Solvents are not necessary but in certain cases they increase the yield. At present, an investigation regarding solvent action and the preparation of a series of new compounds of various phenolic ethers is being studied in this Laboratory.

Summary

1. The rearrangement of a series of alkyl phenyl ethers has been accomplished by the use of boron fluoride.
2. The boron fluoride can be recovered quantitatively.
3. The time required for the rearrangement of alkyl phenyl ethers has been materially shortened by this process.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE BEHAVIOR OF PHENYLACETONITRILE AND ALPHA-PHENYLBUTYRONITRILE WITH SODIUM ETHYLATE[1]

BY MARY M. RISING AND KEITH T. SWARTZ

RECEIVED DECEMBER 31, 1931 PUBLISHED MAY 7, 1932

The isolation of the pure alkali salts of phenylacetonitrile and α-phenylbutyronitrile by Rising in collaboration with Zee,[2a] Muskat and Lowe[2b] and Braun,[2c] and of the former nitrile by Upson,[3] involved the treatment of the nitriles with the alkali metals or amides. As observed by E. von Meyer[4] and his co-workers, and by Upson, and shown quantitatively for phenylacetonitrile by Braun, the reaction of the nitriles with sodium takes the course

$$2C_6H_5CH_2CN + 2\ Na \longrightarrow 2[C_6H_5CHCN]Na + 2H \qquad (1)$$
$$[C_6H_5CHCN]Na + 2H \longrightarrow C_6H_5CH_3 + NaNC \qquad (2)$$

The use of sodamide instead of sodium incurs no reduction of the salts.

It was suggested earlier[2a] that sodium ethylate might prove to be a useful reagent for obtaining the salts of these and other nitriles. The present paper describes the behavior of phenylacetonitrile and α-phenylbutyronitrile with solid sodium ethylate in dry boiling ether in an atmosphere of nitrogen. The ethylate has been used successfully in a great number of condensation reactions of nitriles[5] and the intermediate formation of sodium salts of the nitriles used is ordinarily assumed. We planned to

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[1] The work here described forms part of the dissertation of K. T. Swartz, presented in partial fulfilment of requirements for the doctorate degree at the University of Chicago.

[2] (a) Rising and Zee, THIS JOURNAL, **49**, 541 (1927); **50**, 1699 (1928); (b) Rising, Muskat and Lowe, *ibid.*, **51**, 262 (1929); (c) Rising and Braun, *ibid.*, **52**, 1069 (1930).

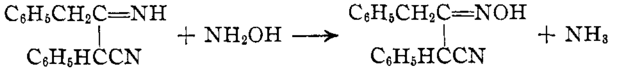
[3] Upson, Maxwell and Parmelee, *ibid.*, **52**, 1971 (1930).

[4] Wache, *J. prakt. Chem.*, **39**, 245 (1889); von Meyer, *ibid.*, **52**, 114 (1895), etc.

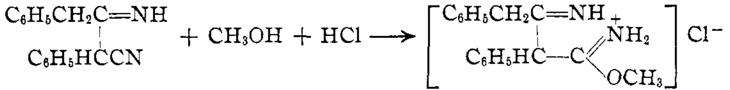
[5] Higson and Thorpe, *J. Chem. Soc.*, **89**, 1455 (1906); Avery and Upson, THIS JOURNAL, **30**, 600 (1908); Daughters, *ibid.*. **39**, 1927 (1917), and others.

isolate the intermediate products in the case of the nitriles studied, using the extremely delicate technique developed by Braun for handling the very unstable salts.

Under the conditions used by us phenylacetonitrile reacts with sodium ethylate to form a considerable quantity of sodium phenylacetonitrile. The major part of the salt formed apparently condenses with phenylacetonitrile to form a dimer of the nitrile, since the main product of the reaction is α,γ-phenyl-α-iminopropionitrile (dimolecular phenylacetonitrile), $C_6H_5CH_2C({=}NH)CH(C_6H_5)CN$, formed in about 25% yield. Sodium phenylacetonitrile was not isolated from the reaction mixture, in which it is soluble, but its presence there, and the quantity formed, were shown by treatment of this mixture with benzyl bromide, and the resulting formation of α,β-diphenylpropionitrile, $C_6H_5CH(CH_2C_6H_5)CN$, in 11% yield. The identity of the dinitrile was established by the analytical data for the compound and by the results of molecular weight determination. Its structure was proved by its conversion into α,γ-diphenyl-β-oximinopropionitrile, $C_6H_5CH_2C({=}NOH)CH(C_6H_5)CN$, and by a study of the products of hydrolysis of the dimer. The equations are

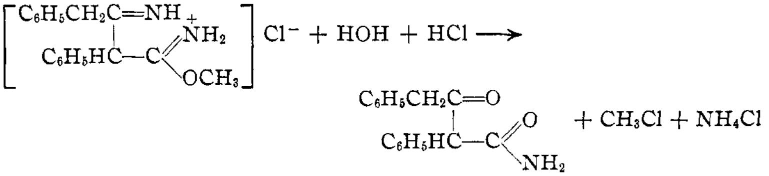


$$\begin{array}{c}C_6H_5CH_2C{=}NH\\ |\\ C_6H_5HCCN\end{array} + NH_2OH \longrightarrow \begin{array}{c}C_6H_5CH_2C{=}NOH\\ |\\ C_6H_5HCCN\end{array} + NH_3 \qquad (3)$$

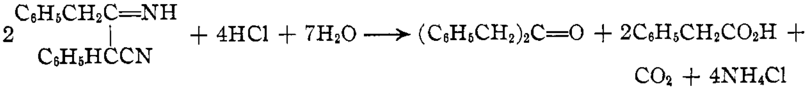


$$\begin{array}{c}C_6H_5CH_2C{=}NH\\ |\\ C_6H_5HCCN\end{array} + CH_3OH + HCl \longrightarrow \left[\begin{array}{l}C_6H_5CH_2C{=}NH^{+}\\ \quad\;\; | \\ C_6H_5HC{-}C\left\langle\begin{array}{l}NH_2\\ OCH_3\end{array}\right.\end{array}\right]Cl^{-} \qquad (4)$$

(not isolated)



$$\left[\begin{array}{l}C_6H_5CH_2C{=}NH^{+}\\ \quad\;\; | \\ C_6H_5HC{-}C\left\langle\begin{array}{l}NH_2\\ OCH_3\end{array}\right.\end{array}\right]Cl^{-} + HOH + HCl \longrightarrow \begin{array}{l}C_6H_5CH_2C{=}O\\ \quad\;\; | \\ C_6H_5HC{-}C\left\langle\begin{array}{l}O\\ NH_2\end{array}\right.\end{array} + CH_3Cl + NH_4Cl \qquad (5)$$



$$2\begin{array}{c}C_6H_5CH_2C{=}NH\\ |\\ C_6H_5HCCN\end{array} + 4HCl + 7H_2O \longrightarrow (C_6H_5CH_2)_2C{=}O + 2C_6H_5CH_2CO_2H + CO_2 + 4NH_4Cl \qquad (6)$$

It is to be concluded that the mononitrile condenses with itself in the presence of sodium ethylate to form the dimer with intermediate formation of the sodium salt of the mononitrile. The product of this aldol-like condensation is the sodium salt of the dimer, which is hydrolyzed to the dinitrile. The dinitrile obtained, of molecular weight 228–235, was a viscous yellow oil of b. p. 222–223° (uncorr.) at 2.75 mm. pressure.

Dimolecular phenylacetonitrile was first prepared by von Meyer,[4] repeating the work of Wache,[4] who studied the behavior of phenylacetonitrile with sodium in ether but failed to isolate the dinitrile. Von Meyer obtained a viscous oil from which he prepared an oxime of melting point 107°, identical with that obtained from cyanodibenzyl ketone, and he concluded that the oil was α,γ-phenyl-β-iminopropionitrile. Atkinson and Thorpe[6] prepared the dimolecular nitrile by heating phenylacetonitrile with sodium in alcohol for half an hour. Rondou[7] obtained the dinitrile by a Grignard reaction.

α-Phenylbutyronitrile, $C_6H_5CH(C_2H_5)CN$, was not found by us to condense with itself under the influence of sodium ethylate. After treatment of this nitrile with the ethylate under the conditions used in the case of phenylacetonitrile, 83% of the mononitrile used was recovered. The material obtained in a reaction of the nitrile with sodium ethylate was treated with methyl alcohol and hydrogen chloride. The products of this reaction were methyl α-phenylbutyrate and a substance of melting point 83° (uncorr.), thought to be α-phenylbutyramide. The amide, hitherto unprepared, was synthesized from α-phenylbutyryl chloride, also previously unknown, and ammonia, and showed a melting point of 83° (uncorr.). The melting point of a mixture of the amides obtained by the two methods was 83°. α-Phenylbutyryl chloride of boiling point 122–125° at 20 mm. was obtained from α-phenylbutyric acid and thionyl chloride.

The investigation of the tautomerism of nitriles is being continued in this Laboratory. An exhaustive study of the conductivities of a series of nitriles is under way, and the results of this work should form a logical basis for selection of nitriles best suited to the study of separation of tautomers. Salts of the nitriles with heavy metals are being studied.

Experimental

1. Reaction of Phenylacetonitrile with Sodium Ethylate in Ether.—Sodium ethylate was prepared from sodium (4 g.) and absolute alcohol (85 cc.) containing 25 cc. of absolute ether in an atmosphere of nitrogen. When the excess of liquids was removed by evaporation, solid white ethylate remained. Phenylacetonitrile (25.5 g., a 25% excess) was dropped into an ether suspension of sodium ethylate in an apparatus essentially like that used by Braun,[2c] the reaction being carried out in an atmosphere of nitrogen. All reagents and apparatus were dried thoroughly. The reaction mixture was refluxed for four hours, then 15 cc. of ligroin was added to precipitate unchanged sodium ethylate. The mixture was allowed to stand overnight; it was then filtered and three volumes of ligroin added to the filtrate to precipitate sodium phenylacetonitrile. The precipitate obtained consisted largely of sodium benzoate.[8] Sodium phenylaceto-

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[6] Atkinson and Thorpe, *J. Chem. Soc.*, **89**, 1906 (1906).

[7] Rondou, *Bull. soc. chim. Belg.*, **31**, 231 (1922).

[8] It is evident that in spite of the precautions used to exclude air from apparatus and reagents some oxygen was present. The formation of benzoic acid may signify the breakdown of sodium phenylacetonitrile as follows

$$[C_6H_5CH{=}C{=}N]Na \longrightarrow C_6H_5CH{=} + NaNC{=}$$

as previously postulated by Rising and Zee,[2a] who obtained benzyl alcohol after the treatment of the salt with aqueous acid. Upson and Thompson [This Journal, **44**, 186 (1922)] obtained benzoic acid from the impure salt following its exposure to air. A study of controlled oxidation of the salt will presently be made.

nitrile was not isolated from the reaction mixture, but its presence there was proved by treatment of a reaction mixture, obtained as just described, with benzyl bromide, whereupon α,β-diphenylpropionitrile was obtained in 11% yield. This nitrile melted at 57.5°[9] (uncorr.), boiled at 163–164° (uncorr.) at 3 mm., and yielded on hydrolysis α,β-diphenylpropionic acid of melting point 81–82° (uncorr.).[10]

2. **α,γ-Diphenyl-β-iminopropionitrile. Preparation.**—The reaction of phenylacetonitrile (46.1 g.) with sodium ethylate (prepared from 7.3 g. of sodium and 140 cc. of alcohol) was carried out as just described. The reaction solution was filtered after being refluxed, and was then treated with water; the ether layer was separated and dried over fused calcium chloride. The ether was then removed by evaporation and the oily residue was distilled, yielding about 16 g. of phenylacetonitrile and 10 g. (a 25% yield) of the dimolecular nitrile, of boiling point 222–223° (uncorr.) at 2.75 mm.

Anal. Calcd. for $C_{16}H_{14}N_2$: C, 82.00; H, 6.03; N, 11.97; mol. wt., 234. Found: C, 81.92, 82.11; H, 6.14, 6.28; N, 11.95, 12.06; mol. wt., 231 (av., benzene as solvent).

Proof of Structure. (a) Oxime Formation.—Treatment of the dinitrile in alcohol with hydroxylamine hydrochloride and barium carbonate (Equation 3) produced an oxime of melting point 106–107°, α,γ-diphenyl-β-oximinopropionitrile.[4,6]

(b) **Hydrolysis.**—(a′) Treatment of the dinitrile with concentrated hydrochloric acid[11] in a bomb tube at 150° for eight hours (Equation 6) produced carbon dioxide, phenylacetic acid[12] of melting point 76° (uncorr.), and dibenzyl ketone[13] of melting point 34–35° (uncorr.). The identity of the ketone was established by its conversion into dibenzyl ketone phenylhydrazone[14] of melting point 125–126° (uncorr.). (b′) Treatment of the dinitrile (4 g.) with methyl alcohol (15 cc.) and hydrogen chloride gas at 0° to saturation (Equations 4 and 5) produced phenylacetophenylacetamide of melting point 163.5–164° (uncorr.) formed in 76% yield.[11] The amide was hydrolyzed by alkali to phenylacetic acid of melting point 75–76° (uncorr.).

3. **α-Phenylbutyryl Chloride.**—α-Phenylbutyric acid (14 g.) was refluxed with thionyl chloride (100 g.) for eight hours. The reaction mixture was fractionated and the fraction of distillate, 14 g. in quantity, of boiling point 122–125° (uncorr.) at 20 mm. was found to be pure butyryl chloride, produced in 89.9% yield.

Anal. Calcd. for $C_{10}H_{11}OCl$: Cl, 19.42. Found: Cl, 19.37, 19.56.

4. **α-Phenylbutyramide.**—Dry ammonia was passed into an ether solution containing 5 g. of α-phenylbutyryl chloride. A vigorous reaction followed and precipitation of the amide and of ammonium chloride occurred. The precipitate was brought on a filter and washed with water to remove the salt. The amide was recrystallized from alcohol and melted at 83° (uncorr.). The yield was 63% of the theoretical. The amide was also obtained, together with methyl α-phenylbutyrate, by treatment of the crude reaction product, obtained by treatment of α-phenylbutyronitrile with sodium ethylate as previously described for phenylacetonitrile, and consisting largely of unchanged α-phenylbutyronitrile, with methyl alcohol and hydrogen chloride at 0°. The melting point of a mixture of the amide obtained by the two methods was 83° (uncorr.).

Anal. Calcd. for $C_{10}H_{13}ON$: C, 73.57; H, 8.03; N, 8.59. Found: C, 73.78, 73.63; H, 8.23, 8.23; N, 8.67, 8.80.

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[9] Meyer, *Ber.*, **21**, 1308 (1888).

[10] Miller and Röhde, *ibid.*, **25**, 2018 (1892).

[11] Walther and Schickler, *J. prakt. Chem.*, **55**, 350 (1897).

[12] Möller and Strecker, *Ann.*, **113**, 64 (1860).

[13] Stobbe, Russwurm and Schulz, *ibid.*, **308**, 175 (1899).

[14] Francis, *J. Chem. Soc.*, **75**, 868 (1899).

Summary

1. Under the conditions used by us sodium ethylate is not a useful reagent for obtaining the sodium salt of phenylacetonitrile.

2. A considerable quantity of sodium phenylacetonitrile is undoubtedly formed in the reaction of the nitrile with sodium ethylate but much of the salt condenses with the mononitrile to form a dinitrile.

3. α-Phenylbutyronitrile was not found to condense with itself under the influence of sodium ethylate in ether.

4. The syntheses of the chloride and amide of α-phenylbutyric acid are reported.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

CARBON TETRABROMIDE AS A BROMINATING AGENT[1]

BY W. H. HUNTER AND D. E. EDGAR

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During the study of certain reactions of carbon tetrabromide and aniline in xylene solution, it was observed that the xylene was brominated. Accordingly, an investigation was started with the point of view of determining the possible use of carbon tetrabromide as a brominating agent. In the case of the majority of compounds studied, bromination with this reagent took place, and when this occurred bromoform was always a by-product. Most of the bromo compounds prepared in this work can be made more easily by other methods, so that, as a rule, the use of carbon tetrabromide does not have any advantages over the commoner methods, but our experiments indicate that there are certain regularities with brominations using carbon tetrabromide that may be very useful, and the most important of these is the preferential side chain bromination of alkylbenzenes.

Experimental Part

Preparation of Carbon Tetrabromide.—The method of Wallach[2] served as a basis for our modified preparation of carbon tetrabromide from acetone and sodium hypobromite. The preparation as described is suitable for the production of large quantities of carbon tetrabromide in good yield. Since bromoform is a by-product in all cases of brominations described here, use was also made of a method similar to Habermann's,[3] involving bromoform and aqueous sodium hypobromite. Although Habermann stated that direct light was necessary, it was found that as good a yield of carbon tetrabromide could be obtained in the complete absence of light.

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[1] The work described in this paper constituted part of a thesis submitted to the graduate faculty of the University of Minnesota by Donald E. Edgar in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1927. This paper was prepared by the junior author after the death of Dr. Hunter.—[L. I. SMITH.]

[2] Wallach, *Ann.*, **275**, 149 (1893).

[3] Habermann, *ibid.*, **167**, 174 (1873).