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# Reduction of Some *N*-substituted Aminoacetonitriles with Lithium Aluminium Hydride

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Reduction of some *N*-substituted (aryl-, benzyl- and cyclohexyl-) aminocetonitriles with lithium aluminium hydride gave besides the expected *N*-substituted ethylenediamines also the corresponding substituted *N*-methylamines in varying yields.

Some mono *N*-substituted ethylenediamines, mainly *N*-monoarylethylenediamines, were needed for further work. For their preparation the reduction of the corresponding substituted aminoacetonitriles with lithium aluminium hydride was taken into consideration.

It is well known that the reduction of nitriles to primary amines proceeds usually with good yields[1,2,3,4,5,6,7]. There is some evidence for the formation of an intermediate imine since in some cases secondary amines were obtained[8,9,10] or, by choice of appropriate reaction conditions, an aldehyde can be obtained[5,6,7]. Soffer and Katz[10] were able to demonstrate in their detailed study that the lithium aluminium hydride reduction of nitriles afforded, besides primary amines, aldehydes, hydrogen, 1,3-diamines and other higher products.

There are also some exceptions known in the case of reduction of $\alpha$- and $\beta$-aminonitriles. Besides the normal reduction, the cyano group is split off[11,12]. However with $\alpha$-branched $\beta$-aminopropionitriles the reduction proceeds normally leading to substituted 1,3-propylenediamines[13,14]. In a recent publication Wadia, Anaud and Dhar[15] reported that *N*-monoalkylaminoacetonitriles can be smoothly reduced with lithium aluminium hydride to the corresponding *N*-monoalkylethylenediamines in 60—70% yield. The formation of any other by-products was not mentioned.

In our experiments we used *N*-phenyl-, *o*-, *m*- and *p*-tolyl, cyclohexyl- and benzylaminoacetonitrile, prepared from the corresponding amines with formaldehyde-bisulfite and potassium cyanide[16,17]. These nitriles, when reduced with 100% excess lithium aluminium hydride in boiling ether, afforded the corresponding ethylenediamines only in low yields (up to 25%), but the corresponding substituted *N*-methylamines were obtained in higher yields. In one experiment the reduction of *N*-phenylaminoacetonitrile was carried out at lower temperature with cooling and the yield of *N*-phenylethylenediamine was raised up to 32.0%, although the formation of *N*-methylaniline couldn't be avoided and it was formed in appreciable amounts. Using boiling tetrahydrofurane as solvent the main reduction product was *N*-methylaniline. When after destruction of excess hydride the aqueous layer gave positive tests for cyanide ion it was evident that the splitting of the cyano group took place during the reduction procedure.

## EXPERIMENTAL

All melting-points were determined with Koflers heating microscope.

The substituted aminoacetonitriles were prepared from the corresponding amines with formaldehyde-bisulfite and potassium cyanide as described in literature[16,17].

*Reduction of substituted aminoacetonitriles with lithium aluminium hydride.*

17 g. of *N*-phenylaminoacetonitrile were dissolved in 70 ml. of anhydrous ether and added dropwise to a stirred suspension of 4.9 g. lithium aluminium hydride in 300 ml. of anhydrous ether, cooled previously to 5°C. The addition lasted two hours. The temperature was maintained at 5°C. After the addition had been completed the mixture was stirred for additional half an hour and excess of lithium aluminium hydride destroyed by adding 20 ml. of water in portions. The ethereal layer was separated, the residue extracted four times with 50 ml. of ether and the combined extracts dried with anhydrous sodium carbonate. After evaporation of the solvent, the residue was dried again with solid potassium hydroxide and amounted to 15 g. After distillation two fractions were obtained.

First fraction, b. p. 77—82°C/13 mm., amounted to 4.6 g. (yield: 33,4%) and was identified as *N*-methylaniline; hydrochloride, m. p. 122°C (reported[18] 121—2°C); acetyl derivative, m. p. 101—2°C (reported[18] 101—2°C), undepressed with an authentic specimen.

The second fraction, b. p. 128—133°C/13 mm., was identified as *N*-phenylethylenediamine 5.6 g.; yield: 32.0% (Lit.[19,20] reported b. p. 142—4°C/15 mm and 143—5°/15 mm. respectively), Diacetyl derivative, m. p. 118°C, (reported[21] 116°C).

Using the above procedure, but performing the reduction in boiling anhydrous tetrahydrofurane, *N*-methylaniline was obtained in 68.3% yield and *N*-phenylethylenediamine in 13.3% yield.

The following reductions were carried out in boiling ether and the results are as follows:

a) *N*-*p*-tolylaminoacetonitrile was reduced to *N*-methyl-*p*-toluidine in 37.5% yield, b. p. 120—128°C/15 mm., hydrochloride: m. p. 119—120°C, (reported[18] 119.5°C) and to *N*-*p*-tolylethylenediamine, b. p. 155—7°C/15 mm. (reported[20] 150°C/15 mm.) in 20.1% yield. Diacetyl derivative, m. p. 108—9°C (reported[21] 107°C), phenylthiourea derivative from the reaction with phenylisothiocyanate had m. p. 119°C.

*Anal.* 3.935 mg. subst.: 0.532 ml. $N_2$ (26°, 731 mm.)
$C_{16}H_{19}N_3S$ (285.40) calc'd: N 14.73%
found: N 14.84%

b) *N*-*o*-tolylaminoacetonitrile afforded *N*-methyl-*o*-toluidine, b. p. 105—112°C/20 mm. (reported[18] 98,5—99°C/17 mm.) in 30.0% yield (hydrochloride: m. p. 124°C) and *N*-*o*-tolyethylenediamine in 18.7% yield. B. p. 152—7°C/15 mm. (reported[20] 157—160°C/15 mm.). Phenylthiourea derivative, m. p. 113°C.

*Anal.* 3.593 mg. subst.: 0.475 ml. $N_2$ (24°, 734 mm.)
$C_{16}H_{19}N_3S$ (285.40) calc'd: N 14.73%
found: N 14.67%

c) *N*-*m*-tolylaminoacetonitrile gave after reduction *N*-methyl-*m*-toluidine, b. p. 107°C/13 mm., 207—8°C (reported[18] 206—7°C) in 60.4% yield. Hydrochloride: m. p. 136—7°C. The second fraction, b. p. 156—160°C/13 mm., was *N*-*m*-tolylethylenediamine, obtained in 16.1% yield. Hydrochloride: m. p. 216—7°C (reported[20] 168°C/28 mm. for the base and m. p. 213°C for the hydrochloride).

Phenylthiourea derivative: m. p. 109°C.

*Anal.* 3.133 mg. subst.: 0.424 ml. $N_2$ (23°, 734 mm.)
$C_{16}H_{19}N_3S$ (285.40) calc'd: N 14.73%
found: N 15.02%

d) *N*-cyclohexylaminoacetonitrile afforded *N*-methyl-cyclohexylamine in 14.8% yield. B. p. 148°C, hydrochloride: m. p. 195°C (reported[18] 145—7°C for the base and m. p. 193°C for the hydrochloride). *N*-cyclohexylethylenediamine was obtained as a fraction with b. p. 95—6°/12 mm. in 19.4% yield. Diphenylthiourea derivative: m. p. 152°C.

*Anal.* 3.164 mg. subst.: 0.397 ml. $N_2$ (25°, 731 mm.)
$C_{22}H_{28}N_4S_2$ (412.61) calc'd: N 13.58%
found: N 13.82%

e) *N*-benzylaminoacetonitrile gave after reduction *N*-methylbenzylamine in 3,5% yield. B. p. 70°C/13 mm., 180°C, hydrochloride: m. p. 176°C (reported[18] 78°C/14 mm. and 180—1°C for the base and m. p. 175°C for the hydrochloride). *N*-benzylethylenediamine was obtained in 25.0% yield, b. p. 134—5°C/18 mm. Diphenylthiourea derivative: m. p. 169°C.

*Anal.* 3.076 mg. subst.: 0.385 ml. $N_2$ (27°, 729 mm.)
$C_{23}H_{24}N_4S_2$ (420.58) calc'd: N 13.33%
found: N 13.66%

## REFERENCES

1. L. H. Amundsen and L. S. Nelson, *J. Am. Chem. Soc.* **73** (1951) 242.
2. D. Y. Curtin and S. M. Gerber, *J. Am. Chem. Soc.* **74** (1952) 4052.
3. R. F. Nystrom, *J. Am. Chem. Soc.* **77** (1955) 2544.
4. R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.* **70** (1948) 3738.
5. Houben-Weyl, *Methoden der organischen Chemie, Band XI/***1***, Stickstoffverbindungen II.*, G. Thieme Verlag, Stuttgart, 1957.
6. V. M. Mićović and M. Lj. Mihailović, *Lithium Aluminium Hydride in Organic Chemistry,* Serbian Academy of Sciences Monograph Vol. 237, Naučna knjiga, Beograd, 1955.
7. N. G. Gaylord, *Reduction with Complex Metal Hydrides,* Interscience Publ., London-New York, 1956.
8. Z. Welvart, *Compt. rend.* **233** (1951) 1121.
9. A. Dornow and K. J. Fust, *Chem Ber.* **87** (1954) 985.
10. L. M. Soffer, and M. Katz, *J. Am. Chem.. Soc.* **78** (1956) 1705.
11. Z. Welvart, *Compt. rend.* **238** (1954) 2536; **239** (1954) 1299.
12. N. J. Leonard, G. W. Leubner and E. H. Burk, *J. Org. Chem.* **15** (1950) 979.
13. H. E. Zaugg and B. W. Horrom, *J. Am. Chem. Soc.* **75** (1953) 292.
14. D. Mazoni, *Compt. rend.* **236** (1953) 1898.
15. P. S. Wadia, N. Anaud and M. L. Dhar, *J. Sci. Ind. Research (India)* **17** B (1958) 24.
16. H. Bucherer and A. Schwalbe, *Ber.* **39** (1906) 2796.
17. E. Knoevenagel, *Ber.* **37** (1904) 4073.
18. I. Heilbron and H. M. Bunbury, *Dictionary of Organic Compounds,* Eyre & Spottiswoode, London, 1953.
19. J. v. Braun, *Ber.* **70** (1937) 979.
20. J. P. Fourneau and Y. de Lestrange, *Bull. soc. chim. France* **1947**, 827.
21. H. E. Newman, *Ber* **24** (1891) 2191.

## IZVOD

### Redukcija nekih *N*-supstituiranih aminoacetonitrila s litijevim aluminijevim hidridom

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Pri redukciji nekih *N*-supstituiranih (aril, benzil i cikloheksil) aminoacetonitrila s litijevim aluminijevim hidridom nastaju pored *N*-supstituiranih etilendiamina i odgovarajući *N*-metilamini s različitim iskorištenjem.

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