in normal hydrochloric acid. This observation makes it seem unlikely that the addition of hydroxyl ion is the first step in the hydrolysis by water, since the rate of such an addition would presumably be decreased by an increase in hydrogen ion concentration.

The loss of a molecule of alcohol from the borate–water adduct can proceed by two possible mechanisms, (I) and (II). In mechanism (II), the carbon–oxygen bond is depicted as breaking, while in formulation (I) the bond remains intact. Whitmore[5] has summarized the literature in which it is shown that in any reaction in which the bond between the neopentyl radical and the rest of the molecule is broken, the neopentyl radical undergoes rearrangement. Whitmore and Rothrock[6] used the melting point of recovered neopentyl alcohol as a criterion of rearrangement.

In order to choose between the two possible mechanisms of hydrolysis, neopentyl borate was prepared and a sample submitted to hydrolysis. Neopentyl alcohol was recovered unchanged, thus demonstrating that the hydrolysis of trineopentyl borate proceeds by mechanism (I). This conclusion is undoubtedly valid for the hydrolysis of other alkyl borates also. By contrast, the esters of another inorganic acid, sulfuric acid, are known[7] to hydrolyze by mechanism (II).

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Summary

1. Twenty-one alcohols were allowed to react with boric acid according to the general method of Bannister. Eighteen borates were secured, sixteen of which had never before been obtained by this method. Ten of these borates are new. Three are crystalline.

2. Physical constants of the new borates and missing constants and analyses of the previously known borates have been determined.

3. The mechanism of hydrolysis of alkyl borates has been studied.

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[5] Whitmore, THIS JOURNAL, **54**, 3274 (1930).

[6] Whitmore and Rothrock, *ibid.*, **52**, 3431 (1930).

[7] Ferns and Lapworth, *J. Chem. Soc.*, **101**, 273 (1912).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY]

The Alkylation and Arylation of Aliphatic Nitriles in Liquid Ammonia

BY F. W. BERGSTROM AND ROBERT AGOSTINHO

Cornell[1] working in these Laboratories found that nitriles react with the alkali amides in liquid ammonia to give crystallizable compounds which were assumed to be formed in accordance with the equation

$$R{\cdot}CN + MNH_2 = RC({=}NH)NHM \qquad (1)$$

(M is an alkali metal)

Hydrolysis of the amidine salt, $RC({=}NH)NHM$, to the corresponding amidine was realized only where R was a phenyl group. Kirssanov and Poliakova[2] observed that sodium amide reacts vigorously with acetonitrile, but were unable to isolate any acetamidine; they are consequently of the opinion that Cornell's preparations are double compounds of the nitrile and the alkali metal amide. Secondary nitriles react with lithium diethylamide to form salts which are readily alkylated.[3] Primary nitriles such as acetonitrile may be alkylated by treating them with an alkyl halide and a fine suspension of sodium amide in benzene or in paraffin oil.[3]

Aliphatic nitriles may also be alkylated by the combined action on them of metallic sodium or sodium amide and an alkyl halide in a solvent.[4] Sodium ethylate or potassium ethylate is a good condensing agent for Claisen type condensations involving aliphatic nitriles; an alkali metal salt of the nitrile is a possible intermediate.[5]

There is accordingly ample evidence for believing that the alkali amides in liquid ammonia will react with nitriles that contain alpha hydrogen atoms to form salts of the type, $RCHNaCN$ or $(RCHCN)^- Na^+$. If this is the case, Cornell's preparations, in so far as the analyses are in agreement with the amidine salt formula, will have the structure, $RCHNaCN{\cdot}NH_3$.

In the present work, acetonitrile was found to react readily with a solution and suspension of sodium amide in liquid ammonia to form a soluble salt, which may be alkylated in accordance with the equation

$$NaCH_2CN + RX = NaX + RCH_2CN \qquad (2)$$

RX is an alkyl halide or alkyl *p*-toluenesulfonate; solvation of the sodium acetonitrile has been disregarded.

Secondary and tertiary nitriles are obtained by reactions which resemble the following

$$\begin{aligned} RCH_2CN + NaCH_2CN &\rightleftarrows RCHNaCN + CH_3CN \qquad (3)\\ RCHNaCN + RX &= R_2CHCN + NaX \end{aligned}$$

The direct introduction of phenyl groups ($R = C_6H_5$) in the manner of equations (2) and (3) may

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[1] E. F. Cornell, THIS JOURNAL, **50**, 3311–3318 (1928).

[2] Kirssanov and Poliakova, *Bull. soc. chim.*, (5) **3**, 1601–1602 (1936).

[3] Ziegler and Ohlinger, *Ann.*, **495**, 84–112 (1932); Ziegler, German Patents 570,594, 581,728, 583,561, *C. A.*, **27**, 4251 (1933); **28**, 1057 (1934); see *Chem. Rev.*, **20**, 451–454 (1937), for references.

[4] Holtzwart, *J. prakt. Chem.*, (2) **39**, 233 (1889); Ramart, *Compt. rend.*, **182**, 1226 (1926).

[5] Wislicenus and Silberstein, *Ber.*, **43**, 1825 ff. (1910); Dorsch and McElvain, THIS JOURNAL, **54**, 2960–2964 (1932); Borsche and Manteuffel, *Ann.*, **512**, 97–111 (1934); *cf.* Bergstrom and Fernelius, *Chem. Rev.*, **20**, 451 ff. (1937).

be accomplished by adding a liquid ammonia solution of potassium amide to a solution of chlorobenzene and potassium acetonitrile in the same solvent; phenylacetonitrile and diphenylacetonitrile are formed in approximately equal amounts. Similar catalytic phenylations have already been described.[6]

Benzoylacetonitrile, $C_6H_5COCH_2CN$, is obtained in fair yield by adding ethyl benzoate to a solution of sodium acetonitrile in liquid ammonia; the addition compound, $C_6H_5C(ONa)(OC_2H_5)CH_2CN$, appears to be formed first, since the corresponding carbinol (Na replaced by H) may be isolated in an impure condition and converted to benzoylacetonitrile by desiccation or by heating.

Experimental

The intramolecular alkylation of γ-chloropropionitrile and the alkylation of phenylacetonitrile in liquid ammonia-ether or in liquid ammonia, respectively, have already been described.[7]

A typical reaction, the butylation of acetonitrile, is carried out in the following manner.

Five hundred ml. of liquid ammonia was run into a three-necked one-liter flask provided with a mercury sealed stirrer, a dropping funnel and a short air condenser, whose purpose was to diminish loss of solvent by foaming or by sudden boiling within the flask. Ferric nitrate (0.2–0.3 g.) was dissolved in the ammonia and 11.5 g. (0.50 atom) of sodium introduced in pieces of 1–2 g. each. When the sodium amide had formed (a gray precipitate replaces the blue solution), 26.6 ml. (0.50 mole) of dry acetonitrile was slowly run in from the dropping funnel with stirring. In a few minutes this was followed by 53.6 ml. (0.50 mole) of *n*-butyl bromide, at such a rate that the reaction did not get out of control and cause the ammonia to boil out of the flask. When all of the solvent had evaporated (about three hours) water was cautiously added to dissolve solid material; the resulting mixture of water and oil was extracted several times with small portions of ether, the latter dried over anhydrous calcium sulfate and fractionated through a short wire spiral column, after removal of the ether by distillation. *n*-Capronitrile (27.1 g., 56%) was collected in the range 159–166° (760 mm.) and di-*n*-butylacetonitrile (10.2 g., 27% calculated on the basis of the butyl bromide) in the range 110–120° (25 mm.). No attempt was made to isolate tributylacetonitrile from the small high boiling residue.

n-Capronitrile was converted to *n*-caproamide by heating an alcoholic solution with 3% alcoholic hydrogen peroxide containing a few drops of sodium hydroxide (three hours at 70°). The caproamide was purified by several crystallizations from water and by sublimation; m. p. 100–101° (lit. 101°). Both the *n*-capronitrile and the dibutylacetonitrile were analyzed and found to have the correct composition.

Butylation of acetonitrile with *n*-butyl *p*-toluenesulfonate by the procedure described gave a 63% yield of *n*-capronitrile and a 20% yield of dibutylacetonitrile, of slightly higher purity than above.

Ethylation of Acetonitrile.—With half molar quantities, as in the above procedure, there was obtained 20.1 g. (58%) of *n*-butyronitrile boiling at 110–120° (760 mm.) and 4.9 g. (20%) of diethylacetonitrile boiling in the range 120–150° (lit. 144–146°). A portion of the first fraction was converted to *n*-butyramide m. p. 113.5–114.5° (lit. 116°), by heating with slightly alkaline hydrogen peroxide. An ethylation of sodium acetonitrile with ethyl *p*-toluenesulfonate gave a 61.5% yield of *n*-butyronitrile.

Benzylation of Acetonitrile.—The relative proportion of reaction products depends upon the rate of adding the benzyl chloride to the liquid ammonia solution of the sodium acetonitrile, and upon the efficiency of the stirring.

Benzyl chloride (0.51 mole) was added during a period of a few minutes to a solution of sodium acetonitrile prepared from one-half mole of sodium amide and one-half mole of acetonitrile. Water was added to the solid residue remaining after evaporation of the ammonia, the insoluble matter filtered, washed three times with small quantities of cold alcohol, and then crystallized from alcohol; m. p. 89.7–90.4°, uncor. (dibenzylacetonitrile). A small residue filtered from the hot alcoholic solution of the above melted at 218–220° uncor. (tribenzylacetonitrile), when crystallized from pyridine. The aqueous alcoholic filtrate of the low melting precipitate contained an oil which was extracted with benzene; the latter was distilled, first to remove solvent, and then in a vacuum to obtain benzylacetonitrile (hydrocinnamonitrile), b. p. 105–108° (about 2 mm.). The undistilled residue was crystallized from alcohol to give more dibenzylacetonitrile.

The yield of liquid benzylacetonitrile was 10 g. or 15.3%, based on the benzyl chloride; the yield of dibenzylacetonitrile was 27.6 g., or 49%, and of tribenzylacetonitrile, 1.2 g., or 2.3%. In a similar run, the weight of benzylacetonitrile was 24.7 g. (38%), and of dibenzylacetonitrile, m. p. 80–83°, 8.3 g. or 16%, probably because of differences in the rate of stirring and of addition of the benzyl chloride.

Anal. (m. p. 88–89°). Calcd. for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.68; H, 7.13; N, 6.33.

Anal. (m. p. 219.6–220.3° uncor.) Calcd. for $C_{23}H_{21}N$: C, 88.70; H, 6.80; N, 4.50. Found: (dried one hour at 105°) C, 88.21; H, 7.00; N, 4.62.

The monobenzylacetonitrile was identified by conversion to hydrocinnamic acid, m. p. 47.2–48.3° (lit. 47°, 48.5°; by long continued heating with alcoholic potassium hydroxide at 100°, addition of excess dilute sulfuric acid and crystallization of the ppt. from ligroin). The dibenzylacetonitrile was partly converted by one hour of heating with 75% sulfuric acid to dibenzylacetamide, m. p. 127–128° (lit. 128–129°).

Ziegler and Ohlinger (ref. 3, p. 110–112) have previously ethylated, butylated and benzylated acetonitrile in solvents other than liquid ammonia.

Condensation of Ethyl Benzoate with Acetonitrile.—One-half mole of ethyl benzoate (75 g.) was added slowly to a liquid ammonia solution of one-half mole of sodium acetonitrile, in accordance with the method described for the butylation of acetonitrile. Ice water (200 ml.) was added after evaporation of the ammonia and the solution filtered to remove iron oxide. Carbon dioxide gas (from Dry Ice) was passed through the solution with cooling and the resulting precipitate filtered; the filtrate was again treated with carbon dioxide to obtain an additional small quantity of solid; the combined yield of material, dried on a porous plate, was 44 g., melting at about 95–114°. Crystallization from ligroin (b. p. 100–140°) gave 25 g. (34%) of benzoylacetonitrile, m. p. 79.5–80.5° (Dorsch and McElvain, ref. 5, report 80–81°). Crystallization of the crude product of another experiment (43 g., m. p. 90–102°) from alcohol gave a white solid melting mostly at 80–102°, but at 80–81° when dried *in vacuo* over concd. sulfuric acid. The m. p. was unchanged after crystallization from water or from 95% ethanol, suggesting that the initial crude product is the carbinol, $C_6H_5C(OH)(OC_2H_5)CH_2CN$, and not $C_6H_5COCH_2CN \cdot C_2H_5OH$.

The aqueous filtrate of the crude reaction product (m. p. 95–114°) when acidified with hydrochloric acid gave 26.5 g. of crude benzoic acid, m. p. 105–112°; the reaction responsible for its formation is unknown.

Catalytic Phenylation of Acetonitrile.—One-tenth of a mole of potassium acetonitrile was prepared in 250 ml. of liquid ammonia contained in a 500-ml. 3-necked flask by adding acetonitrile to an equivalent of potassium amide.

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(6) (a) Wright and Bergstrom, *J. Org. Chem.*, **1**, 179–188 (1936); (b) Seibert and Bergstrom, *ibid.*, in press.

(7) (a) Cloke, Anderson, Lachmann and Smith, THIS JOURNAL, **53**, 2791–2796 (1931); (b) Baldinger and Nieuwland, *ibid.*, **55**, 2851–2853 (1933).

Chlorobenzene (22.5 g., 0.20 mole) was introduced, and this was followed by a liquid ammonia solution of 0.20 mole of potassium amide, siphoned over from another flask[6b] with good stirring. In one-half hour, 10 g. of ammonium bromide was added to stop further reaction, and the ammonia allowed to evaporate. Water (150 ml.) was introduced, and the oily mixture acidified with hydrochloric acid and extracted with ether. The ethereal solution was washed with a little dilute sodium bicarbonate to remove acid, dried over anhydrous sodium sulfate, and distilled, to obtain ether, a small amount of chlorobenzene (at 760 mm.) and then phenylacetonitrile, b. p. 90–95° (7 mm.) (3.62 g., 31%) and diphenylacetonitrile, b. p. 175–183° (7 mm.) (2.7 g., 28%). After several crystallizations from ligroin and from methanol, the latter melted at 73.5–74.5°, and at the same temperature when mixed with diphenylacetonitrile prepared by the method of Anschütz and Römig.[8]

Anal. Calcd. for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.24. Found: C, 86.76; H, 5.89; N, 7.23.

Phenylation of Propionitrile.—In the same manner as above and with fifth molar quantities there was obtained 11.2 g. (43%) of an oil boiling at 105–112° (8 mm.); presumably this is α-phenylpropionitrile (hydratroponitrile), but it was not further identified. The boiling point given by Janssen[9] is 230–232° at about 760 mm.

Summary

1. Acetonitrile reacts with sodium amide in liquid ammonia to form a salt, $NaCH_2CN \cdot xNH_3$ or $(CH_2CN)^-Na^+ \cdot xNH_3$, which can be alkylated to mono, di and trisubstituted acetonitriles, by reaction with an alkyl halide or an alkyl *p*-toluenesulfonate. Under the experimental conditions, very little if any sodium acetamidine can be formed.

2. Potassium acetonitrile can be catalytically phenylated in liquid ammonia to give phenylacetonitrile and diphenylacetonitrile.

3. Ethyl benzoate reacts with sodium acetonitrile to form sodium benzoate and sodium benzoylacetonitrile.

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[8] Anschütz and Römig, *Ann.*, **233**, 349 (1886).

[9] Janssen, *ibid.*, **250**, 137 (1889).

[CONTRIBUTION FROM THE C. W. S. TECHNICAL COMMAND, EDGEWOOD ARSENAL]

Some Analogs of Benzyl Benzoate[1]

BY WALTER H. C. RUEGGEBERG,[2] ABRAM GINSBURG[3] AND RUSSELL K. FRANTZ[4]

A survey of the chemical literature revealed the fact, to the best of our findings, that nothing is known about benzyl benzoate derivatives possessing either chlorine or methyl groups in the aromatic nuclei. Recent developments in this Laboratory necessitated the synthesis of several of these esters.

Gomberg and Buchler,[5] as well as the present authors,[6] have investigated the reaction between benzyl chloride and aqueous sodium benzoate to form benzyl benzoate. Yields of 70–78% of the ester are readily obtainable when this reaction is conducted in an excess of sodium benzoate.

All of the new esters listed in Table I were synthesized after the method of Gomberg and Buchler by refluxing the appropriate benzyl chloride derivative with an aqueous solution of an excess of the suitably substituted sodium benzoate.

Experimental[7]

Materials.—The toluic acids, xylenes and *p*-chlorotoluene were obtained from the Eastman Kodak Company (white label), while the benzoic acid (reagent grade) was obtained from the Mallinckrodt Chemical Works.

The methylbenzenes were chlorinated to the corresponding benzyl chlorides according to the method of Kharasch and Brown.[8] Using 2 moles of the corresponding methylbenzenes, 1 mole of sulfuryl chloride, 0.005 mole of benzoyl peroxide and 0.7 mole of carbon tetrachloride, *p*-chlorotoluene gave an 81% yield of *p*-chlorobenzene, m. p. 26–27°, and of 95.9 purity, as shown by analysis for chlorine. In addition, 18.8 g. of *p*-xylene dichloride, m. p. 99.5–100°, was formed; $ClCH_2C_6H_4CH_2Cl$: Cl, calcd. 40.5; found 40.2. The *p*-, *m*- and *o*-xylenes gave yields of 79, 72 and 73%, with a purity of 92.4, 98.4 and 96.0% and a refractive index $n^{20}{}_D$ of 1.5321, 1.5340 and 1.5403, respectively. The chlorides were used in the ester reaction without further purification.

Using the procedure of v. Braun and Nelles[9] 2,5-dimethylbenzyl chloride was made in 69.9% yield. It boiled at 74–76° (2–3 mm.); $n^{20}{}_D$ 1.5398.

Anal. Calcd. for $C_9H_{11}Cl$: Cl, 22.92. Found: Cl, 22.89.

A fraction of benzyl chloride ($n^{20}{}_D$ 1.5388), made by chloromethylating benzene,[10] was used.

Anal. Calcd. for C_7H_7Cl: Cl, 28.01. Found: Cl, 28.01, 27.98.

The *p*-chlorobenzoic acid was prepared in 80.9% yield by the oxidation of *p*-chlorotoluene with alkaline potassium permanganate. It melted in a sealed capillary at 242°.

Anal. Calcd. for $C_7H_5O_2Cl$: Cl, 22.65. Found: Cl, 22.31.

Preparation of Esters.—One mole of sodium hydroxide in the form of a 16.7% aqueous solution by weight and one mole of the benzoic acid were placed in a 3-necked round-bottom flask equipped with a mercury-seal stirrer, a thermometer and a water-cooled reflux condenser. The reaction flask, immersed in an oil-bath, was brought with stirring to reflux temperature (105–110° bulk temperature) and an amount of the desired benzyl chloride, ranging from 0.25 to 0.5 mole per mole of acid, was added through

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[1] Published with the permission of the Chief, Chemical Warfare Service.

[2] Captain, C. W. S., Army of the United States.

[3] Technician, 3rd. grade, Army of the United States.

[4] Second Lieutenant, C. W. S., Army of the United States.

[5] Gomberg and Buchler, THIS JOURNAL, **42**, 2061 (1920).

[6] Rueggeberg, Ginsburg and Frantz, report on file at Edgewood Arsenal.

[7] Chlorine analyses were by the Parr bomb method.

[8] Kharasch and Brown, THIS JOURNAL, **61**, 2142 (1939).

[9] v. Braun and Nelles, *Ber.*, **67**, 1094 (1934).

[10] Lock, *ibid.*, **74**, 1568 (1941).