through Filter Cel. To the yellow filtrate was added 550 ml. ether and the mixture was cooled to 5°. On addition of 49.5 ml. (0.62 mole) of 35% aqueous sodium hydroxide solution, yellow solid separated. This was collected, washed with ether, and dried; yield, 41 g. (69.6%), m.p. 136–140° (uncorr.). Thirty-four g. of the crude base was taken up in 170 ml. dilute hydrochloric acid and the resulting liquid was treated with charcoal and filtered through Filter Cel. After cooling the filtrate to 0–5°, conc. ammonium hydroxide was added until the mixture was neutral. The yellow solid was collected and dried. Details on yield, purification, and properties of the solid are found in Table I.

4-Amino-1,2-dihydro-6-(p-methylthioanilino)-2-(n-propyl)-s-triazine. To a warm solution of 8.6 g. (0.0274 mole) 4,6-diamino-1,2-dihydro-1-(*p*-methylthiophenyl)-2-(*n*-propyl)-*s*-triazine hydrochloride in 86 ml. water was added 11.2 ml. (0.14 mole) 35% aqueous sodium hydroxide. White solid separated immediately which then changed to an oil on further heating. After 1.5 hr. of heating on a steam bath the mixture was cooled to room temperature, whereupon the oil changed to a gum. The supernatant liquid was decanted and the gum was washed once with water. After decantation, as much water as possible was removed *in vacuo*. Absolute ether was added and the mixture was allowed to stand. The powdery white solid which separated was collected and washed with absolute ether; yield 3 g. (39.4%), m.p. 125.8–129.2°.

Anal. Calcd. for $C_{13}H_{19}N_5S$: N, 25.25; S, 11.56. Found: N, 24.93; S, 11.50.

The hydrochloride was formed from the above base by warming 3 g. (0.0108 mole) of the base with 6 ml. (0.121 mole) of 2.02*N* hydrochloric acid in 15 ml. water. After chilling, the hydrochloride separated as a white powder; yield 2.3 g. (67.9%), m.p. 137–141° (uncorr.). Recrystallization from ethanol gave a white powder, m.p. 158.8–161.4°.

Anal. Calcd. for $C_{13}H_{19}N_5S.HCl$: Cl, 11.30; S, 10.22. Found: Cl, 11.50; S, 10.40.

p-Alkylthioanilines. These compounds, used in the preparation of Ia, b, and c, were prepared through a known method[13] using an iron–acetic acid reduction of the appropriate alkyl *p*-nitrophenylsulfide.[14]

1-(p-Methylthiophenyl) biguanide. The biguanide hydrochloride was obtained in 73% yield by the method of Curd[15] who made 1-(*p*-chlorophenyl) biguanide. The crude hydrochloride, a pink solid with m.p. 215–217° (uncorr.), was used to prepare Ic. Treating a hot aqueous solution of the biguanide hydrochloride with an excess of 35% aqueous sodium hydroxide gave crude pink base; yield, 84%, m.p. 147–150° (uncorr.). After two recrystallizations with water-ethanol (20:1) mixtures, the free base was obtained as yellow platelets, m.p. 152.9–154°.

Anal. Calcd. for $C_9H_{13}N_5S$: N, 31.37. Found: N, 31.36.

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Decyanoethylation of *N,N*-Bis(2-cyanoethyl)amides

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The preparation of 3,3′-iminodipropionitrile from ammonia and acrylonitrile,[1–3] and its reaction with acyl halides to form *N,N*-bis(2-cyanoethyl)amides[4–7] are well known. Some work has been reported on the pyrolytic decyanoethylation of these amides to form β-alanine derivatives, and this route has even been suggested as a possible practical preparative method for β-alanine itself.[8,9] This note deals with a more satisfactory method of decyanoethylation.

Treatment of *N,N*-bis(2-cyanoethyl)amides with bases such as sodium ethoxide and KOH in alcoholic solution leads smoothly to the formation of the corresponding *N*-(2-cyanoethyl)amides at temperatures below 100°, considerably below those necessary for pyrolytic decyanoethylation. A similar reaction was noted in passing by Petersen and Müller with substituted ureas, but the product was not isolated and the yield is unknown.[10]

Both infrared analysis and vapor phase chromatography indicated that 3-ethoxypropionitrile was produced in the decyanoethylation of *N,N*-bis (2-cyanoethyl)benzamide in NaOEt-EtOH, indicating that the alcohol used as solvent forces the reaction to completion by combining with the acrylonitrile formed. The reaction apparently does not proceed in pure benzene.

Further decyanoethylation would lead to a primary amide, which might compete with the ethanol for acrylonitrile, thus explaining why only one mole of acrylonitrile is removed.

Under anhydrous conditions, the reaction proceeds smoothly with *N,N*-bis(2-cyanoethyl)benzamides, acetamides, and benzenesulfonamides. If the reaction is carried out in the presence of water, it leads to an *N*-acyl-β-alanine or to an *N*-(2-carbamoylethyl)amide.

For example, it has recently been shown by Misra and Asthana[11] that alkaline hydrolysis of *p*-chloro-*N,N*-bis(2-cyanoethyl)benzenesulfonamide leads to decyanoethylation and formation of *N*-(*p*-chlorobenzenesulfonyl)-β-alanine. We have found that use of smaller amounts of water leads to formation of *N*-(2-carbamoylethyl)benzamide

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TABLE I

	Starting Material ($AcN(CH_2CH_2CN)_2$)				Product ($AcNHCH_2CH_2CN$)		
Ac	M.P. (°C.)	% N[a] Calcd.	% N[a] Found	Recryst. Yield (%)	M.P. (°C.)	% N[a] Calcd.	% N[a] Found
C_6H_5CO—	109.5–112° (lit. 112°)[4]			60	94–95° (lit. 96–98°)[7]		
o-Cl—C_6H_4CO—	85–87.5°	16.07	15.99	70	82–82.5°	[b]	[b]
p-Cl—C_6H_4CO—	116–117.5°	16.07	15.93	62	154–156°	13.41	13.40
p-NO_2—C_6H_4CO—	150.5–152.5°	20.6	20.64	87	154–155° (lit. 151–153°)[10]		
CH_3CO—	45–48° (lit. 50°, 146°)[4,6]			61	64–65° (lit. 63°)[6]		
p-Cl—$C_6H_4SO_2$—	132.5–133.5° (lit. 132°)[11]			65	91–92.5°	11.43	11.19

[a] Nitrogen analyses are given only for compounds not previously reported in the literature. Infrared spectra of all compounds are in agreement with the structure given. Chlorine and/or carbon-hydrogen analyses also agree. [b] Nitrogen analysis was not run for this compound; chlorine content was found to be 17.06% (calcd. 17.0%).

from *N*,*N*-bis(2-cyanoethyl)benzamide, indicating that decyanoethylation occurs fairly early in the reaction.

The decyanoethylation may even occur in the course of a reduction reaction using alkaline ferrous ion; the product isolated from reduction of *N*,*N*-bis(2-cyanoethyl)-*p*-nitrobenzamide was *p*-amino-*N*-(2-cyanoethyl)benzamide instead of the expected *p*-amino-*N*,*N*-bis(2-cyanoethyl)benzamide.

EXPERIMENTAL

1. *Decyanoethylation. General method.* A number of *N*,*N*-bis(2-cyanoethyl)amides were prepared by known methods from 3,3′-iminodipropionitrile. A solution of 0.5 mole of the amide in a liter of absolute ethanol (or benzene containing a little alcohol) was treated at reflux with 0.2–0.5 g. of sodium (or 1–1.5 g. KOH) dissolved in absolute ethanol.

The solution was refluxed for 2–5 hr., after which time evaporation of the solvent gave an essentially quantitative yield of the *N*-(2-cyanoethyl)amide (often 90% or better in purity by infrared).

This general method was used for the preparation of *N*-(2-cyanoethyl)benzamide and its *o*-chloro, *p*-chloro, and *p*-nitro derivatives as well as *N*-(2-cyanoethyl)acetamide. For decyanoethylation of *p*-chloro-*N*,*N*-bis(2-cyanoethyl)-benzenesulfonamide, more than molar quantities of sodium ethoxide were needed, because of the acidic nature of the product.

One recrystallization of the crude products gave 60–90% recovery of the pure *N*-(2-cyanoethyl)amide. *N*-(2-Cyanoethyl)benzamide and its chloro derivatives were recrystallized from 5 ml. chloroform per gram of crude product; the *N*-(2-cyanoethyl)-*p*-nitrobenzamide from 10 ml. ethanol per gram; the *N*-(2-cyanoethyl)acetamide from 2 g. chloroform plus 4 g. carbon tetrachloride per gram; and the sulfonamide from 10 ml. methylchloroform per gram. Table I summarizes these results.

2. *Hydrolytic decyanoethylation.* A solution of 0.2 g. sodium in 20 ml. butyl alcohol was added to a solution of 0.2 mole *N*,*N*-bis(2-cyanoethyl)benzamide in 400 ml. butyl alcohol at 80°. The mixture was heated at 80–90° for 3 hr., 200 g. of the solvent was distilled off at 260–290 mm. Hg and 21.5 g. precipitate (m.p. 140–150°) was recovered on cooling. This was too high-melting to be the expected *N*-(2-cyanoethyl)benzamide. Recrystallization from 100 ml., then 50 ml. of water, gave 10 g. of *N*-(2-carbamoylethyl)-benzamide, best fraction of which had a m.p. 167–169°; lit. 174–176°.[12] It appears that the butyl alcohol used contained enough moisture to cause partial hydrolysis. The final product contained 14.71% *N* (calcd. for $C_{10}H_{12}N_2O_2$: 14.57%). When 0.2 mole *N*,*N*-bis(2-cyanoethyl)benzamide in 400 ml. 95% ethanol was treated in a similar fashion with 0.5 g. KOH in 30 ml. 95% ethanol, the resulting 40 g. of crude mixture recovered contained both *N*(2-cyanoethyl)-benzamide and *N*-(2-carbamoylethyl)benzamide.

3. *Reductive decyanoethylation.* A boiling suspension of 0.1 mole *N*,*N*-bis(2-cyanoethyl)-*p*-nitrobenzamide in 100 ml. water was added in small quantities to a solution of 0.007 mole $FeSO_4$ in 250 ml. water. Aqueous ammonia was added in small portions with stirring, to make the solution alkaline. The mixture was heated 5 min., then filtered hot. Cooling resulted in recovery of 11.5 g. crude product. Two recrystallizations from 95% ethanol gave 7.5 g. of *p*-amino-*N*-(2-cyanoethyl)benzamide (m.p. 111–115°).

Anal. Calcd. for $C_{10}H_{11}N_3O$: C, 63.4; H, 5.85; N, 22.21. Found: C, 63.58; H, 5.41; N, 22.60.

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