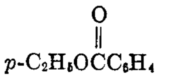
TABLE I
$RNHCH_2CH_2CHOHCH_3$
I

I, R =	Yield, %	B.p. or m.p./mm.	Formula	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N	Infrared spectra[a] μ
C_6H_5—	20	124/1.3 61[b]								2.9, 6.22, 6.65, 7.25, 7.6, 8.9
p-$CH_3OC_6H_4$—	40	162/2[c]	$C_{11}H_{17}NO_2$	67.69	8.71	7.18	67.79	8.50	7.21	2.88, 6.14, 6.55, 7.22, 7.65, 8.8
o-$CH_3OC_6H_4$—	10	152/3[d]								2.88, 6.18, 6.65, 7.25, 7.4, 7.65, 8.8
 $p\text{-}C_2H_5O\overset{\overset{O}{\|}}{C}C_6H_4$	28	104[e]	$C_{13}H_{19}NO_3$	65.81	8.01	5.90	65.81	7.93	6.10	2.88, 5.85, 6.15, 6.5, 7.25, 7.41, 8.95
α-Naphthyl	10	168/1.7[f]	$C_{14}H_{17}NO$	78.13	7.90	6.51	77.73	8.12	6.50	2.9, 6.15, 6.3, 6.55, 7.25, 7.45, 8.95
β-Naphthyl	12	78[g]	$C_{14}H_{17}NO$	78.13	7.90	6.51	77.34[h]	7.81	6.50	2.9, 6.1, 6.22, 6.55, 7.25, 7.4, 8.87

[a] Solids in chloroform and liquids in film. [b] Colorless crystals from hexane; lit.,[4] m.p. 61°. Picrate crystallized from benzene, m.p. 118°. Calcd. for $C_{16}H_{18}N_4O_8$: C, 48.73; H, 4.57; N, 14.21. Found: C, 48.98; H, 4.31; N, 14.20. [c] n^{25}_D 1.5501. [d] Lit.,[4] b.p. 158–160°/8 mm., n^{25}_D 1.5508. [e] The compound was obtained by chilling the benzene filtrate of the reaction mixture after addition of one volume of ether or by chromatography of benzene solution on ethyl acetate-washed alumina and elution with 2:1 benzene–ether. Crystals from benzene. [f] n^{25}_D 1.6553. [g] Colorless crystals from benzene–petroleum ether (b.p. 60–80°). [h] Even though the carbon analysis was low, the infrared spectrum was satisfactory.

and was recovered unchanged on esterification after forty hours at room temperature. Similarly the amino alcohol from α-naphthylamine failed to close either at room temperature or at 80° for four hours.

The synthesis of tetrahydrolepidines in two steps from substituted primary amines is thus a variant from the established methods of synthesis.

Experimental[6]

The following procedure for the preparation of 4-p-anisidino-2-butanol served as a general procedure for the alkylation of other primary amines.

A mixture of p-anisidine (12.3 g.; 0.1 mole) and 1,3-butanediol (10 g.; 0.11 mole) in benzene (60 ml.) containing 2 drops of 4% aqueous sodium hydroxide was refluxed with Raney nickel[7] (20 g.) for 30 hr. The mixture was filtered, nickel washed with ether, and the filtrate was extracted with 10% hydrochloric acid. The acidic extract was made strongly basic and re-extracted into ether. The product obtained after removal of ether was fractionally distilled (see Table I.).

dl-**1,2,3,4-Tetrahydrolepidine.**—A solution of the alcohol I (R = C_6H_5) (200 mg.) in concentrated sulfuric acid (1 ml.) was kept at room temperature for 24 hr. The mixture was poured into crushed ice, made alkaline, and extracted with ether. Removal of ether and distillation yielded 160 mg. (90%) of *dl*-1,2,3,4-tetrahydrolepidine, b.p. 106°/7.5 mm. (lit.,[8] b.p. 110°/8 mm.). The infrared spectra of the compound was indistinguishable from the spectra of authentic compound prepared by sodium and alcohol reduction of lepidine.[9] The N-benzoyl derivative crystallized from alcohol and had m.p. and mixed m.p. with authentic specimen 138° (lit.,[8] m.p. 138°).

The picrate derivative, prepared in benzene solution, crystallized from benzene in yellow, feathery needles and had m.p. and mixed m.p. with authentic specimen 138° (reported[10] m.p. 157°).

Anal. Calcd. for $C_{16}H_{16}N_4O_7$: C, 51.06; H, 4.26; N, 14.89. Found: C, 51.20; H, 4.50; N, 14.74.

dl-**6-Methoxy-1,2,3,4-tetrahydrolepidine.**—The alcohol I (R = p-$CH_3OC_6H_4$) (750 mg.) was dissolved in concentrated sulfuric acid (3 ml.) and immediately poured into crushed ice. The solution was made alkaline and extracted with ether. Removal of ether and distillation of the residue yielded 410 mg. (60%) of *dl*-6-methoxy-1,2,3,4-tetrahydrolepidine, b.p. 118–120°/0.9 mm. (lit.,[5] b.p. 114–115°/0.5 mm.).

Dehydrogenation of the above tetrahydrolepidine (400 mg.) in the presence of palladium–charcoal (10%; 150 mg.) and p-cymene (5 ml.) under reflux in a nitrogen atmosphere for 10 hr. gave after usual work-up 350 mg. (90%) of 6-methoxylepidine; picrate, m.p. 224° (lit.,[11] m.p. 224–225°).

Acknowledgment.—We thank Dr. M. J. Thirumalachar and Dr. D. S. Bhate for their interest in the work.

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(6) Melting points are uncorrected. We are thankful to A. V. Patankar for microanalysis.

(7) Raney nickel was prepared from nickel-aluminum alloy (B.D.H.) according to the method described in A. I. Vogel's "A Textbook of Practical Organic Chemistry," 3rd ed., Longmans, Green and Co., New York, N. Y., 1956, p. 871.

(8) J. C. Sauer and H. Adkins, *J. Am. Chem. Soc.*, **60**, 402 (1938).

(9) A. A. Zats and V. V. Levchenko, *Zh. Obshch. Khim.*, **22**, 2076 (1952); *Chem. Abstr.*, **47**, 9328 (1953).

(10) A. Chichibabin and C. Barkoysky, *Compt. rend.*, **212**, 914 (1941).

(11) A. T. Babayan and N. P. Gambaryan, *Sb. Statei Obshch. Khim., Akad. Nauk SSSR*, **1**, 666 (1953); *Chem. Abstr.*, **49**, 1048 (1955).

Thermal Elimination Reaction of Aliphatic Amine Salts

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Received January 29, 1962

We recently reported[1] the synthesis of highly hindered aliphatic tertiary amine salts of the type

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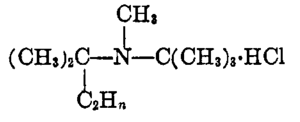
(1) C. Ainsworth and N. R. Easton, *J. Org. Chem.*, **26**, 3776 (1961).

TABLE I

TERTIARY AMINES, $(CH_3)_2CR\overset{CH_3}{N}—C(CH_3)_3$

Compound	R	Hydrocarbon evolved on heating[a]				
		·HCl			·Picrate	
A	$C\equiv CH$	70% W[b]	15% X[c]	15% U[d]	80% W	20% X
B	$CH=CH_2$	90% Y[e]	10% W		95% Y	5% W
C	$CH_2—CH_3$	80% Z[f]	20% W		80% Z	20% W

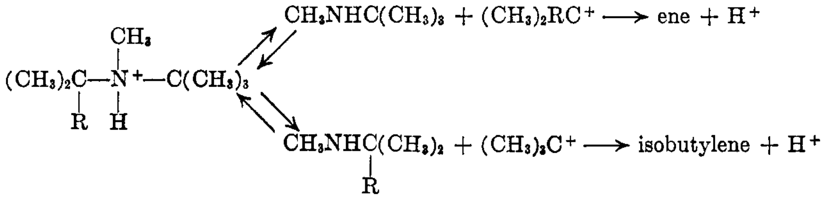
[a] Identified by gas chromatography. A concentrated chloroform solution of the salt was injected into a unit with the following operating conditions: injection chamber temp. 190°; detector temp. 170°; 8-ft. column (3/8-in. i.d.) containing 30% Dow Corning silicone oil DC-300 on 30–60 mesh firebrick, column temp. 100°; helium flow rate at 30 p.s.i. and 25° was 200 cc./min. [b] W is isobutylene, retention time 1.0 min. [c] X is 2-methyl-1-buten-3-yne, retention time 1.4 min. The unsaturated hydrocarbon for comparative purpose was prepared from N-isopropyl-N,N,1,1-tetramethylpropargylammonium iodide.[1] [d] U is unidentified, retention time 2.0 min. In addition, there is a small peak at about 4 min. [e] Y is isoprene, retention time 1.9 min. In addition, there are unidentified peaks at 3.8 and 7.5 min. [f] Z is a mixture consisting of equal amounts of 2-methyl-1-butene, retention time 1.5 min., and 2-methyl-2-butene, retention time 1.7 min. The authentic compounds were prepared according to J. F. Norris and R. Reuter, *J. Am. Chem. Soc.*, 49, 2624 (1927).



$(CH_3)_2\underset{C_2H_n}{C}—\overset{CH_3}{N}—C(CH_3)_3\cdot HCl$

illustrated below. It was noted that, on heating, these relatively low melting salts evolved gas, solidified, and remelted at considerably higher temperatures.

This paper reports a study of the thermal decomposition products of some closely related aliphatic tertiary amine salts of the general formula shown in Table I.[1] It was found that compound A-HCl melted at 140° with gas evolution and quickly solidified to give a higher melting salt that was identified as N,1,1-trimethylpropargylamine hydrochloride. Compound B-HCl behaved in a similar manner when heated, and the new salt was shown by melting point and infrared analysis to be mainly N-methyl-*t*-butylamine hydrochloride. Crystalline compound C-HCl decomposed at its fusion point to give a melt that was not pure but which on recrystallization gave N-methyl-*t*-butylamine hydrochloride.



Next the salts were decomposed in the injection chamber of a gas chromatography unit, and by comparison and combination with known hydrocarbons the products of pyrolysis were determined as shown in Table I. In addition, samples of the gases were collected and identified by infrared analysis.

These observations are consistent with the theory that an E 1 reaction[2] takes place, with the stability of the carbonium ion the chief factor in determining the olefin formed. The carbonium ion $(CH_5)_2RC^+$ is stabilized by a summation of the inductive and the resonance effects, with $R = CH=CH_2 > C_2H_5 > CH_3 > C\equiv CH$.

The elimination reaction also took place in aqueous medium. When compound B·HCl, dissolved in 6 *N* hydrochloric acid, was heated under reflux for one hour, isoprene polymer and N-methyl-*t*-butylamine hydrochloride were formed. The polymer was the same as that formed from isoprene and 6 *N* hydrochloric acid.

The earliest observation of a tertiary amine hydrochloride undergoing change on heating was recorded by Hofmann.[3] Although isolated observations of amine hydrohalide thermal decomposition are recorded,[4] the problem was not systematically investigated. Actually, it was the thermal treatment of quaternary ammonium compounds that received the attention of Hofmann, and from this work his classical degradation rules evolved.

Certain secondary and even primary amine salts[4b] related to this series have been found to

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(2) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 424–427; (b) D. J. Cram, "Olefin Forming Elimination Reactions," in M. S. Newman "Steric Effects in Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1956, pp. 304–348; (c) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp. 472–507.

(3) A. W. Hofmann, *Proc. Roy. Soc.*, 10, 595 (1860), reported the decomposition of trimethylamine hydrochloride into dimethylamine hydrochloride, methyl chloride, and trimethylamine. The reaction once served as a commercial method for the production of methyl chloride from trimethylammonium chloride (by-product of the sugar beet industry) and added hydrogen chloride.

(4) The best sources found that summarize the degradation of amine salts are (a) W. J. Hickinbottom, "Reactions of Organic Compounds," Longmans Green and Co., New York, N. Y., 3rd ed., 1957, p. 416, and (b) C. D. Hurd, "The Pyrolysis of Carbon Compounds," ACS Monograph Series, 1929, p. 310.

undergo thermal fragmentation. Di-*t*-butylamine[5] hydrochloride on melting gave isobutylene and *t*-butylamine hydrochloride. 1,1-Dimethylallylamine hydrochloride[6] heated at 260° decomposed to give isoprene and ammonium chloride.

Important degradation products are obtained by pyrolysis under reduced pressure of certain alkaloid hydrochlorides[7] and we wish to point out that this method might be useful for obtaining degradative compounds from other natural products. Preliminary findings indicate that pyrolysis of N-*t*-butyl-N-methyl tertiary amine hydrochlorides to N-methyl secondary amine salts can be synthetically useful.

Acknowledgment.—The physical data were supplied by H. E. Boaz, D. O. Woolf, Jr. (infrared), and R. R. Pfeiffer and Ann Van Camp (X-ray). W. Hargrove prepared di-*t*-butylamine hydrochloride.

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(5) F. Klages and H. Setz, *Ber.*, **92**, 2606 (1959).

(6) Prepared according to the general method of G. F. Hennion and E. G. Teach, *J. Am. Chem. Soc.*, **75**, 4297 (1953).

(7) M. Gorman, N. Neuss, and K. Biemann, *ibid.*, **84**, 1058 (1962).

Communications TO THE EDITOR

Observations on the Acetylation of Carbohydrates in Aqueous Solution

Sir:

In an attempt to prepare disaccharides containing D-glucose linked through the C-2 hydroxyl group, we considered the use of 1,3,4,6-tetra-*O*-acetyl-α-D-glucose. The preparation of this acetate by acetylation of D-glucose in aqueous solution has been described recently.[1,2]

In our hands, several acetylations of glucose by this method all gave a crystalline product in 60–70% yield which had physical constants in good agreement with those reported by Prey and Aszalos[1] (m.p. 98°, $[\alpha]_D$ +63°) although the specific rotation of our product as well as that of the above authors was very different from the value of +145° previously reported.[3]

Acetyl determination[4] indicated that the product contained five acetyl groups per glucose unit, and no hydroxyl absorption could be detected in the infrared. Gas-liquid partition chromatography[5] showed that the product was a mixture of the α- and β-anomers of penta-*O*-acetyl-D-glucopyranose. No other compound was detected. The two anomers are difficult to separate by fractional crystallization but a synthetic mixture, prepared in the ratio indicated by the optical rotation, had the same melting point and infrared absorption spectrum.

We would also like to point out that the physical constants reported[1] for "sorbital pentaacetate" and "mannitol pentaacetate" are in excellent agreement with those of the corresponding hexaacetates; and when we applied the acetylation method to mannitol, the crystalline product contained no free hydroxyl group and did not depress the melting point of mannitol hexaacetate.

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RECEIVED JULY 11, 1962

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(1) V. Prey and A. Aszalos, *Monatsh. Chem.*, **91**, 729 (1960).

(2) A. Aszalos and V. Prey, *Die Stärke*, **14**, 50 (1962).

(3) R. U. Lemieux and G. Huber, *Can. J. Chem.*, **31**, 1040 (1953).

(4) S. Hestrin, *J. Biol. Chem.*, **180**, 249 (1949).

(5) We would like to thank Dr. M. B. Perry of Queen's University, Kingston, Ont., Can., for the gas chromatographic analysis.

(6) Present address: Corn Products Co., Technical Division, P. O. Box 345, Argo, Ill.

A New Synthesis of Diarylphosphinous Chlorides[1]

Sir:

In spite of the current interest in organophosphorus chemistry, the diarylphosphinous chlorides, Ar_2PCl, remain rather inaccessible and therefore little explored,[2] even though they serve as valuable precursors of other phosphorus compounds. We have devised for these chlorides a new synthesis which appears to have considerable versatility and the potential of making these compounds more readily available.

The reaction of aryldiazonium fluoroborates with arylphosphonous dichlorides is known to give a type of intermediate which may be hydrolyzed to diarylphosphinic acids.[3]

$$ArN_2BF_4 + Ar'PCl_2 \longrightarrow [ArAr'PCl_2{}^+BF_4{}^-] \xrightarrow{H_2O} ArAr'P(O)OH$$

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(1) Supported by Research Grant CY-5507 from the National Cancer Institute, Public Health Service.

(2) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley & Sons, Inc., New York, N. Y., 1950, Chap. 3.

(3) L. D. Freedman and G. O. Doak, *J. Am. Chem. Soc.*, **74**, 2884 (1952).