prepared by making up stock solutions (*ca.* 0.1 *N*) in abs. ethanol of hydrogen chloride, formic acid and triethylamine. Aliquots of these three solutions were combined, 5 to 10 ml. of DMF was added and the solution was made up to *ca.* 100 ml. with abs. ethanol before titrating.

Titration of a solution containing hydrogen chloride, formic acid and triethylammonium chloride gave inflection points at *p*H 6.0, 8.7 and 12.2. Titration of a 1-bromooctane solution in DMF which had stood 324 days gave inflection points at *p*H 6.0, 8.8 and 12.1 while with the 2-bromoöctane–DMF solution (aged 304 days) the inflection points were at *p*H 5.8, 8.8 and 12.0. (The individual *p*H determinations are probably not in error by more than ±0.1 unit.)

Table IV gives the products formed in DMF solutions of 1- (and 2-)bromoöctanes.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE ROHM & HAAS COMPANY]

t-Carbinamines, $RR'R''CNH_2$. I. Reaction with Alkyl Halides and Alkylene Oxides[1]

BY NEWMAN BORTNICK, LEO S. LUSKIN, M. D. HURWITZ, W E CRAIG, L. J. EXNER AND J. MIRZA

RECEIVED NOVEMBER 18, 1955

The reactions of a variety of alkyl halides and alkylene oxides with *t*-butylamine and *t*-octylamine have been investigated. Pure secondary amines were obtained in satisfactory yield. Tertiary amine derivatives were also obtained by the action of methylating agents or of ethylene oxide upon both amines and in low yield by the alkylation of *t*-butylamine with benzyl chloride.

A study has been made of the reactions of *t*-butylamine (I) and of *t*-octylamine (1,1,3,3-tetramethylbutylamine) (II) which are commercially available examples of highly branched primary aliphatic amines, $R(R')(R'')CNH_2$. The results of alkylations by means of alkyl halides and alkylene oxides are reported in this communication.

Pure secondary amines were obtained by the reaction of most alkyl halides with both amines in molar ratios of at least 1 to 2 (Table I). High yields were obtained with reactive halides, such as benzyl chloride and its derivatives, or *n*-alkyl bromides. Substituted alkyl chlorides, such as β-chloroalkyl ethers and 1,2-dichloroethane, reacted very slowly. 2-Bromopropane or 2-bromobutane and *t*-butylamine gave products which were difficult to purify; the corresponding derivatives of *t*-octylamine were obtained in low yield.

The catalytic influence of water was noted in the reactions of II with 1,2-dichloroethane and with 1,2-dibromoethane, for its omission led to complete failure in the former and decreased yield in the latter instance. The effect of water[2] may be due to its behavior as an electrophilic agent in this concerted displacement process.[3]

The action of methyl iodide or dimethyl sulfate on these amines led to a mixture of primary, secondary and tertiary amines (separable by careful fractionation) and quaternary ammonium salts. The use of excess methyl iodide gave the quaternary ammonium derivative of II in good yield.[4]

Both secondary and tertiary amines were also obtained by the reaction of II with ethylene chlorohydrin. In other reactions, the absence (or occasional small yield) of tertiary amines was the result of steric effects which decrease the reactivity of the secondary amines. Under similar conditions, substantial amounts of both secondary and tertiary amines were obtained from the reaction of *n*-butylamine and benzyl chloride. Earlier studies[5] have also indicated the importance of steric factors in the reactions of these amines, although their basicity is comparable to similar, less branched amines.[6]

Efforts were made to force the formation of tertiary amine derivatives of I. The use of excess benzyl chloride followed by slow addition of alkali gave low yields of the desired *t*-butyldibenzylamine. However, similar treatment of II was accompanied by cleavage, and considerable amounts of diisobutylene and tribenzylamine were isolated.

Normal quaternizations giving *t*-octyltrimethylammonium chloride and benzyl-*t*-butyldimethylammonium chloride were carried out. There is some evidence, which is being investigated, that quaternizations of N,N-dialkyl-*t*-octylamines do not always proceed to the expected product.

From the reaction of dichlorodiphenylmethane with *t*-octylamine, N-*t*-octylbenzophenoneimine was prepared in low yield.[7]

No examples of the reaction of *t*-carbinamines with epoxides were found in the literature.[8] Interaction of I or II with ethylene oxide led to secondary and tertiary amines (Table II). Either could be obtained as the principal product by adjustment of the molar ratios of the reactants. Under anhydrous conditions, these reactions proceeded very slowly. Addition of water promoted vigorous and rapid reactions. The water is considered to act as an electrophilic agent which facilitates the opening of the oxirane ring.[9]

Secondary amines were obtained exclusively

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(1) Presented in part before the Division of Organic Chemistry at the 119th Meeting of the American Chemical Society, Cleveland, Ohio, April 10, 1951.

(2) W. R. Boon, *J. Chem. Soc.*, 307 (1947).

(3) C. G. Swain and W. P. Langsdorf, Jr., THIS JOURNAL, **73**, 2813 (1951).

(4) N. Kornblum and D. L. Kendall, private communication.

(5) (a) G. Vavon and L. Bourgeois, *Compt. rend.*, **202**, 1593 (1936); (b) O. L. Brady and F. R. Cropper, *J. Chem. Soc.*, 507 (1950); (c) M. Brander, *Rec. trav. chim.*, **37**, 67 (1917).

(6) G. Vexlearschi, *Compt. rend.*, **228**, 1655 (1949).

(7) L. M. Long, C. A. Miller and H. D. Troutman, THIS JOURNAL, **70**, 900 (1948).

(8) That such reactions are not new, however, may be inferred from the description of di-2-chloroethyl-*t*-butylamine, C. E. Redemann, S. W. Chaikin and R. B. Fearing, *ibid.*, **70**, 1648 (1948); *cf.* also E. L. Carpenter, U. S. Patent 2,453,062 (to American Cyanamid Co.).

(9) C. G. Swain, THIS JOURNAL, **72**, 4578 (1950); S. Winstein and R. B. Henderson in R. C. Elderfield, "Heterocyclic Compounds," Vol. I. John Wiley and Sons, Inc., New York, N. Y., 1950, p. 27; L. Schechter, J. Wynstra and R. P. Kurkjy, *Ind. Eng. Chem.*, **48**, 94 (1956).

TABLE I

N-ALKYL-*t*-CARBINAMINES[a]

Compound	Yield, %	B.p. °C.	B.p. Mm.	$n^{25}D$	d^{25}_{25}	Nitrogen, % Calcd.	Nitrogen, % Found
$R'NHCH_3$[b]	..	73–74[b]		1.3952	0.7323	15.9	15.0
$R'N(CH_3)_2$	..	89–90		1.4020	.7372	13.8	13.7
$R'NHC_2H_5$	50	76–79		1.3941	....	13.8	13.6
$R'NHC_3H_7$-*n*	40	112–114		1.4025	.7443	12.1	11.9
$R'NHCH_2C_6H_5$	84	91	12	1.4941	.8950	8.6	8.5
$R'N(CH_2C_6H_5)_2$	4	142–145	3	M.p. 68–70[c]		5.5	5.5
$R''NHCH_3$[j]	40	165		1.4265	0.7823	9.8	9.5
$R''N(CH_3)_2$[j]	10	174–175		1.4330	.7900	8.9	8.8
$R''NHC_2H_5$	76	168–169		1.4278[d]	.7780[d]	8.9	8.9
$R''NHCH_2CH_2OH$[e]	50	118–120	15	....	....	[e]	[e]
$R''NHC_3H_7$-*n*	83	71–74	7	1.4303	.7848	8.7	8.6
$R''NHCH(CH_3)_2$	25	174–176		1.4268	.7826	8.7	8.4
$R''NHCH_2CH{=}CH_2$	83	184–187		1.4410	.8018	8.3	8.2
$R''NHCH(CH_3)CH_2CH_3$	22	100–102	30	1.4312	.7893	7.6	7.6
$R''NHCH_2CH{=}CHCH_2C(CH_3)_3$	75	123–125	10	1.4501	.8060	5.8	5.7
$R''NHCH_2CH_2OCH_2CH_2OC_4H_9$-*n*	19	103–107	0.3	1.4420	.8761	5.1	5.0
$R''NHCH_2C_6H_5$	77	100–101	1.2	1.4955	.8934	6.4	6.4
$R''NHCH_2C_6H_4$-*p*-Cl	76	137–140	3	1.5081	.9859	5.5	5.5
$R''NHCH_2C_6H_3$-2,4-Cl_2	89	139–143	1.5	1.5187	1.0727	4.9	4.9[f]
$R''NHCH_2C_6H_4$-x-2-C_8H_{17}	46	169–184	1	1.4909	0.8813	4.2	4.1[g]
$R''NHCH_2CH_2OC_6H_5$	85	136–140	0.3	1.4980[d]	.9399[d]	5.6	5.6
$R''NHCH_2CH_2OCH_2CH_2OC_6H_5$	16	143–152	0.35	1.4923	.9603	4.8	4.7
$R''NHCH_2CH_2COH_2CH_2OC_6H_4$-*o*-Cl	23	189–191	3	1.5033	1.0408	4.3	4.2[h]
$R''NHCH_2CONH_2$	56	.....	..	M.p. 102–104[i]		15.0	14.9
$(R''NHCH_2{-})_2$	92	120	0.5	1.4529	0.8413	9.8	9.7
$(R''NHCH_2)_2CH_2$	81	118–121	0.25	1.4553	.8376	9.4	9.4
1,4-$(R''NHCH_2)_2C_6H_4$	65	208–212	1.8	1.4983	.9020	7.8	7.7

[a] $R' = (CH_3)_3C{-}$; $R'' = (CH_3)_3CCH_2C(CH_3)_2{-}$. [b] 1-*t*-Butyl-1-methyl-3-phenylurea needles from isoöctane, m.p. 127–129°, calcd. for $C_{12}H_{18}N_2O$: N, 13.6, found N, 13.8. P. Sabatier and A. Mailhe, *Compt. rend.*, **144**, 957 (1907), reported b.p. 58–60° for the amine, m.p. 118 for the urea. [c] Reference 19 reported b.p. 138° (3 mm.), m.p. 70°. [d] At 20°. [e] Prepared from ethylene chlorohydrin; neut. equiv. calcd. 173; found 171. [f] Calcd. for $C_{15}H_{23}Cl_2N$: Cl, 24.6. Found: Cl, 24.9. [g] Calcd. for $C_{23}H_{41}N$: C, 83.3; H, 12.4. Found: C, 83.3; H, 12.4. Analysis by C. W. Nash. [h] Calcd. for $C_{18}H_{30}ClNO_2$: Cl, 10.8. Found: Cl, 10.9. [i] Recrystallized from ethanol. [j] T. D. Perrine, *J. Org. Chem.*, 16, 1303 (1951), reported b.p. 85–95° (10 mm.) and 107° (10 mm.) for *t*-octylmethylamine and *t*-octyldimethylamine, respectively.

TABLE II

HYDROXYALKYL-*t*-CARBINAMINES[a]

Compound	Yield, %	B.p. °C.	B.p. Mm.	$n^{25}D$	d^{25}_{25}	Nitrogen, % Calcd.	Nitrogen, % Found
$R'NHCH_2CH_2OH$[b]	72	90–92	25	M.p. 43–45		12.0	11.9
$R'N(CH_2CH_2OH)_2$	90	130–137	12	1.4666	0.9830	8.7	8.6
$R''NHCH_2CH_2OH$	69	79–84	0.3	1.4583	.8818	8.0	7.9
$R''N(CH_2CH_2OH)_2$	84	162–170	4	M.p. 50–51		6.5	6.5
$R''NHCH_2CHOHCH_3$	91	109–110	10	1.4515	0.8789	7.5	7.4
$R''NHCH_2C(CH_3)_2OH$	60	93–95	0.9	1.4443	.8678	7.0	6.9
$R''NHCH_2CHOHCH{=}CH_2$	26	83	3	1.4630	.8934	7.0	6.8
$R''NHCH_2CHOHC_6H_5$	23	.....	..	M.p. 100–101.5		5.6	5.6
$R''NHCH_2CHOHCH_2OC_6H_5$	61	160	1.4	M.p. 48–50		5.0	5.0
$(R''NHCH_2)_2CHOH$	82	135–137	0.2	1.4660	0.8871	8.9	8.9

[a] $R' = (CH_3)_3C{-}$; $R'' = (CH_3)_3CCH_2C(CH_3)_2{-}$. [b] R. E. Holmen and D. D. Carroll, THIS JOURNAL, **73**, 1859 (1951).

when substituted derivatives of ethylene oxide were employed. Epichlorohydrin reacted vigorously with II to give 1,3-di-*t*-octylamino-2-propanol. Water was again found to be a necessary constituent of the reaction mixtures.

Some of the alkanolamines were converted by known procedures to chloroalkylamines[10] and to 1-alkylethyleneimines.[11]

Acknowledgments.—We are grateful to R. S. Cook, J. O. van Hook, S. Melamed, C. S. Schmidle, G. E. Gantert and J. L. Rainey, who prepared some of these compounds, and to E. L. Stanley and Thomas P. Callan under whose direction the necessary analyses were performed. We also wish to thank N. Kornblum and D. L. Kendall of Purdue University for permission to include their preparation of *t*-octyltrimethylammonium iodide.

Experimental Section

Starting Materials.—*t*-Butylamine and *t*-octylamine were commercial materials available from the Rohm & Haas Co. Octylbenzyl chloride,[12] 1-chloro-5,5-dimethylhexene-

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[10] K. Ward, Jr., THIS JOURNAL, **57**, 914 (1935).

[11] R. C. Elderfield and H. A. Hagemann, *J. Org. Chem.*, **14**, 622 (1949).

[12] P. L. de Benneville, U. S. Patent 2,525,777 (to Rohm and Haas Co.).

2,[13] 2-phenoxyethyl 2′-chloroethyl ether,[14] 2-*o*-chlorophenoxyethyl 2′-chloroethyl ether[15] and 2-butoxyethyl 2′-chloroethyl ether[16] were prepared according to published methods. The other halides and the epoxides were commercially available materials.

N-*t*-Octylbenzylamine. (a).—Benzyl chloride (III, 380 g., 3 moles) was added rapidly to II (775 g., 6 moles) heated under reflux. After 1 hr., the pot temperature reached 200° and the solid which formed had redissolved. After cooling, the cake was treated with 4 *N* aqueous sodium hydroxide solution (750 ml.). Upon distillation of the oil which separated, 448 g. (3.54 moles) of II was recovered and 504 g. (2.30 moles) of the colorless, oily product, b.p. 100–101° (1.2 mm.), was obtained. This represented a yield of 93% based on unrecovered amine or 76.7% based on III.

Most of the compounds listed in Table I were prepared by this procedure. The reaction mixtures containing I were usually heated at 40–130°.

(b).—III (380 g., 3 moles) was added to refluxing II (378 g., 3 moles). In the course of 2 hr., there was added 50% aqueous sodium hydroxide solution (250 g., 3.1 moles). The temperature gradually fell to 105°. Water was removed continuously during the addition of alkali; a maximum pot temperature of 145° was attained upon completion of the dehydration. The cooled mixture was washed with water and the oil layer was distilled from a modified Claisen flask. The forerun, consisting largely of II and a little benzyl chloride, was treated with excess hydrochloric acid. The insoluble portion was distilled to give 27 g. of diisobutylene, b.p. 102–106°, $n^{25}\text{D}$ 1.4103. The values given for the components of diisobutylene are b.p. 101.5 and 104.5°, $n^{20}\text{D}$ 1.4082 and 1.4158, respectively.[17]

The material which remained after distillation of the octylbenzylamine (obtained in 52.5% yield) solidified on cooling. Recrystallization from methanol gave 76 g. of tribenzylamine as large, colorless, rhombic scales, m.p. 93–94°. An additional 22 g. (m.p. 91–93°) was recovered from the filtrate.

Anal. Calcd. for $C_{21}H_{21}N$: N, 4.87. Found: N, 4.86.

N,N′-Di-*t*-octylethylenediamine.—1,2-Dibromoethane (188 g., 1 mole) was slowly added to a mixture of II (650 g., 5 moles) and water (50 ml.) which was stirred under reflux. Heating was continued for 8 hr. The usual work-up gave 260 g. (92%) of product, b.p. 120° (0.5 mm.). The omission of water led to a yield of 80% under the same conditions.

When II (193.5 g.) was heated under reflux with 1,2-dichloroethane (49.5 g.) for 8 hr., there was no evidence of reaction. Heating for 8 hr. after the addition of water (50 ml.) gave 36 g. (25%) of the diamine.

Methylation of *t*-Octylamine.—The addition of dimethyl sulfate (126 g., 1 mole) to II (130 g., 1 mole) during 5 hr. was accompanied by evolution of heat which maintained the temperature at 60–70°. After standing overnight, the mixture was treated with a solution of sodium hydroxide (44 g.) in water (750 ml.) and heated under reflux for 2 hr. The oil, combined with a benzene extract of the aqueous layer, was dried azeotropically and evaporated under a short packed column to remove most of the solvent. The residual amines were distilled in a Todd precise fractionation assembly (90 cm. × 13 mm.) packed with nichrome helices.[18] There was obtained II (15 g.), an intermediate fraction (4 g.), *t*-octylmethylamine (58 g.), an intermediate fraction (11 g.) and *t*-octyldimethylamine (17 g.).

Methylation of *t*-Butylamine.—A mixture of I (146 g., 2 moles) and xylene (150 ml.) was treated with methyl iodide (142 g., 1 mole) below 40°, then heated at 85° for 3 hr. Upon basification and cooling, the solid which separated was collected and washed thoroughly with acetone. The yield of *t*-butyltrimethylammonium iodide was 28 g. (34%), m.p. 258° dec.

Anal. Calcd. for $C_7H_{18}IN$: N, 5.7. Found: N, 5.7.

The filtrate was distilled under a packed column to give 82 g. of I and 57 g. of wet mixed amines, b.p. 46–104°. After drying over solid caustic, fractionation of the higher amines[18] gave 5 g. of *t*-butylmethylamine and 9 g. of *t*-butyldimethylamine. The latter was converted to *t*-butylbenzyldimethylammonium chloride, m.p. 191–192° dec., in quantitative yield by reaction with III in acetonitrile.

Anal. Calcd. for $C_{13}H_{22}ClN$: Cl^-, 15.5; N, 6.2. Found: Cl^-, 15.4; N, 6.4.

***t*-Octyltrimethylammonium Iodide.**[4]—Methyl iodide (42.6 g., 0.3 mole) was slowly added to II (12.9 g., 0.1 mole) followed by a solution of sodium hydroxide (24 g., 0.6 mole) in water (100 ml.). The mixture was heated under reflux for 5 hr. The crude crystals obtained after chilling were recrystallized from dilute aqueous alkali, then from absolute ethanol. The white crystalline solid, m.p. 262–264° dec., weighed 16 g. (77%), m.p. 264° dec., when recrystallized from ethanol.

Anal. Calcd. for $C_{11}H_{26}IN$: I, 42.5; N, 4.68. Found: I^-, 42.5; N (Dumas), 4.38, 4.48.

Benzylation of Butylamines.—III (126.5 g., 1 mole) and 33% aqueous sodium hydroxide solution (120 g., 1 mole) were added in succession to I (73 g., 1 mole) in benzene (12 ml.) while stirring and heating under reflux. Heating was continued for 12 hr. The products were N-*t*-butylbenzylamine (51% yield) and 10 g. (8% based on III) of N-*t*-butyldibenzylamine,[19] b.p. 142–145° (3 mm.), a colorless distillate which solidified, m.p. 68–70°.

The general procedure applied to 2 moles of I and 1 mole of III (11 hours at 50–130°) gave 82–84% and 4.5% of the above products, respectively.

Similarly the reaction of *n*-butylamine and III (3 hr. at 50–130°) gave N-*n*-butylbenzylamine (58%), b.p. 77° (1 mm.), $n^{25}\text{D}$ 1.4992, d^{25}_{25} 0.9024 (N, calcd., 8.6, found 8.5), and N-*n*-butyldibenzylamine[19] (32%), b.p. 122° (0.4 mm.), $n^{25}\text{D}$ 1.5373, d^{25}_{25} 0.9646 (N, calcd. 5.5, found 5.6), hydrochloride (from water) m.p. 124–126°.

Anal. Calcd. for $C_{18}H_{24}ClN$: Cl, 12.2; N, 4.8. Found: Cl, 12.2; N, 4.8.

N-*t*-Octylbenzophenoneimine.—A mixture of dichlorodiphenylmethane[20] (138 g., 0.58 mole) and II (225 g., 1.75 moles) was heated under reflux for 24 hours. The oil remaining after removal of *t*-octylamine hydrochloride was distilled. The product, b.p. 107–115° (0.5 mm.), solidified and was recrystallized from ethanol. The yield was 43 g. (25%) of a white powder, m.p. 72–73°.

Anal. (by C. W. Nash) Calcd. for $C_{21}H_{27}N$: C, 86.0; H, 9.3; N, 4.8. Found: C, 86.1; H, 9.4; N, 4.7.

2-N-*t*-Butylaminoethanol and 2,2′-(*t*-Butylimino)-diethanol.—Ethylene oxide (88 g., 2 moles) was passed into a solution of *t*-butylamine (292 g., 4 moles) in water (125 ml.) during 45 minutes. The temperature, initially 60°, rose to 75°. The mixture was heated under reflux for 90 minutes, then distilled from a modified Claisen flask and a short air condenser of wide bore, the distillates being collected in receivers cooled in ice-water. The product (145 g.) was obtained as a white, hygroscopic solid, b.p. 80–83° (12 mm.), 90–92° (25 mm.), m.p. 43–45°, and an additional 33 g. was obtained by redistilling the aqueous forerun. The total yield was 76%. From the residue, the tertiary amine (15 g., 9%) was obtained as a pale yellow oil, b.p. 136–139° (12 mm.).

N-*t*-octylaminoalkanols were prepared similarly by the dropwise addition of the appropriate oxide (1 mole) to a mixture of water (100–150 ml.) and *t*-octylamine (2 moles) which contained sufficient dioxane to give a homogeneous solution (Table II).

2,2′-(*t*-Octylimino)-diethanol.—Ethylene oxide was bubbled into *t*-octylamine (259 g.) containing water (18 g.) at 70° until 180 g. was absorbed. The clear reaction mixture was distilled, and the product (375 g., 84%) was obtained as a colorless oil, b.p. 162–170° (4 mm.), which solidified in the receiver, m.p. 50–51°.

2,2′-(*t*-Butylimino)-diethanol was obtained in 90% yield in a similar manner.

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[13] W. D. Niederhauser, U. S. Patent 2,689,873 (to Rohm and Haas Co.).

[14] L. H. Cretcher, J. A. Koch and W. H. Pittenger, THIS JOURNAL, **47**, 1174 (1925).

[15] H. A. Bruson, U. S. Patent 2,107,367 (to Resinous Products and Chemical Co.).

[16] F. F. Blicke and M. F. Zienty, THIS JOURNAL, **63**, 2779 (1941).

[17] C. O. Tongberg, J. D. Pickens, M. R. Fenske and F. C. Whitmore, *ibid.*, **54**, 3706 (1932).

[18] The fractionations were carried out by F. L. Jackson.

[19] R. Labriola, L. Dorronsoro and O. Verruno, *Anales asoc. quim. argentina*, **37**, 79 (1949).

[20] H. Staudinger and H. Freudenberger, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 573.

N,N-Di-2-chloroethyl-*t*-octylamine Hydrochloride.—Thionyl chloride (59.5 g., 0.5 mole) was slowly added to 2,2'-(*t*-octylimino)-diethanol (51.2 g., 0.25 mole) and benzene (40 ml.) at 40°. After the vigorous reaction had subsided, additional thionyl chloride (119 g.) was added rapidly. The mixture was allowed to stand overnight. After evaporation of excess thionyl chloride and solvent, the solid residue was recrystallized from ethanol containing a little acetone. The white powder weighed 54.7 g. (74%), m.p. 135° (with decomposition).

Anal. Calcd. for $C_{12}H_{26}Cl_3N$: N, 4.82; Cl, 36.6. Found: N, 4.81; Cl, 35.9.

N-2-Chloroethyl-*t*-octylamine hydrochloride, m.p. 188–189°, was prepared similarly in 76% yield from 2-*t*-octylaminoethanol.

Anal. Calcd. for $C_{10}H_{23}Cl_2N$: N, 6.14; Cl, 31.1. Found: N, 6.37; Cl, 31.5.

N-*t*-Octylethyleneimine.—Gaseous hydrogen chloride was bubbled into 2-(*t*-octylamino)-ethanol (173 g., 1 mole) dissolved in ether–petroleum ether. The solid hydrochloride, which was collected and dried in air, was added in portions to chlorosulfonic acid (127 g., 1.1 moles). The mixture was heated on a steam-bath for 4 hr., then evaporated under reduced pressure. The residue was slurried with water (500 ml.) and treated with a solution of potassium hydroxide (300 g.) in water (400 ml.). The mixture was steam distilled and the product separated as an oil from the distillate. The aqueous layer was extracted with chloroform and the combined organic layers were dried over anhydrous magnesium sulfate. Upon distillation, the product (64 g., 41%) was obtained as a colorless oil, b.p. 94–98° (25 mm.).

Anal. Calcd. for $C_{10}H_{21}N$: N, 9.0. Found: N, 8.7.

1-*t*-Octyl-2-methylethyleneimine was prepared similarly in 76% yield from 1-*t*-octylamino-2-propanol, b.p. 113–116° (25 mm.), n^{25}_{D} 1.4334, d^{25}_{25} 0.8057.

Anal. Calcd. for $C_{11}H_{23}N$: N, 8.3. Found: N, 8.4.

PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE ROHM & HAAS COMPANY]

t-Carbinamines, RR'R''CNH$_2$. II. Cyanoalkylations and Related Reactions[1]

BY LEO S. LUSKIN, M. J. CULVER, G. E. GANTERT, W E CRAIG AND R. S. COOK

RECEIVED JANUARY 4, 1956

Cyanomethylation of primary *t*-carbinamines did not differ from the reaction of primary aliphatic amines in general. The degree of substitution of the product depended primarily on the molar proportion of the reagents. Cyanomethylation of derivatives of *t*-carbinamines, as well as the reaction of the amines with higher aldehydes and hydrogen cyanide, also proceeded normally, but their reactions with ketone cyanohydrins failed. By contrast, the addition of *t*-carbinamines to ethyl acrylate and especially to acrylonitrile or to methyl methacrylate showed definite steric influences. Reactions of the amines with acrylonitrile and with methyl methacrylate were greatly accelerated by operation under acidic conditions.

A study of the preparation of aminonitriles and related compounds has afforded an opportunity for the comparison of the behavior of highly branched primary amines and their derivatives[2] with other amines.

A large number of α-aminonitriles were prepared from *t*-butylamine (I), *t*-octylamine (II, 1,1,3,3-tetramethylbutylamine) and their secondary amine derivatives. Particular attention was given to the synthesis of glycinonitriles which can be prepared conveniently from commercially available glycolonitrile[3] or from hydrogen cyanide and aqueous formaldehyde solution.

The principal factor which determined the degree of substitution in the cyanomethylation of primary amines was the molar proportions of the reagents. Thus, excellent yields of *monocyanomethylated* amines were obtained by the use of equimolar proportions. Other reaction variables had little effect. These included the nature of the cyanomethylation reagent (glycolonitrile or hydrogen cyanide and formaldehyde added separately), dilution with organic solvents or water, temperature range (30 to 80°) and duration of reaction period.

Dicyanomethylated derivatives of I or II were prepared in excellent yields by charging two molar equivalents of the cyanomethylation reagent per mole of amine. The reactions were accelerated by the addition of small amounts (5 to 10 mole per cent.) of acidic materials, such as mineral acids or acid salts, and by operation at somewhat elevated temperature.

Other, less-branched amines of similar molecular weight gave either mono- or dicyanomethylated derivatives under the same conditions and in comparable yields. The desired product was again obtained in each instance by control of the charge. The yields were not affected by chain length. The properties of these compounds, of which most are new, are listed in Tables I and II.

The results indicate that steric considerations are unimportant in the cyanomethylation of primary amines. The exclusive and facile formation of monocyanomethylated product when desired is a consequence of the large difference between the basic strengths of aliphatic amines and α-aminonitriles. Because of their low basicity,[4] the latter cannot compete with primary amines in their reaction with cyanohydrins.

A variety of derivatives of I and II were cyanomethylated similarly in satisfactory yields (Table III). The lone failure occurred in the attempted cyanomethylation of N-*t*-octyl-2-ethylhexylamine. This result may indicate steric influence, since the isomeric di-*n*-octylamine was successfully converted to the expected nitrile. However, the possibility of decomposition during distillation, which was noted to some extent in other instances, cannot be ruled out.

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(1) Presented in part before the Division of Organic Chemistry at the 119th Meeting of the American Chemical Society, Cleveland, Ohio, April 10, 1951.

(2) N. Bortnick, L. S. Luskin, M. D. Hurwitz, W E Craig, L. J. Exner and J. Mirza, THIS JOURNAL, **78**, 4039 (1956); also forthcoming papers in preparation.

(3) L. J. Exner, L. S. Luskin and P. L. de Benneville, *ibid.*, **75**, 4841 (1953), lists pertinent references.

(4) A. Marxer, *Helv. Chim. Acta*, **37**, 166 (1954).