β-diethylaminoethyl mercaptan[13] in 10 cc. of ether containing two drops of 9 molar alcoholic hydrogen chloride was heated slowly to 70° in an oil-bath, and then kept at about this temperature for twenty hours. The product was treated with a mixture of 25 cc. of 10% sodium hydroxide and 80 cc. of ether. The ether layer was removed, washed with 15 cc. of water, dried, and then filtered. An excess of ethereal hydrogen chloride was added; the ether was decanted; the precipitate was dissolved in 20 cc. of absolute ethanol; and 25 cc. of ether was added. From the cooled solution there separated slowly 4.8 g. (61%) of product which softened at 160° and melted at 169–172°. Recrystallization gave the same melting point range.

Anal. Calcd. for $C_{17}H_{27}Cl_2N_3S$: N, 11.16; S, 8.51. Found: N, 11.15 and 10.95; S, 8.19 and 8.35.

Summary

Lithium diethylamide reacts with α-fluoro-, α-chloro- and α-bromonaphthalene in ether solution to give the rearrangement product, β-diethylaminonaphthalene. One of the products isolated from these reactions is naphthalene, which apparently does not owe its formation to a halogen–metal interconversion reaction.

The lithium dialkylamide reaction in ether proceeds smoothly with 2-chloroquinoline to give 2-dialkylaminoquinolines. One of the types formed by this method is 2-ethyleneiminoquinoline, which when treated with β-diethylaminoethyl mercaptan gives β-(2-quinolylamino)-ethyl β-diethylaminoethyl sulfide dihydrochloride.

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[13] See Albertson and Clinton, THIS JOURNAL, **67**, 1222 (1945); Gilman and Woods, *ibid.*, **67**, 1843 (1945); and Gilman, Plunkett, Tolman, Fullhart and Broadbent, *ibid.*, **67**, 1845 (1945), for the preparation of this mercaptan.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY]

The Action of Bases on Organic Halogen Compounds. III. The Reaction of Potassium Amide with the Naphthyl Halides

BY ROBERT S. URNER AND F. W. BERGSTROM[1]

The action of the alkali amides on the phenyl halides (the fluoride excepted) leads to the formation, in varying amounts, of aniline, diphenylamine, triphenylamine and *p*-aminobiphenyl.[2] Other aromatic halides sometimes give the expected amine, but a rearrangement to the ortho position is often noted, as in the experiments of Gilman and Avakian.[3] The present work is a continuation of investigations of Wright, Chandler, Gilkey and Horning of this Laboratory, and deals with the action of a liquid ammonia solution of potassium amide on the naphthyl halides.

An excess of potassium amide, dissolved in liquid ammonia, removes halogen almost quantitatively from 1-chloronaphthalene, 1-bromonaphthalene and 1-iodonaphthalene with the formation of 2-naphthylamine in 40–55% yields, together with smaller amounts (2–3%) of 1-naphthylamine. The same results are obtained when potassium amide solution is added to an excess of the naphthyl halide. Both reactions follow the equation

$$C_{10}H_7Cl + 2KNH_2 = C_{10}H_7NHK + KCl + NH_3 \quad (1)$$

When hydrolyzed, $C_{10}H_7NHK + H_2O = C_{10}H_7NH_2 + KOH$.

Although fluorobenzene is attacked only to a very slight extent by potassium amide at 20 or 80°,[2a] 1-fluoronaphthalene and potassium amide react slowly at −33° to form 1-naphthylamine; the yield is somewhat improved by carrying out the reaction at room temperatures. A by-product melting at 111° has not yet been identified. Liquid ammonia solutions of the 2-naphthyl halides react with potassium amide to give 2-naphthylamine almost exclusively, with very minor quantities of 1-naphthylamine. Rearrangement therefore does not always occur in the reaction between potassium amide and an aryl halide. It is interesting in this connection that Gilman and co-workers[4] have found that 2-diethylaminonaphthalene is formed in the reaction of lithium diethylamide with 1-fluoronaphthalene, 1-chloronaphthalene and 1-bromonaphthalene. The reaction between potassium amide and 1-fluoronaphthalene may also involve a rearrangement, but to the 4-position of the nucleus.

Experimental

The naphthyl halides were all refractionated white-label preparations of the Eastman Kodak Company, with the exception of 2-fluoro- and 2-chloronaphthalenes, which were made from 2-naphthylamine by known methods. The description of a typical run is given.

Potassium amide was prepared in about 200 ml. of liquid ammonia in a 3-necked 500-ml. flask, by the catalytic action of superficially (flame) oxidized iron wire upon dissolved metallic potassium free from oxide. One neck of the flask was stoppered, one was loosely plugged with cotton and the center neck was closed with a rubber stopper through which passed a glass delivery tube, bent externally at right angles, and reaching almost to the bottom of the flask. The delivery tube was connected by means of a short length of rubber tube (which could be clamped shut if desired) to a tube passing through one of the small necks of a 1000-ml. 3-necked flask. The center opening carried a mercury sealed stirrer, and the third neck was plugged with cotton. This second flask contained 300–500 ml. of liquid ammonia, in which the naphthyl halide was dissolved, at times incompletely. Potassium amide was transferred slowly to the stirred solution and suspen-

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[1] Abstracted from Part II of the Doctor's thesis of R. S. Urner, Stanford University, 1940.

[2] (a) Bergstrom, Wright, Chandler and Gilkey, *J. Org. Chem.*, **1**, 170–178 (1936); (b) Wright and Bergstrom, *ibid.*, **1**, 179–188 (1936).

[3] Gilman and Avakian, THIS JOURNAL, **67**, 349–351 (1945).

[4] Gilman, Crounse, Massie, Benkeser and Spatz, THIS JOURNAL, **67**, 2106 (1945).

sion of the naphthyl halide by loosening the clamp on the rubber tube between the flasks and momentarily closing the open neck of the amide-containing flask with the thumb. A small additional quantity of liquid ammonia was introduced and siphoned over into the 1000-ml. flask in order to wash over all of the potassium amide. At the end of the desired time (one to three hours, generally), ammonium nitrate (one mole per atom of potassium) was introduced to stop the reaction.

The ammonia was allowed to evaporate and 100 ml. of benzene was added to the residue, followed by an equal volume of water. The flask was washed out with several small portions of benzene, the benzene extracts considerably concentrated under reduced pressure of the water tap, and then shaken up with 1:1 hydrochloric acid (about 40 cc.). The precipitate of hydrochloride was washed with benzene and dried at 100°, after which it was converted to an amine mixture by warming with dilute sodium hydroxide solution. One hundred ml. (or more if necessary) of 33% acetic acid was added to the amine with stirring until all but the tar had dissolved. The tar was filtered and the filtrate made basic with ammonium hydroxide; the crude naphthylamine so obtained melted generally in the range of 90-100°, and at 109-110° after crystallizations from dilute ethanol. The mixed melting point with 2-naphthylamine was the same. The picrate melted at 190-191°, uncor., alone or mixed with the picrate of known 2-naphthylamine.

The filtrate from the 2-naphthylamine was extracted several times with 10-ml. portions of benzene. The benzene was shaken with 1:1 hydrochloric acid and the resulting hydrochloride of 1-naphthylamine filtered, washed and warmed with dilute ammonium hydroxide. The slowly solidifying oil melted at 45-47° uncor., and at 50-51° after crystallizations from ligroin; the mixed melting point with known 1-naphthylamine was the same. The picrate, hydrochloride and benzoyl derivatives had the correct melting points. The crude hydrochloride of 1-naphthylamine obtained in the reaction of potassium amide with 1-fluoronaphthalene, melted at about 272-274°; the 1-naphthylamine obtained from it melted, without crystallization, at 46-47°, and therefore contained no appreciable quantity of 2-naphthylamine. In none of the experiments, with the possible exception of those with the fluoronaphthalenes, was any secondary naphthylamine isolated.

TABLE I

Amine	Acetic acid by volume, % 33	50	100
1-$C_{10}H_7NH_2$	3.87	V. sol.	V. sol.
1,1'-$(C_{10}H_7)_2NH$	Insol.	0.017	0.55
2-$C_{10}H_7NH_2$	1.55	3.0	V. sol.
2,2'-$(C_{10}H_7)_2NH$	Insol.	Sl. sol.	0.12

TABLE II

THE REACTION OF POTASSIUM AMIDE WITH THE NAPHTHYL HALIDES[a]

Naphthyl halide	Moles, halide	Moles, KNH_2	Reaction time, hr.	Naphthylamines[b] 1-, %	2-, %	Notes
1-Cl	0.0615	0.119	1.0		45.5	
1-Cl	.123	.0615	3.0	2.0	44.9 (34)	[c]
2-Cl	.0615	.123	1.0	2.1	47.1	
2-Cl	.0695	.0615	1.0	3.2	49 (42)	[d]
1-Br	.024	.0480	1.0	2	43.2	
2-Br	.0241	.0482	2.0	0.8	52.8	
1-I	.0256	.0513	1.5	2.1	44.5	
2-I	.0256	.0513	1.5	2.6	47.5	
1-F	.0747	.0936	3+	63.5	[f]	
1-F	.0247	.0513	120	57.0		[g]
1-F	.272	.139	72	36.0		[h]
1-F	.0685	.274	3	31.3 (78.0)		[i]
2-F	.0247	.0513	3		10.6 (47)	[j]
2-F	.0479	.024	68		3.8 (4.4)	[k]

[a] With the exceptions noted, all reactions were carried out at −33° in accordance with the described procedure. Room temperature reactions required the use of a stainless steel bomb (Bergstrom, *J. Org. Chem.*, 2, 423-425 (1937)). [b] The yields are calculated on the basis of the proper limiting factor in equation (1). Figures in parentheses are calculated on the basis of the halide actually used in the reaction. [c] 1-Chloronaphthalene was recovered, 13.4 g. or 67%. The aqueous solution contained 0.496 equivalent of chloride per mole of potassium amide, in agreement with equation (1). [d] 2-Chloronaphthalene was recovered, 5.5 g. or 49%. The aqueous solution of the reaction product contained 0.505 equivalent of chloride ion per mole of potassium amide used. [e] The iodide ion formed was 97.6% of that calculated from equation (1). [f] The solution was stirred for three hours with the intermediate introduction of 200 ml. more of ammonia. The solvent was allowed to evaporate overnight and the residual solid then hydrolyzed with benzene and water. [g] In a steel bomb at about 30°. [h] In a steel bomb at 27°, with mechanical rocking. The bomb contained 200 g. of ammonia. The benzene extracts of the solid left after evaporating the ammonia were extracted alternately with 1:1 hydrochloric acid and 6 *N* sulfuric acid to remove amines which were weighed as the salts and identified by melting points. The benzene was strongly concentrated and treated with ligroin to give a reddish precipitate (1.44 g., m.p. 103-105°) which melted at 111-112° when crystallized from methanol. The picrate, hydrochloride, hydrosulfate or benzoyl derivative could not be made. Fluorine was absent, and the analysis corresponded more closely to the formula, $C_{18}H_{14}N$ than to the expected di-1-naphthylamine, which also melts at 111° (or 113°). [i] 1-Fluoronaphthalene was recovered, 60.2%. No tar was formed. The reaction took place in the presence of potassium nitrate (6.9 g.) in the hope that amino-fluoronaphthalenes might be prepared. [j] No tar was formed. 2-Fluoronaphthalene was recovered, 2.8 g. or 78%. [k] In a steel bomb at about 25°, with 200 g. of ammonia. 2-Fluoronaphthalene was recovered, 5.5 g. or 79%. A blue-gray solid, m. p. 164-165°, uncor. (0.33 g.), was separated from the benzene extracts in the same manner that the 111-112° melting precipitate in ref. *h* was obtained. It is not certain that this is di-2-naphthylamine, which melts at 170.5°. No cyanide ion was formed.

In connection with this work, some approximate solubilities (in 50 ml. of solvent at 20-25°) have been determined (see Table I).

Summary

1-Chloronaphthalene, 1-bromonaphthalene and 1-iodonaphthalene react with potassium amide in liquid ammonia at −33° to form 1-naphthylamine (2-3%) and the rearranged product, 2-naphthylamine (43-53%). 1-Fluoronaphthalene on the other hand is converted only to 1-naphthylamine. 2-Naphthylamine is the principal product of the action of potassium amide on all of the 2-naphthyl halides.

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