sition 2% MP-635-S,[18] 0.5% Daxad-11,[19] *p*H 3.5, and 2 *M* sodium acetate was prepared the day immediately preceding polymerization and was stored under nitrogen in a tightly stoppered flask. The initiator–activator solution was freshly prepared on the day of polymerization by dissolving 2.150 g. of ammonium persulfate, 1.108 g. of sodium bisulfite and 0.110 g. of cupric sulfate pentahydrate in redistilled, oxygen-free water and diluting to a volume of 100 ml. Four-ounce screw-cap bottles fitted with self-sealing GR-A rubber gaskets which had previously been flushed with nitrogen were used for polymerizations.

Monomer charges were prepared by weighing equimolar quantities of monomers, 40.0000 g. (0.1345 mole) of monomer X and 20.2171 g. (0.1345 mole) of freshly distilled hexamethylenedithiol, into a flask. After swirling gently for 15 minutes, in order to assure complete homogeneity, 5-ml. aliquots (*ca.* 4.7 g.) were withdrawn and added to the polymerization bottles containing 50 ml. of emulsifier–buffer solution and 1 ml. of initiator–activator solution. The bottles were then sealed, capped tightly, and tumbled end-over-end in a 30° constant temperature bath for five days. The latices were coagulated by pouring into 20 ml. of alum coagulant solution prepared by dissolving 100 g. of potassium aluminum sulfate in a solution of 100 ml. of concentrated hydrochloric acid and 1 l. of distilled water. The polymers were isolated by decantation and then washed by decantation with one 50-ml. portion of water and three 50-ml. portions of a 40–10 methanol–water solution. The samples were dried in a vacuum desiccator until a constant weight was obtained.

Inherent viscosities were determined by means of a modified Ostwald viscometer at 25° using 0.200-g. samples dissolved in 50 ml. of chloroform. Polymer was obtained with inherent viscosities from 0.09 to 0.13.

An analytically pure polymer was obtained by dissolving a sample of the crude polymer in 10 ml. of chloroform, filtering through a 100-mesh stainless steel screen and reprecipitating by pouring the solution into a solution of 90 ml. of methanol and 10 ml. of water. The reprecipitated polymer was isolated by decantation and dried under diminished pressure (0.5 mm.) for three days in an Abderhalden vacuum drying apparatus heated to 80°. The polymer thus obtained had an inherent viscosity of 0.134. The infrared spectrum (chloroform) contains bands assignable to an aliphatic ester and ethyl carbamate (1708–1720, 1210–1240 cm.$^{-1}$) and to a carbamate N-H (3420 cm.$^{-1}$).

Anal. Calcd. for $C_{22}H_{41}NO_4S_2$: C, 59.02; H, 9.23; S, 14.32. Found: C, 59.02; H, 9.03; S, 14.62.

Hydrolysis of Polymer XI to Polyampholyte XII.—Four and four-tenths grams of polymer XI having an inherent viscosity of 0.103 was dissolved in 25 ml. of redistilled benzene and placed in a 100-ml. platinum dish. To this solution was added 50 ml. of distilled water and 10.0 g. of sodium hydroxide. The dish was placed in drying oven heated to 60° overnight in an effort to remove the benzene. The dish was then covered with a watch glass, and placed in an autoclave, where it was heated to approximately 125° in a pressure of 24 p.s.i. for eight days. The product was obtained in the form of a partially soluble soap-like oil. Addition of distilled water brought about almost complete water solubility. The water dispersion was filtered through fluted filter paper, the filter paper was washed several times with water, and the combined filtrate and washings were cooled in an ice-bath. The solution was neutralized slowly with constant rapid stirring with very dilute ice-cold hydrochloric acid. A cloudiness began to appear at a *p*H 9. An emulsion-like product was obtained at a *p*H 6. The suspension was diluted to about 600 ml. with water, transferred to dialysis bags and dialyzed for three days. The dialyzed, salt-free product was then transferred to a 1-l. flask and lyophilized to dryness. The product was obtained in the form of a white, fluffy powder which is soluble in wet tetrahydrofuran, 50–50 dioxane–water and anhydrous sulfuric acid. A yield of 3.2 g. (94%) was recovered, m.p. 104–108°. The infrared spectrum (Nujol) contains bands assignable to an amine N-H (3160, 2700 cm.$^{-1}$), to an acid (2700, 1690 cm.$^{-1}$), to a zwitterion (1645–1655 cm.$^{-1}$) and to an $-NH_3^+$ group (1550 cm.$^{-1}$).

Anal. Calcd. for $C_{17}H_{33}NO_2S_2$: C, 58.74; H, 9.57; N, 4.03. Found: C, 58.70; H, 9.70; N, 3.75.

URBANA, ILLINOIS

---

[18] This is a mixed sixteen carbon sodium alkane–sulfonate emulsifier obtained from Dr. Stanley J. Detrick, E. I. du Pont de Nemours and Co.

[19] Obtained from Dewey and Almy, Cambridge, Mass. It is a polymerized sodium salt of an alkyl aryl sulfonic acid.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Cyclopropene. I. The Reaction of 2-Bromocyclopropanecarboxylates with Potassium *t*-Butoxide

BY KENNETH B. WIBERG, ROBERT K. BARNES[1] AND JERRY ALBIN

RECEIVED JANUARY 10, 1957

The reaction of ethyl 2-bromocyclopropanecarboxylate with potassium *t*-butoxide in *t*-butyl alcohol gave ethyl 2-*t*-butoxycyclopropanecarboxylate instead of ethyl cyclopropenecarboxylate. The reaction was shown to involve loss of hydrogen bromide followed by Michael addition of *t*-butyl alcohol by effecting the reaction in a deuterium labeled solvent. Evidence is also presented that the vinyl hydrogen in the intermediate unsaturated ester is sufficiently acidic to exchange easily with the solvent in the presence of potassium *t*-butoxide.

Many investigations have dealt with the effect of "ring strain" on the properties of cyclopropene and related compounds.[2] It should be possible to obtain further useful information on this subject by studying compounds which are more "strained" than cyclopropane, since the unsaturated properties then should become even more prominent. One compound of this type is cyclopropene.[3]

If one considers the model of cyclopropane which has been proposed by Coulson and Moffitt[4] and by Walsh,[5] it would appear that the introduction of a double bond into the molecule would lead to the development of some acetylenic character. This is particularly interesting because of the relatively large difference in properties between the alkenes and the alkynes, as for example in their acidity. In this connection, the corresponding acid cyclopropenecarboxylic acid is also of interest, since whereas butyric and crotonic acids have

---

[1] Taken from part of a thesis submitted by R. K. Barnes to the University of Washington in partial fulfillment of the requirements of the Ph.D. degree, 1955. Shell Oil Co. fellow 1953–1954.

[2] *Cf.* E. Vogel, *Fortschr. Chem. Forsch.*, **3**, 430 (1955).

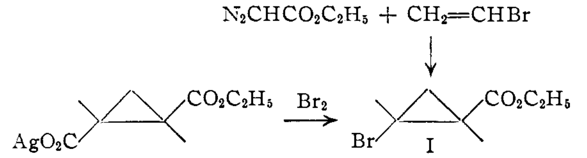
[3] N. J. Demjanov and M. Dojarenko, *Ber.*, **56**, 2200 (1923); M. J. Schlatter, THIS JOURNAL, **63**, 1733 (1941); K. B. Wiberg, Abst. 131st National Meeting, American Chemical Society, Miami, Florida, 1957, p. 39–40.

[4] C. A. Coulson and W. E. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947); *Phil. Mag.*, **40**, 1 (1949).

[5] A. D. Walsh, *Nature*, **159**, 164 (1947); *Trans. Faraday Soc.*, **45**, 179 (1949).

about the same acid dissociation constants, tetrolic acid is about two hundred times as acidic as these acids.[6] To whatever extent cyclopropene resembles ethylene, cyclopropene should resemble acetylene to an even greater extent since it has greater classical "ring strain." Thus an examination of the acidity of cyclopropenecarboxylic acid would be of importance.

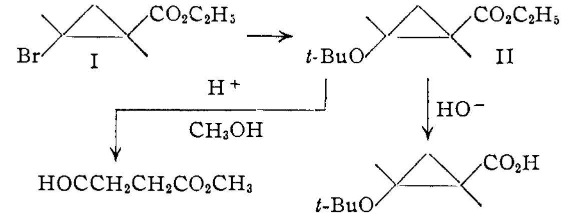
One of the most attractive routes to a derivative of cyclopropenecarboxylic acid is the elimination of hydrogen bromide from a 2-bromocyclopropanecarboxylate. The latter may be prepared by the brominative decarboxylation of the silver salt of a 2-carbalkoxycyclopropanecarboxylic acid or by the reaction of vinyl bromide with diazoacetic ester. The product obtained by either of these methods was identical.

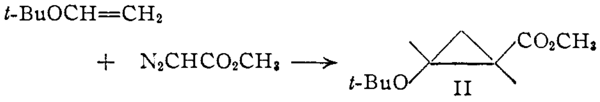


The methyl ester had a dipole moment of 1.82 D. The dipole moment of cyclopropyl bromide is 1.69[7] and that for methyl cyclopropanecarboxylate was found to be 1.81 D. If the carbon–hydrogen bond moments are neglected, the dipole moment of the *trans* isomer is calculated to be 2.0 D. (using 70° as the angle of inclination for the carbomethoxy group).[8] Similarly, the dipole moment for the *cis* isomer was calculated (using 51° as the angle between the two substituents on the cyclopropane ring) to be 1.8 when the methoxy group was directed toward the bromine and 3.5 when it was directed away. The latter is the more likely condition, and thus the dipole moment of the *cis* compound should be greater than the average of these values (2.7). This indicates that the bromo ester has the *trans* configuration.[9]

The halogen in the bromo ester I was quite inert, and it failed to react with either sodium iodide in acetone or with alcoholic silver nitrate solution.[10] Alkaline hydrolysis of I gave 2-bromocyclopropanecarboxylic acid in good yield. Compound I could also be distilled from quinoline at atmospheric pressure without decomposition. However, when compound I was treated with potassium *t*-butoxide in *t*-butyl alcohol, a rapid, slightly exothermic reaction was noted, and a precipitate of potassium bromide was obtained. The product of the reaction was not ethyl cyclopropenecarboxylate but rather a saturated, halogen-free ester.

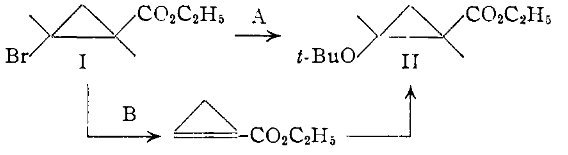
A reasonable possibility for the structure of the new ester II was ethyl 2-*t*-butoxycyclopropanecarboxylate, which corresponds to the observed empirical formula. Confirmation of this structure was found in the hydrolysis of II to a carboxylic acid with base, and by acid cleavage in the presence of methanol to methyl β-formylpropionate. Finally, the methyl ester corresponding to II was prepared by the reaction of *t*-butyl vinyl ether with methyl diazoacetate. Hydrolysis gave a carboxylic acid identical with that from II.





The dipole moment of II was found to be 1.96 D. The difference in calculated moments of the *cis*- and *trans*-esters is too small to be used in determining the configuration of II. However, the fact that prolonged heating of II with potassium *t*-butoxide in *t*-butyl alcohol did not change it indicates that it probably has the more stable configuration, which is undoubtedly *trans*.

It was of interest to determine the course of the reaction. Two routes appear possible. The first involves direct displacement of the halogen by *t*-butoxide ion, and the second involves the formation of ethyl cyclopropenecarboxylate followed by Michael addition of *t*-butyl alcohol.



The first of these possibilities appears the less likely since no other nucleophilic reagent would react with I and since *t*-butoxide ion does not react with isopropyl bromide under the conditions used. The second possibility may also be suspect since it involves the formation of a cyclopropene derivative as an intermediate and it is known that cyclopropene is prepared only with difficulty. A choice between these possibilities may be made by effecting the reaction in *t*-butyl alcohol-*d* as the solvent. The first possibility would lead to the introduction of at most a relatively small amount of deuterium (by exchange at the 1-position), whereas the second would require the introduction of one deuterium.[11]

The reaction was effected using *t*-butyl alcohol-*d* (81 ± 3% estimated from the infrared spectrum), and the product was analyzed using the mass spectrum (Table I). The parent peaks for the *t*-butoxy ester II did not appear, but a peak at mass 158 was found, probably corresponding to internal rearrangement of the ethyl group with the loss of

---

(6) W. Ostwald, *Z. physik. Chem.*, **3**, 241 (1889).

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

(8) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 253.

(9) It is interesting to note that methyl *p*-bromobenzoate, which should have a moment similar to that of the bromo ester, has a dipole moment of 1.82 D. (ref. 8, p. 330).

(10) This is not surprising since cyclopropane derivatives are inert in both the SN1 and SN2 displacement reactions (J. D. Roberts and V. C. Chambers, THIS JOURNAL, **73**, 5034 (1951)).

(11) One might expect that the isotope effect for the introduction of a hydrogen or deuterium at the 1-carbon during a Michael addition would be small in view of the results previously obtained in the neutralization of carbanions (K. B. Wiberg, THIS JOURNAL, **77**, 5987 (1955)).

ethylene. This is a common reaction of ethyl esters. There also was found a smaller peak at mass 171 formed by the loss of a methyl group, probably from either the ester group or the *t*-butoxy group.[12]

TABLE I

MASS SPECTRA OF ETHYL 2-*t*-BUTOXYCYCLOPROPANECARBOXYLATE

	Relative intensities[a] corrected for C^{13}				
Mass no.	*t*-Butoxy ester unlabeled	*t*-Butoxy ester from equilib.	*t*-Butoxy ester from reaction in labeled solvent		Bromo ester
146				5.4	5.8
147				100.0	100.0
148				0.0	0.0
149				96.0	98.0
150				1.0	0.0
158	100.0	100.0	6.2		
159	0.0	1.3	37.4		
160		0.0	100.0		
161			1.2		
164				100.0	100.0
165				0.0	0.0
166				97.0	99.0
167				0.0	0.0
171	100.0	100.0	5.2		
172	0.0	0.0	32.0		
173			100.0		
174			2.0		

[a] The largest peak of each group of peaks was assigned the value 100.0 in order to facilitate comparison.

The mass spectrum of the *t*-butoxy ester prepared in the deuterium labeled solvent was found to contain deuterium and had the following composition: 4% d_0, 26% d_1, 69% d_2 and 1% d_3 (using the 158, 159 and 160 peaks); 4% d_0, 23% d_1 72% d_2 and 1% d_2 (using the 171, 172 and 173 peaks).[13] The amount of d_3 is zero within experimental error. The amounts of d_1 and d_2 correspond well to the expected amounts if two deuteriums were introduced from a solvent having the above composition. Thus, these results indicate that two deuteriums were introduced during the reaction.

The mass spectrum of the above product also had peaks corresponding to the bromo ester reactant.[14] A comparison of these peaks with those of authentic bromo ester showed that no deuterium had been introduced into the reactant during the reaction. The product also was shown to give an insignificant amount of exchange when treated with *t*-butoxide ion in *t*-butyl alcohol-*d* under conditions approximating those used in the reaction. It may be concluded that two deuterium atoms were introduced as an integral part of the reaction which converts I to II.

These results appeared sufficiently important to warrant a careful check. Therefore, methyl 2-bromocyclopropanecarboxylate was prepared from carefully purified 2-bromocyclopropanecarboxylic acid, and this was treated with potassium *t*-butoxide in *t*-butyl alcohol-*d*. The mass spectrum of the product is given in Table II. Starting with alcohol having 94 ± 3% deuterium, the product had 2% d_0, 18% d_1 and 80% d_2. If the monodeutero compound was assumed to have its deuterium evenly distributed between the two possible positions (of the dideutero compound), then each position would have 89% deuterium, which is in good agreement with the composition of the alcohol used as the solvent.

TABLE II

MASS SPECTRA OF METHYL 2-*t*-BUTOXYCYCLOPROPANECARBOXYLATE

	Relative intensities corrected for C^{13}			
Mass no.	Unlabeled	Labeled from reaction	Equilib. at room temp.	Equilib. at 80°
157	100.0	2.5	100.0	100.0
158	0.0	23.2	0.3	28.3
159		100.0	0.0	0.6
160		0.2		0.0
	100% d_0	2% d_0 18% d_1 80% d_2	100% d_0	78% d_0 22% d_1 0.5% d_2

Unlabeled methyl 2-*t*-butoxycyclopropanecarboxylate was equilibrated with the labeled solvent for 0.5 hr. at room temperature and also at the reflux temperature using one-tenth the amount of base used in the above reaction. These conditions bracket those used in the reaction. Essentially no deuterium exchange was found at room temperature, and 22% was found at the reflux temperature. The maximum amount of deuterium which could have been introduced by exchange would then be between these values. Thus we have good confirmation of the above conclusion regarding the number of deuteriums introduced during the reaction.

It was then necessary to determine the location of the two deuteriums. The alkyl group forming the ester can be excluded since deuterium was found in the species in which this alkyl group was lost. Similarly, the *t*-butyl group may be excluded. Four hydrogens then remain which may be substituted by deuterium. Any mechanism which would introduce deuterium would involve the 1-position, and one deuterium is almost certainly in this position. It is unlikely that deuterium had been introduced into the methylene group since no reasonable mechanism may be written for introducing deuterium in this position and since one might expect that both hydrogens would be replaced if either one were to react by exchange, whereas essentially no trideuteroester was found. The most reasonable place for the other deuterium is then at the carbon holding the *t*-butoxy group.

This conclusion may be tested by hydrolyzing the labeled ester to β-formylpropionic ester (III).

---

(12) It should be noted that the ratio of the intensities of the 158 and 171 peaks was not constant. The average value was about three, but it dropped as low as one and went as high as nine. This does not appear to be due to gross amounts of impurities since the infrared spectra of all of the samples were identical, except for those which contained small amounts (~5%) of starting material. This does not affect the conclusions since, within experimental error, the isotopic compositions were the same regardless of which set of peaks was used in the calculations.

(13) The deuterium content of the alcohol samples was determined by infrared spectroscopy with a probable error of about 3%. The deuterium content of the other compounds was determined by mass spectrographic analysis with a probable error of 2% for 171, 172 and 173 peaks of the ethyl ester and an error of 1% for the rest of the spectra. This error is higher than usual because of the relatively low sensitivity for these compounds.

(14) The sensitivity of the mass spectrometer for the *t*-butoxy ester is low, whereas that for the bromo ester is high. Therefore the mass spectrum was easily found in the mixture even though it was present in only a small amount (~5%).

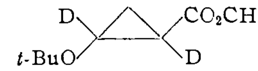
If the conclusion is correct, deuterium should then be found in the aldehyde group since aldehydes do not exchange this hydrogen with a solvent. The other deuterium would be expected to be largely lost under these conditions. The cleavage was effected, and the aldehyde was found to contain 11% d_0, 83% d_1 and 6% d_2 by mass spectrographic analysis (Table III). Here, the maximum percentage of deuterium in one position is 89%, in good agreement with the value found for the *t*-butoxy ester.

TABLE III

MASS SPECTRA OF METHYL β-FORMYLPROPIONATE

Mass no.	Relative intensities corrected for C^{13} Unlabeled	Labeled from reaction
115	4.3	
116	100.0	17.6
117	0.0	100.0
118		6.9
	100% d_0	11% d_0
		83% d_1
		6% d_2

The deuterium was shown to be in the aldehyde position by comparing the NMR spectra of labeled and unlabeled III. The band due to the aldehyde proton was very weak in the labeled sample, and it was estimated from its intensity that this sample had about 90% deuterium in the aldehyde group in excellent agreement with the mass spectrometric data. The *t*-butoxy ester must then have the structure



A reasonable course for the reaction involves the formation of the cyclopropenecarboxylic ester as the first step, followed by exchange of the vinyl hydrogen with the solvent. The argument for the acetylenic character in the vinyl hydrogens of cyclopropene has been given above and one might expect the carbomethoxy group to enhance this acidity. Finally a Michael addition of *t*-butyl alcohol-*d* would give the observed product.

These experiments then show that the cyclopropene ring has considerable acetylenic character, that cyclopropene derivatives may be more easily obtained than previously believed and that cyclopropenecarboxylic esters are particularly reactive in Michael addition reactions.

Acknowledgment.—We wish to thank Dr. C. Reid for the NMR spectra and their interpretation, Mr. B. J. Nist for the mass spectral determinations and Dr. W. Watanabe for supplying us with the procedure for the preparation of *t*-butyl vinyl ether prior to publication. We also wish to thank the Office of Ordnance Research, U. S. Army, for financial assistance, and the Atomic Energy Commission for assistance in purchasing certain equipment for the mass spectrometer.

Experimental[15]

***trans*-Cyclopropane-1,2-dicarboxylic Acid.**—To a stirred solution of 600 g. (6.0 moles) of ethyl acrylate was added 950 g. (5.1 moles) of ethyl diazoacetate at such a rate as would maintain rapid evolution of nitrogen. Only moderate heating was necessary during the addition. Precautions were taken to avoid exposure of the diazo ester to excess heat and acrylate vapors. After the addition, the solution was heated under reflux for 3 hr., and the excess ethyl acrylate was removed by distillation at atmospheric pressure. The residue distilled between 110–118° at 11 mm., $n^{25}\text{D}$ 1.4415, 630 g. The crude ester mixture was distilled through a 12-inch column packed with glass helices and four fractions were collected:

No.	B.p., °C.	Mm.	$n^{25}\text{D}$	G.	%
1	107–109	10	1.4391	243	25.5
2	109–111		1.4402	99	10.5
3	111–115		1.4418	70	7.4
4	115–117		1.4440	169	17.8

Fraction 4 appeared from the infrared spectrum and refractive index to be mainly *trans*-ethyl glutaconate.

Fractions 1 and 2 (342 g., 1.84 moles) were saponified with 415 g. (7.4 moles) of potassium hydroxide in 2.5 l. of methanol. After the initial heat of reaction had dissipated, the solution was heated under reflux for 4 hr. The solvent was removed at 20 mm., water was added and the concentration was continued. The residue was taken up in water, acidified to *p*H 3 with concentrated hydrochloric acid and extracted with seven 200-ml. portions of ether. Concentration of this ether solution gave 140 g. of the crude *trans*-diacid. Continuous ether extraction of the aqueous solution afforded an additional 95.6 g. of less pure *trans*-diacid. Recrystallization of the two fractions separately from acetonitrile produced a total of 156.6 g. (23.5% based on diazoacetic ester) of the *trans*-cyclopropane-1,2-dicarboxylic acid, m.p. 176–177°.[16] A mixed m.p. with authentic *trans*-diacid showed no depression, and the infrared spectra were identical. The acid gave a negative test with bromine in carbon tetrachloride and with potassium permanganate.

Concentration of the mother liquors from the above recrystallizations gave 33.5 g. of a mixture of *cis*- and *trans*-acids contaminated with glutaconic acid. Recrystallization from nitromethane gave pure *cis*-cyclopropane-1,2-dicarboxylic acid, m.p. 138.5–139.8° (5%).

***trans*-Diethyl Cyclopropane-1,2-dicarboxylate.**—A mixture of 34.7 g. (0.266 mole) of the *trans*-diacid, 93.5 ml. of absolute ethanol, 47 ml. of dry toluene and 6 drops of concentrated sulfuric acid was distilled until the vapor temperature reached 78°. The distillate was dried with potassium carbonate and recycled. This procedure was continued three times more. Then 60 ml. of ethanol and 30 ml. of toluene were added, and the solution was distilled at atmospheric pressure to remove most of the solvent and then at reduced pressure giving 46.3 g. (94%) of the diethyl ester, b.p. 117° at 17 mm., $n^{25}\text{D}$ 1.4375.

Anal. Calcd. for $C_9H_{14}O_4$: C, 58.1; H, 7.6. Found: C, 57.8; H, 7.6.

The diamide was prepared in 56% yield by shaking 2.0 g. of the diester with 10 ml. of concentrated ammonium hydroxide solution for three days and recrystallizing the resultant amide from absolute ethanol. It had m.p. 276–277°.

Anal. Calcd. for $C_5H_8N_2O_2$: N, 21.9. Found: N, 21.7.

***trans*-Ethyl Hydrogen Cyclopropane-1,2-dicarboxylate.**—A mixture of 100 ml. of ethanol and 46.3 g. (0.25 mole) of diethyl cyclopropane-1,2-dicarboxylate was heated to boiling, and a solution of 10.4 g. (0.26 mole) of sodium hydroxide in 19 ml. of water was added over a period of 2 hr. The solution was cooled and concentrated at 15 mm. The residue was diluted with 50 ml. of water, concentrated again for a short period of time, and the aqueous solution was then extracted with three 15-ml. portions of ether. The aqueous layer was acidified with concentrated hydrochloric acid to *p*H 3 and extracted with four 40-ml. portions of ether. The ether solution was dried with anhydrous magnesium sulfate, concentrated and distilled to give 18.1 g. (46%) of the half-ester, b.p. 130–134° at 1.5 mm., m.p. 58–60° on recrystallization from ligroin.

Anal. Calcd. for $C_7H_{10}O_4$: neut. equiv., 158.1. Found: neut. equiv., 157.9, 156.4.

---

[15] All melting points and boiling points are uncorrected. Mass spectral data were obtained using a Consolidated Electrodynamics Corp. mass spectrometer model 21-103. Microanalyses were performed by B. Nist, A. Elek and R. Barnes.

[16] C. K. Ingold, *J. Chem. Soc.*, **119**, 305 (1921), reported m.p. 175–176° for the *trans*-diacid and m.p. 139° for the *cis*-diacid.

The monoanilide was prepared in the usual way[17] and recrystallized from water giving needles, m.p. 106.8–107.3°.

Silver Salt of *trans*-Ethyl Hydrogen Cyclopropane-1,2-dicarboxylate.—Ethyl hydrogen cyclopropane-1,2-dicarboxylate (18.1 g., 0.115 mole) was exactly neutralized with 3 *N* ammonium hydroxide, and this solution was added with stirring to 30.6 g. (0.18 mole) of silver nitrate in 200 ml. of water. The silver salt was filtered, washed with water and dried for five days in a vacuum over phosphorus pentoxide at 65° and 15 mm. The salt was ground to a fine powder and dried for two days over phosphorus pentoxide at 100° and 3 mm., ground to a powder again and dried under these conditions for several days. The yield was 28 g. (92%).

Ethyl 2-Bromocyclopropanecarboxylate.—This compound was prepared by two independent methods.

Method A.—The dry, powdered silver salt (27.1 g., 0.106 mole) was placed in a thoroughly dry flask containing a stirrer, condenser and dropping funnel. Dry nitrogen was swept through the system for 2 hr. The exit gas from the system was protected by a concentrated sulfuric acid trap which also served as a bubble counter allowing the observation of the rate of carbon dioxide evolution from the system. A solution of 22.0 g. (0.138 mole) of bromine (dried over phosphorus pentoxide) in 103 g. of carbon tetrachloride (dried and distilled from phosphorus pentoxide) was added to the well-stirred silver salt. Heat and a gas were given off and the addition of bromine was regulated to give a rapid evolution of gas. After the addition was completed, the reaction mixture was allowed to stand for ten minutes and then was heated in a hot water-bath for ten minutes. The solution was cooled and filtered through a sintered glass funnel, and the silver bromide was washed several times with dry carbon tetrachloride. The filtrate was concentrated at atmospheric pressure, and the residue was distilled under reduced pressure giving 0 to 8 g. (0–40%) of the bromo ester, b.p. 89–98° at 13 mm., $n^{25}\text{D}$ 1.4646–1.4688. Redistillation afforded the pure ester, b.p. 76–81° at 18 mm., $n^{25}\text{D}$ 1.4660. The physical properties and derivatives of this compound were identical in all respects with the product obtained by the alternate procedure below.

Method B.—Vinyl bromide (500 g., 4.7 moles) was condensed into a 2-l. stainless steel flask which contained 1 g. of anhydrous copper sulfate, and the flask was attached to an iron condenser. Ethyl diazoacetate (110 g., 0.96 mole) was placed in a glass container which was open at the top and contained a long capillary tube at the bottom which extended down about five inches into the top of the condenser. The dropping bottle was calibrated to deliver 110 g. of the diazo ester in approximately 160 min. The entire system was constructed of iron pipe in order to withstand the pressure which would be developed. When the dropping bottle had been placed in the iron mounting, the system was immediately sealed with a three-inch iron screw cap containing a rubber gasket, and the pressure in the system was adjusted to 90 p.s.i. by the addition of nitrogen. The exit needle valve was adjusted to allow a slight flow of nitrogen through the system. The flask was heated rapidly to 100° and maintained at that temperature for 4 hr. The reaction flask was then cooled in Dry Ice–acetone, the pressure in the system was released and the flask removed.

Vinyl bromide was removed from the crude reaction mixture under reduced pressure, and the residue was poured into 600 ml. of ether. The ether solution was separated from the insoluble polymer, and the ether was evaporated giving 98 g. of an oil. The oil was distilled giving four fractions:

No.	B.p., °C. (4.5 mm.)	$n^{25}\text{D}$	G.
1	45–56	1.4485	9.7
2	56–60	1.4580	10.3
3	60–68	1.4655	21.6
4	68–84	1.4542	13.1

Careful redistillation of fraction 3 gave 17.2 g. (9.3%) of the bromo ester, b.p. 183–186°, $n^{25}\text{D}$ 1.4663.

Anal. Calcd. for $C_6H_9BrO_2$: Br, 41.4; mass weight. 192, 194. Found: Br, 40.2, 40.0; mass weight, 192, 194 (mass spectrometer parent peaks).

This ester was identical to the material obtained by method A. It contained bromine by sodium fusion but did not react with hot alcoholic silver nitrate or with sodium iodide in acetone. The infrared spectrum showed carbonyl absorption at 5.77 μ and no absorption in the carbon–carbon double bond region. It also did not give an unsaturation test with potassium permanganate solution. Fractions 1 and 2 from the crude distillation gave a compound, b.p. 152–158°, $n^{25}\text{D}$ 1.4442–1.4495, whose infrared spectrum compared very well with that of ethyl bromoacetate (20 g., 12.5%). The highest boiling fraction was identified as diethyl fumarate.

2-Bromocyclopropanecarboxylic Acid.—A mixture of 44 g. (0.25 mole) of ethyl 2-bromocyclopropanecarboxylate from method B and 13 g. of sodium hydroxide in 300 ml. of water was heated to reflux with stirring for 0.5 hr. The solution was extracted with ether, acidified with 1:1 nitric acid, and the oil which separated was taken up in 150 ml. of ether. The ether solution was dried over anhydrous sodium sulfate and concentrated giving the crude acid (80%). The acid was recrystallized from water–methanol and then sublimed at 50° and 0.5 mm. giving 28.8 g. (72%) of 2-bromocyclopropanecarboxylic acid, m.p. 66–67°.

Anal. Calcd. for $C_4H_5BrO_2$: Br, 48.4; neut. equiv., 165. Found: Br, 48.2; neut. equiv., 165.

The acid was saturated to potassium permanganate, gave a negative halogen test with hot alcoholic silver nitrate and with sodium iodide in acetone. The carbonyl absorption was at 5.85 μ. The acid obtained from the bromo ester from method A was identical with the above acid as shown by mixed m.p. and comparison of their infrared spectra.

Methyl 2-Bromocyclopropanecarboxylate.—A mixture of 23.2 g. (0.14 mole) of 2-bromocyclopropanecarboxylic acid, 13.4 g. of methanol, 50 ml. of methylene chloride and 0.5 ml. of concentrated sulfuric acid was heated to reflux for 10 hr. The mixture was washed with 25 ml. of water, with two 25-ml. portions of 5% sodium bicarbonate solution and again with water. The organic solution was dried over anhydrous sodium sulfate and concentrated giving 18.0 g. (87%) of the ester. Acidification of the basic solutions gave 4.2 g. of unreacted acid.

The ester was distilled through a 12-inch column packed with Helipak giving 12.6 g. of pure methyl 2-bromocyclopropanecarboxylate, b.p. 172.5–173°, $n^{25}\text{D}$ 1.4751.

Anal. Calcd. for $C_5H_7O_2Br$: C, 33.5; H, 3.9. Found: C, 33.7; H, 4.0.

Attempted Elimination of Hydrogen Bromide from Ethyl 2-Bromocyclopropanecarboxylate. A. Treatment with Quinoline.—A mixture of 2 g. of the bromo ester and 12.9 ml. of purified quinoline was heated at 90–100° for 16 hr. No reaction appeared to take place. The solution was distilled slowly, and the first material obtained was the bromo ester, b.p. 177–190° (94% recovery).

B. Treatment with Triphenylmethylsodium.—The bromo ester (0.90 g.) was dissolved in 30 ml. of dry ether, and 4.65 meq. of triphenylmethylsodium in 18 ml. of ether was added slowly. Each drop of the sodio-compound was decolorized immediately with the formation of a precipitate. Very little low boiling material could be isolated and most of the product appeared to be polymeric. A yield of 0.46 g. of silver bromide (53%) was obtained from aqueous solutions of all of the residues.

Ethyl 2-*t*-Butoxycyclopropanecarboxylate.—A 0.52 *N* solution of potassium *t*-butoxide (20 meq.) in dry *t*-butyl alcohol (38.5 ml.) was added dropwise over a period of 45 min. to a stirred solution of 3.86 g. (20 mmoles) of ethyl 2-bromocyclopropanecarboxylate in 20 ml. of *t*-butyl alcohol. With the addition of the first drop, a white precipitate was observed and a perceptible amount of heat was noted as the addition was continued. When about half of the base had been added, the solution had an approximate *p*H of 10, and at the end of the reaction the *p*H was about 9. The solution was stirred for 20 min. at room temperature and finally heated for 0.5 hr. at reflux. The solution was cooled, filtered and distilled giving 2.34 g. (63%) of ethyl 2-*t*-butoxycyclopropanecarboxylate, b.p. 78–84° at 10 mm., $n^{25}\text{D}$ 1.4350–1.4306. This material appeared to contain about 5% of the bromo ester (from the infrared spectrum).

The ester was dissolved in *t*-butyl alcohol and heated with 5 ml. of 0.52 *N* potassium *t*-butoxide. After 1 hr. the solution was neutralized exactly with acetic acid in dry ether,

---

(17) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 158.

and the *t*-butoxy ester was recovered by distillation (69%), b.p. 76–78° at 10 mm., n^{25}D 1.4288.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.5; H, 9.8. Found: C, 63.1; H, 9.8.

The ester gave a negative test for unsaturation with potassium permanganate solution and did not show absorption in the carbon–carbon double bond region of the infrared spectrum.

2-*t*-Butoxycyclopropanecarboxylic Acid.—A solution of 1 g. (5.37 mmoles) of the *t*-butoxy ester and 10 g. of 15% potassium hydroxide in ethanol was heated to reflux for 0.5 hr. The solution was concentrated under reduced pressure, water was added and the concentration was continued. The residue was extracted with three 20-ml. portions of ether, then acidified with hydrochloric acid and again extracted with three 20-ml. portions of ether. The latter ether extract was evaporated giving 0.70 g. (82%) of 2-*t*-butylcyclopropanecarboxylic acid, m.p. 82–85°. Recrystallization from 30–60° petroleum ether raised the m.p. to 88–89°.

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.7; H, 8.9; neut equiv., 158.1. Found: C, 60.8; H, 9.3; neut. equiv., 158.6.

***t*-Butyl Alcohol-*d*.**—Two moles (148 g.) of dry *t*-butyl alcohol was mixed with 20 ml. (1.0 mole) of deuterium oxide. The mixture was dried using 23 g. (1.0 atom) of sodium and distilled giving 140 g. of the alcohol. This procedure was repeated two or three times more, and the alcohol was finally dried with an additional 2 g. of sodium.

The deuterium content of the alcohol was estimated from the infrared spectrum using the 3.02 and 4.04 μ bands (OH and OD, respectively) and assuming Beer's law to hold. The alcohol used with the ethyl esters had 81 ± 3% deuterium, and that used with the methyl esters had 94 ± 3% deuterium.

Ethyl 2-*t*-Butoxycyclopropanecarboxylate-1,2-d_2.—A solution of 3.45 g. (17.8 mmoles) of ethyl 2-bromocyclopropanecarboxylate in 20 ml. of dry *t*-butyl alcohol was treated with 28.8 ml. of 0.62 *N* potassium *t*-butoxide (17.8 meq.) in *t*-butyl alcohol-*d*. The solution was heated for 0.5 hr. at 90°, and the reaction mixture was worked up as before. There was obtained 1.44 g. (44%) of ethyl 2-*t*-butoxycyclopropanecarboxylate-1,2-d_2. b.p. 74–76° at 10 mm. The infrared spectrum indicated that about 5% of starting material was present. The mass spectrum is recorded in Table I.

Equilibration of Ethyl 2-*t*-Butoxycyclopropanecarboxylate with *t*-Butyl Alcohol-*d*.—The *t*-butoxy ester (0.68 g., 3.65 mmoles) was mixed with 2.88 ml. of 0.62 *N* potassium *t*-butoxide in *t*-butyl alcohol-*d* and allowed to stand for 0.5 hr. The solution was neutralized with acetic acid in dry ether and distilled giving a 44% recovery of the ester, b.p. 74–78° at 10 mm., n^{25}D 1.4285. The mass spectrum is recorded in Table I.

Methyl 2-*t*-Butoxycyclopropanecarboxylate.—To a stirred solution of 5.0 g. (28 mmoles) of methyl 2-bromocyclopropanecarboxylate in 25 ml. of dry *t*-butyl alcohol was added 65 ml. of 0.48 *N* potassium *t*-butoxide (31 meq.) over a period of 15 min. After the addition was completed, the reaction mixture was heated to reflux for 30 min., cooled, filtered and exactly neutralized with acetic acid in dry ether. Distillation gave 2.8 g. (58%) of methyl 2-*t*-butoxycyclopropanecarboxylate, b.p. 66–74° at 10 mm., n^{25}D 1.4292.

Redistillation at atmospheric pressure gave the pure ester, b.p. 192–195°, n^{25}D 1.4295.

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.8; H, 9.3. Found: C, 62.9; H, 9.3.

Hydrolysis gave 75% of 2-*t*-butoxycyclopropanecarboxylic acid, m.p. 89–89.5°, which was identical with that prepared from the ethyl ester.

Reaction of *t*-Butyl Vinyl Ether with Methyl Diazoacetate.—A mixture of 14 g. (0.14 mole) of *t*-butyl vinyl ether[18] and 0.2 g. of powdered anhydrous copper sulfate was heated to boiling, and 7.0 g. (0.07 mole) of methyl diazoacetate was added at such a rate as to maintain boiling. After the addition, the mixture was heated for 20 min., cooled and filtered. Distillation gave 7.0 g. (58%) of methyl 2-*t*-butoxycyclopropanecarboxylate, b.p. 90–97° at 30 mm., n^{25}D 1.4323.

A solution of 4.0 g. of the *t*-butoxy ester and 30 ml. of pentane was treated with 50 ml. of 2% potassium permanganate solution, and the resultant manganese dioxide was removed with sulfur dioxide. The pentane layer was dried with anhydrous sodium sulfate and distilled giving 2.8 g. of the ester, b.p. 95–98° at 30 mm., n^{25}D 1.4316. This ester was identical with that obtained by the reaction of the bromo ester with potassium *t*-butoxide.

Hydrolysis gave 2-*t*-butoxycyclopropanecarboxylic acid, m.p. 89–89.5°, which was identical with the acid obtained from the other esters.

Methyl 2-*t*-Butoxycyclopropanecarboxylate-1,2-d_2.—The reaction was carried out as described above, except that *t*-butyl alcohol-*d* was used as the solvent. There was obtained 44% of the ester, b.p. 108–120° at 60 mm., n^{25}D 1.4303. The mass spectrum is recorded in Table II.

Acid Hydrolysis of Methyl 2-*t*-Butoxycyclopropanecarboxylate.—A mixture of 4 g. (23 mmoles) of methyl 2-*t*-butoxycyclopropanecarboxylate, 100 ml. of methylene chloride, 10 ml. of concentrated hydrochloric acid and 30 ml. of methyl alcohol was heated to reflux for 50 hr. The methylene chloride layer was washed with water, sodium bicarbonate solution and again with water. After drying over anhydrous sodium sulfate, distillation gave 2.0 g. (75%) of methyl β-formylpropionate, b.p. 87–91° at 17 mm., n^{25}D 1.4152. The infrared spectrum of this sample was identical with that of an authentic sample (see below).

The labeled ester was hydrolyzed in the same way and gave 88% of methyl β-formylpropionate-4-d_1. The mass spectrum is recorded in Table III.

Methyl β-Formylpropionate.—A solution of 60 g. of succinic anhydride in 24.6 ml. of methanol was heated for 4 hr. and distilled giving 46 g. (58%) of methyl hydrogen succinate, m.p. 56–57° after recrystallization from carbon disulfide. The half-ester was treated with 200 ml. of benzene and 47.5 g. of thionyl chloride for 12 hr. at the reflux temperature. Distillation gave 43 g. (82%) of the acid chloride, b.p. 87–88° at 15 mm., n^{25}D 1.4390. The Rosenmund reduction was carried out by the general procedure described by Hershberg and Cason[19] using xylene as the solvent. Methyl β-formylpropionate was obtained in 78% yield, b.p. 76–79° at 18 mm., n^{25}D 1.4211. Redistillation gave material having b.p. 82–83° at 22 mm., n^{25}D 1.4195.

The 2,4-dinitrophenylhydrazone was prepared and had m.p. 131.5–132.5° after recrystallization from methanol.

Anal. Calcd. for $C_{12}H_{14}N_4O_6$: C, 46.4; H, 4.6. Found: C, 46.2; H, 4.6.

Equilibration of Methyl 2-*t*-Butoxycyclopropanecarboxylate with *t*-Butyl Alcohol-*d*.—A solution of 2.0 g. (11.6 mmoles) of methyl 2-*t*-butoxycyclopropanecarboxylate in 18 ml. of *t*-butyl alcohol-*d* was treated with 14 ml. of 0.086 *N* potassium *t*-butoxide (1.2 meq.) in *t*-butyl alcohol-*d*. The solution was heated to reflux for 0.5 hr., cooled and exactly neutralized with acetic acid in dry ether. Distillation gave 1.26 g. (63%) of the *t*-butoxy ester, b.p. 95–97° at 30 mm. The mass spectrum is recorded in Table II. In another run, the same quantities of material were used except that the solution was allowed to stand at room temperature for 0.5 hr.

Dipole Moments.—The dipole moments of methyl cyclopropanecarboxylate, methyl 2-bromocyclopropanecarboxylate and methyl 2-*t*-butoxycyclopropanecarboxylate were determined in benzene solution using the method of Guggenheim.[20] The dielectric constants of the solutions were determined using the usual heterodyne beat apparatus.

SEATTLE 5, WASHINGTON

---

[18] W. H. Watanabe and L. E. Conlon, This Journal, **79**, 2828 (1957).

[19] E. B. Hershberg and J. Cason, *Org. Syntheses*, **21**, 84 (1941).

[20] E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).