configuration, and Eu(II) has the Xe, $4f^7$ structure. Accordingly, the Eu(3) position must be stabilized by the interaction of a vacant Eu(II) valence orbital of the proper symmetry with the four nearest 8-ring oxide ions, at O(1), of the zeolite framework. The orbital should be 6s, 5d, or 4f in character, or a hybrid. Perhaps the Eu(II) $5d_{x^2-y^2}$ orbital, which is empty in the ground state, is most likely. The energy of this interaction does not need to be large to explain the positional differences observed.

The bright orange color of the crystal probably results from a Eu(II) f → d transition. For example, the $4f^7 \rightarrow 4f^6\,5d$ electronic transition occurs in the near ultraviolet around 25 000 to 30 000 cm^{-1}.[22] Divalent rare earth ions doped into CaF_2 are known to be deeply colored because of the 4f → 5d transition.[22]

It may be expected that the near-zero-coordinate Eu(II) ion may be catalytically important because of its severe coordinative unsaturation. Indeed, this could be said of every Eu(II) ion in this structure. The 8-ring near-zero-coordinate Ca^{2+} ion in dehydrated Ca_6-A has been shown to be highly active in the isomerization of 1-butene.[23]

The relatively high final error indices for Eu-A can be attributed in part to the disorder present in the structure. Only the average ring geometries can be calculated, but there are three differently occupied kinds of 6 rings and two each differently occupied kinds of 8 and 4 rings. One would expect the conformation of a particular ring to depend upon whether or not it contains a Eu(II) ion. Empirically it is observed that the final error indices increase regularly for the series, Ca_6-A, Sr_6-A, and Eu-A. Ba_6-A decomposes upon dehydration. Together, these observations suggest increasing strain, disorder, and instability with increasing divalent cation size or mass.

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Supplementary Material Available: Listing of the observed and calculated structure factors (2 pages). Ordering information is available on any current masthead page.

References and Notes

(1) A discussion of zeolite nomenclature is available: (a) R. Y. Yanagida, A. A. Amaro, and K. Seff, *J. Phys. Chem.*, **77**, 805 (1973); (b) L. Broussard and D. P. Shoemaker, *J. Am. Chem. Soc.*, **82**, 1041 (1960).
(2) K. Seff and D. P. Shoemaker, *Acta Crystallogr.*, **22**, 162 (1967).
(3) This nomenclature refers to the contents of the unit cell. For example, Ca_4Na_4-A represents $Ca_4Na_4Al_{12}Si_{12}O_{48}$, exclusive of water molecules if a hydrated crystal is considered.
(4) R. Y. Yanagida, T. B. Vance, Jr., and K. Seff, *Inorg. Chem.*, **13**, 723 (1974).
(5) K. Seff, *Acc. Chem. Res.*, **9**, 121 (1976).
(6) P. E. Riley and K. Seff, *Inorg. Chem.*, **13**, 1355 (1974).
(7) N. V. Raghavan and K. Seff, *J. Phys. Chem.*, **80**, 2133 (1976).
(8) P. C. W. Leung, K. B. Kunz, I. E. Maxwell, and K. Seff, *J. Phys. Chem.*, **79**, 2157 (1975).
(9) R. L. Firor and K. Seff, *J. Am. Chem. Soc.*, **98**, 5031 (1976).
(10) R. L. Firor and K. Seff, *J. Am. Chem. Soc.*, **99**, 1112 (1977).
(11) R. L. Firor and K. Seff, *J. Am. Chem. Soc.*, **99**, 6249 (1977).
(12) R. L. Firor and K. Seff, *J. Am. Chem. Soc.*, **99**, 4039 (1977).
(13) R. L. Firor and K. Seff, unpublished work.
(14) "Handbook of Chemistry and Physics", 55th ed, The Chemical Rubber Company, Cleveland, Ohio, 1974, p F190.
(15) H. Bärnighausen, *Z. Anorg. Allg. Chem.*, **342**, 233 (1966).
(16) P. H. Kasai and R. J. Bishop, Jr., U.S. Patent 3 963 830 (1976).
(17) Principal computer programs used in this study: T. Ottersen, COMPARE data reduction program, University of Hawaii, 1973; full-matrix least-squares, P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, UCLA LS4, American Crystallographic Association Program Library (old) No. 317 (revised 1976); FOURIER program, C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, Ames Laboratory Fast Fourier, Iowa State University, 1971; C. K. Johnson, ORTEP, Report No. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(18) These framework parameters were taken from the structure of dehydrated Ca_4Na_4-A.
(19) "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, pp 73–75, 88.
(20) R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 751 (1976).
(21) G. J. McCarthy, *Mater. Res. Bull.*, **6**, 31 (1971).
(22) G. H. Dieke, "Spectra and Energy Levels of Rare Earth Ions in Crystals", Wiley, New York, N.Y., 1968, pp 178, 179.
(23) T. Takaishi, private communication.

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Correlation of Electrochemical Reactivity and Photoelectron Spectra of Aromatic Ketones

Sir:

Gooden and Brauman recently reported[1] on the photodissociation of butyrophenone radical cation and pointed out the possible connection between the photoelectron (pe) spectrum of the ketone and the kinetic sensitivity of the radical cation to incident radiation. These results prompt us to report a

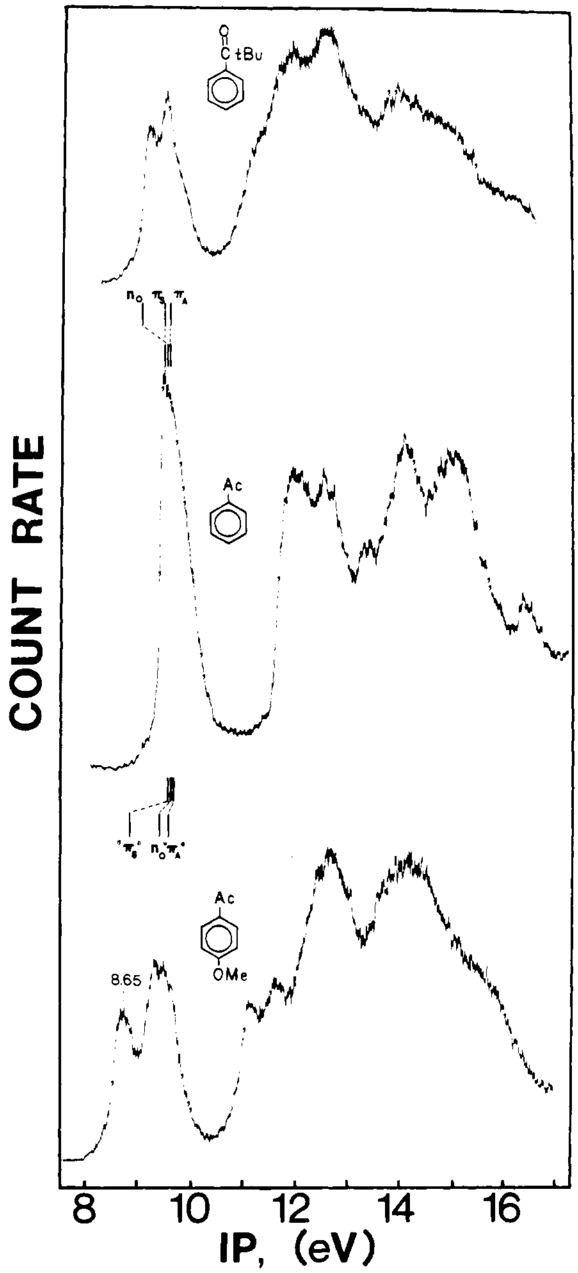
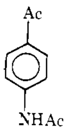
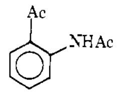
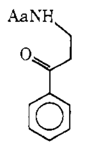
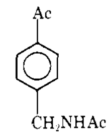


Figure 1. H(I) photoelectron spectra of phenyl *tert*-butyl ketone (top), acetophenone (middle), and *p*-methoxyacetophenone (bottom).

Table I. Photoelectron Spectral Assignments[a] and Electrochemical Ritter Reaction Products[b]

Starting ketone	State	obsd[a] (calcd)[c]				
Acetophenone	"Π_S"	9.46 (9.45)	0.70	0.24		
	n_0	9.50				
	"Π_A"	9.5 (9.50)				
Valerophenone	n_0	9.3	0.37	0.18	0.37	
	"Π_S"	9.46 (9.45)				
	"Π_A"	9.5 (9.50)				
p-Cyanovalerophenone	n_0	9.57			0.89	
	"Π_S"	9.80 (9.90)				
	"Π_A"	10.22 (10.30)				
p-Methylvalerophenone	"Π_S"	9.02 (8.92)				0.88
	n_0	9.32				
	"Π_A"	9.50 (9.50)				

[a] See footnote 3 for symbol designation. In electron volts. [b] Moles/mole of starting material consumed. Yields determined by GLC on a 5-ft SE-30 on Chromosorb W column. Product identification spectroscopically or by comparison with authentic material. [c] Calculated using equation 1, ignoring the effects of the larger alkyl group.

method of assignment of the photoelectron spectra of such ketones and a correlation between the electronic structures of the ionic ground states of substituted examples with their observed electrochemical reactivity.

The pertinent electrochemical results are acetamidations (electrochemical Ritter reactions)[2] carried out potentiostatically with a smooth platinum foil anode in acetonitrile using tetraethylammonium tetrafluoroborate as supporting electrolyte. The position of acetamidation, illustrated here (Scheme I) with valerophenone derivatives, varies widely depending upon the structure of the ketone as shown by Table I.

The pe spectrum of acetophenone (Figure 1, middle) shows the first band maximum at 9.45 eV. The intensity of this band, relative to those of the σ framework, suggests that it arises from the superposition of three bands which correspond to production of the n_0 and two Π ("Π_A", "Π_S")[3] ionic states which are approximately degenerate in this case. We have verified this suggestion through studies of a number of substituted acetophenones. These studies resulted in the observation that members of the para-substituted series show band maxima simply shifted from those of the corresponding monosubstituted derivatives (eq 1).[4]

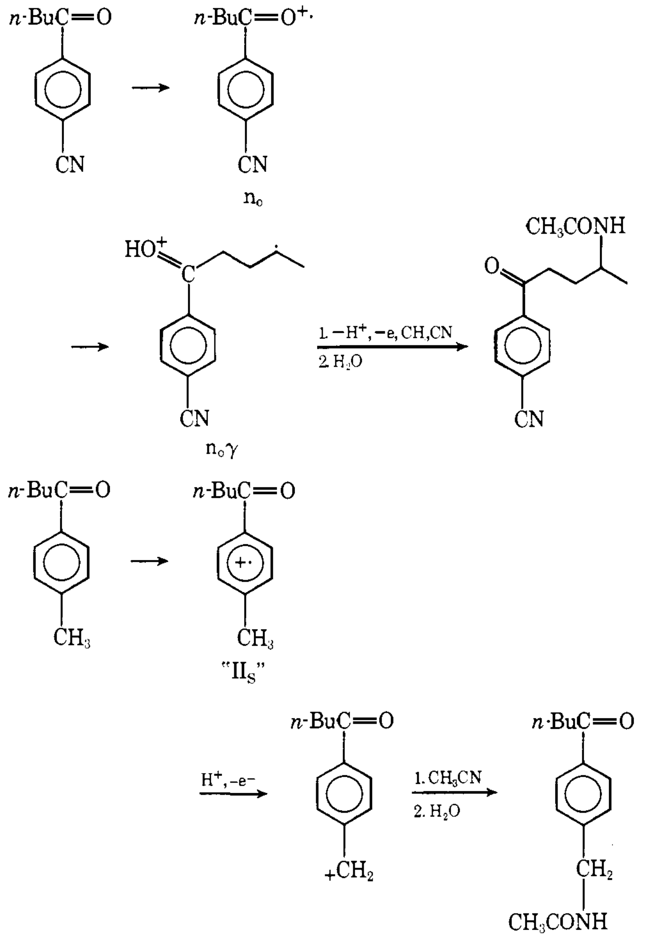
$$\mathrm{IP}\,(p-x-\mathrm{PhA_c}) \simeq \mathrm{IP}\,(\mathrm{Ph}-x) + 0.20\ \mathrm{eV} \qquad (1)$$

This observation furnishes an attractive empirical basis for the pe spectral assignments. For example, the observed spectrum of *p*-methoxyacetophenone (Figure 1, bottom) is assigned as "Π_S", 8.65 eV (eq 1, 8.69 eV) below "Π_A", 9.48 eV (eq 1, 9.43 eV). The n_0 band is observed at 9.3 eV, slightly lower than in acetophenone. Para ring substituents affect one or both of the "Π" states to a greater extent than they do the n_0 state and lift the accidental degeneracy observed for acetophenone.

On the other hand, the n_0 ionic states are more sensitive to the nature of the ketonic alkyl group. The spectrum of phenyl *tert*-butyl ketone (Figure 1, top) shows the n_0 band shifted down to 9.02 eV while the "Π" bands are essentially unchanged. This shift in the n_0 band position, relative to acetophenone (−0.5 eV), is approximately the same as that from acetone to methyl *tert*-butyl ketone (−0.57 eV). The corresponding shifts of the n_0 states of 2-pentanone (−0.24 eV) and 2-hexanone (−0.28 eV), relative to acetone, suggest the n_0 bands for butyrophenone and valerophenone to be near 9.3 eV. The first bands in the spectra of the latter two compounds are broader and have lower onsets than that of acetophenone but the n_0 band maxima are not clearly resolved.

Altogether the pe studies give an indication of the way in which the electronic ground states, of the radical cation derived from such ketones, change with substituents. These variations in ground state are summarized in Table I[6] and can be connected to the electrochemical results through the postulate that the n_0 ionic states may abstract γ hydrogen atoms followed by deprotonation and oxidation of the resulting radical to give, after hydrolysis, the Ritter amide. This is shown in Scheme I for *p*-cyanovalerophenone and it is noted that aliphatic ketones undergo this type of anodic reaction.[2a] The "Π_S" ionic states react by addition of the nucleophile to the ring[2c] or loss of an α proton in the *p*-methylvalerophenone case. The latter reaction is characteristic of alkyl benzene oxidations.[2d] Although

Scheme I



the use of gas phase data to explain electrochemical phenomena must be done prudently, it is often successful,[2b,7] and in this case the pe results demand that the electronic states of the electrochemical intermediates be considered.

The present results nicely compliment those of Gooden and Brauman, although they do reveal complications concerning the nature of the electronic state and structure of the parent ion which is initially formed by electron impact on butyrophenone. The electrochemical results suggest that the observed 3-eV band in the kinetic spectrum of butyrophenone radical cation might arise from a transition originating from the γ radical cation analogous to $n_O\gamma$ of Scheme I.

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References and Notes

(1) R. Gooden and J. Brauman, *J. Am. Chem. Soc.*, **99**, 1977 (1977).

(2) (a) J. Y. Becker, L. R. Byrd, L. L. Miller, and Y.-H. So, *J. Am. Chem. Soc.*, **97**, 853 (1975); (b) L. L. Miller, V. Koch, T. Koenig, and M. Tuttle, *ibid.*, **95**, 5075 (1973); (c) Y.-H. So, J. Y. Becker, and L. L. Miller, *J. Chem. Soc., Chem. Commun.*, 262 (1975); (d) L. Eberson and K. Nyberg, *Tetrahedron*, **32**, 285 (1976).

(3) The ketones discussed here have no symmetry elements. However, we use the "Π_S" designation to refer to the ionic wave function which would be symmetric to a plane perpendicular to that of the aryl group, i.e., ignoring the absence of this symmetry element for the acyl substituent. The "Π_A" designation refers to the ionic wave function which would be antisymmetric with respect to σ_v with the same exception. The n_O symbol refers to the ion with a vacancy localized on oxygen in what would be the σ plane, ignoring the absence of this element for the alkyl group.

(4) Equation 1 relies on literature assignments for nitrobenzene[4a] and benzonitrile:[4b] (a) J. Rabalais, *J. Chem. Phys.*, **57**, 960 (1972). (b) G. Griebel, G. Hohlneicher, and F. Dorr, *J. Electron Spectrosc. Relat. Phenomena*, **4**, 185 (1974).

(5) W. Tam, D. Yee, and C. E. Brion, *J. Electron Spectrosc. Relat. Phenomena*, **4**, 77 (1974). (a) H. Bock, H. Alt, and H. Seidl, *Angew. Chem., Int. Ed. Engl.*, **7**, 885 (1968); R. Brown, *Can. J. Chem.*, **53**, 2446 (1975).

(6) The application of eq 1 to valerophenones does not take into account effects of the longer alkyl chain on the "Π" states.

(7) S. F. Nelson, V. Peacock, and G. R. Wiseman, *J. Am. Chem. Soc.*, **98**, 5269 (1976).

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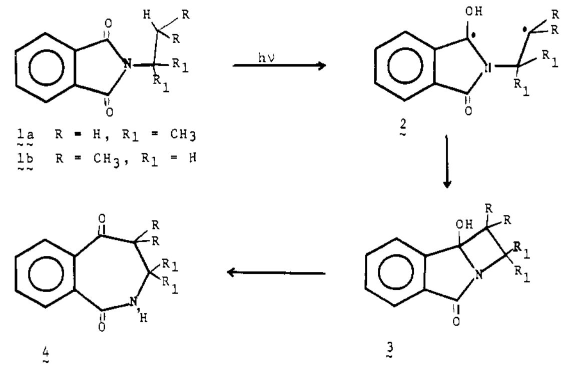
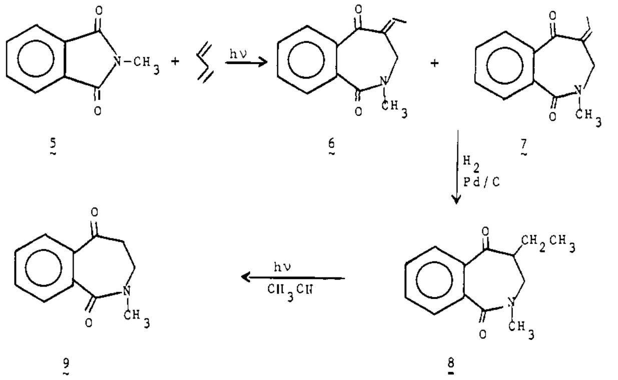
Photochemical Addition of Dienes to *N*-Alkylphthalimides

Sir:

The photochemical rearrangement of *N*-alkylphthalimides to benzazepinediones **1** → **4** via a type II process has been the subject of numerous recent studies.[1-14] The reaction has been shown to be quite general, occurring with O,[3,4] S,[5,6] N,[7,15] and aromatic moieties[2,10,11] incorporated in the *N*-alkyl substituent. Despite the large amount of work on the scope of these reactions there is little mechanistic information available with the exception of reports[1,5,13,14] that some of the reactions occur via the triplet state since they are quenched by dienes.

When we conducted quenching studies on phthalimides **1a**, our results indicated that normal photochemical quenching was not occurring but that the phthalimides were efficiently reacting with the *cis*-piperylene quencher. We investigated this reaction using *N*-methylphthalimide (**5**) and butadiene in order to avoid unnecessary complications from competition with type II processes (i.e., **1** → **4**) and isomer formation. A 1% solution of **5** (3 g) in 2:1 butadiene-acetonitrile was irradiated for 6.5 h with a Hanovia 450-W medium-pressure lamp through quartz. NMR analysis of the semisolid residue from solvent evaporation indicated that 69% of **5** had been converted to product. Silica gel chromatography afforded a 93% yield of product[16] which was shown to consist of a mixture of *anti*- (**6**) and *syn*-3,4-benzo-6,7-dihydro-6-ethylidene-1-methylazepine-2,5-dione (**7**). The structure of the major product follows from chemical and spectroscopic evidence. The ^{1}H NMR spectrum (CDCl$_3$) of the major product (**6**, mp 109-111 °C), after purification by preparative TLC and recrystallization, showed δ 2.05 (d, 3 H, J = 7 Hz), 3.15 (s, 3 H), 4.25 (s, 2 H), 7.1 (q, 1 H, J = 7 Hz), 7.40-8.00 (m, 4 H); IR (CCl$_4$) 1680, 1650 cm^{-1}; m/e 215 (10). The ^{1}H NMR of the minor product **7** showed δ 2.3 (d, 3 H, J = 7 Hz), 3.20 (s, 3 H), 4.05 (s, 2 H), 6.5 (q, 1 H, J = 7 Hz), 7.4-8.0 (m, 4 H).





The anti orientation of the vinyl methyl group in **6** follows from its chemical shift (δ 2.05) when compared with that of the vinyl methyl group in the syn isomer (δ 2.30) which is shifted downfield by the *cis*-carbonyl group. A complementary shift is seen with the vinyl proton in **6** which is shifted downfield by 0.6 ppm from its position in **7**.[17]

Confirmatory evidence for the structure of **6** and **7** was obtained by hydrogenation of the product mixture at atmospheric pressure in ethanol over 5% Pd/C to give the ethyl derivative **8**: NMR (CDCl$_3$) δ 1.0 (t, 3 H, J = 7 Hz), 1.3-1.8 (m, 2 H), 2.7-3.1 (m, 1 H), 3.2 (s, 3 H), 3.5-3.8 (m, 2 H), 7.3 -7.9 (m, 4 H); IR (CCl$_4$) 1690, 1650 cm^{-1}; m/e 217 (26). Irradiation of this material in acetonitrile cleanly converted it to the parent 3,4-benzo-6,7-dehydro-1-methylazepine-2,5-dione (**9**): NMR (CDCl$_3$) δ 2.8-3.1 (m, 2 H), 3.20 (s, 3 H), 3.6-3.8 (m, 2 H), 7.4-7.9 (m, 4 H); IR (CCl$_4$) 1695, 1655 cm^{-1}; m/e 189 (1954). The type II cleavage of the ethyl group[6] clearly establishes the position of the substituent as α to the carbonyl. No evidence for any 7-substituted products was obtained.

Possible mechanisms for this novel reaction,[18] formally a $[_\pi 2 + {}_\sigma 2]$ photochemical cycloaddition, must explain the observed regiospecificity; i.e., the diene always adds with its terminal carbon attached to nitrogen. We suggest the sequence