[Contribution from the Department of Chemistry, University of Nebraska]

STRUCTURE OF THE SALTS OF AROMATIC NITRILES

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In the course of work reported in 1922 from this Laboratory,[2] the impure sodium salt of phenylacetonitrile was isolated. Because of certain properties the authors suggested the nitride structure $(C_6H_5)H{-}C{=}C{=}N{-}Na$ for this substance. It was also suggested that an imide form of the parent nitrile $(C_6H_5)H{-}C{=}C{=}N{-}H$ is an intermediate substance in certain condensation reactions undergoing rearrangement to the nitrile form $((C_6H_5)H{-}\underset{|}{C}{-}C{\equiv}N)H$.

In two papers published recently by Rising and co-workers[3] similar ideas are expressed and the theory concerning tautomerism of the nitriles is more fully developed than in the paper of Upson and Thompson.

Several reactions carried out in this Laboratory favor the nitride structure of the sodium salt.

(I) Decomposition at high temperatures yields stilbene and sodium cyanide.

$$(C_6H_5)H{-}C{=}C{=}N{-}Na \longrightarrow (C_6H_5)H{-}C{=} + NaNC$$
$$2C_6H_5H{-}C{=} \longrightarrow (C_6H_5)H{-}C{=}C{-}H(C_6H_5)$$

(II) An impure silver salt of phenylacetonitrile possessing in all probability the nitride structure was prepared from the sodium salt by interaction with silver nitrate in alcoholic solution. The silver salt on interaction with butyl iodide gave an alkyl derivative of nitride structure, since after decomposition there was isolated butylamine in the form of its hydrochloride.

$$(C_6H_5)H{-}C{=}C{=}N{-}Ag + C_4H_9I \longrightarrow (C_6H_5)H{-}C{=}C{=}N{-}C_4H_9 + AgI$$
$$(C_6H_5)H{-}C{=}C{-}N{-}C_4{-}H_9 \longrightarrow (C_6H_5)H{-}C{=} + C_4H_9{-}N{=}C$$
$$C_4H_9{-}N{=}C + H_2O + HCl \longrightarrow C_4H_9NH_3Cl + HCOOH$$

(III) Spontaneous oxidation of sodium phenylactonitrile in the air leads to the formation of benzoic acid and sodium cyanide

$$(C_6H_5)H{-}C{=}C{=}N{-}Na + O_2 \longrightarrow C_6H_5COOH + NaNC$$

(IV) Toluene and sodium cyanide are formed during the preparation of the salt.

$$2C_6H_5H{-}C{=}C{=}N{-}H + 2Na \longrightarrow 2(C_6H_5)H{-}C{=}C{=}N{-}Na + 2H$$

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[1] Based in part upon theses presented by Robert W. Maxwell and Howard M. Parmelee for the Master of Science degree, University of Nebraska. Presented before the Organic Division of the American Chemical Society at the Minneapolis Meeting, September, 1929.

[2] Upson and Thompson, This Journal, **44**, 181 (1922).

[3] Rising and Zee, *ibid.*, **50**, 1699 (1928); Rising, Muskat and Lowe, *ibid.*, **51**, 262 (1929).

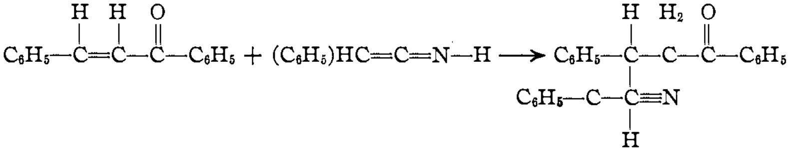
A part of the salt is reduced to toluene and sodium cyanide by the hydrogen liberated in the above reaction.[4]

$$(C_6H_5)H-C=C=N-Na + H_2 \longrightarrow C_6H_5CH_3 + NaNC$$

This reduction which always accompanies the formation of the sodium salt of phenylacetonitrile explains the difficulty experienced by us and by Rising and co-workers in preparing the pure salt.[5] Unless the sodium cyanide is removed it contaminates the salt of the nitrile. Details of the preparation of the salt in pure form will be found in the experimental part.

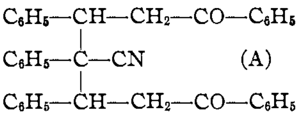
(V) Condensation reactions of the type studied by Avery[6] can be produced by the use of sodium phenylacetonitrile, as well as by the use of sodium methylate and benzyl cyanide.

The work of Avery involves condensation of benzyl cyanide with unsaturated esters and ketones using sodium methylate as the condensing agent. Benzalacetophenone condenses with the sodium phenylacetonitrile in methyl alcohol solution to give a 97% yield of 1,5-dibenzoyl-2,3,4-triphenyl-3-cyanopentane. The same compound is obtained by the use of sodium methylate and phenylacetonitrile



$$C_6H_5-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-C_6H_5 + (C_6H_5)HC=C=N-H \longrightarrow \underset{C_6H_5-\underset{H}{\underset{|}{C}}-C\equiv N}{\underset{|}{C_6H_5-\overset{H}{\overset{|}{C}}}}-\overset{H_2}{C}-\overset{O}{\overset{\|}{C}}-C_6H_5$$

This latter through its imide form gives, with a second molecule of benzalacetophenone, the condensation product obtained by Avery (A). This result constitutes evidence that phenylacetonitrile is tautomerized by sodium methylate as well as by metallic sodium since the two methods give theidentical product.



$$\begin{array}{l} C_6H_5-CH-CH_2-CO-C_6H_5 \\ \qquad\ | \\ C_6H_5-C-CN \\ \qquad\ | \\ C_6H_5-CH-CH_2-CO-C_6H_5 \end{array} \quad (A)$$

Rising, Muskat and Lowe[7] have suggested that sodium phenylacetonitrile exists in two forms designated as "carbide" and "nitride." They explain "the behavior of this salt and of its homolog, sodium α-phenylbutyronitrile, in the reactions studied, upon the assumption of nitride–carbide tautomerism, obviously an extension of the Nef theory with regard to the tautomerism of hydrocyanic acid."

According to our interpretation of the behavior of these salt, there exists only the one form, the "nitride." We would explain condensation reac-

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[4] See in this connection von Meyer, *J. prakt. Chem.*, **22**, 261 (1880).

[5] Zee (Ref. 3) prepared the pure sodium salt of phenylacetonitrile but Rising later was unable to repeat his work. Rising, Muskat and Lowe more recently have prepared the pure potassium salt.

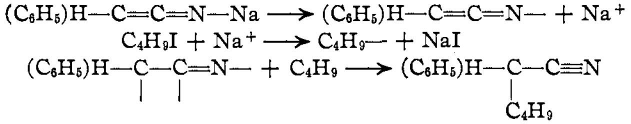
[6] Avery, THIS JOURNAL, **50**, 2512 (1928).

[7] Rising, Muskat and Lowe, *ibid.*, **51**, 263 (1929).

tions of these salts at the carbon atom as involving rearrangement of the anion during the reaction, and condensation at the nitrogen atom as direct replacement of the sodium without rearrangement. Thus just as silver cyanide gives alkyl isocyanides with alkyl halides, so we found that the silver salt of phenylacetonitrile gives a nitrogen derivative on reaction with butyl iodide

$$(C_6H_5)H\text{—}C{=}C{=}N\text{—}Ag + C_4H_9I \longrightarrow (C_6H_5)H\text{—}C{=}C{=}N\text{—}C_4H_9 + AgI$$

Rising, Muskat and Lowe found that the sodium salt condenses with butyl iodide to give α-phenylbutyronitrile. This we believe involves rearrangement of the anion.



$$(C_6H_5)H\text{—}C{=}C{=}N\text{—}Na \longrightarrow (C_6H_5)H\text{—}C{=}C{=}N\text{—} + Na^+$$
$$C_4H_9I + Na^+ \longrightarrow C_4H_9\text{—} + NaI$$
$$(C_6H_5)H\text{—}\underset{|}{C}\text{—}\underset{|}{C}{=}N\text{—} + C_4H_9 \longrightarrow (C_6H_5)H\text{—}\underset{\underset{C_4H_9}{|}}{C}\text{—}C{\equiv}N$$

Experimental Part

Preparation of Sodium Phenylacetonitrile.—In a 500-cc. flask were placed 4.4 g. of sodium in the form of fine shot and 220 cc. of ether which had been specially dried. The flask, connected to a reflux condenser, was warmed on a hot-plate just sufficiently to cause the ether to boil. Dry phenylacetonitrile (23 g.) was added drop by drop, over a period of one hour and thirty minutes. At the end of this time the contents of the flask consisted of a white solid suspended in a yellow solution. The heating was continued for six hours, at the end of which time the sodium had disappeared. All apparatus was specially dried and the reaction mixture was protected from moisture, oxygen and carbon dioxide during the course of the reaction.

The contents of the flask after cooling to 20° deposited a small quantity of white solid. This was removed by filtration under vacuum in an apparatus designed to exclude air and moisture. The solid weighed 1.2 g. and proved to be sodium cyanide. It gave the usual qualitative tests for the cyanide ion and on analysis was found to contain 47.44% Na; calculated for NaCN, 46.93%.

The sodium phenylacetonitrile precipitated from the ethereal filtrate after standing for several days, in the form of frost-like crystals. The salt was removed by filtration in an atmosphere of dry nitrogen and freed from ether in a vacuum desiccator over phosphorus pentoxide. The salt was light pink in color at first and of a yellow color after twenty-four hours. It was distinctly crystalline in character. A yield of 20 g. was obtained.

Anal. Calcd. for C_8H_6NNa: Na, 16.55. Found: Na, 16.57.

The sodium salt is very soluble in the parent nitrile, somewhat soluble in benzene, toluene and xylene and slightly soluble in ether. The reaction mixture contains ether, toluene and unchanged nitrile. The salt is thus quite soluble in the reaction mixture and separates slowly and incompletely. A large excess of ether is desirable since it dilutes the unchanged nitrile and toluene. Cooling increases the rate of precipitation. A second precipitation of the salt usually occurs on long standing of the filtrate.

Identification of Toluene in the Reaction Mixture.—The combined filtrates from five reaction runs, involving a total of 200 cc. of phenylacetonitrile and 1400 cc. of ether, were filtered from precipitated salt and subjected to fractional distillation; 1200 cc. of ether was recovered in the first fraction. The remainder was distilled with an efficient fractionating column. The fraction 110–115°, 54 cc., was again refractionated, yielding

47 cc. boiling at 110–111°, from which there was finally isolated 43 cc. of pure toluene with a boiling point of 110° (corr.). The toluene was further identified by conversion to 2,4-dinitrotoluene; m. p. 70° (corr.).

The higher-boiling fraction yielded a small amount of liquid (unidentified) distilling between 120 and 190°. Between 190 and 240° there was obtained a fraction of 20 cc. consisting chiefly of unchanged phenylacetonitrile. Between 240 and 260° a heavy oil of a red-green color distilled. A small amount of crystalline solid collected in the condenser. These latter were not identified.

Effect of Heat on the Sodium Salt.—The sodium salt obtained from 120 g. of phenylacetonitrile was subjected to rapid heating in a pyrex flask. A small amount of low-boiling liquid was obtained, after which the temperature rose rapidly to 200°. A distillate was obtained of oily appearance and of a green color by reflected light and red by transmitted light. The distillate smelled strongly of ammonia. A considerable amount of crystalline material collected in the condenser tube. This, on recrystallization from alcohol, gave crystals of a wax-like appearance and melting point 123–124°, which is the melting point of stilbene.

Anal. Calcd. for $C_{14}H_{12}$: C, 93.28; H, 6.72. Found: C, 93.41; H, 6.7.

The distillate was treated with an excess of bromine in carbon tetrachloride solution. There appeared almost at once a considerable quantity of fine needle-like crystals. The crystals were removed by filtration and washed well with alcohol. The yield was 4.6 g. The product on recrystallization from hot toluene gave white feathery needles, m. p. 237° (corr.), which is the melting point of stilbene dibromide.

Anal. Calcd. for $C_{14}H_{12}Br_2$: Br, 47.01. Found: Br, 47.11.

The dibromide was converted into tolane by heating with alcoholic alkali. The tolane was precipitated on addition of water, collected and recrystallized from alcohol as white leaflets, m. p. 50–60°. This is the melting point recorded for tolane. These results without doubt identify stilbene as a product of the decomposition of the sodium salt of phenylacetonitrile.

Reactions of the Silver Salt of Phenylacetonitrile.—The silver salt was prepared in an impure form through interaction of the sodium salt and silver nitrate in absolute alcohol solution. There was obtained a white insoluble compound which rapidly became dark in color. This substance decomposes with explosive violence on heating. The silver salt, freshly prepared was mixed with butyl iodide and allowed to stand for twelve hours, after which time a complete reaction had occurred. The mixture possessed a strong odor of isocyanide.

The solution obtained from the reaction mixture of silver salt and butyl iodide was filtered and distilled. The distillate was treated with hydrochloric acid and evaporated to dryness, giving a considerable quantity of white crystalline material. This was purified by recrystallization first from absolute alcohol and then an alcohol–benzene mixture. The substance was butylammonium chloride.

Anal. Calcd. for $C_4H_{12}NCl$: Cl, 32.36. Found: Cl, 32.47.

Condensation of the Sodium Salt of Phenylacetonitrile with Benzalacetophenone.—This condensation was carried out in order to prove that sodium phenylacetonitrile gives the same product that is obtained from phenylacetonitrile using sodium methylate as the condensing agent.

The sodium salt obtained from 2.2 g. of sodium was cooled to the temperature of ice water in a three-necked flask fitted with a stirring device. To this was added 25 cc. of absolute methyl alcohol and then 20 g. of solid benzalacetophenone. The contents of the flask were stirred constantly for three hours, keeping the temperature at 0°. After standing for thirty-six hours there had formed a dense crust of white crystals on the walls of the flask. This was removed, powdered in a mortar and washed with dilute hydrochloric acid to remove sodium compounds, and then with alcohol. There was obtained 24 g. or 93.7% of the theoretical yield of 1,5-dibenzoyl-2,3,4-triphenyl-3-cyanopentane. After recrystallization from chloroform and benzene there was obtained 9.9 g. of pure substance, m. p. 264.5–265.5° (corr.). The substance agrees in every respect with that obtained by Avery.[8]

Anal. Calcd. for $C_{38}H_{31}O_2N$: C, 85.6; H, 6.1; N, 2.6. Found: C, 85.6; H, 5.9; N, 2.5.

This compound has been prepared by Kohler and Allen,[9] who suggest the same structure but who found a melting point of 257°. Avery has shown that this melting point is probably low, due to impurities, and that the corrected melting point is 264.5–265.5°.

Summary

1. A method for the preparation of pure sodium phenylacetonitrile is described.

2. New evidence for the existence of tautomeric forms of the nitrile and for the imide structure of the salt is presented.

3. It has been shown that the sodium salt enters into condensation reactions of the type produced by sodium methylate and phenylacetonitrile.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE PREPARATION OF DIETHYL LEAD DICHLORIDE AND TRIETHYL LEAD CHLORIDE

BY HENRY GILMAN AND JACK D. ROBINSON

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Introduction

Convenient methods have been determined for the ready preparation of diethyl lead dichloride and of triethyl lead chloride in essentially quantitative yields by means of the following reactions carried out in toluene and ether, respectively

$$(C_2H_5)_4Pb + 2HCl \longrightarrow (C_2H_5)_2PbCl_2 \qquad \text{(I)}$$
$$(C_2H_5)_4Pb + HCl \longrightarrow (C_2H_5)_3PbCl \qquad \text{(II)}$$

The most generally used method for the synthesis of diethyl lead dihalides is that elaborated by Grüttner and Krause,[1] and involves the direct action of halogens on tetraethyl lead at low temperatures. In that method they recommend that the triethyl lead halide be first prepared at −60° and then converted to the dihalide as the solution warms

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[8] S. Avery, results soon to be published.

[9] Kohler and Allen, THIS JOURNAL, **46**, 1522 (1924).

[1] (a) Grüttner and Krause, *Ber.*, **49**, 1415 (1916). (b) Other methods, not of preparative value, for the synthesis of diethyl lead dichloride may be found in the following references: Grüttner, *ibid.*, **47**, 3257 (1914); Möller and Pfeiffer, *ibid.*, **49**, 2441 (1916); Goddard and Goddard, *J. Chem. Soc.*, **121**, 256, 482 (1922).