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PHOTOCHEMICAL ANALOGIES IN MASS SPECTRA. AN ORTHO EFFECT.

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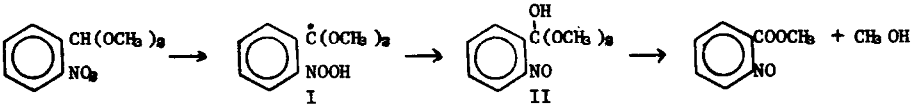
Ortho effects produce a variety of hydrogen transfers in mass spectra (1). In addition, photochemical ortho effects associated with abstraction of adjacent hydrogen by the nitro group on irradiation are well known (2). One of the earliest photochemical reactions to be studied, the conversion of o-nitrobenzaldehyde to o-nitrosobenzoic acid (3), probably proceeds by such a mechanism (eq. 1). Examination of the mass spectra of these two compounds, however, failed to reveal a significant process paralleling photochemical reactivity (4), although some correlation might have been anticipated on the naive basis of parallelism with other observed correlations (5).

In addition to o-nitrobenzaldehyde itself, its acetals formed from smaller alcohols are also known to rearrange photochemically (6). In these cases, the products are esters of o-nitrosobenzoic acid (eq. 2). Because the mass spectral lability of the protected formyl hydrogen in acetals is so great that in general molecular ions are never observed (7), but rather (M - 1) ions are formed, the reinvestigation of the analogy with an acetal of o-nitrobenzaldehyde was deemed worthwhile: here might be a case where according to naive expectation again, a sufficiently labile hydrogen might be transferred to the oxygen of the nitro group for at least a fraction of the molecular ions.

(1)



(2)

Results of mass spectrometric studies indicate that indeed there is evidence for analogous processes on photon impact and electron impact in the dimethyl acetal of o-nitrobenzaldehyde. The intensities of the major peaks of greater mass in the spectrum of methyl o-nitrosobenzoate, relative to the intensity of the molecular ion, are compared in Table I with intensities of

TABLE I

Corresponding Peaks in the Spectra of Methyl *o*-Nitrosobenzoate and *o*-Nitrobenzaldehyde Dimethyl Acetal

m/e	Intensity, ester	Intensity, acetal
165	100 (M^{+})	100 $(M-CH_3OH)^{+}$
135	72	90
120	19	15
104	28	33
92	68	50
77	135	130

corresponding peaks in the spectrum of *o*-nitrobenzaldehyde dimethyl acetal. A suggestive, but not quantitative, correlation between these intensities suggests that the $(M-CH_3OH)^{+}$ ion arises from a process analogous to the photochemical rearrangement, but that the energy distributions of the ion formed from the nitrosobenzoate ester directly and of the ion formed by loss of methanol from the acetal molecular ion are somewhat different. This might be expected simply because the loss of methanol would involve the removal of some energy from the remaining ion. To illustrate this point further, *all* of the metastable ions in the spectrum of the ester were observed in that of the acetal with identical characteristics where these could be measured, except for two instances ($m^* = 44.0, 46.4$) where the widths in the two compounds are the same, but quite different populations of precursors are metastable. Table II indicates the great similarity of the metastable spectra of the compounds. There are many more prominent peaks in the spectrum of the acetal besides those corresponding to those of the ester. An intriguing one is a 25% peak at *m/e* 180, corresponding to the loss of OH from the molecular ion; while this might be taken to support the intermediacy of ions corresponding to species I or II in the electron impact degradation of the acetal, the fact that the (M - 1) ion is the only high-mass ion and the recollection that nitroaromatics lose small amounts of O from molecular ions weaken this hypothesis that an OH radical, and not H and O atoms individually, are lost from the molecular ion. The fact that additional intense ions occur at *m/e* 166 (intensity 410% on the scale of Table I), 149 (44%), 120 (39%), 105 (80%), 91 (125%), and 75 (95%), as well as many additional metastable ions, indicates that the decomposition pathway related to the photochemical rearrangement is only one of a number of competitive routes for decomposition, in fact a minor route. Presumably this route would be totally absent as reported for the parent

TABLE II

Properties of Corresponding Metastable Peaks in the Spectra of Methyl *o*-Nitrosobenzoate and the Dimethyl Acetal of *o*-Nitrobenzaldehyde

Position		Assignment	Intensity Relative to $m^* = 110.4$		Width at Half-Height	
Found	Calcd.		Ester	Acetal	Ester	Acetal
33.9	33.8	77 → 51	0.11 ± 0.01	0.11 ± 0.01	0.3 amu	0.3 amu
34.8	34.7	78 → 52	0.03 ± 0.005	a	0.4 amu	a
44.0	44.0	135 → 77	0.50 ± 0.03	0.10 ± 0.015	0.6 amu	0.7 amu
46.4	46.4	91 → 65	0.14 ± 0.01	0.07 ± 0.01	1.6 amu[b]	1.5 amu[b]
55.5	55.5	104 → 76	0.17 ± 0.01	0.13 ± 0.02	0.7 amu	0.7 amu
56.5	56.5	105 → 77	0.15 ± 0.01	0.16 ± 0.01	0.8 amu	0.8 amu
70.9	70.6	120 → 92	0.09 ± 0.01	0.12 ± 0.01	2.1 amu[b]	a
80.6	80.2	135 → 104	0.12 ± 0.01	0.12 ± 0.01	0.6 amu	0.6 amu
110.4	110.4	165 → 135	1.00	1.00	1.0 amu	0.9 amu

(a) Metastable present only as a shoulder on another more intense metastable

(b) Breadth of metastable introduces large error into measurement

aldehyde if it were not for the greatly increased mass spectral lability of the acetal hydrogen. Because the nitro group's ability to abstract hydrogen is greatly reduced in the ion, the mass spectral reactivity appears then to be bound up with the nature of the carbonyl or related function, as if charge localization in this group were reaction-controlling with respect to the hydrogen transfer. Since the photochemical reaction is indicated to be controlled by excitation of the nitro group (8), a distinction between photochemical and electron-impact behavior in this series, related to different localization of the reaction center in the two types of processes, may be made.

Experimental. The dimethyl acetal of *o*-nitrobenzaldehyde was prepared by warming *o*-nitrobenzaldehyde in methanolic sulfuric acid several days; a center cut from distillation had b.p. 59-61°/*ca.* 10 microns (lit. (9) b.p. 138-139°/11 mm) and no ir carbonyl absorption. Methyl *o*-nitrosobenzoate was prepared by the photochemical rearrangement of the acetal and recrystallized from methanol, m.p. 155-157° (lit. (9) 156.5-157.5°).

Mass spectra were recorded on a Hitachi RMU 6E single-focusing instrument with inlet at both 180°, source at 190°, ionizing voltage at 75 v, and ionizing current at 80 μa. Data reported were determined at least in duplicate.

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