Anal. Calcd. for $C_{10}H_9O_2NS$: N, 6.76. Found: N, 6.77.

A small amount (1.0 g.) of solid melting about 175–250° was insoluble in the hot petroleum ether. This was boiled with about 100 ml. of toluene; the hot mixture was filtered, and the filtrate was cooled in the refrigerator to produce 0.09 g. of crystals of 2,2′-bibenzothiazolyl (II), which were removed and washed with toluene and benzene. The tan platelets melted at about 310°. A melting point of "about 300°" was reported by Hofmann.[5] The analytical sample, white platelets, was obtained by recrystallizing from dioxane and washing with ether.

Anal. Calcd. for $C_{14}H_8N_2S_2$: N, 10.44. Found: N, 10.37.

B. With zinc chloride catalyst. A mixture of 12.5 g. (0.1 mole) of 2-aminobenzenethiol, 29.8 g. (0.2 mole) of diethyl oxalate, and 5 ml. of a 2M solution of fused zinc chloride in absolute ethanol was boiled under reflux for 4 hr., during which time the temperature decreased from 108 to 92°. After cooling, the solution was filtered to remove a small amount of inorganic solid, then worked up as in part A. The 14.4 g. (70%) of crude product, m.p. 69–69.5° (very cloudy melt), on recrystallization from 47 ml. of 63–99° petroleum ether, produced 7.1 g. of crystals melting at 69.8–70.5°. An additional crop of 0.5 g. was obtained from the mother liquor. The material insoluble in the hot petroleum ether weighed 2.7 g., and melted at *ca.* 150–210°. Even after extraction with hot petroleum ether (63–99°), 2.0 g., melting about 160–215°, remained.

2-Benzothiazolecarboxyhydrazide. A mixture of 20.7 g. of I and 6.0 g. of hydrazine hydrate (pract.) in 30 ml. of ethanol was refluxed for 15 min., and then cooled. The light yellow crystals were collected and washed with cold ethanol. They weighed 18.5 g. (95%) and melted without further purification at 175.0–175.6°. Y. Mizuno[4b] reported 2-benzothiazolecarboxyhydrazide to melt at 171°.

Anal. Calcd. for $C_8H_7ON_3S$: C, 49.69; H, 3.65; N, 21.73. Found: C, 49.62; H, 3.55; N, 21.83.

o,o′-Dihydroxyoxanilide (III) *from o-aminophenol. A. On the steam bath.* A mixture of 10.9 g. (0.1 mole) of o-aminophenol and 29.2 g. (0.2 mole) of diethyl oxalate was heated for 1 hr. on the steam bath. After cooling, the solid was removed and washed well with 95% ethanol. The yield was 9.4 g. (69%) of o,o′-dihydroxyoxanilide, melting at about 279–280° (dec.). Meyer and Seeliger[6] reported that this compound melted at 280–282°.

B. At reflux. The reaction was carried out as in part A, except that the mixture was heated at reflux (*ca.* 185°) for about 15 min., instead of on the steam bath. A 12.1 g. (89%) yield, m.p. 281–282° (dec.) was obtained.

C. With zinc chloride catalyst. The reaction was carried out as in part A, except that 5 ml. of a 2M solution of fused zinc chloride in absolute ethanol was added and the mixture heated under reflux for 1 hr. (The temperature fell from 109 to 91°), and worked up as before. The granular solid weighed 11.7 g. (86%) and melted at 283.5–284° (dec.).

When the reactants were heated under reflux in 55 ml. of 95% ethanol containing 0.5 g. of fused zinc chloride, only 3.9 g. (29%) of product was obtained on cooling.

D. With pyridine hydrochloride catalyst in pyridine. A stream of dry hydrogen chloride was passed into 500 ml. of dry pyridine to produce a weight increase of about 6 g. (0.16 mole). After the addition of 30.3 g. (0.207 mole) of diethyl oxalate, the solution was boiled under reflux while a solution of 10.9 g. (0.1 mole) of o-aminophenol in 200 ml. of pyridine was added dropwise, with stirring, over a period of 3 hr. After being heated for an additional 15 min., the solution was allowed to cool and divided into 2 equal parts. One part was poured slowly, with stirring, into 2 l. of water. The pink precipitate was removed and washed with water. A 4.4 g. (65%) yield of III was obtained. About 300 ml. of pyridine was distilled from the second half of the solution, which was then treated with 200 ml. of water, to yield 6.6 g. (97%) of III.

2,3-Quinoxalinediol (IV) *from o-phenylenediamine. A. Without catalyst.* A mixture of 10.8 g. (0.1 mole) of o-phenylenediamine (Eastman Kodak) and 43.9 g. (0.3 mole) of diethyl oxalate was heated for 1 hr. on the steam bath. After cooling, the solid was removed and washed with 95% ethanol. The yield was 14.4 g. (89%) of a gray-green solid, not melting below 300°, as reported by Meyer and Seeliger.[6] After recrystallization from methanol by Soxhlet extraction, the pure material decomposed at 372–373° (Fieser block).

Anal. Calcd. for $C_8H_6O_2N_2$: C, 59.25; H, 3.73. Found: C, 59.41; H, 3.67.

B. With zinc chloride catalyst. A mixture of 10.8 g. (0.1 mole) of o-phenylenediamine and 29.2 g. (0.2 mole) of diethyl oxalate was treated with 5 ml. of 2M solution of fused zinc chloride in absolute ethanol, and heated to boiling. Solid formed in the mixture very rapidly. After the mixture had refluxed for about 20 min., the temperature decreasing from about 100° to 83°, it was allowed to cool, filtered, and the solid washed with 95% ethanol. After combining with a small amount that separated from the filtrate, a yield of 14.1 g. (87%) of IV was obtained.

BLOOMINGTON, IND.

A Study of the Alkylation of 2-Phenylbutanenitrile with Butyl Chlorides[1]

GORDON L. GOERNER AND ANDREW A. HOLZSCHUH

2-Phenylbutanenitrile has been alkylated with the butyl chlorides, using both sodamide and sodium hydride as condensing agents. With sodium hydride, the yields of products were found to be from 3 to 15% less than with sodamide. As predicted on the basis of Newman's *six-member* concept, the highly hindered nitriles thus produced failed to hydrolyze. The "arylation" and alkylation of propionitrile has also been investigated briefly.

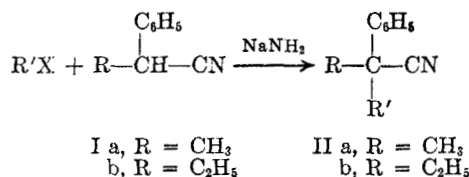Previous papers from this laboratory have reported the alkylation of hydratroponitrile Ia with butyl[2] and amyl halides[3] (see equation page 1347).

In a continuation of these studies 2-phenylbu-

(1) Based in part on the M.S. thesis of Andrew A. Holzschuh, Michigan State University, June 1955. Presented at the 130th meeting of the American Chemical Society, Atlantic City, N. J., September 16–21, 1956.

(2) G. L. Goerner and W. R. Workman, *J. Org. Chem.*, 19, 37 (1954).

(3) R. L. Jacobs and G. L. Goerner, *J. Org. Chem.*, 21, 837 (1956).

$$R'X + R-\underset{\underset{C_6H_5}{|}}{CH}-CN \xrightarrow{NaNH_2} R-\underset{\underset{R'}{|}}{\overset{\overset{C_6H_5}{|}}{C}}-CN$$

I a, R = CH₃   II a, R = CH₃
  b, R = C₂H₅   b, R = C₂H₅

tanenitrile Ib has been alkylated with the butyl chlorides. Although sodamide is the usual condensing agent for the alkylation of nitriles, sodium hydride has been used occasionally in this laboratory for the alkylation of certain substituted phenylacetonitriles with various benyzl chlorides. Since sodium hydride is readily available and easily handled, it appeared desirable to investigate its use as the condensing agent for the work at hand and to compare it with sodamide for this purpose.

Investigation showed that sodium hydride could be used in a manner similar to sodamide. The procedure adopted was essentially the high temperature sodamide method of Ziegler and Ohlinger,[4] with toluene serving as a suitable solvent. Since sodium hydride does not react directly with alkyl halides,[5] the mixture of butyl chloride, nitrile, and solvent could be charged directly into the reaction vessel and the sodium hydride could be added practically all at once at any temperature below the initial reflux temperature. The temperature of the reaction mixture gradually climbed as the reaction progressed and became constant as the reaction reached completion.

With sodamide as the condensing agent, the yields of alkylated nitrile with n-butyl, sec-butyl, and isobutyl chlorides varied from 87 to 93% and were in the order secondary>iso>normal. This order is essentially that observed when hydratroponitrile was alkylated with the butyl and amyl chlorides.[2,3] However with sodium hydride as the condensing agent, the yields were less, ranging from 78% with sec-butyl chloride to 85% with n-butyl chloride. In general the alkylations with sodium hydride proceeded more slowly than those with sodamide. With the sec-butyl and isobutyl chlorides, the alkylation took place at a more rapid rate than with n-butyl chloride. When the former were used, the reaction proceeded with a vigorous, rolling boil under our experimental conditions, the color of the solution soon became rust colored or red, and the sodium hydride was consumed at a reasonable rate. The reaction appeared to be complete in approximately two to three hours and a longer period of heating did not increase the yield appreciably. With n-butyl chloride on the other hand, the reaction appeared sluggish, the dark gray or black color of the sodium hydride persisted longer and at no time did the reaction proceed at the full rolling boil characteristic of the reactions involving the sec-butyl and isobutyl chlorides.

The physical properties of the 2-butyl-2-phenyl-butanenitriles are shown in Table I and the derivatives prepared from them in Table II. The only reaction which these nitriles were found to undergo was reduction to the amine with lithium aluminium hydride. No derivative of nitrile IV was made since it was obtained in such small quantities. The amines were converted into either phenylthioureas or α-naphthylureas. Numerous unsuccessful attempts were made to hydrolyze the nitriles to either amides or acids employing strenuous acidic and basic conditions.

The behavior of these nitriles (I, II, and III) toward hydrolysis is identical with that observed previously with similar highly hindered nitriles prepared in our laboratory. Nitriles with an α-phenyl substituent and with a minimum *effective six-number* of 8 did not hydrolyze under conditions such as those employed in the present work.[2,3] Consequently it was anticipated that the four nitriles prepared here would not undergo hydrolysis since they all have an *effective six-number* of 8 or more. Recently Tsai, Miwa, and Newman[6] have reported that using vigorous acidic conditions, they were able to hydrolyze aliphatic nitriles with a *six number* of 12 fairly readily and a nitrile with a *six-number* of 15 to a limited extent. They also found that amides such as mesitamide were dehydrated by ethylene glycol–alkali to the corresponding nitriles at high temperatures. The discrepancy between our inability to hydrolyze nitriles with an *effective six-number* of 8 and the ability of Newman and co-workers[6] to hydrolyze nitriles with a *six-number* of 12 and 15 arises largely in the use of terms since the effect of a ring is not known precisely. The term *effective six-number*[7] has been used by us[2,3] to denote the number of atoms which are the sixth atom removed from the multiple bonded atom (nitrogen in this case) not counting those carbon atoms which are included in an aromatic ring. On the other hand the term *six-number*[7] customarily refers to those atoms which occupy the six position when no rings are involved From Stuart models it appears that the cyano group in a nitrile such as II above is hindered to approximately the same extent as the cyano group in ethyldiisopropylacetonitrile (*six-number* 15) which was hydrolyzed to a small extent by Newman and co-workers.[6] Indeed it appears that the phenyl group has a shielding effect and hindrance approximately equal to an isopropyl group in the nitriles under consideration.

In 1945 Bergstrom and Agostinho[8] reported the preparation of hydratroponitrile (α-phenylpropionitrile) by the "catalytic phenylation" of propionitrile with chlorobenzene in the presence of

(4) K. Ziegler and H. Ohlinger, *Ann.*, **495**, 84 (1932).

(5) S. J. Cristol, J. W. Ragsdale, and J. S. Meek, *J. Am. Chem. Soc.*, **71**, 1863 (1949).

(6) L. Tsai, T. Miwa, and M. S. Newman, *J. Am. Chem.* **79**, 2530 (1957).

(7) M. S. Newman, *J. Am. Chem. Soc.*, **72**, 4783 (1950).

(8) F. W. Bergstrom and R. Agostinho, *J. Am. Chem. Soc.*, **67**, 2152 (1945).

TABLE I

PHYSICAL PROPERTIES OF 2-BUTYL-2-PHENYLBUTANENITRILES[a]

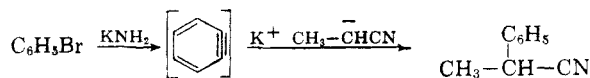| No.	Compound	B.P., °C. (5 Mm.)	n_D^{25}	d^{25}	$N, \%^b$	Effective Six-Number
I	2-Phenyl-2-ethylhexanenitrile	127–128	1.4970	0.9320	6.90	8
II	2-Phenyl-2-ethyl-3-methylpentanenitrile	127–128	1.5037	.9466	6.91	11
III	2-Phenyl-2-ethyl-4-methylpentanenitrile	120–121	1.4969	.9326	7.02	8
IV	2-Phenyl-2-ethyl-3,3-dimethylbutanenitrile	123–126[c]	1.5107	.9571	6.86	14

[a] Determined on redistilled samples. [b] Calculated for $C_{14}H_{19}N$: N, 6.96. [c] Oil crystallized spontaneously after standing overnight. Recrystallized from ligroin, then methanol, m.p. 57.2–58° (corr.).

TABLE II

PROPERTIES OF THE 1-AMINO-2-BUTYL-2-PHENYLBUTANES

$$CH_3—CH_2—\overset{\overset{\displaystyle C_6H_5}{|}}{C}R—CH_2—NH_2$$

R	B.P., °C. (5 Mm.)	D^{25}	n_D^{25}	$N,^a \%$	Phenylthioureas		
					M.P., °C.	$N,^b \%$	$S,^b \%$
n-Butyl	134.0	0.9283	1.5125	6.51	118.5–119	8.04	9.53
s-Butyl	129.5	0.9471	1.5116	6.62	176–177[c]	7.57[c]	
i-Butyl	120.5	0.9279	1.5130	7.06	140.5–141	8.06	9.30

[a] Calculated for $C_{14}H_{23}N$: N, 6.82. [b] Calculated for $C_{21}H_{28}N_2S$: N, 8.23; S, 9.42. [c] α-Naphthylurea. Calculated for $C_{26}H_{30}N_2O$: N, 7.48.

excessive amounts of potassium amide. It was hoped that a similar phenylation could be achieved with sodium hydride instead of potassium amide. However, when such a reaction was carried out using the alkylation procedure already described, only gums and extremely high boiling materials resulted. These materials were largely acid soluble and were presumed to be dimers or trimers of propionitrile. Dimers and trimers, both acid soluble, are known to form when aliphatic nitriles are treated with alkali metals.[9] The special arylation procedure of Bergstrom and Agostinho was next repeated. With potassium amide in liquid ammonia, the results were approximately the same as those reported. Sodamide gave a much smaller yield of hydratroponitrile under these same special conditions. Information coming to our attention since this work was completed makes it appear probable that the arylations described by Bergstrom and Agostinho proceed via the "benzyne" intermediate postulated by Roberts et al.[10] and others.[11] Consequently one would not anticipate that the reaction would proceed in the presence of sodium hydride since it is not a strong enough base to attack the aryl halide.[5] The arylation may be represented by the following equation

$$C_6H_5Br \xrightarrow{KNH_2} \left[\begin{array}{c}\bigcirc\!|\!|\!|\end{array}\right] \xrightarrow{K^+ \ CH_2-\bar{C}HCN} \overset{\overset{\displaystyle C_6H_5}{|}}{CH_3-CH-CN}$$

(9) V. Migrdichian, The Chemistry of Organic Cyanogen Compounds, Reinhold Publishing Corp., New York, 1947, p. 349.

(10) J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, J. Am. Chem. Soc., 78, 601 (1956).

(11) G. Wittig and R. Ludwig, Angew. chem., 68, 40 (1956); W. W. Leake and R. Levine, Chem. and Ind. (London), 37, 1160 (1955).

In the experimental procedure used by Bergstrom and Agostinho, the nitrile was first converted into is potassio derivate by potassium amide, to this was added an equivalent of chlorobenzene followed by a second equivalent of potassium amide. It is during the latter addition that the vigorous arylation occurs.

Since it was found impossible to arylate propionitrile in the presence of sodium hydride and since dimers and trimers were apparently formed from the propionitrile, it appeared desirable to try to alkylate an aliphatic nitrile in the presence of sodium hydride. From the reaction between propionitrile and n-butyl bromide there was recovered about a 23% yield of 2-methylhexanenitrile. This reaction also produced an acid soluble oil, presumed to be either a dimer or trimer, or a mixture of both, which could account for about half the starting nitrile. This reaction was not further investigated.

On the basis of this work, sodium hydride appears to be a satisfactory condensing agent for the alkylation of unsubstituted or substituted phenylacetonitriles. Although the yields from sodium hydride condensations are from 3 to 15% less than those from sodamide condensations (see Table I), the ease of handling and storage and the ready availability of sodium hydride may outweigh the greater yields obtainable with sodamide. Its use, of course, will make unnecessary the preparation of sodamide from liquid ammonia if commercial sodamide is not available. On the other hand, the desirability of using sodium hydride in the alkylation of aliphatic nitriles appears questionable since the latter undergo extensive polymization in its presence.

EXPERIMENTAL[12]

2-Phenylbutanenitrile. The nitrile, prepared by the phosphorus oxychloride dehydration of Eastman practical grade α-phenylbutyramide,[13] distilled at 110–111.5° (9 mm.), n_D^{25} 1.5060; reported[13] b.p. 122–124° (16 mm.), n_D^{25} 1.5070.

The *butyl chlorides* were of Eastman White Label grade and were redistilled before use.

Sodamide. Powdered material, purchased from Farchan Research Laboratories, was placed in small bottles under a nitrogen atmosphere and stored in a desiccator.

Sodium hydride and *lithium aluminum hydride*, obtained from Metallic Hydrides, Inc., were likewise rebottled and stored in a desiccator.

Alkylation of 2-phenylbutanenitrile. (a) *Sodamide method.* All alkylations were carried out using the high temperature procedure of Ziegler and Ohlinger[4] *exactly* as described previously.[2,3] The same molar ratios of reactants were used as before and the reaction mixtures were worked up similarly and distilled through nearly identical equipment. The aqueous layers were saved and titrated for chloride ion. In a typical run using 48.1 g. (0.332 mole) 2-phenylbutanenitrile, 35.6 g. (0.386 mole) sec-butyl chloride, and 15.9 g. (0.408 mole) sodamide, the following fractions were collected at 5-mm. pressure: *Fraction 1*, 0.8 g., b.p. 82–105°, n_D^{25} 1.5005; *Fraction 2*, 1.6 g., b.p. 105–127°, rising almost instantly to 127°, n_D^{25} 1.5039; *Fractions 3–7*, 55.2 g., b.p. 127–128°, n_D^{25} 1.5037 to 1.5039; *Fraction 8*, 5.4 g., b.p. 128–131°, n_D^{25} 1.5040; *residue* and column holdup, about 1 g. Fractions 2 through 8 weighed a total of 62.2 g., yield 93.3%. The chloride ion titrated as 0.332 mole, or 100% based on starting nitrile.

Alkylations carried out with the other butyl chlorides gave the following yields of alkylated product: n-butyl 87%; isobutyl, 90%; tert-butyl, 7.7%.

(b) *Sodium hydride method.* Alkylations using sodium hydride were carried out in the same general manner as those using sodamide. A typical reaction is as follows. Into a 500-ml. three-necked flask equipped with a stirrer, thermometer, reflux condenser, and wide-bore dropping funnel protected by a drying tube was placed a mixture of 48.1 g. (0.332 mole) 2-phenylbutanenitrile, 35.6 g. (0.386 mole) n-butyl chloride, and 50 ml. of dry toluene. The sodium hydride (approximately 10.0 g., 0.416 mole) was weighed by difference from a closed bottle by shaking directly into the dropping funnel where it was immediately covered with 50 ml. of dry toluene. The stirred mixture in the reaction flask was heated to 90° by means of a mantle and the suspension of sodium hydride in toluene was carefully added portionwise during approximately 10 min. (the solid was pushed through the bore of the stopcock with a glass rod or a wire when necessary). During 15 min. the temperature was raised to 104°. Some gas evolution or boiling now occurred. Over the next 6 hr., the temperature of the reaction mixture rose to 116° and became constant. The total time of heating was 9 hr. The color of the mixture progressed through yellow to a dirty mustard color.

Any excess sodium hydride was destroyed by the *cautious addition* (dropwise) of 15 ml. of ethyl alcohol to the cold, stirred reaction mixture, followed by 50 to 75 ml. of water. After the addition of a small amount of Celite, the mixture was filtered and the filter cake washed. The oil layer was separated and the water layer extracted with toluene and ether and saved for chloride analysis. The combined organic layers were dried over anhydrous calcium chloride, the solvent was stripped at the water aspirator, and the residue fractionated through a 2 × 20 cm. column packed with

³/₁₆ in. glass helices. The following fractions were collected at 5-mm. pressure: *Fraction 1*, 2.0 g., b.p. 92–123°, n_D^{25} 1.5005; *Fraction 2*, 2.0 g., b.p. rising instantly to 126°, n_D^{25} 1.4970; *Fractions 3–8*, 53.2 g., b.p. 126–128.5°, n_D^{25} 1.4969 to 1.4973; *Fraction 9*, 1.9 g., b.p. 126.5° dropping to 119°, n_D^{25} *residue* and column holdup, about 4 g. Fractions 2 through 9 weighed a total of 57.1 g., yield 85.6%. The chloride ion titrated as 0.297 mole, or 89.6% based on starting nitrile.

When alkylations were carried out with other butyl chlorides for the time specified, the following yields were obtained: n-butyl, 2 hr., 73%; sec-butyl, from 3 to 7.5 hr., 77 to 80%; isobutyl, from 2.5 to 7 hr., 80%.

Phenylation of propionitrile. The procedure of Bergstrom and Agostinho was followed in detail, using potassium amide, to give (a) 7.3 g. liquid, b.p. 116–140° (20 mm.), n_D^{25} 1.5124, or 27.7% if calculated as hydratroponitrile and (b) 13.9 g., b.p. from 140° (20 mm.) to 162° (3 mm.), n_D^{25} 1.5700, or 33.6% if calculated as diphenylpropionitrile. Bergstrom and Agostinho reported 43% of presumed hydratroponitrile, b.p. 105–112° (8 mm.). Hydratroponitrile has a b.p. 114–116° (19 mm.), 107–110° (11 mm.); n_D^{20} 1.5120, n_D^{25} 1.5090.[3] When sodamide was substituted for potassium amide a smaller yield of material boiling up to 117° (9 mm.) was obtained.

2-Methylhexanenitrile. To a mixture of 36.6 g. (0.67 mole) redistilled propionitrile and 100 g. (0.73 mole) n-butyl bromide in the apparatus described above there was added portionwise 16.0 g. (0.67 mole) sodium hydride in 100 ml. toluene. No noticeable reaction occurred until the mixture was heated to 112°. After heating for 2 to 3 hr., the gray color changed to white. Unreacted sodium hydride was destroyed by the dropwise addition of alcohol, followed by water (care!). The mixture was filtered (Celite) and the oil layer separated, acid washed, water washed and distilled. There was obtained 17.5 g. of 2-methylhexanenitrile (23.6%), b.p. 70–93° (mostly 78–80°) at 30 mm., n_D^{25} 1.4070, d^{25} 0.7985. A second fraction distilled at 100–126°, n_D^{25} 1.4255. (+)-2-Methylhexanenitrile has a reported b.p. 43–50° (9 mm.), d^{25} 0.797.[14]

A sample of the nitrile (1 g.) was hydrolyzed by heating with 5 ml. of 75% sulfuric acid on the steam bath for 20 min. The crystalline amide, m.p. 64–67°, was isolated after pouring the sulfuric acid into ice water. Recrystallization from benzene raised the m.p. to 68.5–69°. 2-Methylhexanamide is reported to melt at 70–72.5°[15] and (+)-2-methylhexanamide at 66°.[14]

Amines. The nitriles were reduced to the corresponding amines with lithium aluminum hydride by the procedure of Amundsen and Nelson[16] as described previously.[3] The amines were recovered in about 65% yield.

Attempted hydrolyses of the hindered nitriles were carried out as follows: (1) heating the nitriles with potassium hydroxide and a high boiling alcohol such as benzyl alcohol or a glycol at temperatures of 190° to 240° for as long as 16 hr.; (2) fusion with 60% potassium hydroxide; (3) heating with sulfuric acid (75 to 95%) or concentrated hydrochloric acid (aqueous under pressure or with dioxane solvent) up to 2 hr. at temperatures as high as 190°. Although a trace of ammonia was observed in some alkaline hydrolyses, only insoluble oily nitrile could be recovered. A water soluble product resulted from some hydrolyses with 90 to 95% sulfuric acid; this was presumed to be a ring-sulfonated product and was not further investigated.

EAST LANSING, MICH.

(12) Melting points and boiling points are uncorrected. All analyses were by Micro-Tech Laboratories, Skokie, Ill.

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(14) P. A. Levene and L. A. Mikeska, *J. Biol. Chem.*, **84**, 571 (1929).

(15) P. Rasetti, *Bull. soc. chim. France*, [3] **33**, 687 (1905).

(16) L. H. Amundsen and L. S. Nelson, *J. Am. Chem. Soc.*, **73**, 242 (1951).