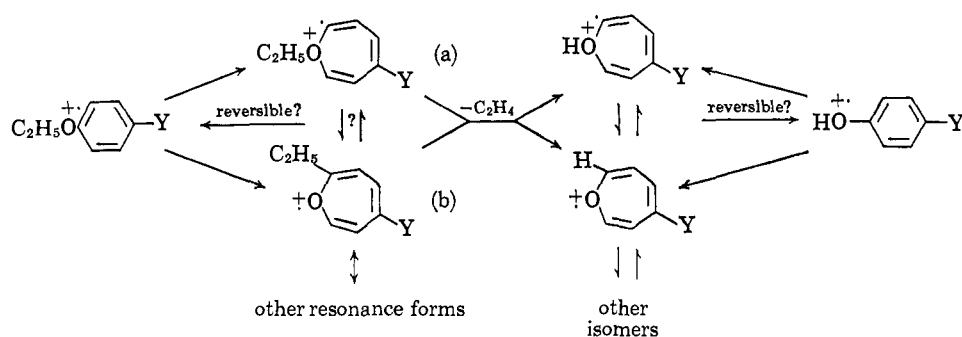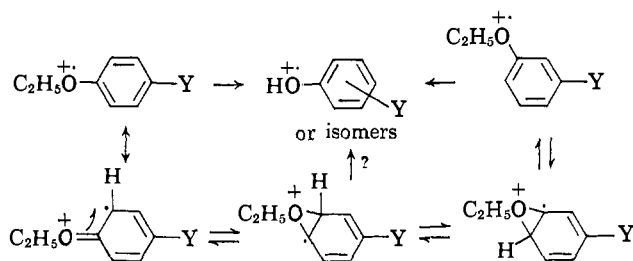**Scheme III**

other resonance forms

other
isomers

stable ions" at m/e 46.4 ($94^+ \rightarrow 66^+$) of 0.23 ± 0.02 ev width[12] and of identical abundance. This indicates[10] that most of the $C_6H_6O\cdot^+$ ions in the spectra of these compounds have the same structure. For all but the CH_3, NO_2, $COOH$, and CHO derivatives, Table I shows[13] that the effect of a particular substituent on the rate of formation and rates of subsequent decompositions of $(M - C_2H_4)\cdot^+$ is independent of the ring position (meta or para) of that substituent.

Schemes III and IV are possible rationalizations for

Scheme IV

or isomers

these data. In Scheme III the oxepin ring is similar to the cycloheptatriene isomer proposed by Meyer and Harrison[14] to explain the partial equilibration of α- and ring-methyl groups in methylethylbenzenes.[15] Other bridged or nonclassical isomers are also possible;[16] a further study to include $C_2D_5OC_6H_4C_2H_5$, $(C_2H_5O)_2$-C_6H_4, $C_2D_5OC_6H_4Y$, and DOC_6H_4Y may yield evidence to support a particular mechanism.

The spectra of m- and p-bromophenetole and m- and p-bromophenol all show the same (in m/e, relative abundance, and shape) "metastable peak" for the reaction $XC_6H_5O\cdot^+ \rightarrow C_6H_5O^+$, as do the corresponding iodo derivatives. These data show that loss of ring position identity can also occur in decompositions of phenols; again, possible rationalizations include isomerizations of M^+ similar to those of Schemes III and IV (replacing C_2H_5 by H). The

(12) T. W. Shannon, F. W. McLafferty, and C. R. McKinney, *Chem. Commun.*, 478 (1966).
(13) At 15 ev further decomposition of $(M - C_2H_4)\cdot^+$ is negligible, except where noted. Thus the 15-ev values correspond to substituent effects on the rates of formation of $(M - C_2H_4)\cdot^+$.[1,11]
(14) F. Meyer and A. G. Harrison, *J. Am. Chem. Soc.*, **86**, 4757 (1964).
(15) Form b should provide better stabilization of the unpaired electron and a better opportunity of randomizing the ring positions than a, but requires the usually unfavorable step of migration of an alkyl group. Possible routes for scrambling include insertion of the oxygen atom into other than the adjacent ring position,[14] reversible contraction of the new seven-membered ring to yield another six-membered ring isomer, and exchange of ring substituents in the seven-membered ring.
(16) Similar formulations have been used to explain the spectra of benzyl alcohol: H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p 169.

spectra of p-nitrophenol and p-nitrophenetole show the same "flat-topped metastable peak,"[12,17] but this is *not* present for the corresponding *meta* compounds.[18]

For the methylphenetoles an additional ring-expansion isomerization[14] may be possible to yield an ethoxycycloheptatriene ion which can also undergo rearrangement loss of C_2H_4 at a different rate. The data of Table I would be explained if this isomerization is favored in one of the isomers.

These results suggest that the similarity in mass spectra of many ortho, meta, and para isomers may be due to randomizing isomerizations of the molecular ions and not just to similarities in decomposition rates of different bonds.

Acknowledgment. The authors are indebted to Drs. F. A. L. Anet and H. A. Morrison for valuable discussions.

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Rearrangements and "Flat-Topped Metastable Ions" in the Mass Spectra of Substituted Nitrobenzenes[1]

Sir:

The mass spectra of nitroaromatic compounds have been studied extensively.[2] Of special interest is the loss of NO from the molecular ion, for which a rearrangement mechanism involving a three-center isomerization to a nitrite structure has been proposed.[2] For some nitroaromatics this NO loss also produces "flat-topped metastable ions,"[3] an unusual and little understood phenomenon. Our observation that the rearrangement loss of C_2H_4 from phenetole is accompanied by the unexpected loss of ring position identity[1] has prompted us to extend our studies of substituent effects to this nitroaromatic rearrangement.

Intensity ratios of the M − 30 ion with respect to the molecular ion at 75 and at 13.8 v, and for the M −

30 — 28 ion with respect to the M — 30 ion at 13.8 v, are given in Table I. Loss of CO is the principal decomposition of $YC_6H_4O^+$ remaining at 13.8; this reaction cannot be eliminated at voltages at which the $YC_6H_4O^+$ is of sufficient intensity to permit significant interpretation. Substituents which can donate electrons by resonance retard the loss of CO from the M — 30 ion when they are in the para position, but accelerate this loss from the meta position. The $YC_6H_4O^+$ and $YC_5H_4^+$ ion abundances at 13.8 have been summed to give approximate values for the substituent effects on the rates of formation of $YC_6H_4O^+$ ions. The data for $-R$ substituents show striking differences between meta and para isomers; the para isomers increase the rates of the rearrangement and other decompositions of the $M \cdot^+$ ion. This acceleration of $YC_6H_4O^+$ formation and the deceleration of all $YC_6H_4O^+$ decomposition reactions point to a specially stabilized structure for these $YC_6H_4O^+$ ions. Valence-bond structures which incorporate stabilization by para $-R$ substituents, but not para $+R$ substituents or meta substituents, are indicated by I and II.[4] The increased rate of loss of CO from $YC_6H_4O^+$ for meta $-R$ substituents may be due to the formation of III. These structures indicate the retention of separate identities of the meta and para positions of the aromatic ring during the course of the elimination of NO and for further decompositions of the $YC_6H_4O^+$, in accord with the Beynon mechanisms.[2] The completely different behavior of the aromatic system in this rearrangement serves to emphasize the loss of structural distinction between meta and para positions in the phenetole rearrangement.[1]
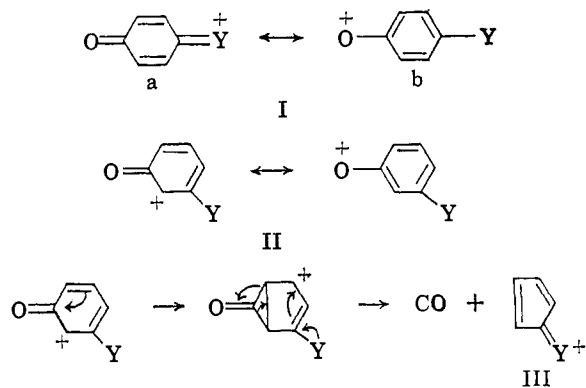
The appearance of a "flat-topped metastable" ion in a spectrum is associated with the release of excess kinetic energy during the decomposition of the parent ion.[3] A "metastable ion" corresponding to the loss of NO from the molecular ion appears in all of the spectra obtained for these compounds. For only five of these compounds, this "metastable ion" has a flat top. The kinetic energy releases associated with these decompositions are compiled in Table II and compared with the σ°_R values for these substituents proposed by Taft.[5] It appears that, for release of NO with kinetic energy, it is necessary to have stabilization of the product ion by the substituent, so that forms such as Ia contribute greatly to the resonance

Table I. Substituent Effects on the Abundances of Key Rearrangement Ions

$$Z_1 = \frac{[YC_6H_4O^+]}{[YC_6H_4NO_2 \cdot^+]} \quad Z_2 = \frac{[YC_6H_4O^+ + YC_5H_4^+]}{[YC_6H_4NO_2 \cdot^+]} \quad Z_3 = \frac{[YC_5H_4^+]}{[YC_6H_4O^+]}$$

Y	Z_1/Z_0, 75 v	Z_1/Z_0, 13.8 v	Z_2/Z_0, 13.8 v	Z_3/Z_0, 13.8 v
H	1.00	1.00	1.00	1.00
p-N(CH₃)₂	1.85	1.06	0.61	<0.05
m-N(CH₃)₂	0.10	0.094	0.12	1.18
p-NH₂	2.62	2.13	1.38	0.13
m-NH₂	0.40	0.42	0.27	1.40
p-OH	2.23	2.08	1.45	0.21
m-OH	0.29	0.23	0.70	4.3
p-OCH₃	3.0	1.81	1.15	0.11
m-OCH₃	0.15	0.19	0.49	3.5
p-F	2.00	2.13	1.63	0.34
m-F	0.50	0.66	0.77	1.05
p-Cl	2.70	2.12	1.79	0.48
m-Cl	0.33	0.47	0.83	2.10
p-Br	2.05	2.42	1.90	0.37
m-Br	0.245	0.72	0.84	1.05
p-C₆H₅	1.33	0.94	0.66	0.23
m-C₆H₅	0.0088	0.083	0.14	2.00
p-CH₃	1.48	1.36	1.08	0.40
m-CH₃	0.50	0.63	0.62	0.71
p-CN	1.70	0.97	1.33	1.40
m-CN	0.42	0.37	0.66	2.12
p-CHO	0.048	0.15	0.09	<0.05
m-CHO	0.087	0.125	0.12	0.67
p-COCH₃	0.20	0.068	0.040	<0.10
m-COCH₃	0.028	0.066	0.010	<0.35
p-NO₂	0.57	0.059	0.034	<0.10
m-NO₂	0.055	0.55	0.53	0.83

hybrid. For all other para substituents, whose resonance parameters are below a certain threshold ($\sigma^\circ_R > -0.40$), the ion is not released with kinetic energy; above this threshold, the amount of energy released is a function of the value of the resonance parameter. Such data demonstrate quantitatively that product ion stability governs rates of mass spectral decomposition reactions, as has been suggested before,[6] in agreement with arguments advanced for solution chemistry;[7] these data further illustrate that product ion stability quantitatively governs the kinetic energy released in the transition state.

Table II. Energy Released in Metastable Decompositions of Nitroaromatic Derivatives

Y	T (ev) released in $YC_6H_4NO \cdot^+ \rightarrow YC_6H_4O^+$	σ°_R
p-N(CH₃)₂	0.84 ± 0.02	-0.55
p-NH₂	0.85 ± 0.04	-0.49
p-OH	0.74 ± 0.06	-0.43
p-OCH₃	0.56 ± 0.06	-0.43
p-C₆H₅	0.38 ± 0.06	-0.09

The appearance of energy release in the decomposition of the p-phenyl compound is not in agreement with the σ_R value[5] based on solution chemistry. We have suggested[8] that increased resonance parameters may be expected for the p-phenyl substituent in mass spectral decompositions; from the substituent value of -0.31 for the formation of benzoyl ion from

(4) J. H. Beynon has suggested such structures to explain his data for metastable ions; seminar, Purdue University, July 1965.

(5) R. W. Taft, J. Phys. Chem., 64, 1805 (1960); R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, J. Am. Chem. Soc., 85, 3146 (1963).

(6) (a) M. M. Bursey and F. W. McLafferty, submitted for publication; (b) F. W. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press Inc., New York, N. Y., 1963, p 318.

(7) (a) M. G. Evans and M. Polanyi, Trans. Faraday Soc., 34, 11 (1938); (b) G. S. Hammond, J. Am. Chem. Soc., 77, 334 (1955).

(8) M. M. Bursey and F. W. McLafferty, ibid., 88, 529 (1966).

p-benzoylbiphenyl,[8] a σ_R value of -0.41 may be calculated by subtraction of the σ_I value of 0.10.[5] The fact that this value exceeds the proposed threshold value for resonance parameters supports our contention based on increased resonance interaction for the benzophenone system.

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(9) To whom requests for reprints should be directed.

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Tropone Dimer. A New Type of Photocycloaddition Reaction

Sir:

Recently much attention has been directed toward molecular orbital symmetry considerations for explaining different behavior in photochemical and thermal reactions.[1-4] Although it is predicted from Woodward and Hoffmann's selection rule[2] that a concerted cycloaddition of (6 + 6) π-type, $n = 3$ in a $4n$ system, would occur photochemically, this type of photocycloaddition has never been reported. We wish to report the first example of (6 + 6) π-type cycloaddition: the photodimerization of tropone.

Irradiation of tropone in 2 N sulfuric acid with a mercury lamp (Toshiba H-400 P) for 140 hr in a Pyrex vessel afforded, on purification using alumina column chromatography, dimer I, mp 220° (7.5%), besides oily product (6.6%), recovered tropone (8%), and a large amount of polymer.

The structure of dimer I was confirmed to be tricyclo[6,4,1,1^{2,7}]tetradeca-3,5,9,11-tetraene-13,14-dione (Ia) from the following physical and chemical evidence. *Anal.* Found for $C_{14}H_{12}O_2$: C, 79.16; H, 5.72; ultraviolet in methanol, 254 mμ (ϵ 8800)[5] and 273 mμ (shoulder); infrared in KBr, 3030 (double bond), 1705 (carbonyl), and 1600 and 723 cm^{-1} (*cis* diene); nmr (100 Mc) in CDCl$_3$, A$_2$B$_2$X$_2$ coupling pattern at τ 4.15 (A protons, 2 H), 4.45 (B protons, 2 H), and 6.58 (X protons, doublet, $J = 6.0$ cps, 2 H) shown in Figure 1a. The assignment of these protons was provided by decoupling technique.[6]

As shown in Figure 1b, a typical A$_2$B$_2$ coupling pattern appeared centered at τ 4.30 when X was saturated, while on saturation of B a singlet was observed for X. The nmr evidence indicated that the molecule was symmetrical, the A and B protons were olefinic, and X was a methine proton.

(1) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).
(2) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).
(3) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965).
(4) K. Fukui, *Tetrahedron Letters*, 2009 (1965).
(5) Cyclohexa-1,3-diene and cyclohepta-1,3-diene have absorption maxima at 256 mμ (ϵ 8000) and 248 mμ (ϵ 7500), respectively (A. I. Scott, "Interpretation of Ultraviolet Spectra of Natural Products," Pergamon Press, New York, N. Y., 1964, p 48).
(6) The authors thank Dr. M. C. Woods for the measurement and discussion of the nmr spectra.
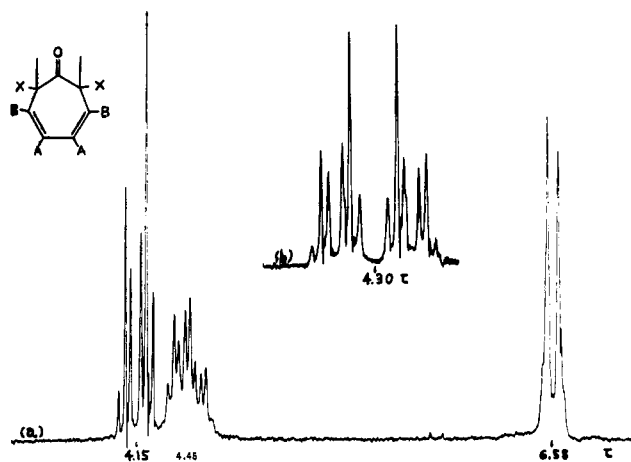

Figure 1.

The mass spectrum of I included peaks with m/e 212 (molecular ion), 149, 141, 106 (M/2), and 78 (base peak).[7] The occurrence of the relatively strong peak of m/e 106 and base peak 78 suggested the cleavage of I to tropone, which exhibits a base peak at m/e 78 corresponding to benzene[8] on electron impact. The dissociation of I to tropone was also brought about by heating. On pyrolysis at 220° in a sealed tube under nitrogen atmosphere, I gave tropone in 60% yield, which was identified by infrared spectrum and the formation of picrate, mp 99°.

On catalytic hydrogenation over 10% palladium–carbon, I took up 4 mole equiv of hydrogen to give an octahydro derivative (II), mp 93°, in almost quantitative yield, which had the following physical properties. *Anal.* Found for $C_{14}H_{20}O_2$: C, 76.25; H, 9.11; infrared in KBr, 1704 cm^{-1} (carbonyl), and no absorption due to double bond; mass spectrum, peaks with m/e 220 (molecular ion), 110, 81, and 67.

Summarizing the evidence cited above, two possible structures, Ia and Ib, can be deduced for dimer I. Evidence for the *trans* form (Ia) rather than the *cis* form (Ib) came from dipole moment measurements.[9] The dipole moment of I taken in benzene at 25° was 0.8 D., strongly supporting Ia for the structure of dimer I (see Chart I).

Chart I
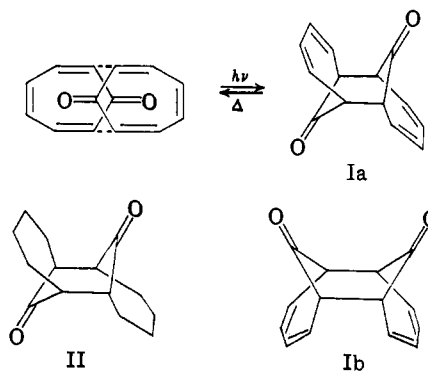
(7) Mass spectra were taken at 70 ev by Dr. S. Hishida, Nippon University, Tokyo, whom the authors acknowledge.
(8) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p 241.
(9) The authors thank Dr. H. Watanabe, Shionogi & Co. Ltd., for the measurement of the dipole moment.