of acid anhydrides and it was possible to prepare the compound by the reaction of potassium N,N-diphenylcarbamate and N,N-diphenylcarbamyl chloride. This product differed from that of Herzog and Budy and the difference seems to lie in the fact that their material was a complex of two molecules of anhydride with one of diphenylamine. Because only a small amount of pure material was required for our purposes, no attempt was made to refine the procedures which are described below.

Experimental Part

Stem corrections were applied to melting points all of which were taken in melting point tubes in an electrically heated copper block.

Potassium N,N-Diphenylcarbamate (I).—The method of preparation was essentially that of Heussermann.[3] An 8.3-g. sample of potassium was added to 100 g. of molten diphenylamine (Eastman Kodak Co. White Label recrystallized) at 90°. After the first vigorous reaction had ceased, the flask was evacuated and heating at 120° was continued for five and one-half hours in order to complete solution of the potassium. A heavy yellow sand-like precipitate settled in the molten diphenylamine. Excess diphenylamine was dissolved by adding 200 ml. of anhydrous ether to the cooled mixture. When carbon dioxide was bubbled through the suspension, the sandy precipitate was replaced by a loose, fine, white powder. The powder was centrifuged, washed seven times with 150-ml. portions of anhydrous ether to remove diphenylamine, and dried. The yield was 55 g. of nearly white powder. Analysis showed that the crude material was far from pure but since the impurity was probably potassium carbonate, purification was not attempted.

N,N-Diphenylcarbamic Anhydride.—About 50 g. of (I) and 40 g. of N,N-diphenylcarbamyl chloride (Eastman White Label recrystallized) were mixed and heated in an oil-bath at 90°. After fifteen minutes, the melt had become a grey paste. The heating was continued for five hours with frequent stirring. Throughout this time, the melt did not change in color but did bubble slightly. When the cooled paste was digested with 150 ml. of boiling methanol, much material dissolved. After the insoluble portion had been centrifuged from the dark red-brown solution, about 30 g. of yellowish crystalline material slowly formed in the solution on cooling in an ice-salt-bath. Recrystallization from methanol resulted only in the formation of 16 g. of material which was more highly colored than the crude product but when this dark-colored material was recrystallized twice in small portions from boiling acetone (2.5 ml. per g.) and once from methanol, 5.5 g. of greyish-yellow crystals were formed which melted at 121.5–122.5° in good agreement with the melting point of 122–123° which is recorded by Herzog and Budy.[2] The analysis, however, indicated that the material was a complex of two molecules of anhydride and one of diphenylamine.

Anal. Calcd. for anhydride: C, 76.43; H, 4.95; N, 6.86; mol. wt., 408. Calcd. for complex: C, 77.93; H, 5.23; N, 7.10; mol. wt., 986 (3 × 329). Found: C, 77.89, 77.69; H, 5.01, 4.94; N, 7.06, 7.38; mol. wt., 321, 329 (Rast micromethod in exaltone).

Experiments showed that recrystallization from absolute ethanol which contained hydrogen chloride yielded a product of melting point of about 129°. Accordingly, 4 g. of the complex was dissolved in 30 ml. of hot absolute ethanol and hydrogen chloride gas was passed into the solution. Cooling of the solution produced fairly large colorless prisms. By repeated crystallization from ethanol–hydrogen chloride and finally from ethanol, a product was finally obtained which melted at 128.5–130°. The following analyses were obtained.

Anal. Calcd. for $C_{26}H_{20}O_3N_2$: C, 76.43; H, 4.95; N, 6.86; mol. wt., 408. Found: C, 76.68, 76.55; H, 4.73, 4.80; N, 7.18, 7.12; mol. wt., 402 (Rast micromethod in exaltone).

Probably the purification could be much improved if the methanolic extract of the reaction mixture were saturated with hydrogen chloride before the product is first crystallized. Several recrystallizations, of which the last should be from ethanol in order to remove traces of hydrogen chloride, should then yield a pure product. The use of hydrogen chloride is effective because the hydrochloride of diphenylamine is stable and soluble in methanol or ethanol.

Proof of Structure of N,N-Diphenylcarbamic Anhydride.—The material of Herzog and Budy[2] probably was the complex of N,N-diphenylcarbamic anhydride and diphenylamine although their analyses, especially for carbon, were not unsatisfactory. However, the compound which was prepared in the present study and which melts at 128.5–130° may be shown to be the anhydride itself on the basis of the following facts.

(1) The analyses and molecular weight agree with the calculated composition and molecular weight of the anhydride.

(2) Ammonolysis yielded 80% of the N,N-diphenylurea (proved by mixed melting point with an authentic sample) which should be formed if 2 moles of ammonia react to form one mole of N,N-diphenylurea and one mole of ammonium diphenylcarbamate. Herzog and Budy also carried out this reaction which by itself is a poor proof of structure.

(3) Hydrolysis with refluxing *N* sodium hydroxide for forty-eight hours produced 90% of the theoretical diphenylamine if it is assumed that one mole of anhydride is hydrolyzed to 2 moles of diphenylamine. In this procedure, the diphenylamine was extracted from the hydrolysate with ether and the quantity was determined by chromatographic-spectrophotometric methods.[4]

(4) Compounds such as diphenyloxanilide, tetraphenylurea, methyl or ethyl N,N-diphenylcarbamate which might be formed during the reaction or purification are excluded on the basis of melting point.

Some Properties of the Anhydride.—N,N-Diphenylcarbamic anhydride is very soluble in chloroform, soluble in benzene, acetone, ethanol, and warm methanol, and slightly soluble in ligroin, ethyl ether, and cold methanol. It can be heated in ethanol or methanol without change and much can be recovered unchanged after refluxing for two hours in ethanol which contains potassium ethoxide. Norite causes decomposition in hot alcoholic solution.

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[3] C. Heussermann, *J. prakt. Chem.*, **58**, 367 (1898).

[4] W. A. Schroeder, E. W. Malmberg, L. L. Fong, K. N. Trueblood, J. D. Landerl and E. Hoerger, *Ind. Eng. Chem.* **41**, 2818 (1949).

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GATES AND CRELLIN LABORATORIES OF CHEMISTRY
CALIFORNIA INSTITUTE OF TECHNOLOGY
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The Synthesis of 1-Methylcyclopropanemethanol

BY SAMUEL SIEGEL AND CLARENCE G. BERGSTROM

As a prelude to a kinetic investigation of the chemical effects of the cyclopropyl group, the previously unknown 1-methylcyclopropanemethanol has been synthesized. Paralleling the work of von Auwers[1] on the thermal decomposition of the pyrazoline resulting from the reaction of diazomethane and ethyl methacrylate, we have found that the corresponding pyrazoline resulting from the reaction of diazomethane and methyl methacrylate gives a mixture of 70%,

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[1] von Auwers and Konig, *Ann.*, **496**, 27, 252 (1932).

1-methylcarbomethoxycyclopropane and 30% methyl tiglate. The lithium aluminum hydride reduction of 1-methylcarbomethoxycyclopropane gave a mixture of compounds from which 1-methylcyclopropanemethanol was isolated by fractional distillation (Fig. 1).

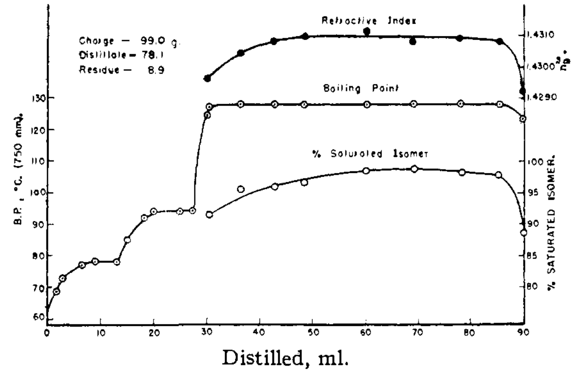

Fig. 1.—Distillation of crude 1-methylcyclopropanemethanol.

Evidence for the structure of 1-methylcyclopropanemethanol, its physical properties and a description of two derivatives, the 3,5-dinitrobenzoate and the α-naphthylurethan are given in the experimental part.

Derfer, Greenlee and Boord[2] have reported an alcohol obtained as a by-product from the reaction of zinc and 1,1,1-tris-(bromomethyl)-ethane as being 1-methylcyclopropanemethanol. In Table I, the compound obtained in the present investigation is compared with that reported by the authors just mentioned.

TABLE I

	This work	D. G. B.
B. p., °C.	128.0 (750 mm.)	120–121 (760 mm.)
d^{20}_4	0.8872	0.9033
n^{20}_D	1.4308	1.4333
M. p. 3,5-dinitrobenzoate, °C.	85.2–85.3	133.3–133.4
Mol. ref.[a]	25.1	24.8
%C[a]	69.91[3]	69.4
%H[a]	11.77[3]	11.7

[a] Calcd. for $C_6H_{10}O$: mol. ref., 25.3; C, 69.72; H, 11.70.

The compound reported by Derfer, Greenlee and Boord obviously is not identical with the compound reported in this paper.

Experimental

Methyl Methacrylate Monomer.—The product obtained by the thermal depolymerization of granular Lucite[4] was found to give the best results. The crude monomer was purified by a rapid distillation through a two-foot Vigreux column, the product boiling at 99–100° being used.

Pyrazoline Intermediate.—Nitrosomethylurea (25 g.) was added slowly to a mixture of 72 ml. of 50% potassium hydroxide and 200 ml. of ordinary ether in a 500-ml. erlenmeyer flask cooled in ice. The ethereal solution of diazomethane was decanted and the aqueous layer swirled twice with two 100-ml. portions of ether which were combined with the first extract. Freshly distilled methyl methacrylate monomer (20 g.) was added. The solution was cooled for a short time after adding the ester and was decolorized in about two hours. The ether was evaporated at the water aspirator. The yield of crude pyrazoline was quantitative.

The pyrazoline was decomposed in a flask attached to a reflux condenser. The rate of decomposition was easily controlled by intermittent application of heat. To complete the reaction the mixture was boiled for one hour. Quantities as high as 50 g. were handled without difficulty. The yield of product was 90%. Both distillation and titration with a bromide-bromate[5] mixture indicated that the product contained 70% 1-methylcarbomethoxycyclopropane and 30% methyl tiglate.

Fractionation of Ester Mixture.—The ester was distilled from a Claisen flask to separate it from a small amount of darkly colored material and then redistilled through a 12 × 915 mm. Todd column[6] packed with glass helices. The product was taken between 123 and 126°. The residue was largely methyl tiglate. If the crude product was wet, an azeotropic mixture of 1-methylcarbomethoxycyclopropane and water was obtained at 77°. Hydrolysis of this fraction followed by treatment of the hydrolyzate with *p*-bromophenacyl bromide gave a *p*-bromophenacyl ester, m. p. 57.5–59.0°, whose mixed melting point with the corresponding derivative of 1-methyl cyclopropanecarboxylic acid showed no depression. The 77° fraction colored anhydrous copper sulfate blue and gave a cloudy solution in benzene. Saponification indicated 43.4, 43.0% ester in the azeotrope.

The Evidence for the Structure of 1-Methylcarbomethoxycyclopropane.—The compound had been previously synthesized by Kohn and Mandelewitsch by the action of zinc on methyl dibromopivalate.[7] The values for the physical constants in parentheses are theirs: b. p. 124.5–126.0° (121–123°); n^{25}_D 1.4208; d^{25}_4 0.9552; mol. ref. 30.3, calcd. 30.1; sapon. equiv. 111, 113, calcd. 114.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.13; H, 8.83. Found[3]: C, 62.95; H, 8.80.

Hydrolysis of the ester yielded 1-methylcyclopropanecarboxylic acid, m. p. 29.5–32.0° (29–31°). The *p*-bromophenacyl ester of 1-methylcyclopropanecarboxylic acid after one recrystallization from an alcohol-water mixture had a m. p. of 59–60°. A second recrystallization caused no change in the m. p.

Methyl tiglate was characterized by the following properties: b. p. 138.0–139.2° (139.4–139.6)[9]; n^{25}_D 1.4338 (n^{20}_D 1.43700)[8]; sapn. equiv. 113, 114 (calcd. 114). Alkaline hydrolysis of the ester gives tiglic acid, m. p. 63.0–63.3° (64°)[9]; *p*-bromophenacyl ester, m. p. 67.0–67.2° (67.9°).[10]

1-Methylcyclopropanemethanol.—1-Methylcarbomethoxycyclopropane was reduced with lithium aluminum hydride by the method of Nystrom and Brown.[11] After the reduction was completed, the product was hydrolyzed with wet ether which was added cautiously to the reaction mixture. The resulting mixture was extracted continuously with ether. A conscious effort was made to avoid contact of the alcohol with strong acids (see last section of Experimental part).

The distillation of the extract proceeded smoothly in the absence of boiling stones. Their presence in the still pot resulted in an uncontrollable frothing of the solution when distillation was attempted.

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[2] Derfer, Greenlee and Boord, THIS JOURNAL, **71**, 175 (1949).

[3] Analysis by Micro-Tech. Lab., Skokie, Illinois.

[4] Purchased from the Chicago Apparatus Company.

[5] Francis, *Ind. Eng. Chem.*, **18**, 821 (1926).

[6] Todd, *ibid.*, **17**, 175 (1945).

[7] Kohn and Mandelewitsch, *Monatsh.*, **42**, 227 (1921).

[8] Naster and Gavriloff, *Bull. soc. chim. Belg.*, **42**, 519 (1933).

[9] von Auwers, *Ann.*, **432**, 70 (1923).

[10] Lund and Langved, THIS JOURNAL, **54**, 4107 (1932).

[11] Nystrom and Brown, *ibid.*, **69**, 1197 (1947).

The results of the distillation of a single batch of the above preparation is shown in Fig. 1. The fraction which boiled at 78° is believed to be ethanol present in the ordinary ether used to decompose the excess lithium aluminum hydride. An azeotrope probably consisting of 1-methylcyclopropanemethanol and water distilled at 94°.

The yield of alcohol, b. p. 124.5–128.0°, is 56% based upon the ester used. The physical constants for the intermediate cut taken between 75.6 and 85.2 ml. are presented in Table I. The alcohol reacts slowly with bromine in carbon tetrachloride.

The α-naphthylurethan was prepared and recrystallized three times from petroleum ether.

Anal. Calcd. for $C_{16}H_{17}O_2N$: C, 75.27; H, 6.71; N, 5.49. Found[8]: C, 75.23; H, 6.66; N, 5.82.

The 3,5-dinitrobenzoate was prepared both in the presence and absence of pyridine. The products were the same, as indicated by the melting point and mixed melting point. The 3,5-dinitrobenzoate after three recrystallizations from alcohol had a m. p. of 85.5–85.7°.

Anal. Calcd. for $C_{12}H_{12}O_6N_2$: C, 51.43; H, 4.32. Found[8]: C, 51.92; H, 4.36.

Oxidation of 1-Methylcyclopropanemethanol.—The alcohol (100 mg.) was dissolved in 5 ml. of water, 1 ml. of 10% sodium hydroxide was added, and potassium permanganate was added in small amounts so that after refluxing for thirty minutes the solution retained the permanganate color. The solution was acidified with 5 *N* sulfuric acid after filtering off the manganese dioxide, and then steam distilled. Titration of the distillate indicated 44 mg. of acid (38% yield). This was converted to the *p*-bromophenacyl ester without isolating the acid from the aqueous solution. After recrystallization from alcohol, 32 mg. of ester was obtained, m. p. 62.5–63.0° (23% yield from the acid). The mixed melting point with an authentic sample of the *p*-bromophenacyl ester of 1-methylcyclopropanecarboxylic acid was 60–62°. The mixed melting point with the corresponding ester of tiglic acid was 49–59°.

The Detection of Unsaturated Isomers.—This was attempted by an analysis of a 0.02 *M* solution of the carbinol in 0.1 *N* sulfuric acid with a bromide–bromate mixture (0.05 *M* in bromine), adding an excess of potassium iodide at definite time intervals and back titrating with standard sodium thiosulfate. The values for the degree of unsaturation were found to increase from 38% after one minute to 86% after seven minutes. Unpublished work by the present authors indicates that a 0.05 *M* solution of cyclopropanemethanol (homolog of the alcohol described in this paper) in 0.1 *N* hydrochloric acid rearranges to an unsaturated isomer to the extent of 23% in 44 hours at 100° so it would appear highly desirable to avoid the use of acids in working with alcohols of this type.

The degree of unsaturation was determined by the titration of 100–200-mg. samples of product taken by intercepting the distillate at the experimental points. The titration was carried out with a 0.05 *M* solution of bromine in carbon tetrachloride and the end-point arbitrarily set as the point at which the bromine color was still visible one minute after adding the bromine solution in 0.04-ml. increments. This technique proved satisfactory for the analysis of 3-butene-1-ol. In a series of experiments involving the reaction of 0.042 molar 1-methylcyclopropanemethanol (of a less carefully purified sample than that reported in Table I) and 0.025 *N* bromine in carbon tetrachloride, the degree of unsaturation was found to increase in a regular manner from 9% after one minute to 54% after 128 min. This suggests that, under the conditions of the analysis, bromine will add to the cyclopropane ring. This would result in low titration values for the purity of the carbinol so it is felt that the values given indicate the minimum purity with respect to any unsaturated isomer.

DEPARTMENT OF CHEMISTRY
ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO 16, ILLINOIS

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A Synthesis of Cyanamide from Barium Carbonate Applicable to Use of Isotopic Carbon

BY SUSANNE VON SCHUCHING AND FREDERICK W. BARNES, JR.

In preparing cyanamide containing C^{14}, it is desirable to use radioactive carbonate as starting material. Reported methods for carrying out this conversion are associated with rather difficult conditions of reaction or with only moderate yields, especially when done in semimicro amounts.[1,2,3]

It was found by us that barium carbonate reacts readily with ammonia in the presence of sodium azide to give cyanamide, the reaction being easily carried out in one step with greater than 94% yield based on carbon. This contrasts with more difficult conditions of reaction when no sodium azide is used.[1] The experimental evidence reported below applies to barium carbonate of normal isotope content. The reaction also has been used in the synthesis of cyanamide from 124 mg. of barium carbonate of which the carbon included 1 mc. of C^{14}. Since the work below was completed, another method of cyanamide synthesis from carbonate with high yield has been reported.[4]

The technique of the condensation was that described by Adamson,[5] except that anhydrous ammonia (passed over potassium hydroxide) was passed briskly into the open end of the test-tube which contained 200 mg. of isotopic barium carbonate and 4 g. of sodium azide. After sixty minutes of heating, the tube was cooled while under the stream of ammonia, and after cautiously destroying the sodium, the content was dissolved in 150 ml. of water and filtered. The clear filtrate was poured slowly into 50 ml. of 0.1 *N* silver nitrate containing 2% ammonia and after twelve hours the yellow-green precipitate was centrifuged off, dissolved in 30 ml. of 3.0 *N* nitric acid, then made up to 50 ml. with water and filtered. Twelve hours after adding 10 ml. of 0.1 *N* silver nitrate to the filtrate, it was made alkaline slowly with 5% ammonia, the centrifuged precipitate then was washed with water until the filtrate was free of silver ion, finally the precipitate was washed with methanol and ether and dried in the desiccator. The precipitate was identified as the silver salt of cyanamide by the following: it was clear yellow, insoluble in water and dilute ammonia, easily soluble in dilute nitric acid.[6] It had no melting point but decomposed violently at about 200°.[3] An analysis for the silver content[7] was made by dissolving the disilver salt in dilute nitric acid and titrating it with ammonium thiocyanate, ferric alum being used as indicator. Calcd. for CN_2Ag_2: Ag, 84.4. Found from three separately synthesized preparations: Ag, 83.5, 83.2, and 83.3. The silver salt was converted to O-methyl isourea monohydrochloride as part of

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(1) German Patent 139,456; *Chem. Zentr.*, **74**, I, 6777 (1903); Franklin, THIS JOURNAL, **44**, 495 (1922); Calvin, Heidelberger, Reid, Tolbert and Yankwich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 158.

(2) Bloch and Schoenheimer, *J. Biol. Chem.*, **138**, 167 (1941); Aroll, *J. Chem. Soc.*, Pt. 2, 1534 (1948); Ullmann, "Enzyklopädie der technischen Chemie," 2nd edit., Vol. II, 109 (1928); German Patent 108,971; *Chem. Zentr.*, **71**, I, 1120 (1900); German Patent 163,320; *Chem. Zentr.*, **76**, II, 1059 (1905).

(3) Beilstein and Geuther, *Ann.*, **108**, 88 (1858).

(4) Murray and Ronzio, THIS JOURNAL, **71**, 2245 (1949).

(5) Adamson, *ibid.*, **69**, 2564 (1947).

(6) Dreschel, *J. prakt. Chem.*, **11**, 301 (1875).

(7) Pink, *Ind. Eng. Chem.*, **17**, 459 (1925).