and cooled in an ice-bath. A vigorous stream of dry hydrogen chloride gas was passed into the solution for a few minutes. A precipitate was obtained immediately. This was filtered off and recrystallized from ethyl alcohol.

Condensation of Dimethylphenol with Crotonaldehyde.—Twelve grams of the dimethylphenol (0.10 mole) and 3.5 or 7.0 g. of crotonaldehyde (0.05 or 0.10 mole) were dissolved in 100 cc. of glacial acetic acid. To this solution was added 20 cc. of concentrated hydrochloric acid. On standing for two days a crystalline precipitate was obtained. This was filtered off, washed with a small amount of glacial acetic acid and then recrystallized from benzene.

Acetates.—Two grams of the condensation product was dissolved in 50 cc. of acetic anhydride and refluxed for two hours. The solution was poured into water and allowed to stand for one day. The resulting crystalline derivatives were recrystallized from dilute ethyl alcohol solution.

Summary

1. Phenols with only one ring position available for reaction were condensed with equi- and multimolar quantities of saturated, unsaturated and aromatic aldehydes. Crystalline condensation products of the alkylidene-di-phenol type were obtained exclusively in all cases.

2. When aldehydes are condensed with properly blocked phenols having only one ring position available for reaction, no Bakelite types of condensation products are formed, indicating that the formation of such types of condensation products requires at least *two* available ring positions in the reacting phenol. In blocked phenols, the possibility for the formation of ether types of condensation products definitely exists, yet, since no such products were formed, it appears that in aldehyde–phenol condensation formation of oxygen–carbon linkages is not favored. The results obtained when multimolar quantities of the aldehyde were used, indicate that the resinous character of Bakelite is not due to ante- or posterior polymerization of the aldehyde, but is due to *multiple diphenylmethane* type of linkages.

3. In the case of the condensation systems involving an unsaturated aldehyde, the catalyst partook in the reaction, a fact never before observed in this type of condensation.

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The Preparation of Cyclopropene

BY MAURICE J. SCHLATTER

Cyclopropene was synthesized in 1922 by Demjanow and Dojarenko[1a] and our entire knowledge regarding this interesting compound is due to the researches[1] carried out by these Russian scientists. In order to make it available in amounts sufficient for an extended investigation of its physical and chemical properties, the conditions attending its formation were studied in some detail. The steps employed in the synthesis are outlined in the accompanying chart.

The yields indicated are conservative, reproducible values obtained on a preparative scale as the result of four to thirty runs at each step. The over-all yield based on these figures and choosing the path (bold-faced arrows) found to be most convenient is 3.3%. Taking into account the quaternary iodide recovered from the dimethylcyclopropylamine formed in the last step, this value becomes 4.7%.

From a detailed study of the decomposition of the quaternary base on platinized asbestos it was shown that the optimum temperature for cyclopropene formation is 320–330°. Dimethylcyclopropylamine and methylacetylene which had been reported[1a] previously were also obtained. A more detailed discussion of the thermal decomposition is given in the experimental part.

Pure cyclopropene was obtained by distilling the hydrocarbons through a Podbielniak column. It distilled at -36 to $-35°$ at 744 mm. and analyzed for C_3H_4. In confirmation of Demjanow and Dojarenko[1] it was found that the olefin reacts energetically with bromine and polymerizes readily. It could not be conveniently stored, even at $-78°$. The[1a] statement that cyclopropene can be regenerated from dibromocyclopropane by treatment with zinc and alcohol was not confirmed. This procedure gave a product consisting to a large extent of cyclopropane. The problem of the reconversion of the stable dibro-

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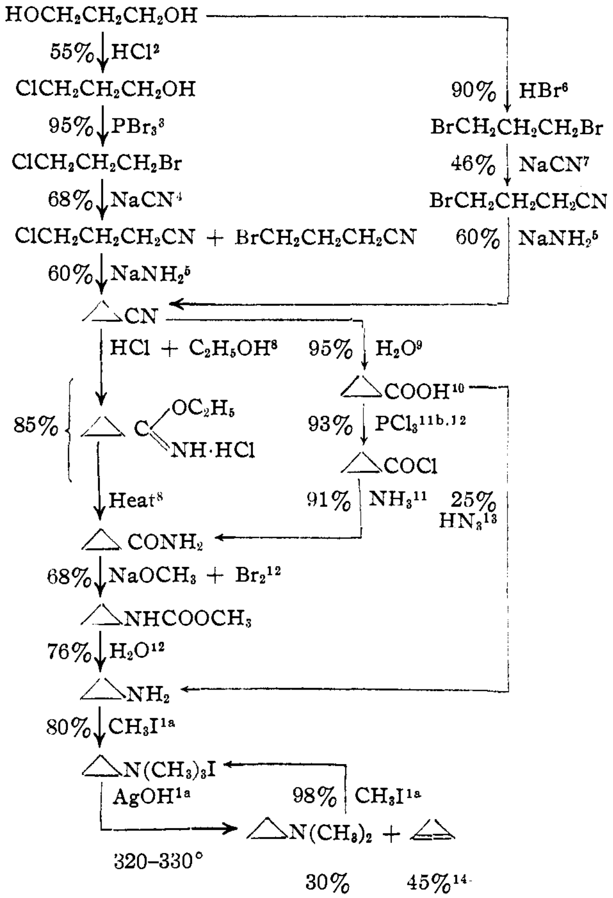
[1] (a) Demjanow and Dojarenko, *Ber.*, **56**, 2200 (1923); *Bull. acad. sci. Russ.*, [6] 297 (1922); (b) *Bull. acad. sci. U. R. S. S.*, [7] 653 (1929); [*C. A.*, **24**, 1848 (1930)].



mide to cyclopropene is of importance in connection with the handling of large amounts of the latter and is the subject of further studies.

Experimental[15]

Trimethylene chlorohydrin was prepared by the methods of Marvel and Calvery[2] and of Hultman, Davis and Clarke.[16] The treatment of trimethylene glycol with the theoretical amount of phosphorus trichloride gave the less satisfactory yield of 40%. An attempt to use thionyl chloride, either alone or in conjunction with pyridine, gave, in addition to chlorohydrin, other products not easily separated by fractional distillation. These interfered with subsequent steps.

Trimethylene chlorobromide was prepared in twenty-mole batches by the method of Cloke, *et al.*,[3] and was used without purifying by distillation.

γ-Chloro- and γ-Bromobutyronitrile from Trimethylene Chlorobromide.—To 765 g. (15.6 moles) of technical sodium cyanide eggs in 1350 ml. of warm water in a 12-liter round-bottom flask surrounded by a water-bath and equipped with a large capacity reflux condenser, was added 3500 ml. of 96% alcohol and 2360 g. (15 moles) of trimethylene chlorobromide. The mixture was warmed and the ensuing vigorous reaction controlled by addition of ice to the bath and by playing a stream of water on the upper part of the flask. After the reaction had subsided, refluxing was continued for an additional hour and then 3.5 liters of alcohol rapidly distilled off. The oil was decanted from the aqueous and solid phases in the flask, these latter extracted thoroughly with chloroform and the extract combined with the oil. The resulting solution was washed with half saturated calcium chloride and with water, the solvent removed and the residue fractionated at reduced pressure; 1193 g. of product (b. p. 89–115° (26 mm.)) was obtained. Analysis of the mixture by fractionation showed it to consist of 67.5% of γ-chlorobutyronitrile (b. p. 94° (26 mm.)) and 32.5% of γ-bromobutyronitrile (b. p. 108 (26 mm.)). This corresponds to a combined yield of 69%.

γ-Bromobutyronitrile from Trimethylene Dibromide.[17]—To 808 g. (4 moles) of trimethylene dibromide in 3200 ml. of 96% alcohol was added 160 g. (3.26 moles) of sodium cyanide in 300 ml. of water. The mixture was shaken thoroughly for five minutes, permitted to react at room temperature for one hour and then refluxed for forty-five minutes. After cooling, the mixture was poured into 9 liters of water, and extracted repeatedly with chloroform. Fractionation at reduced pressure gave 268 g. of recovered trimethylene dibromide and 188 g. of γ-bromobutyronitrile (b. p. 104–107° (23 mm.)) (47% on the basis of trimethylene dibromide consumed).

Cyclopropyl Cyanide from the γ-Halogenbutyronitrile Mixture.—One liter of liquid ammonia and 0.5 g. of hydrated ferric nitrate were placed in a two-liter three-neck flask equipped with mechanical stirrer and dry-ice reflux condenser protected by a soda lime tower; 92 g. (4 moles) of sodium shavings was added over a period of

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(2) Marvel and Calvery in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 519.

(3) Cloke, Anderson, Lachmann and Smith, THIS JOURNAL, **53**, 2794 (1931).

(4) Allen in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 150. This method gives γ-chlorobutyronitrile in the yield indicated. A modification giving a similar yield of a mixture of γ-chloro and γ-bromobutyronitrile (which is equally useful in this synthesis) was employed to facilitate the handling of large batches.

(5) The method used was essentially a large scale modification of the method of Cloke, *et al.*[3] This procedure was equally satisfactory with the pure γ-halogen nitriles or mixtures of them.

(6) Kamm and Marvel in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 28.

(7) The method used was a modification of the procedure of Gabriel, *Ber.*, **22**, 3336 (1889); see Derick and Hess, THIS JOURNAL, **40**, 546 (1918).

(8) Cloke, Knowles and Anderson, *ibid.*, **58**, 2547 (1936).

(9) Henry, *Bull. classe sci. Acad. roy. Belg.*, [3] **37**, 17 (1899) [*Chem. Zentr.*, **70**, I, 975 (1899)].

(10) The yields of this acid by decarboxylation of cyclopropane-1,1-dicarboxylic acid are unsatisfactory. The reaction is being investigated.

(11) Kishner, (a) *J. Russ. Phys.-Chem. Soc.*, **33**, 377 (1901); (b) **37**, 304 (1905) [*Chem. Zentr.*, **72**, II, 579 (1901); **76**, I, 1704 (1905)].

(12) Lipp, Buchkremer and Seeles, *Ann.*, **499**, 13 (1932).

(13) This step has not been described previously in the literature. The conversion of cyclobutanecarboxylic acid directly to the corresponding amine has been reported recently by Heisig, *J. Phys. Chem.*, **43**, 1210 (1939).

(14) This yield is based on dibromocyclopropane isolated.

(15) Melting points reported in this paper are corrected.

(16) Hultman, Davis and Clarke, THIS JOURNAL, **43**, 369 (1921).

(17) The following procedure was worked out in this Laboratory by Messrs. Raymond Clinton and Thurston Skei.

three-quarters of an hour. The mixture was stirred until the blue color had disappeared (one or two hours). In a similarly equipped three-liter three-neck flask (reaction flask) were placed 1.5 liters of liquid ammonia and 4.25 moles of γ-halogenbutyronitrile mixture (pure γ-chloro- or γ-bromobutyronitrile can be substituted for the mixture). The flasks were connected by a 10-mm. glass tube reaching to the bottom of the sodamide flask and extending 1 cm. through a stopper in one neck of the other. By means of air pressure, controlled by a finger over an air bypass, the sodamide suspension was forced over into the reaction flask at such a rate that about one hour was required for the addition; constant stirring was maintained in both flasks. The sodamide flask was rinsed out with 300 ml. of liquid ammonia and the washing added to the reaction mixture. Stirring was continued for four hours,[18] during the first two hours of which the mixture refluxed gently. During the second two hours no more dry-ice was added to the traps and slow evaporation of ammonia took place. The sodamide addition tube was replaced with a dropping funnel and one liter of anhydrous ether slowly added to the solution. The reaction mixture was filtered rapidly through a sintered glass funnel and the filter cake washed with anhydrous ether. The ammonia and ether were removed on a water bath,[19] the residue filtered[20] and then fractionated at 80 mm.; 149 g. of cyclopropyl cyanide (b. p. 69–70° (80 mm.)) (61% yield on the basis of γ-halogenbutyronitrile actually used) and 0.6 mole of γ-halogenbutyronitrile were obtained. A rosin-like residue was left in the distilling flask.

Cyclopropanecarboxylic Acid.—To 336 g. (6 moles) of potassium hydroxide in 1200 ml. of water, was added 268 g. (4 moles) of cyclopropyl cyanide and the mixture refluxed. After initiation of the reaction it was found necessary to cool until the vigorous refluxing subsided. The solution was heated for six hours, cooled in an ice-bath and 1500 ml. (4.5 moles) of 6 *N* sulfuric acid slowly added. Continuous extraction with ether and fractionation of the ether extract yielded 332 g. (96%) of cyclopropanecarboxylic acid (b. p. 80–81° (13 mm.)).

Cyclopropanecarboxamide from the Acid Chloride.—The acid chloride[21] was prepared by the method described by Lipp, *et al.*[12] The amide was prepared by saturating a solution of 171 g. (1.64 moles) of the acid chloride in 1500 ml. of anhydrous ether with ammonia at 0° under anhydrous conditions. Solvent was removed *in vacuo* and the residual fine white powder extracted with chloroform in a Soxhlet extractor. Large colorless prisms separated out; yield 126.5 g. (91%), m. p. 125°.

Cyclopropanecarboxamide from Cyclopropyl Cyanide.—Ethyl imidocyclopropane carboxylate hydrochloride was prepared from 67 g. (1 mole) of cyclopropyl cyanide by the method[8] of Cloke and co-workers. Without isolation of the imido ester salt, volatile materials were removed at reduced pressure, and the solid residue heated in the same vessel in an oil-bath at 130–150°; a stream of ethyl chloride was given off smoothly. To complete the decomposition, the temperature was raised to 165° and the pressure reduced to 20 mm. A small amount of ethyl cyclopropane carboxylate was trapped out. The crystalline residue on recrystallization from ethanol gave 74 g. (87%) of cyclopropanecarboxamide.

Cyclopropylamine from Cyclopropanecarboxamide.—The urethan was prepared in 68% yield according to Lipp, *et al.*[12] It is important that the material be completely worked up within a short time after the methanol has been distilled off.[22] From this, cyclopropylamine was obtained[12] in 76% yield.

Cyclopropylamine from Cyclopropanecarboxylic Acid.—In a one-liter three-neck flask equipped with dropping funnel, mechanical stirrer, gas evolution indicator, and thermometer dipping into the liquid was placed 130 ml. of concentrated sulfuric acid. First 62 g. (0.72 mole) of cyclopropanecarboxylic acid was added slowly, keeping the temperature below 40°; then a solution of hydrazoic acid[23] in chloroform (from 75 g. of sodium azide and found by titration to contain 34.4 g. (0.80 mole) of hydrazoic acid) was added over a period of two hours, maintaining the temperature between 35–40°. Stirring and heating were continued another five hours, at the end of which time gas evolution had almost stopped. The reaction mixture was poured on 200 g. of ice and the resulting mixture steam distilled to remove chloroform and excess hydrazoic acid. Then 250 g. of sodium hydroxide dissolved in a small amount of water was added slowly while the liberated base distilled over into 250 ml. of 3 *N* c. p. hydrochloric acid. Evaporation of the hydrochloric acid solution gave 21.6 g. of solid containing ammonium chloride in addition to cyclopropylamine hydrochloride.

This solid was dissolved in the minimum amount of water and added through a dropping funnel to 30 g. of potassium hydroxide and 5 ml. of water in a distilling flask. The amine which distilled was dried over barium oxide and fractionated; 10.3 g. (25%) of cyclopropylamine (b. p. 49–50° (750 mm.)) was obtained.[24] The following derivatives were prepared: phenyl thiourea,[11] colorless plates from aqueous ethanol, m. p. 125.5°; benzamide,[11] white needles from aqueous methanol, m. p. 99°; picrate, orange needles from ethanol and petroleum ether, m. p. 149°. Identical derivatives were prepared from the amine obtained from the urethan.

Trimethylcyclopropylammonium Iodide from Cyclopropylamine.—To 68 g. (0.73 mole) of cyclopropylamine

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[18] With pure γ-chlorobutyronitrile and γ-bromobutyronitrile, the time of stirring should be two and six hours, respectively (time of refluxing zero and four hours).

[19] In one experiment using pure bromonitrile, crystals of organic material separated out at this point. These crystals were filtered off and recrystallized from absolute alcohol, m. p. 134°. *Anal.* Calcd. for $C_4H_9N_2Br$: C, 29.11; H, 5.50; N, 16.98. Found: C, 29.39; H, 5.79; N, 16.23. This compound dissolved readily in water and gave an immediate test for bromide ion. The substance is probably cyclopropylcarbamidine hydrobromide, $C_3H_5C(NH_2)_2{}^+Br^-$.

[20] With pure γ-chlorobutyronitrile, no solid separates at this point.

[21] Commercial thionyl chloride gave none of the desired product; *cf.* Skraup and Binder, *Ber.*, **62**, 1130 (1929).

[22] Distillation of the residue at 2 mm. yielded two solids boiling at 120–125° (2 mm.) and 155–160° (2 mm.). The low boiling material proved to be unchanged cyclopropanecarboxamide (analysis, mixed m. p.). Recrystallization from alcohol of the higher boiling material gave a compound melting at 100°. *Anal.* Calcd. for C_4H_6ON: C, 57.12; H, 7.19; N, 16.66. Found: C, 57.16; H, 7.17; N, 16.63. The compound is probably N-cyclopropyl-N'-carboxycyclopropyl urea $C_3H_5NHCONHCOC_3H_5$; *cf.* Hofmann, *Ber.*, **14**, 2725 (1881); **15**, 754 (1882).

[23] Von Braun, *Ann.*, **490**, 125 (1931).

[24] A similar experiment with 20 g. of isobutyric acid yielded 80% of the theoretical amount of isopropylamine.

hydrochloride in 150 ml. of methanol and 400 g. (2.82 moles) of methyl iodide was added 160 g. of potassium hydroxide in 800 ml. of methanol, with stirring, over a period of three hours, keeping the temperature at 30–40°. The mixture was refluxed for an additional two hours; evaporation to dryness *in vacuo* at 40° gave 551 g. of solid. This yielded 137 g. (83%) of trimethylcyclopropylammonium iodide on extraction with chloroform for ninety-six hours in a Soxhlet extractor.

Trimethylcyclopropylammonium Iodide from Dimethylcyclopropylamine.—To 40 g. (0.47 mole) of dimethylcyclopropylamine (see below) in 400 ml. of absolute alcohol was added 100 g. (0.704 mole) of freshly distilled methyl iodide with stirring over a period of fifteen minutes. The mixture was allowed to stand overnight. A large crop of white crystals separated out; yield 104 g. (96%), m. p. 274° dec.

Anal. Calcd. for $C_6H_{14}NI$: C, 31.71; H, 6.23; N, 6.17; I, 55.90. Found: C, 31.79; H, 6.24; N, 6.20; I, 55.99.

Thermal Decomposition of the Quaternary Base.—Trimethylcyclopropylammonium hydroxide was prepared from 22.7 g. (0.1 mole) of quaternary iodide by Demjanow's[1a] procedure. The solution was concentrated *in vacuo* at 40°, taking care to avoid carbonate formation by the use of nitrogen-filled apparatus. The concentrated base (approx. 20 ml.) was brownish and cloudy, and was used in this form. The pyrolysis tube was made by blowing a test-tube bottom on a piece of 30-mm. Pyrex tubing 12 cm. in length with neck constricted to hold a small two-hole rubber stopper. A condenser made from 8-mm. tubing was sealed to the tube 8 cm. from the bottom. The rubber stopper carried a gas inlet tube (for sweeping the system with carbon dioxide) and a short-stem dropping funnel which projected 0.5 cm. through the stopper.[25] A hydrostatic head was maintained on the liquid to be added by connecting the sidearm of a filter flask to the top of the dropping funnel. The filter flask was fitted with a rubber stopper carrying a funnel with a 30-cm. stem; this reached the bottom of the flask and was filled with water. The bulb of the pyrolysis tube was lined with a layer of 20% platinized asbestos, 3-mm. thick. The condenser attached to the pyrolysis tube was connected to a 100 ml. receiver which was followed by a 100 ml. spiral gas wash bottle containing 3 *N* hydrochloric acid (to absorb trimethylamine and any dimethylcyclopropylamine which did not condense in the receiver). This, in turn, was connected to a gasometer containing saturated sodium chloride.[26] After sweeping the air from the apparatus with carbon dioxide, the pyrolysis tube was heated to the desired temperature by a metal bath and the concentrated solution of base added over a period of ten to twelve min. This yielded 1600–1800 ml. of gas at the optimum temperature (320–330°). The apparatus was flushed out with 800 ml. of carbon dioxide which was combined with gas in the gasometer. Bromination (see below) of gas obtained under optimum conditions gave 8–9.5 g. of 1,2-dibromocyclopropane (material boiling below 50° (25 mm.)) and 1.5–2 g. of higher boiling residue.

The contents of the hydrochloric acid wash bottle were poured into the receiver and the combined solutions evaporated to dryness *in vacuo*. The mixed amine hydrochlorides were treated with alkali and steam distilled. Drying of the amines over potassium hydroxide and subsequent fractionation gave dimethylcyclopropylamine, b. p. 60.1° (748 mm.); n^{20}_D 1.3999; d^{25}_4 0.7607; picrate, yellow needles (from ethanol), m. p. 196.5° dec.

A series of more than twenty decompositions, each of one-tenth mole of quaternary iodide, was carried out at temperature intervals within the range 250 to 450°. It was found that at temperatures below 320° the ratio of hydrocarbons to dimethylcyclopropylamine formed decreased rapidly while there was very little change in the ratio of cyclopropene to methylacetylene. At 250° the total hydrocarbon formed was less than one-third that obtained at the optimum temperature. As the temperature of the decomposition was increased above 330°, the total volume of hydrocarbon obtained decreased somewhat and the ratio of cyclopropene to methylacetylene obtained fell off rapidly. At the optimum temperature (320 to 330°) this ratio was about 10:1, while at 450° it dropped to 1:1.5. The condition of the catalyst improved with use for the first three or four times, but after this was somewhat erratic in its behavior. From this it is seen that the ratio of hydrocarbons to amine appears to be affected by the condition of the catalyst, though the ratio of cyclopropene to methylacetylene depends primarily on the temperature. A variation in the ratio of hydrocarbon to amine is not seriously disadvantageous as the amine may be quantitatively reconverted[1a] to the quaternary salt. In some experiments products isolated from decomposition of the quaternary base accounted for 85–90% of the quaternary iodide.

Examination of Hydrocarbon Pyrolysis Products.—The presence of an acetylenic hydrocarbon was confirmed by testing samples of gas with cuprous chloride dissolved in ethanolamine; a yellow precipitate was obtained. The relative amounts of cyclopropene and methylacetylene in the mixture were determined by passing further samples from the gasometer (corresponding to 0.1 mole quaternary iodide) into excess bromine at 0° over a period of one and one-half hours. The bromine and bromide were then treated with sodium bisulfite to remove excess bromine, washed with water, dried with calcium chloride and distilled. The portion boiling to 50° (25 mm.) was collected and found to be nearly pure dibromocyclopropane; the weight of the residue was taken as an index of the amount of methylacetylene present.

One hundred and fifty grams of the combined bromination product from a series of pyrolyses at various temperatures, on careful fractionation, yielded 117 g. of 1,2-dibromocyclopropane (b. p. 57–58° (50 mm.); m. p. −1 to +1°; n^{20}_D 1.5360; d^{25}_4 2.0838), 11.9 g. of 1,1,2,2-tetrabromopropane (b. p. 110–112° (10 mm.); n^{20}_D 1.6162; d^{25}_4 2.668), 6.1 g. of 1,1,3,3-tetrabromopropane (b. p. 122–123° (10 mm.); n^{20}_D 1.6198; d^{25}_4 2.683), and small intermediate fractions.

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(25) It is important that this dropping tube does not project into the hot zone of the pyrolysis tube.

(26) The gasometer was made from two 2.5 liter bottles. The rubber stopper of the first carried a gas inlet tube and differential pressure manometer flush with the stopper and a 12-mm. tube reaching to the bottom of the bottle. This was connected by rubber tubing to a similar tube reaching to the bottom of the second bottle. The gasometer was calibrated. Gas could be drawn into or displaced from the first bottle by lowering or raising the second bottle.

Isolation of Cyclopropene.—Three liters of hydrocarbon pyrolysis products, dried with magnesium perchlorate and freed of carbon dioxide with ascarite, was fractionated at atmospheric pressure (744 mm.) in a small Podbielniak column.[27] Approximately 700 ml. of gas distilled over at −36 to −35°; the residue, 3 to 4 ml. of slightly yellow somewhat viscous oil, gave no further distillate on warming to room temperature. As the original sample contained methylacetylene as well as cyclopropene, this seems to indicate that cyclopropene can combine with methylacetylene as well as with itself. The ratio of hydrogen to carbon was determined on three 10-ml. samples of pure hydrocarbon gas by burning in a semi-micro combustion furnace.

Anal. Calcd. for C_3H_4: H/C ratio, 1.33. Found: 1.332, 1.346, 1.320.

Acknowledgment.—The author wishes to acknowledge his indebtedness to Dr. E. R. Buchman for suggesting the problem and to him and to Professor H. J. Lucas for guidance during the course of the investigation. Thanks are also due to Professor J. B. Cloke for suggestions relating to the preparation of cyclopropyl cyanide and to Mr. Alf O. Reims and to Mr. Herbert Sargent for aid with some of the preparations.

Summary

The preparation of cyclopropene by the thermal decomposition of trimethylcyclopropylammonium hydroxide on a platinum catalyst was studied in detail. The optimum temperature for cyclopropene formation was found to be 320°.

Pure cyclopropene was obtained by fractional distillation of the hydrocarbons obtained by pyrolysis of the quaternary base. It boils at −36° at 744 mm.

Cyclopropylamine was prepared from trimethylene glycol by several paths. The individual steps were investigated from a preparative point of view.

PASADENA, CALIF. RECEIVED JANUARY 28, 1941

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[27] The author wishes to acknowledge the assistance of Dr. B. H. Sage and Mr. Robert Dourson, of the American Petroleum Institute Laboratories at this Institute, in carrying out this distillation.

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 822]

The Crystal Structure of Melamine

BY E. W. HUGHES

In an earlier paper[1] the crystal structure of dicyandiamide, the dimer of cyanamide, was reported. I have now completed a similar investigation of melamine, or cyanuric triamide, the trimer of cyanamide, with the results described below.

The earlier crystallographic investigations of melamine are recorded in Groth. The most recent investigation is that of Heydrich.[2] He found the substance to be monoclinic holohedral with axial ratios $a:b:c = 1.4121:1:0.9728$ and $\beta = 112°16'$. The birefringence is strongly negative and he placed the acute bisectrix about 6° from a in acute β. The latter observation is undoubtedly wrong but he gives refractive indices which are at least approximately in accord with the structure found below and from the method used in measuring the indices it appears possible that he has made an error only in recording the position of the bisectrix. Indeed, the true position makes with c an angle about equal to that made with c by his bisector, but in obtuse β, and such an error might easily be made by reading a circle backward or by reversing the sign of a sine in a calculation.

The Unit Cell and Space Group

The material at first used in this investigation was from Eastman Kodak Company. Later a sample was obtained from the research laboratories of the American Cyanamid Company and a third sample was prepared by heating guanidinium carbonate according to the directions of Krall.[3] The latter claimed by this method to have prepared an isomer of melamine, the much sought "isomelamine," but in two attempts only ordinary melamine was obtained. Crystals from the different sources yielded identical diffraction patterns.

The best crystals were obtained by slow evaporation of seeded water solutions in flasks with cotton wad stoppers. The crystals stick tenaciously to surfaces on which they grow and it was necessary, in order to get good specimens, to turn the growing crystals over daily with a fine glass

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[1] Hughes, THIS JOURNAL, **62**, 1258 (1940).

[2] Heydrich, *Z. Krist.*, **48**, 278 (1910–1911).

[3] Krall, *Proc. Chem. Soc.*, **29**, 377 (1913).