sample of 1,1′-binaphthyl[19] was recovered unchanged when subjected to the conditions used to reduce 1,2-binaphthylene.

COLUMBUS 10, OHIO

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[19] Kindly supplied by Mr. Daniel Lednicer.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY]

Cyclopropanes: The Cyclopropyl Carbanion[1,2]

BY H. M. WALBORSKY AND F. M. HORNYAK

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2,2-Diphenylcyclopropanecarboxylic acid was prepared by the condensation of 1,1-diphenylethylene with ethyl diazoacetate and by the condensation of methyl acrylate with diphenyldiazomethane. The acid was resolved into its enantiomorphs and converted to optically active 2,2-diphenylcyclopropyl cyanide. The optically active cyanide derivative underwent facile racemization when treated with lithium diisopropylamide. The cyclopropyl carbanion was unable to retain its geometric configuration.

Introduction

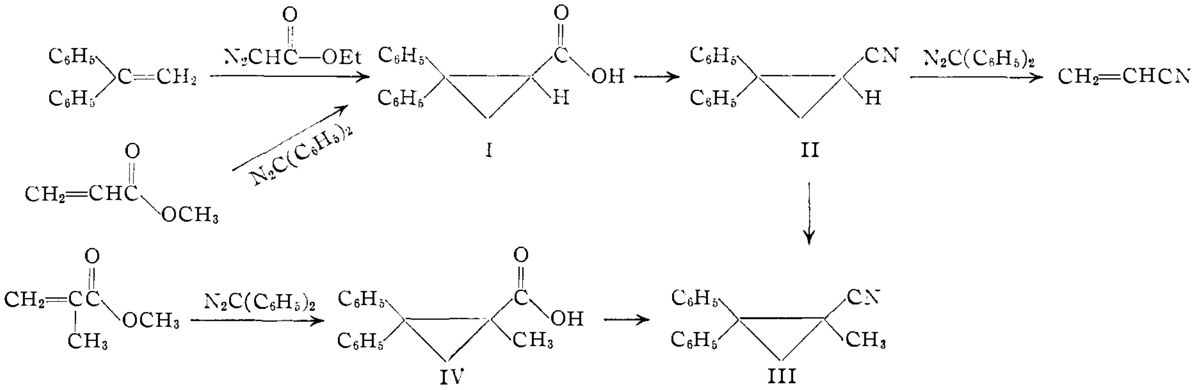
Many claims for the existence of optically stable carbanions have appeared in the literature. In nearly all cases, subsequent work has shown these reports to be in error. It had been reported that 2-nitrobutane[3] and 2-nitroöctane[4] gave, on treatment with base, optically active salts. Kornblum[5] and Theilacker[6] demonstrated that the activity was due to an alkyl nitrate contaminant and that nitro compounds formed inactive salts.

Wallis and Adams[7] reported that optically active 12-phenyl-12-B-benzoxanthenethioglycolic acid on treatment with sodium and liquid ammonia yielded optically active 12-phenyl-B-benzoxanthene. It was believed that the desulfurization reaction involved a carbanion intermediate which retained its asymmetry. Wittig and co-workers[8] repeated the work but could not duplicate the results.

The only case of an optically active carbanion which has not been refuted is found in a communication by Letsinger[9] who described the production of an optically active acid from the reaction of optically active 2-iodoöctane with *sec*-butyllithium and subsequent carbonation of the lithium exchange product.

Many other experiments have demonstrated that carbanions which can resonate with an adjacent group cannot retain optical activity such as the racemization of 2-dimethylamine-9-methylfluorene by lithium,[10] methylethylacetonitrile by lithium diethylamide,[11] and the facile racemization of ethyl ethylmethylacetate by sodium ethylate.[12]

In all of the above cases there are no obvious barriers to the planarity and, therefore, to the racemization of the intermediate carbanion. Thus it became of interest to prepare a molecule whose carbanion would possess a barrier to planarity and to determine whether or not this carbanion could retain its configuration. To this end the synthesis of optically active 2,2-diphenylcyclopropylcyanide (II) was undertaken.



2,2-Diphenylcyclopropyl Cyanide.—A successful synthesis of 2,2-diphenylcyclopropanecarboxylic acid (I) from ethyl diazoacetate and 1,1-diphenylethylene was accomplished in 46% yield using a procedure similar to that of Drake and Sweeney.[13] Previous syntheses of this acid gave yields of 5–7%.[14] It was found that purity of the product was enhanced by using freshly prepared ethyl diazoacetate and controlling the saponification time of the ester.

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[1] This paper is based on a portion of the thesis submitted by F. M. Hornyak in 1955 to the Florida State University in partial fulfillment of the requirements for the Ph.D. degree in Chemistry.

[2] Presented in part at the 126th Meeting of the American Chemical Society, New York, N. Y., September, 1954.

[3] R. Kuhn and H. Albrecht, *Ber.*, **60**, 1277 (1927).

[4] R. L. Shriner and J. H. Young, THIS JOURNAL, **52**, 3332 (1930).

[5] N. Kornblum, *et al.*, *ibid.*, **69**, 307 (1947).

[6] W. Theilacker, *Z. angew. Chem.*, **59A**, 175 (1947).

[7] E. S. Wallis and F. H. Adams, THIS JOURNAL, **55**, 3838 (1933).

[8] G. Wittig, F. Widal and R. Bohnert, *Ber.*, **83**, 359 (1950).

[9] R. L. Letsinger, THIS JOURNAL, **72**, 4842 (1950). The experimental portion of this work has yet to be formally published.

[10] K. Ziegler and A. Wenz, *Ber.*, **83**, 359 (1950).

[11] M. Heintzeler, *Ann.*, **569**, 7 (1950).

[12] J. Kenyon and D. P. Young, *J. Chem. Soc.*, 216 (1940).

[13] N. L. Drake and T. R. Sweeney, *J. Org. Chem.*, **11**, 67 (1946).

[14] H. Wieland and O. Probst, *Ann.*, **530**, 274 (1937); A. Burger, *et al.*, THIS JOURNAL, **71**, 3307 (1949); M. Hamada and A. Okamoto, *Batyu Kagaku*, **18**, 70 (1953); A. D'yakonov, *J. Gen. Chem.* (*U. S. S. R.*), **21**, 1986 (1951).

An alternate method for the preparation of I was found in the reaction between diphenyldiazomethane and substituted ethylenes.[15] The reaction between methyl acrylate and diphenyldiazomethane occurred at room temperature with the evolution of nitrogen to yield methyl 2,2-diphenylcyclopropanecarboxylate. Although only 85% of the theoretical amount of nitrogen was evolved, no pyrazoline derivative could be isolated.[16] The ester was saponified in good yield to the acid which was shown to be identical to the acid I previously prepared. This method is preferred to the ethyl diazoacetate procedure due to its technical simplicity, comparable yields and purer products.

2,2-Diphenylcyclopropyl cyanide (II) was prepared through the dehydration of the amide (formed by treatment of I with thionyl chloride and finally with cold aqueous ammonia) by phosphorus pentoxide in the presence of triethylamine as recommended for acid-sensitive compounds.[17] This method was adopted since dehydration by thionyl chloride produced a very impure nitrile in low yields. The nitrile II was prepared in 57% yield by the more direct method of condensing acrylonitrile and diphenyldiazomethane. This method could not be utilized conveniently for the preparation of optically active II but was useful for the preparation of racemic II. Haller and Benoist[18] and more recently Brown and Piehl[19] have demonstrated that cyclopropyl phenyl ketone can be alkylated by using a strong base such as sodamide or sodium triphenylmethyl. In this work it was found advantageous to use lithium diisopropylamide as the base since, as has been pointed out by Hamell and Levine,[20] it is a stronger base than sodium triphenylmethyl. Lithium diisopropylamide was shown to react almost instantaneously with II (see Experimental) and upon the addition of methyl iodide gave a 58% yield of III.

To demonstrate that no rearrangement occurred during the alkylation III was independently synthesized. Methyl methacrylate and diphenyldiazomethane were condensed to yield methyl 1-methyl-2,2-diphenylcyclopropanecarboxylate. The ester was saponified, converted to the amide and dehydrated by phosphorus pentoxide to the nitrile which was shown to be identical to that obtained by the alkylation of II.

Results and Discussion

The concept that the cyclopropane ring system possesses double bond character is supported by a great deal of evidence. Dipole moment,[21] ultraviolet absorption spectra[22] and molar refraction[23] studies are consistent with this idea. One of the most important pieces of evidence bearing on this point is found in the work of Freed and Sancier[24] who demonstrated that iodine and cyclopropane form an addition compound at low temperatures. There is also a great deal of chemical data which indicates double bond character in the cyclopropane ring.[25]

If, indeed, the cyclopropane ring has sufficient double bond character, this would suggest the possibility that a cyclopropyl carbanion might behave similarly to a carbanion formed on a trigonal carbon atom (alkenyl anion). Curtin and Harris[26] have shown that a carbanion formed on a trigonal carbon retains its geometric position. Thus *cis*- and *trans*-2-*p*-chlorophenyl-1,2-diphenyl-1-bromoethylene when treated with *n*-butyllithium at −20° and followed by carbonation gave rise to the *cis*- and *trans*-acids, respectively. Moreover, Dreiding and Pratt[27] have extended this work to the synthesis of angelic acid by the carbonation of the lithium derivative prepared from *trans*-2-bromo-2-butene.

If the carbon–nitrogen double bond is considered, such as in oximes and azomethines, this system is isoelectronic with the alkenyl anion system, and the stereochemical properties of the carbon–nitrogen double bond should be related to those of an alkenyl anion. Indeed, stereoisomeric forms of oximes[28] and azomethines[29] have been isolated and it is evident that in these cases a pair of electrons can occupy a fixed position in space.

It is seen that an alkenyl anion, when formed, is capable of maintaining its steric configuration. Since the cyclopropane ring is believed to have some properties of a carbon–carbon double bond the question arises as to whether a pair of electrons on a cyclopropane ring carbon will be subject to similar influences or interactions and thus preserve its spatial configuration. In connection with this point, Kincaid and Henriques[30] made rough calculations on the ethylenimine ring system, which is isoelectronic with the cyclopropyl carbanion, and predicted that they should be resolvable.

The results of our experiments on the optically active nitrile II clearly showed that the cyclopropyl carbanion is incapable of retaining its steric configuration. When I ($\alpha^{23}\text{D}$ $-307 \pm 6°$) was treated with lithium diisopropylamide, at room temperature, complete racemization occurred in less than 15 seconds.[31] Lowering the reaction temperature to that of Dry-Ice–acetone mixture also resulted in complete loss of optical activity. The alkylation of II at room temperature yielded an alkylated product which was completely racemized.

The mode of racemization brings up some interesting points. The usual mechanism proposed for the racemization of optically active nitriles[11] in-

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(15) H. Staudinger, *et al.*, *Ber.*, **49**, 1928 (1916); P. C. Guha and D. K. Sankaran, *ibid.*, **70**, 1688 (1937).

(16) Many times pyrazolines are preferentially formed or are by-products in this type of reaction. For examples see reference 15.

(17) S. M. McElvain and R. L. Clarke, THIS JOURNAL, **69**, 2657 (1947).

(18) A. Haller and E. Benoist, *Ann. Chim.*, [IX], **17**, 25 (1923).

(19) F. J. Piehl and W. G. Brown, THIS JOURNAL, **75**, 5023 (1953).

(20) M. Hamell and R. Levine, *J. Org. Chem.*, **15**, 162 (1950).

(21) M. T. Rogers and J. D. Roberts, THIS JOURNAL, **68**, 843 (1946); M. T. Rogers, *ibid.*, **69**, 2544 (1947).

(22) L. I. Smith and E. R. Rogier, *ibid.*, **73**, 3840 (1951).

(23) V. A. Slabey, *ibid.*, **76**, 3603 (1954).

(24) S. Freed and K. M. Sancier, *ibid.*, **74**, 1273 (1952).

(25) For a review with pertinent references see E. E. Royals, "Advanced Organic Chemistry," Prentice–Hall, Inc., New York, N. Y., p. 210–213.

(26) D. Y. Curtin and E. E. Harris, THIS JOURNAL, **73**, 2716, 4519 (1951).

(27) A. S. Dreiding and R. J. Pratt, *ibid.*, **76**, 1902 (1954).

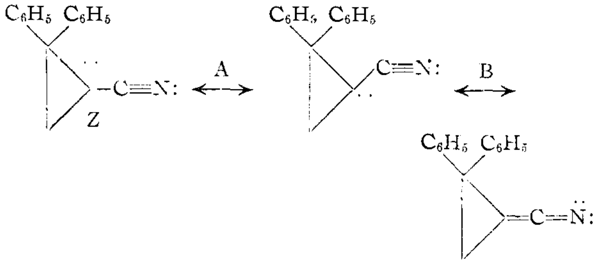
(28) A. Hantzsch and A. Werner, *Ber.*, **23**, 11 (1890); **24**, 13 (1891).

(29) W. Manchot and J. R. Furlong, *ibid.*, **42**, 3030 (1909).

(30) I. F. Kincaid and F. C. Henriques, Jr., THIS JOURNAL, **62**, 1474 (1940).

(31) Dr. S. H. Harper, Kings College, London, has kindly informed us that in the saponification of *cis*-chrysanthemonitrile by KOH in ethylene glycol he obtained a mixture of *cis*- and *trans*-acids due to epimerization.

volves the ion going through a planar transition state. The cyclopropane ring should present a barrier to this mode of racemization. If racemization occurs through a planar transition state



caused by a resonance hybrid B or by the swing through or inversion of the pair of electrons similar to the ammonia molecule A, either path would involve a strained, high energy, intermediate according to Brown's I Strain theory.[32] Apparently the strain involved is not sufficient to prevent the molecule from passing through this high energy barrier.

Kenyon and Young[12] reported a 100% racemization of methyl phenylmethylacetate by sodium methylate in 20 hours at room temperature. Refluxing the optically active methyl ester of I in a concentrated solution of sodium methylate in methanol for 15 hours yielded the acid I (apparently due to alkyl–oxygen fission)[33] and an oil which on saponification also gave I. Both acid products isolated showed *ca.* 85–90% retention of activity. Saponification of the ester by refluxing potassium hydroxide produced the acid with at least 87% of its activity. This parallels the findings of Brown and Piehl[19] who have shown that the behavior of ethyl cyclopropanecarboxylate toward sodium triphenylmethyl and sodamide is similar to that of esters which contain no α-hydrogens.

Experimental[34]

2,2-Diphenylcyclopropanecarboxylic Acid (I).—A large excess of 1,1-diphenylethylene[35] (100 g., 0.55 mole) held at 160° was treated with ethyl diazoacetate[36] (11.4 g., 0.10 mole) with good stirring, over a period of 6 hours. The addition was interrupted after the first few drops until gas evolution began. The temperature in the reaction vessel was maintained at 160–165° and a total corrected volume of 1880 ml. of nitrogen (84%) was collected. The cooled reaction mixture was refluxed with a solution of 6.0 g. of potassium hydroxide in 75 ml. of ethanol for one hour with stirring. The alcohol was removed *in vacuo* and the pasty residue diluted with water. The aqueous layer was separated and the organic layer washed several times with water. The aqueous layers were combined, washed twice with ether and the ether washings combined with the organic layer. The ethereal solution was dried over anhydrous sodium sulfate and on vacuum distillation yielded almost all of the excess olefin used. The aqueous layers were cooled in ice and slowly acidified with dilute hydrochloric acid. The solid precipitate was filtered, washed with water, and dried giving 16 g. of crude I. Recrystallization from methanol and a few drops of water gave 11 g. (46%) of acid melting at 170–171°[14] which had a neutralization equivalent of 236 (calcd. 238). It did not react with permanganate or bromine in carbon tetrachloride.

Resolution of I.—Thirty-one grams (0.13 mole) of acid was dissolved in 200 ml. of acetone with gentle warming. When solution was complete, 52 g. (0.13 mole) of anhydrous brucine alkaloid was added and the mixture again warmed and stirred to form a clear solution. On cooling in an icebox overnight a crop of crystals was obtained. The crop was recrystallized from acetone by allowing the solution to undergo a slow evaporation at room temperature. In this way crops of brucine salt crystals weighing 3–5 g. were separated and their specific rotations taken. A negative specific rotation, $[\alpha]^{23}\text{D}$ −112°, was the maximum value obtainable. In like manner the mother liquor from the original crop was subjected to a slow evaporation and crops were obtained which had specific rotations, $[\alpha]^{23}\text{D}$ as high as +30°.

To hydrolyze the brucine salt the following procedure was found advantageous. The brucine salt was dissolved in a minimum amount of acetone and the solution cooled in an ice-bath. Concentrated hydrochloric acid was then added slowly with stirring until a precipitate formed and the mixture was acid to litmus. On addition of water the precipitate dissolved. The acetone was partially removed *in vacuo* and cold dilute hydrochloric acid added to make the mixture distinctly acid during which a second precipitate appeared. (The first precipitate was probably brucine hydrochloride.) The acid was fully precipitated by addition of water and filtered. After thorough washing with water and drying, 2,2-diphenylcyclopropanecarboxylic acid was obtained. The brucine salts having $[\alpha]^{23}\text{D}$ −112° and $[\alpha]^{23}\text{D}$ +30°, gave the levorotatory and dextrorotatory acids, respectively, having $[\alpha]^{24}\text{D}$ −216 ± 6° and $[\alpha]^{24}\text{D}$ +212 ± 6° and melting at 150–151°. The brucine salt having $[\alpha]^{23}\text{D}$ −40° afforded the racemic acid.

2,2-Diphenylcyclopropanecarboxamide.—Prepared in the usual manner,[14] m.p. 178–179°, from ethanol. A sample of dextrorotatory I, $[\alpha]^{23}\text{D}$ +212 ± 6° gave the amide with $[\alpha]^{23}\text{D}$ +133 ± 5° and m.p. 120–121°. The levorotatory acid having $[\alpha]^{23}\text{D}$ −200 ± 6° gave the amide with $[\alpha]^{23}\text{D}$ −121 ± 5° and m.p. 121–122°.

2,2-Diphenylcyclopropyl Cyanide (II).—A mixture of the amide, 1.00 g. (0.0042 mole), 5 ml. of dry triethylamine and 1.5 g. (0.01 mole) of phosphorus pentoxide in 10 ml. of dry thiophene-free benzene was heated for 45 minutes and allowed to stand overnight. The mixture was diluted with water and extracted with ether. The ether extract was washed successively with dil. hydrochloric acid, aqueous sodium carbonate, water and dried over Drierite. The solvent was evaporated to yield 0.76 g. of crude nitrile which after one recrystallization from ethanol gave 0.65 g. (71%) of pure product, m.p. 107–108°. The crystals seemed to contain solvent and were resublimed *in vacuo* at 80° before analysis.

Anal. Calcd. for $C_{16}H_{13}N$: C, 87.63; H, 5.98; N, 6.39. Found: C, 87.81; H, 5.84; N, 6.49.

A sample of dextrorotatory amide having $[\alpha]^{23}\text{D}$ +133 ± 5° gave the nitrile with $[\alpha]^{23}\text{D}$ +304 ± 6° and melting at 136–138°. The levorotatory amide with $[\alpha]^{23}\text{D}$ −121 ± 5° gave nitrile with $[\alpha]^{23}\text{D}$ −307 ± 6° and melting at 137–138°. Equal amounts of enantiomorphs were mixed and gave m.p. 103–107°.

Alternate Synthesis of II.—A solution of 0.032 mole of diphenyldiazomethane[37] and 0.064 mole of acrylonitrile in 100 ml. of benzene was allowed to stand at room temperature until the red color disappeared. The excess acrylonitrile and the solvent were removed *in vacuo* and the residue crystallized from methanol to give II in 64% yield, m.p. and mixed m.p. 106–107°. The addition of diazodiphenylmethane to refluxing acrylonitrile gave an identical yield of product.

1-Methyl-2,2-diphenylcyclopropylcyanide (III).—An ether solution of lithium diisopropylamide[20] (0.01 mole) was refluxed with 1.00 g. (0.0045 mole) of racemic II for two minutes, then treated with 5 ml. of methyl iodide and refluxed for 45 minutes. The reaction mixture was hydrolyzed with water and extracted with ether. The ether solution was washed with dilute acid, water and dried over anhyd. sodium sulfate. Evaporation of the solvent yielded 61 mg. (58%) of III, m.p. 141–142°.

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[32] H. C. Brown, R. S. Fletcher and R. B. Johannesen, THIS JOURNAL, **73**, 212 (1951).

[33] J. F. Bunnett, M. M. Robison and F. C. Pennington, *ibid.*, **72**, 2328 (1950).

[34] All m.p.'s and b.p.'s are uncorrected. Optical rotations were taken on the Kern full-circle polarimeter (manufactured by Kern and Co. Ltd., Arrau, Switzerland). The concentrations used were 1% in acetone (unless otherwise stated).

[35] C. F. H. Allen and S. Converse, "Organic Syntheses," Coll. Vol. **I**, John Wiley and Sons, Inc., New York, N. Y., p. 226.

[36] E. B. Womack and A. B. Nelson, *Org. Syntheses*, **24**, 56 (1944).

[37] L. I. Smith and K. L. Howard, *ibid.*, **24**, 53 (1954).

Anal. Calcd. for $C_{17}H_{15}N$: C, 87.51; H, 6.48; N, 6.00. Found: C, 87.64; H, 6.55; N, 6.03.

In an identical experiment 0.100 g. of optically active 2,2-diphenylcyclopropanecarbonitrile with $[\alpha]^{24}D$ $-307 \pm 6°$, and melting at 137–138° gave 60 mg. of product which showed an angle of rotation of zero and melted at 140–142.5°. When this product was mixed with active starting material the melting point was 110–115°.

Reaction of Optically Active II with Lithium Diisopropylamide.—A 0.05-g. quantity of nitrile, $[\alpha]^{24}D$ -307 ± 6, in 5 ml. of anhydrous ether was added to 10 ml. of an ethereal solution of lithium diisopropylamide (0.005 mole) and agitated for 10 seconds. The mixture was then immediately poured into ice and dilute hydrochloric acid and shaken. The ether layer was washed in the usual manner and dried. Evaporation gave a quantitative yield of crude nitrile which melted at 94–105° and showed an angle of rotation of 0.00 ±0.025° when dissolved in 2.5 ml. of acetone.

Low Temperature Racemization of II.—A 0.078-g. quantity of nitrile, $[\alpha]^{23}D$ $-307 \pm 6°$, was added to 25 ml. of lithium diisopropylamide solution prepared and cooled as in the previous low temperature alkylation. Stirring was continued for 10 minutes. The solution was then quickly poured into water and shaken. The nitrile was then separated as described in the room temperature racemization. After recrystallizing the crude product from methanol, 22 mg., m.p. 105.5–107°, was obtained. A mixed m.p. with inactive nitrile was 106–107°. When the entire pure yield was dissolved in 1.5 ml. of acetone the angle of rotation was 0.0 ± 0.025°. For complete retention of activity the polarimeter angle would have been as high as −4.40°. No activity was found in the mother liquors or impurities.

1-Benzyl-2,2-diphenylcyclopropyl Cyanide.—Five milliliters of lithium diisopropylamide solution, containing 0.001 mole, was treated with 0.100 g. of II. The nitrile dissolved giving a reddish-brown coloration. A 0.15-g. quantity of purified benzyl chloride was added and the mixture was allowed to stand at room temperature for two days. During this time small crystals appeared. The mixture was evaporated to dryness, water added and the organic product separated by ether extraction. The product was recrystallized from methanol–ether twice and melted at 164.5–165.2°. It was relatively insoluble in methanol. The yield of benzylated nitrile was 0.042 g. (30%).

Anal. Calcd. for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53. Found: C, 89.05; H, 6.15; N, 4.57.

Reaction of Diphenyldiazomethane and Methyl Acrylate.—A solution of 0.044 mole of diphenyldiazomethane in 50 ml. of petroleum ether was added in 5- to 10-ml. portions, with stirring, at room temperature to 10 g. (0.116 mole) of methyl acrylate. Each portion decolorized with the evolution of nitrogen which was collected over water. The addition time was about 3.5 hours and a total volume (corrected to S.T.P.) of 850 ml. of nitrogen was collected (85%). The solvent was removed *in vacuo* and the residue distilled giving 5.2 g. (52%) of an oil boiling at 170–175° at 2 mm. When seeded with a sample of solid ester prepared by the action of diazomethane on 2,2-diphenylcyclopropanecarboxylic acid the distillate solidified, m.p. 35–38°; refluxing for 1 hour with a twofold equivalent amount of potassium hydroxide in methanol and working up, yielded 4.0 g. of acid which melted at 169–171°. A mixed melting point with the acid obtained from diazoacetic ester and 1,1-diphenylethylene was 169–171°.

Methyl 2,2-Diphenylcyclopropanecarboxylate.—An 11.5 g. (0.049 mole) quantity of II was treated with 100 ml. of an ethereal solution containing about 2.8 g. (0.068 mole) of diazomethane was slowly added until bubbling ceased and the mixture was distinctly yellow. The mixture was allowed to stand overnight, then washed with water and dried over sodium sulfate. The aqueous washings on acidification gave a quantity of unreacted acid. Evaporation of the ether and distillation gave 7.5 g. (56%) of ester boiling at 160–165° at 3.5 mm. After one year the sirupy ester crystallized to a white solid melting at 39–41°.

Esterification of the optically active acid (specific rotation) $[\alpha]^{24}D$ $-204 \pm 6°$) in the same manner gave the active ester with $[\alpha]^{24}D$ $-217 \pm 6°$, boiling at 165° at 4 mm. The ester remained an oil until seeded with a minute amount of solid racemic ester. It then became a white solid melting at 46–47.6°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.86; H, 6.65.

The Action of Bases Upon Methyl 2,2-Diphenylcyclopropylcarboxylate. A. Potassium Hydroxide.—Four milliliters of 95% ethanol, 0.065 g. of ester $[\alpha]^{24}D$ $-217 \pm 6°$, and 0.1 g. of potassium hydroxide were refluxed for 14 hours, becoming brown in color. At the end of this time the alcohol was removed *in vacuo* and water added. The solution was centrifuged and a clear brownish yellow liquid obtained. On acidification with hydrochloric acid, 2,2-diphenylcyclopropanecarboxylic acid (m.p. 168–170° was obtained weighing 0.05 g., $[\alpha]^{24}D$ $-184 \pm 6°$).

B. **Sodium Methylate.**—Two grams of sodium was dissolved in 5 ml. of methanol. A 0.225-g. quantity of ester, $[\alpha]^{24}D$ $-217 \pm 6°$, was added and the solution was refluxed for 15 hours. The alcohol was then removed *in vacuo* and the residue dissolved in 2 ml. of water and extracted with ether. The aqueous layer on acidification gave 0.03 g. of 2,2-diphenylcyclopropanecarboxylic acid, $[\alpha]^{24}D$ $-185 \pm 11°$. Saponification of the ether layer material gave the acid with $[\alpha]^{23}D$ $-195 \pm 6°$.

Boiling the active ester with sodium hydride in dry benzene for 6 hours followed by saponification gave the active acid with $[\alpha]^{23}D$ $-194 \pm 5°$. There was no apparent reaction.

Methyl 1-Methyl-2,2-diphenylcyclopropylcarboxylate.—Methyl methacrylate (10 g.), held at 135°, was treated with a solution of 0.044 mole of diphenyldiazomethane in 50 ml. of low boiling petroleum ether over a period of three hours. After addition was complete a corrected volume of 695 ml. of nitrogen (at S.T.P.) was obtained (71%). The reaction mixture was then distilled and a fraction boiling at 153–154° at 1 mm. was collected. Recrystallization from methanol gave 8.8 g. of pure white crystals (75%) melting at 92–92.2°. The product gave negative tests for nitrogen and unsaturation.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.13; H, 6.94.

1-Methyl-2,2-diphenylcyclopropanecarboxylic acid was obtained in 79% yield by saponification of the ester with alcoholic potassium hydroxide. The acid, m.p. 182–183°, had a neutralization equivalent of 249 (calculated 252).

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.99; H, 6.67.

1-Methyl-2,2-diphenylcyclopropanecarboxamide was prepared in 55% yield by treating the acid with thionyl chloride and subsequently with cold aqueous ammonia. The amide was obtained in two forms one melting at 78–80° from ethanol which after melting had m.p. 149–150°. Sublimation of the high melting form gave the low melting form.

Anal. Calcd. for $C_{17}H_{17}ON$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.37; H, 6.99; N, 5.56.

1-Methyl-2,2-diphenylcyclopropylcyanide.—The dehydration was carried out with phosphorus pentoxide by the method described for the dehydration of 2,2-diphenylcyclopropanecarboxamide. The nitrile was obtained in 75% yield and melted at 141.3–142.8°. A mixed melting point with the product obtained from the methylation of 2,2-diphenylcyclopropanecarbonitrile was not depressed.

TALLAHASSEE, FLORIDA