calculated on the basis of hydrogen uptake, the presence of any appreciable amounts of unreduced acetylenes (which would, however, lead to high hydrogen uptake values) would be more serious. Careful scanning of the infrared absorption spectra of the two compounds, however, revealed no trace of acetylenic absorption.

It is a pleasure to acknowledge the considerable contribution made to this work by Professors Prelog and Cope, whose coöperation in supplying samples has been of the greatest assistance.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Reaction of Cyanogen Halides with the Silver Salts of Carboxylic Acids

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The reaction of cyanogen halides with the silver salts of carboxylic acids was studied. The major products were found to be the corresponding nitrile, acid and anhydride. The yields of these three compounds varied with the solvent employed, the yield of nitrile being highest (32%) in acetonitrile, the yield of acid being highest (82%) in nitromethane and the yield of anhydride (88%) in trichloroethylene. It is postulated that an intermediate acyl cyanate is formed and this material reacts further to give rise to nitrile and anhydride.

The silver salt–bromine degradation of Hunsdiecker has been widely used to prepare alkyl halides.[1] Recently, this reaction has been employed in the preparation of complex C^{14}-carboxyl labeled acids according to the following sequence (eq. 1).[2] Considering the relative ease by which C^{14}-labeled cyanogen halides can be prepared from labeled alkali metal or silver cyanides[3] and the similarity of such compounds with a halogen molecule, a modification and extension of the Hunsdiecker reaction using cyanogen halides instead of bromine was studied. Other than the usual chemical interest in the reaction of pseudohalogens, it also was of interest to see if replacement of an unlabeled carboxyl group by a labeled cyanide group could be achieved in one step (eq. 2).

$$RCOOH \xrightarrow[2,\ Br_2]{1,\ Ag^{\oplus}} RBr \xrightarrow{C^*N^{\ominus}} RC^*N \xrightarrow{H_2O} RC^*OOH \quad (1)$$

$$R{-}COOAg + C^*NX \longrightarrow R{-}C^*N + AgX + CO_2 \quad (2)$$

In 1947,[4] Zappi and Bouso described a similar reaction, and in their work solid alkali metal salts of carboxylic acids were pyrolyzed in the presence of cyanogen halides at temperatures between 200–300° and nitriles were isolated in variable yields. When this reaction was performed with C^{14}-carboxyl labeled benzoic acid, Douglas, Eccles and Almond[5] observed that no displacement occurred, the evolved carbon dioxide was not labeled and the generated benzonitrile was labeled. On the other hand, when a carboxyl labeled aliphatic acid was used in the pyrolysis reaction, the carbon dioxide was labeled and the nitrile was not radioactive.[5] Evaluation of these conflicting results must await further work.

It was obvious that the drastic conditions used in this alkali metal salt and cyanogen halide reaction would limit the usefulness of the reaction to acids of simple structure if, indeed, displacement did occur. If, however, the reaction could be run with the silver salts of carboxylic acids under the conditions of the silver salt–bromine degradation of Hunsdiecker, the reaction might become a valuable method for the introduction of C^{14} into organic compounds. In line with this concept are the findings of Haszeldine and Jander[6] who report that when the silver salt of an aliphatic trifluorocarboxylic acid is allowed to react with nitrosyl chloride under the conditions of the Hunsdiecker reaction, an alkylnitroso compound and carbon dioxide are obtained.

Although the mechanism of the Hunsdiecker reaction is not clearly understood,[1] the most likely route would involve the reaction of a bromine cation, $Br^{\oplus}$, with the silver salt to form an acylhypohalite which, in turn, would decompose to alkyl halide and carbon dioxide. From what is known of the chemistry of the cyanogen halides,[7] it is clear that under certain conditions these compounds do generate $CN^{\oplus}$, and it appears that cyanogen chloride would be more likely to do this than cyanogen bromide and the bromide more likely than the iodide.[8] In the present work, cyanogen bromide was utilized since it is easier to handle than the gaseous cyanogen chloride and the easily subliming cyanogen iodide. Furthermore, since the main aim of the study was to obtain a good yield of nitrile, most experiments were not performed under identical conditions. The acid chosen for the most investigations was γ-phenylbutyric acid since this acid shows the features of both an aromatic ring and an aliphatic acid.

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[2] S. Bergström, K. Pääbo and M. Rottenberg, *Acta Chem. Scand.*, **6**, 1127 (1952); S. Bergström, M. Rottenberg and J. Voltz, *ibid.*, **7**, 481 (1953); S. Bergström, K. Pääbo and M. Rottenberg, *ibid.*, **7**, 1001 (1953); D. R. Howton, R. H. Davis and J. C. Nevenzel, THIS JOURNAL, **76**, 4970 (1954).

[3] S. Graf, M. Engelman, H. B. Gillespie and A. M. Graf, *Cancer Research*, **11**, 388 (1951); F. Weygand and H. Simon in Houben-Weyl, "Methoden der Organischen Chemie," Vol. IV, part 2, Georg Thieme Verlag, Stuttgart, 1955, p. 558.

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[5] D. E. Douglas, J. Eccles and A. E. Almond, *Can. J. Chem.*, **31**, 1127 (1953).

[6] R. N. Haszeldine and J. Jander, *J. Chem. Soc.*, 4172 (1953).

[7] V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publishing Corp., New York, N. Y., 1947, p. 97; D. T. Mowry, *Chem. Revs.*, **42**, 189 (1948).

[8] G. Lord and A. A. Woolf, *J. Chem. Soc.*, 2546 (1954); T. Kikindai, *Bull. soc. chim. France*, **18**, 799 (1951).

It was found that when the silver salt of γ-phenylbutyric acid was allowed to react with cyanogen bromide in carbon tetrachloride, the reaction was sluggish compared to the Hunsdiecker reaction. No carbon dioxide could be observed in the cold or at room temperature. Only after heating on a steam-bath was carbon dioxide evolved. The main product of the reaction was not the expected nitrile but the anhydride of the acid. The yield of nitrile was 9% and of anhydride was 75%. The silver salt mixture isolated from the reaction mixture was shown to contain silver cyanate. In several cases, approximately equimolecular amounts of anhydride and cyanate were found.

The formation of an anhydride in the reaction of silver salts is well known. For example, the anhydrides of mono- and dicarboxylic acids are obtained when their silver salts are allowed to react with iodine. Thus, silver phthalate gives phthalic anhydride and silver hypoiodite which, in turn, disproportionates into silver iodate and silver iodide.[9] Also, silver trifluoroacetate and iodine in benzene form trifluoroacetic anhydride.[10] By analogy, a reasonable explanation for the formation of anhydride and cyanate in the cyanogen halide reaction can be represented as shown below (eq. 3, 4, 5) and involves the formation of an intermediate acyl cyanate which can react with silver salt to form an anhydride or can decompose to give rise to a nitrile and carbon dioxide. Since such a postulate indicates a bimolecular displacement reaction for the formation of the anhydride, the influence of different solvents has been investigated. The solvents used and the results obtained are summarized in Table I.

$$\text{RCOOAg} + \text{CNBr} \longrightarrow \text{RCOOCN} + \text{AgBr} \quad (3)$$

$$\text{RCOOCN} + \text{RCOOAg} \longrightarrow \text{RCOOCOR} + \text{AgOCN} \quad (4)$$

$$\text{RCOOCN} \longrightarrow \text{RCN} + \text{CO}_2 \quad (5)$$

TABLE I

REACTION OF SILVER SALTS OF CARBOXYLIC ACIDS WITH CYANOGEN BROMIDE IN VARIOUS SOLVENTS

	Solvent, %					
	Carbon tetrachloride	Nitromethane	Acetonitrile	N,N-Dimethylformamide	Nitrobenzene	Trichloroethylene
Nitrile	9	5	32	17	21	5
Anhydride	75	15	28	8	64	88
Acid	1	82	36	40	5	5

It is seen that the best yields of nitrile are obtained when a solvent of high dielectric constant is employed, the dielectric constants for acetonitrile, nitrobenzene and N,N-dimethylformamide being 37.5, 35.7 and 37.6, respectively.[11] However, when the solvent was nitromethane, a compound also possessing a dielectric constant of 37.5,[11] the yield of nitrile was very low. Simultaneously, the yield of acid was high and this reaction must be attributed to the acidic nature of the solvent. The yield of acid was also high in acetonitrile, an acidic solvent, and N,N-dimethylformamide. In this last solvent, the N,N-dimethylamide of γ-phenylbutyric acid also was formed, and this reaction may account for the liberation of free starting acid. Although no definite decision can be given as to the role of solvent in the formation of anhydride, since the various reactions were not run under the same conditions, it does seem apparent that a solvent of low dielectric constant favors the formation of this species. Such a conclusion clearly shows the oversimplification of the above postulated mechanistic pathway for the formation of the anhydride. The assumption of an intermediate acyl cyanate, nevertheless, offers a reasonable explanation for the concomitant formation of the anhydride and the silver cyanate and also accounts for the formation of the nitrile and carbon dioxide.

An alternate pathway for the formation of nitrile also must be considered. It is known that when the anhydride of a carboxylic acid is heated with potassium cyanate in benzene, imides are formed[12] and that imides on mild heating decompose to a nitrile and an acid.[13] Accordingly, silver cyanate and the anhydride, products of the silver salt–cyanogen bromide reaction, could react similarly to yield an imide which could decompose to a nitrile and an acid. It was found that under the same or similar conditions to those used in the silver salt–cyanogen bromide reaction, no imide, nitrile or acid was formed when pure silver cyanate and an anhydride were allowed to react.

Two exploratory experiments were performed with silver γ-phenylbutyrate and the other cyanogen halides. With cyanogen iodide in carbon tetrachloride, the products were 1.5% nitrile, 68% anhydride and 18% acid while with cyanogen chloride the yields were 7% nitrile, 73% anhydride and 8% acid. In addition, in this latter case, 3-phenylpropyl chloride was isolated in 2% yield. This is the only case among all the experiments where a halide was isolated and, indeed, this is surprising since cyanogen chloride should be the halide least likely to yield an $X^{\oplus}$ ion. The non-occurrence of halide in the cyanogen halide reactions explains the fact that in no instance could Simonini ester formation be demonstrated.[1]

To extend the scope of this reaction, a brief study was made with a typical aromatic acid, benzoic acid, and a typical aliphatic acid, decanoic acid. In both cases cyanogen bromide was employed and it was found that the results did not differ from those obtained with γ-phenylbutyric acid. It is of interest to note that no aromatic ring substitution was found with either acid containing an aromatic nucleus. Such substitutions have been observed in the Hunsdiecker reaction with aromatic acids containing activating groups on the ring.[14]

Finally, it can be stated that the difference between the alkali metal salt–cyanogen bromide reaction with benzoic acid run under pyrolytic conditions and the reaction performed with silver

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[12] K. Brunner, *Ber.*, **47**, 2671 (1914).

[13] F. Krafft, *ibid.*, **23**, 2389 (1890).

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benzoate in an organic solvent are that, in the former case, besides benzonitrile, also benzamide and cyaphenin, the trimer of benzonitrile, are isolated[4,5] but no anhydride, whereas in the latter case mainly anhydride, nitrile and acid are the products, but no amide or cyaphenin is formed. The yield of nitrile is better when the reaction is run under the pyrolytic conditions.

Experimental[15]

All solvents were purified and carefully dried. The silver salts of the carboxylic acids were prepared in the usual manner[16] and they were either dried in a vacuum oven at 60° or in a vacuum desiccator over phosphorus pentoxide at room temperature for at least 24 hr. Their purity was checked by combustion analysis.

The cyanogen halides cyanogen chloride,[17] cyanogen bromide[18] and cyanogen iodide[19] were prepared by metathesis of the halogens with alkali metal cyanides. The cyanogen bromide, before being added to the silver salts, was dried in carbon tetrachloride over phosphorus pentoxide.

All liquid reaction products were distilled through a 20" wire-screen filled column of 12-plate efficiency if not otherwise mentioned.

Determination of Cyanate Ion. (a) Quantitative Test.[20]—A sample of the silver salt mixture obtained from the reaction of the silver salt of a carboxylic acid with the cyanogen halide was mixed in a mortar with cobaltous acetate and potassium chloride. Addition of a few drops of acetic acid followed by mixing produced a blue color when cyanate-ion was present.

(b) Quantitative Test.[20] Cyanate Carbon.—A sample of silver salt from the reaction mixture was treated with excess 1 *N* hydrochloric acid and the evolved carbon dioxide absorbed in standardized sodium hydroxide solution. If stronger acid concentrations were used, the cyanide was also hydrolyzed to formate and the carbon values were too high.

Cyanate Nitrogen.—The residual acidified mixture above was made alkaline with 1 *N* potassium hydroxide solution and the liberated ammonia absorbed in standardized sulfuric acid solution. Stronger potassium hydroxide solution hydrolyzed also the cyanide.

Silver cyanate was prepared from potassium cyanate and silver nitrate[21] and dried in a desiccator over phosphorus pentoxide. Following the above procedure a freshly prepared and dried sample of silver cyanate was analyzed.

Anal. Calcd. for AgOCN (149.90): C, 8.01; N, 9.34. Found: C, 7.84; N, 9.22.

In the same manner a well dried sample of silver cyanide was analyzed.

Anal. Calcd. for AgCN (133.90): C, 8.97; N, 10.46. Found: C, 0.0; N, 0.0.

An equimolecular mixture of the silver salts of decanoic, cyanic, hydrocyanic and hydrobromic acids was prepared and dried in a desiccator over phosphorus pentoxide. A sample was analyzed as above.

Anal. Calcd. for AgOCN in mixture [AgOOC-$(CH_2)_5$-CH_3 (279.26); AgOCN (149.90); AgCN (133.90); AgBr (187.80)] : C, 1.60; N, 1.87. Found: C, 1.44; N, 1.81.

Experiments with Silver γ-Phenylbutyrate and Cyanogen Bromide.—(a) In Carbon Tetrachloride as the Solvent; Addition of the Cyanogen Bromide to the Silver Salt.—A suspension of 108.4 g. (0.4 mole) of silver salt in 800 ml. of carbon tetrachloride was distilled until 100 ml. of distillate had been collected and then cooled in an ice-bath. A solution of 47 g. (0.45 mole) of cyanogen bromide in 315 ml. of carbon tetrachloride was added dropwise with stirring over a period of 1 hr. No carbon dioxide evolution could be detected. Upon heating on a steam-bath to reflux temperature, a slow evolution of carbon dioxide began. Heating and stirring were continued for 5 hr. At the end of the heating period the carbon dioxide evolution had stopped. The silver salts were filtered and washed several times with carbon tetrachloride. The carbon tetrachloride solution was extracted three times with 2 *N* sodium carbonate solution.

The alkaline aqueous extracts were combined and were acidified with 6 *N* sulfuric acid. The acidic aqueous solution was extracted with ether in an apparatus for continuous extraction. After removal of the ether the residue was distilled under reduced pressure to a cold finger and 422 mg. (0.6%) of γ-phenylbutyric acid, m.p. 47–48°, was obtained.

Subsequent extraction of the carbon tetrachloride layer with 4 *N* sodium hydroxide solution did not yield any extractable material. The carbon tetrachloride solution, washed with water until neutral, was dried with Drierite. The solvent was removed and the residue was fractionally distilled. The forerun (0.5 g., b.p. 120–126° (10 mm.)) was shown not to contain 3-phenylpropyl bromide (b.p. 120.5–121.5° (20 mm.)). The next fraction was a colorless oil, b.p. 126–127° (10 mm.), and was γ-phenylbutyronitrile, (lit.[22] b.p. 129–131° (10 mm.)), yield 5 g. (8%).

A sample of the nitrile was hydrolyzed with 25% ethanolic potassium hydroxide and gave in 80% yield γ-phenylbutyric acid.

The distillation residue crystallized at room temperature to a waxy substance which was insoluble in 2 *N* sodium hydroxide solution and which had a m.p. 25–28°. Recrystallization of a sample from ether-petroleum ether at −30° yielded γ-phenylbutyranhydride, m.p. 28–29°. The infrared spectrum was identical with that of an authentic sample.

Anal. Calcd. for $C_{20}H_{22}O_3$ (310.38): C, 77.39: H, 7.14. Found: C, 77.39; H, 7.41.

A sample of the distillation residue (13 g.) was refluxed overnight with 350 ml. of 10% aqueous sodium hydroxide solution. The alkaline solution was saturated with potassium carbonate and was continuously extracted with ether for 24 hr. No alcoholic material could be detected in this ether extract. The aqueous phase of this extraction was acidified with 6 *N* sulfuric acid (acid to congo red). This acidic mixture was continuously extracted with ether for 24 hr. The ether extract was dried with magnesium sulfate and yielded γ-phenylbutyric acid (95%), m.p. 45–47°. Hence, the non-distillable fraction consisted of 46.9 g. (75%) of the anhydride of γ-phenylbutyric acid.

The silver salts from the reaction were treated with 500 ml. of 6 *N* hydrochloric acid using a vibrating mixer. A violent evolution of hydrocyanic acid occurred and the mixture warmed up. The mixture was filtered through a mat of filter aid. The filter cake was shaken several times with portions of diisopropyl ether, and the filtrate was extracted several times with the same solvent. The combined ether extracts yielded 4 g. (6%) of γ-phenylbutyric acid, m.p. 45–47°.

γ-Phenylbutyranhydride was prepared by refluxing a mixture of 32.8 g. (0.2 mole) of acid with 200 ml. of acetic anhydride and 200 ml. of pyridine for 3 hr. After removal of the excess reagents under reduced pressure the residue was fractionally distilled, yield 21 g. (68%). This compound can only be distilled with losses due to decomposition, b.p. 200–205° (3 mm.), m.p. 28–29°. The compound shows strong absorption peaks in the infrared at 5.5, 5.83 and 9.7 μ.

Anal. Calcd. for $C_{20}H_{22}O_3$ (310.88): C, 77.39; H, 7.14. Found: C, 77.48; H, 7.35.

(b) In Carbon Tetrachloride as the Solvent; Addition of the Silver Salt to the Cyanogen Bromide.—A solution of 47 g. (0.45 mole) of cyanogen bromide in 1200 ml. of carbon tetrachloride was cooled to 0°, and a 10-g. portion of silver salt was added. After 10 minutes, the mixture was brought to reflux on a steam-bath, whereupon carbon dioxide evolution commenced. Over the period of 1 hr. 108.4 g. (0.4 mole) of silver salt was added and the heating and stirring

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(15) Quantitative analyses by the Microanalytical Laboratory of the Department of Chemistry, University of California, Berkeley.

(16) J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, p. 271.

(17) G. H. Coleman, R. W. Leeper and C. C. Schulze, in "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., New York, N. Y., 1946, p. 90.

(18) G. Brauer, "Handbuch der präparativen anorganischen Chemie," F. Enke Verlag, Stuttgart, 1954, p. 505.

(19) B. Bak and A. Hillebert, *Org. Syntheses*, **32**, 29 (1952).

(20) H. E. Williams, "Cyanogen Compounds," 2nd Ed., Edward Arnold and Co., London, 1948, p. 400.

(21) H. Hecht, "Präparative anorganische Chemie," Springer-Verlag, Berlin, 1951, p. 112.

(22) I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. IV, rev ed., Oxford University Press, New York, N. Y., 1953, p. 110.

was continued for 10 hr. Processing in the usual way (see above) gave 500 mg. (1%) of γ-phenylbutyric acid from the sodium carbonate extract, 7.3 g. (12%) of nitrile and 44 g. (71%) of anhydride.

(c) **In Nitromethane as the Solvent.**—The silver salt (108.4 g., 0.4 mole) was suspended in 400 ml. of carbon tetrachloride, and 400 ml. of the solvent was distilled. Nitromethane (700 ml.) was then added, and over the period of 1.5 hr. 50 g. (0.47 mole) of cyanogen bromide in 350 ml. of nitromethane was added, with stirring, to the reaction mixture. During the first 0.5 hr. of the addition the reaction mixture was at room temperature and no carbon dioxide evolution occurred. The reaction mixture was then heated to slow reflux and the addition of cyanogen bromide continued. At this elevated temperature carbon dioxide evolution occurred and the heating was continued for 8.5 hr. The silver salts were filtered and washed well with carbon tetrachloride. The filtrate was processed in the usual way. The neutral fraction gave 3 g. (5%) of pure nitrile and 9.3 g. (15% assuming pure γ-phenylbutyranhydride) of crude anhydride. This crude anhydride gave a weakly positive Beilstein test for halogen. The acidified alkaline extract yielded 54 g. (82% assuming pure γ-phenylbutyric acid) of crude acidic material. This material had a m.p. of 42–45° and it gave a positive Beilstein test. When this material was distilled, approximately 4 g. of higher boiling material was obtained as a tarry distillation residue which gave a strongly positive Beilstein test.

(d) **In Acetonitrile as the Solvent.**—To a suspension of 80 g. of silver salt in 1200 ml. of purified acetonitrile containing 2 g. of cuprous cyanide, 36 g. of cyanogen bromide dissolved in 350 ml. of acetonitrile was added during the course of 2.5 hr. Upon initial heating a blue color developed which later discharged. During the entire reaction carbon dioxide was evolved. After an additional hour of heating the reaction mixture was allowed to stay at room temperature overnight.

The usual working-up procedure was modified due to the water solubility of acetonitrile. The acetonitrile layer was diluted with a large volume of carbon tetrachloride, the aqueous layer was saturated with sodium chloride, and the reaction mixture was processed in the normal manner. A yield of 32% nitrile, 28% anhydride and 36% acid was obtained.

(e) **In N,N-Dimethylformamide as the Solvent.**—A mixture of 108.4 g. (0.4 mole) of silver salt with 1500 ml. of N,N-dimethylformamide was prepared. The mixture was stirred and heated on a steam-bath and a solution of 45 g. (0.43 mole) of cyanogen bromide in 450 ml. of carbon tetrachloride was added during 1.5 hr. The carbon dioxide evolution was rather slow. The mixture was heated on the steam-bath overnight. After 8 hr. of heating there was still some carbon dioxide evolution. To the cooled mixture was added carbon tetrachloride in order to precipitate more of the silver salts. These were filtered and washed with the same solvent. Shaking the filtrate with 2 *N* sodium carbonate solution precipitated more silver salts which were filtered. The sodium carbonate extracts were continuously extracted with ether for three days in order to extract the water-soluble N,N-dimethylformamide. The acidified aqueous phase yielded 26 g. (40%) of pure γ-phenylbutyric acid. The combined carbon tetrachloride layers were dried with magnesium sulfate. After removal of the solvent a brown oil was obtained which was fractionated with a column; 6 g. (10%) of pure γ-phenylbutyronitrile was obtained, b.p. 126–127° (10 mm.). On further heating the distillation residue began to decompose. The distillation was interrupted. This residue was a liquid in which crystallization could not be induced by seeding with γ-phenylbutyranhydride. The residue was subjected to a fast distillation in a Claisen flask. This operation separated a fraction which boiled mainly between 150 and 180° at a pressure of 1 mm. from a distillation residue which solidified. This solidified material eventually yielded 5.3 g. (8%) of γ-phenylbutyranhydride. In a third distillation, using again a column, the fraction with b.p. 150–180° (1 mm.) was split into 4 g. (7%) of γ-phenylbutyronitrile and a distillation residue (20 g., dark brown) which did not solidify and which contained nitrogen. This water-insoluble oil was refluxed with 500 ml. of 10% aqueous sodium hydroxide solution until the water-insoluble layer had disappeared and until the evolution of dimethylamine ceased. The mixture from the hydrolysis yielded after acidification and after purification 16 g. (24%) of γ-phenylbutyric acid. Hence the dark oil consisted largely of N,N-dimethyl-γ-phenylbutyramide, b.p. 151–152° (1.5 mm.) (see below).

N,N-Dimethyl-γ-phenylbutyramide.—A solution of 68 g. (0.37 mole) of distilled γ-phenylbutyryl chloride[23] dissolved in 300 ml. of hexane was added with shaking to 860 ml. of an ice-cold commercial 25% aqueous solution of dimethylamine. The amide separated as an oil which did not solidify and was separated and dissolved in methylene chloride. The methylene chloride solution was washed with 2 *N* sodium carbonate solution and with water and dried with magnesium sulfate. After removal of the solvent the amide was distilled, 60 g. (84%) of a yellow oil. It distilled with decomposition at 151–152° (1.5 mm.). Upon cooling the distillate to Dry Ice temperature, large glassy crystals are formed, which melt around 20°. The amide can be recrystallized from methylene chloride–hexane, but care must be exerted since the compound is highly hygroscopic. The analytical sample was dried in a high vacuum for 24 hr. at 60° and sealed under vacuum.

Anal. Calcd. for $C_{12}H_{17}ON$ (191.26): C, 75.35; H, 8.96; N, 7.32. Found: C, 75.41; H, 8.87; N, 7.24.

(f) **In Nitrobenzene as the Solvent.**—A mixture of the silver salt (108.4 g., 0.4 mole) and 1500 ml. of purified nitrobenzene was heated on a steam-bath. During the course of 0.5 hr. 45 g. (0.43 mole) of cyanogen bromide dissolved in 450 ml. of carbon tetrachloride was added dropwise. The carbon dioxide evolution was slow and heating was continued overnight. The bulk of the solvents was distilled under reduced pressure. Carbon tetrachloride was added in order to precipitate the silver salts which were filtered. Extraction with 2 *N* sodium carbonate solution and subsequent acidification yielded 3 g. (5%) of γ-phenylbutyric acid. The carbon tetrachloride extracts, after fractional distillation, gave 12 g. (21%) of nitrile and 39.6 g. (64%) of anhydride.

(g) **In Trichloroethylene as the Solvent.**—The reaction was carried out in the usual manner using 108.4 g. (0.4 mole) of silver salt and 1500 ml. of purified trichloroethylene. The mixture was heated on a steam-bath in an atmosphere of dry nitrogen, and 45 g. (0.43 mole) of cyanogen bromide dissolved in 450 ml. of carbon tetrachloride were added during 1 hr. The carbon dioxide evolution was slow, and heating and stirring was continued for 9 more hours. The silver salts were filtered, washed with carbon tetrachloride and dried for 24 hr. in a desiccator at room temperature *in vacuo* over phosphorus pentoxide. Their weight was 68.5 g. Using the usual working-up procedure the following yields and products were obtained: 3.5 g. (5%) of γ-phenylbutyric acid from the sodium bicarbonate extract, 2.9 g. (5%) of nitrile and 55 g. (88%) of anhydride. Assay of a sample of the silver salt mixture: cyanate-C, 2.85%; cyanate-N, 3.28%. This is equimolecular to 52.3 g. of anhydride. Found: 55 g. of anhydride.

Silver Benzoate and Cyanogen Bromide.—From a mixture of 91.6 g. (0.4 mole) of silver salt and 2000 ml. of carbon tetrachloride, 500 ml. of solvent was distilled. Then 45 g. (0.43 mole) of cyanogen bromide dissolved in 450 ml. of carbon tetrachloride was added to the heated solution during the course of 1 hr. The carbon dioxide evolution was rather slow. The stirring and the refluxing were continued for 14 more hours. The weight of the dried silver salts was 70 g. Using the usual working-up procedure the following yields and products were obtained: From the sodium bicarbonate extract 5 g. (10%) of benzoic acid, which was purified by sublimation, m.p. 121–122°; 2 g. (5%) of benzonitrile, b.p. 80–81° (8 mm.) (lit.[24] 69° (10 mm.)); and 31.5 g. (70%) of benzoic anhydride, b.p. 210–220° (20 mm.), m.p. 41–43° (lit.[25] same b.p., m.p. 43°). The silver salts were treated with dilute (1:1) hydrochloric acid. This mixture was exhaustively extracted with ether, and after removal of the solvent 4 g. (8%) of benzoic acid was obtained. The assay of a sample of the silver salt mixture gave: cyanate-C, 2.16%; cyanate-N, 2.64%. This is equimolecular to 29.2 g. of benzoic anhydride. Found: 31.5 g. of anhydride.

Separation of a Mixture of Benzonitrile, Benzimide[26] and

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[23] H. Rupe, *Ann.*, **395**, 118 (1913).

[24] I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. I, rev. ed., Oxford University Press, New York, N. Y., 1953, p. 256.

[25] H. T. Clarke and E. J. Rahrs, in "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 91.

[26] F. Krafft, *Ber.*, **23**, 2389 (1890).

Benzoic Acid.—If equimolecular amounts of the above listed compounds were dissolved in carbon tetrachloride, a quantitative separation could be performed by extraction of the acid with saturated sodium bicarbonate solution, the imide with 2 *N* sodium hydroxide solution, leaving the benzonitrile in the carbon tetrachloride.

Experiments with Silver Decanoate and Cyanogen Bromide.—From a mixture of 111.6 g. (0.4 mole) of silver salt and 700 ml. of carbon tetrachloride, 100 ml. of solvent was distilled. Afterwards 47 g. (0.45 mole) of cyanogen bromide dissolved in 450 ml. of carbon tetrachloride was added at room temperature over the period of 45 minutes. No carbon dioxide evolution could be observed. The mixture was refluxed on a steam-bath for 12 hr. The carbon dioxide evolution was slow. Using the usual working-up procedure the following yields and products were obtained: 49 g. (75%) of anhydride[27] and 10.7 g. (17%) of nitrile, b.p. 109–110° (10 mm.) (lit.[28] 243.7°). Only traces of acid were recovered in this experiment.

In a second experiment, where the cyanogen bromide was added to the heated mixture over a period of 1.5 hr., the carbon dioxide evolution was complete after a total heating time of 3 hr. The yield of nitrile was 4.5 g. (7%).

Experiment with Silver γ-Phenylbutyrate and Cyanogen Iodide.—Cyanogen iodide (39 g., 0.25 mole) dissolved in 400 ml. of carbon tetrachloride was added in the usual manner in portions to 62.4 g. (0.23 mole) of the silver salt in 600 ml. of carbon tetrachloride heated on a steam-bath over a period of 1 hr. The carbon dioxide evolution ceased about 0.5 hr. after the last addition of cyanogen iodide. The reaction mixture was refluxed with stirring overnight. After the usual working-up procedure 0.5 g. (1.5%) of nitrile, 24.2 g. (68%) of anhydride and 6.8 g. (18%) of acid were obtained.

Silver γ-Phenylbutyrate and Cyanogen Chloride.—Approximately 60 ml. (excess) of cyanogen chloride (b.p. 13°) was distilled over the period of 1.5 hr. directly into a slurry of 112 g. (0.41 mole) of the silver salt and 1100 ml. of carbon tetrachloride at room temperature. The reaction flask was equipped with a cold finger condenser filled with Dry Ice and *n*-butyl Carbitol. The content of the cold finger was then replaced with a Dry Ice and methanol mixture and the temperature in the cold finger kept at −20 to −10°. The reaction mixture was heated to about 60–70° and stirring was continued. There was a great initial carbon dioxide evolution, but the evolution came to an end after about 1 hr., albeit cyanogen chloride was still escaping. The mixture was stirred and refluxed for 7 more hours. Using the usual working-up procedure 4.0 g. (7%) of nitrile, 45.1 g. (73%) of anhydride, 5.4 g. (8%) of acid and 1.2 g. (2%) of 3-phenylpropyl chloride[29] were obtained.

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(27) J. M. Wallace and J. E. Copenhaver, THIS JOURNAL, **63**, 699 (1941).

(28) Reference 24, p. 421.

(29) J. B. Conant and W. R. Kirner, THIS JOURNAL, **46**, 232 (1924).

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[CONTRIBUTION FROM THE ROHM & HAAS CO.]

Chemistry of the 1,4-Diamino-1,3-butadienes. I. Preparation[1]

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1,4-Bis-(dimethylamino)-2-butyne (I), on heating with sodium, was rearranged to 1,4-bis-(dimethylamino)-1,3-butadiene (II). The preparation and rearrangement of several homologs of I are described. On standing at room temperature, II is isomerized to a geometric isomer. Infrared evidence is adduced to assign the initial form the *cis,trans* and the new isomer, the *trans,trans* structure. In the presence of potassium bases, dimerization of I rather than intramolecular rearrangement occurred. This mixture of isomeric dimers was itself subject to rearrangement. The structures of the dimeric products were not definitely ascertained. The mechanism for these transformations of I is discussed.

We have found that 1,4-bis-(dimethylamino)-2-butyne (I) may be rearranged to 1,4-bis-(dimethylamino)-1,3-butadiene (II) by means of finely divided metallic sodium.

$$\underset{\text{I}}{(CH_3)_2NCH_2C{\equiv}CCH_2N(CH_3)_2} \xrightarrow{\text{Na}} \underset{\text{II}}{(CH_3)_2NCH{=}CHCH{=}CHN(CH_3)_2}$$

II had first been prepared in these laboratories by McKeever and Nemec[2] by passage of I over chromium oxide-containing catalysts at 300–450° in the vapor phase. Our present discovery has permitted the facile preparation of II on a large laboratory scale.

In order to control this exothermic rearrangement, dried, redistilled I was added dropwise to a stirred boiling mixture of hexane and metallic sodium dispersed in xylene.[3] From 50 g. to 300 g. of I, depending on its purity, could be converted to II per gram of sodium. The product was isolated in yields of 80 to 90% of the theoretical by distillation without prior removal or destruction of the catalyst. Alfin catalyst[4] (55% yield), metallic lithium (81% yield), metallic potassium (9% yield) and sodamide (12% yield) were catalysts of limited utility, while sodium acetylide and metallic calcium were inactive.

This rearrangement was extended to the 1,4-diamino-2-butyne derivatives shown in Table I. These were prepared by means of the cuprous chloride-catalyzed Mannich reaction[5,6] applied to acetylene and to the intermediate 3-dialkylamino-1-propynes. Properties of the corresponding 1,4-diamino-1,3-butadienes are shown in Table II. Dispersed sodium alone was not a satisfactory catalyst for the isomerization of many of the higher

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(1) Given in part at the 123rd Meeting of the American Chemical Society, Los Angeles, Calif., March 16, 1953.

(2) C. H. McKeever and J. W. Nemec (Rohm & Haas Co.), U. S. Patent 2,617,827 (Nov. 11, 1952); *C. A.*, **48**, 1429 (1954). Their product was probably the *trans,trans*-modification. The similar rearrangement of 3-amino-1-butynes to the corresponding 1,3-butadienes over activated alumina at 250–300° has been described recently by W. Reppe, *Ann.*, **596**, 12 (1955).

(3) V. L. Hansley, *Ind. Eng. Chem.*, **43**, 1759 (1951); U. S. Patent 2,394,608 (E. I. du Pont de Nemours & Co.) Feb. 12, 1946; *C. A.*, **40**, 2598 (1946). We wish to thank the U. S. Industrial Alcohol Division of National Distillers, Inc., for samples of these dispersions.

(4) A. A. Morton, *Ind. Eng. Chem.*, **42**, 1488 (1950); A. A. Morton, E. E. Magat and R. L. Letsinger, THIS JOURNAL, **69**, 950 (1947).

(5) (a) C. Mannich and F. T. Chang, *Ber.*, **66**, 418 (1933). (b) W. Reppe, E. Keyssner and O. Hecht, U. S. Patent 2,273,141 (General Aniline & Film Corp.) Feb. 17, 1942; *C. A.*, **36**, 3807 (1942). (c) W. Reppe, *Ann.*, **596**, 12 (1955).

(6) The processes which have permitted the satisfactory preparation of these materials at low pressures of acetylene were worked out in collaboration with Dr. J. O. Van Hook, Dr. L. R. Freimiller and Dr. J. S. Strong and are described in the Experimental section.