanti, A. Galli, A. Giradini-Guidoni, and G. G. Volpi, *Trans. Faraday Soc.*, **64**, 124 (1968).
(15) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964).
(16) T. Yonezawa, K. Shimizu, and H. Kato, *Bull. Chem. Soc. Jap.*, **40**, 1302 (1967).
(17) P. R. Story and M. Saunders, *J. Amer. Chem. Soc.*, **84**, 4876 (1962); P. R. Story, *et al.*, *ibid.*, **85**, 3630 (1963); H. G. Richey, Jr., and R. K. Lustgarten, *ibid.*, **88**, 3136 (1966); R. K. Lustgarten, M. Brookhart, and S. Winstein, *ibid.*, **89**, 6350 (1967); M. Brookhart, R. K. Lustgarten, and S. Winstein, *ibid.*, **89**, 6352 (1967).
(18) G. A. Olah and A. M. White, *ibid.*, **91**, 3954, 3956, 5801 (1969); G. A. Olah, J. R. DeMember, C. Y. Liu, and A. M. White, *ibid.*, **91**, 3958 (1969); G. Klopman, *ibid.*, **91**, 89 (1969).
(19) Most of the extensive literature may be found in ref 3 and 4 and in L. Friedman and A. T. Jurewicz, *ibid.*, **91**, 1800 (1969).

In the additions to cyclopropanes, the characteristic features which have demonstrated protonated cyclopropane intermediates are (1) direct hydrogen–deuterium exchange with solvent which leads to multiple introduction (or elimination) of deuterium, (2) scrambling of deuterium or carbon label in the 1-propyl products, and (3) formation of products that arise from 1,1 and 1,2 addition as well as 1,3 additions. Up to now, the above have been found only in unsubstituted cyclopropane.[1,2]

These features completely disappear in additions to methylcyclopropane. The 1,3 additions of HCl and CH_3COCl have been reported.[2,4] The 1,3 additions of CF_3COOH and Br_2 to form 2-butyl trifluoroacetate and 1,3-dibromobutane are described in the Experimental Section. Most definitive is the addition of DCl which produced 2-chlorobutane-4-*d* exclusively.[2] The additions thus take place *via* the more stable 2-butyl cation rather than C_4 protonated cyclopropanes.

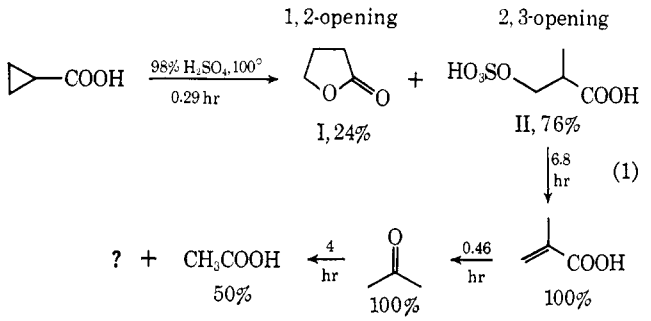
In order to discover new examples of protonated cyclopropane intermediates (in monocyclics), a study was initiated on the addition of H_2SO_4 and D_2SO_4 to cyclopropanecarboxylic acids and cyclopropyl ketones. Although scuh electron-withdrawing substituents would reduce the stability of the protonated cyclopropane, it seemed likely that the destabilization would be even greater in the classical alkyl cation.

Additions Proceeding *via* Protonated Cyclopropanes

Cyclopropanecarboxylic Acid. This acid reacts with 98% H_2SO_4 at 100°. The sequence of products, half times, and yields are summarized in eq 1. The products were identified by direct comparison of nmr bands with those of authentic material.[20] The half-time for conversion of 2-methylacrylic acid to acetone in the reaction mixture was identical with that found in independent experiments in which 2-methylacrylic acid was the initial reactant. This further identifies 2-methylacrylic acid. All of the carboxylic acids, lactones, and ketones are present in their protonated forms in 98% H_2SO_4.

When the reaction was conducted in 98% D_2SO_4, the nmr triplets of I (C-2 and C-4) appeared as superimposed doublet and triplet and the quintet (C-3) was an unresolved envelope. This immediately demon-

(20) An exception was II. The solution of II in 98% H_2SO_4 showed doublets (J = 7 cps) at δ 1.42 and 4.56 and a multiplet at 3.17–3.58 in good accord with the proposed identification.

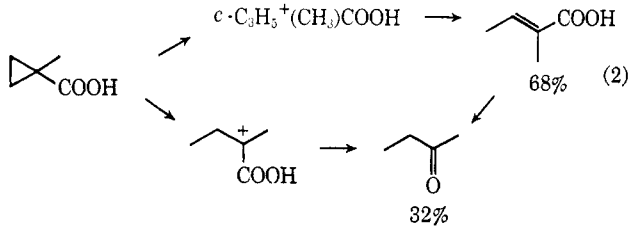


strated the presence of deuterium on all three carbons and particularly on C-3. The nmr spectrum was unchanged with time showing that I is inert to direct deuteration. All three band areas were equal showing that the entering deuteriums were statistically scrambled.

The nmr bands of II also indicated statistical scrambling of deuterium. The doublets of the α-methyl and C-3 appeared as superimposed singlet and doublet in D_2SO_4, and the relative areas were unchanged.

Experiments are in progress to determine the number of deuteriums introduced and the extent of direct deuteration of cyclopropanecarboxylic acid.

1-Methylcyclopropanecarboxylic Acid. The half-life of this acid is <5 min at 100° and 8 hr at 25°, both in 98% H_2SO_4. The initial products are 68% tiglic (*cis*-2-methyl-2-butenoic) acid[21] and 32% 2-butanone[22] (64 and 36% at 25°). Although tiglic acid degrades to 2-butanone under the reaction conditions, this is much slower (half-life 22 hr at 100°) and 2-butanone is a direct product as well as a secondary product, eq 2. The 2-butanone degrades further (half-life > 1 day) to acetic acid, a trace of propionic acid, and unknown products. The most likely route for the direct production of 2-butanone is *via* the carbonium ion as shown in eq 2 since such species are known to form ketones.[23]



Tiglic acid was isolated from a run in 98% D_2SO_4. The nmr showed methyls:vinyl H:COOH as 4.50:0.76:1. The nmr bands of the two methyl groups are nearly coincident so that the placement of the 1.50 methyl deuteriums could not be made with confidence from the nmr. However, the multiple deuteration (total of 1.84 introduced) and deuterium scrambling (1.50 on methyls and 0.34 on C-3) implicate protonated cyclopropane intermediates, particularly since tiglic acid does not deuterate under the reaction conditions.

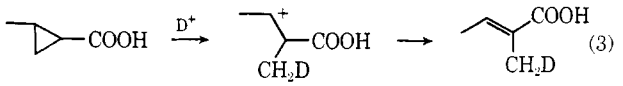
The C-3 nmr band was an unresolved envelope rather than the quartet of the undeuterated acid. This indicated comparable amounts of H and D on C-4. It also provided a little evidence for the *a priori* expectation that the α-methyl would not be deuterated.

2-Butanone produced in D_2SO_4 was completely α-deuterated, but this is of no significance since 2-butanone itself undergoes rapid α-deuteration at 100°.

Although the results with cyclopropanecarboxylic acid and its 1-methyl derivative leave many details unanswered, they do demonstrate that the characteristics of protonated cyclopropane intermediates appear in suitably chosen substituted cyclopropanes.

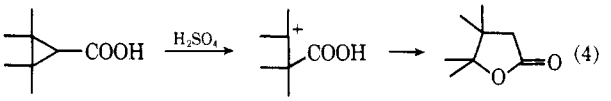
Additions Proceeding *via* Classical Cations

2-Methylcyclopropanecarboxylic Acid. Ring opening in 98% H_2SO_4 has a half-time of 0.5 day at 25° and 5 min at 100°. The initial product is tiglic acid in >90% yield. Tiglic acid from a run in 98% D_2SO_4 at 100° showed methyls:vinyl H:COOH of 5.1:1:1. The shapes of the doublet and quartet were identical with those of normal tiglic acid which indicated that the single D had been introduced on the α-CH_3, eq 3. The broadened α-CH_3 band lay under the doublet of the C-4 methyl, and it was not possible to resolve and directly compare the areas of the two methyl bands.



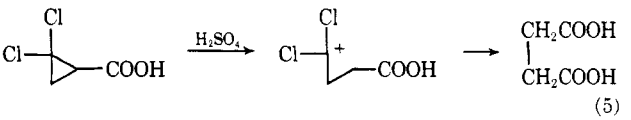
2,2,3,3-Tetramethylcyclopropanecarboxylic Acid. In eq 3, opening to a secondary alkyl cation prevailed. It was to be expected that the presence of *gem*-dimethyl substituents would lead to opening to a *t*-alkyl cation, eq 4.

Ring opening was complete in 3 days in 98% H_2SO_4 at 25°. The dominant product is 3,3,4,4-tetramethylbutyrolactone (eq 4) which was identified by melting point (98–100°, lit.[24] mp 100°) and nmr spectrum.[25] The yield was 72% (nmr band areas) and 62% (isolated). The low yield is probably a result of polymerization of the intermediate cation and its conjugate alkene. Participation by the carboxyl group in stabilizing the intermediate carbonium ion may be a factor.



In comparing eq 3 and 4, there is one puzzling feature. In eq 3, the ring opening was 2,3 whereas in eq 4 it is 1,2.

2,2-Dichlorocyclopropanecarboxylic Acid. Chloro substituents stabilize carbonium ions nearly as effectively as alkyl groups.[26] Direct opening to $-C^+Cl_2$ was expected and the formation of succinic acid (nmr band at 3.19 in 98% H_2SO_4) in 100% yield, eq 5, substantiated this expectation.



(21) Nmr spectrum in 98% H_2SO_4: superimposed singlet (1.94) and doublet (2.02, J = 7 cps) and a quartet (7.81, J = 7 cps) in the ratio 6:1.

(22) Nmr spectrum in 98% H_2SO_4: triplet (1.26, J = 7 cps), singlet (2.85), and multiplet 2.97–3.50.

(23) For examples and references see N. Deno, G. W. Holland, Jr., and T. Schulze, *J. Org. Chem.*, **32**, 1496 (1967).

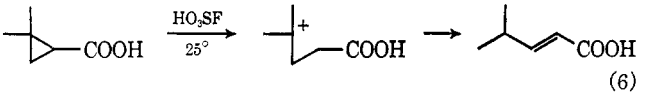
(24) H. E. Baumgarten, *J. Amer. Chem. Soc.*, **75**, 979 (1953).

(25) Varian NMR Spectra Catalog, Varian Associates, Palo Alto, Calif., 1962, spectrum no. 214.

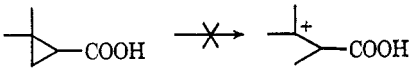
(26) R. H. Martin, F. W. Lampe, and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 1353 (1696).

2,2-Dimethylcyclopropanecarboxylic Acid. In 98% H_2SO_4, the products were polymeric. This in itself suggests the 1,2 opening to a *t*-alkyl cation, eq 6, rather than the 2,3 opening, eq 7. The latter would be expected to tautomerize quickly to the protonated α,β-unsaturated acid, a structural type which is stable in 98% H_2SO_4.[27]

In HO_3SF, a carboxylic acid was produced in >90% yield (by nmr) which could be isolated by dilution and CH_2Cl_2 extraction. The nmr spectrum of the acid in CCl_4 provided reasonably definitive identification of the product as *trans*-4-methyl-2-pentenoic acid, eq 6. The spectrum consisted of a doublet (1.06, J = 6.5 cps, *gem*-dimethyl), multiplet (2.29–2.85, C-4), doublet (5.77, J = 15.5 cps, C-2, fine splitting evident), multiplet of 4 peaks (7.07, C-3), and a singlet (12.00, COOH) in the ratios 6:1:1:1:1. The J = 15.5 indicates a *trans* CH=CH. The first four-band systems were shifted downfield to 1.10, 2.40–3.03, 6.18, and 8.00 in 98% H_2SO_4. These shifts are comparable to those of other α,β unsaturated acids when converted to their protonated forms in strong acids.[27]



(6)

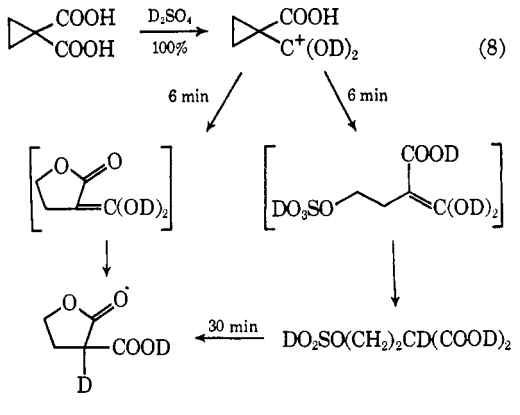


(7)

The Displacement Mechanism

1,1-Cyclopropanedicarboxylic acid was reported to form 2-carboxybutyrolactone in 96% H_2SO_4 at 121°.[28] A more detailed examination at 100° by nmr shows that the initial products are equal amounts of the lactone and another species which is most probably HO_3SOCH_2-$CH_2CH(COOH)_2$, identification described in Experimental Section. This latter species changes to the lactone so that after 4 hr at 100°, only lactone is present.

In D_2SO_4, the lactone was shown to contain deuterium only at C-2.[28] The mechanism proposed[28] must be slightly modified to account for nucleophilic attack by HSO_4^- as well as the internal COOH. Equation 8 summarizes the sequences and accounts for deuterium on C-2.



(8)

(27) N. Deno, C. U. Pittman, Jr., and M. J. Wisotsky, *J. Amer. Chem. Soc.*, 86 4370 (1964).

(28) J. Bus, H. Steinberg, and T. J. deBoer, *Tetrahedron Lett.*, 1979 (1966).

Cyclopropylcarbonium ions undergo concerted ring opening and nucleophilic attack on the β-carbon, and this is their primary mode of decomposition.[29] Addition of a proton to the C=O of a cyclopropanecarboxylic acid or a cyclopropyl ketone generates a cation that can be written as a hydroxy-substituted cyclopropyl carbonium ion and could undergo the analogous type of ring opening. Equation 8 illustrates this mechanism. The formation of products derived from both COOH and HSO_4^- attack is strong evidence for a nucleophilic displacement on a carbonium ion.

It is curious that cyclopropane mono- and dicarboxylic acids show such different modes of opening, eq 1 and 8.

trans-1,2-Cyclopropanedicarboxylic acid is inert to both ring opening and deuteration for 1 day in 98% D_2SO_4 at 100°.

During the course of this work, a paper appeared on the opening of a series of cyclopropyl methyl ketones in sulfuric acid.[30] In every case 1,3 opening occurred to the cyclic oxonium ion derived from the 5-hydroxy-2-alkanone.[30] This result had been previously found for cyclopropyl methyl ketone and the 5-hydroxy-2-pentanone had been isolated by dilution and identified.[31] In view of the strict 1,3 opening, protonated cyclopropane intermediates seem unlikely despite this suggestion in the literature.[30] It is attractive to formulate these openings as analogous to that in eq 8.

Conclusions

For the ring openings observed herein, a simple principle correlates the data. Protonated cyclopropanes are intermediate in stability between primary and secondary carbonium ions.[2,6] Where a secondary or tertiary alkyl cation can form by H^+ addition, the reaction proceeds *via* these classical intermediates. Where only primary carbonium ions or COOH destabilized ions are available, the reaction proceeds by the alternant nonclassical protonated cyclopropane path.

However, there are reasons for doubting the generality of the above. The trimethylbutyl cation exhibits a single nmr band at −180°[32] so that the bridged (protonated cyclopropane) geometry is within 2–3 kcal of that of the tertiary cation and is likely of the order of 12 kcal[33] more stable than isomeric secondary alkyl cations. Similarly, in the 2,4-dimethyl-2-pentyl cation, the protonated cyclopropane geometry is within 6.5 kcal of the energy of the *t*-alkyl cation whereas at least the barrier to forming the secondary cation (by 1,2 H^- shift) is much larger.[34] In bicyclic systems, the bridged geometry can be more stable than secondary and even tertiary alkyl cations.[17]

Although the present study adds no insight regarding the structures of protonated cyclopropanes, we wish to

(29) N. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *J. Amer. Chem. Soc.*, 87, 4533 (1965).

(30) C. U. Pittman, Jr., and S. P. McManus, *ibid.*, 91, 5917 (1969).

(31) Ph.D. Thesis of A. S. Kushner, directed by H. G. Richey, Jr., Pennsylvania State University, 1966, p 117; Ph.D. Thesis of D. LaVietes, Pennsylvania State University, 1969, p 70.

(32) Dr. E. Namenworth, ref 14 of G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, 89, 4739 (1967).

(33) Secondary alkyl cations are 15 kcal less stable than tertiary (ref 6; M. Saunders and E. L. Hagen, *ibid.*, 90, 2436 (1968); D. M. Brouwer, *Rec. Trav. Chim. Pays-Bas*, 88, 9 (1969)).

(34) D. M. Brouwer and J. A. Van Doorn, *ibid.*, 88, 573 (1969); D. M. Brouwer, *ibid.*, 87, 1436 (1968).

comment briefly on this problem. Divalent hydrogen (edge protonated) and pentavalent carbon (corner protonated) structures have been favored for protonated cyclopropanes. On the basis of a nonstatistical 45:17:38 distribution of deuterium on C-3:C-2:C-1 (in the 1-propyl products from 57% D_2SO_4 and cyclopropane), Baird and Aboderin offered an ingenious argument to show that products arose from edge-protonated cyclopropane.[1] The validity of this conclusion is now questioned. A wide variety of additions of deuterated reagents to cyclopropane give the statistical 44:28:28 distribution.[2] The two examples of nonstatistical distribution (57% D_2SO_4 and DCl[2]) are curious in view of the report that more nucleophilic conditions (pH 6 in water), where c-$C_3H_6D^+$ lifetimes should be shorter and equilibration less complete, give statistical distribution.[3] Further, the largest deviation from statistical, 17% rather than 28% D on C-2, is not far from statistical. Most damaging is an internal inconsistency. Baird and Aboderin's description would require the C-3:C-1 and C-1:C-2 deuterium ratios to be *greater* than the statistical 1.5 and 1.0. The C-3:C-1 ratio is only 1.2, *less* than statistical.

What can be emphasized is that the rapidity of c-$C_3H_6D^+$ isomerizations means that edge and corner protonated structures are of comparable stability, a conclusion which appears to extend to ring protonated cyclopropanecarboxylic acid judging from the statistical distribution of deuterium observed in the products from cyclopropanecarboxylic acid.

Experimental Section

Nmr Spectra. All spectra were recorded on a Varian A-60 and band positions are expressed in δ (parts per million downfield from tetramethylsilane). In H_2SO_4 or HO_3SF, CH_2Cl_2 or $(CH_3)_4N^+$ (3.10) were used as secondary standards.

2-Butyl Trifluoroacetate. The nmr spectrum of a solution of methylcyclopropane in CF_3COOH consists of a δ 0.96 triplet (J = 7 cps, 3-4), 1.36 doublet (J = 6.5 cps, C-1), 1.48–2.03 multiplet (C-3), and a 5.02 sextet (J = 6.5 cps, C-2) in the area ratios 3:3:2:1. This spectrum identifies the product as 2-butyl trifluoroacetate.

1,3-Dibromobutane. Addition of Br_2 to methylcyclopropane in the presence of 1% iron filings at 10° gave 1,3-dibromobutane. The product was identified by its boiling point and nmr spectrum. The latter (in CCl_4) consisted of a 1.76 doublet (J = 6.5 cps, C-4), 2.0–2.5 multiplet (C-2), 3.4–3.9 multiplet (C-1), and 4.28 sextet (J = 6.5 cps, C-3) in the area ratios 3:2:2:1.

$HO_3SOCH_2CH_2CH(COOH)_2$. The nmr spectrum in 98% H_2SO_4 consisted of a multiplet at 2.67–3.20 and triplets at 4.30 (J = 9 cps) and 4.66 (J = 7.5 cps) in the area ratios 2:2:1. Under the same conditions, the nmr spectrum of 2-carboxybutyrolactone consisted of multiplets at 2.65–3.30 and 4.48–5.02 in the ratio 2:3. The identification of the sulfate rests on it being different from the lactone, its quantitative conversion to lactone, and the satisfactory nmr spectrum. Of particular importance in the latter is the position of the $-CH_2OSO_3H$ at 4.30, which is in the region of other primary alkyl hydrogen sulfates. For example, the nmr band of the α-CH_2 is 4.52 for $CH_3CH_2OSO_3H$ and 4.39 for $CH_3CH_2CH_2OSO_3H$, both in 98% H_2SO_4.

Preparation of Cyclopropanecarboxylic Acids. Cyclopropanecarboxylic acid was purchased.[35] 1,1-Cyclopropanedicarboxylic acid was prepared by hydrolysis of the dimethyl ester.[36,37] *trans*-1,2-Cyclopropanedicarboxylic acid was prepared as described.[38] 2,2-Dichlorocyclopropanecarboxylic acid was prepared in 44% yield by $KMnO_4$ oxidation of 1,1-dichloro-2-vinylcyclopropane.[39,40]

2-Methylcyclopropanecarboxylic acid was prepared by a Wittig reaction on propylene oxide.[41] A solution of 44.8 g (0.20 mol) of triethylphosphonoacetate in 25 ml of diglyme was added to a mixture of 25 ml of diglyme and 10.8 g (0.23 mol) of 51% NaH in mineral oil. When hydrogen evolution ceased, 14.5 g (0.25 mol) of propylene oxide in 25 ml of diglyme was added. The mixture was stirred for 1 day at 25° and 3 hr at 140°. A solution of 30 g of NaOH in 50 ml of water was added in the cold. The mixture was refluxed 15 hr, diluted with 200 ml of cold water, and washed with three 100-ml portions of ether.

Acidification to pH 2 with 25% H_2SO_4, extraction with six 50-ml portions of ether, drying the ether over $MgSO_4$, and distillation through a spinning band column gave 11.1 g (55%) of 2-methylcyclopropanecarboxylic acid, bp 90–97° (15 mm).[42]

1-Methylcyclopropanecarboxylic acid was prepared in 68% yield by saponification of the methyl ester. The acid had bp 105–111° (40 mm, lit.[43] bp 111°) and mp 32–34° (lit.[43] mp 34°). The ester was prepared by adding a mixture of 50 g of methyl methacrylate and 188 g of CH_2I_2 over 2 hr to 65 g of Zn–Cu couple[44] and 200 ml of ether stirred at reflux. The decanted solution was washed with excess 1 M aqueous HCl, washed with water, and dried over K_2CO_3. Distillation on a spinning band column produced 11 g (20%) of methyl 1-methylcyclopropanecarboxylate, bp 118–121° (lit.[43] bp 124°).

2,2-Dimethylcyclopropanecarboxylic acid[45] and 2,2,3,3-tetramethylcyclopropanecarboxylic acid[46] were prepared as described.

The nmr spectra of all of the above acids and the intermediates used to prepare them are reported in the Ph.D. Thesis of D. LaVietes (Pennsylvania State University, 1969).

Acknowledgment. Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this work and for funds to purchase the nmr spectrometer.

(35) Aldrich Chemical Co., Milwaukee, Wis.
(36) W. H. Perkin, Jr., *J. Chem. Soc.*, **47**, 801 (1885).
(37) A. W. Dox and L. Yoder, *J. Amer. Chem. Soc.*, **43**, 2097 (1921).
(38) K. B. Wiberg, R. K. Barnes, and J. Abin, *ibid.*, **79**, 4994 (1957).
(39) K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *ibid.*, **86**, 762 (1964).
(40) Purchased from Columbia Chemicals Co., Columbia, S. C.
(41) For other examples, see A. Maercker, *Org. Reactions*, **14**, 387 (1965).
(42) Bp *cis* acid 91.5°, bp *trans* acid 97°: D. E. Applequist and A. H. Peterson, *J. Amer. Chem. Soc.*, **82**, 2372 (1960).
(43) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 2719 (1961).
(44) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).
(45) E. R. Nelson, M. Maienthal, L. A. Lane, and A. A. Benderly, *J. Amer. Chem. Soc.*, **79**, 3467 (1957).
(46) A. P. Meshcheryakov and I. E Dolgii, *Bull. Acad. Sci. USSR*, 864 (1960).