in contrast to ring expansion in the hydroxy, methyl, and fluoro analogs to form substituted tropylium ions.[48] Similarly, the apparently greater ability of the methoxyl than of the hydroxyl group to stabilize the charge is reflected in a pronounced shift of charge retention between complementary products upon replacing the hydroxyl group on C-3 of 4,6-dideoxy-D-xylohexose dithioacetal with methoxyl;[49] and the intensities of the substituted benzoylium ions in the spectra of neopentyl *p*-methoxy- and *p*-nitrobenzoates are, respectively, increased and decreased relative to the unsubstituted ester, in accord with the charge-stabilizing and -destabilizing effects of the substituents.[50]

Consideration of the spectra of the isomeric nitrobiphenyls and the dimethoxynitrophenol emphasizes the importance of charge distribution and stabilization in directing the decomposition reactions of ionized molecules. Functional groups that serve as preferred sites for charge localization or that interact with other parts of the molecule to alter its ability to accommodate the charge can thus exert profound effects on mass spectra. In favorable cases, correlation of selected spectral features with Hammett or related substituent constants has been good enough to serve as a basis for quantitative prediction.[11,23] In view of the large number of competing and consecutive reactions contributing to the mass spectra of nitroarenes, the attainment of correlations adequate for such prediction seems unlikely. Nonetheless, these concepts can be highly useful in rationalizing differences among the spectra of isomers, and conversely, one would hope, in assigning probable isomeric structures when sufficient spectral data are available.[51]

(48) J. M. S. Tait, T. W. Shannon, and A. G. Harrison, *J. Am. Chem. Soc.*, 84, 4 (1962).
(49) D. C. DeJongh and S. Hanessian, *ibid.*, 88, 3114 (1966).
(50) W. H. McFadden, K. L. Stevens, S. Meyerson, G. J. Karabatsos, and C. E. Orzech, *J. Phys. Chem.*, 69, 1742 (1965).

(51) NOTE ADDED IN PROOF. Two additional relevant papers have appeared very recently: J. Harley-Mason, T. P. Toube, and D. H. Williams, *J. Chem. Soc.*, B396 (1966); T. H. Kinstle, J. R. Althaus, and J. Stam, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstracts, p S-141. As reported in the latter paper, the mass spectra of β-nitrostyrenes show primary loss of OH and of CO, in close analogy to *o*-nitrobiphenyl.

Studies in Mass Spectrometry. XIX.[1] Evidence for the Occurrence of Aromatic Substitution Reactions upon Electron Impact

J. Ronayne, D. H. Williams, and J. H. Bowie

Contribution from the University Chemical Laboratory, Cambridge, England.
Received June 20, 1966

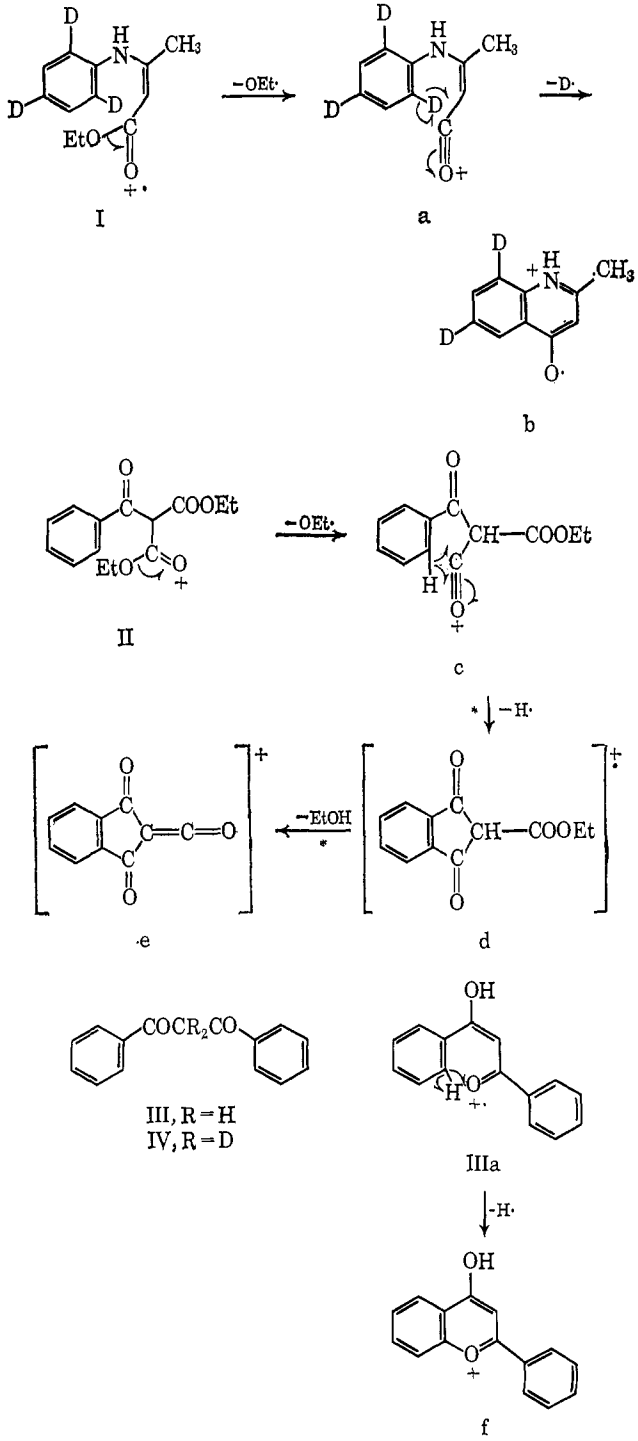
Abstract: The mass spectra of a number of compounds of the general formula $C_6H_5CH{=}CHCOR$ contain intense M − 1 peaks, which largely arise through the loss of a hydrogen atom from the aromatic ring. Selective deuteration experiments suggest that the phenyl hydrogens become equivalent in the molecular ion. The M − 1 species is probably formed *via* an intramolecular aromatic substitution reaction which can occur in the molecular ion and results in the formation of a relatively stable benzopyrylium cation.

In investigations of the behavior of β-keto esters,[2] β-diketones,[3] and enamines[4] upon electron impact we have uncovered reactions which are believed to correspond to intramolecular substitution reactions occurring in the mass spectrometer. Thus, ethyl 3-(2′,4′,6′-d_3-phenylamino)but-2-enoate (I) was shown to eliminate C_2H_5DO and C_2H_6O from its molecular ion in the ratio 85:15, and the loss of a deuterium atom from the aromatic ring was rationalized in terms of an intramolecular acylation of the aromatic ring by the acylium ion a to give the stabilized quinolinium ion b *via* loss of a deuterium atom.[4] Similarly, the successive losses of C_2H_5O, H, and C_2H_6O (as established by appropriate metastable peaks) from diethyl benzoylmalonate (II) demanded the elimination of an aromatic hydrogen atom to form the final ion, which was formulated as e.[2] Once more, it seemed reasonable that the driving force for the elimination of an aromatic hydrogen might be the intramolecular "Friedel–Crafts acylation" of the aromatic ring in the acylium ion c; ethanol could then be eliminated from d to furnish e.

The second type of aromatic substitution reaction which we have suggested may occur upon electron impact involves the formation of a completely aromatic benzopyrylium ion.[3] Thus, dibenzoylmethane (III) exhibits a pronounced M − H ion in its spectrum, which still corresponds to the loss of a hydrogen atom from the molecular ion in the spectrum of the d_2 derivative IV. It was concluded that the driving force for the loss of the aromatic hydrogen atom, which is of necessity eliminated in the formation of the M − 1 species, lay in the formation of the oxonium ion f[3] from a molecular ion IIIa of III.

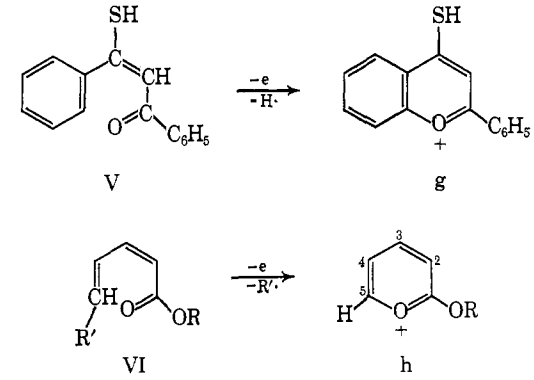
Reactions which bear some analogy to our sugges-

(1) Part XVIII: J. T. B. Marshall and D. H. Williams, *Tetrahedron*, in press.
(2) J. H. Bowie, D. H. Williams, S.-O. Lawesson, and G. Schroll, *J. Am. Chem. Soc.*, 87, 5742 (1965).
(3) J. H. Bowie, D. H. Williams, S.-O. Lawesson, and G. Schroll, *J. Org. Chem.*, 31, 1384 (1966).
(4) H. J. Jakobsen, S.-O. Lawesson, J. T. B. Marshall, G. Schroll, and D. H. Williams, *J. Chem. Soc.*, in press.

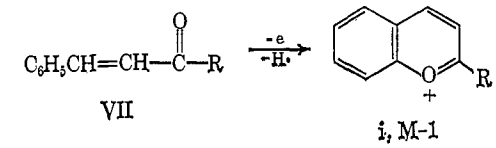


tions have recently been postulated to occur in other classes of compounds. Shannon and co-workers[5] have reported that thio derivatives of β-diketones such as V lose hydrogen in the mass spectrometer to form the postulated resonance-stabilized ion g. Vinylic 5,6-cleavage is important in the spectra of 2,4-dienoates (see VI), probably because aromatic oxonium ions such as h may be produced.[6]

Such reactions are of obvious chemical and diagnostic interest, and we have therefore undertaken a study of the mass spectra of a series of compounds of the general formula VII, with the aid of extensive dueterium label-

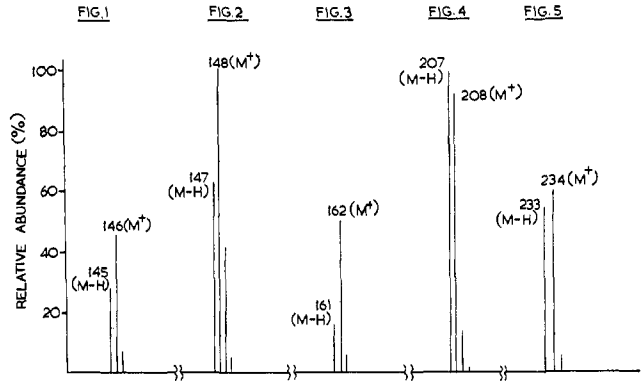


ing. Our aim was to show that abundant M − 1 ions are a fairly general feature of the mass spectra of such compounds and that the M − 1 ions are formed by loss of a hydrogen atom from the aromatic ring, presumably to give ions of the general formula i.



Discussion and Results

The compounds which have been investigated are summarized in formulas VIII–XII, and the molecular ion regions of their mass spectra are reproduced in Figures 1–5. It can be seen that M − 1 ions are

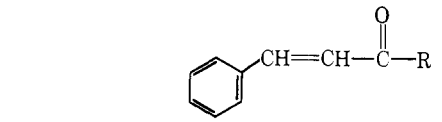


Figures 1–5. Molecular ion regions in the mass spectra of benzalacetone (VIII), cinnamic acid (IX), methyl cinnamate (X), benzalacetophenone (XI), and dibenzalacetone (XII), respectively.

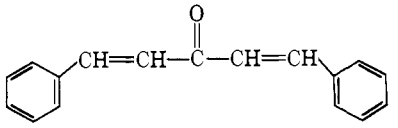
pronounced in the spectra of all these compounds. Surprisingly, only the M − 1 ion from the chalcone (XI) seems to have attracted attention previously[7,8] and only in one case[7] has there been an attempt to rationalize its formation, in terms of the structure j.

All the compounds studied are synthetically available from various base-catalyzed condensation reactions involving benzaldehyde. 2,4,6-d_3-Benzaldehyde (XV, $d_1 = 2\%$, $d_2 = 15\%$, $d_3 = 83\%$) was therefore prepared from 2,4,6-d_3-aniline (XIII)[9] *via* the nitrile XIV.

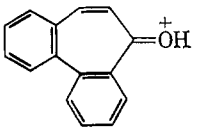
(5) S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Australian J. Chem.*, **18**, 673 (1965).
(6) W. K. Rohwedder, A. F. Mabrouk, and E. Selke, *J. Phys. Chem.*, **69**, 1711 (1965).
(7) J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Am. Chem. Soc.*, **63**, 1865 (1959).
(8) Y. Itagaki, T. Kurokawa, S. Sasaki, C.-T. Chang, and F.-C. Chen, *Bull. Chem. Soc. Japan*, **39**, 538 (1966).
(9) A. P. Best and C. L. Wilson, *J. Chem. Soc.*, 241 (1946).



VIII, R = CH_3
IX, R = OH
X, R = OCH_3
XI, R = C_6H_5

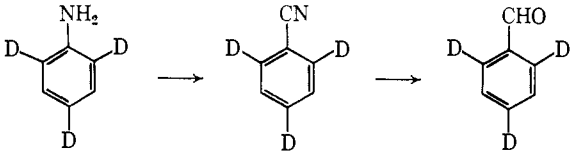


XII

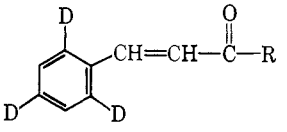


j

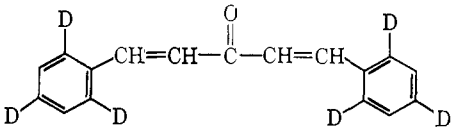
Appropriate condensation reactions then furnished the labeled derivatives VIIIa–XIIa.



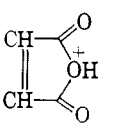
XIII XIV XV



VIIIa, R = CH_3
IXa, R = OH
Xa, R = OCH_3
XIa, R = C_6H_5



XIIa



k

The mass spectra of the deuterated derivatives contained M − H and M − D ions of approximately equal abundance. The ratios in which hydrogen atoms and deuterium atoms are expelled from the molecular ions of these derivatives are summarized in Table I. The

Table I. Relative Proportions of Hydrogen and Deuterium Lost from the Molecular Ions of the Deuterated Compounds VIIIa–XIIa

Compound	Hydrogen lost, %	Deuterium lost, %
VIIIa	49	51
IXa	49	51
Xa	40	60
XIa	49	51
XIIa	49	51

calculations for each compound (VIIIa–XIa) are based upon an isotopic purity (d_1 = 2%, d_2 = 15%, d_3 = 83%) which was established from the mass spectrum of the common precursor 2,4,6-d_3-benzaldehyde (XV); the incorporation of two benzaldehyde molecules into dibenzalacetone (XIIa) leads to a calculated isotopic purity of d_3 = 1%, d_4 = 6%, d_5 = 25%, d_6 = 68%. The effects of ^{13}C isotopes have been obviated in the usual manner.[10] With the exception of methyl cinnamate (Xa), the calculations show that deuterium and hydrogen are lost in almost identical amounts. In all cases, the driving force for the loss of an aromatic deuterium atom is thought to be associated with the formation of an aromatic oxonium ion i. It is noteworthy that the formation of such ions requires the isomerization of a *trans* to a *cis* double bond in the mass spectrometer. However, such a transformation is known to be a facile process in 70-ev spectra as evidenced by the occurrence of abundant *m/e* 99 ions, corresponding to k, from dialkyl maleates *and* fumarates.[11]

Two explanations can account for the only *partial* loss of deuterium from the molecular ions of VIIIa–XIIa. First, it is possible that the hydrogen is lost from the aromatic ring from which deuterium is lost. Second, the hydrogen could be lost from some point in the molecule other than the phenyl ring of the styryl group. Since the results summarized in Table I are qualitatively the same for all the compounds (VIIIa–XIIa), the former explanation seemed more attractive. Additional deuterated derivatives have therefore been prepared to distinguish between these two possible explanations.

The compound selected for more exhaustive deuterium labeling was chalcone (XI, benzalacetophenone). d_5-Acetophenone (XVI, d_3 = 1.5%, d_4 = 16.5%, d_5 = 82%) was prepared by Friedel–Crafts acylation of d_6-benzene and on condensation with benzaldehyde afforded 2,3,4,5,6-d_5-benzalacetophenone (XIb). Chlorination of d_8-toluene gave d_6-benzal chloride (XVII), which was converted to d_6-benzaldehyde (XVIII, d_5 = 3%, d_6 = 97%) by hydrolysis; condensation of XVIII with acetophenone furnished the d_6 derivative (XIc). More exhaustive chlorination of d_8-toluene gave XIX which was converted to d_5-benzaldehyde (XX, d_4 = 3%, d_5 = 97%) *via* d_5-benzoic acid and d_5-benzyl alcohol; condensation of XX with acetophenone led to 2′,3′,4′,5′,6′-benzalacetophenone (XId). Finally, base-catalyzed exchange of acetophenone in deuteriomethanol gave d_3-acetophenone (XXI, d_2 = 2%, d_3 = 98%), which on condensation with benzaldehyde gave d_1-benzalacetophenone (XIe).

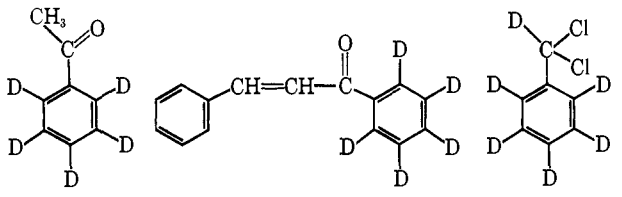
The results for the various labeled benzalacetophenones (XIa–XIe) are summarized in Table II. The figures establish that in the formation of the M − 1 ion from benzalacetophenone (XI), the hydrogen atom which is eliminated originates very largely (85%, if one assumes no isotope effect[12]) from the phenyl ring of the styryl group. It is gratifying that there is a clear distinction between the two aromatic rings of benzalacetophone (XI), only 6% of the M − 1 peak being formed by elimination of a hydrogen atom from the

(10) See, for example, K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 5.

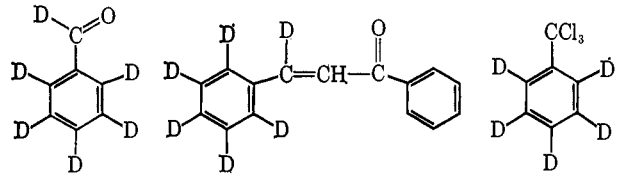
(11) J. H. Bowie, D. H. Williams, P. Madsen, G. Schroll, and S.-O. Lawesson, *Tetrahedron*, in press.

(12) In practice there will almost certainly be an isotope effect, but a fairly wide range of values has been observed for mass spectral processes so far investigated[13] and therefore no reliable estimate can be made for these cases. However, it is noteworthy that the results presented in Table II account completely for hydrogen lost in the formation of an M − 1 species by replacement of all 12 hydrogens by deuterium. The results therefore suggest that any isotope effect is small.

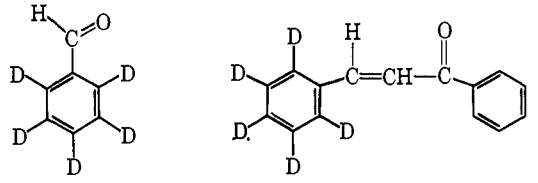
(13) J. K. Macleod and C. Djerassi, *Tetrahedron Letters*, 2183 (1966).



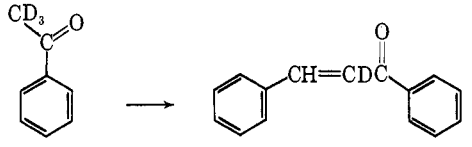
XVI XIb XVII



XVIII XIc XIX



XX XId



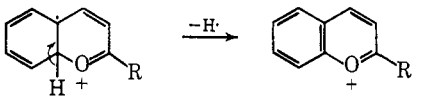
XXI XIe

phenyl ring of the benzoyl group (again assuming no isotope effect[12]). The β-hydrogen of the α,β-unsaturated ketone group is eliminated to a small extent (compare data for XIc and XId) but the α-hydrogen atom is not expelled to any significant extent in the formation of the M − 1 species.

Table II. Relative Proportions of Hydrogen and Deuterium Lost from the Molecular Ions of Deuterated Benzalacetophenones XIa–e

Compound	Hydrogen lost, %	Deuterium lost, %
XIa	49	51
b	94	6
c	6	94
d	15	85
e	100	0

The difference in the figures obtained when the styryl ring is labeled only in the *ortho* and *para* positions and when labeled completely correspond to complete equivalence of the aromatic hydrogens in this ring prior to the loss of a hydrogen atom from the molecular ion, if one assumes no isotope effect (*i.e.*, three-fifths of the 85% deuterium lost from the d_5 derivative XId is 51%, which corresponds exactly to the value observed for XIa). In view of our earlier conclusion that any isotope effect must be small (see ref 12), our experiments provide strong, but not unequivocal, evidence for randomization of these aromatic hydrogens prior to fragmentation. Such randomization could occur if, instead of loss of a hydrogen radical being concerted with C–O bond formation (see IIIa → f), 1 exists as a reaction intermediate and scrambling occurs in the styryl ring *via* a series of hydrogen shifts in 1 (prior to the loss of a hydrogen radical which affords i). Deuterium scrambling would not, of course, be observed in the labeled derivatives if only 1,3- and/or 1,5-hydrogen shifts occurred in 1.[14] Attention is drawn to the contrasting absence of complete scrambling in the cyclization of the carbonium ion a to the ion-radical b.



1 i, M−1

In summary, compounds of the general formula VII which we have investigated all show intense M − 1 peaks which are partly derived by expulsion of hydrogen from the aromatic ring. In the case of benzalacetophenone (XI), the hydrogen is lost almost exclusively from the styryl ring and, by analogy, this situation probably holds in the other compounds also. The results are consistent with (1) randomization of phenyl hydrogens in the molecular ion, and (2) formation of a relatively stable M − 1 oxonium ion i by means of an intramolecular aromatic substitution reaction.

Experimental Section

Mass spectra were obtained using an AEI MS 9 mass spectrometer operating at 70 ev and a source pressure of 0.1–0.5 × 10^{-6} mm. Samples were introduced through a heated inlet system at a temperature of approximately 150°.

Isotopic purities of condensation products from 2,4,6-d_3-benzaldehyde (XV) are in general based upon the isotopic purity of XV. In those cases where the isotopic purities of the condensation products could be directly checked, the results were the same as for the labeled benzaldehyde within 1%.

2,4,6-d_3-Benzaldehyde (XV). 2,4,6-d_3-Aniline (XIII, 4.5 g)[9] was diazotized and the diazotized solution added to a solution of cuprous cyanide in aqueous potassium cyanide. The mixture was refluxed on a water bath for 30 min, and the resulting yellow oil was separated by steam distillation. The crude product was extracted with ether (three 30-ml portions); evaporation of the ether extract gave crude 2,4,6-d_3-benzonitrile (XIV, 2.2 g). This material in dry ether (30 ml) was added to a suspension of anhydrous stannous chloride (8 g) in dry ether (70 ml) saturated with dry hydrogen chloride. The mixture was allowed to stand overnight. The resulting aldimine stannichloride was steam distilled and the crude product extracted with ether. Evaporation of the ether and distillation of the residue gave 2,4,6-d_3-benzladehyde [XV, 1.1 g, mol wt (mass spec) 109, d_1 = 2%, d_2 = 15%, d_3 = 83%].

2,4,6-d_3-Benzalacetone (VIIIa). 2,4,6-d_3-Benzaldehyde (XV, 70 mg) and acetone (120 mg) were condensed in the presence of 10% aqueous sodium hydroxide (1 ml). Ether extraction of the product and evaporation of the extract gave crude material (75 mg) which was purified by crystallization from ethanol to give 2,4,6-d_3-benzalacetone (VIIIa, mp 38–40°, mol wt (mass spec) 149, d_1 = 2%, d_2 = 15%, d_3 = 83%) as pale yellow plates. The isotopic purity was calculated from the M − CH_3 ion.

2,4,6-d_3-Cinnamic Acid (IXa). 2,4,6-d_3-Benzaldehyde (XV, 50 mg), malonic acid (100 mg), and pyridine (3 ml) were heated on a water bath for 2 hr. Dilute hydrochloric acid was then added until all the cinnamic acid had precipitated. The precipitate was isolated, washed well with water, and recrystallized from water to give 2,4,6-d_3-cinnamic acid [IXa, 56 mg, mp 122–124°, mol wt (mass spec) 151].

Methyl 2,4,6-d_3-Cinnamate (Xa). 2,4,6-d_3-Cinnamic acid (IXa, 20 mg) in ether (10 ml) was treated with a solution of diazomethane in ether until there was a persistent yellow color. The solution was allowed to stand overnight and the ether then evaporated. The

(14) The authors acknowledge helpful discussion with Dr. I. Fleming and Dr. W. J. Richter on the possible existence of 1 as a discrete reaction intermediate.

residue crystallized on standing to give methyl 2,4,6-d_3-cinnamate [Xa, 12 mg, mp 33–35°, mol wt (mass spec) 165, d_1 = 3%, d_2 = 14%, d_3 = 83%]. The isotopic purity was calculated from the M − OCH_3 ion.

2′,4′,6′-d_3-Benzalacetophenone (XIa). 2,4,6-d_3-Benzaldehyde (40 mg), acetophenone (40 mg), and absolute ethanol (3 ml) were mixed and 10% aqueous sodium hydroxide then added until the solution became cloudy. The mixture was shaken for 30 min, and the solid which separated from solution was then isolated by filtration. Recrystallization of the crude product from aqueous methanol gave 2′,4′,6′-d_3-benzalacetophenone [XIa, 65 mg, mp 55–57°, mol wt (mass spec) 211].

2,4,6,2′,4′,6′-d_6-Dibenzalacetone (XIIa). 2,4,6-d_3-Benzaldehyde (40 mg), acetone (10 mg), and absolute ethanol (3 ml) were mixed, and 10% aqueous sodium hydroxide (2 ml) was added. The mixture was shaken for 30 min and the solid product then isolated by filtration. The crude material was recrystallized from absolute ethanol giving 2,4,6,2′,4′,6′-d_6-dibenzalacetone [XIIa, mp 109–112°, mol wt (mass spec) 240, d_3 = 1%, d_4 = 6%, d_5 = 25%, d_6 = 68% as calculated from the isotopic purity of the precursor benzaldehyde].

2,3,4,5,6-d_5-Benzalacetophenone (XIb). 2,3,4,5,6-d_5-Acetophenone (XVI, d_3 = 1.5%, d_4 = 16.5%, d_5 = 82%) was prepared by a standard Friedel–Crafts reaction between d_6-benzene and acetic anhydride in the presence of aluminum chloride. This material (XVI) was then condensed with benzaldehyde as described previously to give XIb.

d_6-Benzaldehyde (XVIII). d_8-Toluene (2 ml) was heated gently under reflux and a rapid stream of chlorine passed into the solution in the presence of sunlight. When the temperature of the liquid had reached 208°, the reaction was stopped, and the resulting d_6-benzal chloride was hydrolyzed with aqueous 25% calcium hydroxide solution. The product was isolated *via* ether extraction and distilled to give d_6-benzaldehyde [XVIII, 1.0 g, mol wt (mass spec) 112, d_5 = 3%, d_6 = 97%]. The mass spectrum of the material showed it to be quite pure.

d_6-Benzalacetophenone (XIc). This material was prepared by condensation of d_6-benzaldehyde (XVIII) with acetophenone in the presence of 10% aqueous sodium hydroxide as previously described.

2,3,4,5,6-d_5-Benzaldehyde (XX). The chlorination of d_8-toluene (2 ml) was carried out as described for the preparation of d_6-benzaldehyde (XVIII), except it was continued until the temperature of the liquid had reached 232°. The resulting trichloride (XIX) was then hydrolyzed with 25% aqueous calcium hydroxide, and the d_5-benzoic acid was filtered off and dried. This material was then reduced to the alcohol with lithium aluminum hydride and the alcohol then oxidized to the corresponding aldehyde by refluxing in sunlight with N-chlorosuccinimide (1.3 g), pyridine (1.3 ml), and carbon tetrachloride (20 ml).[15] The mixture was acidified with dilute hydrochloric acid, and the organic layer was removed and washed well with water, 2 *N* sodium hydroxide (10 ml), and finally again with water (three 10-ml portions). The carbon tetrachloride solution was dried and evaporated and the residue purified by distillation to give 2,3,4,5,6-d_5-benzaldehyde [XX, 250 mg, mol wt (mass spec) 111, d_4 = 3%, d_5 = 97%].

2′,3′,4′,5′,6′-d_5-Benzalacetophenone (XId). This material was prepared by condensing d_5-benzaldehyde (XX) with acetophenone in the presence of 10% aqueous sodium hydroxide as previously outlined.

α-d_1-Benzalacetophenone (XIe). Benzaldehyde (40 mg) and 1′,1′,1′-d_3-acetophenone (XXI)[16] were condensed in the presence of 10% aqueous sodium deuteroxide (1 ml) and deuteriomethanol (3 ml), and the product was obtained as detailed previously.

Acknowledgment. J. R. gratefully acknowledges the receipt of a Science Research Council postgraduate award.

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Unusual Mass Spectral Fragmentation of 21-Oxoaspidoalbidine-Type Alkaloids[1]

Keith S. Brown, Jr., Wolfango E. Sanchez L., Antonio de A. Figueiredo, and Joaquim M. Ferreira Filho

Contribution from the Centro de Pesquisas de Produtos Naturais, Faculdade de Farmácia e Bioquímica, Rio de Janeiro ZC-82, Brazil. *Received May 27, 1966*

Abstract: The mass spectra of indole alkaloids of the 21-oxoaspidoalbidine type show an unusual fragmentation pattern, giving an ion at *m/e* 160 as (usually) the base peak. Using the known alkaloid dichotamine and two new alkaloids of this group isolated from *Aspidosperma exalatum*, with deuterations and high-resolution mass spectral measurements, a rationale for this unprecedented fragmentation was developed. The first step, loss of CO_2, prohibits the normal aspidospermine-type fragmentation and leads instead to ion fragments including C-20 and one or both aliphatic carbons of the dihydroindole ring. All major peaks in the spectra are assigned tentative origins and structures on the bases of their established molecular formulas and their shifts in deuterated materials.

In recent years, there has been reported an increasing number of aspidospermine-type indole alkaloids, having the ethyl side chain oxidized at terminal C-21 and cyclized onto C-19 to form a hemiazaacetal lactone (I).[2–4] Early in the work on these compounds,[5] the unusual fact was noted that the alkaloids did not undergo the normal aspidospermine-type skeletal fragmentation in the mass spectrometer, but rather gave a prominent fragment of mass 160 (almost always as the base peak) with further important fragments at *m/e* 132, 136, 161, and 174. Other prominent fragmenta-

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