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Amine Oxides. IX. Comparison of the Elimination Reactions Forming Olefins from the N-Oxides and Methohydroxides of Amines of the Type R₂CHCH₂N(CH₃)₂^{1,2}

BY ARTHUR C. COPE AND DANIEL L. ROSS

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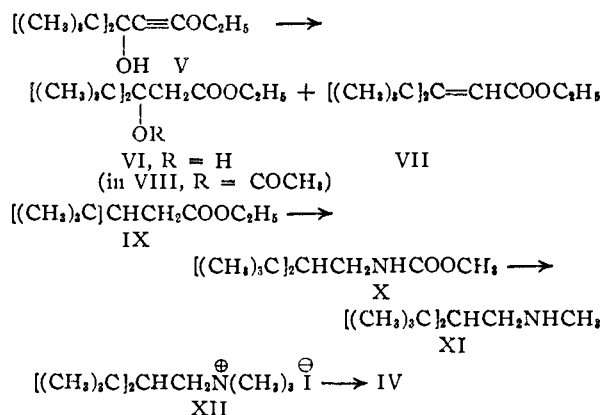
Four tertiary amines of the type R₂CHCH₂N(CH₃)₂ have been prepared and converted to the N-oxides and methohydroxides. Thermal decomposition of the amine oxides formed olefins, R₂C=CH₂, in yields of 80% (R = C₂H₅), 77% (R = n-C₃H₇), 80% (R = i-C₃H₇) and 73% (R = t-C₄H₉), indicating little influence on olefin yields by β-alkyl substitution. Yields of the same olefins from the Hofmann elimination reaction likewise showed little variation, and were 77, 73, 67 and 81%, respectively.

This paper reports a comparison of the pyrolyses of N-oxides of tertiary amines and corresponding methohydroxides containing a highly substituted β-carbon atom. Previous work had indicated that in the Hofmann elimination reaction the attack of hydroxide ion on an α-carbon atom forming an alcohol and a tertiary amine becomes more important as branching increases at the β-carbon atom.³ This finding was interpreted as being the result of an inductive effect of the β-substituents lowering the acidity of the β-hydrogen atom, and thus increasing the importance of the competing reaction. On the other hand, the results of pyrolyses of amine oxides containing β-alkyl groups indicate that this reaction is relatively insensitive to inductive effects, the yields of olefins generally ranging from 70 to 85%.^{1,4}

In this research a series of four amines of the structure R₂CHCH₂N(CH₃)₂ in which R is ethyl (I), n-propyl (II), isopropyl (III) and t-butyl (IV) was prepared and submitted to the amine oxide pyrolysis and the Hofmann elimination reaction. An increase in carbon substitution on the γ-carbon atoms in this series should result in a corresponding increase in inductive effects transmitted to the β-carbon atom and should thereby provide a test of the sensitivity of the two reactions to these effects.

The amine I was prepared by reduction of N,N-dimethyl-2-ethylbutyramide, obtained by the reaction of 2-ethylbutyryl chloride and dimethylamine. Amines II and III were obtained by methylation with formaldehyde and formic acid of the primary amines formed by reduction of the corresponding dialkylacetonitriles (prepared from ethyl cyanoacetate by alkylation, partial hydrolysis and decarboxylation). The amine IV was synthesized by a reaction sequence beginning with the addition of ethoxyacetylenemagnesium bromide to hexamethylacetone, which formed the ethynylcarbinol V in 88% yield. Treatment with dilute sulfuric acid of a solution of the carbinol V in tetrahydrofuran gave in nearly quantitative yield a mixture containing about 60% of the β-hydroxy ester VI and 40% of the α,β-unsaturated ester VII. The proportion of VII in the mixture was raised to 84% by dissolving V in water-

tetrahydrofuran (2:1), and treating the resulting two-phase system with dilute sulfuric acid. Attempted dehydration of VI by treatment with thionyl chloride and pyridine appeared to result in some skeletal rearrangement, but VI could be converted to the acetate VIII by treatment with isopropenyl acetate, and pyrolysis of the resulting acetate afforded the pure unsaturated ester VII. Hydrogenation of VII followed by a Curtius reaction gave the urethan X, which was reduced with lithium aluminum hydride to the N-methylamine XI. Methylation of XI with methyl iodide and sodium bicarbonate yielded the methiodide XII,



part of which was reduced with lithium aluminum hydride⁵ to the tertiary amine IV. The properties of the picrates and methiodides of the amines I-IV are listed in Tables I and II. The yields of olefins obtained by pyrolysis of the N-oxides and methohydroxides of the amines I-IV are listed in Table III.

Several conclusions can be drawn from these data. The yields of olefins formed in the amine oxide pyrolyses were relatively insensitive to inductive and steric effects in the four compounds studied. However, that the ease of elimination in this reaction may be influenced by steric effects is shown by the case in which R = t-C₄H₉; this amine oxide decomposed spontaneously (as it was formed in aqueous methanol solution) to the olefin and dimethylhydroxylamine. Such facile decomposition of amine oxides previously has been observed only when the amine oxide group is attached directly to a tertiary carbon atom (see ref. 1, including footnote 18). The recovery of 27% of the tertiary amine in this case almost certainly

(1) Paper VIII in this series, A. C. Cope, E. Ciganek, C. F. Howell and E. E. Schweizer, *J. Am. Chem. Soc.*, **82**, 4663 (1960).

(2) Supported in part by the Office of Ordnance Research, U. S. Army, under Contract No. DA-19-020-ORD-4542.

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

(4) A. C. Cope, C. L. Bumgardner and E. E. Schweizer, *J. Am. Chem. Soc.*, **79**, 4730 (1957).

(5) By a procedure described by A. C. Cope, E. Ciganek, L. J. Fleckenstein and M. A. P. Meisinger, *ibid.*, **82**, 4651 (1960).

TABLE I
 N,N-DIMETHYL TERTIARY AMINE PICRATES

Picrate of amine	M.p., °C.	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
I	94.7-96.2	C ₁₄ H ₂₂ N ₄ O ₇	46.92	47.00	6.19	6.29	15.64	15.46
II	100.6-101.7	C ₁₆ H ₂₆ N ₄ O ₇	49.73	49.49	6.78	6.85	14.50	14.26
III	175.5-176.5	C ₁₆ H ₂₆ N ₄ O ₇	49.73	50.04	6.78	6.88	14.50	14.35
IV	150.5-152.0	C ₁₈ H ₃₀ N ₄ O ₇	52.16	52.21	7.30	7.51	13.52	13.50

 TABLE II
 ALKYLTRIMETHYLAMMONIUM IODIDES

Methiodide of amine	Yield, %	M.p., °C.	Formula	Carbon, %		Hydrogen, %		Iodine, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
I	96	239.0-240.5 d.	C ₉ H ₂₂ NI	39.86	39.83	8.18	8.08	46.80	46.67
II	99	227-229 d. ^a	C ₁₁ H ₂₆ NI	44.15	44.39	8.76	8.74	42.41	42.22
III	97	252.5-253.5 d.	C ₁₁ H ₂₆ NI	44.15	43.87	8.76	8.48	42.41	42.41
IV	88	239.0-239.5 d.	C ₁₃ H ₃₀ NI	47.77	47.81	9.23	9.19	38.78	38.61

^a G. Koller and E. Kandler, *Monatsh.*, **58**, 213 (1931), report m.p. 215° d. and no analysis for this methiodide.

 TABLE III
 YIELDS OF R₂C=CH₂ AND R₂CHCH₂N(CH₃)₂

R	From pyrolysis of R ₂ CHCH ₂ N(CH ₃) ₂		From pyrolysis of R ₂ CHCH ₂ N(CH ₃) ₂ OH ^a		Ref. 3, olefin yield, %
	Olefin, %	Amine, %	Olefin, %	Amine, %	
C ₂ H ₅	80	..	77, 49 ^a	14, 40 ^a	43
<i>n</i> -C ₃ H ₇	77	..	73	14	31
<i>i</i> -C ₃ H ₇	80	..	67	25	..
<i>t</i> -C ₄ H ₉	73	27 ^b	81	12	..

^a By the procedure of ref. 3 (see text). ^b Isolated as the result of incomplete oxidation of the amine (see text).

is due to partial oxidation of the dimethylhydroxylamine to formic acid and subsequent formation of the amine formate, as has been proved to be the case for N,N-dimethyl-1-methylcyclooctylamine.¹

In the Hofmann elimination reaction, it is evident from the data of Table III that much higher yields of olefin were obtained when the quaternary bases were concentrated to sirups and distilled under reduced pressure, rather than decomposed by distillation of aqueous solutions at atmospheric pressure (the procedure of ref. 3). Distillation in the presence of a large amount of water probably favors nucleophilic attack by hydroxide ion on an N-methyl group forming methanol and the tertiary amine.

The yields of olefins from the Hofmann elimination reactions (Table III) also are relatively insensitive to branching of the β -substituents. The small but probably significant decreases in yield of olefin as R increases in size from ethyl to *n*-propyl to isopropyl may be a result of two steric effects. As a consequence of the *trans* relationship of the trimethylammonium group and the β -hydrogen atom required for a concerted *trans* elimination, the two β -alkyl groups and the trimethylammonium group are forced to take positions on the same side of the molecule (see Fig. 1). As the size of the β -alkyl groups increases, interactions between these groups and the nitrogen function should become significant and increase the energy of the transition state for the elimination, thereby allowing the competing attack by hydroxide ion on an N-methyl group to become more important. In addition, as the size of the β -alkyl groups increases, greater steric interference with the incoming nucleophile which attacks the β -hydrogen atom would be expected.

It is of interest to compare the results of the present work with those of Smith and Frank⁶ who decomposed the quaternary bases of the corresponding β -monosubstituted amines of the type

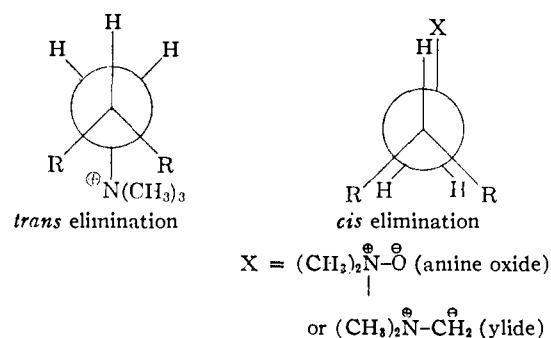


Fig. 1.—Conformations required for *cis* and *trans* elimination.

RCH₂CH₂N(CH₃)₂ and obtained the following yields of olefins: 86% (R = C₂H₅), 78% (R = *i*-C₃H₇), and 20% (R = *t*-C₄H₉). These results were interpreted as due to electronic effects because it was believed that the bulk of the R group did not have much steric effect on the approach of hydroxide ion to the β -hydrogen atom. However, while there is a drop in yield of only 8% (compare a similar drop of 11% in Table III) when R is changed from ethyl to isopropyl, the drop of 58% when R is changed to tertiary butyl as compared to isopropyl is so large that we believe steric effects must be involved.

The surprisingly high yield of olefin in the present study when the β -carbon atom is substituted with two *t*-butyl groups requires explanation. Examination of molecular models shows that it is virtually impossible for this quaternary base to attain the conformation required for *trans* elimination (Fig. 1). Indeed, the steric interactions of the *t*-butyl groups and the nitrogen function should favor the conformation required for *cis* elimination, and this may explain the very facile elimination of the corresponding amine oxide. Another steric effect of the β -*t*-butyl groups that may be important is their mutual repulsion when the β -carbon atom in the amine derivative is tetrahedral. This repulsion should be relieved upon formation of the

(6) P. A. S. Smith and S. Frank, *J. Am. Chem. Soc.*, **74**, 509 (1952).

olefin in which the same carbon atom is trigonal and the *t*-butyl groups are farther apart. Thus it appears likely that the high degree of branching in the *t*-butyl compound does inhibit the normal *trans* concerted elimination reaction mechanism in favor of some other mechanism without resulting in a lowering of the yield of olefin. A reasonable explanation for the high yield of di-*t*-butylethylene from the Hofmann reaction that is consistent with the steric features of this system is offered by the formulation of a cyclic intramolecular *cis* elimination mechanism proceeding *via* an α -carbanion or ylide as proposed by Wittig and Polster⁷ and later supported by tracer studies⁸ as one possible mechanism for the Hofmann elimination reaction. Work is in progress to determine whether an ylide mechanism is involved in the formation of di-*t*-butylethylene from the quaternary base.

The mono-*t*-butyl compound of Smith and Frank may be a borderline case in which the β -substituent is sufficiently bulky to suppress normal *trans* elimination, but interaction with the trimethylammonium group is not great enough to favor a *cis* elimination process.

Experimental⁹

N,N-Dimethyl-2-ethylbutylamine (I) was prepared in 71% yield from 2-ethylbutyl chloride by the procedure described for the preparation of cyclohexylmethyl dimethylamine from cyclohexanecarbonyl chloride¹⁰; b.p. 83.5–84.0° (148 mm.), n_D^{25} 1.4123.

N,N-Dimethyl-2-*n*-propylpentylamine (II) and **N,N-dimethyl-2-isopropyl-3-methylbutylamine (III)** were prepared from the monoalkyl cyanoacetic esters¹¹ which were alkylated by treatment with sodium ethoxide and the corresponding alkyl bromides. The resulting dialkyl cyanoacetic esters were saponified and decarboxylated to the dialkylacetone nitriles, which were reduced with lithium aluminum hydride by the procedure of Amundsen and Nelson¹² to the primary amines. The tertiary amines were prepared by methylation with formaldehyde and formic acid.

Hexamethylacetone.—The method of Bartlett and Schneider¹³ was used with slight modifications. It was found that the use of sodium sand finer than 1–2 mm. in diameter led to an uncontrollably vigorous reaction. Ethyl pivalate¹⁴ was substituted for methyl pivalate. Distillation of the material obtained from 84.1 g. of ethyl pivalate afforded (after some forerun) a total of 72.4 g. (78% calculated as di-*t*-butylcarbinol) of a mixture which contained predominantly di-*t*-butylcarbinol and some of the corresponding ketone, collected from 151–164° (mostly 164°). Oxidation of the distillate with nitric acid gave 58.2 g. of hexamethylacetone, b.p. 152–154°, n_D^{25} 1.4170.

3-Ethoxyethynyl-2,2,4,4-tetramethylpentan-3-ol (V).—In a 3-l. round-bottomed flask fitted with a reflux condenser, pressure-equalizing dropping funnel and magnetic stirrer ethylmagnesium bromide was prepared under nitrogen from 19 g. (0.782 mole) of magnesium turnings and 110 g. of ethyl bromide in 350 ml. of ether. The mixture was stirred for 20 min. after addition of the ethyl bromide was completed and then an additional 350 ml. of ether was added. The Grignard reagent was cooled in an ice-bath and a solution of 60.3 g. (0.86 mole) of ethoxyacetylene¹⁵

in 350 ml. of ether was added with stirring over a 1-hr. period. The mixture was allowed to warm to room temperature and was refluxed for 1 hr. The resulting two-phase mixture containing ethoxyacetylenemagnesium bromide was stirred at room temperature and a solution of 55.6 g. (0.39 mole) of hexamethylacetone in 250 ml. of ether was added over a 1-hr. period. The mixture became homogeneous after about one-half of the ketone had been added. The mixture was stirred for 45 min. and was then refluxed for 3 hr. and allowed to cool and stand overnight under nitrogen.

The mixture was poured with stirring onto a mixture of 670 g. of ice, 715 ml. of water and 277 g. of ammonium chloride. The mixture was shaken in a separatory funnel, the organic phase was separated, and the aqueous phase was extracted with two 350-ml. portions of ether. The combined organic phase and extracts were washed with 350 ml. of water and dried over magnesium sulfate. The ether was distilled on a steam-bath and the residue was distilled through a short Vigreux column, giving 72.9 g. (88%) of the acetylenic carbinol V, b.p. 87.5–88.0° (1.9 mm.), n_D^{25} 1.4622.

Anal. Calcd. for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39. Found: C, 73.63; H, 11.49.

Ethyl 3-*t*-Butyl-4,4-dimethyl-2-pentenoate (VII) and **Ethyl 3-*t*-Butyl-3-hydroxy-4,4-dimethylpentanoate (VI)** by Acid-catalyzed Rearrangement of V.—In a 2-l. round-bottomed flask equipped with a magnetic stirrer, a mixture of 648 ml. of water, 300 ml. of tetrahydrofuran and 68.7 g. (0.323 mole) of V was cooled to 10° and 64.8 ml. of dilute sulfuric acid (10 g. diluted to 100 ml. with water) was added with stirring. Stirring was continued at room temperature for 4 hr. at which time 261 ml. of 1 *N* sodium bicarbonate was added with stirring and most of the tetrahydrofuran was removed under reduced pressure. The resulting two-phase mixture was extracted with a total of 650 ml. of ether. After drying over magnesium sulfate and filtering, the ether was removed leaving 70.6 g. of a mixture containing approximately 84% of the α,β -unsaturated ester and 16% of the β -hydroxy ester. This mixture was distilled carefully through a Podbielniak-type column giving, after a small forerun, a total of 50.2 g. (73%) of VII of 95.5% purity (as determined by gas chromatography,¹⁶ the remainder being the β -hydroxy ester) boiling at 85–90° (2.8–3.1 mm.). The distillation residue (17.3 g.) consisted of 38% of the α,β -unsaturated ester and 62% of the β -hydroxy ester.

An analytical sample of VI had b.p. 108–108.5° (2.1 mm.), n_D^{25} 1.4542.

Anal. Calcd. for $C_{13}H_{26}O_3$: C, 67.78; H, 11.38. Found: C, 67.85; H, 11.62.

An analytical sample of VII had b.p. 91–94° (2.1 mm.), n_D^{25} 1.4590; λ_{max} 217 m μ in ethanol, ϵ 4,078.

Anal. Calcd. for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39. Found: C, 73.27; H, 11.45.

Ethyl 3-Acetoxy-3-*tert*-butyl-4,4-dimethylpentanoate (VIII).—A mixture containing 0.179 mole of VI of approximately 90% purity (the remainder being the α,β -unsaturated ester) was placed in a 250-ml. round-bottomed flask with 180 g. (1.8 mole) of isopropenyl acetate and 0.25 g. of *p*-toluenesulfonic acid. The flask was attached to a 45 × 1.5-cm. column packed with glass helices. The pot temperature was raised to 110° and the isopropenyl acetate was allowed to flood about half way up the column. Acetone slowly distilled and was removed periodically. After 11 hr., about 8.8 ml. of acetone had distilled. The system was kept under total reflux overnight after which an additional 2.3 ml. of acetone was removed over a period of 1.5 hr. At this point, the column was heated, and about 70 ml. of isopropenyl acetate was distilled during a period of 3 hr. The flask was cooled, 0.11 g. of sodium acetate was added, and the remaining isopropenyl acetate was removed under reduced pressure.

The residue was dissolved in an equal volume of ether and washed successively with two 25-ml. portions of water, 25 ml. of saturated sodium bicarbonate solution, two 25-ml. portions of water and dried over magnesium sulfate.

The solution was filtered, the ether was removed under reduced pressure, and the residue was distilled through a semi-micro column giving, after 6.5 g. of forerun boiling

(16) On 80% by weight of 1,2,3-tris-(2-cyanoethoxy)propane on 48–80 mesh firebrick at 180°.

(7) G. Wittig and R. Polster, *Ann.*, **599**, 13 (1956).

(8) F. Weygand, H. Daniel and H. Simon, *Chem. Ber.*, **91**, 1691 (1958). However, see "Organic Reactions," Vol. XI, John Wiley and Sons, Inc., New York, N. Y., 1960, p. 329.

(9) Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy for analyses.

(10) A. C. Cope and E. Ciganek, *Org. Syntheses*, **39**, 19 (1959).

(11) E. R. Alexander and A. C. Cope, *J. Am. Chem. Soc.*, **66**, 886 (1944).

(12) L. H. Amundsen and L. S. Nelson, *ibid.*, **73**, 242 (1951).

(13) P. D. Bartlett and A. Schneider, *ibid.*, **67**, 141 (1945).

(14) A. Brändström, *Arkiv Kemi*, **1**, 481 (1950).

(15) Prepared essentially by the method of E. A. Braude and O. H. Wheeler, *J. Chem. Soc.*, 320 (1955), but distilled before use.

at 73–105° (1.6 mm.), 43.3 g. (89%) of VIII boiling at 105.5–109° (1.6 mm.), n_D^{25} 1.4590.

Anal. Calcd. for $C_{15}H_{25}O_4$: C, 66.14; H, 10.36. Found: C, 66.49; H, 10.59.

Ethyl 3-*t*-Butyl-4,4-dimethyl-2-pentenoate by Acetate Pyrolysis.—A solution of 32.9 g. of VIII in 33 ml. of pentane was dropped through a vertical 10-mm. column with a 15-cm. section packed with glass helices heated at 300°. A slow stream of nitrogen was passed through the column, and the solution was added at a rate of about 16 drops per minute. The bottom of the column was connected directly to a trap cooled in Dry Ice-acetone. After addition was complete (about 4 hr.), the column was cooled and was washed with 10 ml. of pentane. The contents of the trap were allowed to melt and washed with two 30-ml. portions of saturated sodium bicarbonate solution and two 30-ml. portions of water, and then dried over magnesium sulfate.

After filtration and removal of the pentane, the residue was distilled through a semi-micro column, giving 22.0 g. of ethyl 3-*t*-butyl-4,4-dimethyl-2-pentenoate (VII), b.p. 79–80° (1.9–2.0 mm.), and 3.0 g. of recovered β -acetoxy ester. This represents a 94% yield based on unrecovered β -acetoxy ester. An infrared spectrum of the product was identical in every respect with that of a sample prepared by acid-catalyzed rearrangement of V.

Ozonization of VII.—A stream of oxygen delivering about 13 mg. of ozone per minute was passed through a solution of 1.44 g. of VII in 40 ml. of dry ethyl acetate maintained at –20° for 1 hr. This solution was added to a solution prepared from 1.2 g. of 2,4-dinitrophenylhydrazine, 6 ml. of concentrated sulfuric acid, 9 ml. of water and 30 ml. of ethanol. The solution was boiled on a steam-bath until about 10 ml. of solvent had evaporated, and then cooled in a refrigerator. The precipitate was collected by filtration and weighed 0.54 g. (27% calculated as ethyl glyoxylate 2,4-dinitrophenylhydrazine). The precipitate was recrystallized twice from aqueous ethanol, giving orange platelets (m.p. 126–127.5°) of ethyl glyoxylate 2,4-dinitrophenylhydrazine. A mixed melting point with an authentic sample, prepared as described below, showed no depression, and the infrared spectra of the two samples were identical.

The mother liquors from the ozonization were mixed with 100 ml. of water and 40 g. of sodium hydroxide and refluxed for 24 hr. The resulting mixture was steam distilled. The distillate was saturated with salt, extracted with ether and the extracts were dried. Distillation of the ether left a residual liquid. Gas chromatography on a 30% by weight Silicone oil (Dow-Corning no. 550) on a 48–80 mesh firebrick column showed hexamethylacetone to be the only component other than ether and ethanol. The infrared spectrum of a sample collected from the effluent gas from the column was identical with that of an authentic sample.

Ethyl Glyoxylate 2,4-Dinitrophenylhydrazine.—The procedure of Rigby¹⁷ was used. Diethyl *D*-tartrate (2.06 g.) was stirred with a mixture of 3.5 g. of 80% sodium bismuthate and 7 ml. of 3.3 *M* phosphoric acid solution for 3.3 hr. The mixture was filtered into a solution of 4 g. of 2,4-dinitrophenylhydrazine in 20 ml. of sulfuric acid, 30 ml. of water and 100 ml. of ethanol. An immediate yellow precipitate formed which was collected by filtration and represented a quantitative yield of the derivative. Two recrystallizations from ethanol gave an analytical sample, m.p. 126.0–127.5°.

Anal. Calcd. for $C_{16}H_{16}N_4O_6$: C, 42.56; H, 3.57; N, 19.85. Found: C, 42.59; H, 3.62; N, 19.79.

Ethyl 3-*t*-Butyl-4,4-dimethylpentanoate (IX).—To a solution of 48.0 g. of ethyl 3-*t*-butyl-4,4-dimethyl-2-pentenoate (VII) in 300 ml. of glacial acetic acid in a 500-ml. pressure bottle was added 3.0 g. of platinum oxide. The solution was shaken in a hydrogen atmosphere at 30 p.s.i. and room temperature. The theoretical amount of hydrogen was absorbed over a period of 1 hr. The solution was filtered and concentrated to a volume of about 70 ml. under reduced pressure with gentle heating (55°). The residue was diluted with 220 ml. of water and extracted with five 55-ml. portions of pentane. The combined pentane extracts were washed with 50 ml., then 30 ml. of saturated sodium bicarbonate solution and with 50 ml. of water, and dried over magnesium sulfate. Following filtration and removal of the pentane, the residue was distilled through a semi-micro column, giving 44.9 g. (93%) of IX boiling at 80–82° (2.6 mm.),

(17) W. Rigby, *J. Chem. Soc.*, 1907 (1950).

n_D^{25} 1.4421. An analytical sample had b.p. 76.5° (2.1 mm.), n_D^{25} 1.4414.

Anal. Calcd. for $C_{13}H_{26}O_2$: C, 72.84; H, 12.23. Found: C, 72.99; H, 12.46.

3-*t*-Butyl-4,4-dimethylpentanoic Acid Hydrazide.—In a glass-lined 300-ml. bomb was placed a solution of 53.7 g. of IX in 100 ml. of ethanol and 50 g. of 95% hydrazine. The bomb was pressurized to 500 p.s.i. of nitrogen and heated at 150° for 96 hr. Attempts to prepare this compound under milder conditions resulted in no reaction, while shorter periods of heating gave incomplete reaction. The bomb was cooled and vented, and the solution was concentrated under reduced pressure to a waxy solid that weighed 49.7 g. (100% yield would be 48.8 g.). This material was of sufficient purity to be used in the Curtius reaction. An analytical sample was prepared by several recrystallizations from pentane followed by sublimation at 65–70° (1.0 mm.), m.p. 89–92°.

Anal. Calcd. for $C_{11}H_{24}ON_2$: C, 65.95; H, 12.08; N, 13.99. Found: C, 65.99; H, 11.78; N, 13.80.

Methyl N-(2-*t*-Butyl-3,3-dimethyl)-butyl Carbamate (X).—Fifteen milliliters of ether was added to a solution of 2.82 g. of sublimed 3-*t*-butyl-4,4-dimethylpentanoic acid hydrazide in 20 ml. of water and 1.40 g. of concentrated hydrochloric acid and the mixture was cooled with stirring in an ice-salt-bath. At 5° some of the hydrazide hydrochloride precipitated, and 5 ml. of water was added to make stirring possible. To this mixture, which was maintained below 5° throughout the reaction by the addition of small pieces of Dry Ice, a solution of 1.06 g. of sodium nitrite in 2.8 ml. of water was added dropwise during a period of 5 min.; 3 ml. of ether was added, and the mixture was stirred for 20 min. at 5°. The mixture then was extracted in a separatory funnel with three 5-ml. portions of ether. The combined extracts were washed with 3 ml. of saturated sodium bicarbonate solution followed by two 5-ml. portions of water, and dried over calcium chloride for 30 min. in a refrigerator. The solution was decanted, diluted with 25 ml. of methanol, and the ether was distilled through a semi-micro column until the head temperature reached 64°. A vertical condenser was attached, and the mixture was heated under reflux overnight. The methanol was removed under reduced pressure leaving a thick oil that solidified after it was dried at 1 mm. for several hours. The crude product weighed 2.89 g. (95%), m.p. 57–60°. An analytical sample was prepared by sublimation at 60° (1.0 mm.), m.p. 56.0–58.5°.

Anal. Calcd. for $C_{12}H_{25}O_2N$: C, 66.93; H, 11.70; N, 6.51. Found: C, 66.87; H, 11.81; N, 6.54.

In other preparations on a larger scale, the crude hydrazide (prepared as described above) was used.

N-Methyl-2-*t*-butyl-3,3-dimethylbutylamine (XI).—To a slurry of 1.0 g. of lithium aluminum hydride in 50 ml. of ether in a three-necked 100-ml. round-bottomed flask fitted with a reflux condenser, dropping funnel and magnetic stirrer, under an atmosphere of dry nitrogen, was added a solution of 2.15 g. of crude X in 10 ml. of ether over a period of 20 min. The mixture was then refluxed gently overnight. The mixture was hydrolyzed by adding in succession 1 ml. of water, 0.85 ml. of 20% sodium hydroxide solution and then 3.7 ml. of water, followed by stirring for 2 hr. The solution was filtered and the resulting white precipitate was washed several times with ether. The combined ether solutions were extracted with a total of 38 ml. of 10% hydrochloric acid. The hydrochloric acid washes were cooled in an ice-bath and 10 g. of sodium hydroxide was added. This mixture was extracted with five 10-ml. portions of ether, which were combined and dried over potassium hydroxide pellets. The solution was decanted and the ether was removed under reduced pressure. The residue was distilled through a semi-micro column giving 1.25 g. (73%) of XI, b.p. 88–89° (21 mm.), n_D^{25} 1.4475.

The picrate of XI was prepared by adding 4 ml. of a saturated ethanolic solution of picric acid to a solution of 126 mg. of the amine in 4 ml. of ethanol. The picrate (198 mg., 67%) melted at 172.5–175.0° after three crystallizations from ethanol.

Anal. Calcd. for $C_{17}H_{28}N_4O_7$: C, 50.99; H, 7.05; N, 13.99. Found: C, 50.88; H, 7.11; N, 14.01.

N,N,N-Trimethyl-2-*t*-butyl-3,3-dimethylbutylammonium Iodide (XII).—A solution of 22.3 g. of XI in 130 ml. of

methanol was stirred under gentle reflux with 72.5 g. of methyl iodide and 28 g. of sodium bicarbonate for 24 hr., at which time an additional 72.5 g. of methyl iodide was added. Stirring and heating were continued; 48 hr. later 30 g. of methyl iodide was added. After a total of 144 hr. of heating, the solution was cooled, filtered and concentrated to dryness under reduced pressure. The residual white solid was extracted with four 200-ml. portions of boiling chloroform. The combined extracts were cooled, filtered and concentrated to dryness. The residue was recrystallized from 800 ml. of acetone, giving 24.1 g. of the methiodide. An additional 13.3 g. was recovered from the mother liquors. The total yield was 37.4 g. (88%) (for properties of XII see Table II).

N,N-Dimethyl-2-*t*-butyl-3,3-dimethylbutylamine (IV).—In a 1-l. three-necked flask fitted with a reflux condenser and a magnetic stirrer, under an atmosphere of nitrogen, a suspension of 25.1 g. of XII in 450 ml. of tetrahydrofuran was stirred under reflux with 17.4 g. of lithium aluminum hydride for 96 hr. After cooling in an ice-bath, 35.6 ml. of 15% sodium hydroxide solution was slowly added dropwise with stirring. Following this, 71.5 ml. of 30% potassium hydroxide solution was added and the mixture was steam distilled until the distillate was neutral (about 2.75 l.). The distillate was acidified with 20 ml. of concentrated hydrochloric acid and concentrated to dryness under reduced pressure. The residue was dissolved in 75 ml. of water, made basic by the cautious addition of 80 ml. of a cold 50% sodium hydroxide solution, and the product was extracted with four 50-ml. portions of ether and one 50-ml. portion of pentane. The combined extracts were dried over potassium hydroxide pellets. The solvent was distilled and the residue distilled through a semi-micro column, giving 12.5 g. (88%) of IV, b.p. 98–99° (27 mm.), n_D^{20} 1.4483.

Anal. Calcd. for $C_{12}H_{27}N$: C, 77.76; H, 14.68; N, 7.56. Found: C, 77.84; H, 14.66; N, 7.74.

In another experiment in which the reaction time was 24 hr., the yield was 72%.

Tertiary amine picrates were prepared as described above and are listed in Table I. The picrates of I and II were recrystallized from 1:1 ethanol-water. The picrates of III and IV were recrystallized from ethanol.

Quaternary iodides of I, II and III (Table II) were prepared by stirring an ether solution of the tertiary amine with an excess of methyl iodide for 48 hr. They were recrystallized from acetone or 5:1 ethyl acetate-ethanol.

Amine Oxides.—The N-oxides of I, II and III were prepared by a method illustrated by the following procedure.

N,N-Dimethyl-2-propylpentylamine N-Oxide.—To a solution of 5.62 g. of N,N-dimethyl-2-propylpentylamine in 30 ml. of absolute methanol was added 15 ml. of 30% hydrogen peroxide solution. The mixture was stirred, and small portions were tested periodically with phenolphthalein indicator, a pink color indicating the presence of unoxidized amine. An additional 6 ml. of hydrogen peroxide was added after a 10-hr. period. After the mixture had been stirred for 24 hr. no pink color was observed with phenolphthalein, and a few drops of an aqueous suspension of platinum black was added to decompose excess hydrogen peroxide. After the solution had stirred overnight, the evolution of oxygen had ceased. The mixture was filtered and the residue was washed with several small portions of methanol. The combined filtrate and washings were then concentrated, initially at 20 mm. at 35°, and finally at 0.2 mm. at room temperature, to a glassy solid.

N,N-Dimethyl-2-*t*-butyl-3,3-dimethylbutylamine N-oxide was prepared under similar conditions, but in an atmosphere of nitrogen, for it required from 10 to 30 days of contact with hydrogen peroxide before a phenolphthalein spot test gave no pink color. Because this amine oxide spontaneously decomposed at room temperature, the solution was concentrated by distillation under reduced pressure and the product was collected in a trap cooled with Dry Ice-acetone. The small amount of residual amine oxide was pyrolyzed as described below.

Quaternary hydroxides were prepared as illustrated by the following procedure.

N,N,N-Trimethyl-2-propylpentylammonium Hydroxide.—To a solution of 10.1 g. (0.0338 mole) of N,N,N-trimethyl-2-propylpentylammonium iodide in 150 ml. of water was added 0.0676 mole of silver hydroxide freshly prepared from 11.5 g. of silver nitrate and 5.4 g. of sodium hydroxide. This mixture was allowed to stir for 24 hr. and then filtered. The residue was washed with water until the washings were neutral to pH paper. A drop of the combined filtrates gave no precipitate when tested with acidified silver nitrate solution. The combined filtrates were concentrated to a thick jelly at 20 mm. at a temperature below 45°, and finally at 0.1–1.0 mm. at room temperature.

Pyrolysis of Amine Oxides and Trimethylammonium Hydroxides.—The concentrated amine oxide or quaternary base was heated under reduced pressure (1–10 mm.) in a round-bottomed flask connected through a short Vigreux column to a series of two traps, the first cooled with Dry Ice-acetone, and the second with liquid nitrogen. The temperature was raised slowly until decomposition was complete as indicated by the complete distillation of the products from the reaction flask.

The two traps were washed with pentane and their contents were combined with the washes and extracted with several portions of cold 10% hydrochloric acid followed by several portions of water. The pentane solutions were dried over magnesium sulfate. The pentane was distilled through a semi-micro column and the residual olefin distilled through the same column. By making the aqueous washes strongly basic, recovered tertiary amines were obtained.

For the decomposition of I, inasmuch as the product had b.p. 65°, no pentane was used in the above procedure and 0.25-mole quantities were pyrolyzed. After washing the olefin with 10% hydrochloric acid and water, it was dried by cooling in Dry Ice-acetone, transferred to a pear-shaped flask, and distilled from a small piece of sodium.

Decomposition of N,N,N-Trimethyl-2-ethylbutylammonium Hydroxide at Atmospheric Pressure.—A solution of 0.20 mole of the quaternary base in 700 ml. of water was placed in a 2-l. round-bottomed flask and heated by means of an electric heating mantle. The distillate was collected in a trap cooled in Dry Ice-acetone over a period of 3 hr. No detectable organic material distilled with the first 500 ml. of water. During the distillation of the last 200 ml., the flask temperature rose from 105° to 169° and decomposition occurred. The last 10 ml. of material in the flask was distilled under slightly reduced pressure (100 mm.). The trap contents were allowed to melt, the organic phase was separated and washed with five 10-ml. portions of 10% hydrochloric acid and one 10-ml. portion of water, and the product was distilled as described above.

The acid washes were combined with the aqueous phase and 10 ml. of concentrated hydrochloric acid and then evaporated to dryness under reduced pressure. The residual solid was dissolved in 100 ml. of water and made strongly basic with 50% sodium hydroxide solution to give the recovered tertiary amine.

The yields of olefins and recovered tertiary amines are listed in Table III.

Olefins.—The olefins obtained in the yields listed in Table III were analytically pure. All but 1,1-di-*t*-butylethylene showed strong infrared absorption at 890 cm^{-1} , while in that hydrocarbon the band was shifted to 900 cm^{-1} . Observed physical constants were in good agreement with some reported earlier: $(C_2H_5)_2C=CH_2$, b.p. 64–65°, n_D^{20} 1.3941 (lit.¹⁸ b.p. 64.5–65.0°, n_D^{20} 1.3948); $(n-C_3H_7)_2C=CH_2$, b.p. 114–115°, n_D^{20} 1.4115 (lit.¹⁹ b.p. 117.3° at 751 mm., n_D^{20} 1.4136); $(i-C_3H_7)_2C=CH_2$, b.p. 99–100°, n_D^{20} 1.4055 (lit.¹⁹ b.p. 102.4–102.5° at 741 mm., n_D^{20} 1.4079); $(t-C_4H_9)_2C=CH_2$, b.p. 148–150°, n_D^{20} 1.4340 (lit.²⁰ b.p. 150.3° at 760 mm., n_D^{20} 1.4339).

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