References and Notes

(1) Presented in part at the 2nd Joint CIC/ACS Conference Montreal, Canada, May 29–June 2, 1977.
(2) Available from Columbia Organic Chemical Co., Inc., P.O. Box 9696, Columbia, S.C. 29290.
(3) W. G. Finnegan and W. P. Norris, *J. Org. Chem.*, **28**, 1139 (1963).
(4) This reaction was first demonstrated by Dr. F. D. Marsh.
(5) W. P. Norris and W. G. Finnegan, *J. Org. Chem.*, **31**, 3293 (1966), made $CF_3C{\equiv}CCl$ in trace amounts by the reaction of cupric chloride with the zinc derivative.
(6) A. M. Shchekotikhin, V. S. Blagoveshchenskii, U. V. Sidorenko, and O. K. Denisov, *Zh. Vses. Khim. Ova.*, **7**, 580 (1962); also USSR Patent 169 522 (March 17, 1965) [*Chem. Abstr.*, **63**, 2897 (1965)], synthesized both $CF_3C{\equiv}CCl$ and $CF_3C{\equiv}CBr$ by gas-phase dehydrohalogenation of $CF_3CCl{=}CHCl$ and $CF_3CBr{=}CHBr$, respectively, with NaOH at 210–290 °C in 19–27% yields.
(7) $CF_3C{\equiv}CX$ compounds (X = Cl, Br, I) have also been prepared by the halogenation of $CF_3C{\equiv}CLi$: Dr. E. Kloster Jensen, the University of Oslo, personal communication.
(8) E. Augdahl, E. Kloster-Jensen, V. Devarajan, and S. J. Cyvin, *Spectrochim. Acta, Part A*, **29**, 1329 (1973).
(9) E. Augdahl, E. Kloster-Jensen, V. Devarajan, and S. J. Cyvin, *Aust. J. Chem.*, **26**, 269 (1973).
(10) A. Bjørseth and K. M. Marstokk, *J. Mol. Struct.*, **13**, 191 (1972).
(11) N. I. Delyagina, B. L. Dyatkin, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **No. 7**, 1666 (1974).
(12) R. D. Chambers, "Fluorine in Organic Chemistry", Wiley, New York, N.Y., 1973, pp 223 ff.
(13) E. K. Raunio and T. G. Frey, *J. Org. Chem.*, **36**, 345 (1971).
(14) W. E. Truce and G. J. W. Tichenor, *J. Org. Chem.*, **37**, 2391 (1972).
(15) R. D. Smith and H. E. Simmons, *Org. Synth.*, **41**, 72 (1961).
(16) H. C. Brown and H. L. Gewandter, *J. Org. Chem.*, **25**, 2071 (1960).
(17) W. R. Cullen and D. S. Dauson, *Can. J. Chem.*, **45**, 2887 (1967).
(18) J. A. Jackson, *J. Polym. Sci.*, **10**, 2935 (1972).
(19) W. T. Flowers, R. N. Haszeldine, and P. G. Marshall, *Chem. Commun.*
(20) J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.*, 3488 (1962).
(21) S. K. M. Ehrenstorfer, *J. Polym. Sci., Part A*, **7**, 969 (1969).

Effects of Bridgehead Substituents on the Mass Spectral Fragmentation Pathways for the 9-Methyl-9-azabicyclo[3.3.1]nonane Framework

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Received May 17, 1977

The mass spectral fragmentations of the 9-methyl-9-azabicyclo[3.3.1]nonane nucleus functionalized at a bridgehead position with H (**1**), OH (**2**), OCH_3 (**3**), $OCOCH_3$ (**4**), $NHCH_3$ (**5**), Cl (**6**), and CN (**7**) are reported. The productions of the base ions were found to be strongly dependent on the nature of the bridgehead substituent. For the parent amine **1** the base ion is formed by α cleavage of the 1,2 bond, loss of cyclopropane (carbons 2, 3, and 4), and loss of hydrogen from carbon 6. For the bridgehead hydroxy and methylamino derivatives the most abundant ions arise from α scission of the 1,2 bond, loss of ethylene (carbons 2 and 3), and loss of hydrogen from carbon 5. Bridgehead methyl ether **3** gives rise to its base peak via α cleavage of the 1,2 bond, loss of cyclopropane, and loss of the *O*-methyl group. Acetate **4** takes part in a Hofmann–Loeffler type abstraction of an acetyl hydrogen by the initially generated nitrogen radical cation (in concert with the expulsion of ketene), followed by α cleavage of the 1,2 bond and loss of cyclopropane in route to its base peak. The α-amino chloride merely expels chlorine to produce its base ion. The 1-cyano derivative **7** forms its base peak by cleavage of the 4,5 bond, formation of an iminium radical by attack of the carbon radical (produced from the previous α cleavage) on the cyano carbon, homolytic scission of the bond between carbon 1 and the iminium carbon, and finally cleavage of the 2,3 bond. Other less important fragmentation sequences are also discussed.

Investigations focused on the performance of bridgehead functionalized bridged bicyclic compounds have proven to be of tremendous value in the elucidation of the relationships between structure and reactivity.[2,3] During the last few years heterobicyclic materials (in which the heteroatom is adjacent to the bridgehead carbon atom which bears the bridgehead functionality) have been subjected to various theoretical and experimental tests, the results of which have provided some very interesting postulates pertaining to the relative degrees of stabilization (or destabilization) by resonance and/or induction via the heteroatom.[4–6] In this report, the substantial effects of a bridgehead substituent on the electron-impact-induced fragmentation patterns for the 9-methyl-9-azabicyclo[3.3.1]nonane (granatanine) system (**1–7**) are described.[7,8]

1, X = H
2, X = OH
3, X = OCH_3
4, X = $OCOCH_3$
5, X = $NHCH_3$
6, X = Cl
7, X = CN

Previous reports concerned with interpretations of the mass spectra of compounds in the granatanine system have dealt exclusively with substrates having functionality at the 3 position.[9] In all cases, homolytic cleavage of a carbon–carbon bond adjacent to the nitrogen was shown to be the primary fragmentation process leading ultimately to the production of the base ion.[10] In a recent report from this laboratory it was disclosed that, with certain 1-alkoxy-9-methyl-9-azabicyclo[3.3.1]nonanes, the Hofmann–Loeffler hydrogen-abstraction process can compete effectively with the usual α-cleavage mechanism.[11] For three of the compounds whose mass spectra have been examined in the present study, scission of the 1,2 bond does *not* ultimately result in the formation of the base ion. Furthermore, for the remaining four compounds, wherein cleavage of the 1,2 bond is the predominant initial fragmentation step, the nature of the bridgehead substituent exerts considerable influence on subsequent fragmentations, particularly those leading to the base ions.

Results and Discussion

Table I collects the relative intensity data for the important ions derived from electron impaction of the various bridgehead functionalized 9-methyl-9-azabicyclo[3.3.1]nonanes **1–7**.[12] Inspection of the data reveals that two fragmentation pathways are common to all of the compounds investigated; these sequences are outlined in Chart I. Following α cleavage to produce a′, cyclopropane (or its equivalent) is expelled to provide radical cation b, which in turn goes on to cation c by the loss of a hydrogen atom.[13] In support of the process involving the expulsion of cyclopropane (a′ → b), appropriate

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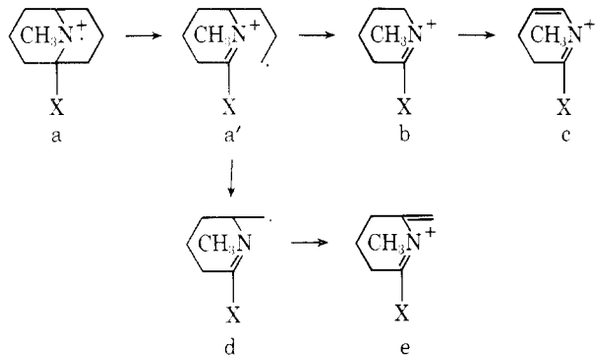
Table I. Relative Intensity Data for Bridgehead Substituted Amines

			m/e; ion; %			
1,[a] X = H	2,[a] X = OH	3[a] X = OCH_3	4,[a] X = $OCOCH_3$	5,[a] X = $NHCH_3$	6,[a] X = Cl	7,[a] X = CN
139; a; 27	155; a; 71	169; a; 52	197; a; 44	168; a; 63	173; a; 46	164; a; 26
138; m; 2	154; g; 5	154; g; 68	169; d; 5	153; g; 20	145; d; 9	136; d; 3
111; d; 5	138; m; 1	141; d; 22	168; e; 2	140; d; 20	144; e; 52	135; e; 19
110; e, n; 35	137; l; 4	140; e; 98	155; b, h; 92	139; e; 100	138; m; 100	122; b; 12
97; b; 25	127; d; 23	138; m; 1	154; c, g; 40	138; m; 3	137; l; 29	121; c; 41
96; c; 100	126; e; 100	127; b; 79	138; m; 21	137; l; 3	131; b; 88	110; n; 100
	113; b, f; 100	126; c; 94	137; l; 65	126; b; 78	130; c; 84	
	112; c; 95	112; f; 100	127; j; 22	125; c; 56	110; n; 77	
	110; n; 4	110; n; 19	126; k; 80	110; n; 16		
			113; i; 100			
			112; f; 76			
			110; n; 16			

[a] Registry no.: **1**, 491-25-8; **2**, 56258-84-5; **3**, 63989-30-0; **4**, 63989-31-1; **5**, 63989-32-2; **6**, 51209-45-1; **7**, 63989-33-3.

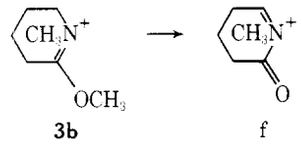
Chart I



metastable peaks were detected for alcohol **2** (*m/e**, 82.4), ether **3** (*m/e**, 95.5), and amine **5** (*m/e**, 94.5). Furthermore, for bridgehead alcohol **2** a mass-analyzed ion kinetic energy (MIKE) spectrum[14] positively confirmed the loss of cyclopropane from the *m/e* 155 ion (**2a'**) as the *only* pathway leading to the production of the *m/e* 113 ion (**2b**). Immonium ion **1c** is the base peak in the mass spectrum of granatanine itself.

In the other fragmentation scheme common to all of the granatanines of the present study, radical cation a' expels ethylene (substantiated by the mass-analyzed ion kinetic energy spectrum for the amino alcohol **2**) to generate radical cation d, which then can lose a hydrogen from carbon 5 to give cation e. The a' → d → e processes are responsible for the base peaks in the mass spectra of the bridgehead hydroxy and methylamino derivatives **2** and **5**, respectively.

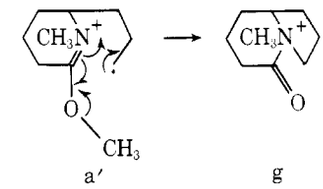
For the α amino bridgehead methyl ether **3**, the base peak (f) is derived from radical cation **3b** by the loss of the methyl group bonded to oxygen (eq 1). The **3b** → f step is supported



(1)

by a metastable peak at *m/e** 98.8 and is in complete agreement with the results previously reported for several other 1-alkoxy-9-methyl-9-azabicyclo[3.3.1]nonanes.[11]

Bridgehead methyl ether **3** also gives rise to an abundant ion (*m/e* 154) formed by the loss of methyl radical from the molecular ion. This process (a' → g) is formulated as taking place as shown in eq 2. If the loss of methyl radical and the C(2)–N bond formation occur simultaneously with the α cleavage (a → a'), the process is essentially a Wagner–Meerwein type migration.[11,15] In addition to **3**, bridgehead acetate **4** and amine **5** exhibit the types of cleavages depicted in eq 1 and 2.



(2)

The base peak (i) of amino acetate **4** is produced by yet another fragmentation sequence (Chart II). In a manner analogous to the hydrogen-transfer step of the condensed-phase Hofmann–Loeffler reaction, the molecular ion **4a** (an amininium ion) abstracts an acetyl hydrogen and simultaneously expels ketene to generate the ammonium alkoxy radical h, which undergoes α scission to give the isomeric species h'; loss of cyclopropane from h' provides the most intense ion in the spectrum (i). The fragmentations outlined in Chart II have ample precedence in the mass spectra of various 1-substituted secondary and tertiary alkoxy granatanines.[11] The availability of activated (by the carbonyl group) hydrogens suitable for abstraction by nitrogen via an intramolecular six-membered transition state, and the fact that a small neutral molecule (ketene) can be eliminated in concert with the hydrogen transfer are responsible for the pathway illustrated in Chart II. Moreover, Green and co-workers have recently demonstrated conclusively that the Hofmann–Loeffler reaction can indeed take place in the mass spectrometer.[16]

Two other fragmentation sequences are also found in the mass spectrum of acetate **4**. Radical cation h' can lose ethylene to provide j, which can go on to k by the loss of a hydrogen

Chart II

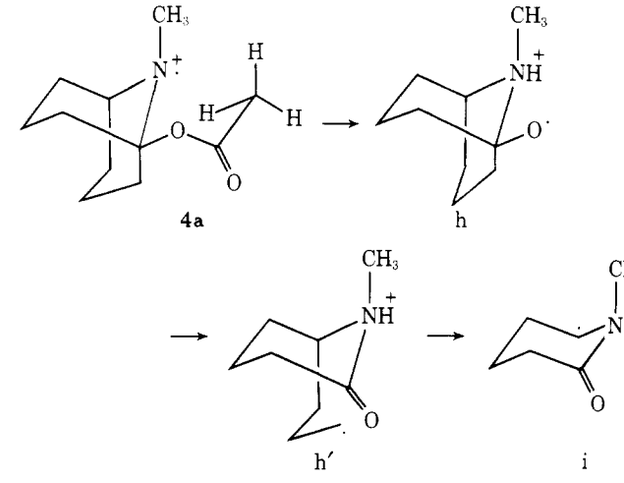
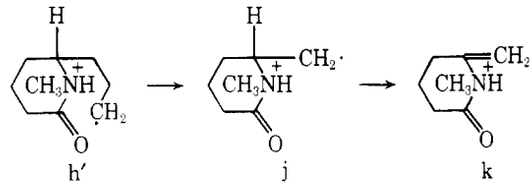
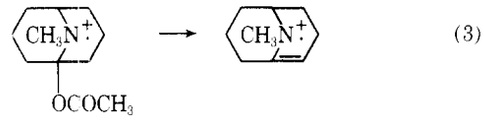


Chart III



atom (Chart III). Finally, amino acetate **4** also displays a relatively highly abundant ion at *m/e* 137 which corresponds to the elimination of acetic acid from the molecular ion to generate the bridgehead enamine radical cation l (eq 3). Of the

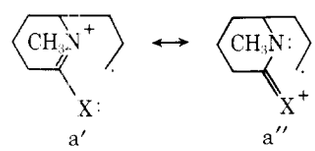


(3)

other substrates investigated, only the bridgehead chloride **6** presents a relatively important signal for the a → l transformation.[17]

The α amino chloride **6** gives rise to the base peak in its mass spectrum by still another primary fragmentation mechanism: the loss of atomic chlorine from the molecular ion to give immonium ion m (Chart IV). The **6a** → m transformation has been documented previously,[11] and has also recently been found to take place in the somewhat related 2-chloro-4-phenylquinuclidine system.[18,19] The fact that a *trans*-azacyclohexene (m) can indeed be generated derives support from the extraordinarily high rate of solvolysis of α-amino bridgehead chlorides.[6c] As indicated in Chart IV, immonium ion m eliminates ethylene to produce n. Among the other substrates examined here only the acetoxy derivative **4** shows a relatively intense signal for the bridgehead immonium ion m.

For the bicyclic amines **1–6**, the α-cleavage process within the molecular ion occurs predominantly (if not exclusively) at the 1,2 bond (see a in Chart I) so that the 1-heteroatom can assist in stabilizing the cleaved species a′ by resonance (a″).



With the bridgehead nitrile **7**, such resonance is not likely; moreover, cleavage of the 1,2 bond provides **7a′** which is destabilized via resonance and induction by the electron-withdrawing cyano group. Consequently, the 4,5 bond is preferentially cleaved in route to the base ion (Chart V). Radical **7o** attacks the cyano carbon to produce isomeric radical **7p** which undergoes α cleavage to afford the resonance-stabilized radical **7q** which loses 2-cyanoethyl radical to provide the base ion n. The **7o** → **7p** transformation is completely analogous to that observed in the condensed state with the bornyl radical.[20]

Chart IV

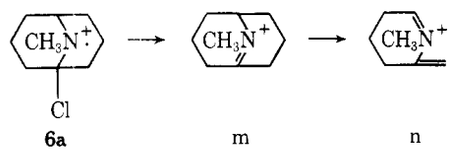
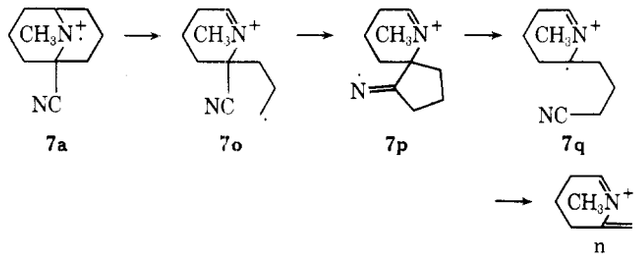


Chart V



Conclusion

It is clear from the above discussions that the nature of the bridgehead substituent plays an extremely important role in directing the fragmentation paths, particularly those leading to the base ions. The directive role of the α substituent manifests itself even though the fragmentations are triggered by the ionization of the nitrogen atom. In summary, it should be emphasized that four different initial fragmentations are responsible for the productions of the base ions: α cleavage of the 1,2 carbon–carbon bond (compounds **1, 2, 3, 5**), α cleavage of the bond between the bridgehead carbon and the substituent (compound **6**), α cleavage of the 4,5 carbon–carbon bond (compound **7**), and hydrogen abstraction from the side chain by nitrogen (compound **4**). The knowledge gained here on the strong dependence of the important fragmentation pathways on the nature of a substituent α to a nitrogen should be highly valuable in studies engaged in the elucidation of the structures of alkaloids utilizing mass spectrometry.

Experimental Section

Mass spectra were obtained with an A.E.I. MS-9 mass spectrometer operating at an ionization voltage of 70 eV and at a source temperature of about 175 °C. The mass-analyzed ion kinetic energy (MIKE) spectra were measured with the Varian MAT-311 instrument focused on the mass/charge value of 155 and operated at 3 kV. ^{1}H NMR spectra were measured on a Varian Associates T-60 instrument. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are not corrected; boiling points are also uncorrected. All substrates were purified by preparative gas chromatography (with a Varian Aerograph 90-P apparatus equipped with a 5 ft. × 0.25 in. stainless-steel column packed with 20% SE-30 on Chromosorb G) immediately prior to mass spectral measurements; the column temperatures employed for sample collection were about 190 °C (which established that the substrates are thermally stable under the conditions used for mass spectrometry). Compounds **1**,[6] **2**,[6] **5**,[21] and **6**[6] are known and were prepared according to published procedures. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor Mich.

1-Methoxy-9-methyl-9-azabicyclo[3.3.1]nonane (3). To a 200-mL round-bottomed flask was added 3.10 g (0.02 mol) of amino alcohol **2** and 50 mL of cold thionyl chloride. After 1, the solution was heated at reflux for 60 h, after which the thionyl chloride was distilled. After cooling to room temperature, methanol and then saturated aqueous sodium carbonate solution were added, and the resulting solution was extracted with methylene chloride. The combined organic extracts were dried (Na_2SO_4) and concentrated on a rotary evaporator to a liquid whose GC analysis indicated the presence of **2** and **3** in the ratio 14:86. Amino ether **3** was isolated by preparative thick-layer chromatography (silica gel, methanol) and distillation (bp ~85 °C, 0.25 Torr): NMR ($CDCl_3$) δ 3.09 (s, 3 H, OCH_3), 2.96 (m, 1 H, NCH), 2.20 (s, 3H, NCH_3), 2.2–1.2 (m, 12 H, CH_2).

Anal. Calcd for $C_{10}H_{19}NO$: C, 70.96; H, 11.31; N, 8.27. Found: C, 71.00; H, 11.27; N, 8.20.

9-Methyl-9-azabicyclo[3.3.1]non-1-yl Acetate (4). A solution of 646 mg (3.72 mmol) of amino chloride **6**, 7 mL of glacial acetic acid, 1 mL of acetic anhydride, and 1 g of anhydrous sodium acetate was stirred at room temperature for 2 days, after which methylene chloride and sufficient 10% aqueous sodium hydroxide solution to render the mixture basic were added. The layers were separated and the aqueous phase was extracted with methylene chloride. The combined organic extracts were dried over Na_2SO_4 and concentrated to 851 mg of liquid, most of which was acetic anhydride. Preparative GC provided pure amino acetate **4**: mp 63–66 °C; NMR ($CDCl_3$) δ 3.13 (m, 1 H, NCH), 2.52 (s, 3 H, NCH_3), 2.2–1.2 (m, 12 H, CH_2), 2.00 (s, 3 H, $OCOCH_3$); IR ($CHCl_3$) 1720 cm^{-1}.

Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10. Found: C, 66.62; H, 9.77; N, 7.02.

1-Cyano-9-methyl-9-azabicyclo[3.3.1]nonane (7). To a solution of 545 mg (3.14 mmol) of amino chloride **6** in 30 mL of *N,N*-dimeth-

ylformamide (distilled from CaO) was added 1.5 g of sodium cyanide. The mixture was stirred at room temperature under nitrogen for 4 days, after which methylene chloride and water were added. The layers were separated and the organic phase was washed with water, dried (Na_2SO_4), and concentrated to 40 mg of liquid from which pure amino nitrile **7** was obtained by preparative GC: NMR ($CDCl_3$) δ 2.88 (m, 1 H, NCH), 2.68 (s, 3 H, NCH_3), 2.3–1.2 (m, 12 H, CH_2); IR ($CHCl_3$) 2240 cm^{-1}.

Acknowledgments. The author is grateful to Mrs. Margaret Johnson for measuring the mass spectra of compounds **1–7**, to Dr. Woodfin V. Ligon, Jr., for the MIKE spectra, and to Professor John R. Wiseman for providing partial support.

Registry No.—Thionyl chloride, 7719-09-7; sodium cyanide, 143-33-9.

Supplementary Material Available. Bar graphs of the mass spectra of compounds **1–7** (7 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Correspondence concerning this manuscript should be directed to the author at the Organic and Polymer Chemistry Branch, General Electric Corporate Research and Development Center, Schenectady, N.Y. 12301.
(2) R. C. Fort, Jr., and P. v. R. Schleyer, *Adv. Alicycl. Chem.*, **1**, 283 (1966).
(3) R. C. Fort, Jr., "Carbonium Ions", Vol. 4, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1973; W. Parker, R. L. Tranter, C. I. F. Watt, L. W. K. Chang, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96**, 7121 (1974), and references therein.
(4) Reduction of α-amino bridgehead ethers: P. G. Gassman and B. L. Fox, *J. Am. Chem. Soc.*, **89**, 338 (1967); J. O. Reed and W. Lwowski, *J. Org. Chem.*, **36**, 2864 (1971); P. Kovacic, J.-H. Liu, E. M. Levi, and P. D. Roskos, *J. Am. Chem. Soc.*, **93**, 5801 (1971); S. J. Padegimas and P. Kovacic, *J. Org. Chem.*, **37**, 2672 (1972).
(5) Solvolysis reactions: (a) R. D. Fisher, T. D. Bogard, and P. Kovacic, *J. Am. Chem. Soc.*, **95**, 3646 (1973); (b) P. G. Gassman, R. L. Cryberg, and K. Shudo, *J. Am. Chem. Soc.*, **94**, 7600 (1972); (c) C. A. Grob and A. Sieber, *Helv. Chim. Acta*, **50**, 2531 (1967); (d) T. A. Wnuk and P. Kovacic, *J. Am. Chem. Soc.*, **97**, 5807 (1975); (e) W. P. Meyer and J. C. Martin, *J. Am. Chem. Soc.*, **98**, 1231 (1976).
(6) Syntheses and properties of bridgehead olefins: (a) C. B. Quinn and J. R. Wiseman, *J. Am. Chem. Soc.*, **95**, 1342 (1973); (b) C. B. Quinn and J. R. Wiseman, *J. Am. Chem. Soc.*, **95**, 6120 (1973); (c) H. O. Krabbenhoft, J. R. Wiseman, and C. B. Quinn, *J. Am. Chem. Soc.*, **96**, 258 (1974).
(7) For reports dealing with the mass spectra bridgehead-substituted bridged bicyclic compounds; see: (a) Z. Dolejsek, S. Hala, V. Hanus, and S. Landa, *Collect. Czech. Chem. Commun.*, **31**, 435 (1966); (b) J. W. Greidanus, *Can. J. Chem.*, **49**, 3210 (1971); (c) D. C. DeJongh and S. H. Schrader, *J. Am. Chem. Soc.*, **88**, 3881 (1966); (d) A. G. Yurchenko, F. N. Stepanov, S. S. Isaeva, B. M. Zolotarev. V. I. Kadenstev, and O. S. Chizhov, *Org. Mass Spectrom.*, **3**, 1401 (1970).
(8) For reports dealing with the mass spectra of bicyclo[3.3.1]nonanes, see: (a) R. Nicoleti and A. Gambacurta, *Org. Mass. Spectrom.*, **7**, 699 (1973); (b) J. Cable, J. K. MacLeod, M. R. Vegar, and R. J. Wells, *Org. Mass. Spectrom.*, **7**, 1137 (1973); (c) J. R. Dalton, G. J. James, and J. G. Morris, *J. Chem. Eng. Data*, **20**, 125 (1975); (d) J. A. Peters, B. van de Graaf, P. J. W. Schuyl, T. M. Wortel, and H. van Bekkum, *Tetrahedron*, **32**, 2735 (1976).
(9) R. D. Guthrie and J. F. McCarthey, *J. Chem. Soc. C.*, 1207 (1966); (b) W. M. Bryant, III, A. L. Burlingame, H. O. House, C. G. Pitt, and B. A. Tefertiller, *J. Org. Chem.*, **31**, 3120 (1966).
(10) Similar results have been observed for the tropane system: (a) E. C. Blossey, H. Budzikiewicz, M. Ohashi, G. Fodor, and C. Djerassi, *Tetrahedron*, **20**, 585 (1964); (b) J. Parello, P. Longevaille, W. Vetter, and J. A. McCloskey, *Bull. Soc. Chim. Fr.*, 2787 (1963); (c) J. E. Dewhurst, J. J. Kaminski, and J. H. Supple, *J. Heterocycl. Chem.*, **9**, 507 (1972).
(11) H. O. Krabbenhoft, *J. Org. Chem.*, **41**, 1774 (1976).
(12) Bar graphs of the mass spectra of the compounds **1–7** appear in the microfilm edition; see paragraph at end of paper regarding supplementary material.
(13) For alcohol **2** the loss of hydrogen from radical ion b can occur from carbon 6 (to give **2c**) or from the hydroxyl group (to give **2f**). An attempt to distinguish between these two pathways by examining the mass spectrum of partially deuterated **2**-OD gave inconclusive results.
(14) R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, "Metastable Ions", Elsevier, Amsterdam, 1973, pp 42–44.
(15) F. Komitsky, Jr., J. E. Gurst, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 1398 (1965).
(16) M. M. Green, J. M. Moldowan, M. W. Armstrong, T. L. Thompson, K. L. Sprague, A. J. Hass, and J. J. Artus, *J. Am. Chem. Soc.*, **98**, 849 (1976).
(17) By measuring the mass spectrum of 9-methyl-9-azabicyclo[3.3.1]non-1-ene[6c] itself, it was found that the ions at *m/e* values of 136, 122, 109, 108, 94, 82, 81, 68, and 67 are daughters of **1** (H. O. Krabbenhoft, Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 1974).
(18) H. Achenbach, J. Worth, W. Schneider, and H. Bochow, *Org. Mass Spectrum*, **10**, 111 (1975); see also B. E. Maryanoff and R. O. Hutchins, *J. Org. Chem.*, **37**, 3475 (1972).
(19) The loss of bridgehead chloride is also responsible for the base peak in the bicyclo[3.3.1]nonane (H. O. Krabbenhoft, Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 1974) and adamantane[7a] systems.
(20) J. A. Berson, C. H. Olsen, and J. S. Walia, *J. Am. Chem. Soc.*, **84**, 3337 (1962).
(21) C. B. Quinn, Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 1973.