[CONTRIBUTION FROM THE RESEARCH LABORATORY OF RALPH L. EVANS ASSOCIATES]

sym-Dialkylethylenediamines

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Although a number of unsymmetrically substituted dialkylethylenediamines have been prepared by several general methods,[1] only a few members of the symmetrical series have been described. The *sym*-dimethyl and diethyl compounds were obtained through the Hinsberg reaction[2,3,4] or by way of dinitrosophenyl derivatives.[5] The direct condensation of methylamine with ethylene dihalides was first successfully tried by Gibbs,[6] and recently a 50% yield of *sym*-dimethylethylenediamine was obtained through this reaction.[7] Dialkylidene ethylenediamines, formed readily from ethylenediamine and two molecular equivalents of an aldehyde, yield the dialkyl compounds when reduced with sodium and alcohol or sodium amalgam. *sym*-Diisobutylethylenediamine was synthesized in this manner.[8]

Our interest was centered in the preparation of higher dialkylethylenediamines, and because of previous experience[9] we decided to attempt the direct condensation of ethylenediamine with two moles of alkyl halide. The new bases, obtained in 84–98% yields, were shown to be secondary amines by means of the Hinsberg test and the formation of dinitroso derivatives. They are oily liquids or low-melting solids with slight odor and strongly basic reaction, soluble in ether, benzene, ligroin, and glacial acetic acid; less soluble in alcohol; insoluble in water. Dilute mineral acids form salts of low solubility.

Experimental

With the exception of decyl bromide the alkyl chlorides were used in the condensation, and the general procedure was as follows:

A mixture of the alkyl halide (1 mole) and 95% ethylenediamine (0.5 mole) was heated in an oil-bath under reflux for three hours to boiling temperature. A solid formed gradually during the reaction and, after the mixture had cooled, 1500 ml. of a 10% aqueous sodium hydroxide solution was added with stirring. The mixture was extracted with ether. The ether extracts were dried with anhydrous sodium sulfate and filtered, and the solvent was evaporated. The residue was suspended in 1500 ml. of 10% caustic soda solution and extracted again with ether, yielding the pure base.

The dipicrates, yellow prisms, were prepared in alcoholic medium and recrystallized from alcohol.

The dihydrochlorides were formed by bubbling dry hydrogen chloride gas through the solution of the base in anhydrous ether, and were then recrystallized from alcohol.

TABLE I

DIALKYLETHYLENEDIAMINES, ($RNHCH_2CHCNHR$)

R	Yield, %	Base m. p., °C.	Dipicrate M. p., °C.	Dipicrate Carbon, % Calcd.	Dipicrate Carbon, % Found	Dipicrate Hydrogen, % Calcd.	Dipicrate Hydrogen, % Found	Dihydrochloride, m. p., °C.
n-Octyl	84	−22 to −20	108					275–276[a]
n-Decyl	94	0–2	111	51.13	50.79	6.77	6.49	251–252
n-Dodecyl	97	15–17	112	53.40	53.42	7.26	7.22	246–248
n-Tetradecyl	98	24–26	148	55.38	55.22	7.69	7.69	210–212
n-Hexadecyl	93	34–35	108	57.14	56.88	8.07	8.25	221–223
n-Octadecyl[b]	98	62–64						197–199

[a] *Anal.* Calcd. for $C_{18}H_{40}N_2 \cdot 2HCl$: C, 60.50; H, 11.76. Found: C, 60.51; H, 11.70. [b] Base recrystallized from ethyl acetate. *Anal.* Calcd. for $C_{38}H_{80}N_2$: C, 80.85; H, 14.18. Found: C, 81.48; H, 14.40.

Summary

1. The straight-chain, even-numbered, symmetrical dialkylethylenediamines from C_8 to C_{18} were synthesized by condensing highly concentrated (95%) ethylenediamine with alkyl halides, using two moles of the halide to one mole of ethylene diamine.

2. The bases were characterized in form of their dipicrates and dihydrochlorides.

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RECEIVED MARCH 14, 1946

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