Peri Effects in the Mass Spectra of Some 8-Substituted 1-Naphthoic Acids and 1-Naphthylcarbinols

PAUL H. CHEN*

Philip Morris Research Center, Richmond, Virginia 23261

DONALD C. KLEINFELTER

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916

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The mass spectra of several 8-substituted 1-naphthoic acids and 1-naphthylcarbinols have been examined to determine if peri interactions are involved in the fragmentation. The substituents at the C_8 position include CH_3O, CH_3, Br, and NO_2. The spectrum of the 8-methoxy acid shows a strong $M - CH_3OH$ ion due to peri interaction whereas its isomeric 2-methoxy acid does not. The loss of water in the spectra of the 8-methyl acid and alcohol and of HBr from the 8-bromo alcohol are indicative of interaction between peri substituents. The expulsion of these neutral molecules from the molecular ion is presumably facilitated by the peri cyclization to form a stable product. The weak molecular ion and facile loss of the 8 substituent in the spectra of the 8-bromo and 8-nitro acids are interpreted as being due to peri interactions. The presence of $M - H_2O$ and $M - OH - OH$ ions in the spectrum of the 8-nitro alcohol also indicates the interaction between the peri substituents.

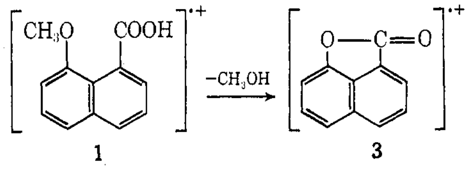
Proximity effects in peri-substituted naphthalenes in solution chemistry have been reported by us in our previous paper[1] and by a number of other workers.[2] From a geometrical consideration peri substituents are much closer to one another than identical ortho substituents. Since ortho effects in the mass spectra of aromatic compounds are very common,[3] one should also observe peri effects in the mass spectra of 1,8-disubstituted naphthalenes. However, there has been considerably less work published on peri effects in mass spectral fragmentations[4-7] than on ortho effects,[3] presumably owing to the fact that the peri-substituted naphthalene derivatives are not so easily available as the ortho-substituted aromatic compounds.

The present study concerns itself with analyses of the mass spectra of several 8-substituted 1-naphthoic acids and 1-naphthylcarbinols to determine whether peri interactions are involved in the electron impact induced fragmentation. Wherever possible, the mass spectra of these peri-substituted naphthalenes are compared with those of corresponding isomers of naphthalene or with appropriate benzene derivatives.

Results and Discussion

8-Substituted 1-Naphthoic Acids.—The mass spectrum of the unsubstituted parent 1-naphthoic acid obtained by us is similar to that reported by McLafferty and Gohlke[8] and hence will not be reproduced here. Its major fragmentation processes are loss of the hydroxyl radical and subsequent loss of carbon monoxide. These two processes have been substantiated by the observation of an appropriate metastable ion determined by the defocusing technique.[9]

The mass spectrum (Figure 1) of 8-methoxy-1-naphthoic acid (1) shows a very strong peak at m/e 170 owing to loss of CH_3OH from the molecular ion. The strong loss of methanol as well as the presence of a strong metastable ion for this loss and of a very weak metastable ion for the transition from the m/e 185 ion to the m/e 170 ion suggest that the methanol loss is primarily, though not exclusively, a one-step loss from the molecular ion. The similar direct methanol loss is absent in the mass spectrum (Figure 1) of the isomeric 2-methoxy-1-naphthoic acid (2). A metastable defocusing measurement indicates that the weak m/e 170 ion in the 2-methoxy acid 2 is attributed to loss of the methyl radical from the M − OH ion (m/e 185). This drastic difference observed in the spectra of isomeric 1 and 2 can be explained by the formation of a stable lactone ion 3 in the former through peri ring closure,[10] whereas in the latter a similar 1,2 cyclization would lead to the unlikely formation of a very strained four-membered ring compound ion. The fact that a one-step loss of methanol from compound 2 is absent suggests that the methoxy methyl and the carboxyl hydroxy cannot interact to lose methanol even though a stable quinoid ion like 4 could be formed from such an



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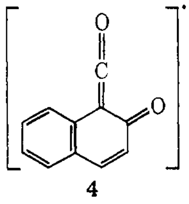

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[1] D. C. Kleinfelter and P. H. Chen, *J. Org. Chem.*, **34**, 1741 (1969).

[2] For an extensive review of naphthalene peri interactions, see V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).

[3] For examples of ortho effects, see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, pp 197, 200, 220, 279, 516, 636.

[4] (a) J. H. Bowie, P. J. Hoffmann, and P. Y. White, *Tetrahedron*, **26**, 1163 (1970); (b) J. H. Bowie and P. Y. White, *J. Chem. Soc. B*, 89 (1969); (c) B. M. King, D. A. Evans, and K. Biemann, *Org. Mass Spectrom.*, **3**, 1049 (1970).

[5] (a) J. Harley-Mason, T. P. Toube, and D. H. Williams, *J. Chem. Soc. B*, 396 (1966); (b) J. H. Beynon, B. E. Job, and A. E. Williams, *Z. Naturforsch., A*, **21**, 210 (1966).

[6] J. L. Smith, J. L. Beck, and W. J. A. VandenHeuvel, *Org. Mass Spectrom.*, **5**, 473 (1971).

[7] (a) D. L. Fields and T. H. Regan, *J. Org. Chem.*, **36**, 2986 (1971); (b) R. Marchelli, W. D. Jamieson, S. H. Safe, O. Hutzinger, and R. A. Heacock, *Can. J. Chem.*, **49**, 1296 (1971).

[8] F. W. McLafferty and R. S. Gohlke, *Anal. Chem.*, **31**, 2076 (1959).

[9] (a) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Nature (London)*, **204**, 67 (1964); (b) P. Schulze and A. L. Burlingame, *J. Chem. Phys.*, **49**, 483 (1968).

[10] Reference 2, p 593.

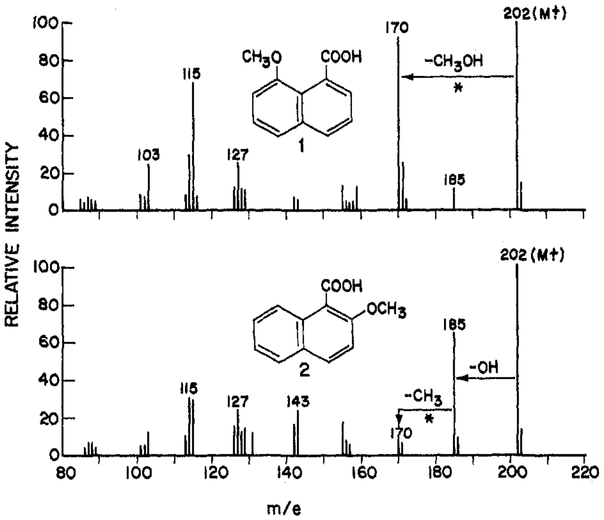


Figure 1.—Mass spectra (70 eV) of 8-methoxy-1-naphthoic acid (1) and 2-methoxy-1-naphthoic acid (2).

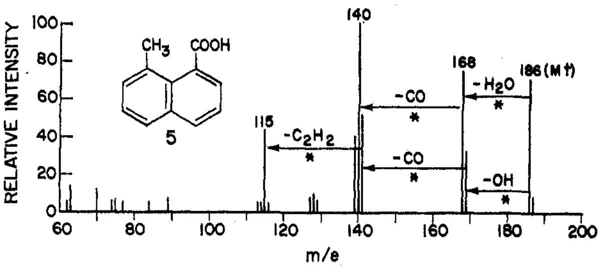


Figure 2.—Mass spectrum (70 eV) of 8-methyl-1-naphthoic acid (5).

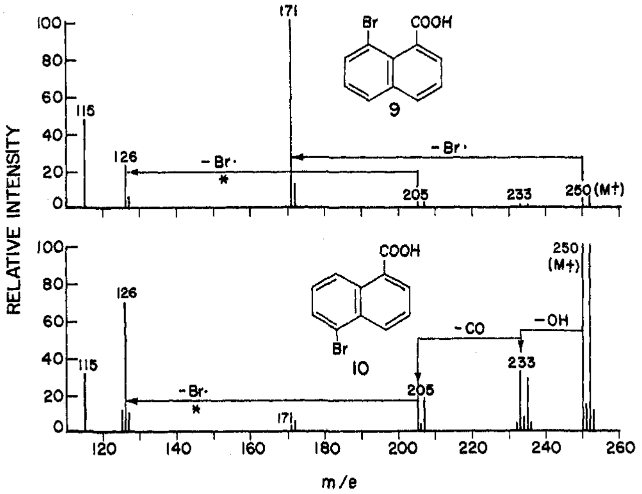
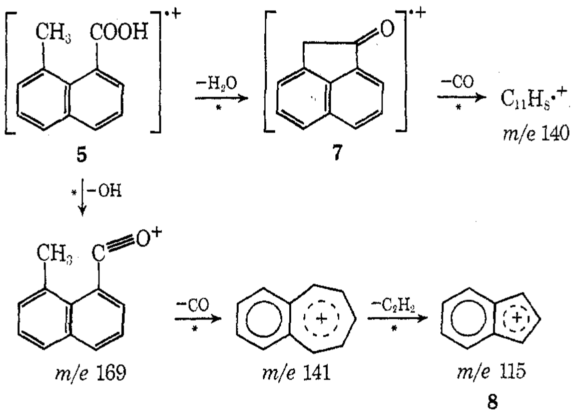


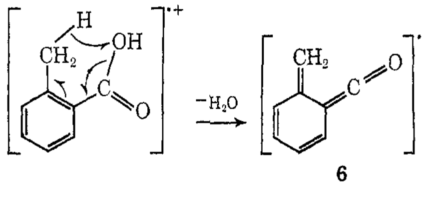
Figure 3.—Mass spectra (70 eV) of 8-bromo-1-naphthoic acid (9) and 5-bromo-1-naphthoic acid (10).

SCHEME I



interaction (compound 2). This is understandable because such a mechanism for the elimination of methanol would require a transfer of a methyl radical, a process which is much more difficult than a similar transfer of a hydrogen atom.

The mass spectrum (Figure 2) of 8-methyl-1-naphthoic acid (5) exhibits a strong M − H_2O peak (*m/e* 168) owing to the interaction of the two peri substituents. The direct loss of water from the molecular ion is substantiated by the presence of an appropriate metastable ion determined by the defocusing technique. This also indicates, at least in part, that the M − H_2O ion is not due to thermal elimination. A comparison of the fragmentation pattern of the 8-methyl acid **5** with its isomeric 2-methyl-1-naphthoic acid is not possible owing to the unavailability of the latter compound. However, a ready comparison can be made with *o*-toluic acid, which also shows strong loss of water from the molecular ion.[8,11] In *o*-toluic acid the water loss is facilitated by the formation of ion **6**,



whereas in the 8-methyl acid **5**, the same loss is more than likely facilitated by the formation of the acenaphthenone ion (**7** in Scheme I) through peri ring closure, assuming that no ring expansion occurs prior to water loss. The stabilization of the M − H_2O ion in compound **5** by the resonance interaction between substituents is unlikely because peri substituents are separated by three carbon atoms and may therefore be likened to meta substituents. The major fragmentation processes of compound **5** are shown in Scheme I. An asterisk in the scheme indicates the presence of a metastable ion determined by the defocusing technique.[9] The *m/e* 115 ion, which is strong in the spectrum of **5** as well as many of the other peri-substituted naphthalene derivatives, probably has a structure like the indenyl ion (**8**),[12] the ethenyltropylium ion,[13] or the phenylcyclopropenyl cation.[13] The chemical composition of the *m/e* 115 ion has been established to be C_9H_7 by the exact mass measurement.

The striking differences between the mass spectra (Figure 3) of 8-bromo-1-naphthoic acid (**9**) and 5-bromo-1-naphthoic acid (**10**) are the following: (1) while the M − Br peak (*m/e* 171) is extremely strong in compound **9**, the corresponding peak is very weak[14] in compound **10**; (2) while the molecular ion peaks are weak in **9**, the corresponding peaks are strong in **10**; (3) the peaks due to the fragmentation of the carboxyl group, *i.e.*, *m/e* 205, 207, 233, and 235, are much more

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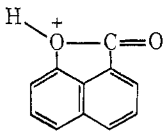
[11] T. Aczel and H. E. Lumpkin, *Anal. Chem.*, **33**, 386 (1961).

[12] R. T. Aplin and S. Safe, *Chem. Commun.*, 140 (1967).

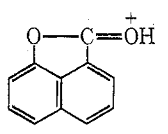
[13] H. Schwarz and F. Bohlmann, *Org. Mass Spectrom.*, **7**, 395 (1973).

[14] While the singly charged ion is very weak, the doubly charged ion of M − Br is much more abundant.

prominent in the spectrum of **10** than in that of **9**. The fragmentation behavior of the 8-bromo acid is also different from that of *o*-bromobenzoic acid[15] in that the latter shows very strong molecular ion peaks and a very weak peak corresponding to the loss of bromine from the molecular ion. The facile loss of the bromine atom in the spectrum of the 8-bromo acid **9** is most likely assisted by the presence of the peri carboxyl group. This effect is analogous to that observed in naphthalene solution chemistry, where the presence of a carboxyl group peri to a nitro or halo substituent appears to make the substituents labile and more easily replaced than ones in analogous ortho-substituted compounds.[16] The interactions between the two peri substituents can be attributed to steric effects, electronic effects, and neighboring-group participation. With relation to the steric effect, it has been reported that large steric interactions in the molecule would cause the molecular ion to be less stable and hence to have a greater tendency to decompose to relieve the steric strain.[17] In solution chemistry, in addition to steric effects, direct dipolar field effects have been reported to exert some influence on the pK_a values of the 8-substituted 1-naphthoic acids.[18] It is not known to what extent this field effect would influence the molecular ion intensity. The expulsion of the bromine atom from the molecular ion may not be a simple bond cleavage but may involve a tight transition state where the carboxyl group participates in the elimination, thereby lowering the activation energy.[19] The low activation energy for the process of bromine elimination is supported by the experimental observation that the relative abundance of the M − Br ion remains prominent at low ionizing voltage. The formation of stable protonated lactones like **11a** and/or **11b** may be postulated to follow the loss of the bromine atom. The metastable defocusing measurement indicates that the *m/e* 126 ion in both **9** and **10** originates from the M − COOH ions (*m/e* 205, 207) by the loss of a bromine atom.



11a



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The mass spectra of 8-nitro-1-naphthoic acid (**12**) and its isomeric 5-nitro-1-naphthoic acid (**13**) are shown in Figure 4. The 8-nitro acid **12** has a weak molecular ion and a very strong M − NO_2 ion, whereas the 5-nitro acid **13** has a strong molecular ion and a moderate M − NO_2 ion. The strong molecular ion in the spectrum of **13** is expected because aromatic compounds normally have high molecular ion intensities. The strong molecular ion was also reported for the mass spectrum of *o*-nitrobenzoic acid.[20] The weak molecular ion and the strong M − NO_2 ion in the spectrum of **12** are likely due to some sort of interaction between the two peri substituents. This is in accord with the mass spectral fragmentation behavior of the 8-bromo acid (*vide supra*) and with a report published elsewhere.[21] As shown in Figure 4, the strong *m/e* 115 ion in both **12** and **13** is derived from the *m/e* 171 and 143 ions, presumably by the loss of C_2O_2[20a] and CO, respectively. The ionic formula of the *m/e* 115 ion has been determined to be C_9H_7 by the accurate mass measurement.

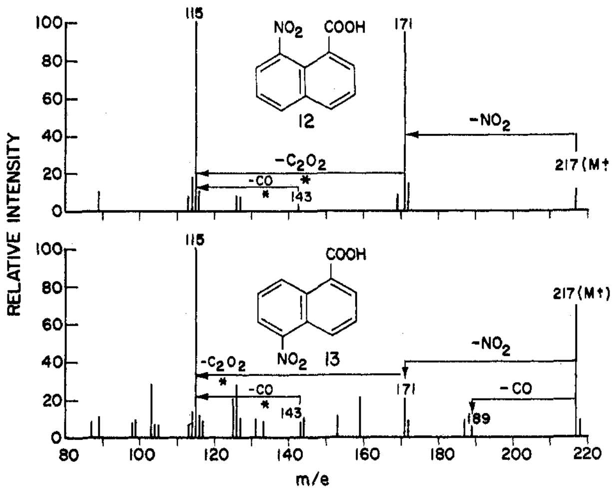

Figure 4.—Mass spectra (70 eV) of 8-nitro-1-naphthoic acid (**12**) and 5-nitro-1-naphthoic acid (**13**).

Williams[5a] and Beynon[5b] reported independently that the loss of CO from the molecular ion was observed in 1-nitronaphthalene but not in nitrobenzene or 2-nitronaphthalene. They both proposed that the peri carbon (C_8) atom was involved in this unique loss of CO. We also observed the loss of CO from the molecular ion of the 5-nitro acid **13** but not from that of the 8-nitro acid (see Figure 4). This is in agreement with Williams and Beynon's observations. However, in the 5-nitro acid, part of the CO loss could come from the carboxyl group.

8-Substituted 1-Naphthylcarbinols.—The mass spectral fragmentation behavior of the unsubstituted 1-naphthylcarbinol (**14**) has been described[22] very recently with the aid of deuterium- and ^{13}C-labeled derivatives. The most prominent fragmentation process is the loss of 29 mass units (CHO) from the molecular ion. This is an important decomposition pathway for most of the naphthylcarbinols examined in this study.

In contrast to the mass spectrum of the 8-methoxy acid **1**, which shows distinguished peri interaction by the loss of methanol from the molecular ion, the spectrum (Figure 5) of 8-methoxy-1-naphthylcarbinol (**15**) shows little or no loss of either CH_3OH or H_2O from interaction of the peri substituents.[23] The metastable defocusing measurement suggests that the weak *m/e*

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[15] Mass Spectral Data, No. 2891, Dow Chemical Co., Midland, Mich.

[16] (a) H. G. Rule and A. J. G. Barnett, *J. Chem. Soc.*, 175, 2728 (1932); (b) H. G. Rule and H. M. Turner, *ibid.*, 317 (1935).

[17] (a) K. Biemann and J. Seibl, *J. Amer. Chem. Soc.*, **81**, 3149 (1959); (b) P. Natalis in "Mass Spectrometry," R. I. Reed, Ed., Academic Press, New York, N. Y., 1965, pp 379–399; (c) C. E. Brion, J. S. Haywood-Farmer, R. E. Pincock, and W. B. Stewart, *Org. Mass Spectrom.*, **4**, 587 (1970).

[18] (a) M. Hojo, K. Katsurakawa, and Z. Yoshida, *Tetrahedron Lett.*, 1497 (1968); (b) K. Bowden and D. C. Parkin, *Can. J. Chem.*, **47**, 185 (1969).

[19] For examples of neighboring-group participation reactions in the mass spectral fragmentation, please see (a) R. G. Cooks, N. L. Wolfe, J. R. Curtis, H. E. Petty, and R. N. McDonald, *J. Org. Chem.*, **35**, 4048 (1970); (b) R. H. Shapiro and K. B. Tomer, *Org. Mass Spectrom.*, **3**, 333 (1970); (c) J. M. Pechine, *ibid.*, **5**, 705 (1971).

[20] (a) F. Benoit and J. L. Holmes, *Org. Mass Spectrom.*, **3**, 993 (1970); (b) K. B. Tomer, T. Gebreyesus, and C. Djerassi, *ibid.*, **7**, 383 (1973).

[21] E. F. H. Brittain, C. H. J. Wells, H. M. Paisley, and D. J. Stickley, *J. Chem. Soc. B*, 1714 (1970).

[22] H. Schwarz and F. Bohlmann, *Org. Mass Spectrom.*, **7**, 29 (1973).

[23] While there is little or no peri interaction in the electron impact induced fragmentation, the same 8-methoxy alcohol exhibits a strong intramolecular H bonding in solution chemistry (see ref 1 and P. H. Chen, Ph.D. Thesis, The University of Tennessee, Knoxville, Tenn., 1967).

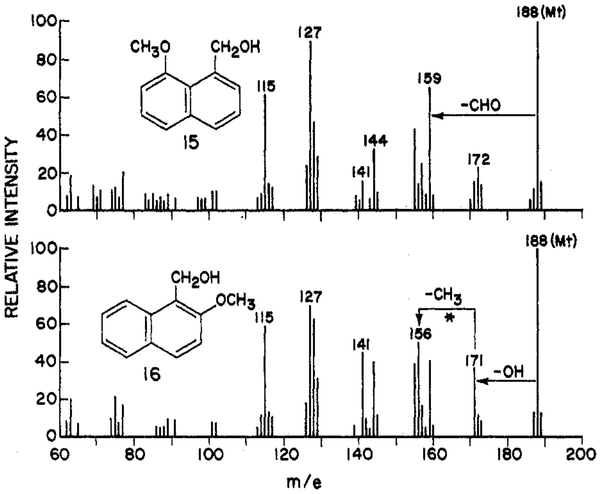


Figure 5.—Mass spectra (70 eV) of 8-methoxy-1-naphthylcarbinol (**15**) and 2-methoxy-1-naphthylcarbinol (**16**).

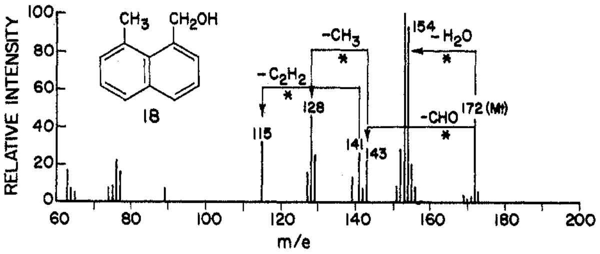
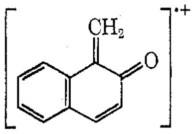


Figure 6.—Mass spectrum (70 eV) of 8-methyl-1-naphthylcarbinol (**18**).

156 ion is primarily due to two-step elimination from the molecular ion. The absence of significant water loss from the molecular ion is understandable because its formation would require an unfavorable eight-membered cyclic transition state. The reason for little or no direct methanol loss from the 8-methoxy alcohol **15** molecular ion is obscure. It may be related to competing reaction such as the loss of CHO or other fragment(s), or to the possible ring expansion which occurs prior to or during the fragmentation of the molecular ion. Fragmentations are directed by either the hydroxymethyl or methoxy functions. The peaks at *m/e* 115, 126, 127, 128, and 141 are characteristic of naphthalene derivatives. The mass spectrum (Figure 5) of 2-methoxy-1-naphthylcarbinol (**16**) is similar to that of its 8-methoxy isomer **15** except that the M − OH ion (*m/e* 171) and M − OH − CH_3 ion (*m/e* 156) are more prominent for the 2-methoxy isomer **16**. The driving force for the production of the strong *m/e* 156 ion in the spectrum of the 2-methoxy isomer may be due to the formation of a resonance-stabilized structure like **17**.



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The mass spectrum (Figure 6) of 8-methyl-1-naphthylcarbinol (**18**) exhibits two strong peaks at *m/e* 154 and 153 owing to loss of water and successive losses of water and the hydrogen radical, respectively. As shown in Scheme II, the M − H_2O ion presumably bears the structure of acenaphthene (**19**), which eliminates a hydrogen atom to form an acenaphthenyl ion (**20**). The proposed structures of **19** and **20** are based on the assumption that no ring expansion occurs prior to or during water loss. The other major fragmentation processes are also shown in Scheme II.

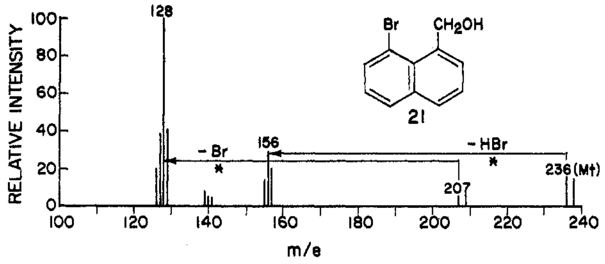
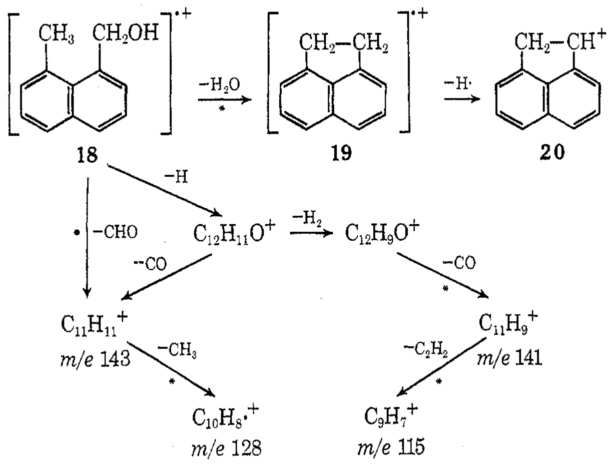
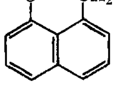


Figure 7.—Mass spectrum (70 eV) of 8-bromo-1-naphthylcarbinol (**21**).

SCHEME II



Loss of HBr from the molecular ion is also observed in the spectrum (Figure 7) of 8-bromo-1-naphthylcarbinol (**21**), which is indicative of interaction between the two peri substituents. A deuterium-labeling experiment confirms that the hydroxyl hydrogen is lost with the bromine atom in the HBr elimination. The M − HBr ion may have a structure like **22**. The relatively weak molecular ion peaks (*m/e* 236 and 238) are in line with the mass spectra of the 8-bromo and 8-nitro acids (see Figures 3 and 4). The metastable defocusing measurement indicates that the base peak ion (*m/e* 128) originates from the *m/e* 207 and 209 ions by loss of a bromine atom. The ionic formula of the *m/e* 128 ion has been determined to be $C_{10}H_8$ by the accurate mass measurement. Presumably it has the structure of naphthalene.



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The mass spectrum (Figure 8) of 8-nitro-1-naphthylcarbinol (**23**) shows a weak molecular ion and strong fragment ions at *m/e* 127, 128, 115, and 141 which are characteristic peaks of naphthalene derivatives. The weak molecular ion and the presence of the M − H_2O ion (*m/e* 185) and the M − OH − OH ion (*m/e* 169) are indicative of the interaction between the peri substituents. Similar water elimination from the molecular ion has been reported in the mass spectrum of *o*-nitrobenzyl alcohol.[20a] The loss of water and the expulsion of hydroxyl radical from the M − OH ion have been substantiated by the observation of an appropriate metastable ion determined by the defocusing technique. The elimination of water can be postulated by a transfer of a naphthylcarbinyl hydrogen to the neighboring nitro group; the two peri substituents in the rearranged molecular ion (with or without ring expansion) then interact to lose water. Examination of the spectrum of compound **23** with a deuterium replacing the hydroxyl hydrogen revealed that, in addition to a loss of 18 mass units (OD) from the deuterated molecular ion, a loss of 17 mass units (OH) was also observed. Corrections have been made for the hydroxyl loss from the undeuterated molecular ion and also for the ^{13}C contribution. This indicates that either the hydroxyl group formed by a hydrogen transfer to the nitro group is responsible for the OH loss from the deuterated molecular ion or the deuterium in CH_2OD moiety undergoes deuterium–hydrogen exchange prior to hydroxyl loss. The strong *m/e* 141 ion is derived from the *m/e* 169 and 185 ions by the loss of 28 and 44 mass units,[24] respectively. The former loss is presumably due to elimination of CO, which is frequently observed in the mass spectra of aromatic nitro compounds.[25] The *m/e* 141 ion loses a molecule of HCN to the *m/e* 114 ion. The loss of CO and HCN are also observed in the decomposition of *m/e* 155 to *m/e* 127 and of *m/e* 142 to *m/e* 115, respectively.

Experimental Section

Preparation of Naphthoic Acids and Naphthylcarbinols.—Methods or literature references for preparation of most of these compounds have been given in our previous paper[1] except for the compounds described below. The 5-nitro-1-naphthoic acid was prepared by the method of Ekstrand.[26] The 2-methoxy-1-naphthoic acid was prepared by the method of Werner and Seybold,[27] and its corresponding alcohol was synthesized by lithium aluminum hydride reduction of the acid. The 5-bromo-1-naphthoic acid was prepared by the procedure of Short and Wang.[28] The compounds had melting points in agreement with the values reported in the literature.

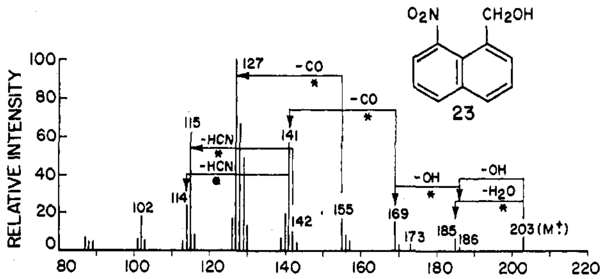

Figure 8.—Mass spectrum (70 eV) of 8-nitro-1-naphthylcarbinol (**23**).

Mass Spectra.—Mass spectra were obtained on a CEC 21-104 mass spectrometer except for the data on the metastable ion and accurate mass measurements. Samples were introduced *via* the direct insertion probe at ambient temperature with a source thermocouple reading of 250°. The metastable ion measurements were obtained with a CEC 21-110B double-focusing mass spectrometer by the defocusing technique similar to the method used by Schulze and Burlingame.[9b] The accurate mass measurements were also done on a CEC 21-110B with a resolution of about 10,000. Deuterium labeling of the hydroxyl hydrogen was done by dissolving the alcohol in chloroform, then adding D_2O, and subsequent evaporating of solvent and D_2O to obtain the deuterated alcohol.

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Registry No.—**1**, 5991-56-0; **2**, 947-62-6; **5**, 19310-98-6; **9**, 1729-99-3; **10**, 16726-67-3; **12**, 2216-13-9; **13**, 1975-44-6; **15**, 19190-42-2; **16**, 40696-22-8; **18**, 10336-29-5; **21**, 14938-58-0; **23**, 19190-46-6.

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[24] The assignment of the loss of 44 mass units has some degree of uncertainty because of the presence of a broad flat-topped metastable peak indicating a large kinetic energy release in the fragmentation process.

[25] (a) S. Meyerson, I. Puskas, and E. K. Fields, *J. Amer. Chem. Soc.*, **88**, 4974 (1966); (b) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Ind. Chim. Belg.*, **29**, 311 (1964).

[26] J. Ekstrand, *J. Prakt. Chem.*, **38**, 154 (1888).

[27] A. Werner and W. Seybold, *Chem. Ber.*, **37**, 3661 (1904).

[28] W. F. Short and H. Wang, *J. Chem. Soc.*, 991 (1950).