[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

ACTION OF BASIC REAGENTS ON BENZONITRILE TO FORM TRIAZINES[1]

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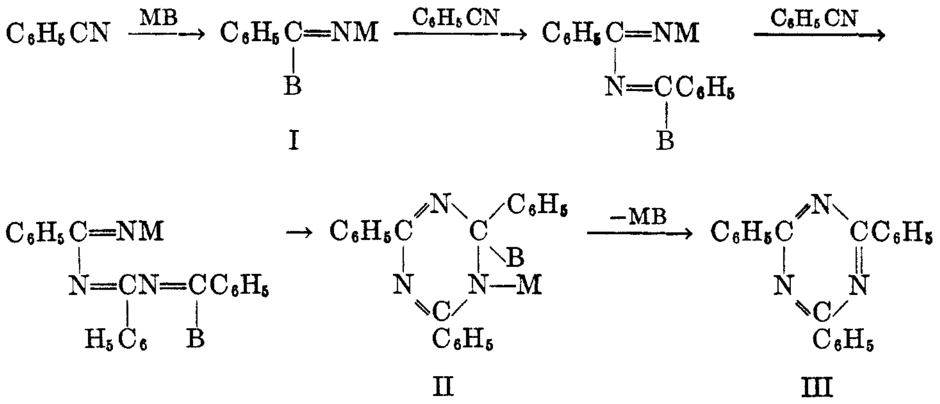
Metallic basic reagents (MB) may react with benzonitrile to form not only simple addition compounds (I) but also further cyclic condensation products. The most common of the cyclic products are dihydrotriazines (II, M = H, B = alkyl or aryl) and the triazine (III). The latter is a trimer of benzonitrile. Earlier workers have reported the formation of dihydrotriazines with various basic reagents such as lithium alkyls and aryls (1), sodium (2), and phenyllithium (1), and the formation of the aromatic triazine with basic reagents including diethylzinc (3) and lithium (1). Grignard reagents have given the ketimine (I, M = H, B = alkyl or aryl) in ethyl ether but have produced the triazine (III) in refluxing xylene. A 25% yield of the triazine along with a small amount of the dihydrotriazine has been reported with phenylmagnesium bromide (1).



We have studied the reactions of benzonitrile with sodium hydride and with certain metallic derivatives of secondary amines. With sodium hydride in benzene, there was isolated a 14% yield of the dihydrotriazine (IV) which was dehydrogenated almost quantitatively to the triazine (III) in refluxing nitrobenzene or even in xylene. In most experiments, however, a mixture of the dihydrotriazine and the triazine or the triazine alone was obtained. The best over-all yield of the triazine from benzonitrile was 25% (30% conversion yield). The structure of the dihydrotriazine (IV) was established by hydrolysis in the presence of sulfuric acid to form benzaldehyde and benzoic acid in the ratio of

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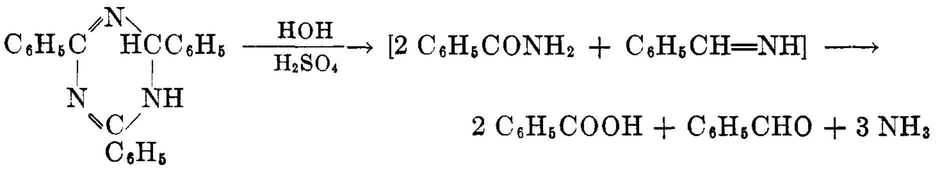
approximately one to two. Some of the dihydrotriazine underwent dehydrogenation to the triazine. The hydrolysis may be indicated as:



IV

The reaction of benzonitrile with sodiomethylaniline or with N-methylanilinomagnesium bromide in ethyl or *n*-butyl ether produced the triazine (III) in yields up to 28% (conversion yields up to 39%). None of the dihydrotriazine derivative [II, M = H, B = N $(CH_3)C_6H_5$] was isolated. The yield was much lower with diethylaminomagnesium bromide. Catalytic amounts of the metallic derivatives of methylaniline or of sodium hydride produced only very small yields of the triazine.

The trimerization of benzonitrile to the triazine (III) has also been effected by acids. Fuming sulfuric acid was used by Pinner and Klein (4), but no yield of the triazine was reported. We have obtained only a 16% yield with this acid. Cook and Jones (2) have reported a 40% yield of the triazine using chlorosulfonic acid.

EXPERIMENTAL

Reaction with sodium hydride. A 500-ml. three-necked flask was fitted with a sealed stirrer, thermometer, dropping-funnel, and reflux condenser protected by a drying tube. The system was purged with nitrogen and 11.5 g. (0.48 mole) of sodium hydride (Du Pont)[2] was charged to the flask and covered immediately with 50 ml. of dry, thiophene-free benzene. Benzonitrile (51.5 g., 0.5 mole) was added through the dropping-funnel. The mixture was stirred and heated at 70–85° for five hours. During this time it turned to a dark red gel. After cooling, 100 ml. of benzene was added and neutralization was effected by the careful addition, over a period of two hours, of 30 g. of glacial acetic acid in 60 ml. of benzene. Considerable gas evolution occurred during neutralization; this gas was presumably hydrogen produced by decomposition of the excess sodium hydride. Water and ether were added and the suspended solid was filtered off. A second crop of solid was obtained by concentrating the organic phase from the filtrate and filtering again. A cut of 9.5 g. of benzonitrile was recovered by distilling the filtrate at reduced pressure. The solid material was heated with toluene at 100°, a considerable amount of undissolved solid was filtered off, and the filtrate was allowed to cool. The crystals from the filtrate were recrystallized from toluene, yielding 7.2 g. (14%, 18% conversion yield) of 1,2-dihydro-2,4,6-triphenyl-*s*-triazine (IV) as pale yellow needles, melting at 171–172°.

Anal. Calc'd for $C_{21}H_{17}N_3$: C, 80.99; H, 5.51; N, 13.53.

Found: C, 80.55; H, 5.51; N, 13.35.

Cryoscopic molecular weight determinations in naphthalene gave values of 300 ± 3; the calculated value is 311.

The *dihydrotriazine*, on refluxing a few minutes in nitrobenzene or xylene, was converted nearly quantitatively to 2,4,6-triphenyl-*s*-triazine, m.p. 228–229°. The melting point was

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[2] We are indebted to the Electrochemical Department, E. I. du Pont de Nemours and Co., Niagara Falls, N. Y., for a generous supply of sodium hydride.

not depressed by admixture with a sample of the triazine prepared from benzonitrile by action of fuming sulfuric acid (4).

A sample of the dihydrotriazine was hydrolyzed as follows: a 300-ml. two-necked flask was fitted with a short Vigreux column connected to a condenser and receiver. The system was purged with nitrogen and the flask was charged with 50 ml. of 15% sulfuric acid and 2 g. of the dihydrotriazine. The mixture was heated to boiling and about 25 ml. of distillate was slowly collected. The distillate was extracted with ether and the ether extract dried and concentrated yielding 0.4 g. of benzaldehyde which was identified by its 2,4-dinitrophenylhydrazone (m.p. 235–236°) and by air-oxidation to benzoic acid (m.p. 119–120°). The residue from the distillation was extracted thoroughly with ether. The ether extract was extracted with saturated sodium bicarbonate solution, washed with water, and the ether removed. There remained 1.1 g. of the aromatic triazine, m.p. after recrystallization, 228–229°. On acidification of the bicarbonate extract and saturation with salt, benzoic acid separated. It was taken up in ether. On removal of the ether, 1.0 g. of benzoic acid remained; m.p. 119–120° after recrystallization from hot water. The benzoic acid and benzaldehyde were obtained in the ratio 2.2:1; the calculated ratio is 2:1.

On repeating the reaction of benzonitrile with other samples of sodium hydride obtained from Du Pont[2] there were obtained either the aromatic triazine or mixtures of the dihydrotriazine and the triazine in yields of 15–25%.

Reaction with sodiomethylaniline. To a suspension of approximately 0.087 mole of the reagent, prepared by means of sodium amide, in 75 ml. of ether was added 27 g. (0.262 mole) of benzonitrile in 50 ml. of ether. After stirring and refluxing for two hours, the mixture was decomposed with cold dilute hydrochloric acid. The solid (1.8 g.) was collected. The ether phase of the filtrate was distilled yielding 17.2 g. (64% recovery) of benzonitrile (b.p. 80–81° at 20 mm.) and a solid residue (1.7 g.). The combined solids were recrystallized from toluene yielding 3.1 g. (12%, 39% conversion yield) of the triazine (III) (m.p. 228–229°). The yield was only 1% (5% conversion yield) using 0.0087 mole of the reagent and 0.262 mole of benzonitrile and refluxing the mixture for 20 hours.

When the reaction was carried out with 0.087 mole of the reagent and 0.262 mole of benzonitrile in refluxing *n*-butyl ether for 12 hours, the yield of the triazine was 2.8 g. (11%, 25% conversion yield).

Reaction with N-methylanilinomagnesium bromide. To ethylmagnesium bromide, prepared from 5 g. (0.046 mole) of ethyl bromide and 1.07 g. (0.044 mole) of magnesium in 50 ml. of ethyl ether was added 5.2 g. (0.044 mole) of methylaniline. After stirring for 30 minutes, 14.2 (0.138 mole) of benzonitrile in 50 ml. of ether was added and the mixture refluxed for two hours. The mixture was worked up as described above for sodiomethylaniline, yielding 1.1 g. (6%, 12% conversion yield) of the triazine (m.p. 228–229°).

Better yields of the triazine were obtained when the reaction was carried out in refluxing *n*-butyl ether. The yield was 4 g. (21%, 32% conversion yield) after 12 hours using a three to one ratio of the nitrile to the reagent, and was 5.2 g. (28%, 35% conversion yield) after the same time with equivalent amounts of the reactants. The yield was only 1% after 12 hours using a ten to one ratio of the nitrile to the reagent. When the ratio of nitrile to reagent was three to one and the time extended to 24 hours, none of the triazine was isolated; instead, there was obtained a solid melting above 300° which was insoluble in various organic solvents.

The reaction of benzonitrile (0.135 mole) with diethylaminomagnesium bromide (0.045 mole) in refluxing ethyl ether for two hours gave only a 2% (10% conversion) yield of the triazine.

SUMMARY

Benzonitrile reacted with sodium hydride to form 1,2-dihydro-2,4,6-triphenyl-*s*-triazine which on dehydrogenation gave 2,4,6-triphenyl-*s*-triazine. The structure of the dihydrotriazine was established by hydrolysis.

Benzonitrile was also trimerized to the triazine by certain metallic derivatives of secondary amines.

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(3) Frankland and Evans, *J. Chem. Soc.*, **37**, 563 (1880).
(4) Pinner and Klein, *Ber.*, **11**, 764 (1878).