sublimed, code 1082) to the solution of 0.755 g (5.0 mmol) of squaryl dichloride, the mixture was stirred for 1 hr at 20° and another 20 hr at reflux under the conditions of the experiment described in (A). Work-up as before furnished four chromatographic bands, from which the following compounds were isolated: band I, 0.126 g (6.8%) of crude **4**, mp 163° (from benzene-hexane); band II, 0.291 g (15.6%) of crude **2**, mp 130-131° (from benzene-hexane); band III, 0.119 g (10.2%) of crude **1**, mp 95° (from benzene-chloroform) (lit. 97-97.2°,[17] 98°,[3a] 94-95° [1]), undepressed on admixture of authentic[1] compound; band IV, 0.328 g (21.0%) of crude **3**, mp 204-208° dec (from benzene-hexane).

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Registry No.—**2**, 28480-68-4; **3**, 51065-83-9; **4**, 2892-40-2; squaryl dichloride, 2892-63-9; benzene, 71-43-2.

References and Notes

(1) B. R. Green and E. W. Neuse, *Synthesis*, 46 (1974).

(2) Symmetry considerations predict a conrotatory mode of ring opening for this 4-π electrocyclic process, although its stereospecificity cannot be assessed in the example **2** → **4**.

(3) (a) W. Ried and D. P. Schäfer, *Chem. Ber.*, **102**, 4193 (1969); (b) W. Ried and H. Kohl, *ibid.*, **104**, 2896 (1971).

(4) W. Ried, A. H. Schmidt, and W. Kuhn, *Chem. Ber.*, **104**, 2622 (1971).

(5) Cyclobutenones lacking the capability for chelation of this type generally[4,6] show $\nu_{C=O}$ in the region of 1750-1790 cm^{-1}; in rare instances, frequencies as low as 1740 cm^{-1} have been recorded.[7]

(6) See, for example, E. J. Smutny, M. C. Caserio, and J. D. Roberts, *J. Amer. Chem. Soc.*, **82**, 1793 (1960); W. Ried and W. Kunstmann, *Angew. Chem.*, **80**, 121 (1968); *Chem. Ber.*, **102**, 1422 (1969).

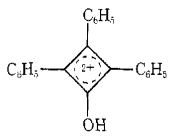
(7) W. Ried and D. P. Schäfer, *Chem. Ber.*, **103**, 2225 (1970); W. Ried and F. Bätz, *Justus Liebigs Ann. Chem.*, **755**, 32 (1972).

(8) This nmr pattern, for which there is precedence in the spectra of 1-phenylcyclobutene-3,4-dione[9a] and some 1-chloro-2-phenylcyclobutene derivatives,[9b] rules out the alternative structure of the 3-hydroxy-1,2,3-triphenylcyclobuten-4-one isomer expected to give a 4:11 intensity ratio of the low-field to high-field phenyl proton signals.

(9) (a) W. Ried and A. H. Schmidt, *Angew. Chem.*, **84**, 1048 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 997 (1972). Much of the pioneering work done by Roberts' and Ried's schools on unsaturated four-membered ring ketones is covered in this review on phenylcyclobutenediones. (b) Y. Kitahara, M. C. Caserio, F. Scardiglia, and J. D. Roberts, *J. Amer. Chem. Soc.*, **82**, 3106 (1960).

(10) In the sterically more favorable case of 1-phenylcyclobutene-3,4-dione as the substrate, Ried and Schäfer[3a] observed the $AlCl_3$-catalyzed 1,3-addition of aromatics (involving positions 2 and 4 of the four-membered ring system) to proceed without restriction.

(11) The existence of suitably substituted cyclobutenyl and oxocyclobutenyl cations in acidic solution,[12a] and even in the solid state,[12b-d] has been demonstrated. On the other hand, protonation (at oxygen) of the oxocyclobutenyl cation, which would give the formally dicationic species



is most unlikely to occur in the environment of our experiments, as highly acidic conditions are required even for the generation of the tetraphenyl-substituted dication,[13] in which a higher extent of stabilization through charge delocalization is expected than in the hydroxytriphenyl species drawn above.

(12) (a) G. A. Olah, J. M. Bollinger, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3667 (1969); (b) H. H. Freedman and A. M. Frantz, *ibid.*, **84**, 4165 (1962); H. H. Freedman and A. E. Young, *ibid.*, **86**, 734 (1964); (c) G. Seitz and H. Morck, *Chimia*, **26**, 368 (1972); (d) W. Ried and R. Lantzsch, *Justus Liebigs Ann. Chem.*, **756**, 173 (1972).

(13) G. A. Olah and G. D. Mateescu, *J. Amer. Chem. Soc.*, **92**, 1430 (1970).

(14) R. C. De Selms, C. J. Fox, and R. C. Riordan, *Tetrahedron Lett.*, 781 (1970).

(15) L. I. Smith and H. H. Hoehn, *J. Amer. Chem. Soc.*, **63**, 1180 (1941).

(16) W. Ried and R. Lantzsch, *Synthesis*, 303 (1970).

(17) A. T. Blomquist and E. A. LaLancette, *J. Amer. Chem. Soc.*, **83**, 1387 (1961).

Birch Reduction of *N*-Methylindoline

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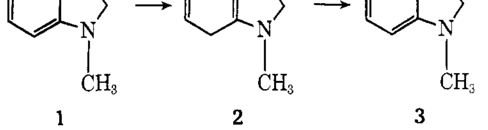
Pursuant to a need for some intermediate compounds in our development of certain synthetic routes, we investigated the Birch reduction of *N*-methylindoline[2] (**1**). It has been suggested[3] that **3** is the probable product of this reaction and that in the case of *N,N*-dimethyl-*p*-toluidine[4] a mixture of 2,3-dihydro-*N,N*-dimethyl-*p*-toluidine and 2,5-dihydro-*N,N*-dimethyl-*p*-toluidine are the products.

Our conditions for the reduction require lithium in liquid ammonia-tetrahydrofuran-isopropyl alcohol, and, upon subjection of **1** to this reaction, *N*-methyl-4,7-dihydroindoline (**2**) is the sole product. Our experience with the reduction of **1** and its product **2** indicates that no **3** is formed during the reduction. However, **2** is a very labile substance with respect to rearrangement to **3** and extreme care is required to prevent this rearrangement from occurring. As one might expect, exposure of **2** to acidic substances accelerates the conversion to **3**. For example, using commercial CCl_4 or $CDCl_3$, which may contain even trace amounts of HCl, will cause **3** to develop. We also found that the following drying agents also cause the **2** to **3** reaction: $CaCl_2$, Na_2SO_4, K_2CO_3, $MgSO_4$, and $CaSO_4$. However, **2** appears stable, neat or in ether solutions, when stored in the cold (0°) over solid KOH. Product **2** can be distilled without rearrangement but rigorous treatment of the glassware with ammonium hydroxide is necessary to prevent rearrangement from happening.

One can, of course, produce **3** directly from the reduction by purposely exposing the reduction product to acid during work-up. One such method is distillation from a small amount of acidic ion-exchange resin.

The structures for **2** and **3** follow directly from their spectral and analytical data. For **2** in its nmr spectrum the broad singlet of 2 H at τ 4.4 and the 4 H in the τ 7.2 region are fully characteristic of the 1,4-diene in a cyclohexane ring. In the case of **3**, it has three separate single proton vinyl resonances at τ 4.1, 4.9, and 5.6. The first two are multiplets and the third is a broad doublet in a chemical shift region typical of a β-vinylenamine type. In addition **3** gives a uv spectrum with λ_{max} 3306 (ϵ 5200) indicative of the conjugated enamine.

It appears from these results that **1** indeed gives the normal product (**2**) from the Birch reduction and that **2** can be used in some synthetic operations with due caution. Also one can easily prepare **3** from **1** and it too may be of use in synthetic sequences.



1 **2** **3**

It would seem to be a logical extension of our results that *N,N*-dialkyl aromatic amines will in general give the usual unconjugated diene as the sole primary product. However, due caution must be taken to see that the very facile rearrangement of the unconjugated to the conjugated diene does not take place.

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.

Acknowledgment. This investigation was supported by a Public Health Service Research Career Development Award (No. GM-70,394-01) from the Institute of General Medical Sciences.

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.*

(3) S. O'Brien and D. C. C. Smith, *J. Chem. Soc.*, 4609 (1960).

(4) B. Millward, *J. Chem. Soc.*, 26 (1960).

Degradation of Tertiary Amines *via* Aminimines

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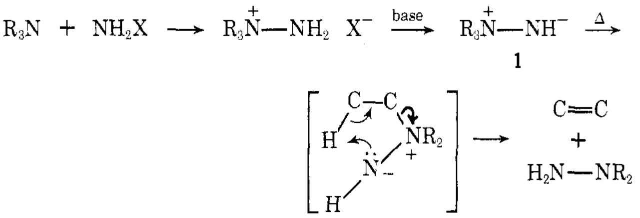
In 1879 Fischer reported[1] that, when 1,1,1-triethylhydrazinium hydroxide is refluxed in water, 1,1-diethylhydrazine is formed (eq 1). He formulated the reaction as also producing ethylene, but mentioned no experimental evidence for it; perhaps this was merely equation balancing. However, since he had 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.

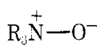
$$(CH_3CH_2)_3\overset{+}{N}—NH_2\,OH^- \xrightarrow[H_2O]{\Delta} (CH_3CH_2)NNH_2 + CH_2{=}CH_2 \quad (1)$$

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.

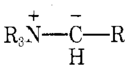
Scheme I



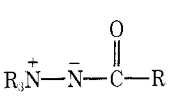
Presumably under proper conditions, though perhaps not in water, the elimination would occur *via* an aminimine inner salt 1,[4] and therefore would be a nitrogen analog of the Cope elimination[5] of amine oxides 2, and the α,β' mechanism of elimination in some hindered quaternary ammonium ions *via* 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


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

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