

period of 8 hours, giving 6.66 g. (74% of product),  $n_{23}^D$  1.4965.

$\alpha, \alpha$ -Methylisobutylbenzylazo-2(4-methylpentane) (IVd). (A) Silver Nitrate Oxidation.—The hydrazine IIIId was oxidized with silver nitrate as described above, except that the reaction mixture was worked up after only 4 hours of shaking. From 28.8 g. (0.114 mole) of distilled hydrazine was obtained 13.95 g. (49%) of yellow oil,  $n_{26}^D$  1.4851,  $d_{25}^{25}$  0.8911, the distillation being effected over a period of 2.5–3.5 days at  $10^{-4}$  to  $10^{-6}$  mm. using a bath temperature of 50–65°.

Silver nitrate oxidation of undistilled hydrazine in ethanolic solution gave similar results, under the same conditions, the yield of azo compound being 62%.

(B) Mercuric Oxide Oxidation.—The oxidation was carried out in the manner described for preparing IVc. High vacuum distillation yielded 72% of the azo compound.

$\alpha$ -Phenylethylazoisopropane (IVe).—The oxidation was carried out in the manner described for preparing IVc except that yellow mercuric oxide was used, and the solids were removed by filtration after stirring for only 4.5 hours. From 10.33 g. (0.058 mole) of acetone  $\alpha$ -phenylethylhydrazine, which was hydrogenated and oxidized, was obtained 6.75 g. of green liquid residue. Distillation through an 8-inch center tube column gave 4.9 g. (49%) of a yellow liquid, b.p. 48° (0.5 mm.),  $n_{26}^D$  1.4917,  $d_{25}^{25}$  0.9100.

Cyclohexanone azine was prepared according to the procedure of Perkin and Plant<sup>42</sup> in 88% yield, m.p. 34.5–35.5°, b.p. 116° (3–4 mm.),  $n_{26}^D$  1.5250 (77%, m.p. 33°).<sup>42</sup>

Reaction of Cyclohexanone Azine and Phenyllithium. 1-Phenylbicyclohexyl and 1,1-Diphenylbicyclohexyl.—After stirring for 24 hours, the reaction mixture from 65 g. (0.34 mole) of cyclohexanone azine in 225 ml. of anhydrous ether and a 0.72 molar solution of phenyllithium in 550 ml. of ether gave 94 g. of brownish-red viscous oil, the solvent being removed under nitrogen and reduced pressure. Distillation under nitrogen gave five fractions and a residue, 13.2 g., ether soluble: fraction I, 17 g., b.p. 76–115° (1.5–3.2 mm.),  $n_{23}^D$  1.5346; fraction II, 7.5 g., b.p. 120–151° (2.0–5 mm.); fraction III, 13 g., b.p. 145–147° (2.0–5 mm.),  $n_{23}^D$  1.5410; fraction IV, 11.5 g., b.p. 146–151° (2.2–3 mm.),  $n_{26}^D$  1.5476; fraction V, 4.8 g., b.p. 160–180° (3 mm.), liquid and solid.

Fraction I (17 g.), which gave a positive Brady test, was added to a saturated sodium bisulfite solution composed of 80 g. of sodium bisulfite, 120 g. of water and 30 ml. of ethanol, with stirring. The solid, 11.5 g., which formed was filtered by suction after 0.75 hr., and washed with ether. The filtrate was extracted with ether until the ether layer

(42) W. H. Perkin, Jr., and S. G. P. Plant, *J. Chem. Soc.*, **125**, 1503 (1924).

was no longer yellow, and dried over magnesium sulfate. Removal of the solvent left 9.5 g. of yellow-red liquid, which gave a negative Brady test. Distillation under nitrogen through a center tube column gave 6 g. of colorless material, in several fractions, b.p. 65–84° (3–5 mm.),  $n_{23}^D$  1.5232– $n_{24}^D$  1.5454, giving a negative test for nitrogen, but decolorizing a bromine–chloroform solution. The boiling point of one of the fractions was 245° (760 mm.). These properties are consistent for a mixture of phenylcyclohexane<sup>30,43</sup> (b.p. 83–85° (4.5 mm.)<sup>30</sup>; b.p. 239° (750 mm.),  $n_{18}^D$  1.5274<sup>43</sup>) and 1-phenylcyclohexene-1<sup>44,45</sup> (b.p. 251–253<sup>44</sup>; 128° (16 mm.),  $n_{20}^D$  1.5695<sup>45</sup>).

Successive redistillation of the combined fractions II, III and IV gave 12.3 g. of light yellow, constant boiling and constant refractive index material in 4 cuts, b.p. 147° (2.5 mm.),  $n_{23}^D$  1.4561. The elemental analyses for this material indicated the sample to be most probably a mixture of 1-phenylbicyclohexyl and 10% cyclohexanone 1-phenylcyclohexylhydrazone (or possibly 7.1% cyclohexanone azine). The addition of 2 g. of the final distilled material to 5 ml. of acetone with vigorous stirring, while cooling in an ice-bath, gave an amorphous white solid, 1.5 g., m.p. 38–42°. Recrystallization from acetone, by standing overnight in the freezer, yielded 1.3 g. of fibrous looking white solid, m.p. 45–46°, which is believed to be 1-phenylbicyclohexyl. Purification also could be effected by sublimation of the initial crude solid.

*Anal.* Calcd. for  $C_{15}H_{26}$ : C, 89.19; H, 10.81. Found: C, 88.82; H, 11.01.

From fraction V was filtered approximately 2.0 g. of white solid. Recrystallization from ethanol gave a beautiful crystalline white solid, 1,1-diphenylbicyclohexyl, 1.65 g., m.p. 183–183.5° (m.p. 178–178.5° uncor., from acyloin condensation of ethyl 1-phenylcyclohexanecarboxylate<sup>30</sup>).

*Anal.* Calcd. for  $C_{24}H_{30}$ : C, 90.5; H, 9.5. Found: C, 90.8; H, 9.29.

**Acknowledgment.**—We wish to acknowledge gratefully the generous support of this work by the National Science Foundation, Grant NSF 1453. We also wish to express our appreciation to Dr. R. Hiskey for his many helpful and useful suggestions during the progress of this work.

(43) H. Gelissen and P. H. Hermans, *Ber.*, **59**, 662 (1926).

(44) P. E. Verkade, J. Coops, Jr., C. J. Maan and A. Verkade-Sandbergen, *Ann.*, **467**, 217, 232 (1928).

(45) S. Nametkin and N. Iwanoff, *Ber.*, **56**, 1805 (1923).

BROOKLYN 1, N. Y.

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

## Three-membered Rings. The Preparation of Some 1,2-Cyclopropanedicarboxylic Acids

BY LAYTON L. MCCOY<sup>1</sup>

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The base condensation of an  $\alpha$ -halo-ester with an  $\alpha, \beta$ -unsaturated ester leads to 1,2-cyclopropanedicarboxylic acid diesters; subsequent saponification gives the diacids. Two general procedures for the preparation of the diesters are described, one using sodium methoxide and the other sodium hydride in oil. The mixtures of stereoisomers obtained are unusual in that the less stable (*cis*) isomer is often the major component.

In connection with some other work on three-membered rings, both of the isomers of 1,2-cyclopropanedicarboxylic acid were required in considerable quantity. These acids have been prepared in a variety of ways,<sup>2</sup> the various procedures

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(2) (a) E. Buchner and A. Papendieck, *Ann.*, **273**, 232 (1892); (b) C. K. Ingold, *J. Chem. Soc.*, **119**, 305 (1921); (c) W. H. Perkin, *ibid.*, **87**, 358 (1905); (d) M. Conrad and M. Guthzeit, *Ber.*, **17**, 1186

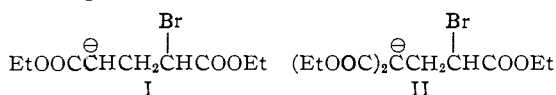
being examples of some of the general methods for the preparation of cyclopropane compounds.<sup>3</sup>

(1884); (e) E. Buchner, *ibid.*, **23**, 703 (1890); (f) H. von Pechmann, *ibid.*, **27**, 1891 (1894); (g) K. B. Wiberg, R. K. Barnes and J. Albin, *THIS JOURNAL*, **79**, 4994 (1957).

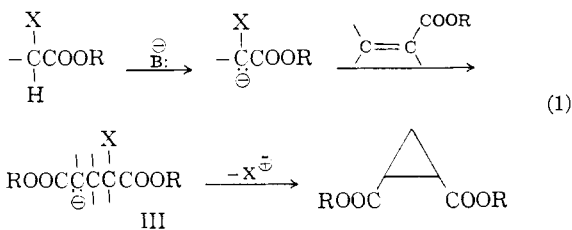
(3) With the exception of the recently discovered techniques involving the addition of carbenes to olefins, a summary of these methods is given in "Chemistry of Carbon Compounds," E. H. Rodd, editor, Elsevier Publ. Co., Amsterdam, the Netherlands, 1953, Vol. IIa, pp. 23–25. The carbene method apparently is of too recent origin to have been reviewed; references to its use are somewhat scattered.

These methods usually require several steps from readily available starting materials, and the over-all yields may be rather low. Of the procedures described for the preparation of the desired acids,<sup>2</sup> the best—fewest steps and greatest over-all yield—is that given by Wiberg, Barnes and Albin.<sup>2c</sup> However, this method does use diazoacetic ester, and on a large scale this may be rather hazardous; also, the ester product mixture requires rather careful fractional distillation to separate the major by-product, diethyl glutaconate, from the desired products, diethyl *cis*- and *trans*-1,2-cyclopropane dicarboxylates. None of the other previously described preparations is completely satisfactory.

Re-examination of the procedures for preparing cyclopropanes resulted in the conclusion that those methods involving basic conditions had in common a specific type of intermediate. The most obvious feature of this intermediate is the three-carbon chain with a carbanion at one end, and an appropriate group, usually halogen, at the other end; cyclopropane formation occurs by elimination of the group as an anion. A second feature is the presence at the carbanion end of the three carbon chain of some group, often carbalkoxy, which can stabilize the anion, and assist in its initial formation under basic conditions. Other structural features usually will be of secondary importance.<sup>4</sup> Two examples of these intermediates are I, from diethyl  $\alpha$ -bromoglutarate treated with hot methanolic



potassium hydroxide,<sup>2b</sup> and II, a species from the reaction of diethyl sodiomalonate with ethyl  $\alpha,\beta$ -dibromopropionate.<sup>2d</sup> The latter intermediate can arise by Michael addition of the diethyl malonate anion to ethyl  $\alpha$ -bromoacrylate (formed by elimination of hydrogen bromide from the dibromide) followed by equilibration of the resulting anion with II.<sup>5</sup> Based on these required features and the two examples shown, a simple method for the preparation of these intermediates suggested itself. The proposed synthetic path is the base condensation of an  $\alpha$ -halo-ester with an



See, for instance, P. S. Skell and A. Y. Garner, *THIS JOURNAL*, **78**, 3409, 5430 (1956).

(4) It is fairly obvious that a group which can be eliminated readily as an anion cannot be present on the middle carbon of the three-carbon chain. If there were, then elimination leading to an olefin almost certainly would prevail rather than elimination leading to a cyclopropane. Also, if it is assumed that the 1,3-elimination is not concerted, and that the actual and potential carbanions can interact (possibly equilibrate), then the presence of a substituent which could stabilize a negative charge on the middle carbon atom cannot be allowed. In this situation, elimination giving the olefin would again prevail.

(5) Michael, *Am. Chem. J.*, **9**, 112 (1887); *J. prakt. Chem.*, **35**, 132, 349 (1887).

$\alpha,\beta$ -unsaturated ester leading to an intermediate of the type III, and subsequently to a 1,2-dicarbalkoxycyclopropane.<sup>6</sup> This paper is an initial report on this reaction; Table I summarizes the results considered in the following discussion.

**1,2-Carbalkoxycyclopropanes.**—Two general methods for the preparation of these compounds were developed; these are described in the Experimental section. Method B using sodium hydride dispersion in oil<sup>7</sup> was the second procedure developed, but it proved to be the more versatile. Method A using sodium methoxide as the basic reagent was found to be satisfactory only with unsubstituted acrylic acid esters. However, in these cases, method A does give slightly better yields, and consequently the two methods tend to complement each other.

In general, the distilled diesters (mixtures of stereoisomers) were saturated to 2% potassium permanganate and showed no bands in their infrared spectra between 6.0–6.75  $\mu$  (carbon-carbon double bonds). However, in a few runs a small amount of unsaturated material was indicated by the permanganate test and in some of these cases a small band at about 6.1–6.2  $\mu$  was present in the infrared spectra. All of the crystalline diacids obtained from the diesters were saturated to potassium permanganate.

A number of by-products may be present in the crude reaction mixture. Only two appear to have any significance, and their relative importance depends on the Experimental procedure followed. In method B, the only appreciable by-product, other than some tarry material, has been of the acetoacetic ester type, and this occurs only when a haloacetate ester is used. This acetoacetic ester type product is undoubtedly a mixture, but it probably consists mostly of the  $\alpha,\gamma$ -dihaloacetoacetic ester and only to a small extent of the mixed condensation products. This condensation of haloacetate esters is known to occur readily.<sup>8</sup> It is quite possible that this type of by-product could be markedly reduced by using hindered esters such as *t*-butyl chloroacetate. In any case, the condensation product can be removed readily; it is present in the reaction mixture as the sodium salt, and this is soluble in water.

This same type of by-product has been observed in method A. However, by the procedure described in the Experimental section, and in those cases where method A is applicable, this by-product occurs to only a very minor extent. A more important by-product is that formed by addition of

(6) After completion of the work presented in this paper, one example of this reaction was found in the literature. D. H. Deutsch and E. R. Buchman, *Experientia*, **6**, 462 (1950), re-examined the structure of "1,3-cyclobutanedicarboxylic acid" obtained by treating ethyl  $\alpha$ -chloropropionate with ethanolic sodium ethoxide. They concluded that the diacid was actually 1-methyl-1,2-cyclopropanedicarboxylic acid; they showed that the yield of the diacid could be increased by using a 1:1 ratio of ethyl acrylate and ethyl  $\alpha$ -chloropropionate under the original reaction conditions. In a footnote they indicated that they intended to investigate the generality of the method for preparing cyclopropanes. Apparently they have published nothing on this reaction since then.

(7) (a) Sodium hydride dispersed in a mineral oil is available from Metal Hydrides, Inc., Beverly, Mass. (b) Ordinary, dry sodium hydride was found to be ineffective under the experimental conditions used in this work.

(8) W. Wislicenus, *Ber.*, **43**, 3532 (1910).

TABLE I

Olefin	Halogen comp.	Method <sup>a</sup>	Ester	Yield, %	
				Acid <sup>b</sup>	trans
CH <sub>2</sub> =CHCOOMe	ClCH <sub>2</sub> COOEt	A	45 <sup>c</sup>	26 <sup>d</sup>	22 <sup>d</sup>
	ClCH <sub>2</sub> COOEt	B	34 <sup>e</sup>	..	..
	BrCH <sub>2</sub> COOEt	A	22 <sup>e</sup>	..	..
	BrCH <sub>2</sub> COOEt	B <sup>e</sup>	23	0	58
	CH <sub>3</sub> CHClCOOMe	A	70	63	14
	CH <sub>3</sub> CHClCOOMe	B <sup>e</sup>	55	32	28
CH <sub>2</sub> =C(COOEt)   CH <sub>3</sub>	ClCH <sub>2</sub> COOEt	A	<3.5	..	..
	CH <sub>3</sub> CHClCOOMe	B	60	72	<3
CH <sub>3</sub> CH=CHCOOEt	ClCH <sub>2</sub> COOEt	A	8	..	..
	CH <sub>3</sub> CHClCOOMe	B	65	..	66 <sup>f</sup>
CH <sub>3</sub> CH=CHCOOMe EtOOCCH=CHCOOEt	ClCH <sub>2</sub> COOEt	B	29	(16) <sup>g</sup>	10 <sup>g</sup>
	ClCH <sub>2</sub> COOEt	A	0	..	..

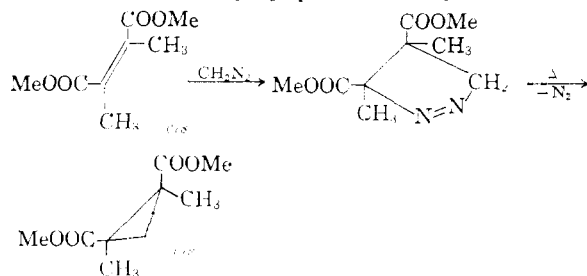
<sup>a</sup> See Experimental section. <sup>b</sup> These are the percentage yields of the pure diacids from the cyclopropane diesters. <sup>c</sup> These ester products had essentially the same physical constants including the infrared spectra; only the ester obtained in 45% yield was studied to determine the isomer ratio. <sup>d</sup> The separation of these acids was carried out a number of times. Although the ratio of the two isomers varied somewhat, the percentage yield of *trans* isomer was fairly constant, and in no case was there less of the *cis* isomer than the *trans*. <sup>e</sup> These reactions were run hot; see Experimental section. <sup>f</sup> Only one of the two possible *trans* isomers was isolated. <sup>g</sup> These yields are probably not significant in terms of the isomer ratio actually present; see Experimental section.

the methoxyl group to the unsaturated ester. This addition occurs readily, probably more so than does (1). For this reason, it was found best to use two moles of the unsaturated ester, one for the desired reaction leading to type III intermediates, and one to take up the methoxyl groups. The resulting  $\beta$ -methoxypropionate ester can be separated readily from the higher boiling cyclopropane derivative by distillation. A third by-product, an  $\alpha$ -methoxy ester, may be formed by a displacement reaction on the halo ester. Evidence concerning this possibility is meager, but it appears to be important only with bromo compounds.

**1,2-Cyclopropanedicarboxylic Acids.**—Saponification of the diester products gave mixtures of the isomeric dicarboxylic acids. These mixtures were separated into their components as described in the Experimental section. The results are shown in Table I.

Except for the isomers of 1,3-dimethyl-1,2-cyclopropanedicarboxylic acid, the diacids isolated in this work are known compounds that have been made by standard procedures.<sup>3</sup> In general, these procedures leading to cyclopropanes give, when stereoisomers are possible, predominantly or exclusively the more stable (usually *trans*) isomer.<sup>9</sup>

(9) Specific exceptions occur when pyrazolines obtained from tri-, or better, tetrasubstituted olefins are thermally decomposed to give cyclopropanes. The steric relations originally present in the olefin will be maintained in the cyclopropane. For example

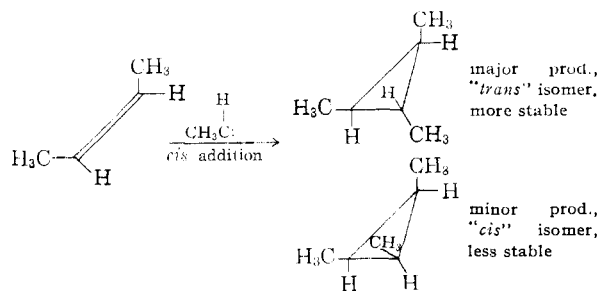


v. Auwers and König, *Ann.*, **496**, 252 (1932). Similarly, carbenes add to olefins by stereospecific *cis* addition, thus yielding cyclopropanes with the same steric relations as the starting olefin; W. von E. Doering and P. LaPlante, *This Journal*, **78**, 5447 (1956). However, the

For example, by treating the appropriate  $\alpha$ -bromoglutaric acid diester with boiling methanolic potassium hydroxide, Ingold obtained yields of 36% *trans*- and 3% *cis*-1,2-cyclopropanedicarboxylic acid,<sup>2b</sup> and 20% *trans*- and 5% *cis*-1-methyl-1,2-cyclopropanedicarboxylic acid.<sup>10</sup> Similarly, by treating boiling ethyl acrylate with ethyl diazoacetate and saponifying the resulting diester, Wiberg, Barnes and Albin obtained yields of 24% *trans*- and 5% *cis*-1,2-cyclopropanedicarboxylic acid.<sup>2e</sup> As shown in Table I, the ratios of stereoisomers obtained in the present work are quite different. Substituent, solvent and temperature effects have not been thoroughly evaluated. However, the preliminary results presented here indicate that high reaction temperatures and  $\beta$ -substituents in the acrylate ester favor *trans* isomers, while low temperatures and  $\alpha$ -substituents in either or both of the reacting esters favor the *cis* isomer.

The procedures described in this paper are probably the simplest available for the preparation of 1,2-cyclopropanedicarboxylic acids. They complement other methods which usually lead to the more stable (*trans*) isomers. Although the present work has been limited to the preparation of diacids,

use of unsymmetrical diazo compounds or carbenes in these procedures would give a mixture of two isomers in which the more stable ("*trans*") isomer would predominate. For example



*cis* isomers may also be formed preferentially in the dicarboxylation of some cyclopropanepolycarboxylic acids through the intervention of cyclic anhydride formation.

(10) C. K. Ingold, *J. Chem. Soc.*, **127**, 387 (1925).

there is no obvious reason why other functional groups (carbonyl, nitro, nitrile, etc.) cannot be used in place of either or both of the carboxyl groups. These possibilities, the stereochemistry of the reaction and certain other extensions are being investigated.

### Experimental<sup>11</sup>

**General Methods of Preparing 1,2-Cyclopropanedicarboxylic Acid Diesters.** A. **Sodium Methoxide.**—The acrylic acid ester (2 or more moles) and the  $\alpha$ -halo ester (1 mole) were treated with sodium methoxide (1 mole) (a commercial grade of 95% purity was used), finely powdered, added in small portions. The reaction temperature was maintained at about 15–35° by cooling with an ice-bath when necessary. The reaction was usually only mildly exothermic and it was controlled readily by the rate of addition of the sodium methoxide and by the use of the cooling bath; the reaction mixture ordinarily remained fluid, but if it did become thick or viscous, considerable caution was observed in further addition of sodium methoxide as localized heating, although rare, occasionally resulted followed by a more vigorous or even violent reaction.<sup>12</sup> Stirring was continued for an hour or so after complete addition of the sodium methoxide; occasional cooling was sometimes necessary during this period. The reaction mixture then was poured into slightly more than enough water to dissolve the sodium halide, and the organic phase was washed with water and then saturated aqueous sodium chloride. The organic material was dried (MgSO<sub>4</sub>) and then distilled. Low boiling (at about 15 mm. pressure) material consisting of unreacted acrylic acid ester, the corresponding  $\beta$ -methoxy-propionate ester, and some  $\alpha$ -methoxy ester corresponding to the halo ester were separated readily from the higher boiling cyclopropane diesters. The pot residue was usually a dark red or black tar.

B. **Sodium Hydride Dispersed in Oil.**—A suspension of sodium hydride (1 mole, in oil<sup>13a</sup>) in dry toluene (100 ml.) was treated under nitrogen with the  $\alpha$ -halo ester (1 mole) and  $\alpha,\beta$ -unsaturated ester (1 mole) added dropwise. Gas evolution was immediate and mild, but occasionally became more vigorous. The reaction temperature was maintained at about 20–40° by using a cooling bath when necessary. The reactions studied so far were controlled readily by the use of the cooling bath and regulating the rate of addition of the ester mixture. (A larger volume of solvent may be advantageous in some cases to reduce the foaming tendency occasionally observed during gas evolution.) After addition of the ester mixture, stirring, and cooling as necessary, was continued until gas evolution was complete. A small amount of methanol was added dropwise with stirring to decompose any residual sodium hydride, and then sufficient water to dissolve the sodium halide was added. The toluene solution was washed with water and saturated aqueous sodium chloride. It was dried (MgSO<sub>4</sub>) and distilled. The high boiling cyclopropane derivative was readily separated from the toluene. Usually, the pot residue consisted solely or predominantly of the clear mineral oil in which the sodium hydride was dispersed.

Acidification of the aqueous washes from either procedure caused separation of an oil. The amount of oil was negligible except in procedure B when a halo-acetate was used. The oil appeared to be a mixture of acetoacetic esters.

The 1,2-cyclopropanedicarboxylic acid diesters were mixtures of stereoisomers. Although this resulted in rather large boiling ranges, the diesters usually did not appear to be contaminated with other materials. Most of the diester fractions were saturated to 2% potassium permanganate. The major exceptions were the diesters obtained from the crotonate esters. Even in those cases where unsaturation was detected, the unsaturated material appeared to be present in only small amount. In all cases there was negligible distillate in the range of 30–40° (usually even more) both above and below the boiling range of the diester.

The diesters (0.020–0.025 mole) were saponified by re-

fluxing with a 50% excess of 15% aqueous sodium hydroxide. Solution of the diester was complete in about one or two hours, but refluxing usually was continued for a total time of about four or five hours. The disodium salt of 1,2-dimethyl-1,2-cyclopropanedicarboxylic acid was insoluble; all of the other salts in this work were soluble under the conditions used. The basic solutions were concentrated under reduced pressure (about 15 mm.) and 40° bath temperature to remove alcohols. Dissolution of the thick mushes so obtained was done in the minimum amount of water. These solutions were acidified with a slight excess of concentrated hydrochloric acid and then continuously extracted for 24–36 hours with alcohol-free ether. Drying (MgSO<sub>4</sub>) the ethereal solutions and then removal of the ether on a steam-bath left mixtures of the stereoisomeric acids; some of these mixtures crystallized readily, but most remained as clear glasses.

The mixtures of isomeric diacids were usually obtained in about 80–95% yield, but in some cases considerable losses were encountered in the separation and purification of the isomers. Each of the mixtures presented a different problem in separation. Usually, a rough idea of the isomer ratio was obtained by a crude fractional crystallization. In those cases where the *trans* isomer predominated, this isomer usually could be obtained without difficulty by direct crystallization from a suitable solvent, the *cis* isomer being obtained from the mother liquors. In those cases where the *cis* isomer predominated, the mixtures were treated with a 20–50% excess of acetic anhydride based on the estimated amount of *cis* isomer. These mixtures were warmed on the steam-bath for 15 minutes, and then while still on the steam-bath the acetic acid and excess acetic anhydride were removed in a stream of dry air. The residual material was then sublimed (100°/10 mm.) to separate the *cis*-anhydride from the *trans*-diacid (or in some cases a polymeric *trans*-anhydride).

**1,2-Cyclopropanedicarboxylic Acid. Method A.**—Methyl acrylate (388 g., 4.5 moles), ethyl chloroacetate (245 g., 2 moles) and sodium methoxide (114 g., 95% active, 2.0 moles) gave 154 g., 45% yield, of 1-carbomethoxy-2-carbomethoxycyclopropane, b.p. 101–114° (15 mm.), *n*<sub>D</sub><sup>20</sup> 1.4416. Saponification gave 22% *trans*-1,2-cyclopropanedicarboxylic acid, m.p. 177–177.5° (CH<sub>3</sub>CN), and 26% *cis*-1,2-cyclopropanedicarboxylic acid (as the anhydride), m.p. 58–60° (sublimed). In another saponification, the *cis*-diacid, m.p. 139–142° (CH<sub>3</sub>NO<sub>2</sub>), was obtained, and converted by acetic anhydride to the *cis*-anhydride, m.p. 58–60° (toluene). The *trans* isomer had a mixed m.p. 177–177.5° with a sample, m.p. 176–177.5°, prepared by the method of Wiberg, Barnes and Albin<sup>2a</sup> (supplied by J. Albin); the infrared spectra were the same. The *cis*-anhydride had a mixed m.p. 58–60° with a sample, m.p. 58–60° (supplied by J. Albin); the infrared spectra were the same.<sup>13</sup>

In another run using one-fourth the quantities and substituting ethyl bromoacetate for the chloro compound, 22% of the diester was obtained. It had physical constants, including the infrared spectrum, essentially identical with those reported above.

**Method B.**—Methyl acrylate (43 g., 0.5 mole), ethyl chloroacetate (61 g., 0.5 mole) and sodium hydride (12 g., 52.5% by wt. in oil, 0.5 mole) gave 34% of the diester having physical constants, including the infrared spectrum, the same as reported above. When this reaction was repeated using ethyl bromoacetate in place of the chloro compound, the reaction would not take place in the usual temperature range (~20–40°). However, the reaction did go smoothly at the boiling point of the mixture (~100–110°) and then gave 23% of the diester, b.p. 95–103° (10 mm.), *n*<sub>D</sub><sup>20</sup> 1.4402; the infrared spectrum was somewhat different from that obtained previously for the diester mixture. Saponification gave 58% of the *trans*-diacid, m.p. 176–177° (CH<sub>3</sub>CN); none of the *cis*-diacid could be isolated from the mother liquors.

**1-Methyl-1,2-cyclopropanedicarboxylic Acid. Method A.**—Methyl acrylate (69 g., 0.8 mole), methyl  $\alpha$ -chloropropionate (49 g., 0.4 mole) and sodium methoxide (22.8 g., 95% active, 0.4 mole) gave 49 g., 70% yield, of dimethyl 1-methyl-1,2-cyclopropanedicarboxylate, b.p. 105–109° (15 mm.), *n*<sub>D</sub><sup>20</sup> 1.4432. Saponification gave 14% of the *trans*-diacid, m.p. 170° (CH<sub>3</sub>CN), and 63% of the *cis*-diacid (as

(11) Melting points and boiling points are uncorrected. Infrared spectra were taken on a Perkin-Elmer model 21 infrared spectrophotometer with a sodium chloride prism.

(12) Although no solvents were used in the present procedure, any hydrocarbon or ether solvent probably would be satisfactory as a diluent.

(13) Ingold (ref. 2b) reported m.p. 175–176° for the *trans*-diacid, m.p. 139° for the *cis*-diacid, and m.p. 59° for the *cis*-anhydride.

the anhydride), m.p. 45–47° (sublimation).<sup>14</sup> In a separate saponification, the *cis*-diacid, m.p. 139–141° (CH<sub>3</sub>CN), was isolated, and converted by acetic anhydride to the *cis*-anhydride, m.p. 46–47° (sublimation).

Ethyl methacrylate (22.8 g., 0.2 mole), ethyl chloroacetate (12.3 g., 0.1 mole) and sodium methoxide (5.7 g., 95% active, 0.1 mole) gave 0.7 g. of material boiling about 112° (13 mm.), *n*<sub>D</sub><sup>20</sup> 1.4462, and containing appreciable unsaturated substance, in this case, probably the starting methacrylate ester; the infrared spectrum showed a band at about 6.12  $\mu$ , and generally indicated a mixture. Therefore, any of the desired ester must have been present in less than 3% yield.

**Method B.**—This run was made at the boiling point of the mixture to obtain some idea of the effect of temperature on the reaction. Methyl acrylate (26 g., 0.3 mole), methyl  $\alpha$ -chloropropionate (37 g., 0.3 mole) and sodium hydride (7.2 g., 52.5% by wt. in oil, 0.3 mole) gave 28.5 g., 55% yield, of the diester, b.p. 98–99° (12 mm.), *n*<sub>D</sub><sup>20</sup> 1.4422. Saponification gave 28% of the *trans*-diacid, and 32% of the *cis*-diacid (as the anhydride).

**1,2-Dimethyl-1,2-cyclopropanedicarboxylic Acid. Method B.**—Ethyl methacrylate (11 g., 0.1 mole), methyl  $\alpha$ -chloropropionate (12 g., 0.1 mole) and sodium hydride (2.4 g., 52.5% by wt. in oil, 0.1 mole) gave 12 g., 60% yield, of 1,2-dimethyl-1-carbomethoxy-2-carbomethoxycyclopropane, b.p. 110–113° (14 mm.), *n*<sub>D</sub><sup>20</sup> 1.4453. Saponification gave <3% of the *trans*-diacid, m.p. 229–231°, and 72% of the *cis*-diacid (as the anhydride), m.p. 52–54°. In another saponification, the *cis*-diacid, m.p. 115–117° (CH<sub>3</sub>NO<sub>2</sub>), was isolated and converted by acetic anhydride to the *cis*-anhydride, m.p. 55–57° (methylcyclohexane), or m.p. 56–57° (sublimed).

**3-Methyl-1,2-cyclopropanedicarboxylic Acid. Method A.**—Ethyl crotonate (80 g., 0.7 mole), ethyl chloroacetate (43 g., 0.35 mole) and sodium methoxide (20 g., 95% active, 0.35 mole) gave 5.5 g., 8% yield, of diethyl 3-methyl-1,2-cyclopropanedicarboxylate, b.p. ~128° (19 mm.), *n*<sub>D</sub><sup>20</sup> 1.4419.

**Method B.**—Methyl crotonate (30 g., 0.3 mole), ethyl chloroacetate (37 g., 0.3 mole) and sodium hydride (7.2 g., 52.5% by wt. in oil, 0.3 mole) gave 16 g., 29% yield, of 3-methyl-1-carbomethoxy-2-carbomethoxycyclopropane, b.p. 108–120° (13 mm.), *n*<sub>D</sub><sup>20</sup> 1.4438. Saponification of the diester resulted in about 95% yield of the mixed diacids. Unfortunately, no really satisfactory procedure was found for separating and purifying these isomers; consequently, the yield of "pure" isomers is poor, and yields probably are not significant with respect to the isomer ratio actually present in the mixture. The *trans* isomer was isolated in 10% yield, m.p. 148–149°<sup>16</sup> (CH<sub>3</sub>CN) by crystallization from

(14) C. K. Ingold (ref. 10) reported a m.p. 168° for the *trans*-diacid, m.p. 142° for the *cis*-diacid, and b.p. 154–157° (19–20 mm.) for the *cis*-anhydride. However, Deutsch and Buchman (ref. 6) have indicated that the diacid obtained from ethanolic sodium ethoxide on ethyl  $\alpha$ -chloropropionate and reported previously as 1,3-cyclobutanedicarboxylic acid is actually 1-methyl-1,2-cyclopropanedicarboxylic acid. The *cis*-anhydride reported for this compound does have m.p. 47°.

(15) K. v. Auwers and O. Ungemach, *Ann.*, **511**, 152 (1934), reported a m.p. 230–231° for the *trans*-diacid, m.p. 115–117° for the *cis*-diacid, and m.p. 54–56° for the *cis*-anhydride.

(16) (a) M. C. Ettlinger, S. H. Harper and F. Kennedy, *J. Chem.*

acetonitrile. In a separate saponification, the diacid mixture was treated with acetic anhydride as described previously. By sublimation, a mixture of needles (major) and oil (minor) was obtained on the "cold finger." Assuming these to be the two *cis*-anhydrides, a total of 16% yield of the *cis* isomers was obtained. The oil and needles could not be separated completely, but when the bulk of the oil was removed on porous plate, the crude solid remaining had m.p. 75–80°.<sup>16a</sup>

**1,3-Dimethyl-1,2-cyclopropanedicarboxylic Acid. Method B.**—Ethyl crotonate (17 g., 0.15 mole), methyl  $\alpha$ -chloropropionate (18 g., 0.15 mole) and sodium hydride (3.6 g., 52.5% by wt. in oil, 0.15 mole) gave 19 g., 65% yield, of 1,3-dimethyl-1-carbomethoxy-2-carbomethoxycyclopropane, b.p. 107–113° (12 mm.), *n*<sub>D</sub><sup>20</sup> 1.4433. Saponification of the diester gave a mixture of diacids from which one isomer could be separated readily by crystallization from nitromethane or acetonitrile in 66% yield, m.p. 199–201°. A sample sublimed for analysis had m.p. 203°.

*Anal.* Calcd. for C<sub>7</sub>H<sub>10</sub>O<sub>4</sub>: C, 53.16; H, 6.37; neut. equiv., 79. Found: C, 52.94; H, 6.54; neut. equiv., 79.

This diacid when treated with acetic anhydride gave a very viscous anhydride (possibly polymeric) which had in its infrared spectrum bands at 5.58 and 5.78  $\mu$ . Based on these bands, its low solubility in acetonitrile and nitromethane, and its high melting point, this diacid is one of the *trans* isomers, probably 1<sup>4</sup>,3<sup>2</sup>-dimethyl-1<sup>2</sup>,2<sup>1</sup>-cyclopropanedicarboxylic acid.<sup>17</sup> No other pure isomer was isolated.

**1,2,3-Cyclopropanetricarboxylic Acid. Method A.**—Diethyl fumarate (34 g., 0.2 mole), ethyl chloroacetate (12 g., 0.1 mole) and sodium methoxide (5.7 g., 95% active, 0.1 mole) gave no triester, only a dark colored tar. The infrared spectrum of this material had a strong, sharp band at 6.12  $\mu$ . This result is explained adequately as described in footnote 4. The initial product would again be an  $\alpha,\beta$ -unsaturated ester, and this could react further leading to various unsaturated oligomeric substances.

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*Soc.*, 922 (1957), reported a m.p. 138°, passing into a dimorphic form, m.p. 150°, for the *trans* isomer. The lower melting form was not observed in the present work. They also reported a m.p. 80° for the anhydride of one of the *cis* isomers, but no melting point was given for the anhydride of the second *cis* isomer. (b) The separation of the isomers from a mixture such as that obtained in the present work has presented difficulties in earlier work: F. R. Goss, C. K. Ingold and J. F. Thorpe, *J. Chem. Soc.*, **123**, 3342 (1923); see the comments and corrections by Ettlinger, *et al.*, on the results of this work.

(17) In all of the known pairs of isomers observed in this work, the *trans* isomer is the less soluble, usually quite markedly so, in acetonitrile and nitromethane. None of the *trans* isomers melts below about 150°, and none of the *cis* isomers has a melting point above about 150°. The infrared spectra of all of the *cis*-anhydrides have bands at 5.40–5.45 and 5.65–5.70  $\mu$ . These bands are what might be expected for a succinic anhydride attached to a cyclopropane ring [Jones and Sandorfy in Weissberger's "Technique of Organic Chemistry," Vol. IX, Interscience Publishers, Inc., New York, N. Y., p. 456; D. H. R. Barton, P. de Mayo and Mohammed Shafiq, *J. Chem. Soc.*, 140 (1958)]. The ethyl crotonate starting material is undoubtedly *trans*, and if it is assumed that this same relation holds in the cyclopropane, then the steric relation of the groups is determined as indicated above.