filtered solution yielded a liquid which on gas chromatography (Carbowax, 155°) showed three components. The major product (*ca.* 55%) was isolated and shown to have an infrared and nmr spectrum identical with those of 3-keto-*endo*-tricyclo-[5.2.1.$0^{2,6}$]decane (**2**).

Registry No.—**5**, 13970-41-7; **6**, 13970-42-8; **8**, 13865-12-8; **9**, 13865-13-9; *p*-nitrophenylhydrozone of **9**, 13865-14-0; 2,4-dinitrophenylhydrazone of **9**, 13865-15-1; **11**, 13865-16-2; **14**, 13970-43-9.

Acknowledgments.—We are grateful to the Petroleum Research Fund (No. 1676-A1) and the Research Council, Rutgers, The State University, for generous financial support.

The Mass Spectra of Small-Ring Heterocycles. I. Some 1-Alkyl-2-phenyl-3-aroylazetidines

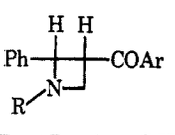
J.-L. IMBACH,[1a] EARL DOOMES, NORMAN H. CROMWELL,[1b] HENRY E. BAUMGARTEN,[1b] AND RICHARD G. PARKER[2]

Avery Laboratory of Chemistry, The University of Nebraska, Lincoln, Nebraska 68508

Received March 20, 1967

The mass spectra of nine 1-alkyl-2-phenyl-3-aroylazetidines (I–IX) are described, and a method for distinguishing between *cis*- and *trans*-aroylazetidines is presented and discussed. An unusual, simple fission of the 1-alkyl–nitrogen bond is also described. The preparation and characterization of three new azetidines (VII, VIII and IX) are described.

No reference to the mass spectra of azetidines has appeared in the literature. In conjunction with other studies being carried out in this laboratory[3] and in an attempt to establish a method for distinguishing between the *cis* and *trans* isomers by mass spectroscopy, the mass spectra of the following 1-alkyl-2-phenyl-3-aroylazetidines were determined: *trans*-1-*t*-butyl-2-phenyl-3-benzoylazetidine (I; series **1**; Figure 1), *trans*-1-*t*-butyl-2-phenyl-3-benzoyl-3-deuterioazetidine (II; series **1**; Figure 2), *cis*-1-*t*-butyl-2-phenyl-3-benzoylazetidine (III; series **1**; Figure 3), *trans*-1-*t*-butyl-2-phenyl-3-*p*-phenylbenzoylazetidine (IV; series **2**; Figure 4), *trans*-1-*t*-butyl-2-phenyl-3-*p*-phenylbenzoyl-3-deuterioazetidine (V; series **2**; Figure 5), *cis*-1-*t*-butyl-2-phenyl-3-*p*-phenylbenzoylazetidine (VI; series **2**; Figure 6), *trans*-1-cyclohexyl-2-phenyl-3-*p*-phenylbenzoylazetidine (VII; series **3**; Figure 7), *trans*-1-cyclohexyl-2-phenyl-3-*p*-phenylbenzoyl-3-deuterioazetidine (VIII; series **3**; Figure 8), and *cis*-1-cyclohexyl-2-phenyl-3-*p*-phenylbenzoylazetidine (IX; series **3**; Figure 9).



series 1, R = *t*-Bu; Ar = C_6H_5
series 2, R = *t*-Bu; Ar = *p*-$C_6H_5C_6H_4$
series 3, R = C_6H_{11}; Ar = *p*-$C_6H_5C_6H_4$

It might be expected that the predominant process occurring when the aroylazetidines are subjected to electron impact would be the removal of one of the nonbonding electrons from one of the heteroatoms. It is generally accepted that nitrogen is capable of stabilizing a positive charge more readily than oxygen[4] and, in fact, in the somewhat similar case of tropinone,[5] where the nitrogen and carbonyl functions are also separated by three bonds, the entire fragmentation pattern may be rationalized on the basis of the removal of an electron from nitrogen. However, in the present case, the carbonyl group is adjacent to an aromatic system and a positive charge on oxygen would be stabilized by resonance interaction with the aromatic ring. Therefore, although electron-shift mechanisms can be drawn to account for the origin of all major fragments by removal of an electron from nitrogen, the removal of a nonbonding electron from oxygen is undoubtably an important process for these azetidines, especially in the formation of the fragment which allows *cis* and *trans* isomers to be easily distinguished.

Previous studies of *cis* and *trans* isomers have generally been more or less successful in establishing distinct fragmentation patterns for each isomer[6] based on relative differences in intensities of certain key fragments. This technique requires that the spectra of both *cis* and *trans* isomers be available for comparison.

In the 2-phenyl-3-aroylazetidines it is possible to distinguish between *cis* and *trans* isomers by the presence or absence of specific fragments in the mass spectrum. Although pairs of isomers of known configuration were available for comparison in the present study, it should be possible to apply these results to future cases in similar and related systems where both isomers are not available or are of unknown configuration. This possibility is being investigated in other systems.

(1) (a) ENSCM Universite de Montpellier, 8 Rue Ecole Normale, Montpellier 34, France. (b) To whom inquiries should be addressed.

(2) Texaco Fellow in Chemistry, 1966–1967.

(3) (a) E. Doomes and N. H. Cromwell, *Tetrahedron Letters*, 4037 (1966). (b) J.-L. Imbach, E. Doomes, R. P. Rebman, and N. H. Cromwell, *J. Org. Chem.*, **32**, 78 (1967).

(4) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 117.

(5) H. Budzikiewicz, C. Djerassi, and D. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p 92.

(6) (a) L. D. D'Or, J. Momigny, and P. Natalis in "Advances in Mass Spectroscopy," R. M. Elliot, Ed., The Macmillan Co., New York, N. Y., 1963, p 370. (b) D. A. Bak and K. Conrow, *J. Org. Chem.*, **31**, 3608 (1966). (c) Reference 5, p 144. (d) H. Budzikiewicz, C. Djerassi, and D. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Holden-Day, Inc., San Francisco, Calif., 1964, Vol. I, pp 81, 102, 220; Vol. II, p 61. (e) K. Biemann and J. Seibl, *J. Am. Chem. Soc.*, **81**, 3149 (1959). (f) V. I. Zaretskii, N. S. Wulfson, V. G. Zaikin, L. M. Kogan, N. E. Voishvillo, and I. V. Torgov, *Tetrahedron*, **22**, 1399 (1966).

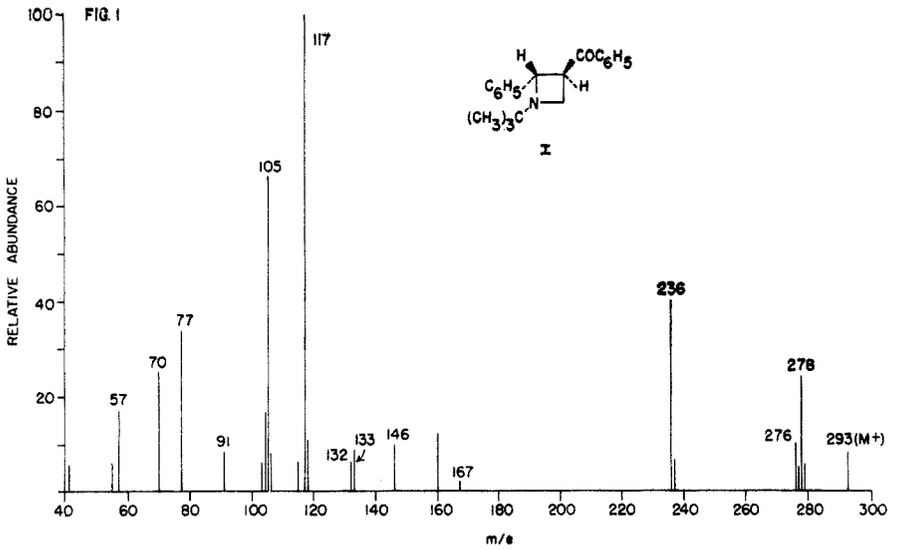


Figure 1.

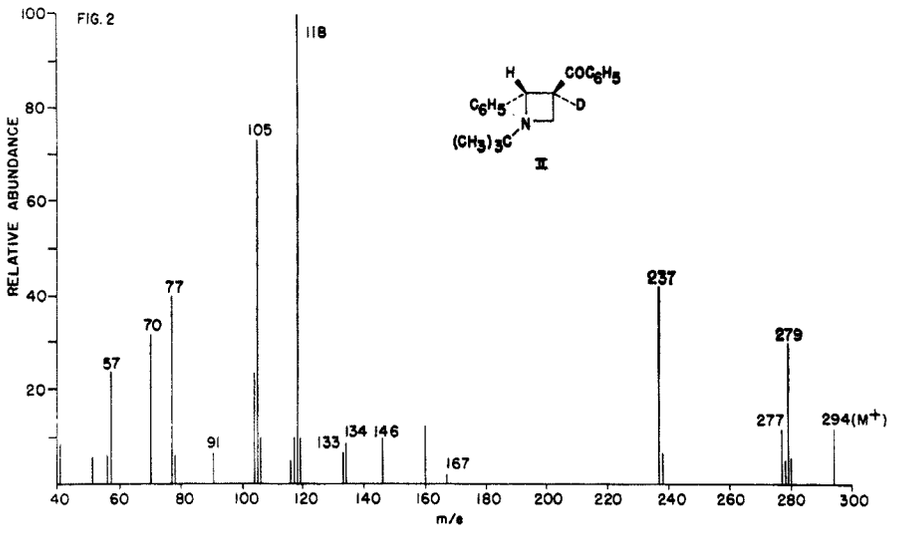


Figure 2.

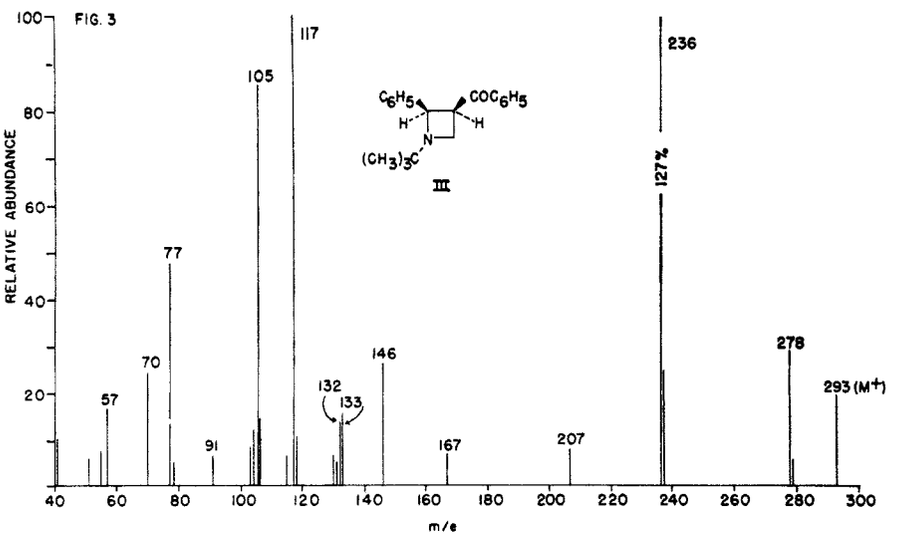


Figure 3.

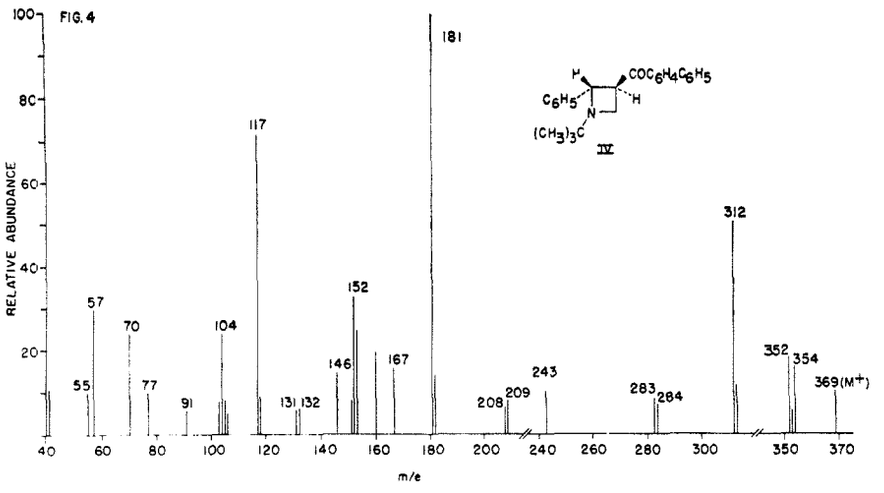


Figure 4.

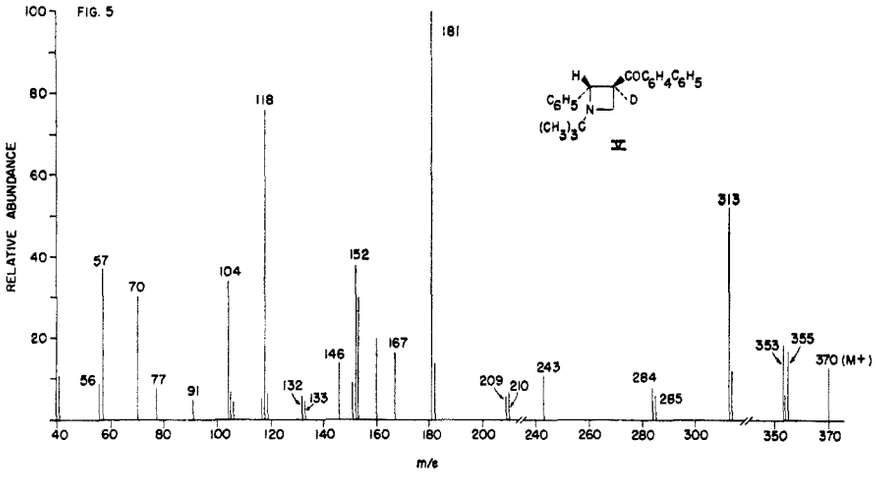
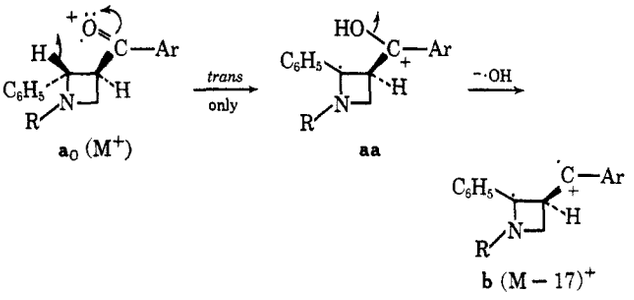


Figure 5.

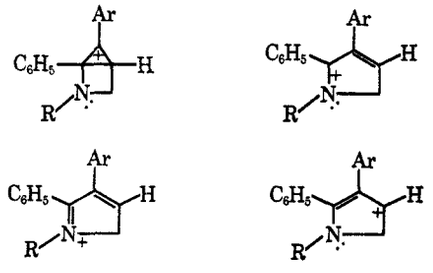
Thus, the mass spectrum of each *trans* compound studied shows an ion at M − 17 and an easily observable metastable ion corresponding to the transition M to M − 17. Both of these ions are absent in the spectra of the *cis* isomers. This obvious difference in the spectra may be rationalized on the basis of a rearrangement of the C-2 hydrogen onto the carbonyl group in the *trans* isomers (**aa**), followed by loss of hydroxyl radical to yield the diradical ion **b**.[7] Since this β hydrogen is geometrically unavailable in the *cis* isomers, the rearrangement cannot occur. The fact that the *cis* isomers do not undergo this rearrangement process indicates also that the C-4 hydrogens (also β) do not take part in this process. The rearrangement of the C-2 hydrogen is undoubtably enhanced by its benzylic nature and the subsequent formation of a benzyl radical.



The over-all fragmentation pattern for each series was deduced by means of deuterium labeling at C-3 in the *trans* isomers, by substitution of biphenyl for phenyl in the aroyl group, by substitution of cyclohexyl for *t*-butyl at the 1 position, and by observation of the metastable ions listed in Table I. Although the *trans* isomer is shown in the schemes, the schemes are general for both isomers except where indicated. The relative abundances of the fragments are presented in Figures 1–9.

The main fragmentation process might be expected to proceed *via* cleavage of the bonds α to the nitrogen

(7) Although ion **b** is formulated as a diradical ion, other formulations are possible. Four alternatives to the diradical ion are shown.



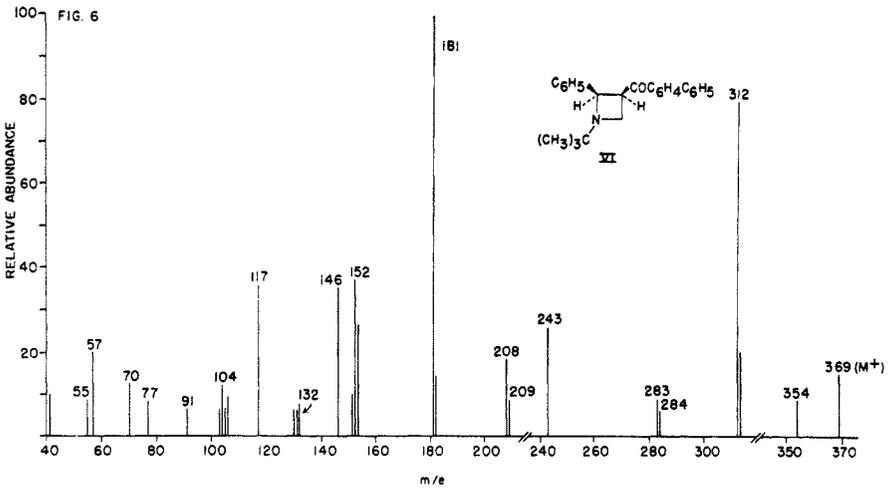


Figure 6.

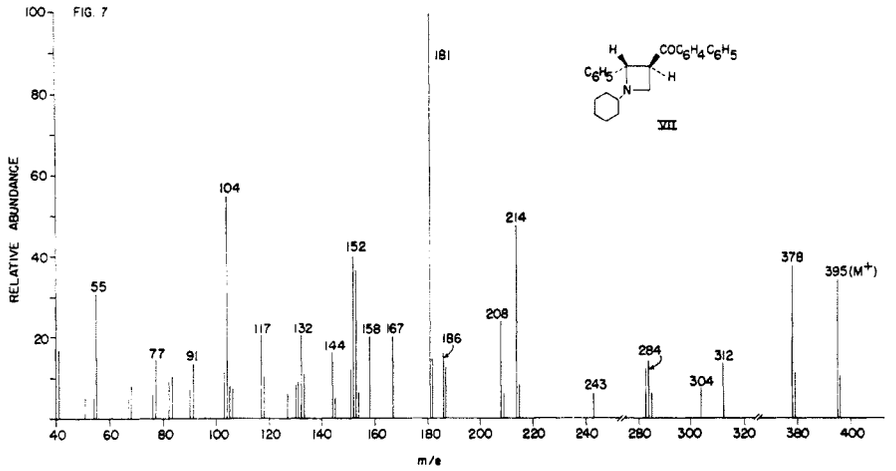


Figure 7.

TABLE I

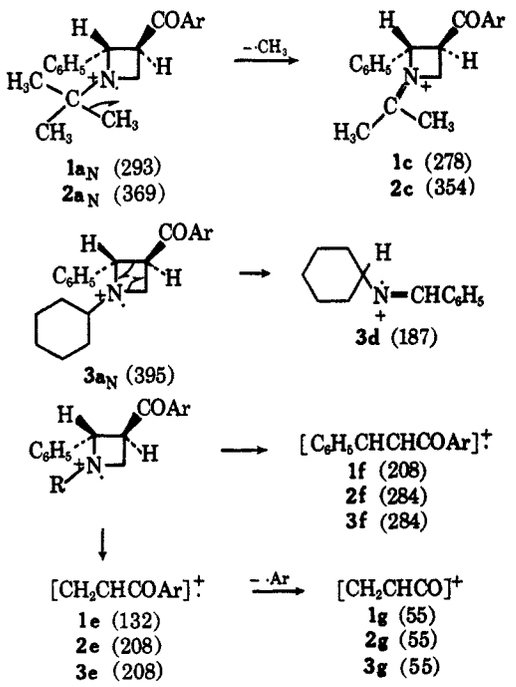
METASTABLE TRANSITIONS IN THE MASS SPECTRA OF SOME 1-ALKYL-2-PHENYL-3-AROYLAZETIDINES

Observed	Transition	Calcd
	a to b (*trans* only)	
259.9	293 → 276 (series 1)	259.96
335.7	369 → 352 (series 2)	335.78
362.0	395 → 378 (series 3)	361.73
	a to h	
190.0	293 → 236 (series 1)	190.09
263.9	369 → 312 (series 2)	263.80
246.5	395 → 313 (series 3)	246.44
	i to j	
56.3	105 → 77 (series 1)	56.46
129.4	181 → 153 (series 2)	129.33
129.5	181 → 153 (series 3)	129.33

and this process appears to be favored in series 1 and 2 (Scheme I) where a methyl radical is cleaved from the *t*-butyl group ($a_N \rightarrow c$), in a ring-opening reaction in Series 3 ($a_N \rightarrow d$), and in ring cleavages yielding fragments containing no nitrogen ($a_N \rightarrow e$, $a_N \rightarrow f$).[8] Fragments **e** and **f** could also arise from ions like **c**.

(8) The formation of e and f requires the cleavage of one C–N bond and one C–C bond α to the nitrogen and their formation may be rationalized on the basis on an initial α cleavage.

SCHEME I



There also appears to be a tendency for cleavage of the 1-alkyl group ($a_N \rightarrow h$) (Scheme II), formation of

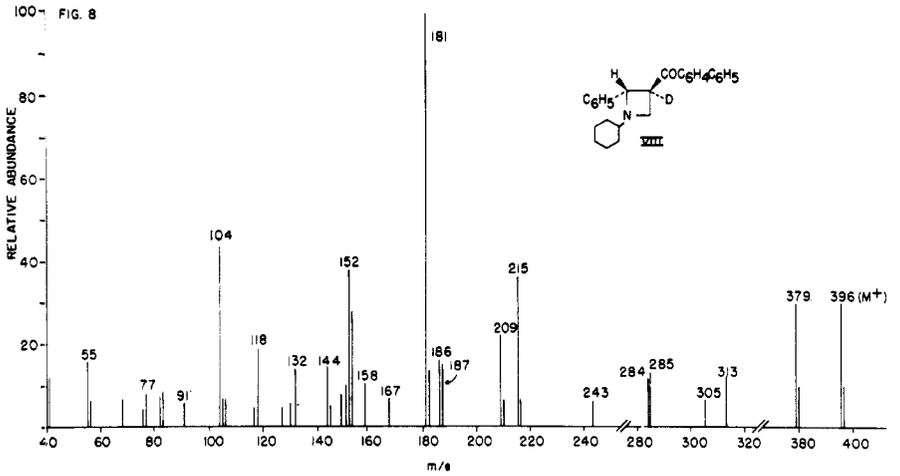


Figure 8.

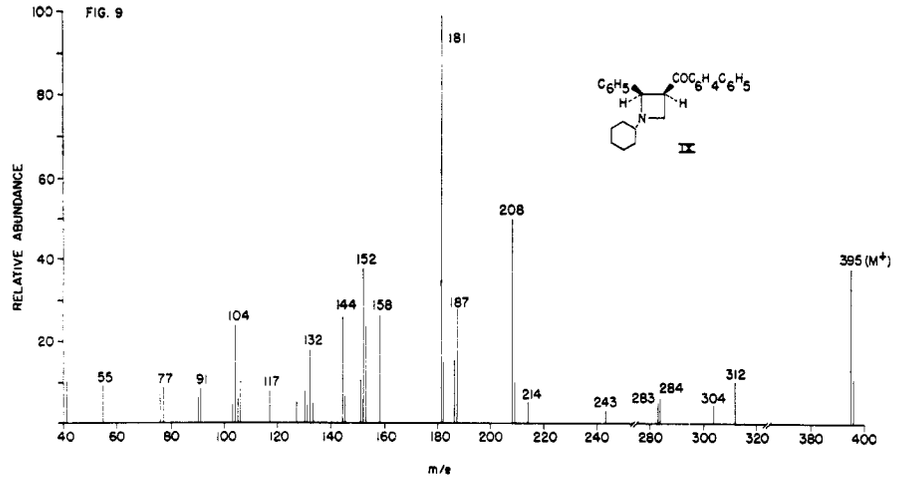
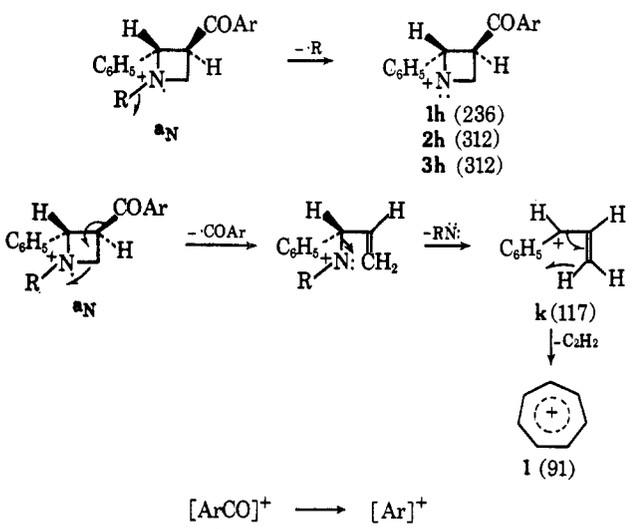


Figure 9.

SCHEME II



$[ArCO]^+$	$[Ar]^+$
1i (105)	**1j** (77)
2i (181)	**2j** (153)
3i (181)	**3j** (153)

aroyl ion **i** (and subsequently, aryl ion **j**) and formation of the benzylallyl cation **k**.

α cleavages also appear to play an important role in the secondary fragmentation processes. It is probable that fragments **m**, **n**, **o**, **p**, **q**, **r**, and **s** are formed by α cleavages (Scheme III, p 3128).

Simple fission of the 1-alkyl-nitrogen bond ($\mathbf{a}_N \rightarrow \mathbf{h}$) is considered to be unusual as it is generally stated that this process is not significant in amine spectra.[9] However, this process appears to be highly favored in these azetidines, perhaps owing to a relief of steric crowding through loss of the bulky alkyl group.

Within each series, it is apparent that the *cis* isomer generally gives certain fragments in greater abundance than does the *trans* isomer. This difference in abundance can be explained on the basis of relief of steric strain between the two, large *cis* groups. For example, **o** and **e** are more intense in the *cis* isomers owing to preferential ring cleavages which are strain relieving. A similar observation has been made by Bak and Conrow[6b] for the mass spectra of some cyclobutane carboxylates.

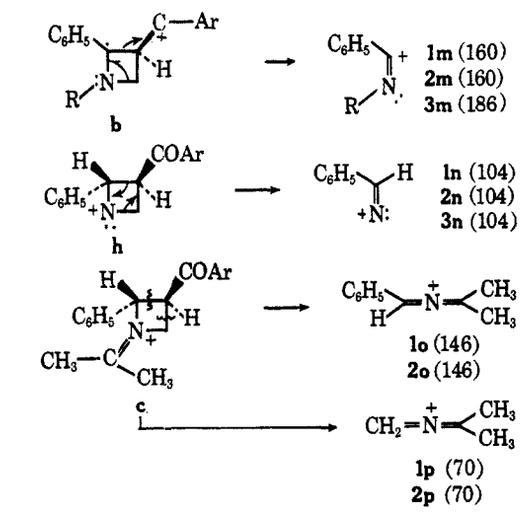
The appearance of *m/e* 133 (**t**) in *trans* isomer I and *m/e* 209 (**t**) in *trans* isomers IV and VII is attributed to a ring cleavage reaction of **aa** (Scheme IV) while the appearance of the same ions in the *cis* isomers is attributed to a ring cleavage of $\mathbf{a}_0$, followed by a seven-centered rearrangement.[10]

The appearance of *m/e* 186 in series **3** can arise in two ways: $\mathbf{3a}_0 \rightarrow \mathbf{3b} \rightarrow \mathbf{3m}$ or by loss of a hydrogen

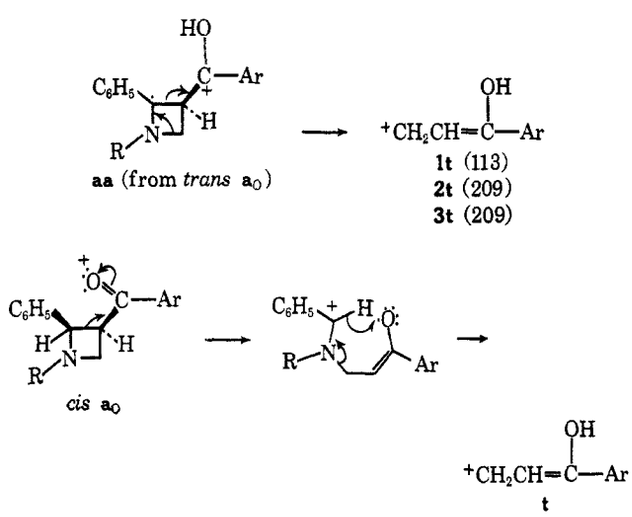
(9) H. C. Hill, "Introduction to Mass Spectrometry," Heyden and Sons Ltd., London, 1966, p 91.

(10) (a) N. C. Rol, *Rec. Trav. Chem.*, **84**, 413 (1966). (b) S. D. Sample, D. A. Lightner, O. Buchardt, and C. Djerassi, *J. Org. Chem.*, **32**, 997 (1967).

SCHEME III



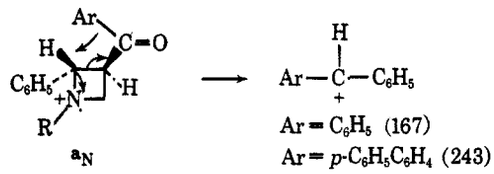
SCHEME IV



from **3d**. Since the composition of the fragments is identical, the two processes cannot be separated in the present system.

The ring opening of *cis* isomers may be facilitated by a relief of steric strain between the large *cis* groups.

An interesting rearrangement also appears to occur in these azetidines. Thus, all spectra from the azetidines containing the benzoyl group have a peak at *m/e* 167 which is shifted to *m/e* 243 in the azetidines containing the *p*-phenylbenzoyl group but which is not shifted by deuterium labeling at C-3. This rearrangement probably results in formation of the arylphenylmethyl (or its tropylium analog) ion.



A similar rearrangement has also been noted in this laboratory in the mass spectra of some similarly substituted aziridines.

Experimental Section

Mass Spectra.—The mass spectra were determined with a Perkin-Elmer–Hitachi RMU-6D mass spectrometer operating at 80 ev. The samples were introduced directly into the ion source[11] under the following conditions: series **1**—source, 80°, and sample, 50°; series **2**—source, 160°, and sample, 110°; and series **3**—source, 170°, and sample, 115° (except IX, which was determined at source, 230°, and sample, 180°).

***cis*- and *trans*-1-*t*-Butyl-2-phenyl-3-benzoylazetidine (I, II, and III).**—The preparation and characterization of I, II and III are described in ref 3b.

***cis*- and *trans*-1-*t*-Butyl-2-phenyl-3-*p*-phenylbenzoylazetidine (IV, V, and VI).**—The preparation and characterization of IV, V and VI are described in ref 3a.

***cis*- and *trans*-1-Cyclohexyl-2-phenyl-3-*p*-phenylbenzoylazetidine (VII, VIII, and IX).**—Compound IX was prepared from 2-(α-cyclohexylaminobenzyl)-4′-phenylacrylophenone (X) using the procedure given in ref 3b.

Compound X was prepared from α-bromoethyl-4′-phenylchalcone[3a] and 2 equiv of cyclohexylamine by the procedure given in ref 3b. Compound X, mp 90–91° (*n*-hexane), had the following spectral properties:[12] infrared absorption (CCl_4) at 1660 cm^{-1} (C=O) and nmr peaks ($CDCl_3$) at 415 to 480 cps (broad multiplet, 14 H, aromatic), 337 cps (singlet, 1 H, vinyl), 329 cps (singlet, 1 H, vinyl), 305 cps (singlet, 1 H, benzyl), and 40 to 165 cps (broad multiplet, 12 H, cyclohexyl and NH).

Anal. Calcd for $C_{28}H_{29}NO$: C, 85.02; H, 7.39; N, 3.53. Found: C, 84.75; H, 7.45; N, 3.53.

Azetidine IX, mp 172–173° (methanol), had the following spectral properties: infrared absorption (CCl_4) at 1684 cm^{-1} (C=O) and nmr peaks ($CDCl_3$) at 410 to 470 cps (broad multiplet, 14 H, aromatic), 278 cps (doublet, J = 8.5 cps, 1 H, benzyl), 180 to 270 cps (multiplet, 3 H, C-3 and C-4 protons), and 30 to 150 cps (broad multiplet, 11 H, cyclohexyl).

Anal. Calcd for $C_{28}H_{29}NO$: C, 85.02; H, 7.39; N, 3.53. Found: C, 84.95; H, 7.38; N, 3.53.

Treatment of IX with sodium methoxide in methanol yielded the *trans* isomer VII, mp 142–143° (methanol), which showed the following spectral properties: infrared absorption (CCl_4) at 1680 cm^{-1} (C=O) and nmr peaks ($CDCl_3$) at 425 to 480 cps (broad multiplet, 14 H, aromatic), 264 cps (doublet, J = 7 cps, 1 H, benzyl), 186 to 270 cps (broad multiplet, 3 H, C-3 and C-4 protons), and 30 to 160 cps (broad multiplet, 11 H, cyclohexyl).

Anal. Calcd for $C_{28}H_{29}NO$: C, 85.02; H, 7.39; N, 3.53. Found: C, 85.16; H, 7.57; N, 3.40.

Treatment of IX with sodium methoxide in deuterated methanol (CH_3OD) yielded the 3-deuterioazetidine, VIII, mp 142–143° (methanol) which showed the following spectral properties: infrared absorption (CCl_4) at 1680 cm^{-1} (C=O) and nmr peaks ($CDCl_3$) at 425 to 480 cps (broad multiplet, 14 H, aromatic), 265

(11) The P-E-H Mg-150 Direct Introduction System has been described by H. W. Major, Jr., and A. W. Struck at the Fourteenth Annual Conference on Mass Spectroscopy and Allied Topics, Dallas, Tex., May 1966.

(12) The infrared spectra were determined with a Perkin-Elmer Model 21 spectrometer and the nmr spectra were determined with a Varian A-60 spectrometer using tetramethylsilane as an internal standard.

cps (singlet, 1 H, benzyl), 228 cps and 193 cps (doublets, J = 7 cps, 1 H each, methylene protons), and 30 to 160 cps (broad multiplet, 11 H, cyclohexyl).

Registry No.—I, 10235-75-3; II, 10235-76-4; III, 10231-03-5; IV, 13871-53-9; V, 13871-54-0; VI, 13871-55-1; VII, 13871-56-2; VIII, 13871-57-3; IX, 13970-36-0; X, 13871-58-4.

Acknowledgment.—This work was supported in part by U. S. Public Health Service Grant CA-02931 (J.-L. I., E. D. and N. H. C.) and by National Science Foundation Grant GP-4915 (R. G. P. and H. E. B.). The mass spectrometer was purchased in part from funds supplied by National Science Foundation Grant GP-3765.

Oxidation of Primary, Secondary, and Tertiary Amines with Neutral Permanganate. A Simple Method for Degrading Amines to Aldehydes and Ketones

SURJAN S. RAWALAY AND HAROLD SHECHTER

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

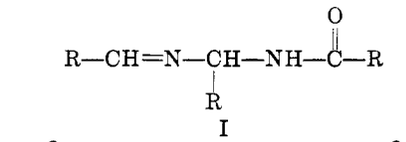
Received May 10, 1967

Primary, secondary, and tertiary amines containing hydrogen on carbon α to nitrogen are oxidatively hydrolyzed to the corresponding aldehyde(s) and/or ketone(s) by buffered permanganate in warm aqueous t-butyl alcohol. The new method is efficient, rapid, experimentally simple, and general for degrading each group of a primary, secondary, or tertiary amine if it is appropriately substituted.

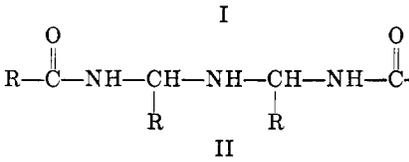
Degradation of complex amines to identifiable products has always been a classic problem of proof of structure. Methods involving base-catalyzed decomposition of quaternary ammonium compounds (the Hofmann degradation),[1a] thermolysis of amine oxides,[1a] and cleavage of amines with cyanogen bromide (the von Braun reaction)[1b] are of great significance to the practice and theory of organic chemistry. As structural methods, however, they are frequently limited by their impracticality and complexity, and products are usually formed which must be degraded by repetitious and/or subsequent operations. Reactions for oxidative-degradations of various amines[2,3] to carbonyl compounds and their derivatives have been reported which involve use of potassium permanganate,[2a] manganese dioxide,[2b] chromic acid,[2c] N-bromosuccinimide,[2d] osmium tetroxide,[2e] mercuric acetate,[2f] 2,3-dichloro-1,4-naphthoquinone,[2g] silver persulfate,[2h] ozone,[2i] chlorine dioxide,[2j] oxygen,[2k] benzoyl peroxide,[2l] alkyl hydroperoxides,[2m] peroxymonosulfuric acid,[2n] and nitrous acid.[2c]

Recently it has been found[4] that amines are oxidized photolytically to imines by benzophenones; the amines are thus degradable to lower amines and the corresponding aldehydes or ketones upon hydrolysis of the intermediate imines. In the present research it is reported that oxidation of primary, secondary, and tertiary amines with neutral permanganate and rapid isolation of the reaction products result in an advantageous method for degrading amines to aldehydes and ketones.

Amines containing hydrogen on carbon bonded to nitrogen (R_2CHNR_2) are rapidly oxidized[2a] by neutral permanganate in aqueous t-butyl alcohol at 25–30°. Primary and secondary amines are converted primarily to imines (RCH=NH) and to enamines (RCH=CRNHR) and/or Schiff bases (RCH=NR), respectively; under these conditions the imines and the Schiff bases usually undergo addition of the parent amines to give ammonals and aminals ($H_2NCHRNHR$ and $RNHCHRNR_2$) with subsequent oxidation, hydration or addition of the initial amine, and oxidative degradation to complex products such as I and II.



I



II

Tertiary amines, depending on their structures, are oxidized to enamines and/or undergo oxidative fragmentation to Schiff bases and products derived from the substituent removed.[2a]

It has been presently found that amines (Table I) containing hydrogen on the carbon α to nitrogen are oxidatively hydrolyzed to the corresponding aldehyde(s) and/or ketone(s) by neutral permanganate in warm (60–80°) aqueous t-butyl alcohol and by rapid isolation of products. The method is general for degrading each group of a primary, secondary, or tertiary amine if it is appropriately substituted. A portion of the chemistry involved in the new degradation method involves oxidation of the amines and hydrolysis of the intermediate imines and enamines as is

(1) (a) A. C. Cope and E. R. Trumbull, *Org. Reactions*, **11**, 317 (1960). (b) H. A. Hageman, *ibid.*, **7**, 198 (1953).

(2) For lead references, see (a) H. Shechter, S. S. Rawalay, and M. Tubis, *J. Am. Chem. Soc.*, **86**, 1701 (1964), and H. Shechter and S. S. Rawalay, *ibid.*, **86**, 1706 (1964). (b) E. F. Curragh, H. B. Henbest, and A. Thomas, *J. Chem. Soc.*, 3559 (1960). (c) F. E. Newmann and C. W. Gould, *Anal. Chem.*, **25**, 751 (1953). (d) S. Dunstan and H. B. Henbest, *J. Chem. Soc.*, 4905 (1957). (e) N. Y. Dem'yanov and Z. I. Shuikina, *J. Gen. Chem. USSR*, **6**, 350 (1936). (f) N. J. Leonard and D. F. Morrow, *J. Am. Chem. Soc.*, **80**, 371 (1958). (g) H. B. Henbest and P. Slade, *J. Chem. Soc.*, 1558 (1960). (h) R. G. R. Bacon and W. J. W. Hanna, *Proc. Chem. Soc.* (London), 305 (1959). (i) W. Strecker and M. Baltes, *Ber.*, **54**, 2693 (1921). (j) L. A. Hull, G. T. Davis, D. H. Rosenblatt, H. K. R. Williams, and R. C. Weglein, *J. Am. Chem. Soc.*, **89**, 1163 (1967). (k) Z. I. Shuikina, *J. Gen. Chem. USSR*, **7**, 983 (1937). (l) D. Buckley, S. Dunstan, and H. B. Henbest, *J. Chem. Soc.*, 4901 (1957). (m) H. E. De La Mare, *J. Org. Chem.*, **25**, 2114 (1960). (n) R. J. Kennedy and A. M. Stock, *ibid.*, **25**, 1901 (1960). (o) P. A. S. Smith and R. N. Loeppky, *J. Am. Chem. Soc.*, **89**, 1147 (1967).

(3) E. Muller and Houben-Weyl, "Methoden Der Organischen Chemie," Vol. XI/I, V. E. B. Georg Thieme Verlag, Stuttgart, 1952, pp 976–984; S. S. Rawalay, Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1962.

(4) S. G. Cohen and R. J. Baumgarten, *J. Am. Chem. Soc.*, **87**, 2996 (1965).