Experimental Section

Preparation of 4,7-Dihydro-*N*-methylindoline (2). A 1-l. three-necked flask equipped with a mechanical stirrer, Dry Ice condenser, and gas inlet and outlet was purged with nitrogen. Ammonia was passed through a KOH gas washing tower, and about 500 ml was collected in the reaction flask. To the ammonia a solution of *N*-methylindoline (10 g, 0.075 mol) in tetrahydrofuran (100 ml) was added along with isopropyl alcohol (45 g, 0.75 mol). To this stirring mixture was added lithium ribbon (1.6 g, 0.23 g-atom) in small pieces, and the reaction was allowed to continue until the blue color had discharged, usually about 0.5 hr. At this point an aliquot of the reaction mixture was quenched in an ether–water mixture, and the ether layer was examined by nmr to determine if all aromatic protons had disappeared. Usually an additional 0.5 g of lithium was required in order to effect complete reduction and the blue color persisted for an hour or so. At this point another aliquot was checked by quenching and nmr analysis and more lithium was added if necessary. When complete reduction was indicated, the ammonia was allowed to evaporate under nitrogen flow. A mixture of water and ether (100 ml each) was added and the organic layer was washed rapidly with water and dried over solid KOH pellets. Concentration of the ether layer and rapid distillation in an apparatus carefully washed with ammonium hydroxide and dried gave 2 (8.6 g, bp 39–41° (0.07 mm)) in 86% yield; nmr (neat) τ 4.4 (s, 2 H), 6.95–7.6 (m, 8 H), 7.7 (s, 3 H).

Anal. Calcd for $C_9H_{13}N$: C, 79.95; H, 6.69. Found: C, 80.08; H, 9.58.

Preparation of 4,5-Dihydro-*N*-methylindoline (3). The identical reaction as described above for the preparation of 2 was conducted again upon *N*-methylindoline (10 g). Work-up of the reaction was also identical except that *ca.* 100 mg of Dowex 50W-X2 200–400 mesh hydrogen form cation-exchange resin was added to the pot and then the product was slowly distilled to give 3 (8.1 g, bp 69–73° (3 mm)): nmr (neat τ 4.1 (m, 1 H), 4.9 (m, 1 H), 5.6 (d, 1 H), 6.8–8.7 (m, 7 H), 7.5 (s, 3 H); uv λ_{max}(*i*-PrOH) 306 (ϵ 5200).

Anal. Calcd for $C_9H_{13}N$: C, 79.95; H, 9.69. Found: C, 79.90; H, 9.62.

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References and Notes

(1) Fellow of the Alfred P. Sloan Foundation.
(2) *This compound has been subjected to Birch conditions, but the results were incomplete and not rigorously conclusive. See footnote 3.*
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Degradation of Tertiary Amines *via* Aminimines

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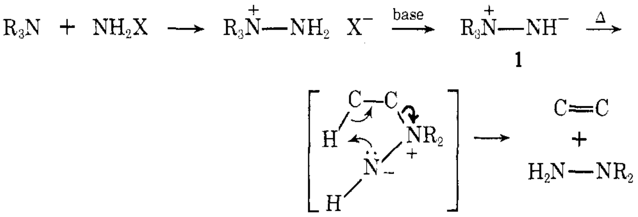
In 1879 Fischer reported[1] that, when 1,1,1-triethylhydrazinium hydroxide is refluxed in water, 1,1-diethylhydrazine is formed (eq 1). He formulated the reaction as also producing ethylene, but mentioned no experimental evidence for it; perhaps this was merely equation balancing. However, since he had previously shown[2] that some hydrazinium hydroxides give alcohols by a displacement process, he might have had unreported evidence that ethanol was not formed from the ethyl compound.

$$(CH_3CH_2)_3\overset{+}{N}—NH_2\ OH^- \xrightarrow[H_2O]{\Delta} (CH_3CH_2)NNH_2 + CH_2{=}CH_2 \quad (1)$$

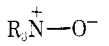
If such eliminations could be effected generally, they might furnish a useful alternative to the Hofmann and Cope degradations, particularly since hydrazinium salts can be formed readily from tertiary amines.[1b,3] The overall plan for such a degradation is indicated in Scheme I.

Scheme I



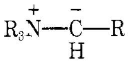
$$R_3N + NH_2X \longrightarrow R_3\overset{+}{N}—NH_2\ X^- \xrightarrow{base} \underset{1}{R_3\overset{+}{N}—NH^-} \xrightarrow{\Delta}$$

Presumably under proper conditions, though perhaps not in water, the elimination would occur *via* an aminimine inner salt 1,[4] and therefore would be a nitrogen analog of the Cope elimination[5] of amine oxides 2, and the α,β' mechanism of elimination in some hindered quaternary ammonium ions *via* the ylides 3.[6] Eliminations from the similar aminimide inner salts 4 have been reported,[7] but these occurred only at rather high temperatures.



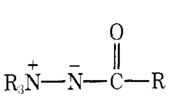
$R_3\overset{+}{N}—O^-$

2



$R_3\overset{+}{N}—\underset{H}{\overset{-}{C}}—R$

3



$R_3\overset{+}{N}—\overset{-}{N}—\overset{O}{\overset{\|}{C}}—R$

4

Accordingly, we have investigated the elimination from two hydrazinium salts in the presence of strong base (potassium *tert*-butoxide) and have obtained respectable yields of olefins. The two systems studied, *sec*-butyl and cyclohexyl, were selected as likely to reveal most quickly the characteristics and utility of the scheme. The results are what one might anticipate for a Cope-like process, a syn elimination in 1 through a cyclic transition state.

The hydrazinium chlorides were prepared from dimethyl-*sec*-butylamine and dimethylcyclohexylamine by several minor variations of Sommer's method[3a] employing hydroxylamine-*O*-sulfonic acid (the excellent method of Tamura, *et al.*,[3c] had not yet appeared when this investigation was begun). The yields were quite variable and sometimes rather low. The best yields, based on amine, were obtained in aqueous potassium carbonate to which a small amount of ethylenediaminetetraacetic acid (EDTA) was added in an effort to minimize heavy metal catalyzed side reactions. This procedure was adopted to avoid the use of excess amine as the required base.[1b,3a] It was found to be advisable to use freshly prepared hydroxylamine-*O*-sulfonic acid, since the commercial product is rather unstable and some lots gave poor results.

These hydrazinium salts displayed no detectable acidity in 0.1 *N* NaOH, and therefore their pK_a is greater than 13. When the solutions in aqueous sodium hydroxide were refluxed for 1 hr, no olefin was formed, and after acidification with hydrochloric acid the original hydrazinium salts were recovered. Since it has been reported[4] that potassium *tert*-butoxide suffices for the preparation of trimethylaminimine, this base was used in subsequent studies. The elimination from dimethyl-*sec*-butylhydrazinium chloride proceeded smoothly in refluxing *tert*-butyl alcohol containing a small excess of potassium *tert*-butoxide, giving a mixture of butene isomers in 73% isolated yield. The ratio of isomers, as determined by glc, was found to be 64.5% 1-butene, 10.5% *cis*-2-butene, and 25% *trans*-2-butene. This ratio is very nearly identical with that found for the Cope elimination of dimethyl-*sec*-butylamine oxide,[8] 67:12:21, and probably can be interpreted as implying a similar mechanism.

The elimination from dimethylcyclohexylhydrazinium chloride in refluxing *tert*-butyl alcohol-potassium *tert*-butoxide gave only a 32% yield of cyclohexene, as determined by glc. This, however, is significantly better than the 7% yield reported for the Hofmann elimination from trimethylcyclohexylammonium chloride in the same medium.[9] When dimethyl sulfoxide was substituted for *tert*-butyl alcohol as the solvent, the yield was increased to 52%. Whether this is a solvation effect[10] or merely due to the higher boiling point of the solvent could not be ascertained, since cyclohexene cannot be distilled from the reaction mixture at 80° and direct injection into the heated port of a gas chromatograph would vitiate the attempt at temperature control.

The procedure reported here has several characteristics that may render it particularly advantageous for the degradation of amines and the synthesis of olefins: (a) the temperature required is lower than that usually employed in the Hofmann degradation and the yields were better, especially from the cyclic amine; (b) the conversion of a tertiary amine to a hydrazinium salt does not require strong oxidizing agents, as does the preparation of an amine oxide; (c) since the nitrogenous product of the elimination, a 1,1-disubstituted hydrazine, usually can be further alkylated at the 1-nitrogen atom to regenerate a hydrazinium salt,[11] sequential degradation by a repetetive methylation procedure should be possible, as in Hofmann's approach; (d) some of the side reactions encountered in the Cope reaction[12] are less likely with the aminimines. A probable disadvantage is that migrations from N-1 to N-2, especially of allylic and benzylic groups, may be expected.[13]

Experimental Section

Hydroxylamine-*O*-sulfonic acid was prepared by the method of Gösl and Meuwsen.[1b] Dimethyl-*sec*-butylamine was prepared by Eschweiler-Clarke methylation of *sec*-butylamine. The dimethylcyclohexylamine was a commercial sample.

Dimethyl-*sec*-butylhydrazinium Chloride. Dimethyl-*sec*-butylamine (5 g, 50 mmol) was suspended in a vigorously stirred cold solution of 8 g of potassium carbonate sesquihydrate (50 mmol) in 20 ml of water containing 0.1 g of EDTA. A cold solution of 5.6 g (50 mmol) of hydroxylamine-*O*-sulfonic acid in 10 ml of water was added over 40 min. Methanol (180 ml) was added and the precipitated K_2SO_4 was filtered. The filtrate was adjusted to pH 7 by addition of hydrochloric acid, and the solvent was removed in a rotary evaporator. Acetone was added to the syrupy residue to promote crystallization of the hydrazinium chloride. The salt was purified by dissolving in methanol, filtering to remove a small amount of K_2SO_4, evaporating, and reprecipitating with acetone. After drying at 100° the product weighed 5.5 g (73%), mp 170°.

Anal. Calcd for $C_6H_{17}N_2Cl$: N, 18.37. Found: N, 18.36.

Nmr ($CDCl_3$) δ 6.75 (br, 2 H, NH_2), 3.7 (br, 1 H), 3.50 [d, 6 H, $N(CH_3)_2$], 1.46 (d, 3 H + 1 H), 1.05 (t, 3 H). The C-3 methylene of the *sec*-butyl group appears to be widely split by the adjacent chiral atom into two broad regions, one centered at δ 2.35 (1 H) and the other buried under the C-1 methyl doublet at δ 1.46.

Dimethylcyclohexylhydrazinium Chloride. Following a similar procedure, 6.35 g (50 mmol) of dimethylcyclohexylamine gave 3.2 g (35%) of the hydrazinium salt: mp 225-227°; nmr ($CDCl_3$) δ 6.75 (br, 2 H, NH_2), 3.75 (br, 1 H), 3.50 [s, 6 H, $N(CH_3)_2$], 2.47 (br, 2 H, 2,6-equatorial), 1.97 (br, 2 H, 2,6-axial), 1.8-1.3 (m, br, 6 H).

Anal. Calcd for $C_8H_{19}N_2Cl$: N, 15.70. Found: N, 15.68.

When 2 equiv of either of the hydrazinium salts was added to 0.1 *N* NaOH, the pH as determined by a glass electrode remained at 13; therefore the pK_a's of these compounds must be at least that great.

Eliminations. A. To a solution of 2.25 g (20 mmol) of potassium *tert*-butoxide in 10 ml of *tert*-butyl alcohol was added 2.42 g (16 mmol) of dimethyl-*sec*-butylhydrazinium chloride. The mixture was refluxed for 90 min, using a slow stream of nitrogen to sweep the gaseous products through the condenser into a Dry Ice cooled trap. The contents of the trap were transferred to a chilled vial and weighed, yield 0.58 g (73%). The nmr spectrum indicated that the material collected consisted solely of the isomeric *n*-butenes. The ratio of isomers was determined by glc on a 6 ft × 0.125 in. column packed with saturated $AgNO_3$ in phenylacetonitrile supported on 80-100 mesh Chromosorb P, using a flame ionization detector and electronic integration.

B. Dimethylcyclohexylhydrazinium chloride, 1.6 g (9 mmol), was added to a solution of 1.2 g (10 mmol) of potassium *tert*-butoxide in 15 ml of *tert*-butyl alcohol and the mixture was refluxed for 3 hr. The presence of cyclohexene was indicated by the nmr of the reaction mixture, and the amount was determined by glc on a 6-ft silicone (SE-30) column, using toluene as an internal standard, yield 0.24 g (32%).

C. Two grams (11 mmol) of dimethylcyclohexylhydrazinium chloride was added to a solution of 1.3 g (12 mmol) of potassium *tert*-butoxide in 15 ml of dimethyl sulfoxide, and the mixture was refluxed for 90 min. After cooling, glc indicated a 52% yield of cyclohexene.

Registry No.—Dimethyl-*sec*-butylhydrazinium chloride, 51051-67-3; dimethyl-*sec*-butylamine, 921-04-0; hydroxylamine-*O*-sulfonic acid, 2950-43-8; dimethylcyclohexylhydrazinium chloride, 51051-68-4; dimethylcyclohexylamine, 98-94-2.

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A Convenient Synthesis of Primary Benzhydrylamines

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Our need for relatively large quantities of primary benzhydrylamines (1) prompted the search for a general synthetic pathway. The well-known condensation of xanthydrol (**2a**) with primary amides[1] appeared to be a good method for bonding nitrogen to the benzhydryl position. Though previous attempts to hydrolyze *N*-9-xanthylacetamide to amine **1a** failed,[2] **1a** has recently been prepared by alkaline hydrolysis of the corresponding ethyl carbamate (**5**).[3] Similarly, we have found that benzyl *N*-9-xanthylcarbamate (**3a**), prepared from **2a** and benzyl carbamate (**4**),[4] is readily hydrolyzed to 9-aminoxanthene (**1a**) by refluxing in 95% EtOH containing 15% KOH. That amine **1a** was indeed obtained was shown by its conversion to carbamate **5** (Scheme I), identical in every respect with the compound obtained by condensation of **2a** with urethane.