

I**b**, a "nonbasic fraction" consisting of 64% veratraldehyde (IIIc), 22% ethyl 3,4-dimethoxybenzyl ether (IIIb), and 7% each of homoveratrole (IIIId) and veratrole (IIIh).

A number of trial runs on papaverine irradiation in isopropyl alcohol were attempted using 800 ml of a 10^{-3} M solution. For example, after 3 hr of irradiation, tlc showed the presence of five new trace spots positive to iodoplatinic acid. However, upon continued irradiation these spots began to disappear as did that for the papaverine starting material. Evaporation of the solvent left residues weighing two to four times as much as that of the total starting material and preliminary attempts at isolation of any specific pure products were not successful.

Irradiations conducted in a similar manner, except using benzene as solvent, showed no photolysis products on tlc. In one case, an Hanovia Type L (450 W) lamp was used and no new product could be detected after 2 days of irradiation. The solvent was evaporated and the residue found to be only unreacted papaverine. Under these conditions, product spots could be observed using methanol solvent after 2 hr and in less than 1 hr using isopropyl alcohol as solvent.

Irradiation of Phenanthridine.—Phenanthridine (0.91 g or 0.0048 M) was dissolved in a mixture of 992 ml of 95% ethanol and 8 ml of concentrated hydrochloric acid and the resulting solution was placed in a 1000-ml Pyrex flask. This was stoppered, inverted, and placed in the sunlight. After 14 days of irradiation, the solvent was removed *in vacuo*, the residue was dissolved in

methanol, the solution evaporated, and the residue triturated with benzene-ether. This left a brown oil whose nmr spectrum showed the disappearance of the downfield singlet due to the proton at the 6 position (next to nitrogen) and the appearance of a characteristic upfield triplet and quartet of an ethyl group. Essentially the same result was obtained when 5 l. of the same solution was irradiated for 41 hr in an Hanovia immersion reactor (450-W Type L lamp) under nitrogen and using a Pyrex filter. Gas chromatography showed the residue to be contaminated with about 10% phenanthridine. The gas chromatographic separation yielded a white solid which was then recrystallized from *n*-heptane to give 6-ethylphenanthridine, mp 55° (lit.¹⁸ mp 54–55°). The mass spectrum was exactly analogous with that reported¹⁹ for 2-ethylpyridine (as opposed to other ethylpyridines) and constituted additional proof of structure.

Registry No.—I, 58-74-2; I hydrochloride, 61-25-6; IV, 229-87-8.

Acknowledgment.—The authors are indebted to Drs. R. C. Anderson and W. M. Moore of Utah State University for many helpful discussions and comments.

(18) A. Pictet and A. Hubert, *Ber.*, **29**, 1186 (1896).

(19) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., New York, N. Y., 1962, p 134.

The Electron-Impact Fragmentation of Dimethylaminoacetone and 2-Dimethylaminocyclohexanone

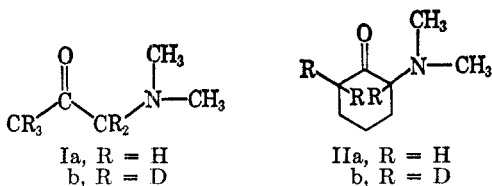
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The mass spectra of dimethylaminoacetone and 2-dimethylaminocyclohexanone have been analyzed with the help of their deuterated analogs. Fragmentation patterns are interpreted as being virtually exclusively directed by the nitrogen function with insignificant fragmentation direction by the carbonyl group.

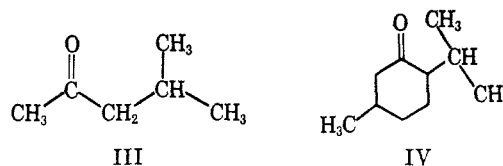
As a prelude to studying the photochemistry of some amino ketones, and particularly the intramolecular interactions of the amino and ketone functions, it was deemed of interest to study the electron impact fragmentation of some model compounds. It has been suggested a number of times in the literature that mass spectra, particularly of aliphatic ketones, can be correlated with photochemistry. The presence of an amino function (strongly directing in electron impact fragmentation) in the same molecule as a carbonyl (highly reactive photochemically) might be expected to test severely this correlation. This paper reports an analysis of the mass spectra of dimethylaminoacetone (Ia) and 2-dimethylaminocyclohexanone (IIa) assisted by the spectra of the deuterio analogs Ib and IIb.



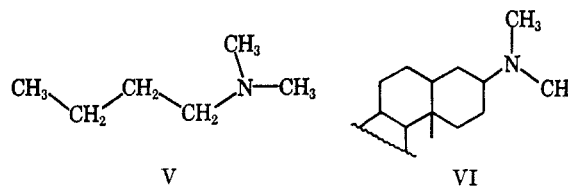
Figures 1–4 give the 80-eV mass spectra of Ia, Ib, IIa, and IIb, respectively.

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It is perhaps most instructive to compare these spectra with those of similar structure, but in which first the nitrogen is replaced by carbon and, alternatively, the carbonyl group is replaced by CH_2 . For the first comparison, mass spectra of 4-methyl-2-pentanone² (III) and menthone³ (IV) are particu-



larly useful. For the second comparison, spectra of dimethyl-*n*-butylamine⁴ (V) and a number of dimethylamino steroids⁵ (VI) are available. For the



(2) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966, Figure 8.5, p 124.

(3) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc. San Francisco, Calif., 1964, Figures 1-12 and 1-13, p 23.

(4) R. S. Gohlke and F. W. McLafferty, *Anal. Chem.*, **34**, 1281 (1962).

(5) L. Dolejs, V. Hanus, V. Cerny, and F. Sorm, *Collect. Czech. Chem. Commun.*, **28**, 1584 (1963); Z. Pelah, D. H. Williams, H. Budzikiewicz, and C. Djerassi, *J. Amer. Chem. Soc.*, **87**, 574 (1965).

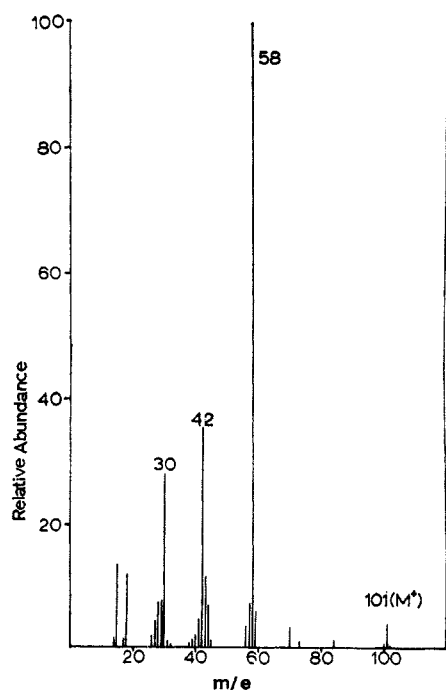


Figure 1.—Mass spectrum of dimethylaminoacetone.

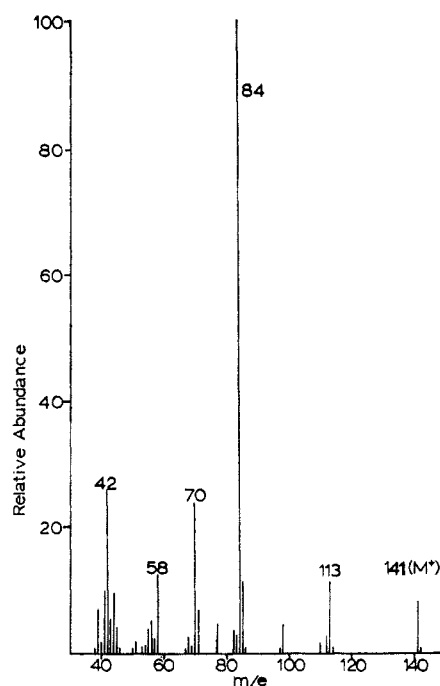


Figure 3.—Mass spectrum of 2-dimethylamino-cyclohexanone.

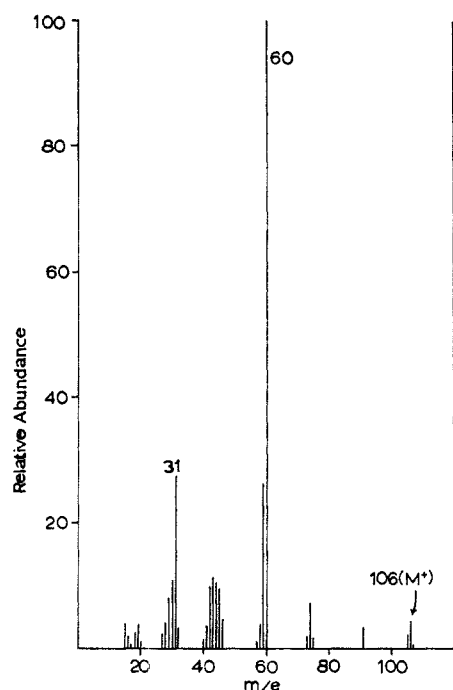


Figure 2.—Mass spectrum of pentadeuteriodimethylaminoacetone.

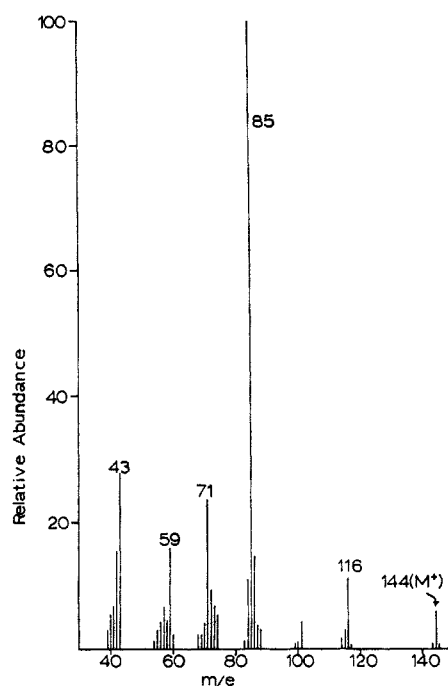
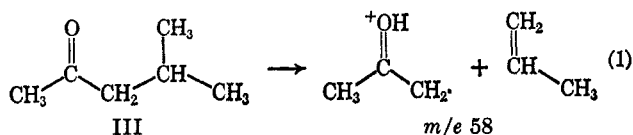


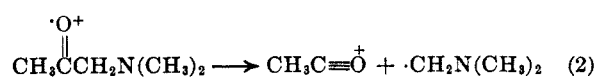
Figure 4.—Mass spectrum of trideuterio-2-dimethylamino-cyclohexanone.

first comparison, it is noted² that III yields a base peak at m/e 43 for $\text{CH}_3\text{C}\equiv\text{O}^+$, which is typical for all methyl ketones and, of second intensity, the m/e 58 McLafferty rearrangement ion (eq 1). The amino

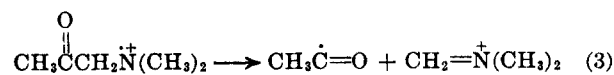


analog Ia, on the other hand, exhibits a relatively minor m/e 43 peak, with the base peak being at m/e 58. Inspection of the Ib spectrum, however, shows that the m/e 58 peak in Ia cannot be that arising from process 1, since there is virtually nothing at m/e 63.

The m/e peak has, instead, shifted to m/e 60, indicating the presence of only two deuterium atoms. Based upon comparisons with the spectrum⁴ of V, the m/e peak in Ia must be due to the $\text{CH}_2=\text{N}^+(\text{CH}_3)_2$ ion. Thus, process 2, the ubiquitous one for methyl



ketones, has been supplanted by process 3 in the



present case. If the molecular ion of process 2 were formed at all, some McLafferty rearrangement should

have been observed. The complete absence of this process provides strong evidence for an assumed localized ionization⁶ at the nitrogen as the directive force in the fragmentation.

An interesting sidelight in the Ia and Ib spectra is provided by the m/e 30 peak of Ia which changes to m/e 31 in the deuterio analog. A metastable peak was observed at m/e 15.6, with the calculated value of 15.5 being that for a m/e 58 to 30 process. The ordinary interpretation of this ($\text{CH}_2=\text{N}^+(\text{CH}_3)_2 \rightarrow \text{CH}_2=\text{N}^+\text{H}_2$) would predict a shift to m/e 32 rather than the observed m/e 31. This process will be examined in more detail.

For the second comparison (II vs. IV and VI), it is noted³ that the base peak in the mass spectrum of IV is that resulting from process 1 since we are no longer dealing with a methyl ketone. If this same process held in regard to IIa, the base peak would be expected to appear at m/e 98, with a shift to m/e 101 in IIb. Examination of Figures 3 and 4 indicates that this is far from being the case, although here this process has not been completely eliminated as in the case of Ia. The base peak of IIa can be assigned to the $\text{CH}_2=$

(6) F. W. McLafferty, "Determination of Organic Structures by Physical Methods," F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, p 93.

$\text{CHCH}=\text{N}^+(\text{CH}_3)_2$ ion (m/e 84 in IIa and m/e 85 in IIb) in complete accordance with observations⁵ in the VI systems where no carbonyl is present.

Our results⁷ on the photochemistry of Ia and IIa will be reported subsequently. Those interested in making correlations between electron-impact fragmentation and photochemistry have an opportunity, in the meantime, to predict the latter based upon the spectra reported here.

Experimental Section

The mass spectra were taken using an Hitachi Perkin-Elmer RMU-6E mass spectrometer (80 eV, 100°, all-glass inlet).

Dimethylaminoacetone and 2-dimethylaminocyclohexanone were purchased from Aldrich Chemicals and purified by distillation at reduced pressure.

The deuterated analogs were prepared by warming a mixture of ketone and deuterium oxide with a trace of anhydrous sodium carbonate. The ketone was then isolated by extraction with anhydrous ether and the entire procedure was repeated until complete deuteration (as evidenced by mass spectrometry) of all the protons adjacent to the carbonyl was achieved.

Registry No.—Ia, 15364-56-4; Ib, 15364-57-5; IIa, 6970-60-1; IIb, 15364-59-7.

(7) F. R. Stermitz and V. P. Muralidharan, unpublished results.

The Preparation of (+)-N-Methyl-1-(1-naphthyl)ethylamine and the Determination of Its Optical Purity by Nuclear Magnetic Resonance^{1a}

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Optically pure 1-(1-naphthyl)ethylamine (1) was converted into the optically pure N-methyl derivative (2) by methylation of the benzenesulfonamide, followed by cleavage with sodium naphthalene radical anion. It is suggested that this method is a generally useful one for the N-alkylation of optically active amines without loss of optical purity. The optical purities of 1 and 2 were determined by nmr spectroscopic analysis of the O-methylmandelamides. This approach to the estimation of the optical purity of primary and secondary amines appears to have broad applicability.

In connection with other work in progress in these laboratories, it became necessary to prepare optically pure N-methylamines of type $\text{R}_1\text{R}_2\text{CHNHCH}_3$ from the corresponding primary amines, $\text{R}_1\text{R}_2\text{CHNH}_2$. The purpose of the present paper is to describe, through the example of the conversion of (+)-1-(1-naphthyl)ethylamine ("Resoline," 1) to (+)-N-methyl-1-(1-naphthyl)ethylamine (2), a procedure for N-methylation which results in no loss of optical purity and a method for determining the optical purity of primary and secondary amines by nmr spectroscopy which gives accurate estimates and is simple to apply.

One approach to the preparation of 2 involved reduction of the formamide of 1 (3) with lithium aluminumhydride² in ether. However, reaction for 18 hr afforded only a low yield of the desired product with the recovery of a considerable amount of unreacted

starting material.³ An alternative approach, the methylation of the benzenesulfonamide of 1 (4) and subsequent cleavage of the N-methyl derivative (5) by commonly reported procedures,⁴ was investigated. Attempted cleavage of 5 with cold, concentrated sulfuric acid,⁵ 25% aqueous sulfuric acid at reflux,⁶ 25% aqueous hydrochloric acid at reflux,⁷ or KOH in dimethyl sulfoxide⁸ failed to yield the desired product.⁹

(3) The difficulty of the reduction of some monosubstituted amides has been noted previously; cf. V. M. Mićović and M. L. Mihailović, *J. Org. Chem.*, **18**, 1190 (1953).

(4) The cleavage of sulfonamides has been discussed by S. Searles and S. Nukina, *Chem. Rev.*, **59**, 1077 (1959).

(5) T. L. Fletcher, M. E. Taylor, and A. W. Dahl, *J. Org. Chem.*, **20**, 1021 (1955). This procedure led to extensive decomposition of the starting material.

(6) Previous failures to cleave sulfonamides with dilute sulfuric acid (<40%) have been recorded (J. Halberkann, *Ber.*, **54**, 1665 (1921)).

(7) A. Jindra and F. Sipos, *Chem. Listy*, **44**, 235 (1950); *Chem. Abstr.*, **45**, 5569 (1951).

(8) F. C. Chang [*Tetrahedron Lett.*, No. 6, 305 (1964)] has reported the cleavage of toluenesulfonates under similar conditions.

(9) C-N bond cleavage of benzylic sulfonamides has been reported by P. A. Briscoe, F. Challenger, and P. S. Duckworth, *J. Chem. Soc.*, 1755 (1956). The nature of the products (other than recovered starting material) in the present study are unknown.

(1) (a) This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-67; (b) Public Health Service Postdoctoral Fellow, 1966-1967; (c) Public Health Service Predoctoral Fellow, 1964-1966.

(2) J. Ehrlich, *J. Amer. Chem. Soc.*, **70**, 2286 (1948).