nitrile and phenylacetonitrile respectively for acetonitrile.

This novel variant of the alkene-nitrile reaction has since been extended to the synthesis of Δ^1-pyrrolines, dihydropyridines, and other *N*-heterocyclic systems which will be reported in the near future.

EXPERIMENTAL

2,4,4,6-Tetramethyl-5,6-dihydro-1,3-oxazine(I). Acetonitrile (55 ml., 1.05 mole) was added dropwise with stirring to 500 g. of 92% sulfuric acid at 6–7° during 0.5 hr. Then 128 ml. (118.2 g., 1 mole) of 2-methyl-2,4-pentanediol was added dropwise with stirring over 4 hr. at 8–10°. The resulting solution was poured with stirring on 1 kg. of cracked ice and the mixture was half-neutralized with 40% sodium hydroxide solution, then extracted with several portions of chloroform. The acid layer was then made alkaline with 40% sodium hydroxide and the basic oil which separated was extracted with several portions of ether. The combined ether extracts were dried over anhydrous potassium carbonate, and after removal of the ether the residual oil was distilled through a 30-cm. vacuum-jacketed Vigreux column. There was obtained 61.4 g. (44%) of a water-soluble colorless liquid with ammoniacal odor, b.p. 56°/24 mm. (146–147°/750 mm.), n_D^{25} 1.4370; reported[3] b.p. 146.8–147°, n_D^{25} 1.4358.

Anal. Calcd. for $C_8H_{15}ON$: N, 9.93. Found, 9.95. The picrate melted at 153–154° (uncorr.); reported,[3] 152–153°.

Alkaline cleavage of I. The method of Smith and Adkins[3] was used to treat 24 g. (0.17 mole) of I. A colorless amine(II) was obtained in 75% yield (15 g.), b.p. 174–175°, n_D^{20} 1.4350. A specimen of 4-amino-4-methyl-2-pentanol[4] distilled at atmospheric pressure at 174–175°, n_D^{20} 1.4340. The caprylates of II and 4-amino-4-methyl-2-pentanol were prepared by mixing 1 mmole of each with 1 mmole of caprylic acid. The mixtures solidified almost immediately and the resulting solids were recrystallized twice from dry acetone. The melting point of each was 84–85° and the mixed melt showed no depression.

4,4,6-Trimethyl-2-phenyl-5,6-dihydro-1,3-oxazine. Benzonitrile (20.6 g., 0.2 mole) was added dropwise with stirring to 100 g. of 92% sulfuric acid at 2–4° over 20 min. Then 23.6 g. (0.2 mole) of 2-methyl-2,4-pentanediol was added dropwise with stirring at 3–6° during 2 hr. The product was isolated in the same manner as for I. A pale yellow oil (19.1 g., 47%), b.p. 103–106°/3 mm. was obtained. Two recrystallizations from ethanol-water (the compound was dissolved at room temperature and the solution was then strongly cooled) gave colorless crystals, m.p. 34–35° (reported,[5] 32°).

Anal. Calcd. for $C_{13}H_{17}ON$: N, 6.90. Found, 7.01. The picrate melted at 159–161° (corr.); reported,[5] 162.5–164°.

4,4,6-Trimethyl-2-benzyl-5,6-dihydro-1,3-oxazine. The procedure for this preparation was similar to the one above. Phenylacetonitrile (11.7 g., 0.1 mole) was added to 50 g. of 92% sulfuric acid followed by 11.8 g. (0.1 mole) of 2-methyl-2,4-pentanediol. A yellow oil (5.7 g., 26%) was obtained, b.p. 116–119°/5 mm., n_D^{20} 1.5125.

Anal. Calcd. for $C_{14}H_{19}ON$: N, 6.45; found, 6.39. The picrate melted at 125–126°.

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(4) M. Kohn, *Monatsh.*, **25**, 141 (1904).

(5) M. Kahan, *Ber.*, **30**, 1319 (1897).

Amines. III. Characterization of Some Aliphatic Tertiary Amines[1]

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The literature on simple aliphatic tertiary amines and their characterization is surprisingly sparse. Even the commercially available triethylamine[3] has not been reported characterized by such common derivatives as the methiodide or the methotosylate. Frequently when methiodide derivatives have been prepared and reported—there are at least five references to the methiodide of *N*-ethyldimethylamine,[4] two each for that of *N*,*N*-diethylmethylamine[4a,4b] and of *N*-isopropyldimethylamine[4a,5] and one for that derivable from *N*-*tert*-butyldimethylamine[6]—no melting data were given. The present investigation was undertaken to provide systematic and comparative characterization of a series of closely related simple aliphatic tertiary amines. This included the fully *N*-methylated ethyl-, diethyl-, isopropyl-, diisopropyl-, and *tert*-butylamines, and triethylamine. Although the *tert*-butyldimethylamine is the only new compound, the other amines, except for triethylamine, have been poorly characterized in the literature.

The tertiary methylamines were prepared by the Eschweiler-Clarke method.[7] The preparative data are presented in Table I. Physical constants, including freezing points, refractive indices, densities, molar refractivities, and Eykman constants are summarized in Table II. The chemical derivatives are listed in Tables III and IV.

EXPERIMENTAL

Eschweiler-Clarke N-methylation. Reactions were carried out in a magnetically stirred glass system closed except for a gas effluent tube which carried off the evolved carbon dioxide

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(1) Previous paper, J. Radell, L. Spialter, and J. Hollander, *J. Org. Chem.*, **21**, 1051 (1956).

(2) Dr. Joseph A. Pappalardo, of the University of Dayton, worked on this investigation under the Summer Expert Employment Program of the Wright Air Development Center.

(3) Available from Union Carbide Chemicals Co., 30 East 42nd Street, New York 17, N. Y.

(4) (a) N. Collie and S. B. Schryver, *J. Chem. Soc.*, **57**, 767 (1890); (b) L. Wagner, *Z. Kryst. Mineral.*, **43**, 148 (1907); (c) R. Müller, *Ann.*, **108**, 1 (1858); (d) W. Lossen, *Ann.*, 181, 364 (1876); (e) Z. H. Skraup and Wiegmann, *Monatsh.*, **10**, 107 (1889).

(5) H. Malbot and A. Malbot, *Bull. soc. chim. France*, [3], **7**, 136 (1892).

(6) W. Hanhart and C. K. Ingold, *J. Chem. Soc.*, 997 (1927).

(7) (a) W. Eschweiler, *Ber.*, **38**, 880 (1905); (b) H. T. Clarke, H. B. Gillespie and S. Z. Weisshaus, *J. Am. Chem. Soc.*, **55**, 4571 (1933); (c) M. L. Moore, *Org. Reactions*, **5**, 307 (1949).

TABLE I

PREPARATIVES DATA FOR VARIOUS TERTIARY AMINES

Amine Prepared	Moles of Reactants: Parent amine	Formic acid	Formaldehyde	Yield, %[a]	Boiling Point, °C. Found (740 Mm.)	Analyses[b] Calcd./Found: C	H	N
$EtN(Me)_2$	1[c]	5	2.2	38	35.8–35.9[d]	65.69 65.62	15.16 15.32	19.15 19.40
$(Et)_2NMe$	1[e]	5	2.2	79	65.1–65.3[f]	68.90 68.72	15.03 15.09	16.07 15.94
i-$PrN(Me)_2$	1[g]	10	4.4	71	65.5–65.7[h]	68.90 68.85	15.03 14.95	16.07 15.80
i-$PrN(Me)_2$	1[g]	5	2.2	35[a]	—	—	—	—
$(i\text{-}Pr)_2NMe$	1[i]	5	2.2	79	111.7–112.0[j]	72.97 73.09	14.87 14.76	12.16 12.47
t-$BuN(Me)_2$	1[k]	5	2.2	76	89.6–89.9	71.21 71.39	14.94 14.72	13.84 14.10

[a] The yields are based on weights of distillate fractions with an average boiling range of 1.4°, except for the 35% yield in the 2nd i-$PrN(Me)_2$ run. [b] All analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. [c] Ethylamine (Sharples). [d] Lit. values (unspecified pressures): 37.5°, M. Kohn and O. Morgenstern, *Monatsh.*, **28**, 479 (1907); 36–38°, ref. (6); 37–39°, F. Schlegel, *Ber.*, **64B**, 1739 (1931). [e] Diethylamine (Sharples). [f] Lit. values (unspecified pressures): 63–65°, B. Emmert, *Ber.*, **42**, 1507 (1909); 66°, G. M. Robinson and R. Robinson, *J. Chem. Soc.*, **123**, 532 (1923); 66–69°; A. P. Terent'ev, A. N. Kost, and S. M. Gurvich, *Zhur. Obshchei Khim.*, **23**, 615 (1953). [g] *iso*-Propylamine (Union Carbide Chemical). [h] Lit. values (unspecified pressures): 67–67.5°, A. Skita and F. Keil, *Monatsh.*, **53/54**, 753 (1929). [i] Di-*iso*-propylamine (Sharples). [j] Lit. values (unspecified pressures): 109–112°, J. Klages, G. Nober, F. Kircher, and M. Bock, *Ann.*, **547**, 1 (1941). [k] *tert*-Butylamine (Rohm and Haas).

TABLE II

PHYSICAL CONSTANTS FOR VARIOUS TERTIARY METHYLAMINES

Amine	F.P.	n_D^{25}	n_D^{20}	d_4^{25}	d_4^{20}	Molar Refractivity, 25° Calcd.[a]	Found	Eykman Constant[b]
$EtN(Me)_2$	−140	1.3702	1.3720	0.6694	0.6751	24.46	24.73	0.7391 ± 0.0014
$(Et)_2NMe$	−196 (glass)[c]	1.3865	1.3891	0.7016	0.7061	29.09	29.01	0.7357 ± 0.0002
i-$PrN(Me)_2$	−196 (glass)[c]	1.3874	1.3905	0.7106	0.7151	29.09	28.90	0.7287 ± 0.0005
$(i\text{-}Pr)_2NMe$	−196 (glass)[c]	1.4082	1.4109	0.7495	0.7535	38.35	37.94	0.7257 ± 0.0003
t-$BuN(Me)_2$	− 90	1.4021	1.4041	0.7377	0.7419	33.72	33.41	0.7261 ± 0.0004

[a] Bond refractivity values used were those for the sodium-D line given by Y. K. Syrkin and M. E. Dyatkina, *Structure of Molecules and the Chemical Bond*, p. 201, Interscience Publ. Inc., New York, 1950. [b] See ref. (12). The values here represent the mean values over the range 20 to 25°. [c] These could not be crystallized.

through a reflux condenser and thence a gas flowmeter.[8] The formalin solution was added to the amine dissolved in 88% formic acid. Sufficient heat (60 to 90°) was applied to maintain carbon dioxide evolution of 200–500 cc./min. In less than an hour gas evolution ceased and the system was heated at reflux temperature for 4 hr. The product was worked up by acidification, concentration by evaporation, alkalization, distillation, drying over potassium hydroxide, and final fractionation from sodium in a dry nitrogen, carbon dioxide-free atmosphere. Table I contains preparative conditions and yields. To maintain purity, the products were divided into 1–5 ml. portions and sealed under nitrogen in individual ampoules.

Physical constants. Freezing points were determined by chilling samples in sealed ampoules with liquid nitrogen-cooled pentane mixtures and repeatedly observing freezing and melting points. Temperature values are estimated to be better than ±5°. As indicated in Table II, three of the amines could not be induced to crystallize, but froze to glassy supercooled liquids at the temperature of liquid nitrogen.

Refractive index measurements were made with a thermostated American Optical Spencer Abbe refractometer. Densities were determined with a pycnometer.

Chemical derivatives. The methiodides and methotosylates[9] were satisfactorily prepared by both conventional procedures,[10] with the additional precaution in the solventless method of using small quantities and special care because of the high amine reactivity and exothermicity on quaternization. The methotosylates were recrystallized from ethyl acetate containing some methanol. All crystals were dried in a vacuum oven at 60 to 90°.

On exposure to the laboratory atmosphere over a 3 to 4 day period, all of the methiodides acquired a yellow color except the one from *tert*-butyldimethylamine. The intensity of the yellow color, in decreasing order, was $Et_3N = Et_2NMe > EtNMe_2 > i\text{-}PrNMe_2 = i\text{-}Pr_2NMe > t\text{-}BuNMe_2$.

Melting points of the methiodides were determined on a Kofler micro hot stage and represent corrected values. Those for the methotosylates had to be determined in sealed capillary tubes by the Thiele tube method because of the pronounced hygroscopicity of these latter derivatives.

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(8) Flowrater, range of 100 to 3000 cc./mm., manufactured by the Fischer and Porter Co., Hatboro, Pa.

(9) These are the quaternary ammonium derivatives arising from reaction of a tertiary amine with methyl iodide and methyl *p*-toluenesulfonate, respectively.

(10) R. L. Shriner and R. C. Fuson, *The Systematic Identification or Organic Compounds*, p. 149, John Wiley and Sons, Inc., New York, 2nd Ed., 1940.

TABLE III

METHIODIDES OF TERTIARY AMINES

			Analyses, % Calcd./Found			
Amine	M.P. (Corr.)[a]	Formula	C	H	N	I
EtN(Me)$_2$	300–301[b,c]	$C_5H_{14}NI$	27.92 27.87	6.56 6.31	6.51 6.64	59.01 58.94
(Et)$_2$NMe	298–299[b,c]	$C_6H_{16}NI$	31.45 31.42	7.04 6.76	6.11 6.29	55.40 55.22
i-PrN(Me)$_2$	294–295[b]	$C_6H_{16}NI$	31.45 31.49	7.04 6.94	6.11 6.36	55.44 55.45
(*i*-Pr)$_2$NMe	252–253[b]	$C_8H_{20}NI$	37.36 37.39	7.84 7.73	5.45 5.52	49.35 49.44
t-BuN(Me)$_2$	240–241[b]	$C_7H_{18}NI$	34.58 34.73	7.46 7.30	5.76 5.92	52.20 52.46
(Et)$_3$N	280–281[b]	$C_7H_{18}NI$	34.58 34.51	7.46 7.19	5.76 5.93	52.20 52.05

[a] A Kofler micro hot stage apparatus was used. [b] Decomposes. [c] Sublimes.

TABLE IV

METHOTOSYLATES OF TERTIARY AMINES

			Analyses, % Calcd./Found			
Amine	M.P.[a]	Formula	C	H	N	S
EtN(Me)$_2$	185–188	$C_{12}H_{21}O_3NS$	55.57 55.77	8.16 8.18	5.40 5.67	12.36 12.56
(Et)$_2$NMe	132–135	$C_{13}H_{23}O_3NS$	57.11 57.20	8.48 8.20	5.12 5.06	11.73 11.78
i-PrN(Me)$_2$	187–190	$C_{13}H_{23}O_3NS$	57.11 57.00	8.48 8.58	5.12 5.18	11.73 11.72
(*i*-Pr)$_2$NMe	109–111	$C_{15}H_{27}O_3NS$	59.77 60.65	9.03 8.96	4.65 4.74	10.64 10.22
t-BuN(Me)$_2$	184–187	$C_{14}H_{25}O_3NS$	58.50 58.43	8.77 8.44	4.87 4.95	11.15 11.48
Et$_3$N	88–91	$C_{14}H_{25}O_3NS$	58.50 58.04	8.77 9.22	4.87 5.02	11.15 11.11

[a] Melting points are uncorrected and were obtained in sealed capillary tubes.

DISCUSSION

The physical properties of the aliphatic tertiary amines, as listed in Table II, appear rather similar to those of highly branched alkanes of comparable molecular weight and structure. The densities and refractive indices are, respectively, about 0.04–0.05 and 0.01–0.02 units higher than those of the hydrocarbon analogs wherein the amino-nitrogen has been replaced by the C-H group.[11] The Eykman constants[12] for the amines are 0.025–0.030 units lower. The amines except for the case of ethyldimethylamine, are also lower-melting. For this reason and others, such as chemical stability, ease and low cost of synthesis, they may be useful as low temperature thermometric, heat exchange, hydraulic, or lubricative fluids.

Agreement between calculated (from bond refractivities) and found values for molar refractivity is not as good as one might expect in view of the simplicity of the tertiary amine structures and absence of hydrogen bonding, unsaturation, etc., which disturb additive molecular parameters in the case of more complex molecules. The agreement is no better (and is sometimes worse) when atomic

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(11) American Petroleum Institute Research Project 44 at National Bureau of Standards, *Selected Values of Properties of Hydrocarbons*, U. S. Government Printing Office, Washington, D. C., Nov. 1947.

(12) The Eykman equation [J. F. Eykman, *Rec. trav. chim.*, 14, 185 (1895)] is a temperature-invariant relation between the density and index of refraction of a liquid. The equation has the form:

$$\frac{n^2 - 1}{n + 0.4} \times \frac{1}{\mathrm{d}} = \mathrm{C_e}$$

where n and d are the refractive index and liquid density, respectively, at the same temperature, and C_e, the Eykman Constant, which is a fixed parameter characteristic for a particular compound. Critical evaluations of this equation have been given by S. S. Kurtz, Jr., S. Amon, and A. Sankin [*Ind. Eng. Chem.*, **42**, 174 (1950)] and R. R. Dreisbach [*Ind. Eng. Chem.*, **40**, 2269 (1948)]. These authors show its superiority in temperature invariance over the well-known Lorentz-Lorenz molecular refractivity equation.

refractivity values of other authors[13] are used. The refractivity increment per methylene group appears to be less than the estimated value of 4.65 generally given.[13]

The Eykman constant was computed over the range 20–26° and appears constant within the estimated limits of experimental error.

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[13] (a) W. Hückel, *Theoretische Grundlagen der Organischen Chemie*, 4th Ed., Vol. II, p. 142, Akademische Verlag., Leipzig, Germany, 1943. (b) A. I. Vogel, *A Textbook of Practical Chemistry*, 3rd Ed., p. 1035, Longmans, Green and Co., Inc., New York, N. Y., 1956. (c) R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, 2nd Ed., p. 107, John Wiley and Sons, Inc., New York, N. Y., 1940.

High Temperature Chlorination of Dioxane to Give Trichloroacetyl Chloride

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Several workers[1–4] have reported the chlorination of *p*-dioxane at temperatures of 130–160° to give a number of chlorinated dioxanes. Boeseken, *et al.*[2] noted that the ring was broken and that "acid chlorides were probably present" when dioxane was subjected to prolonged chlorination at 130–150°.

When trichloroacetyl chloride was isolated from the products of a dioxane chlorination experiment, the work described below was carried out to determine the extent to which trichloroacetyl chloride was formed. Although the experiment was stopped before the ultimate yield of trichloroacetyl chloride was obtained, sufficient information was obtained to show that trichloroacetyl chloride is a major product of the prolonged high temperature chlorination of dioxane. The factors which account for the different results of the previous and present work are the temperature, which was kept near or above 160° when trichloroacetyl chloride was formed, and the large excess of chlorine which was used in this work.

EXPERIMENTAL

Two hundred and sixty g. (2.95 moles) of *p*-dioxane was heated to 90° in a flask equipped with a condenser, an inlet tube, and a thermometer. Chlorine was added at a rate of 20 to 30 g. per hr. At the end of 60 hr. the pot temperature had risen to 115° and the net weight increase was 530 g. Infrared analysis indicated less than 2% carbonyl chloride present. Chlorination was continued at 155–160° for 11 hr. Distillation of the crude products at 75 mm. gave 144 g. of trichloroacetyl chloride, b.p. 47–48, n_D^{24} 1.4662, confirmed by the infrared spectrum. The residue was then chlorinated for 15 hr. at 165–180° after which reduced pressure distillation yielded 88 g. of trichloroacetyl chloride. Again the distillation residue was chlorinated at 175–190° for 10 hr.; no condenser was used and the vent gases were passed directly into a cold trap. During this period 160 g. was collected. Distillation of the condensate gave 84 g. of trichloroacetyl chloride. The pot residue solidified on cooling. Infrared and chlorine analysis showed the solid to be hexachloroethane. The total yield of trichloroacetyl chloride was 316 g. (1.74 moles).

An attempt was made to distill the reaction residue (462 g.) at 2 mm. The column and condenser immediately plugged with hexachloroethane. According to the infrared spectrum, the residue contained above 20% hexachloroethane.

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[1] C. L. Butler and L. H. Cretcher, *J. Am. Soc.*, **54**, 2987 (1932).

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[3] J. J. Kucera and D. C. Carpenter, *J. Am. Chem. Soc.*, **57**, 2346 (1935).

[4] R. K. Summerbell, R. R. Umboeffer, and G. R. Lappin, *J. Am. Chem. Soc.*, **69**, 1352 (1947).

Preparation of Malonaldehyde bis-Bisulfite, Sodium Salt

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Malonaldehyde (I) reacts with 2-thiobarbituric acid to give a characteristic pink coloration. This reaction is useful for the estimation of 2-deoxysugars and nucleosides containing 2-deoxysugars. For this purpose, it is considered important to have a stable derivative of I, since I has been reported[1] as an unstable crystalline monomer. This report is concerned with the preparation of a stable crystalline bisulfite addition compound suitable for investigations of reactions of I.[2]

EXPERIMENTAL[3]

A suspension of 10 ml. of malonaldehyde bis(dimethyl acetal)[4] in 5.5 ml. of 3.7% aqueous hydrochloric acid was shaken for 1 min. in a water bath at 60° to effect dissolution. The resulting yellow solution was kept at room temperature for 40 hr. and then cooled to 4°. A freshly prepared saturated solution of sodium *meta*-bisulfite was chilled in an ice bath

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[1] R. Hüttel, *Ber.*, **74**, 1825 (1941).

[2] U. S. Patent No. 2,671,800 has been granted for a related process for preparing bisulfite addition products of malonaldehyde [*Chem. Abstr.*, **49**, 4014 (1955)]. However, no proof of identity of the proposed compounds is recorded, and apparently no physical or chemical studies were undertaken to characterize the compounds.

[3] Microanalyses for C, H, S, and Na were performed by Dr. W. C. Alford and his associates.

[4] Obtained from Kay-Fries Chemicals, Inc., 180 Madison Ave., New York 16, N. Y.