[Contribution from the Department of Chemistry, Clark University]

PREPARATION OF TRIMETHYLENEDIAMINES

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The purpose of this paper is to report on the preparation of a number of β-alkylaminopropionitriles and the conversion of some of these to the corresponding monoalkyltrimethylenediamines. The by-products obtained in the synthesis of both classes of substances are also described.

The reaction between acrylonitrile and primary amines was carried out according to the method of Holcomb and Hamilton (1). When an excess of amine is used, the main product of the reaction is the monosubstituted amine. A small yield of the disubstituted amine is also obtained in most cases. Catalytic reduction of the monosubstituted product results in the formation of the monoalkyltrimethylenediamine in good yield as well as a small amount of the secondary amine in accordance with the mechanism of von Braun, *et al.* (2).

In the present research the mononitrile was prepared from cyclohexylamine and both mono- and di-nitriles were prepared from *n*-dodecylamine, *n*-butylamine, and benzylamine. The monocyclohexyl and dodecyl derivatives were reduced to the corresponding primary and secondary amines. Of the compounds prepared, β-cyclohexylaminopropionitrile, β-dodecylaminopropionitrile, and β-butylaminopropionitrile have been reported by Hoffman and Jacobi (3); γ-cyclohexylaminopropylamine has been described by Tarbell, *et al.* (4), and the β-benzylaminopropionitrile has been reported by King and MacMillan (5). These workers give substantially the same physical properties for the nitriles and amines as those obtained in the present work, but did not report on the by-products of their reactions.

In this investigation, the mononitriles were obtained as colorless liquids while the dinitriles were isolated as pale yellow liquids. The nitriles were reduced with Raney nickel catalyst prepared according to the procedure of Covert and Adkins (6). Methanol saturated with ammonia was used as a solvent in order to repress formation of the secondary amine, according to the suggestion of Schwoegler and Adkins (7). The experimental results and analytical data are given in Table I for the nitriles and in Table II for the amines. The methods used for preparation of these substances are described below.

EXPERIMENTAL PART

N-(γ-Cyclohexylaminopropyl)-N′-phenyl urea. The phenyl urea derivative of cyclohexylaminopropylamine was prepared in the usual manner and recrystallized twice from ethanol. Colorless crystals, m.p. 202–203°, were obtained.

Anal. Calc'd for $C_{16}H_{25}N_3O$: N, 15.26. Found: N, 15.07.

Bis-γ-cyclohexylaminopropylamine. This substance was obtained as a higher-boiling fraction in the preparation of cyclohexylaminopropylamine. The product was isolated as a small amount of pale yellow liquid, boiling range 210–224° at 11 mm.

β-Dodecylaminobispropionitrile. This substance was obtained as a high-boiling fraction in the preparation of β-dodecylaminopropionitrile. It was isolated as a colorless liquid boiling at 182–184° at 1 mm.

γ-Dodecylaminopropylamine. To 40 ml. of methanol which had been saturated with ammonia at 0° was added 40 g. of β-dodecylaminopropionitrile. The solution was reduced in the presence of Raney nickel at 1400 lbs. of hydrogen and at 120–130° for four hours. After filtration and removal of the volatile components, the residue was distilled under diminished pressure. Yield, 35 g. (86%) of N-dodecyltrimethylenediamine, b.p. 137–141° at 1 mm. The product was a colorless liquid which solidified in the receiver to a colorless waxy solid, m.p. 24.5–25.5°.

Bis-γ-dodecylaminopropylamine. This substance was obtained as a higher-boiling fraction in the preparation of γ-dodecylaminopropylamine. It was isolated as a pale yellow liquid, boiling range 190–210° at 1 mm.

TABLE I

NITRILES

SUBSTANCE	B.P., °C./MM.	YIELD, %	LIT. REF.	ANALYSES N, %	
				Calc'd	Found
β-Cyclohexylaminopropionitrile	144–145/11	70	(3)	18.41	18.30
β-*n*-Dodecylaminopropionitrile	152–156/2	91	(3)	11.75	11.41
β-*n*-Dodecylaminobispropionitrile	182–184/1	—	—	14.42	14.20
β-*n*-Butylaminopropionitrile	102–105/10	70	(3)	22.20	22.00
β-*n*-Butylaminobispropionitrile	120–128/10	—	—	23.45	23.33
β-Benzylaminopropionitrile	181–184/24	84	(5)	17.50	17.34
β-Benzylaminobispropionitrile	173–175/3–4	—	—	19.70	19.49

TABLE II

AMINES

SUBSTANCES	B.P., °C./MM.	YIELD, %	LIT. REF.	MOL. WT.		ANALYSES N, %	
				Calc'd	Found	Calc'd	Found
γ-Cyclohexylaminopropylamine	85–89/2	74	(4)	156	165	17.93	17.68
Bis-γ-cyclohexylaminopropylamine	210–224/11	—	—	296	300	14.22	14.05
γ-Dodecylaminopropylamine	137–141/1	86	—	242	237	11.55	11.76
Bis-γ-dodecylaminopropylamine	182–184/1	—	—	468	457	8.98	9.29

β-Butylaminobispropionitrile. The dinitrile was isolated as a high-boiling fraction from the residue remaining after the distillation of β-butylaminopropionitrile. A small amount of a pale yellow liquid, boiling range 120–128° at 10 mm., was obtained.

β-Benzylaminobispropionitrile. A small yield of the disubstituted amine, β-benzylaminobispropionitrile, boiling at 173–175° at 4 mm., was obtained on further distillation of the residue obtained from the distillation of β-benzylaminopropionitrile.

SUMMARY

The preparation of β-alkylaminopropionitriles and β-alkylaminobispropionitriles by the reactions of amines with acrylonitrile and the preparation of γ-alkylaminopropylamines and of bis-γ-alkylaminopropylamines by reduction

of the corresponding β-alkylaminopropionitriles are described. Of the substances discussed, β-dodecylaminobispropionitrile, β-butylaminobispropionitrile, β-benzylaminobispropionitrile, N-(γ-cyclohexylaminopropyl)-N′-phenyl urea, bis-γ-cyclohexylaminopropylamine, γ-dodecylaminopropylamine, and bis-γ-dodecylaminopropylamine have not been reported previously.

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