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Charge Migration through Sigma Bonds in a Fragment Ion from 5,5′-Divaleryl-2,2′-spirobiindan under Electron Impact

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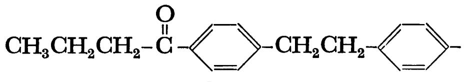
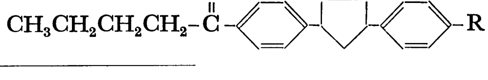
In order to examine the nature of charge and radical electron migration in mass spectral fragment ions, 5,5′-di-*n*-valeryl-2,2′-spirobiindan (**3**) was prepared and its mass spectrum was measured. The successive loss of two propylene molecules from the molecular ion to give peaks at *m/e* 346 (**b**) and 304 (**c**) was clearly indicated by observing appropriate metastable ion peaks. As the radical electron is one of the prerequisites for these fragmentations to occur, the results demonstrate that the charge and radical electron can migrate through sigma bonds in fragment ion **b**, since the two *n*-valerophenyl groups cannot be brought into close proximity even with C–C bond fission of the spiro ring. While the strongest peak at *m/e* 331 (**a**) is ascribable to the ordinary α-fission of the carbonyl group in **3**, a moderately intense peak at *m/e* 289 (**d**) can adequately be explicable by the similar α-fission of the carbonyl group in ion **b**, the process of which again involves radical electron migration prior to fragmentation.

Electron impact induced fragmentation patterns of organic compounds in a mass spectrometer have been widely rationalized with application of the concept of localized positive charge and localized unpaired electron in the molecular ion.[2] Wachs and McLafferty[3] presented a typical example using a series of substituted 1-(4-*n*-butyrophenyl)-2-phenylethanes (**1**). They suggested that the random removal of an electron from any part of a given molecule was followed by rapid localization of charge and unpaired electron at a particular site. The concept was shown by Howe and Williams[4] not to be inconsistent with the quasi-equilibrium theory of mass spectra.

In certain cases, however, a dynamic distribution of charge appears to operate in fragment ions. For instance, Mandelbaum and Biemann[5] examined mass spectra of 1,3-diphenylcyclopentane derivatives (**2**) of unknown stereochemistry, and concluded that charge would be free to migrate among distant functional groups, and the distribution of charge would be governed by the ionization potentials of the various sites. Kinstle and Oliver[6] also showed that charge would migrate in fragment ions in some instances, though it is difficult to predict the extent of charge mobility in a particular ion.

Although some proposals were made,[7] the precise


(1)


(2)

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[1] To whom the correspondence should be addressed.

[2] F. W. McLafferty, *Chem. Commun.*, **1966**, 78. See, also, H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco (1967), pp. 9—14.

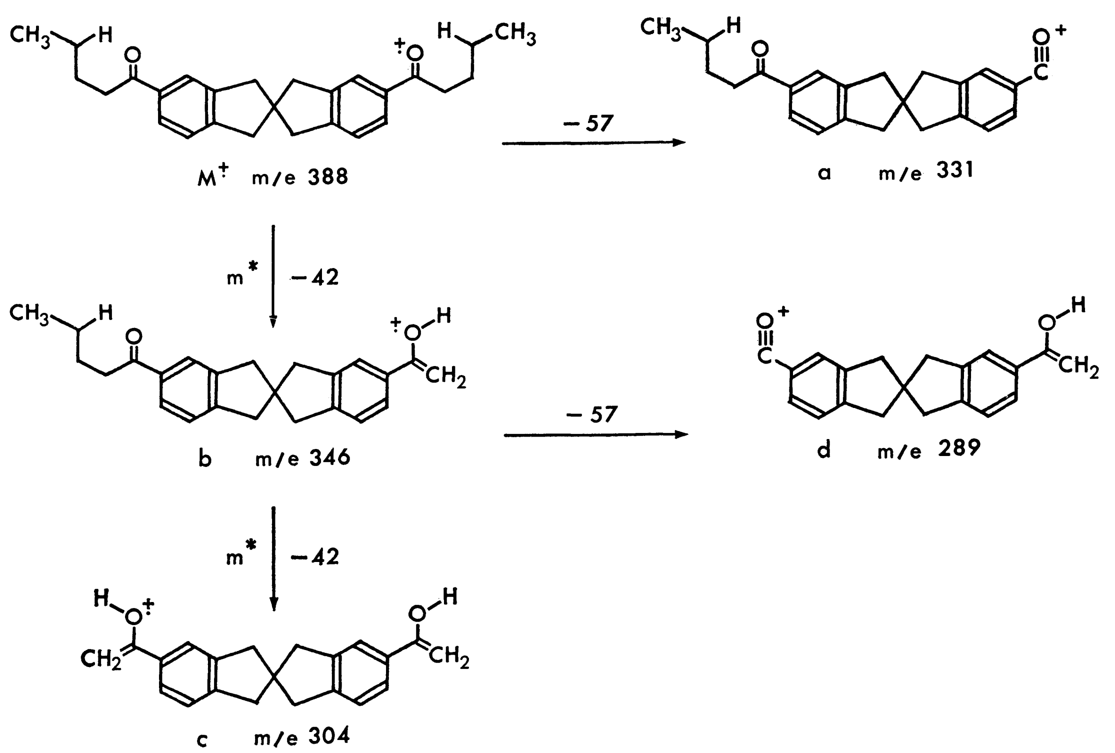
[3] T. Wachs and F. W. McLafferty, *J. Amer. Chem. Soc.*, **89**, 5044 (1967).

[4] I. Howe and D. H. Williams, *ibid.*, **90**, 5461 (1968).

[5] A. Mandelbaum and K. Biemann, *ibid.*, **90**, 2976 (1968).

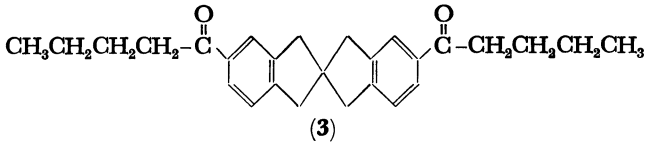
[6] T. H. Kinstle and W. R. Oliver, *ibid.*, **91**, 1864 (1969).

[7] W. Vetter, W. Meister, and W. J. Richter, *Org. Mass Spectrom.*, **3**, 777 (1970).



Scheme 1

mechanism of this charge and unpaired electron migration is still unknown. One obvious possibility is that the charge might transfer from one functional group to the other through the space, instead through the sigma bonds, if two groups approach closely enough to permit spatial overlap of their orbitals, as pointed out by Wagner.[8] In order to clarify this point, we have examined the mass spectrum of 5,5′-di-*n*-valeryl-2,2′-spirobiindan (**3**), which apparently cannot be in the conformation that the two phenyl groups approach each other.



(**3**)

Results and Discussion

5,5′-Di-*n*-valeryl-2,2′-spirobiindan (**3**) was prepared by Friedel-Crafts condensation of *n*-valeryl chloride with 2,2′-spirobiindan, which, in turn, was synthesized from diethyl dibenzylmalonate through 2,2′-spirobiindan-1,1′-dione according to the procedure of Leuchs *et al.*[9,10] The structure of the product was confirmed by IR, UV, and NMR spectral analyses (see, Experimental Section).

The mass spectrum of **3**, shown in Fig. 1, is fairly simple, and the fragmentation sequences are summarized in Scheme 1. As is seen, the molecular ion undergoes two competing fragmentations. An α-fission of the carbonyl group in one of the side chains with loss of a butyl radical produces a peak at *m/e* 331 (ion **a**), whereas the McLafferty cleavage gives a peak at *m/e* 346 (ion **b**). Although the peak at *m/e* 331 is the strongest in the spectrum taken at 70 eV, lowering of impact electron energies resulted the sharp decrease of its intensity relative to that of the ion **b**. This trend is in good agreement with the recent convincing argument[11] on the intensity ratio of peaks from simple cleavage and rearrangement reactions.

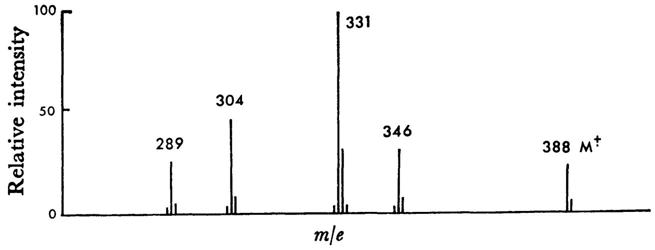


Fig. 1. The mass spectrum of 5,5′-di-*n*-valeryl-2,2′-spirobiindan (**3**).

The most pronounced feature of the spectrum is the appearance of a moderately intense peak at *m/e* 304. The well-defined metastable ion peaks were observed for the processes *m/e* 388 ($M^{+\cdot}$)→*m/e* 346 and *m/e* 346→*m/e* 304, indicating the successive elimination of two propylene molecules from the molecular ion. The exact mass measurement of the *m/e* 304 ion (**c**) (304.150) agreed with the calculated value of $C_{21}H_{20}O_2$ (304.146). With decreasing impact electron energies the intensity ratio of **c**/**b** markedly decreased, and this also suggests the step-wise fragmentation. These results clearly indi-

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8) P. J. Wagner, *ibid.*, **3**, 1307 (1970).

9) H. Leuchs and D. Radulescu, *Ber.*, **45**, 189 (1912).

10) H. Leuchs and L. Lock, *Ber.*, **48**, 1432 (1915).

11) P. Brown, *Org. Mass Spectrom.*, **3**, 1175 (1970).

cate that the first McLafferty cleavage of one side chain in **3** was followed by the second McLafferty cleavage of the other side chain. Therefore, the transfer of the ion radical from one site to the other through several sigma bonds is required in the fragment ion **b**, as the radical electron is one of the prerequisites for mass spectral reactions to occur.

There would be three possible routes of formation of ion **d**, since ion **a**, **b**, or **c** could be a precursor ion. A route from ion **a** with elimination of propylene must involve a biradical ion intermediate generated by unpairing of the carbonyl π-electrons and may appear highly improbable.[12] This is also supported by the intensity ratio of **d**/**a** that was almost independent of impact electron energies. The alternative route from ion **c** with loss of a methyl radical may assume ketonization of ion **c** prior to fragmentation, and the process would not be important because enol-keto interconversion in a fragment ion was usually not observed.[13]

The most adequate explanation for the formation of ion **d** is, therefore, from ion **b** with loss of a butyl radical, as indicated in Scheme 1. Although the process is not confirmed by observing an appropriate metastable ion peak, this fragmentation reaction is mechanistically quite feasible, for it merely involves an α-fission of the carbonyl group. Thus, the fragmentation of **b** to **d** is, again, explicable only by assuming the radical electron migration in ion **b**.

Since in our compound **3** the two *n*-valerophenyl groups cannot be brought into close proximity even with C–C bond fission of the spiro ring, the above results clearly demonstrate that the charge and radical electron can migrate through sigma bonds. After completion of the present work, a paper by Lengyel, Uliss, and Mark on the same subject has appeared.[14] Their results are consistent with our conclusions presented above. It is, however, still unknown whether or not any particular structural limitations and odd- or even-electronic nature of fragment ions can be correlated with the effective charge migration. Studies are in progress in our laboratory to attempt to provide further insight in such problems.

Experimental

All melting points were determined on a Kofler hot stage and are uncorrected. Infrared spectra (IR) were taken as potassium bromide disks using a Nihon Bunko IR-G instrument. Ultraviolet spectra (UV) were measured by a Hitachi EPS-3T spectrophotometer. Nuclear magnetic resonance spectra (NMR) were taken on a Varian A-60 spectrometer, and the peak positions are recorded in ppm from internal tetramethylsilane standard. Mass spectra were measured by a Hitachi RMU-7 mass spectrometer under the following conditions: ionizing voltage 70—14 eV, ion accelerating voltage 1800 V, total emission current 80 μA, ion source temperature 250°C.

*5,5′-Di-*n*-valeryl-2,2′-spirobiindan (3).* To a solution of 0.46 g of 2,2′-spirobiindan (mp 60—62°C)[9,10] in 10 m*l* of methylene dichloride, 0.55 g of *n*-valeryl chloride and 0.6 g of aluminum chloride were added and the mixture was allowed to stand for 26 hr at room temperature. After the addition of diluted hydrochloric acid under cooling, the mixture was extracted with chloroform. The extracts were combined and evaporated *in vacuo*. The residual brown oil was chromatographed on silica gel. The pure product of **3** was obtained by recrystallization from petroleum ether, mp 73°C, yield 0.56 g, IR (KBr) 1675 cm^{-1} (aromatic ketone); UV $\lambda_{\text{max}}^{\text{EtOH}}$ 258 mμ (ε 30200); NMR (CCl_4) 0.94 (6H, deformed t, J=6 Hz), 1.1—2.0 (8H, broad m), 2.83 (4H, t, J=6 Hz), 2.93 (8H, s), 7.16 (2H, d, J=8 Hz), 7.67 (4H, m).

Found: C, 83.61, H, 8.03%. Calcd for $C_{27}H_{32}O_2$: C, 83.46; H, 8.30%.

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[12] J. Cable, G. W. Adelstein, J. Gore, and C. Djerassi, *Org. mass Spectrom.* **3**, 439 (1970). See, also, F.W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York (1966), pp. 138—149.

[13] H. Nakata and A. Tatematsu, This Bulletin, **42**, 1678 (1969); J. Diekman, J. K. MacLeod, C. Djerassi, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **91**, 2069 (1969). See, however, D. J. McAdoo, F. W. McLafferty, and J. S. Smith, *ibid.*, **92**, 6343 (1970).

[14] I. Lengyel, D. B. Uliss, and R. V. Mark, *J. Org. Chem.*, **35**, 4077 (1970).