The Synthesis of Some N-Arylethylenimines

By Harold W. Heine, Brij. L. Kapur, John L. Bove, Richard W. Greiner, Karl H. Klinger and Clair Mitch

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Recently the synthesis of N-phenylethylenimine by the treatment of N-β-bromoethylaniline hydrobromide with alkali in 70% alcohol was described.[1] In the present study this method of cyclization has been extended to the preparation of five new N-arylethylenimines. The N-β-bromoethylaniline hydrobromides used as precursors to the N-arylethylenimines were prepared by treating the corresponding N-β-hydroxyethylanilines with hydrobromic acid.

As noted with N-phenylethylenimine, the N-*p*-tolyl-, N-*m*-tolyl- and N-*o*-tolylethylenimines polymerize readily when exposed to carbon dioxide from the air, when emulsified with water or when treated with small amounts of acid. The N-*m*-chloro- and N-*o*-chlorophenylethylenimines under the same conditions polymerize at a slower rate. The formation and characterization of these polymers are now being studied in our laboratories and will be reported in detail presently.

The properties and analytical data of the N-arylethylenimines are given in Table I and those of the N-β-bromoethylaniline hydrobromides and the N-β-hydroxyethylanilines in Table II.

TABLE I

YIELDS AND PROPERTIES OF N-ARYLETHYLENIMINES

N-Arylethylenimine	Mol. formula	Yield,[a] %	B.p. °C.	Mm.	n^{20}_{D}	Nitrogen, % Calcd.	Found
p-Tolyl	$C_9H_{11}N$	65	76–77	8	1.5429	10.5	10.6
m-Tolyl	$C_9H_{11}N$	71	73–75	8	1.5446	10.5	10.9
o-Tolyl	$C_9H_{11}N$	57	73–75	8	1.5469	10.5	10.3
m-Chlorophenyl	C_8H_8NCl	62	92–93	10		9.11	9.06
o-Chlorophenyl	C_8H_8NCl	52	94–97	10	1.5718	9.11	9.05

[a] Yield after two distillations.

Experimental

N-Arylethylenimines.—The method[1] previously described for the preparation of N-phenylethylenimine was employed. For purpose of further characterization each of the N-arylethylenimines was converted into the corresponding N-β-bromoethylaniline hydrobromide by treatment with 48% hydrobromic acid.[1] Mixed melting points of these hydrobromides and the hydrobromides prepared from the anilinoethanols and hydrobromic acid failed to depress the melting points recorded in Table II.

N-β-Bromoethylaniline Hydrobromides.—These compounds were prepared by the procedure described by Pearlman[4] for the synthesis of N-β-bromoethylaniline hydrobromide. The N-β-bromoethyl-*o*-toluidine, the N-β-bromoethyl-*m*-chloroaniline and the N-β-bromoethyl-*o*-chloroaniline hydrobromides were recrystallized from absolute ethanol while the *p*-methyltoluidine homolog was recrystallized from chloroform and the *o*-methyltoluidine homolog was precipitated from a chloroform solution by the addition of ether.

N-β-Hydroxyethylanilines. General Procedure (A).—In a one-liter round-bottomed flask was placed two moles of the appropriately substituted aniline and one mole of ethylene chlorohydrin. The mixture was refluxed gently for 10–12 hours. The reaction mixture was then cooled and made alkaline with 10% sodium hydroxide. Two layers were formed. The top layer was removed and saved. The bottom layer was extracted with ether and the ethereal extracts combined with the top layer. After drying over anhydrous sodium sulfate the solution was filtered and the ether removed. The residue was subjected to a vacuum distillation. The first fraction contained the unreacted aniline. The second fraction was collected usually over a 15° range and then redistilled twice.

In the case of N-β-hydroxyethyl-*p*-toluidine and N-β-hydroxyethyl-*m*-chloroaniline the reaction mixture (after being treated with alkali) was subjected to a steam distillation to remove the unreacted aniline. The residue was then extracted with ether, the ethereal extracts dried, the ether removed and the product distilled.

General Procedure (B).—In a pressure bottle was placed one mole of the appropriately substituted aniline and one-half mole of liquefied ethylene oxide. The bottle was stoppered and heated at 120° by means of heating tape for 8 hours. The reaction vessel was shaken during the entire reaction time. The mixture was cooled and vacuum distilled. In each case a small forerun of unreacted aniline was collected. The physical constants of the substituted ethanols prepared by these two methods checked with one another. This method was not tried with *m*-chloroaniline.

TABLE II

YIELDS AND PROPERTIES OF N-β-BROMOETHYLANILINE HYDROBROMIDES AND N-β-HYDROXYETHYLANILINES

Compound	Mol. formula	Yield,[a] %	M.p., °C.	Bromine, % Calcd.	Found
N-β-Bromoethyl-*p*-toluidine	$C_9H_{13}NBr_2$	64	180–181	54.2	53.9
N-β-Bromoethyl-*m*-toluidine	$C_9H_{13}NBr_2$	87	120–121	54.2	54.1
N-β-Bromoethyl-*o*-toluidine	$C_9H_{13}NBr_2$	77	210–213	54.2	54.2
N-β-Bromoethyl-*m*-chloroaniline	$C_8H_{10}NBr_2Cl$	61	145–146	50.7	50.5
N-β-Bromoethyl-*o*-chloroaniline	$C_8H_{10}NBr_2Cl$	66	189–191	50.7	50.2

Compound	Mol. formula	Yield,[b] % Procedure A	Procedure B	B.p. °C.	Mm.	n^{20}_{D}	Nitrogen, % Calcd.	Found
N-β-Hydroxyethyl-*p*-toluidine[c]	$C_9H_{13}NO$	60	61	155–157	8	1.5659	..	..
N-β-Hydroxyethyl-*m*-toluidine	$C_9H_{13}NO$	50	50	156–159	10	1.5678	9.26	9.54
N-β-Hydroxyethyl-*o*-toluidine[d]	$C_9H_{13}NO$	50	57	144–146	7	1.5707	..	..
N-β-Hydroxyethyl-*m*-chloroaniline	$C_8H_{10}NOCl$	64	..	174–177	10	1.5892	8.15	8.11
N-β-Hydroxyethyl-*o*-chloroaniline[e]	$C_8H_{10}NOCl$	61	28	156–157	11	1.5858	8.16	8.06

[a] Yield after two recrystallizations. [b] Yield after two distillations. [c] Melting point 41–42°. Prepared by Adams[2] who reported a melting point of 42–43° and b.p. 153–155° (4 mm.). [d] Prepared by Dains[3] who reported a b.p. 172° (12 mm.). Also prepared by Adams[2] who reported a b.p. 145–150° (3 mm.) and n^{20}_{D} 1.5675. [e] Prepared by Adams[2] who reported n^{20}_{D} 1.5185 and b.p. 148–152° (3 mm.).

DEPARTMENT OF CHEMISTRY
BUCKNELL UNIVERSITY
LEWISBURG, PENNSYLVANIA

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[1] H. W. Heine, B. L. Kapur and C. Mitch, THIS JOURNAL, **76**, 1173 (1954).

[2] R. Adams and J. B. Segor, *ibid.*, **45**, 785 (1923).

[3] F. B. Dains, R. Q. Brewster, J. S. Blair and W. C. Thompson, *ibid.*, **44**, 2637 (1922).

[4] W. Pearlman, *ibid.*, **70**, 871 (1948).