rosaniline was perhaps the product since Hofmann[7] obtained it similarly by the action of carbon tetrachloride.

It will be noted in Table III that benzotribromide was the product of two reactions. This compound is described here for the first time, as far as the writers are aware. A search of the literature revealed only one mention[8] of this compound and that was in a statement to the effect that benzotrichloride (or bromide) is readily hydrolyzed by water or potassium hydroxide to benzoic acid. It was found that several hours of heating with 10% sodium hydroxide was required to bring about hydrolysis of a 3-g. sample.

Benzotribromide ($C_7H_5Br_3$).—Benzotribromide resulted from the reaction of two equivalents of carbon tetrabromide with one of benzyl bromide and also from one equivalent of carbon tetrabromide with one of benzal bromide. Hydrolysis of the product resulted in the formation of benzoic acid.

Benzotribromide is a colorless crystalline material, very soluble in alcohol or ether, less soluble in petroleum ether, insoluble in water: m. p. 56–57°.

Anal. Calcd.: Br, 72.91. Found: Br, 72.76, 72.61 (Stepanoff); 72.85 (alc. $AgNO_3$).

Summary

1. Carbon tetrabromide will react with various organic materials through the exchange of a bromine atom for a hydrogen. Bromoform is always the by-product of such bromination.

2. Carbon tetrabromide brominates selectively the side chains of the benzene hydrocarbons instead of attacking the ring.

3. Duryl monobromide, benzotribromide, and an addition product of durene and carbon tetrabromide are described.

[7] Hofmann, *J. prakt. Chem.*, **77**, 191 (1859); **87**, 226 (1862).

[8] Fry, THIS JOURNAL, **36**, 1043 (1914).

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE WALKER CHEMICAL LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

SUBSTITUTED PHENYLACETONITRILES AND DERIVATIVES. 1-PHENYL-1-CYANOCYCLOPROPANE, ALPHA-PHENYL-GAMMA-HYDROXYBUTYRONITRILE, ALPHA-PHENYL-GAMMA-CHLOROBUTYRONITRILE AND ALPHA-PHENYLCROTONONITRILE[1]

BY EDWIN C. KNOWLES AND JOHN B. CLOKE

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In the development of a series of investigations on sundry cyclic ketimines, imino esters and heterocyclic nitrogen compounds, supplies of α-alkyl and α-aryl-γ-chlorobutyronitriles and alkyl and aryl substituted cyclopropyl cyanides were required. The present paper describes the preparation of one of the chloro and two of the cyclic compounds.

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[1] This paper is from the first part of a thesis presented by Edwin Chandler Knowles in June, 1931, to the Graduate School of the Rensselaer Polytechnic Institute in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

The Preparation of 1-Phenyl-1-cyanocyclopropane, $\overline{\mathrm{CH_2CH_2C}}\mathrm{(C_6H_5)}$-CN.—Two methods have been developed for the preparation of 1-phenyl-1-cyanocyclopropane (I). In the first method one mole of phenylacetonitrile (XIII) in ether was first treated with two moles of sodium amide, and this reaction mixture was then allowed to react with ethylene chlorobromide or dibromide under suitable conditions to give 40–45% yields of (I). This procedure, therefore, constitutes an extension of the work of Bodroux and Taboury[2] on the alkylated phenylacetonitriles to the alkylene derivatives.

The first stage in the formation of (I) by the foregoing method involves the reaction of the sodium amide with (XIII) to give the monosodium salt. In accordance with the views of Rising[3] and others the carbide tautomer of this salt may then be assumed to react with the ethylene chlorobromide to give primarily sodium bromide and α-phenyl-γ-chlorobutyronitrile (XIV).

$$\mathrm{ClCH_2CH_2Br + Na^{+-}CH(C_6H_5)CN = ClCH_2CH_2CH(C_6H_5)CN + Na^{+-}Br} \quad (1)$$

In the third stage of the reaction, (XIV) may be supposed to react with the excess sodium amide and with the salt of (XIII) to give the tautomeric carbide and nitride salts, and, finally, the carbide salt may be regarded as undergoing a very rapid internal condensation to give (I) and sodium chloride

$$\mathrm{ClCH_2CH_2C^-(Na^+)(C_6H_5)CN = \underline{CH_2CH_2C}(C_6H_5)CN + Na^+Cl^-} \quad (2)$$

The mechanism which has been suggested for the latter ring closure is the same as that which has been given in detail for the preparation of cyclopropyl cyanide from γ-chlorobutyronitrile.[4]

That the formation of (I) by Method 1 actually goes through the stages as sketched above seems clear from other considerations. Thus, in the first place, slightly less than one equivalent of ammonia is liberated for each mole of (XIII) which is used, even though twice as much sodium amide is present. In the second place (XIV), whose existence as an intermediate has been postulated in Equation 1, has been found to react with sodium amide to give (I). This reaction, which is formulated in Equation 2, constitutes the second method for the preparation of (I).

α-Phenyl-γ-chlorobutyronitrile.—Compound (XIV) was obtained by the action of thionyl chloride on α-phenyl-γ-hydroxybutyronitrile in pyridine solution

$$\mathrm{HOCH_2CH_2CH(C_6H_5)CN + SOCl_2 = ClCH_2CH_2CH(C_6H_5)CN + SO_2 + HCl} \quad (3)$$

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[2] Bodroux and Taboury, *Bull. soc. chim.*, **7**, 666 (1910); *Compt. rend.*, **150**, 531, 1241 (1910).

[3] Rising and Zee, THIS JOURNAL, **49**, 541–545 (1927); **50**, 1699–1707 (1928); Rising, Muskat and Lowe, *ibid.*, **51**, 262 (1929).

[4] Cloke, Anderson, Lachmann and Smith, *ibid.*, **53**, 2791 (1931).

This procedure was suggested by the work of Darzens[5] on the replacement of hydroxyl in alcohols and hydroxy esters by chlorine.

α-Phenyl-γ-hydroxybutyronitrile.—The hydroxynitrile which was required in Equation 3 was prepared by the action of ethylene chlorohydrin on the sodium salt of (XIII).

$$HOCH_2CH_2Cl + Na^{+-}CH(C_6H_5)CN = HOCH_2CH_2CH(C_6H_5)CN + Na^+Cl^- \quad (4)$$

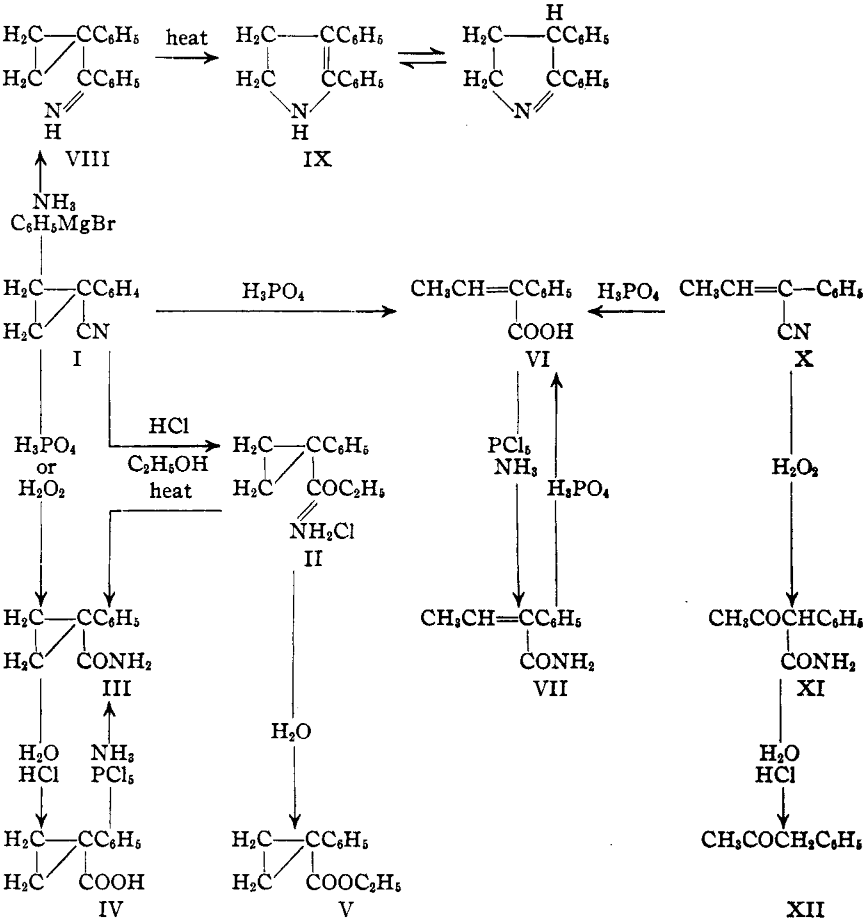
The Structure of the 1-Phenyl-1-cyanocyclopropane.—At one time it appeared likely that our nitrile (I) which was obtained by Method 1 might be one of the geometrical isomers of the isomeric α-phenylcrotononitrile (X), since the amide which was obtained from (I) was found to have the same melting point as that which had been reported by Pfeiffer, Engelhardt and Alfuss[6] for the α-phenylcrotonamide (VII). It seemed possible, therefore, that the isomeric (X) might either have arisen directly from (I) by a ring rupture or from the rearrangement of α-phenylvinylacetonitrile, which might have been the initial product by Method 1. Now, however, several lines of evidence point unquestionably to the cyclopropane structure (I).

In the first place nitrile (I) is different from (X). Thus (I) was saponified by phosphoric acid and also by alkaline hydrogen peroxide to give the amide of 1-phenylcyclopropanecarboxylic acid (III), which was distinct from the amide (VII) which can be prepared from the α-phenylcrotonic acid (VI) by the action of phosphorus pentachloride and ammonia. It is true that the amides melted at practically the same temperature, but they had distinct crystalline structures and gave a decidedly lower mixed melting point. Moreover, the real (X) was difficultly saponified by hydrogen peroxide and dilute alkali to give α-phenylacetoacetamide (XI), which was recognized from its analysis and from the fact that it gave methyl benzyl ketone (XII) on hydrolysis. It is also of interest to note that (I) reacted with hydrogen chloride and ethanol to give the imino ester hydrochloride (II), which in turn gave the amide (III) on heating, whereas the isomeric nitrile (X) failed to react under these conditions. Finally (I) and (X) gave characteristic ketimines.

The saponification of (I) with hot phosphoric acid gave not only the amide (III) but also the acid (VI), which originated as the result of a ring rupture. *The acid, indeed, was the main product.* Cyanocyclopropane itself under the same conditions gave cyclopropanecarboxylic acid. The corresponding acid (IV) was obtained from the amide (III) by saponification with boiling dilute hydrochloric acid. That no ring rupture had occurred in this reaction was established by the reconversion of the acid (IV) into the amide (III) by means of phosphorus pentachloride and ammonia.

[5] Darzens, *Compt. rend.*, **152**, 1314, 1601 (1911).

[6] Pfeiffer, Engelhardt and Alfuss, *Ann.*, **467**, 189 (1928).



That the nitrile (I) could not be the α-phenylvinylacetonitrile was shown, on the one hand, by its failure to react significantly either with bromine in carbon tetrachloride or with alkaline potassium permanganate solution, and, on the other hand, by its saponification to the acid (IV) which failed to rearrange to (VI) when it was treated with a base. Independent work of Gilman and Harris[7] and by the writers on the vinylphenylacetic acid has established this point.

That the nitrile (I) is not the geometric isomer of (X) and that it actually has the cyclic structure (I) was finally established beyond question by the complete analogy which exists between the behavior of phenylcyclopropyl ketimine, $\underline{CH_2CH_2C}HC(=NH)C_6H_5$,[8] and the 1-phenylcyclopropyl phenyl ketimine (VIII), which has been prepared from (I) by the Grignard

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[7] Gilman and Harris, THIS JOURNAL, **53**, 3544–3545 (1931).

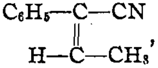
[8] Cloke, *ibid.*, **51**, 1174 (1929); Doctorate Dissertation, University of Chicago.

reaction. Thus, the two ketimine hydrochlorides react with water at almost the same rate, and, second, and this is of most significance, both ketimines rearrange to give the corresponding pyrrolines, *e. g.*, (IX). An account of this work will appear later. Finally, it may also be noted that the structure (I) would likewise be indicated from the second method of synthesis, namely, from (XIV), since the γ-chlorobutyronitrile gives cyanocyclopropane under the same conditions.

α-Phenylcrotononitrile.—The nitrile (X), which was required in connection with the study of the structure of (I), was obtained in a 36% yield by the condensation of acetaldehyde with benzyl cyanide in the presence of sodium ethylate at 0°

$$CH_3CHO + H_2C(C_6H_5)CN = CH_3CH{=}C(C_6H_5)CN + H_2O \qquad (5)$$

Pfeiffer, Engelhardt and Alfuss, who obtained the nitrile by another method, assigned to it the *cis* configuration, namely,



$$\begin{matrix} C_6H_5{-}C{-}CN \\ \| \\ H{-}C{-}CH_3 \end{matrix}$$

, in view of the fact that the compound is very slowly esterified. Our failure to transform it into the ethyl imino ester hydrochloride constitutes evidence of the same type for this structure.

Experimental Part

Preparation of 1-Phenyl-1-cyanocyclopropane by Method 1.—A one-liter, three-necked, round-bottomed flask was provided with a 500-cc. dropping funnel, a mechanical stirrer, which operated through a mercury seal, and a reflux condenser. The open ends of the funnel and condenser were provided with drying tubes. In the later runs a suction arrangement, which is illustrated in Fig. 1, was also attached to the apparatus, whereby the contents of the flask could be transferred to the funnel without the necessity of their exposure to the moist air of the laboratory. Finally the apparatus was thoroughly dried with a current of warm dry air.

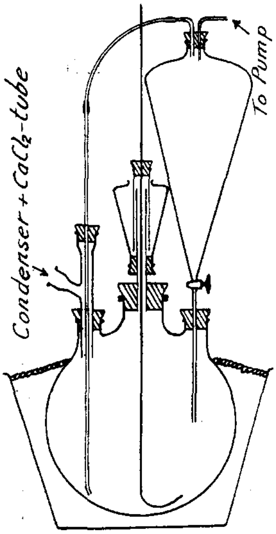


Fig. 1.

A weight of 75 g. (1.92 moles) of Kahlbaum's sodium amide was halved and each part was converted into a flocculent condition under about 200 cc. of anhydrous ether by a process of elutriation. Throughout this alternate process of grinding and decantation care was taken to avoid as much as possible the direct exposure of the sodamide to moist air. In passing it may be added that no explosive decompositions have occurred with us since we have ground the sodium amide under ether, although several took place before. The finely ground compound was at once transferred to the reaction flask with 400–450 cc. of the ether under which it had been pulverized. One mole (117 g.) of phenylacetonitrile[9] was then added to the well-stirred sodium amide suspension from the dropping funnel with sufficient rapidity to give a vigorous refluxing of the ether. As soon as all of the nitrile

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[9] Adams and Thal, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1922, Vol. II, p. 9.

had been added and the vigor of the reaction began to abate, the mixture was refluxed gently on a water-bath for four to five hours, whereby about 0.9 mole of the monosodium salt was formed upon the basis of the quantity of ammonia evolved. Longer periods of refluxing did not serve to increase this amount of salt. Furthermore, no noticeably increased yields of the desired nitrile were obtained when the reaction was carried out in an atmosphere of nitrogen, although the color of the reaction mixture was lighter in this case.

At the end of this first stage in the preparation the yellow to dark red reaction mixture was cooled and transferred, preferably by means of the suction arrangement, to the 500-cc. dropping funnel. A weight of 130 g. (0.9 mole) of redistilled Eastman Kodak Co. ethylene chlorobromide[10] in twice its volume of anhydrous ether was then poured into the flask, which at this stage was cooled in an ice–salt bath to −15°. The stirrer was started, and as soon as the solution was thoroughly cold, the sodium salt mixture in the funnel was added to the chlorobromide solution at such a rate that scarcely any refluxing of the ether could be detected.[11] Following the addition of the salt mixture, which required about two hours, the stirring was continued during the next seven hours, while the temperature of the bath was allowed to rise to that of the room. At this stage the temperature of the bath was raised to the point where droplets of ether began to collect in the condenser, where it was held for an hour, and finally it was raised sufficiently to give a gentle refluxing, which was maintained for two hours while the stirring was continued. At the end of this period the evolution of ammonia had completely ceased.

At the conclusion of the foregoing operation enough water was added to the mixture in the flask to dissolve the solid material. The ether layer was then separated and dried over anhydrous sodium sulfate for ten hours. Distillation of the dry filtered ether solution under diminished pressure on the water-bath gave 15 g. of a fraction which boiled from 81–83° at 1 mm.; this was mainly benzyl cyanide. The continuation of the distillation under the same pressure but with direct heating gave 91.5 g. of the main product, which boiled from 110–113°, and 18–20 g. of a tarry residue which was not examined. Redistillation of the main fraction through a modified Claisen–Vigreux flask with a 1.8 × 30 cm. column gave 60–64 g. of distillate which boiled from 98–100° at less than 1 mm.; this corresponds to a 44% yield upon the basis of the benzyl cyanide used. The freshly distilled product was a colorless oil with a slightly aromatic odor.[12] This liquid boiled from 250–253° at 751 mm. with little decomposition. It possessed a density, d_4^{20}, of 1.0156 and a refractive index, n_D^{20}, of 1.3676, which correspond to a molecular refractivity, $MR_D^{20}(n^2)$ of 43.24 as compared with the calculated value of 43.10.

Anal. Subs., 8.44 mg., 9.78 mg.: N_2 (corr.), 0.657 cc.; N_2 (corr.), 0.763 cc. Calcd. for $C_{10}H_9N$: N, 9.79. Found: N, 9.72, 9.75.

Preparation of 1-Phenyl-1-cyanocyclopropane by Method 2.—The 1-phenyl-1-cyanocyclopropane was also prepared by the action of 8.1 g. of sodium amide on 31.5 g. of α-phenyl-γ-chlorobutyronitrile in 200–250 cc. of liquid ammonia by a process similar

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[10] In one run in which 42 g. of sodium amide, 58 g. of benzyl cyanide and 92 g. of ethylene dibromide were employed, 12 g. of product was obtained. This yield could doubtless be improved.

[11] In one experiment in which the ethylene chlorobromide was added to the sodium salt mixture, the result was practically as good as in the procedure described, although we believe the latter method is safer.

[12] The last traces of benzyl cyanide may be removed from the final product by its condensation with benzaldehyde in accordance with the process of Meyer and Frost, *Ann.*, **250**, 157 (1889).

to that of Cloke, Anderson, Lachmann and Smith. A 73% yield (18.5 g.) of product was obtained.

α-Phenyl-γ-chlorobutyronitrile.—In the first run 77 g. (0.48 mole) of α-phenyl-γ-hydroxybutyronitrile from the following preparation and 38 g. (0.48 mole) of pyridine were placed in a 500-cc. three-necked flask, which was equipped with a reflux condenser, a mechanical stirrer and a dropping funnel. To this solution, which was cooled by the immersion of the flask in an ice-bath, 57 g. (0.48 mole) of thionyl chloride was slowly added from the dropping funnel with constant stirring. At the end of this addition the mixture was heated in a water-bath at 80–85° for thirty minutes. Water was then added and the heating was continued for about two hours. At this stage the mixture was cooled and extracted with ether. The ether extract in turn was extracted with dilute acid, which was followed by water, 10% sodium carbonate solution and finally by several portions of water. The ether extract was then dried over calcium chloride and distilled in a Claisen flask. The fraction which boiled from 97–135 at 3–4 mm. and which weighed 50 g. was redistilled in a Claisen–Vigreux flask. Two fractions were collected: the first (15 g.) was collected between 98–125°; and the second (31.5 g.), which was taken for analysis, boiled from 127–129° at 3–4 mm.; d_4^{20} 1.1251; n_D^{20} 1.5327; mol. ref. calcd., 49.42; found (n^2 formula), 49.51. The product was an oily liquid with a pleasant aromatic odor and was tinged slightly yellow, doubtless on account of the presence of a trace of impurity.

Anal. Subs., 11.12 mg.: N_2 (S. T. P. corr.), 0.699 cc. Calcd. for $C_{10}H_{10}NCl$: N, 7.80. Found: N, 7.88.

In a second run the α-phenyl-γ-hydroxybutyronitrile was mixed with a small excess of pyridine in the dropping funnel and added to the thionyl chloride which was contained in the flask. This procedure, however, reduced the yield of the desired product to 13 g., which was less than half of the amount which was obtained in the first run.

α-Phenyl-γ-hydroxybutyronitrile.—A weight of 120 g. (1.03 mole) of benzyl cyanide was allowed to react with 40 g. of sodium amide in the presence of 200 cc. of anhydrous ether. Enough ether was then added to bring the total volume to about 700 cc., and the mixture was refluxed gently on the water-bath for four hours with constant stirring. Here the water-bath was replaced by an ice-bath and, as soon as the mixture was well chilled, 85 g. (1.06 mole) of ethylene chlorohydrin was added slowly and with constant stirring over a period of about two hours. The ice-bath was then removed and the stirring was continued at room temperature for five hours, when the amount of precipitate seemed to have become constant. Enough water was then added to dissolve all of the solid, when the ether layer was separated and dried over anhydrous sodium sulfate. Three fractions were obtained: the first (34 g.) was mainly benzyl cyanide; the second (64 g. of b. p. 160–168° at 2–3 mm.) was primarily the desired nitrile; while the residue was not examined. Redistillation of the middle fraction gave a product of b. p. 146–149° at 1.5–2.0 mm., and this was taken for analysis. The freshly distilled compound was a nearly colorless and very viscous oily substance. A sample which had been allowed to stand for two years was found to have changed into a pasty wax-like substance. The density of the freshly distilled compound, d_4^{20}, was 1.065; and its index of refraction, n_D^{20}, was 1.5411.

Anal. Subs., 0.3125 g.: CO_2, 0.8500; H_2O, 0.1976. Subs., 19.91 mg., 17.18 mg.: N_2 (S. T. P. corr.) 1.394, 1.183 cc. Calcd. for $C_{10}H_{11}ON$: C, 74.49; H, 6.88; N, 8.69. Found: C, 74.18; H, 7.08; N, 8.76, 8.61.

Mol. wt. Subs., 0.2725; ethyl acetate, 17.38 g.; boiling point rise, 0.265°. Calcd. for $C_{10}H_{11}ON$: mol. wt., 161.09. Found: 158.7.

In a second run, in which the sodium salt of benzyl cyanide in ether was added to a 25% excess of ethylene chlorohydrin, the yield of nitrile was somewhat smaller than by the above process. In a third run, which was similar to the first, but in which the temperature of the reaction flask was lowered to −15° during the addition of the chlorohydrin, a larger quantity of benzyl cyanide was recovered, but the yield of the hydroxy compound was not materially increased.

1-Phenyl-2-methyl-1-cyanocyclopropane, $\overline{CH_2CH(CH_3)C}(C_6H_5)CN$.—Two moles (80 g.) of finely pulverized sodium amide in about 200 cc. of anhydrous ether was treated with 0.9 mole (105 g.) of benzyl cyanide as in the preparation of the 1-phenyl-1-cyanocyclopropane. To this mixture, which was cooled in an ice-bath, 0.9 mole (180 g.) of propylene dibromide was added. A very vigorous reaction ensued. The completion of the reaction gave 26 g. of a colorless oil with a slightly ethereal odor of b. p. 257–260° at 761 mm.; d_4^{20} 1.0115; n_D^{20} 1.5316.

Anal. Subs., 13.880 mg.: N_2 (corr.), 0.982 cc. Calcd. for $C_{11}H_{11}N$: N, 8.91. Found: N, 8.84.

The Amide of 1-Phenylcyclopropanecarboxylic Acid.—By the general process of Radziszewiski[13] the 1-phenyl-1-cyanocyclopropane was converted into the amide by the first method. The fine, glistening, needle-shaped crystals melted at 81–83° when heated rapidly and at 95–96° when heated slowly. The product which had been dried at 50–60° under diminished pressure for several hours softened at 96° and melted completely at 97–98° (uncorr.) or at 100–101° (corr.). From these results it was assumed that the air-dried product was hydrated. No evidence was secured which suggested the ring rupture of the amide below 250°.

Anal. Subs., 11.69 mg.: N_2 (corr.), 0.803 cc. Calcd. for $C_{10}H_{11}ON$: N, 8.69. Found: N, 8.59.

Mol. wt. (Rast) Subs., 2.59 mg.; camphor, 24.52 mg.; freezing point lowering, 26.13°. Calcd. for $C_{10}H_{11}ON$: mol. wt. 160.1. Found: 161.7.

The foregoing amide was also obtained in a second way by the heating of ethyl imino-1-phenylcyclopropane-carboxylate hydrochloride to approximately 110°.

By a third method 2 g. of nitrile was heated at 140° with 30 g. of "100%" phosphoric acid (70 g. of 85% H_3PO_4 + 30 g. of P_2O_5) for three and one-half hours by the Berger–Olivier[14] method. The cooled acid solution was poured onto cracked ice, the aqueous solution was extracted with ether, and the ether was finally extracted twice with sodium hydroxide solution and once with water. Evaporation of the dried and filtered ether extract gave the amide of m. p. 100–101° (corr.) after two recrystallizations.

The Rupture of the Ring in the Formation of α-Phenyl-crotonic Acid from 1-Phenyl-1-cyanocyclopropane.—The acidification of the sodium hydroxide solution from the preceding reaction gave the acid of m. p. 135.5–137°[15] after two recrystallizations.. A mixed melting point determination with the acid which was obtained from α-phenylcrotononitrile by the same method gave no depression.

The Action of Hot Phosphoric Acid on Cyanocyclopropane.—The unsubstituted cyclopropyl cyanide by the foregoing saponification method gave the cyclopropanecarboxylic acid, which gave an anilide of m. p. 110–111° by the method of Autenrieth and Pretzell.[16]

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[13] Radziszewiski, *Ber.*, **18**, 355 (1885); McMaster and Langreck, THIS JOURNAL, **39**, 103 (1917).

[14] Berger and Olivier, *Rec. trav. chim.*, **46**, 600–604 (1927).

[15] Dimroth and Feuchter, *Ber.*, **36**, 2238 (1903).

[16] Autenrieth and Pretzell, *ibid.*, **38**, 2548 (1905).

1-Phenylcyclopropanecarboxylic Acid.—By the saponification of the amide of the 1-phenylcyclopropanecarboxylic acid with boiling concentrated hydrochloric acid, the corresponding acid was obtained. The dry needle-like crystals melted at 86–87° (uncorr.). That no ring rupture had occurred in this reaction was demonstrated by the reconversion of the acid into the original amide by means of phosphorus pentachloride and ammonia.

α-Phenylcrotononitrile.—A solution of 160 g. (1.36 moles) of benzyl cyanide, 250 g. of absolute alcohol and 88 g. (2 moles) of acetaldehyde, which was prepared by the depolymerization of paraldehyde, was chilled to −5° and treated gradually with 15 cc. of freshly prepared 20% sodium ethylate so that the temperature did not rise above 0°. The yellowish-red solution was then placed in a refrigerator for a day, when an additional 10-g. portion of acetaldehyde was added, which was followed by a further sixteen-hour stand in the ice box. Three hundred cc. of water was then added to the mixture, which was well shaken, and the oily layer was separated and washed with another 300-cc. portion of water. The fractionation of the dried oil gave finally 70 g. (35.8% yield) of the nitrile, b. p. 100–103° at 1 mm. or less. The freshly distilled oily compound was colorless with a somewhat musty unpleasant odor, but it turned slightly yellowish on standing. It boiled at 244–246° at 751 mm. with a marked discolorization: d_4^{20} 1.013, n_D^{20} 1.5555, MR_D^{20} 45.41; calcd., 45.10.

Anal. Subs., 10.844 mg.: N_2 (corr.), 0.841 cc. Calcd. for $C_{10}H_9N$: N, 9.79. Found: N, 9.70.

Excessively alkaline solutions were found to be disadvantageous for the foregoing condensation, since they led to the formation of large amounts of resinous tarry materials, which was also the case when the condensation of ethylidene chloride and benzyl cyanide with sodium amide was attempted. Moreover, the use of such condensing agents as acetic acid–acetic anhydride, alcoholic ammonia and piperidine was unsuccessful.

α-Phenylacetoacetamide.—With the expectation of obtaining α-phenylcrotonamide, the α-phenylcrotononitrile was subjected to the action of alkaline hydrogen peroxide. The pure white solid which was formed was insoluble in cold water, fairly soluble in ether, alcohol and acetone and readily soluble in dioxane. The dried sample melted at 177–178°. Solutions of the compound in acetone and dioxane did not appear to be changed by long exposure to an ultraviolet light.

Anal. Subs., 10.478 mg., 11.838 mg.: N_2 (corr.), 0.642 cc.; N_2 (corr.) 0.749 cc. Calcd. for $C_{10}H_{11}NO_2$: N, 7.91. Found: N, 7.66, 7.91.

Mol. wt. Subs., 1.108 mg., 0.871 mg.; camphor, 10.576 mg., 10.099 mg.; temperature lowering, 23.73, 19.68°. Calcd. for $C_{10}H_{11}NO_2$: mol. wt. 177.09. Found: 176.6, 175.3.

Methyl Benzyl Ketone from the α-Phenylacetoacetamide.—In order to establish the identity of the acetoacetamide it was saponified with boiling concentrated hydrochloric acid. The semicarbazone into which the resulting ketone was converted melted at 188.5–189.5°, whereas the recorded value[17] for this derivative of the methyl benzyl ketone is 188–189°, although higher values have been reported.

α-Phenylcrotonic Acid from the Nitrile.—The saponification of α-phenylcrotononitrile by the hot phosphoric acid method gave the acid, m. p. 136–137°.

α-Phenylcrotonic Acid from Phenylvinylacetic Acid.—In order to show that phenylvinylacetic acid would rearrange to give the isomeric crotonic acid, the following program was followed. First phenylvinylcarbinol was prepared from 48.5 g. of magnesium, 314 g. of bromobenzene, 580 cc. of anhydrous ether and 92 g. of freshly prepared acrolein

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[17] Wolff, *Ann.*, **325**, 146 (1902).

by a modification of the process of Klages and Klenk.[18] The carbinol was then converted into 1-phenyl-1-chloropropene-2 by the saturation of its ether solution with dry hydrogen chloride,[18,19] which gave, with certain modifications, 215 g. of the chloride. Finally a Grignard reagent was prepared by a special procedure from 18 g. of magnesium, 100 cc. of ether and 30 g. of the chloride in five volumes of ether. This reagent was then carbonated as usual, and the salt was decomposed in a cold acid solution. Evaporation of the ether extract of the acid under diminished pressure left 7–8 g. of a brownish oil, which crystallized after several hours in an ice–salt bath and which was presumably the phenylvinylacetic acid. This was then treated with 15 cc. of 10% sodium hydroxide solution, and from this the α-phenylcrotonic acid was prepared. The acid was characterized by its melting point and by its transformation into the *p*-nitrobenzyl ester, m. p. 80–81°, and the amide.

Summary

1. 1-Phenyl-1-cyanocyclopropane can be obtained in 40–45% yields by the condensation of ethylene chlorobromide with phenylacetonitrile by means of sodium amide. The same cyclic compound has been prepared in 73% yield by the action of sodium amide on α-phenyl-γ-chlorobutyronitrile. Several derivatives and reactions of the cyclic nitrile have been described in connection with a critical proof of its structure.
2. The preparation of 1-phenyl-2-methyl-1-cyanocyclopropane has been described.
3. α-Phenyl-γ-chlorobutyronitrile can be obtained by the action of thionyl chloride on α-phenyl-γ-hydroxybutyronitrile in pyridine solution.
4. α-Phenyl-γ-hydroxybutyronitrile has been obtained in a 40% yield by the action of ethylene chlorohydrin on the sodium salt of phenylacetonitrile.
5. α-Phenylcrotononitrile has been prepared in a 36% yield by the condensation of acetaldehyde with benzyl cyanide.
6. The action of alkaline hydrogen peroxide solution on α-phenylcrotononitrile led to the formation of α-phenylacetoacetamide.
7. The preparation of α-phenylcrotonic acid from the α-phenylcrotononitrile, the 1-phenyl-1-cyanocyclopropane and by a Grignard synthesis has been described.

Other papers will follow on the extension of the work described in this paper to other analogous compounds and their derivatives.

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[18] Klages and Klenk, *Ber.*, **39**, 2552 (1906).

[19] Klages, *ibid.*, **35**, 2650 (1902).