[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN 1, N. Y.]

Ionic Polymerization. XVI. Reactions of 1-Cyclopropylethanol–Vinylcyclopropane[1-3]

BY C. G. OVERBERGER AND A. E. BORCHERT

RECEIVED MARCH 18, 1960

The pyrolysis of 1-cyclopropylethyl acetate yielded cyclopentene and smaller amounts of vinylcyclopropane and 1,4-pentadiene while the sulfuric acid-catalyzed dehydration of 1-cyclopropylethanol produced vinylcyclopropane, 2-methyltetrahydrofuran and small amounts of both cyclopentene and 1,4-pentadiene. The pyrolysis of 1-cyclopropylethyl S-methyl xanthate yielded vinylcyclopropane and a trace amount of 1,4-pentadiene while a simultaneous rearrangement of 1-cyclopropylethyl S-methyl xanthate produced 1-cyclopropylethyl methyl dithiolcarbonate. Mechanisms for these thermal and acid-catalyzed rearrangements are discussed.

Introduction

Vinylcyclopropane is the first member in a series of vinylcycloalkanes which have been prepared pure and polymerized in this Laboratory. Recently the preparation and polymerization of isomeric methylvinylcyclohexane have been reported.[4] The purpose of this paper was to evaluate several reactions of the precursor 1-cyclopropylethanol and to describe a synthesis of vinylcyclopropane.

Demjanov and Dojarenko[5] prepared vinylcyclopropane by a Hofmann exhaustive methylation of 1-cyclopropylethylamine. More recently, Van Volkenburgh, *et al.*,[6] and Slabey[7] have reported that the dehydration of 1-cyclopropylethanol with, respectively, a catalytic amount of sulfuric acid and a heated alumina catalyst yielded vinylcyclopropane together with isomeric products. The ready availability of methyl cyclopropyl ketone[8] made a transformation of 1-cyclopropylethanol a logical route for monomer synthesis. A repetition of the mineral acid-catalyzed dehydration of 1-cyclopropylethanol with complete identification of products,[6] the preparation of both 1-cyclopropylethyl acetate and 1-cyclopropylethyl S-methyl xanthate and the pyrolyses of the latter esters are described. The use of gas phase chromatography greatly facilitated the purification and isolation of products.

Discussion

1-Cyclopropylethanol and 1-Cyclopropylethyl Acetate.—Methyl cyclopropyl ketone[8] was reduced with lithium aluminum hydride,[6] 90%, and a mixture of 1-cyclopropylethanol[9] and pentanol-2 was obtained. Distillation yielded 1-cyclopropylethanol, pure by G.P.C. (gas phase chromatography), and this alcohol was esterified with a mixture of acetic anhydride and sodium acetate.[10] Acetylation with acetyl chloride was not practical since the cyclopropyl ring opened and yielded a mixture of products.[11,15]

Pyrolysis of 1-Cyclopropylethyl Acetate.—The pyrolysis[10,12] of 1-cyclopropylethyl acetate at 510–515° yielded a mixture of products, 87%. Cyclopentene, the major component, 69%, was identified with the aid of G.P.C. and infrared analysis, and the properties of this material were identical with those found for authentic cyclopentene which was obtained from the pyrolysis of cyclopentyl acetate. Similar methods aided in the identification of vinylcyclopropane, 12%, 1,4-pentadiene, 10%,[13] and isoprene and *trans*-1,3-pentadiene which were present in small amounts. Evidence that small quantities of gaseous products, such as propylene, probably were produced during the pyrolysis was also obtained.

The formation of cyclopentene probably resulted from either a one-step elimination–rearrangement (b) or from a two-step reaction (a) in which vinylcyclopropane was an intermediate, as illustrated in Fig. 1. Evidence for a two-step reaction was found when a solution of an olefin mixture containing vinylcyclopropane in acetic acid was subjected to the same pyrolytic conditions and both cyclopentene and 1,4-pentadiene were obtained. The pyrolysis of a mixture of 1,3-pentadiene and acetic acid, however, failed to yield a cyclized product; and the pyrolysis of 1,5-pentadiyl acetate yielded 1,4-pentadiene and only a trace amount of cyclopentene as evidenced by G.P.C. These latter observations coupled with the fact that the residue from the pyrolysis of 1-cyclopropylethyl acetate contained no detectable rearranged non-olefinic products made unlikely the possibility that other isomeric species were responsible for the formation of cyclopentene.

The major proportion of cyclopentene formed during the pyrolysis of 1-cyclopropylethyl acetate undoubtedly arose from a thermal rearrangement of vinylcyclopropane. The identities of the products indicated that a concerted cleavage of the three-membered ring had occurred mainly in the direction of ring substitution.[14] If the direction had been reversed, isomeric 1,3-pentadiene would have been the favored product.

---

[1] This is the 16th in a series of papers concerned with ionic polymerization.

[2] For the previous paper in this series see C. G. Overberger and M. G. Newton, THIS JOURNAL, **82**, 3622 (1960).

[3] This paper comprises a portion of a dissertation submitted by A. E. Borchert in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

[4] C. G. Overberger and J. E. Mulvaney, THIS JOURNAL, **81**, 4697 (1959).

[5] N. J. Demjanov and M. Dojarenko, *Ber.*, **55B**, 2718 (1922).

[6] R. Van Volkenburgh, K. W. Greenlee, J. M. Derfer and C. E. Boord, THIS JOURNAL, **71**, 3595 (1949).

[7] V. A. Slabey, *ibid.*, **74**, 4930 (1952).

[8] Peninsular Chem. Research, Inc., Gainesville, Fla.

[9] N. J. Demjanov and S. Pinegin, *J. Russ. Chem. Soc.*, **43**, 510 (1911).

[10] C. G. Overberger and D. Tanner, THIS JOURNAL, **77**, 369 (1955).

[11] P. Bruylants and A. Dewael, *Bull. Classe. Sci. Acad. roy. Belg.*, **14**, 140 (1928).

[12] C. G. Overberger, A. Fischman, C. W. Roberts, L. H. Arond and J. Lal, THIS JOURNAL, **73**, 2540 (1951).

[13] Prepared in this Laboratory by Dr. H. Yuki; J. S. Daraday, Ed. "Encyclopedia of Hydrocarbon Compounds," Vol. 2A, Chemical Publishing Co., New York, N. Y., 1952.

[14] E. P. Kohler and J. B. Conant, THIS JOURNAL, **39**, 1404 (1917).

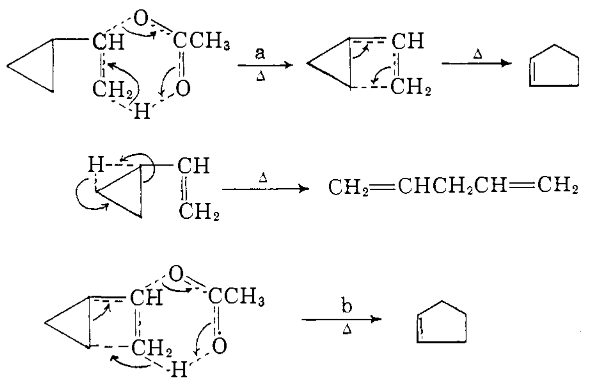


Fig. 1.—Pyrolysis of 1-cyclopropylethyl acetate.

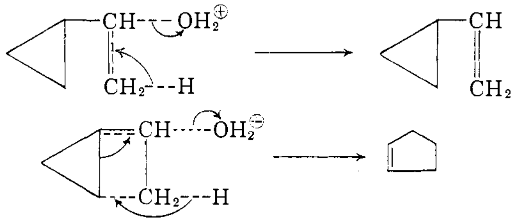
Sulfuric Acid-catalyzed Dehydration of 1-Cyclopropylethanol.—The procedure of Van Volkenburgh, *et al.*,[6] was followed and a mixture of olefins, 10%, which contained vinylcyclopropane, 83%, and small amounts of 1,4-pentadiene, 4%, and cyclopentene, 9%, was obtained. In addition, a 10% conversion to 2-methyltetrahydrofuran was found to accompany the major reaction of ring opening which resulted in the formation of unsaturated alcohols and unsaturated hydroxyethers.

The formation of olefins by a mechanism proceeding through a cyclopropylcarbinyl type carbonium ion[15] was considered, and vinylcyclopropane, cyclopentene and 1,4-pentadiene could have arisen from rearrangements of a 1-cyclopropylethyl carbonium ion. However, the formation of an oxygenated product indicated that a direct acid-catalyzed ring opening was operative to a significant extent. A combination of acid-catalyzed ring opening and dehydration is proposed to best explain these transformations without suggesting any detailed intermediate or transition state.

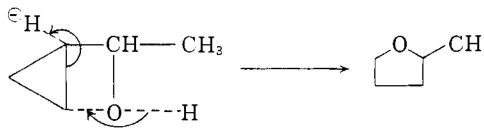
Figure 2: A preference for heterolytic ring scission in the direction of substitution probably was operative and a similarity to the observations described for the pyrolysis of 1-cyclopropylethyl acetate was noted. A possible ethylidenecyclopropane intermediate, which had been proposed for acid-catalyzed dehydrations,[16] was considered to be of little utility to the mechanism of olefin formation.

Reactions which involved ring opening could introduce the ionic conditions favorable to the formation of the unsaturated alcohols and unsaturated hydroxyethers which were observed.

(a) Acid-catalyzed dehydration



(b) Acid-catalyzed ring opening



(c) Combination of acid-catalyzed dehydration and ring opening

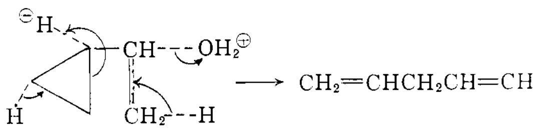


Fig. 2.—Sulfuric acid-catalyzed dehydration of 1-cyclopropylethanol.

Pyrolysis of 1-Cyclopropylethyl S-Methyl Xanthate.—1-Cyclopropylethyl S-methyl xanthate was prepared by a standard procedure[17] and isolated. The pyrolysis of this ester yielded vinylcyclopropane and trace amounts of 1,4-pentadiene and a lower boiling unidentified olefin, which might have been ethylidenecyclopropane. Conversion to olefins was 47–52% and vinylcyclopropane, 95%, was readily isolated and purified. The pyrolysis of 1-cyclopropylethyl S-methyl xanthate was used for the preparation of vinylcyclopropane suitable for polymerization studies.[18] The small amount of 1,4-pentadiene produced during the latter pyrolysis could have arisen from a coördinated elimination–rearrangement reaction, Fig. 3, or from a thermal isomerization of vinylcyclopropane. Since the transition state in thermal elimination in esters was considered to possess some degree of double bond character,[19] conditions favorable to a rearrangement probably were present. The comparatively low temperature (130–230°) reaction conditions made it appear unlikely that an isomerization of vinylcyclopropane would take place, but this possibility cannot be ruled out entirely and was not tested by experiment at these temperatures.

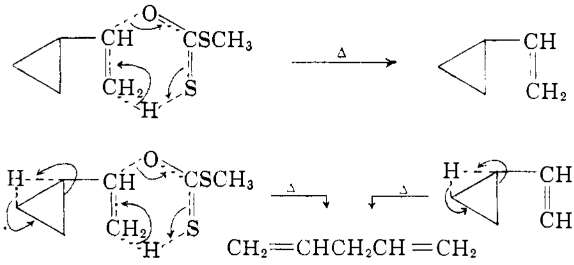


Fig. 3.—Elimination in the pyrolysis of 1-cyclopropylethyl S-methyl xanthate.

A thermal rearrangement was found to accompany the thermal elimination during the pyrolysis of 1-cyclopropylethyl S-methyl xanthate (I) and a mixture of two components which were stable at 360° was obtained. Fractionation at atmospheric pressure yielded the major, higher boiling component, 1-cyclopropylethyl methyl dithiolcarbonate (II), Fig. 4. The unidentified lower boiling, unsaturated component may have arisen from an alternate displacement by thion sulfur on an unsubstituted ring carbon to yield a 3-pentenyl methyl dithiolcarbonate. The rearrangement of xanthates[20]

---

[15] J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 2509 (1951).

[16] C. F. H. Allen and R. Boyer, *Can. J. Research*, **9**, 159 (1933).

[17] R. A. Benkeser and J. J. Hazdra, THIS JOURNAL, **81**, 228 (1959).

[18] C. G. Overberger, A. E. Borchert and A. Katchman, International Polymer Symposium, Moscow, 1960.

[19] C. H. DePuy and R. E. Leary, THIS JOURNAL, **79**, 3705 (1957).

[20] I. M. McAlpine, *J. Chem. Soc.*, 1114 (1931).

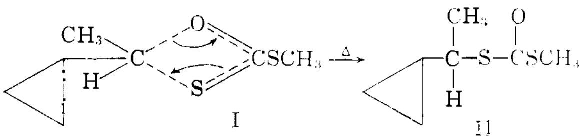


Fig. 4.—Rearrangement in the pyrolysis of 1-cyclopropylethyl S-methyl xanthate.

has been reported and dithiolcarbonates have been isolated.[21] The degree to which this undesirable rearrangement occurred during the pyrolysis of 1-cyclopropylethyl S-methyl xanthate indicated that the latter system possessed an inherent property which favored such a co-reaction. Steric factors undoubtedly are operative, but electronic factors associated with the α-carbon atom are viewed to be more important. The presence of the cyclopropyl group probably increased the electrophilicity of the α-carbon atom[22] which would facilitate the easy displacement by nucleophilic thion sulfur. It was noted that the pyrolysis of 3-cyclohexenylmethyl S-methyl xanthate,[23] where the electronic effects exerted by the ring are too distant to influence significantly the course of elimination, proceeded to 80% conversion to 4-methylenecyclohexene. In addition, the reported favored rearrangement from thion sulfur to carbonyl oxygen[24] would be expected to contribute to the driving force for rearrangement.

Infrared absorptions in the ranges 3099–3072 and 3033–2995 cm.$^{-1}$ due to carbon–hydrogen stretching modes in the three-membered carbocyclic system[25] have aided in the identification of products in the elimination and rearrangement reactions which involved 1-cyclopropylethanol and its derivatives. This analytical tool was of value in the identification of 1-cyclopropylethanethiol, which was obtained from the saponification of 1-cyclopropylethyl methyl dithiolcarbonate. The latter mercaptan was treated with 2,4-dinitrofluorobenzene[26] and a crystalline 1-cyclopropylethyl 2′,4′-dinitrophenyl sulfide also was obtained.

A description of the polymerization of vinylcyclopropane, the characterization of crystalline polyvinylcyclopropane and a discussion of reactions which yielded modified polyvinylcyclopropanes will be presented separately.[18]

Experimental

Instrumental Analysis.—Gas phase chromatography (G.P.C.) measurements were made on a Perkin–Elmer model 154-B vapor fractometer. A Perkin–Elmer model 112-G single beam infrared spectrophotometer was used to obtain carbon to hydrogen stretching frequencies in the 2850–3100 cm.$^{-1}$ region and a Perkin–Elmer model 21 double beam instrument serviced the 2–15 μ infrared region.

1-Cyclopropylethanol 9.—From 84.1 g. (1 mole) of methyl cyclopropyl ketone,[8] n^{25}_D 1.4222, and 9.6 g. (0.25 mole) of lithium aluminum hydride, a mixture of alcohols boiling at 121–123° (751 mm.), 77.3 g., 90%, was obtained. G.P.C. showed that 2-pentanol was present to approximately 5%, and rectification through a 14" packed column yielded 1-cyclopropylethanol boiling at 123–123.5° (755 mm.), n^{25}_D 1.4292, d^{25}_4 0.8848, M_D 25.11, (calcd. 25.33), C–H absorptions at 3007 and 3080 cm.$^{-1}$, O–H absorption at 3600 cm.$^{-1}$ [lit.[6] b.p. 123.5° (760 mm.), 80%, n^{20}_D 1.4316, d^{20}_4 0.8893].

1-Cyclopropylethyl Acetate.—A mixture of 90 g. (1.05 moles) of 1-cyclopropylethanol, n^{25}_D 1.4292, 214 g. (2.09 moles) of acetic anhydride and 37 g. of fused sodium acetate was allowed to react at 90° for 18 hr.,[10] cooled and added to chopped ice. The aqueous phase was extracted with ether and the organic phase, after drying, was distilled to yield material boiling at 135–141° (755 mm.), 108.3 g., 84%, which was further rectified through a 14" packed column to yield 1-cyclopropylethyl acetate boiling at 139–140° (755 mm.), 102 g., n^{25}_D 1.4140, d^{25}_4 0.9262, C–H absorptions at 3010 and 3086 cm.$^{-1}$, C=O absorption at 1735 cm.$^{-1}$. The latter ester gave a single absorption in G.P.C.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.58; H, 9.44; M_D, 34.70. Found: C, 65.71; H, 9.67; M_D, 34.59.

Pyrolysis of 1-Cyclopropylethyl Acetate.—Pyrolysis[10,12] was carried out at 510–515° in a 12 × 7/8" Pyrex glass tube packed with 7 × 7 mm. Pyrex glass Raschig rings and at an ester flow rate into the column of 0.2 ml./min. at a positive nitrogen pressure. From 123.7 g. (0.965 mole) of 1-cyclopropylethyl acetate, n^{25}_D 1.4140, 52 g., 87%, of an olefin mixture boiling at 25–45° (755 mm.) was obtained. A non-olefinic residue, 11 g., 91% conversion, was shown to be unreacted 1-cyclopropylethyl acetate.

Rectification of the olefin mixture, which contained 6 components, through a 90 theoretical plate concentric tube column yielded 9 fractions. A fraction boiling at 25–29° (755 mm.) was mainly 1,4-pentadiene by a comparison of G.P.C. graphs and infrared spectra with authentic 1,4-pentadiene.[13] Material boiling at 39.5–41.5° (755 mm.) was mainly vinylcyclopropane, while cyclopentene **A** boiled at 44° (755 mm.), 69%, n^{25}_D 1.4202, d^{25}_4 0.7664, M_D 22.50, C–H absorptions at 3060, 1615 and 905 cm.$^{-1}$.

Anal. Calcd. for C_5H_8: C, 88.16; H, 11.84. Found for cyclopentene A: C, 88.30; H, 11.74.

Cyclopentyl acetate, boiling at 152° (755 mm.), n^{25}_D 1.4290 [lit.[27] b.p. 152.5–153° (760 mm.), n^{20}_D 1.4318] was prepared and pyrolyzed as above (575–580°) to yield cyclopentene B boiling at 43.5–44° (755 mm.), 81%, n^{25}_D 1.4196, d^{25}_4 0.7630, M_D 22.57 [lit.[28] b.p. 41–42° (atm.), n^{25}_D 1.4190]. Compounds A and B were identical in both G.P.C. and infrared analysis, and an absorption at 3060 cm.$^{-1}$ [29] was found in the infrared spectrum of each of these materials.

Pyrolysis of Vinylcyclopropane.—A solution of 3 g. (0.044 mole) of an olefin mixture consisting of vinylcyclopropane, 68%, cyclopentene, 31%, and 1,4-pentadiene, 0.3%, and 15 ml. of glacial acetic acid was pyrolyzed[10,12] at 500–520° at a flow rate of 0.2–0.3 ml./min. Distillation of the pyrolysate yielded 1.5 g. (50% recovery) of material boiling in the range 20–42.5° (755 mm.). The recovered material contained cyclopentene, 70%, vinylcyclopropane, 28%, and 1,4-pentadiene, 3%.

Dehydration of 1-Cyclopropylethanol.—The procedure of Van Volkenburgh, *et al.*,[6] was followed. A mixture of 20 g. (0.232 mole) of 1-cyclopropylethanol, n^{25}_D 1.4298, and 4 drops of sulfuric acid, sp. gr. 1.84 g./ml., was boiled in a small distillation assembly. The initial pot temperature was 95° and rose to a 150° value after 10 days whereupon a light green distillate, 10 ml., which had collected was distilled to yield 1.4 g., 8.9%, of a 3-component olefin mixture boiling 25–45° (755 mm.) and 2.05 g., 10%, of 2-methyltetrahydrofuran, n^{25}_D 1.4056, boiling at 76–80° (755 mm.). Vinylcyclopropane, 83%, 1,4-pentadiene, 4%, and cyclopentene, 9%, were identified with the aid of G.P.C. and infrared analysis.

The darkly colored pot residue was washed and, after drying, was fractionated. G.P.C. and infrared analysis indicated that the material boiling at 126–170° (755 mm.) consisted largely of unidentified, unsaturated alcohols while that boiling at 170–182° (755 mm.) contained unidentified, unsaturated hydroxyethers.

---

(21) P. V. Laakso, *Suomen Kemi*, **16B**, 19 (1943).

(22) J. D. Roberts and V. C. Chambers, THIS JOURNAL, **73**, 5030 (1951).

(23) C. G. Overberger and A. E. Borchert, results to be published.

(24) C. L. O'Connor and H. R. Nace, THIS JOURNAL, **74**, 5454. (1952).

(25) S. E. Wiberly, S. C. Bunce and W. H. Bauer, *Anal. Chem.*, **32**, 217 (1960).

(26) R. W. Bost, J. C. Turner and R. D. Norton, THIS JOURNAL, **54**, 1985 (1932).

(27) A. I. Vogel, *J. Chem. Soc.*, 1809 (1948).

(28) H. Adkins and S. H. Watkins, THIS JOURNAL, **73**, 2184 (1951).

(29) E. K. Plyler and N. Acquista, *J. Research Natl. Bur. Standards*, **43**, 37 (1949), reported a 3067 cm.$^{-1}$ value for cyclopentene.

1-Cyclopropylethyl S-Methyl Xanthate.—A general procedure for xanthate preparation[17] was employed. From 46.2 g. (0.495 mole) of 1-cyclopropylethanol, $n^{25}D$ 1.4292, there was obtained 1-cyclopropylethyl S-methyl xanthate boiling at 70° (0.2 mm.), 45.7 g., 52.3%, $n^{25}D$ 1.5454, d^{25}_4 1.0878, C–H absorptions at 3005 and 3082 cm.$^{-1}$, additional absorptions at 1225 and 1050(s) cm.$^{-1}$.

Anal. Calcd. for $C_7H_{12}OS_2$: C, 47.69; H, 6.86. Found: C, 47.84; H, 7.02.

Pyrolysis of 1-Cyclopropylethyl S-Methyl Xanthate.—1-Cyclopropylethyl S-methyl xanthate was pyrolyzed[10,12] as previously described for 1-cyclopropylethyl acetate. From 21 g. (0.119 mole) of 1-cyclopropylethyl S-methyl xanthate, $n^{25}D$ 1.5454, and at 200–245°, 3.7 g., 46%, of material boiling at 25–40° (755 mm.) was obtained. The latter material was washed with 50 ml. of cold 5% aqueous sodium bicarbonate, dried over calcium hydride and distilled from sodium metal to yield 1.1 g. of a 3-component olefin mixture.

Alternatively, 1-cyclopropylethyl S-methyl xanthate (116.8 g., 0.66 mole) was boiled in a small distillation assembly. Ebullition commenced at a pot temperature of 130° and the temperature slowly rose to a steady 230° value at which it was maintained for an additional 2 hr. The distillate was treated as above to yield 20 g., 44.5%, of an olefin mixture consisting of vinylcyclopropane, 95%, 1,4-pentadiene, trace amount, and an unidentified olefin, trace amount. Rectification through a 90 theoretical plate concentric tube column yielded vinylcyclopropane boiling at 40.5–40.8° (755 mm.), $n^{25}D$ 1.4104, d^{25}_4 0.7157, C–H absorptions at 3005, 3019, 3083, 1645(s), 1020(s), and 905(s) cm.$^{-1}$ [lit.[7] b.p. 40.19° (760 mm.), $n^{20}D$ 1.4138, d^{20}_4 0.72105, 54% from 1-cyclopropylethanol by dehydration over alumina].

Anal. Calcd. for C_5H_8: C, 88.16; H, 11.84; MD, 23.34. Found: C, 88.03; H, 12.02; MD, 23.60.

1-Cyclopropylethyl Methyl Dithiolcarbonate.—The pot residue, S-methyl xanthate, above, was a two-component mixture as evidenced by G.P.C. Pyrolysis at 360° failed to cleave this material. Distillation of 61.8 g. of this material through a 7″ Vigreux column followed by rectification through a 14″ packed column yielded a yellow oil boiling at 236–237° (759 mm.), 25.2 g., $n^{25}D$ 1.5358, d^{25}_4 1.0908, which was pure in G.P.C. Absorptions at 3002 and 3082 cm.$^{-1}$ indicated that the cyclopropyl group had remained intact, and additional absorptions at 1645(s) and 868(s) cm.$^{-1}$ were noted for 1-cyclopropylethyl methyl dithiolcarbonate.

Anal. Calcd. for $C_7H_{12}OS_2$: C, 47.69; H, 6.86; S, 36.37. Found: C, 47.54; H, 7.00; S, 36.20.

1-Cyclopropylethanethiol.—1-Cyclopropylethyl methyl dithiolcarbonate (14 g., 0.079 mole), $n^{25}D$ 1.5334, was saponified essentially according to the procedure of Shriner, *et al.*[30] The mixture was acidified with acetic acid since mineral acids could open the cyclopropyl group. The aqueous phase was extracted with ether and the organic phase, after washing with 5% aqueous sodium bicarbonate and drying, was distilled to yield 1-cyclopropylethanethiol boiling at 115–115.5° (758 mm.), 2.5 g., 31%, $n^{25}D$ 1.4626, d^{25}_4 0.8836, C–H absorptions at 3004 and 3079 cm.$^{-1}$.

Anal. Calcd. for $C_5H_{10}S$: C, 58.76; H, 9.86; S, 31.37; MD, 31.50. Found: C, 58.85; H, 9.50; S, 31.78; MD, 31.83.

1-Cyclopropylethanethiol was treated with 2,4-dinitrofluorobenzene essentially according to the procedure of Bost, *et al.*,[26] and an orange-yellow crystalline sulfide melting at 74.5–75° was obtained.

Acknowledgment.—The assistance given by Miss M. Caldera, Mr. S. Abramowitz and Dr. R. Bauman in obtaining and interpreting infrared data was deeply appreciated. This research was supported by the United States Air Force under Contract No. AF 33(616)-5253, monitored by the Materials Laboratory, Wright Air Development Center, Wright–Patterson Air Force Base, Ohio.

Summary.—(1) 1-Cyclopropylethyl acetate was prepared and pyrolysis of this material yielded cyclopentene and smaller amounts of vinylcyclopropane and 1,4-pentadiene. (2) 1-Cyclopropylethanol yielded vinylcyclopropane, 2-methyltetrahydrofuran and small amouuts of both 1,4-pentadiene and cyclopentene when subjected to sulfuric acid-catalyzed dehydration. (3) 1-Cyclopropylethyl S-methyl xanthate was prepared and pyrolysis of this material yielded vinylcyclopropane and 1-cyclopropylethyl methyl dithiolcarbonate.

(30) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., Fourth Ed., 1956, p. 236.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA, MINNEAPOLIS 14, MINN.]

Inductive Effects on the Acid Dissociation Constants of Mercaptans[1]

BY MAURICE M. KREEVOY, EDWIN T. HARPER, RICHARD E. DUVALL, HERBERT S. WILGUS, III, AND LEROY T. DITSCH

RECEIVED MARCH 24, 1960

The acid dissociation constants of a number of mercaptans have been measured by a variety of methods. These constants, along with some taken from the literature, have been correlated with the Taft σ^*-parameters. The correlation holds for eleven mercaptans but fails for thiophenol and hydrogen sulfide. The former is attributed to a resonance effect, the latter to a steric effect on solvation.

A knowledge of the acid dissociation constants of simple mercaptans is fundamental to an understanding of the chemistry of these compounds for two reasons. First, many important reactions of mercaptans may proceed through the mercaptide ions, and secondly the acid dissociation constants can give important information about the distribution of electrons in mercaptans.[2] In spite of this, there seem to be only a small number of such constants available,[2–10] and most of these are

---

(1) This research was supported, in part, by the U. S. Army Medical Research and Development Command through contract DA-49-193-MD-2027 and in part by the National Science Foundation through grant No. N.S.F.-G5434. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) M. Calvin in S. Colowick, *et al.*, "Glutathione," Academic Press, Inc., New York, N. Y., 1954, Chap. 1.

(3) G. Schwarzenbach, *Helv. Chim. Acta*, **15**, 1468 (1932).

(4) G. Schwarzenbach and H. A. Egli, *ibid.*, **17**, 1176 (1934).

(5) G. Schwarzenbach and A. Epprecht, *ibid.*, **19**, 169 (1936).

(6) G. Schwarzenbach and H. A. Egli, *ibid.*, **22**, 260 (1939).

(7) D. L. Yabroff, *Ind. Eng. Chem.*, **32**, 257 (1940).

(8) W. H. Fletcher, THIS JOURNAL, **68**, 2726 (1946).

(9) J. Maurin and R. A. Paris, *Compt. rend.*, **232**, 2428 (1951).

(10) F. G. Bordwell and H. M. Anderson, THIS JOURNAL, **75**, 6019 (1953).