

***n*-Octyl Disulfide.**—The same methods were used for this compound: boiling point 178–183° (5 mm.); yield, by the iodine reaction, 69%; by the peroxide reaction, 52%. It also is a new compound. *Anal.* Calcd. for $C_{18}H_{34}S_2$: S, 22.10. Found: S, 22.04.

Lauryl Disulfide.—This compound melts just a little above room temperature (34.5°)¹⁰ and special handling was necessary. The procedure was similar at the start, although a greater amount of time was necessary to form the Bunte salt. After the iodine was added, the liquid product, already tending to solidify, was crystallized from alcohol with a charcoal treatment; yield 35%; melting point 33–34°. In using the peroxide reaction, it was found that the lauryl Bunte salt was not soluble in cold aqueous alcohol. It was therefore filtered off and dissolved in aqueous 1,4-dioxane. The peroxide and acid were added. After the mixture had been allowed to stand in the cold for several days, the product appeared slowly as a solid. It was filtered and recrystallized from alcohol. This appears to be the better way to prepare the compound as the crude product was nearly pure, yield 70%.

***n*-Octadecyl Disulfide.**—Eight and one-half grams of octadecyl bromide (prepared after "Organic Syntheses," Vol. XV, p. 24) was dissolved in 25 cc. of alcohol and mixed

(10) Fore and Bost, *THIS JOURNAL*, **59**, 2557 (1937).

with a solution of 5 g. of sodium thiosulfate in 15 cc. of water. After refluxing together for eight to ten hours, iodine was added until the color remained. Then about 50 cc. of a sodium bisulfite solution was added to remove the excess iodine. After filtration, the white product was recrystallized repeatedly from glacial acetic acid and from alcohol, using charcoal in some instances. The melting point remained constant at 54–56°. The compound is reported¹⁰ to melt at 62°, while octadecyl alcohol melts at 59°. It appeared that a trace of the alcohol contaminated the product, and because of the great similarity between the two, could not be removed. This is borne out by the fact that the sulfur analysis is only a fraction of a per cent. low, yield about 49%. *Anal.* Calcd. for $C_{36}H_{76}S_2$: S, 11.24. Found: S, 10.80.

Summary

Present knowledge of the scope of the reactions of Bunte salts with iodine and with hydrogen peroxide as preparative methods has been extended to include the preparation of normal alkyl disulfides. Two of those prepared are new compounds.

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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Hydrogenation of β -Iminonitriles

BY HOMER ADKINS AND GERALD M. WHITMAN¹

Since imines have been hydrogenated under milder conditions than have nitriles,² it seemed probable that aminonitriles, as well as diamines, could be obtained by the hydrogenation of iminonitriles. Only β -iminonitriles are available so that the present study has been confined to this type of compound.³ Five iminonitriles of the type $RCH_2C=NHCHRCN$ were prepared by the Thorpe reaction from RCH_2CN where R was hydrogen, methyl, ethyl, *n*-propyl or phenyl.

All attempts, using Raney nickel or copper chromite as catalysts, to hydrogenate these compounds to β -aminonitriles were unsuccessful. Ether, ethanol, dioxane and methylcyclohexane were used for the reaction medium. The hydrogenations were attempted at temperatures from 75 to 245°. The amount of hydrogen allowed to react was varied from 0.1 to 1.0 mole per mole of iminonitrile. In all cases the iminonitrile was re-

covered unchanged from the reaction mixture, along with various amounts of diamine and cleavage products which were formed as the result of the reaction of three or more moles of hydrogen per mole of iminonitrile.

The complete hydrogenation of the five iminonitriles took place readily over Raney nickel. Where R was methyl, ethyl or propyl, the diamine $RCH_2CHNH_2CHRCH_2NH_2$ was isolated in yields of 60 to 70% after hydrogenation for two to three hours at 130–150°. Where R was H, the yield of diamine, $CH_3CHNH_2CH_2CH_2NH_2$, isolated was lower (41%). Where R was phenyl the yield of the diamine $C_6H_5CH_2CHNH_2CH(C_6H_5)CH_2NH_2$ was low (27%); because of the tendency for cleavage, the chief product (50% yield) was the monamine $C_6H_5CH_2CHNH_2CH(C_6H_5)CH_3$.⁴

The iminonitriles where R was H, CH_3 , C_2H_5 or C_3H_7 also gave primary amines, containing one less carbon than the iminonitrile, in yields of 7 to 15%. For example, $CH_3C=NHCH_2CN$ gave

(1) Du Pont Fellow 1939–1940.

(2) Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., 1937, p. 55.

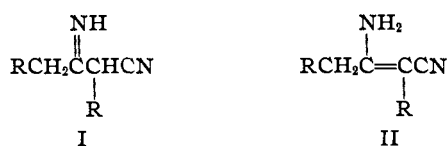
(3) Bruylants [*Bull. soc. chim. Belg.*, **33**, 307 (1923)] reported the synthesis of $C_6H_5C=NH(CH_2)_3CN$, the only compound of a type described in the literature in which the imino group is not β to the cyano group. We were unable to duplicate Bruylant's synthesis.

(4) For the purpose of comparison this amine was prepared by the hydrogenation over Raney nickel of $C_6H_5CH_2COCHC_6H_5CH_3$ in the presence of ammonia, according to the method of Schwogler and Adkins, *THIS JOURNAL*, **61**, 3499 (1939).

$\text{CH}_3\text{CHNH}_2\text{CH}_3$. A comparison of the amine produced by hydrogenation with an amine of known structure showed it to be of the type $\text{RCH}_2\text{CHNH}_2\text{CH}_2\text{R}$ in each case where R was CH_3 , C_2H_5 or C_3H_7 . That is to say, in the case of the aliphatic iminonitriles the cyano group was removed by hydrogenolysis, while where R was C_6H_5 only the nitrogen of the cyano group was lost by hydrogenolysis. However, in the latter case there was also a small amount of cleavage between carbon atoms for 2% of phenethylamine was isolated.

The question arose as to whether these cleavage products resulted from the hydrogenolysis of the diamines or from a precursor of them. The diamines, $\text{RCH}_2\text{CHNH}_2\text{CHRCH}_2\text{NH}_2$, where R is CH_3 , C_2H_5 or $n\text{C}_3\text{H}_7$, were shaken with hydrogen under 200 atm. over Raney nickel for three and one-half hours at 150° . Where R was C_2H_5 or C_3H_7 the recovery of unchanged diamine was 93–94% along with about 3% of higher boiling products. Where R was CH_3 there may have been a few per cent. of the diamine cleaved, while where R was H a similar amount of change took place at 135° ; but it seems doubtful that the rate of hydrogenolysis of any of these diamines is sufficient to account for the cleavage products resulting from the action of hydrogen on the iminonitriles.

The inactivity toward hydrogenation of the imino group makes it doubtful whether the structure of the compounds called "iminonitriles" is represented by formula I.



Auwers and Wunderling⁵ have presented evidence based upon the molar refraction and dispersions, that the enamine structure in II is valid. Observations by Anderson and Teresi⁶ upon the Raman spectrum of the iminonitrile, where R is n -propyl, suggests the same conclusion.

Intramolecular hydrogen bonding might offer an explanation of the inactivity of the groups, although the linear nature of the nitrile group makes chelation improbable. It seemed worthwhile to determine the apparent molecular weight in different solvents and concentrations. A part of the numerical data from these studies are pre-

sented in Fig. 1, the degree of association being expressed in terms of the polymerization number n , which is the apparent molecular weight divided by the formula weight.

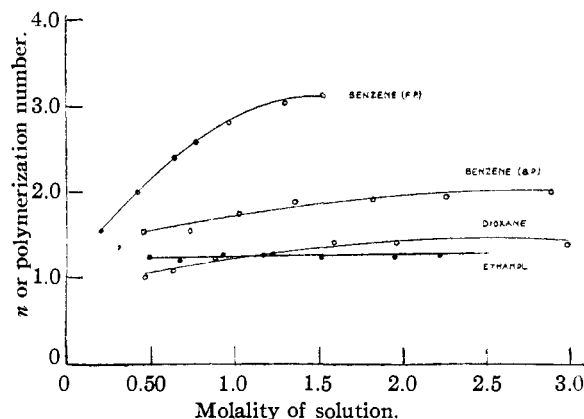


Fig. 1.—Association of 2- n -propyl-3-iminoanthonitrile.

The more significant results may be summarized as follows. The "polymerization number" for 2- n -propyl-3-iminoanthonitrile at the freezing point of benzene increased from about 1.5 to over 3 when the concentration of the iminonitrile was increased from 0.2 to 1.52 molal. At the boiling point of benzene the value of n reached a maximum of about two. In ethanol at its boiling point the value of n was about 1.2, and this value was independent of the concentration of the nitrile in the solvent. The values of the apparent molecular weight varied from 202 to 213 as compared with 212 for a complex of the nitrile and alcohol. These figures show clearly that with this nitrile a dimer or trimer exists in benzene, while in alcohol it is not polymerized but adds a molecule of the solvent.

The behavior of the nitrile in dioxane at its boiling point was similar to that in ethanol, although there was a small change in the value of "n" with change in concentration, and the maximum value of n was a little greater than in ethanol.

The 3-(phenylimino)-butyronitrile behaved in general like the open chain compound. That is, the compound was dimeric in boiling benzene while in alcohol it apparently combined with the solvent.

Neither n -butyl cyanide nor 3-piperidinocinnamonitrile, $\text{C}_6\text{H}_5\text{C}(\text{NC}_5\text{H}_{10})=\text{CHCN}$, showed association at the freezing point of benzene, so that it is clear that the association of the iminonitriles is dependent upon the hydrogen of the imino or amino group.

(5) Auwers and Wunderling, *Ber.*, **64**, 2758 (1931).

(6) Unpublished work in this Laboratory.

While these results are interesting in themselves, they do not throw much light upon the peculiarities in the results of the hydrogenation studies. It was hoped that 3-(phenylimino)-butyronitrile, which is associated in benzene, would show the same resistance to hydrogenation as the iminonitriles, while 3-piperidinocinnamouitrile, which is not associated in benzene, would reduce readily at a low temperature.

The hydrogenations of the butyronitrile took place readily, but the only product isolated was aniline. The yields were 73 to 84%. This indicates that the chief reaction is cleavage between the nitrogen and the carbon of the imino group. However, 8% of 1,3-diaminobutane was isolated. There was also isolated a compound $C_{12}H_{25}N_3$, in which only two of the three nitrogens had basic properties. The formula of this compound may be $C_4H_9NHCH(CH_3)CH_2CH_2NHCH(CH_3)CH_2CN$.

The hydrogenation of 3-piperidinocinnamouitrile was potentially interesting, not only because of its lack of dimerization in benzene, but because in it is fixed the enamine structure suggested by Auwers for the β -iminonitriles. However, the only reaction detected was the hydrogenolysis of the piperidino group.

Experimental

3-Iminobutyronitrile.—Powdered sodium (78 g.) in 800 ml. of dry benzene was placed in a three-necked flask provided with a reflux condenser, stirrer and dropping funnel. Acetonitrile (246 g.) was added slowly. The reaction may not begin immediately, but it proceeds with considerable violence when once under way, so that provision must be made for external cooling. Methane is evolved and if proper precautions are not taken large amounts of benzene may be carried up into the condenser. The acetonitrile was added slowly over a period of two and one-half hours at such a rate as to maintain refluxing of the reaction mixture. The mixture was refluxed for three hours after the addition of the nitrile. A mixture of sodium cyanide and the sodium derivative of 3-iminobutyronitrile crystallized out from the cold reaction mixture and was removed by filtration. The solid was suspended in a liter of ether, and water was added slowly until the solid disappeared. The ether layer was separated, dried over calcium chloride and the ether distilled. After a few hours the residue crystallized, giving 121 g. of crude product. After recrystallization from benzene 91 g., m. p. 63–71°, was obtained. Von Meyer⁷ has shown that the compound exists as a stable form, m. p. 50–54°, and a labile form, m. p. 79–84°. The semicarbazone of 3-ketobutyronitrile melted at 164–164.5°, resolidified and melted again at 216°.⁸

(7) Von Meyer, *J. prakt. Chem.*, [2] **52**, 84 (1895).

(8) (a) Von Meyer, *ibid.*, **78**, 499 (1908); (b) Bruylants, *Chem. Zentr.*, **94**, I, 85 (1923).

2-Methyl-3-iminovaleronitrile.⁹—This compound was prepared from ethyl cyanide (528 g.) in ether solution according to the general procedure given above. The ether and unreacted ethyl cyanide were distilled out of the reaction mixture and the residue allowed to stand, whereupon 84 g. of crystals separated. The residue was distilled and 137 g., b. p. 107–112° (2 mm.), obtained. Recrystallization of the crude products (221 g.) from benzene, gave 160 g. of a solid, m. p. 44–46°.

The ethyl cyanide was obtained by refluxing sodium cyanide (785 g.) in 3 liters of water with ethyl bromide (1405 g.) for seventy-two hours. Fractionation of the mixture of dried ethyl bromide and cyanide through a 75-cm. Vigreux column gave a recovery of 538 g. of ethyl bromide and 268 g. of ethyl cyanide.

2-Ethyl-3-iminocapronitrile.—*n*-Propyl cyanide (400 g.) was dimerized in ether solution (500 ml.) with sodium (67 g.). Four hours were required for the addition of the nitrile, and the mixture was then poured into cold water, the ether layer separated and the water layer extracted with ether. There was obtained by fractionation 160 g. of iminonitrile at 137–142 (7 mm.). Refractionation gave 157 g., b. p. 114–117° (2 mm.), n_D^{25} 1.5051 to 1.5060, which solidified when allowed to stand in a refrigerator. Recrystallization from dilute alcohol gave colorless shining plates, m. p. 41–42.5°. The compound has not previously been reported as a solid.^{10,11} *n*-Propyl cyanide (405 g.), b. p. 113–115°, was made from *n*-propyl bromide (1246 g.) and sodium cyanide (637 g.) in 650 ml. of water and 1200 ml. of methanol during a reaction period of forty hours under reflux. The fraction of b. p. 70–98° was collected, treated with fused calcium chloride and the nitrile layer dried over calcium chloride. The dried product was then fractionated through a Vigreux column.

2-*n*-Propyl-3-iminoanthronitrile¹² was prepared as previously described.

2,4-Diphenyl-3-iminobutyronitrile.—Sodium (29 g.) was dissolved in dry ethanol (450 ml.) and benzyl cyanide (292 g.) added rapidly. The mixture was heated twenty minutes on a steam-bath and 500 ml. of water added. The oil separated from two such preparations was extracted with ether and the ether extract washed with water. The ether was distilled and the residual oil distilled until the distillate was no longer milky. The residue was extracted with ether and the ether solution dried over calcium chloride. After the distillation of the ether the residue was distilled from a flask having indentations below the side arm, like a Vigreux column. The desired product (248 g.), b. p. 203–205° (1 mm.), n_D^{20} 1.5693, was obtained.

The product, purified as described above, partially crystallized upon standing for four weeks. Recrystallization was obtained from 95% alcohol to give colorless prisms, m. p. 112–115°, but since there was no apparent difference between the hydrogenation of the solid and the oil, the material to be hydrogenated was simply distilled from Raney nickel.

Benzyl cyanide (203 g.) was recovered at various steps in the process of isolating the desired product. Cyanbenzylene (45 g.), b. p. 230–237° (1 mm.), m. p. 107–107.5°

(9) Von Meyer, *J. prakt. chem.*, [2] **38**, 336 (1888).

(10) Wache, *ibid.*, [2] **39**, 245 (1889).

(11) Baerts, *Bull. soc. chim. Belg.*, **31**, 421 (1922).

(12) Wiley and Adkins, *THIS JOURNAL*, **60**, 914 (1938).

TABLE I
PHYSICAL DATA ON PREVIOUSLY UNREPORTED COMPOUNDS

Compound	B. p. or m. p., °C.	Press., mm.	n_D^{20}	d_4^{20}	Molar refraction		Formula	Analyses, %	
					Calcd.	Found		Calcd.	Found
1,3-Diamino-2-methylpentane	110	88	1.4580	0.8643	36.75	36.68	C ₆ H ₁₂ N ₂	N, 24.14	24.11
Chloroplatinate	237	(dec.)	C ₆ H ₁₂ Cl ₂ N ₂ Pt	Pt, 37.1	36.95
1,3-Diamino-2-ethylhexane	99	17	1.4554	.8645	45.99	45.29	C ₈ H ₂₀ N ₂	N, 19.44	19.47
Dihydrochloride	153-165	C ₈ H ₂₂ Cl ₂ N ₂	Cl, 32.62	32.47
5-Aminononane	78	20	1.4264	0.7824	47.18	46.91	C ₉ H ₂₁ N	N, 9.98	9.95
Hydrochloride	178-180	C ₉ H ₂₂ ClN	Cl, 19.78	19.89
Picrate	149.5-150	C ₁₅ H ₂₄ N ₄ O ₇	N, 15.05	15.34
4-Methyl-5-aminononane	87-90	18	1.4323	C ₁₀ H ₂₁ N	N, 8.91	9.05
Picrate	153.5-154.5	C ₁₅ H ₂₄ N ₄ O ₇	N, 14.51	14.59
1,3-Diamino-2-propylheptane	100	5	1.4557	0.8531	55.22	54.84	C ₁₀ H ₂₁ N ₂	N, 16.28	16.24
Dihydrochloride	106-110	(dec.)	C ₁₀ H ₂₃ Cl ₂ N ₂	Cl, 28.95	28.56
1,3-Diamino-2,4-diphenylbutane	166-168	1.5	1.5803	1.0599	75.73	75.48	C ₁₄ H ₂₀ N ₂	C, 80.00	80.16
Dihydrochloride	>280	C ₁₄ H ₂₂ Cl ₂ N ₂	H, 8.33	8.57
1,3-Diphenyl-2-aminobutane	142.5	51-54	1.5660	1.0193	72.30	72.01	C ₁₄ H ₁₉ N	C, 85.28	85.34
Hydrochloride	174-175.5	C ₁₄ H ₂₀ ClN	H, 8.51	8.66
Picrate	190.5-191.5	C ₂₂ H ₂₂ N ₄ O ₇	Cl, 13.58	13.61
3-Nitrophthalimide	152-153	N, 12.33	12.32	
Phenylthiourea	146.5-147	C ₂₄ H ₂₀ N ₂ O ₄	N, 7.00	7.37
2,4-Diphenyl-1-aminobutane	144.5	1	1.5728	C ₂₂ H ₂₂ N ₂ S	N, 7.78	7.62
3-Nitrophthalimide	129.5	C ₁₄ H ₁₃ N	N, 6.22	6.48
Phenylthiourea	191-191.5	C ₂₄ H ₂₀ N ₂ O ₄	N, 7.00	7.32
							C ₂₂ H ₂₂ N ₂ S	N, 7.78	8.05

(from 95% alcohol), was also obtained. This compound was the chief product when the description of the procedure of Atkinson and Thorpe¹³ for the preparation of 2,4-diphenyl-3-imino-butyrionitrile was strictly followed. The method of Lees and Thorpe¹⁴ was not found satisfactory.

3-(Phenylimino)-butyrionitrile.—Aniline (144 g.) dissolved in acetic acid (154 g.) and water (300 ml.) was added rapidly with stirring to a suspension of 3-imino-butyrionitrile (125 g.) in water (500 ml.). After standing for thirty minutes the reaction mixture was cooled in an ice bath. The solid product was filtered off and recrystallized from dioxane. The first crop weighed 86 g., while an additional 83 g. was obtained by diluting the mother liquor with water. The m. p. was 116-117° for both crops of crystals.⁸

3-Piperidinocinnamionitrile.—Ethyl phenylpropionate¹⁵ (412 g., b. p. 132-134° (8 mm.), n_D^{20} 1.5504) was prepared by the esterification of phenylpropionic acid¹⁶ (660 g.) with dry ethanol and hydrogen chloride. The amide was made by the reaction of the ester (412 g.) and concentrated ammonium hydroxide (1250 ml.) during four and one-half days with frequent agitation. The crude product (210 g.) which separated was washed with 150 ml. of cold 75% alcohol. The yield of amide, m. p. 107.5-108.5°, was 154 g.

The amide (102 g.), phosphorus oxychloride (58 g.) and pulverized sodium chloride (45 g.) were heated, under a reflux condenser attached to an apparatus for gas adsorption, at 75° in an oil-bath until the evolution of gas diminished. The temperature of the bath was then raised gradually to 100-105° and maintained there for four hours.

The liquid portion of the cold reaction mixture was dissolved in an equal volume of ether. A water solution of the solid portion of the reaction mixture was extracted with ether and both ether solutions washed with a 10%

water solution of sodium carbonate. The combined ether solutions were dried over calcium chloride and distilled. The nitrile (53 g.) came over at 101-105° (12 mm.) m. p. 41°.

Pure dry piperidine (8.15 g.) was added slowly to the nitrile (12 g.) with cooling, and allowed to stand thirty minutes. Raney nickel (5 g.) was added and the mixture distilled. The desired product (17.6 g.) came over at 165-175° (0.5 mm.), m. p. 91.5-92.5°. Recrystallization from petroleum ether (b. p. 60-68°) or a mixture of methanol and water gave products which melted at 94-95° and 92-93°, respectively.

2,4-Diphenyl-1-aminobutane.—1,3-Diphenyl-4-nitrobutanone-1 (20 g.)¹⁷ in dioxane (100 ml.) took up 4.2 moles of hydrogen within 1.6 hours at 70-126° over Raney nickel (8 g.) under a pressure of 150 atm. The amine (12.5 g.), b. p. 132-133° (0.5 mm.), n_D^{20} 1.5642 gave neutral equivalents of 227 and 228 as compared with a calculated value of 225. The 3-nitrophthalimide, m. p. 129.5° (from 95% alcohol), was prepared by the method of Alexander and McElvain.¹⁸ The phenylthiourea of the amine had a m. p. 191-191.5° (from alcohol).

1,3-Diphenyl-2-aminobutane.—Benzyl cyanide (117 g.) was added at a rate to maintain refluxing, to a stirred suspension of sodamide¹⁹ (39 g.) in 350 ml. of ether. The mixture was refluxed fifteen minutes, cooled and methyl iodide (142 g.) added slowly. After refluxing for two hours the mixture was cooled, decomposed with water and the product extracted with ether. After drying over calcium chloride the ether was distilled and 2-phenylpropionitrile²⁰ (94 g.) distilled at 88-94° (8 mm.) along with benzyl cyanide (10 g.).

The crude nitrile was slowly added to the Grignard reagent from 405 g. of benzyl chloride in 1250 ml. of ether. After refluxing for three hours and stirring for twelve hours, the addition product was decomposed with ice and 20%

(13) Atkinson and Thorpe, *J. Chem. Soc.*, **89**, 1906 (1906).

(14) Lees and Thorpe, *ibid.*, **91**, 1287 (1907).

(15) Perkin, *ibid.*, **45**, 174 (1884).

(16) "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1932, Vol. 12, p. 60.

(17) Kohler and Drake, *This Journal*, **45**, 2144 (1923).

(18) Alexander and McElvain, *ibid.*, **60**, 2285 (1938).

(19) Vaughn, Vogt and Nieuwland, *ibid.*, **56**, 2120 (1934).

(20) Baldinger and Nieuwland, *ibid.*, **55**, 2851 (1933).

sulfuric acid. The 1,3-diphenyl-2-butanone²¹ (143 g.) was distilled at 152–153 (2 mm.), n_D^{25} 1.5597.

The ketone (50 g.) in 40 ml. of dioxane with 8.5 g. of ammonia was shaken with Raney nickel (5 g.) for five hours under 100 atm. of hydrogen at 150°. The dioxane was distilled, the residue taken up in ether and treated with concentrated hydrochloric acid until it was acid to congo red. The acid solution was extracted with two 150-ml. portions of ether, whereupon the amine hydrochloride crystallized out of the acid layer. The latter was made alkaline with a 50% solution of potassium hydroxide and extracted with 250 ml. of ether. The ether layer was washed with alkali, dried over potassium hydroxide and distilled.

The 1,3-diphenyl-2-aminobutane (24 g., n_D^{25} 1.5657) distilled at 133–138°. The amine partially crystallized upon standing, m. p. 50–51°. When recrystallized from petroleum ether (b. p. 60–68°) the melting point was as high as 54°. The 3-nitrophalimide had a melting point 152–153° (from alcohol).

Hydrogenations.—In general 30 to 40 g. of an iminonitrile dissolved in 80 ml. of ether or dioxane was allowed to react with hydrogen at 200 to 300 atm., over about 5 g. of Raney nickel, for two to three hours at 120 to 150°. The steel reaction vessel (270 ml. void), catalyst and procedures, were those ordinarily used in this Laboratory. The products were separated by fractionation and the formation of salts or other derivatives of the amines. The types of derivative used for characterization (and in some cases for isolation of small amounts of an amine) are indicated in Table I.

Summary

Five iminonitriles of the type $RCH_2C=NH-$

(21) Levy and Jullien, *Bull. soc. chim.*, [4] 45, 941 (1929).

CHRCN have been prepared by the Thorpe reaction from nitriles RH_2CN where R was hydrogen, methyl, ethyl, *n*-propyl or phenyl, and submitted to hydrogenation over Raney nickel. The corresponding diamines were obtained in yields averaging about 60%, but in no case was it possible to selectively hydrogenate the imino group and obtain an aminonitrile.

All of the iminonitriles gave cleavage products upon hydrogenation. In the first four nitriles listed above the predominant cleavage involved the removal of the cyano group, while with $C_6H_5-CH_2C=NHCHC_6H_5CN$ only the nitrogen of the cyano group was lost to any considerable extent.

Two substituted iminonitriles, 3-(phenylimino)-butyronitrile and 3-piperidinocinnamitrile underwent cleavage almost exclusively at the imino group.

Molecular weight determinations in benzene indicated that the compound $C_3H_7CH_2C=NH(C_3H_7)CN$ exists as a trimer at the freezing point of benzene and as a dimer at the boiling point of benzene. In an alcohol solution di- or trimerization does not occur, but the alcohol adds to the iminonitrile.

The behavior of the iminonitriles upon hydrogenation lends support to the concept that they have the structure $RC(NH_2)=CRCN$.

MADISON, WISCONSIN

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[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES]

Chain Structure of Linear Polyesters—Trimethylene Glycol Series

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In previous papers^{1,2,3} results have been reported on the crystalline nature and the chain molecule configurations of linear polyesters of high molecular weight. These results have been based on the measurement of X-ray fiber patterns obtained from oriented fibers. In the case of the crystalline members of the ethylene glycol and decamethylene glycol series, it has been shown that the chain molecules are arranged parallel to the fiber axis and are essentially planar zigzag in configuration. In addition it was found that in these series the molecules exhibit typical paraffinic packing in the plane perpendicular to the chain

axes.⁴ At the same time there is good evidence that the mutual alignment of the chemical repeating units in adjacent chain molecules is sometimes variable within the same compound (polymeric mixture), so that several apparently stable arrangements of the planar chains, corresponding to various angles of "tilt" of the dipole layers, may co-exist in a given polycrystalline aggregate. As might be expected this is particularly true in the decamethylene series² where the dilution of the polar ester groups is great and the energy between different arrangements is therefore small.⁵

(1) C. S. Fuller and C. L. Erickson, *THIS JOURNAL*, 59, 344 (1937); 61, 3601 (1939).

(2) C. S. Fuller and C. J. Frosch, *ibid.*, 61, 2575 (1939).

(3) C. S. Fuller and C. J. Frosch, *J. Phys. Chem.*, 43, 323 (1939).

(4) Polyethylene succinate appears to be an exception to this rule. However, evidence has been found⁴ which indicates that under certain conditions it also can be made to exhibit paraffinic packing.

(5) T. Schoon, *Z. physik. Chem.*, B39, 385 (1938); *Ber.*, 72, 1821 (1939).