Neighboring-Group Participation Reactions in the Mass Spectral Fragmentations of Some Azulenes. Comparisons with Solvolytic Processes[1]

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Participation by the azulene ring has been demonstrated in several fragmentation reactions of a variety of 4-substituted azulenes. Evidence for such participation comes from metastable ion abundances, appearance potential data, rate characteristics obtained from spectra run at various electron energies, and comparisons between isomeric compounds. Some striking contrasts between participation in the mass spectrometer and related processes in the solvolysis of the corresponding neutral molecules are identified and explained. It appears that the structures of the substituted azulenes are retained in the molecular ions formed upon electron impact; neither ring opening, nor substituent randomization, nor isomerization to the naphthalene molecular ion occurs. Our data indicate, however, that β cleavage, at least in the cases of the isomeric methylazulenes, is followed by structural isomerization.

Participation by aryl groups in solvolysis reactions has been studied in detail in many systems.[2] Work in this laboratory has been directed toward a thorough exploration of such reactions of azulene derivatives.[3] Marked rate enhancement has been observed in the solvolysis of esters of 2-(1-azulyl)ethanol relative to the 4- and 6-azulyl isomers.[3] The high electron density at C_1 in azulenes and the fact that the azulene analog of the phenylethylenonium ion possesses tropylium ion stabilization only if the spiro fusion to azulene is at C_1 appear to account for this observation.

Our interest in bond formation upon electron impact[4] and in the relationships between reactions in solution and those occurring upon electron impact in the gas phase led us to study the mass spectra of azulenes bearing CH_3, CH_2CO_2H, $CH_2CO_2CH_3$, CH_2CH_2OAc, or CH_2CH_2OTs substituents at C_1, C_4, or C_6. Evidence was sought for azulyl participation reactions related to those which occur in solution, a possibility suggested by the fact that positions 1 and 3 in the ground state of the unrearranged azulene molecular ion should have relatively high electron densities, the positive charge being preferentially delocalized over the seven-membered ring. Recently Shapiro and Jenkins[5] presented results of a study of aryl participation in the electron impact fragmentation of 1-bromo-2-phenylethane and its ring-substituted analogs. Identifying bond forming reactions by their typical low frequency factors and low activation energies,[6] and by the abundance of their metastable ions compared with those due to competing simple cleavages,[7] they suggested that phenonium ion formation accompanied bromine radical loss from 1-bromo-2-phenylethane. Their results on the higher ω-bromophenylalkanes also showed strong similarities to solution processes, including the fact that the formation of the spiro[3.5] $C_9H_{11}^+$ ion was relatively unimportant. Aryl participation in the mass spectrometer has also been suggested in other 1-substituted 2-phenylethanes,[8] but still more recently Grützmacher[9] has reported appearance potential data for a series of ω-bromophenylalkanes which he interprets as providing evidence against phenonium ion formation. A somewhat different interpretation of his appearance potential results, consistent with a phenonium ion intermediate, is made herein.

A fundamental problem encountered in mass spectrometry concerns ion structure. The question of whether the azulene and the naphthalene molecular ions isomerize prior to fragmentation has been answered in the affirmative for the parent compounds,[10] although several new methods of ion structure determination[6,11] were not available to the original investigators. Since neither azulene nor naphthalene can fragment by low energy, simple bond cleavages, this isomerization may be a consequence only of relatively long molecular ion lifetimes; hence, it seemed desirable to investigate the question of molecular ion isomerization in the methylnaphthalenes and methylazulenes. If substituent identity is retained in these rapidly fragmenting molecular ions, the $(M - 1)^+$ ion abundance should vary with the position of the methyl group. The isomeric azulene derivatives bearing more complex substituents also provided an opportunity to study the question of substituent randomization.

The ease of thermal decarboxylation of the isomeric azulylethanoic acids shows wide variations, but, unlike the reactivity order for the 2-azulylethyl tosylate solvolyses, the 4 isomer is most reactive and the 1 isomer is least reactive.[3] The corresponding electron impact reaction was investigated in order to establish whether the rate of decarboxylation varies with the position of the substituent and, if so, to seek mechanistic parallels with the thermal process. The mass spectra of the corresponding methyl esters were also studied for the bond forming reactions and isomer dependence that they might show.

Results and Discussion

Tables I–VI give relative abundances of the major ions observed in the mass spectra of some 2-azulylethyl

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(1) This paper is part II in the series, Nonbenzenoid Aromatic Systems. For part I, see R. N. McDonald and W. S. Stewart, *J. Org. Chem.*, **30**, 270 (1965).

(2) B. Capon, *Quart. Rev.*, **18**, 45 (1964).

(3) R. N. McDonald, J. R. Curtis, H. E. Petty, and N. L. Wolfe, unpublished results.

(4) Reviewed in R. G. Cooks, *Org. Mass Spectrom.*, **2**, 481 (1969).

(5) R. H. Shapiro and T. F. Jenkins, *ibid.*, **2**, 771 (1969).

(6) R. G. Cooks, I. Howe, and D. H. Williams, *ibid.*, **2**, 137 (1969), and references therein.

(7) F. W. McLafferty and R. B. Fairweather, *J. Amer. Chem. Soc.*, **90**, 5915 (1968).

(8) W. J. Richter and W. Vetter, *Org. Mass Spectrom.*, **2**, 781 (1969). Also compare J. Dickman, J. B. Thompson, and C. Djerassi, *J. Org. Chem.*, **32**, 3905 (1967).

(9) H. F. Grützmacher, *Org. Mass Spectrom.*, **3**, 131 (1970).

(10) R. J. Van Brunt and M. E. Wacks, *J. Chem. Phys.*, **41**, 3195 (1964).

(11) M. M. Bursey and F. W. McLafferty in "Carbonium Ions," Vol. 1, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., 1968, Chapter 8.

TABLE I

PARTIAL MASS SPECTRA OF TOSYLATES $ArCH_2CH_2OTs$[a]

Compd	Ar	Mol ion	M·+ − Ts·	M·+ − TsO·	M·+ − TsOH	M·+ − $TsOH_2$·	M·+ − $TsOCH_2$·
1[b]	1-Az	20	≤0.5	≅0	58	≅20	100
2	3-NO_2-1-Az	14	0.1	0	100	0.3	71
3	3-$COCH_3$-1-Az	31	0.1	≤2	46	0.2	100
4	4-Az	56	100	5	32	54	17
5	6,8-Di-Me-4-Az	43	100	5	17	34	24
6	6-Az	64	0	≤1.5	100	12	18
7	1-Naphthyl	8	0.1	3	100	17	33

[a] Ts = *p*-toluenesulfonyl, Az = azulyl. Ion abundances have been corrected for isotopic contributions. See Experimental Section for instrumental conditions. See footnote 19 for explanation of upper limits. [b] Underwent facile decomposition to the sulfonic acid in the ion source, spectrum found by subtraction.

TABLE II

PARTIAL MASS SPECTRAL OF ACETATES $ArCH_2CH_2OAc$[a]

Compd	Ar	Mol ion	M·+ − Ac·	M·+ − AcO·	M·+ − AcOH	M·+ − $AcOH_2$·	M·+ − $AcOCH_2$·
8	1-Az	20	0.3	4	78	30	100
9	4-Az	100	52	6	58	74	20
10	6,8-Di-Me-4-Az	100	49	8	15	20	32
11	6-Az	47	0.7	≤1	100	25	16
12	1-Naphthyl	7	0.3	≤2	100	37	37

[a] Ac = acetyl. See also footnote *a*, Table I.

TABLE III

PARTIAL MASS SPECTRA OF ALCOHOLS $ArCH_2CH_2OH$[a]

Compd	Ar	Mol ion	M·+ − H·	M·+ − HO·	M·+ − H_2O·	M·+ − CHO·	M·+ − CH_2O	M·+ − $HOCH_2$·	M·+ − C_2H_3O·
13	1-Az	19	0	0	0	0	0	100	0
14	3-NO_2-1-Az	24	0	0	0	0	0	100	0
15	4-Az	100	7	14	14	50	8	37	81
16	6,8-Di-Me-4-Az	100	8	12	8	26	12	11	77
17	6-Az	100	1.5	3.5	3.5	3	15	68	8
18	1-Naphthyl	45	0	0	2	0	17	100	0

[a] See footnote *a*, Table I.

TABLE IV

PARTIAL MASS SPECTRA OF ACIDS $ArCH_2CO_2H$[a,b]

Compd	Ar	Mol ion	M·+ − H·	M·+ − HO·	M·+ − H_2O	M·+ − CO_2	M·+ − HCO_2·
19	1-Az	17	0	0	0	0	100
20	4-Az	100	2	2	5	12	59
21	6,8-Di-Me-4-Az	100	2	2	3	11	18
22	6-Az	100	1	8	0.8	5	39

[a] See footnote *a*, Table I. [b] Compounds were each introduced twice and scanned several times at 80° source temperature, maintaining identical instrumental conditions throughout. A similar set of data was obtained at 130°. See text for comments regarding thermal decarboxylation.

TABLE V

PARTIAL MASS SPECTRA OF METHYL ESTERS Ar of CH_2CO_2Me[a]

Compd	Ar	Mol ion	M·+ − MeO·	M·+ − MeOH	M·+ − CH_2CO_2	M·+ − CH_3CO_2·
23	1-Az	28	0	0	0	100
24	4-Az	100	9	10	26	41
25	6,8-Di-Me-4-Az	100	9	6	12	16
26	6-Az	100	3	3	≤4	56

[a] See footnote *a*, Table I.

tosylates, 2-azulylethyl acetates, 2-azulylethanols, azulylethanolic acids, methyl azulylethanoates, and methylazulenes. Data for some naphthalene analogs are also included.

There is a remarkable distinction between the spectra of the tosylates substituted at the 4 position of the azulene nucleus and the remaining tosylates (Table I). In the 4-substituted isomers, **4** and **5**, δ cleavage[12] with loss of $CH_3C_6H_4SO_2$· gives the *base peak*, but in none of the remaining compounds does this process *even occur*. Some structural feature peculiar to the 4-substituted compounds must cause this unusual cleavage of these sulfonic esters. An immediate consequence of these observations is that, in this reaction at least, the azulene substituents do not lose their identity, nor does azulene/naphthalene molecular ion isomerism occur. The composition of the δ-cleavage product ion in compound **4** was established by exact mass measurement. Several lines of evidence indicate that $CH_3C_6H_4SO_2$· loss does

(12) The terms α, β, γ, and δ cleavage are employed following standard mass spectrometric usage, as defined in ref 21, p 2. The α bond links the azulene nucleus with the substituent.

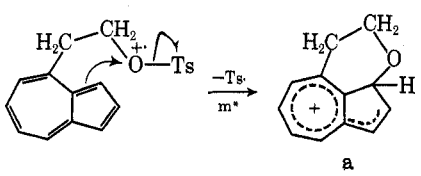
TABLE VI
PARTIAL MASS SPECTRA OF METHYLAZULENES AND METHYLNAPHTHALENES[a,b]

Compound	Mol ion	M·+ − H·	M·+ − H· − C_2H_2
1-Methylazulene (**27**)	59	100	24
4-Methylazulene (**28**)	100	81	28
5-Methylazulene (**29**)	100	70	27
6-Methylazulene (**30**)	100	56	24
2-Methylnaphthalene (**31**)	100	73	17
1-Methylnaphthalene (**32**)[c]	100	79	24

[a] See footnote *a*, Table I. [b] Compounds were each introduced twice and scanned several times at 120–130° source temperature. [c] Data for this compound taken from E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, "Atlas of Mass Spectral Data," Vol. 2, Interscience, New York, N. Y., 1969, pp 762–765.

not occur by simple O–S bond cleavage but is accompanied by bond formation: (i) the process is not typical of sulfonic esters and only occurs in one type of azulene isomer, (ii) the most abundant metastable decompositions of the molecular ions of compounds **4** and **5** are due to $CH_3C_6H_4SO_2\cdot$ loss (in compound **4** the metastable ion associated with δ cleavage has more than ten times the abundance of that associated with *p*-toluenesulfonic acid elimination), (iii) the lowest appearance potential process in compound **4** is $CH_3C_6H_4SO_2\cdot$ loss,[13] (iv) at a nominal 15 eV, compound **4** has only two daughter ions of appreciable abundance and they arise by $CH_3C_6H_4SO_2\cdot$ and $CH_3C_6H_4SO_3H$ loss (33 and 32% relative abundance, respectively). These facts would seem to indicate that the δ-cleavage reaction has the typical energy/rate characteristics[14] associated with bond forming reactions. An especially significant indication that bond formation is involved is the successful competition seen in the metastable region against *p*-toluenesulfonic acid elimination, a reaction which itself involves bond formation (like acetic elimination from acetates,[15] it almost certainly proceeds *via* a six-membered transition state). In agreement with this is the fact that in compounds **2**, **3**, **6**, and **7**, in which competition by δ cleavage was absent, the M·+ → M·+ − TsOH process gave abundant metastable ions.

A possible mechanism for the δ-cleavage reaction, consistent with the above, invokes participation by the electron-rich C_3 center. Formation of a charged monovalent oxygen ion is not required, as it would be for simple cleavage, but instead an extremely stable tropylium-like ion a is the suggested product.



a

An identical azulyl participation reaction is evident in the mass spectra of the 2-(4-azulyl)ethyl acetates, **9** and **10**, and here again the reaction gives an ion of less than 1% relative abundance in the 1- and 6-substituted isomers, **8** and **11**, and in the 1-naphthyl analog **12** (see Table II and Figure 1). Exact mass measurements, metastable ion abundances and low electron energy data indicated that bond formation in the 4 isomers paralleled that found for the 4-substituted tosylates. Thus in **9** the M·+ − 43 ion, *m/e* 171, had the composition $C_{12}H_{11}O$, while the metastable peak corresponding to formation of this ion from the molecular ion had an abundance equal to that corresponding to elimination of acetic acid, and at low electron energy the abundances of both these ions rose relative to all other fragment ions. The only significant difference between the two classes of compounds lies in the proportion of the total ion current carried by the δ-cleavage products: 26 and 27% for the tosylates **4** and **5** but only 12 and 14% for the acetates **9** and **10**. Since it is reasonable to assume identical product ion structures, this difference could reflect the difference in radical stabilities[16] and the arylsulfonyl radical can reasonably be expected to be more stable than the acetyl radical. The mass spectra of the isomeric 2-azulylethanols (Table III) show the occurrence of δ cleavage, leading to the M·+ − H· ion, in the 4-substituted alcohols, **15** and **16**. However, the low stability of the H· radical[17] and the occurrence of new competitive processes combine to make the δ-cleavage product of moderate abundance only. A very low abundance M·+ − H· ion is also observed for the 6 isomer, but the 2-(4-azulyl)ethanols, **15** and **16**, are still clearly distinguished from the other isomers. An interesting result emerged when an attempt was made to further study M·+ − H· formation by labeling the hydroxyl hydrogen in compound **15** by cointroduction of the sample and D_2O into the ion source.[18] Incorporation of up to three atoms of deuterium was observed, presumably due to exchange of the hydrogen atoms at C_1 and C_3 as well as the hydroxyl hydrogen. A similar exchange has been observed on treating the alcohol **15** with D_2O in carbon tetrachloride solution.[3]

A second aryl participation reaction, also exclusive[19,20] to the 4-substituted compounds, is encompassed in the data of Tables I–III. Loss of HO·, $CH_3CO_2\cdot$, and $CH_3C_6H_4SO_3\cdot$ from the ethanols, acetates, and tosylates, respectively, occurs only for the 4-substituted azulenes. This is a more important process than is δ cleavage in the 4-azulylethanols, but far less important in the corresponding acetates and tosylates. Another indication, in addition to the isomer specificity, that the reaction does not merely involve γ cleavage is the fact

(13) Some thermal elimination of *p*-toluenesulfonic acid apparently occurred in compound **4** as the appearance potential of the M·+ − TsOH ion was marginally lower than the ionization potential of the compound. For this reason the appearance potential of the accompanying electron impact induced elimination could not be determined. The thermal process probably comprised a very minor portion of the observed M·+ − TsOH ion abundance at 70 eV, as witnessed by the fact that only slight changes were observed in the spectrum over an 80–200° range of source temperature.

(14) See ref 4; also note that the reaction is atypical in that it has a high "apparent" activation energy (*vide infra*).

(15) Compare W. Benz and K. Biemann, *J. Amer. Chem. Soc.*, **86**, 2375 (1964).

(16) See R. H. Shapiro and J. Turk, *Org. Mass Spectrom.*, **2**, 1067 (1969), for a determination of relative radical stabilities by mass spectrometry. Note, however, that, if ionization in the substituent rather than in the azulene ring is necessary for δ cleavage (*vide infra*), then the difference between the sulfonate and acetate ionization potentials would be more significant than radical stabilities.

(17) $\Delta H_f°(H\cdot)$ = 52.1 kcal/mol, $\Delta H_f°(HO\cdot)$ = 9.3 kcal/mol, D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, NBS Tech. Note 270-3, U. S. Government Printing Office, Washington, D. C., 1968.

(18) J. S. Shannon, *Aust. J. Chem.*, **15**, 265 (1962).

(19) Upper limits are quoted in the tables when a low abundance peak could not be resolved from a more abundant isotope ion. (A resolution of 40,000 at mass 150 is required to resolve the $^{12}CH/^{13}C$ doublet.)

(20) At low electron energy, the difference between the 4-substituted azulenes and the other isomers as regards the importance of γ cleavage became much more pronounced.

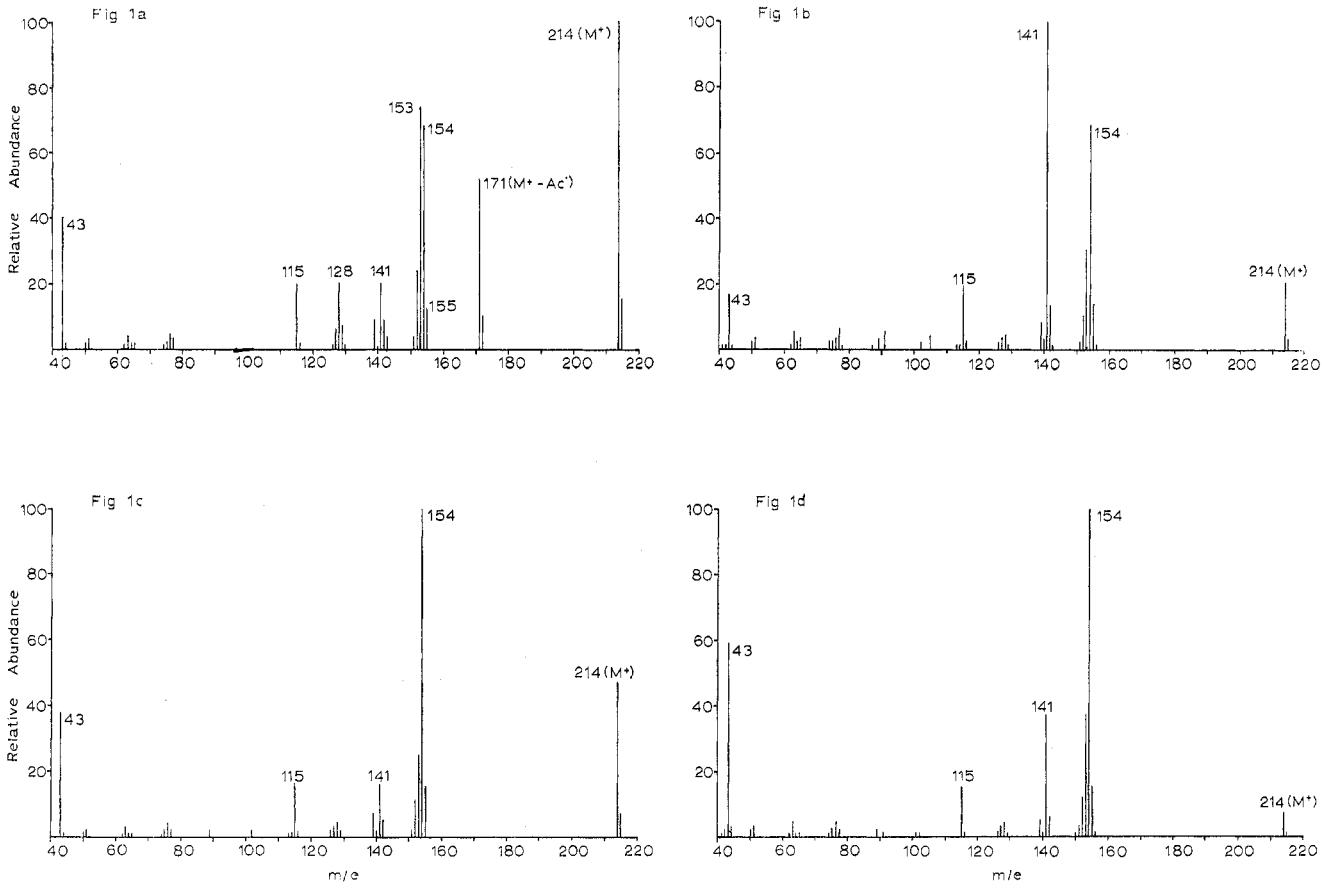
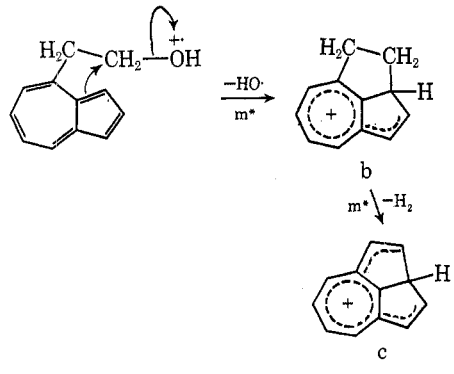


Figure 1.—The mass spectra (70 eV) of (a) 2-(4-azulyl)ethyl acetate (**9**), (b) 2-(1-azulyl)ethyl acetate (**8**), (c) 2-(6-azulyl)ethyl acetate (**11**), and (d) 2-(1-naphthyl)ethyl acetate (**12**).

that such a cleavage would yield a primary carbonium ion, an almost unknown process in alcohol mass spectra.[21] Azulyl participation involving C_3 can account for the observed results and appearance potential data on compound **15** are consistent with this interpretation (*vide infra*). The possibility of formation of a 4-azulylethylenonium product ion is considered unlikely, partly in view of the absence of the $M\cdot^+ - HO\cdot$ ion in the 1-azulylethanols, **13** and **14**, where such ion formation should be favored. This point is discussed in more detail later. The suggested mechanism for γ cleavage is illustrated below. The more highly strained product b should be less stable than the δ-cleavage product (a),



and, consequently, γ cleavage is generally less important. In the particular case of the 2-(4-azulyl)ethanols, however, the stability of HO· relative to the H· radical[17,22] results in γ cleavage being somewhat more important than δ cleavage. Further evidence that γ cleavage, like δ cleavage, does indeed involve some form of azulyl participation, comes from the spectra of the 2-(1-naphthyl)ethanol derivatives, **7**, **12**, and **18**. Neither γ nor δ cleavage occurs in these naphthalene compounds which show very simple spectra dominated by β cleavage and $C_{12}H_{10}\cdot^+$ formation.

Fragmentation patterns may be used, with due caution, to deduce ion structures.[6] It is therefore of note that the substituted alcohols **15** and **16** exhibit $M\cdot^+ - 19$ ions which are considerably more abundant than those of the other compounds in Table III, and that a metastable ion confirms the sequence $M\cdot^+ - HO\cdot \rightarrow (M\cdot^+ - HO\cdot) - H_2$ in compound **15**. If b does represent the $M\cdot^+ - HO\cdot$ ion, then facile loss of H_2 to give the interesting[23] ion c could be expected. It must be noted, however, that an ion m/e 153 is present in all the isomeric tosylates and acetates (Tables I and II), where it may arise by H· loss from the $M\cdot^+ - TsOH$ and $M\cdot^+ - AcOH$ ions.

A minor feature of our results is that azulyl participation reactions may occur, to a small extent, in the 6-substituted azulene derivatives. The alcohol **17**, for instance, exhibited $M\cdot^+ - H\cdot$ and $M\cdot^+ - HO\cdot$ ions

(21) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectra of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, Chapter 2.

(22) Mass spectrometric intramolecular aromatic substitutions[4] can provide useful indications of relative radical stabilities. Data have been reported suggesting a lower energy requirement for HO· displacement than for H· displacement from analogous compounds which give identical product ions: R. G. Cooks and S. W. Tam, *Org. Mass Spectrom.*, **1**, 583 (1968).

(23) Compare K. Hafner and J. Schneider, *Justus Liebigs Ann. Chem.*, **624**, 37 (1959).

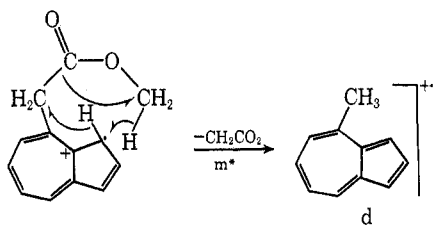
and the acetate **11** gave a 0.7% ion shown by exact mass measurement to be due to δ cleavage. A similar observation applies to the data of Table V.

The 2-(4-azulyl)ethanols **15** and **16** showed two additional processes which involve bond formation and which are either absent or of negligible importance in the isomeric naphthalene and azulene compounds. These are the fragmentations leading to abundant $M\cdot^+ - 29$ and $M\cdot^+ - 43$ daughter ions. Exact mass measurements on compound **15** showed that the neutrals lost are CHO· and C_2H_3O·, respectively. Furthermore, metastable ions indicated that the formation of both daughter ions occurred directly from the molecular ion, while low electron energy measurements showed that both processes possess low activation energies. Formyl radical loss from an alcohol is, of course, unusual[21] although it does occur in benzyl alcohol.[18] Hydrogen transfer to C_3 may well be part of this sequence in compound **15** and a complex rearrangement must also be involved in the $M\cdot^+ - C_2H_3O$· process.

Except for the 1-azulyl derivatives, all the 2-arylethanols studied underwent the McLafferty rearrangement with elimination of a molecule of formaldehyde. This process is also important in 2-phenylethanols,[24] and may be absent in the 2-(1-azulyl)ethanols, **13** and **14**, partly because of the strong propensity for β cleavage in these compounds.

The availability of the arylethanoic acids, **19–22**, and their methyl esters, **23–26**, provided the opportunity to further investigate the scope of aryl participation in the mass spectrometer. In neither the acids nor the esters is γ or δ cleavage an important process (Tables IV and V); yet bond forming reactions involving a specific site on the aromatic ring were observed. These reactions cannot be classified as mass spectrometric aryl participations if this term is restricted to the loss of a radical by an apparent simple bond cleavage which in fact depends on the formation of a new single bond to the atom bearing the leaving group; the reactions are, nevertheless, rather closely related to the γ and δ cleavage already discussed. The processes of interest, both most important in the 4-azulene derivatives, **20**, **21**, **24**, and **25**, are (i) CO_2 loss from the acids and CH_2CO_2 loss from the methyl esters, and (ii) H_2O loss from the acids and MeOH loss from the esters.

The data (Table IV) for the decarboxylation are tempered by the occurrence of thermal decarboxylation as evidenced by large variations in the $M\cdot^+ - CO_2/M\cdot^+$ ratio with source temperature. (The ratio doubled for both 4-azulylethanoic acid and 6-azulylethanoic acid on raising the source temperature from 80 to 130°.) The spectra are nevertheless of considerable interest for the contrast between 1-azulylethanoic acid (**19**) which shows no decarboxylation, even at 300°, and the 4-azulylethanoic acids where decarboxylation is a major process at relatively low source temperatures and completely swamps molecular ion formation at higher temperatures. Elimination of CH_2CO_2 from the molecular ions of compounds **24** and **25** was confirmed by appropriate metastable peaks; exact mass measurements on **25** established the composition of the product ion, and low energy spectra showed that this process, together with methanol loss, has the lowest energy requirement of all the fragmentations of **24** and **25**. These data, together with the observed isomer specificity (Table V), are consistent with the mechanism shown. Representation of the product as the 4-methylazulene molecular ion follows from the similarities in daughter



d

and metastable ions observed for the further decomposition of d and for the fragmentation of 4-methylazulene (*vide infra*); however, it is not claimed that a methylnaphthalene or isomeric methylazulene structure can be excluded. Decarboxylation of the acids **20** and **21**, whether thermal or electron impact induced, might involve a similar hydrogen transfer to C_3; these spectra are also closely related to those of the corresponding methylazulenes.

The second reaction type, dehydration of the acids and methanol elimination from the esters, predominates in the 4-azulene derivatives. Meyerson and Leitch[25] found that ω-phenylalkanoic acids require at least a six-membered transition state for appreciable dehydration. Moreover, while esters can lose methanol by 1,2 elimination, frequently the hydrogen is abstracted from a distant activated site.[26] Metastable ions verifying electron impact dehydration were found only in the 4-azulene derivatives. It therefore seems probable that the hydrogen atom at C_3 is eliminated and that C_3—C(=O) bond formation accompanies the elimination.

Appearance potential data for compounds **4** and **15** allow some amplification regarding the mechanisms of the γ- and δ-cleavage processes. The ethylene group effectively isolates the azulene ring from the functional part of the substituent and the observed ionization potentials of the two compounds (7.3 and 7.1 eV, respectively) are in satisfactory agreement with the best reported value (7.4 eV)[27] for the IP of azulene itself. The appearance potentials of the products of δ cleavage in compounds **4** and **15** and the γ cleavage product in **15** are all 3.2 eV above the respective ionization potentials; yet loss of $C_7H_7SO_2$· is the lowest energy fragmentation process in **4**. This is interpreted to mean that the lowest ionization potential in these compounds corresponds to removal of an electron from the azulene ring to give a molecular ion which cannot undergo γ or δ cleavage. These latter processes, therefore, seem to require ionization in the substituent (OTs or OH), and this proposal is supported by the fact that the ionization potential of ethanol is 10.5 eV.[28] The appearance potentials for the rearrangement processes occurring in compound **15** are, therefore, similar to the energy

(24) N. M. M. Nibbering and T. J. deBoer, *Org. Mass Spectrom.*, **1**, 365 (1968).

(25) S. Meyerson and L. C. Leitch, *J. Amer. Chem. Soc.*, **88**, 56 (1966).

(26) R. E. Wolff, M. Greff, and J. A. McCloskey, *Advan. Mass Spectrom.*, **4**, 193 (1968).

(27) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," National Standard Reference Data System, National Bureau of Standards, Washington, D. C., 1969, p 78.

(28) Reference 27, p 124.

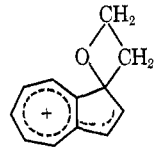
required for ionization in the substituent.[29] In this sense the activation energies (approximated by AP-IP) for the rearrangements occurring in compound **15**, at least, must be considered low. The observation of identical appearance potentials for the ions formed by γ and δ cleavage in compound **15** reflects the balance between ring strain in the ionic products and the relative stabilities of the respective radical products.

The question as to why azulene/naphthalene molecular ion isomerism does not occur in compounds **4** and **15** at energies below that required for the γ and δ cleavages may be answered by Van Brunt and Wacks' suggestion[10] that the heat of formation of the species of molecular ion common to azulene and naphthalene is some 2 eV higher than that of the ground state azulene molecular ion. A similar situation should obtain in the substituted compounds and it only requires that the frequency factor for the complex isomerization be lower than that for the cleavage processes to explain the absence of isomerization. It is therefore also quite reasonable that processes such as β cleavage should show isomer dependence. In fact, a most striking feature of the β-cleavage process in all the compounds examined was its enhanced importance in the 1-substituted azulenes. Approximating the extent of this reaction by the [β-cleavage ion]/[$M\cdot^+$] abundance ratio, values of 0.28 and 0.30 are found for the 2-(4- and 2-(6-azulyl)-ethyl tosylates, **4** and **6**, while the ratio is 5.0 for the 1-azulyl isomer. Similar data apply to the other series of compounds. This order of reactivity follows product ion stability, it being well known that, in the ground state, the equivalent 1 and 3 positions of azulene are the centers of highest electron density[32] and are, therefore, best able to stabilize carbonium ion substituents. As expected, β cleavage is also very important in the naphthalenes **7**, **12**, and **18**. In the light of the above arguments and the data on aryl participation, it is suggested that the azulene carbon skeleton is intact in the molecular ions formed by the compounds here examined.

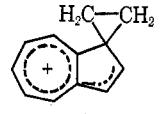
The methylazulenes, **27–30**, and 2-methylnaphthalene (**31**) were investigated in a further study of ion isomerization. The spectra (Table VI) were run in duplicate under as nearly identical conditions as possible. The $M\cdot^+ - H\cdot$ ion, formed by β cleavage, was the base peak in the 1-methylazulene spectrum, but in all the other compounds the molecular ion was the base peak. There is, therefore, no evidence for molecular ion isomerization; however, there is evidence for isomerization of those β cleavage ions which undergo further fragmentation. This is found in the fact that the only significant differences in the spectra of compounds **27–32** are the $[M\cdot^+ - H\cdot]/[M\cdot^+]$ ratios; otherwise fragmentation patterns, daughter ion abundances, doubly charged ion abundances, and metastable ions, including the characteristic broad metastable ion at *m/e* 93.8 (*m/e* 141 → *m/e* 115), are almost identical. These results imply formation of structurally identical $M\cdot^+ - H\cdot$ ions with similar internal energies.[6]

Conclusions

This work has produced much more direct evidence for aryl participation in gas phase ions than has previously been obtained. The operation of this phenomenon has dramatic effects upon the mass spectra. Another notable aspect of our study has been the demonstration that the prominent azulyl participation reactions (γ and δ cleavage), which occur in the mass spectrometer in the 2-azulylethanols and their esters, bear little relation to the azulyl participation reactions observed in the solvolysis of these esters. Azulyl participation upon electron impact is almost completely specific to the 4-azulene derivatives, but in the acetolysis of tosylates **1**, **4**, and **6** marked rate enhancement (rate ratio of 68,000) relative to 2-phenylethyl tosylate is observed only for compound **1**.[3] Two major mechanisms for the electron impact reaction can account for this difference and for much of the other data presented. They differ in whether it is the substituent or the azulene ring which mainly bears the charge/radical character in those forms of the molecular ion undergoing the participation reactions. If the azulene nucleus is ionized, the most important resonance forms will be those in which the charge is delocalized over the seven-membered ring and the radical delocalized between C_1 and C_3. This formulation invokes a radical center in the aryl participation process[33] and is also less satisfactory in accounting for the observed appearance potential results than is the alternative mechanism[29] in which the ring is not ionized and the electron density at C_3 is comparable to that in azulene itself. Both formulations predict stabilized product ions **a** and **b** for the two participation reactions in the 4-substituted azulenes while analogous stabilized product ions could not be formed from any of the other isomers.[34] The 1-substituted compounds could, however, use the relatively high electron density in the five-membered ring and form stabilized spiro cations, e and f, the latter being



e



f

(29) Those aspects of Grützmacher's criticism[9] of a previous postulation[5] of gas phase phenonium ion formation which are based on ionization and appearance potential data may be invalid because ionization within the substituent, *viz.*, on the bromine atom in 2-phenylethyl bromide, may be a necessary aspect of aryl participation. Such a mechanism has the advantages that (i) the electron density of the aryl system is not decreased, and (ii) the electron density on carbon is decreased by the adjacent charge; both these facts should promote aryl participation. This mechanism is also in accord with our appearance potential results as well as those of Grützmacher.[30] The suggestion that the charge must be located in the substituent for aryl participation to occur also finds credence in the examples of phenonium ion formation reported by Richter and Vetter.[8] In their compounds, the charge was localized on a heteroatom in the substituent.

(30) While we do not intend to argue for or against phenonium ion formation[31] in 2-phenylethyl bromide, it is noteworthy that Grützmacher's appearance potential data *can* be interpreted in terms of this bridged ion. Thus the AP (10.1 eV[9]) of the $M\cdot^+ - Br\cdot$ ion derived from 2-phenylethyl bromide is almost identical with the values found for various ring-substituted 2-phenylethyl bromides and with the IP of simple alkyl bromides, *e.g.*, *n*-butyl bromide has IP = 10.1 eV; see ref 27, p 212.

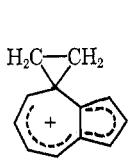
(31) The low resolution mass spectra of 2-phenylethyl *p*-toluenesulfonate, 2-phenylethyl *p*-nitrobenzenesulfonate, and 2-(*p*-methoxyphenyl)ethyl *p*-nitrobenzenesulfonate showed no ions which suggested the occurrence of aryl participation: R. G. Cooks and R. N. McDonald, unpublished results.

(32) E. Heilbronner in "Nonbenzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience, New York, N. Y. 1959, Chapter 5.

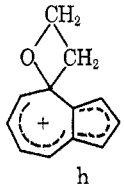
(33) For arguments against radical participation in solution, see M. M. Martin, *J. Amer. Chem. Soc.*, **84**, 1986 (1962).

(34) Note that the analogy between the γ- and δ-cleavage processes may not be complete. It is *possible* that δ cleavage *follows* molecular ion isomerization to a species having a C_3–O bond, but γ cleavage must be concerted with C_3–CH_2 bond formation. Drawing our terminology from solvolytic processes, the latter case corresponds to both participation and assistance, the former just to participation.

the solvolytic intermediate.[3] The fact that neither γ nor δ cleavage is observed in the 1-substituted compounds seems to be largely due to the exceptional stability of the β-cleavage product. Alternative formulations, such as g and h, for the δ- and γ-cleavage products in the 4-azulyl derivatives, lack the tropylium-type



g



h

stabilization which characterizes a and b and fail to account for the clear distinction between 4- and 6-substituted azulenes. It is just this fact, namely, that azulylethylenonium ions possessing tropylium-type stabilization should only be possible for azulenes with the attached side chain at position 1, 2, or 3 on the ring, which dictates the nature of the azulyl participation reaction observed in solution.

In the light of the above considerations and especially the apparently greater stability (δ *vs.* γ cleavage) of the ion a relative to the ion b, we predict that a significant rate enhancement should be observed for the solvolysis of 3-(4-azulyl)prop-1-yl arenesulfonate esters relative to the corresponding 3-(6-azulyl)prop-1-yl esters. Experiments are under way to test the validity of this prediction.[34a]

Taken together, the data for the compounds studied here include a considerable amount of evidence, much admittedly indirect, that upon ionization the azulene nucleus remains intact and that this structural integrity is maintained even in those relatively high energy molecular ions which undergo the rearrangements and simple cleavages described.

Experimental Section

The syntheses of several of the compounds used in this study have been described: 1-methylazulene,[35] 1-azulylethanoic acid,[35] 2-(1-azulyl)ethanol,[35] 4-methylazulene,[36] 2-(4-azulyl)ethanol,[37] 6,8-dimethyl-4-azulylethanoic acid,[38] methyl 6,8-dimethyl-4-azulylethanoate,[38] 6-methylazulene,[39] 6-azulylethanoic acid,[38] and 2-(1-naphthyl)ethanol[40] (synthesized from 1-naphthylacetic acid obtained from Aldrich Chemical Co.). All compounds were purified by column chromatography or recrystallization prior to mass spectrometric analysis and, with the single exception of compound **1**, no evidence for impurities was evident in any of the mass spectra. The preparation and characterization of the new compounds used in this study will be reported elsewhere.[3]

Mass spectra were recorded using an AEI MS-9 spectrometer, under the following standard conditions: electron energy, 70 eV, trap current 100 μA; inlet system, direct insertion; source temperature, 140–180°; repeller potential, +5 V; accelerating voltage, 8 kV. It is from these spectra that the data in Tables I–VI are taken. In addition, almost all spectra were recorded at electron energies in the range 12–18 eV. The spectra of the acetic acid derivatives (**19–22**) were determined in duplicate at source temperatures of 80 and 120°, all instrumental parameters being held constant. 2-Methylnaphthalene and the methylazulenes (**27–30**) were also run in duplicate with careful control of source temperature (120–130°) and other parameters. Exact mass measurements were made by peak matching, using perfluorotributylamine to provide reference ions. A resolution of not less than 12,000 was used and the results were accurate to better than 10 ppm.

Ionization and appearance potentials were measured at 100 μA trap current, and 170° source temperature. Samples were introduced directly into the source but it proved difficult to maintain steady ion currents for the times necessary and errors of as much as 0.5 eV may have resulted. Duplicate determinations showed the reproducibility lies within this range. Benzene and krypton were used as standards and the difference in the IP values agreed, within 0.3 eV, with the expected difference (4.7 eV). Ion currents were recorded as fractions of the 70 eV value and the semilog plot method[41] of calculation was used, with measurements being taken at 0.1–1% of the 70-eV abundances.

Registry No.—**1**, 26154-60-9; **2**, 26154-61-0; **3**, 26154-62-1; **4**, 26154-63-2; **5**, 26154-64-3; **6**, 26211-00-7; **7**, 4735-54-0; **8**, 26154-65-4; **9**, 26154-66-5; **10**, 26154-67-6; **11**, 26154-68-7; **12**, 26157-05-1; **13**, 26157-06-2; **14**, 26157-07-3; **15**, 13935-44-9; **16**, 26157-09-5; **17**, 26157-10-8; **18**, 773-99-9; **19**, 26157-12-0; **20**, 26157-13-1; **21**, 26157-14-2; **22**, 26157-15-3; **23**, 23702-20-7; **24**, 26157-17-5; **25**, 26157-18-6; **26**, 26156-73-0; **27**, 769-31-3; **28**, 17647-77-7; **29**, 1654-55-3; **30**, 1654-52-0; **31**, 91-57-6; **32**, 90-12-0.

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(34a) NOTE ADDED IN PROOF.—Preliminary experiments indicate that some rate enhancement indeed occurs while C_3 participation is indicated by the isolation of what appears to be the C_4–$(CH_2)_3$–C_3 ring closed compound.

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