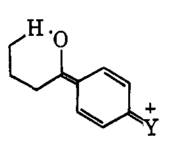
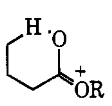
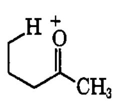


b′



d



e

(e).[8,17] Note that the *m*-NH_2 derivative, in which such resonance donation would be greatly reduced, exhibits a low Z/Z_0 value; the *p*-Ph derivative should have an increased number of canonical forms in which the radical site is removed from the carbonyl group.[18]

Thus for this rearrangement in butyrophenones two substituent effects with ρ values of opposite sign appear to be operative; these effects are consistent with the postulation that the unpaired electron site serves as a driving force for rearrangement.[8]

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[17] A similar formulation will rationalize the increased abundance of the (M − C_2H_4) ion in ethyl benzoate compared to that in butyrophenone.

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

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The Influence of the Charge and Radical Sites in Unimolecular Ion Decompositions[1]

Sir:

The concept of localized charge[2] as a driving force for unimolecular decomposition reactions induced by electron impact has been used by a number of authors to explain and correlate a large variety of reactions observed in mass spectra.[3] As an extension of this concept, it has been proposed that most decomposition reactions which yield abundant ions can be interpreted as being initiated by the positive charge or the unpaired electron at a particular site.[3c–5] However, for particular cases it has been postulated that the localized charge is not involved in the formation of an abundant ion,[6] and it has been pointed out that the usefulness of such a concept to rationalize decomposition pathways is not proof of its validity.[7]

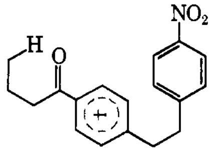
We report here mass spectral data for a series of aromatic ketones in which the characteristic ketone fragmentation pathways are almost completely eliminated in one of the members of the series by a minor structural change; the most logical explanation is that this structural change has moved the site of charge localization to a position isolated from the ketone moiety.

In Table I are listed the ion intensities (based on the molecular ion) of the characteristic fragment ions and the ionization potentials of the molecular ion of a series of *para*-substituted butyrophenones. Previous work[8] on the effect of substituents (Y) on the formation of the YPhCO ion in the spectra of YPhCOR indicates that the intensity of this ion compared to the molecular ion in the latter four compounds in Table I should be approximately the same since the substituent groups present will have nearly identical σ values. In all but one of the spectra of butyrophenones which we have examined, this M − 43 ion is the most abundant in the spectrum. In the spectrum of *p*-[2-(*p*-aminophenyl)ethyl]butyrophenone (III) this decomposition has been virtually eliminated. The same dramatic effect is observed for the M − C_2H_4 rearrangement ion.

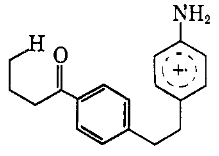
Table I. Characteristic Ions in the 75-ev Spectrum of *para*-Substituted Butyrophenones, *p*-$YPhCOCH_2CH_2CH_3$

Y	M	M − 15	M − 28	M − 43	M − 71	IP, ev[a]
H	100	7.9	28.9	470	230	9.38
$PhCH_2$	100	9.0	128	2650	47[b]	8.69
p-$NO_2PhCH_2CH_2$ (I)	100	5[b]	94	3000	2	9.10
p-$C_3H_7COPhCH_2CH_2$ (II)	100	5	99	2600	40	8.91
p-$NH_2PhCH_2CH_2$[c] (III)	100	<1	<1[d]	8	1	8.14

[a] Ionization potentials, ±0.2 ev, determined by previous method.[5] [b] Corrected for isotopic contributions. [c] The most intense ion of this spectrum, *m/e* 106, has an abundance of 975. [d] Value decreased upon lowering the ionizing voltage to a point 10 ev above ionization potential.



I



III

Again the substituent effects[5] on this reaction, although not a simple function of σ values, indicate that the *p*-amino substitution should have only a small effect on the abundance of this ion. However, a significant change in the molecular ion caused by the *p*-amino substitution is indicated by the substantial reduction that occurs in the ionization potential. The latter value is similar to the ionization potentials of arylamines[5,9] (8.14 ev for *p*-aminotoluene[9]) and substantially lower than the values for *p*-alkylphenyl alkyl ketones.[5,10] This is consistent with a shift of the charge site to the ring not bearing the keto moiety.[11,12]

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[1] The generous financial support of the National Institutes of Health (GM 12755 and FR 00354) is gratefully acknowledged. The Hitachi RMU 6D mass spectrometer used in this work was purchased through National Science Foundation Grant GP 4335.

[2] F. W. McLafferty in "Determination of Organic Structures by Physical Methods," F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, p 93.

[3] See, for example: (a) J. S. Shannon, *Tetrahedron Letters*, 801 (1963); (b) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, and "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. 2, Holden-Day, Inc., San Francisco, Calif., pp 1–3; (c) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966.

[4] F. W. McLafferty, *Chem. Commun.*, 78 (1966).

[5] F. W. McLafferty and T. Wachs, *J. Am. Chem. Soc.*, **89**, 5043 (1967).

[6] (a) M. Spiteller-Friedmann and G. Spiteller, *Monatsh. Chem.*, **96**, 104 (1965); (b) G. Spiteller, M. Spiteller-Friedmann, and R. Houriet, *ibid.*, **97**, 121 (1966); the authors acknowledge valuable discussions with Professor Spiteller.

[7] P. Bommer and K. Biemann, *Ann. Rev. Phys. Chem.*, **16**, 481 (1965).

[8] M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 529 (1966).

[9] G. F. Crable and G. L. Kearns, ASTM E-14 Mass Spectrometry Conference, Chicago, Ill., June 1961, p 205.

[10] S. Pignataro, A. Foffani, G. Innorta, and G. Distefano, *Z. Physik. Chem.* (Frankfurt), **49**, 291 (1966).

[11] G. A. Junk and H. J. Svec, *J. Am. Chem. Soc.*, **89**, 790 (1967), have reported evidence that the ionization potential of a polyfunctional molecule is determined by the functionality of lowest ionization potential.

[12] Charge localization offers an explanation for other features of the spectrum of II. Secondary ions whose formation involves reaction at the second ketone moiety after initial decomposition at the first, such

These data appear to be consistent with a localization of the charge and radical site in the vicinity of the aminobenzyl group for most of the molecular ions formed from III. If ionization occurs by loss of an electron from the butyrophenyl ring in III, transfer of charge to the other ring apparently occurs rapidly, in keeping with the quasi-equilibrium theory.[13] Spiteller has objected to this theory, postulating that the bombarding electrons excite a particular site in the molecule before ionization.[14] It would appear to us that the cross section of the butyrylphenyl group for such a primary excitation[14] would not be greatly different in compounds I and III, in sharp contrast to the observed difference in their reactivities.

Previous correlative evidence[2-4] for the increase in reactivity upon ionization of the carbonyl group[15] is similar to the evidence for other functional groups, thus supporting the application of the localized charge concept in interpreting and predicting the mass spectra of other types of compounds.

as (M − C_2H_4 − C_2H_4), (M − C_2H_4 − C_3H_7), and (M − C_2H_4 − C_4H_7O), are of very low abundance and may be due in part to the loss of C_2H_4 from the center of the molecule. Also, abundances of the (M − C_2H_4) and (M − C_3H_7) ions of this compound do not exhibit the statistical factor of 2 expected in comparison to the compounds in which one C_3H_7CO group is replaced by H or NO_2.

[13] A. L. Wahrhaftig, "Mass Spectrometry," R. I. Reed, Ed., Academic Press Inc., New York, N. Y., 1965, p 137, and references cited therein.

[14] G. Spiteller and M. Spiteller-Friedmann, *Ann. Chem.*, **690**, 1 (1965).

[15] This is similar to its reactivity increase upon excitation to the n,π* state, which suggests similar transition states for the analogous unimolecular reactions induced by photon and electron impact.[4] This does not rule out, however, the possibility that some mass spectral decompositions arise from other excited states, such as those similar to intermediates in thermal reactions.[6] Note also that these effects were observed in odd-electron ions, whose behavior is known to differ from that of even-electron ions.[3,4]

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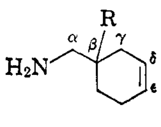
One-Step Synthesis of Bridged Aziridines

Sir:

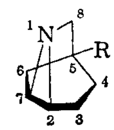
Recently, the chemistry of aziridines,[1] the simplest nitrogen heterocycles, has received increasing interest in the field of synthetic organic chemistry because of their high reactivity and also in relation to nitrene chemistry.[2] We wish to report the first synthesis of 1-azatricyclo[3.2.1.0^{2,7}]octane derivatives which have been known only as hypothetical intermediates in alkaloid chemistry.[3]

This method consists of oxidation of δ,ε-unsaturated primary amines **1** to highly strained bridged aziridines **2** and represents a new method for aziridine synthesis.

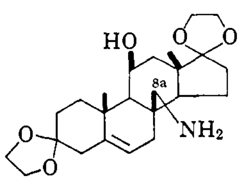
In connection with study on 8β-functionated steroids, N-chlorination of the amine **3** was attempted. Treatment of **3** with 1 equiv of N-chlorosuccinimide (NCS) in methylene chloride yielded, as a basic product, the aziridino compound **4a**[4] [90%; $C_{24}H_{35}O_5N$; mp 261–262°; $[\alpha]^{28}D$ −8.0° (ethanol)]. The structure of **4a** is assigned on the basis of the following evidence.



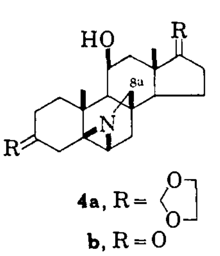
1a, R = CH_3
b, R = H



2



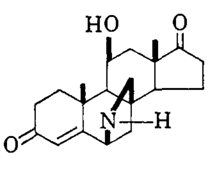
3



4a, R =
b, R = O

Compound **4a** has a lower pK_a value (7.17) than the 8.81 of **3**. No double bond absorption is observed in its infrared and Raman spectra. A sharp singlet for C-8a protons at τ 7.16 and a signal for a vinyl proton at 4.79 in **3** are absent in the nmr spectrum of **4a**, and an AB-type quartet (*J* = 11.4 cps) appeared at τ 6.38 and 7.40. Corroborative evidence for **4a** was obtained by transformation into the known compound **7** [$C_{22}H_{35}O_3N$; mp 215–219°; $[\alpha]^{23}D$ +127.8°; λ_{max} 241.0 mμ (ε 15,800); ν_{max} 3610, 3450 (-OH), 2800, 2770 (-N-$(CH_3)_2$), 1733 (C=O), 1667, 1617 cm^{-1} (Δ^4-3-keto)].

Cautious hydrolysis of **4a** with dilute hydrochloric acid gave the diketone **4b** [$C_{20}H_{29}O_3N$; mp 226–230° dec; $[\alpha]^{23.5}D$ +89.0°; λ_{max} 284.5 mμ (ε 110); ν_{max} 3640 (OH), 1736, 1710 cm^{-1} (C=O)], which on basic treatment was converted into the pyrrolidine **5** [$C_{20}H_{29}O_3N$; mp 270–280° dec; $[\alpha]^{24}D$ +129.3° (methanol); λ_{max} 240.7 (ε 14,000), 325 mμ (ε 176); ν_{max}^{Nujol} 3345 (OH), 1736 (C=O), 1674, 1616 cm^{-1} (Δ^4-3-keto)]. Quaternization with methyl iodide in the presence of potassium carbonate afforded the salt **6** [$C_{22}H_{34}O_3NI \cdot 0.5H_2O$; mp 272–277° dec; $[\alpha]^{24}D$ +93.6° (methanol); λ_{max} 221.7 mμ (ε 22,500); ν_{max}^{Nujol} 3350 (OH), 1738 (C=O), 1660, 1604 cm^{-1} (Δ^4-3-keto)], which was treated with zinc to give **7**. This compound was prepared from the corresponding 8β-cyano-11-oxo-Δ^5-steroid **8** in an unequivocal manner.[5]



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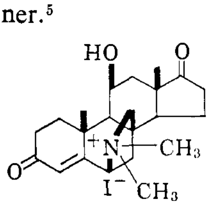

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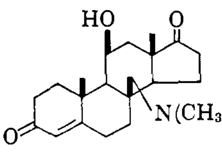

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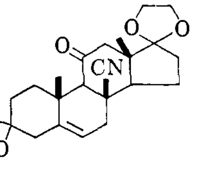

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[1] P. E. Fanta in "Heterocyclic Compounds with Three and Four Membered Rings," Part 1, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter 2.

[2] L. Horner and A. Christmann, *Angew. Chem.*, **75**, 707, (1963); R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

[3] G. Büchi, D. L. Coffen, K. Kocsis, P. E. Sonnet, and F. E. Ziegler, *J. Am. Chem. Soc.*, **88**, 3099 (1966); J. W. Huffman, T. Kamiya, and C. B. S. Rao, *J. Org. Chem.*, 32, 700 (1967).

[4] Satisfactory elemental analyses have been obtained for all compounds with formulas cited. Unless otherwise stated, infrared spectra were measured in chloroform, ultraviolet spectra in 95% ethanol, and specific rotation in chloroform.

[5] The synthetic pathway will be described in detail in a full paper.