Figure 1. Resonance energies per electron.

which π energies are calculated by a semiempirical Pople-type SCF–MO method and in which allowances are made for σ-bond compression energies (see Table I and Figure 1b). These SCF–MO results probably represent the best estimates of resonance energies available,[13] and the high correlation with the resonance theory values (correlation coefficient is 0.998 for total resonance energy and 0.991 for resonance energy per π electron) attests to a utility of the resonance method in calculating resonance energies. Since the formal procedure can be carried out by hand in a few seconds as delineated later in this paper, the simpler theory should be the method of choice for determination of resonance stabilization.

The reasons for the consonant results remain obscure. The VB results are obtained from a method that is little more than a simple recipe, albeit a quantum mechanical recipe. Perhaps the results ought to be accepted in the same pragmatic spirit that HMO results are accepted. Additional work will show whether or not the approach has wider applicability. The results do indicate that VB theory limited to Kekule structures is a viable concept.

Resonance between Kekule structures gives rise to several types of exchange integrals, of which only two are used in this work. γ_1 refers to resonance between two structures related by a permutation of three bonds within a six-membered ring, and γ_2 involves the permutation of five bonds within two annelated rings. The resonance energy of benzene is therefore γ_1 with the lowest energy electronic transition equal to 2.0 γ_1. The analogous values for azulene are γ_2 and 2.0 γ_2. The ratio of γ_2 to γ_1 is given by the ratio of the electronic transitions, 7000 and 2600 Å, respectively, $\gamma_2/\gamma_1 = 0.37$.[14] Actual evaluation of the integrals using bond lengths of 1.40 Å gives $\gamma_2/\gamma_1 = 0.36$.[1,15]

The Kekule structures are enumerated by writing a single structure and using the concept of the structure count (SC) as described in a recent paper.[16] One can easily demonstrate that the γ_1 exchange integrals can then be enumerated by excision of each ring of the structure in turn, with summation of the SC's for the residual systems. The γ_2 integrals are enumerated

(13) See the papers by B. A. Hess, Jr., and L. J. Schaad for a different viewpoint, J. Amer. Chem. Soc., 93, 305, 2413 (1971); J. Org. Chem., 36, 3418 (1971).
(14) S. P. McGlynn, L. G. Vanquickenborne, M. Kinoshita, and D. G. Carroll, "Introduction to Applied Quantum Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1972, pp 214–217.
(15) C. A. Coulson and W. T. Dixon, Tetrahedron, 17, 215 (1962).
(16) W. C. Herndon, Tetrahedron, 29, 3 (1973).

by excision of adjacent rings two at a time and application of the same procedure.

The structures are assigned equal weights in the resonance hybrid, and a zero overlap approximation is used. The total resonance energies must then be twice the sum of exchange interactions divided by the number of Kekule structures K. Resonance energies are therefore given by the formula $RE = 2(n_1\gamma_1 + 0.37n_2\gamma_2)/K$.

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Photochemistry of 4-tert-Butyl-2,6-dimethylpyrylium Perchlorate. Evidence for an Oxoniabenzvalene Intermediate

Sir:

We wish to report a study of the photochemistry of 4-tert-butyl-2,6-dimethylpyrylium perchlorate (1), the products from which provide strong evidence for the intermediacy of an oxoniabenzvalene, i.e., an oxygen analog of benzvalene.

Irradiation of the pyrylium salt 1 in water (λ >270 nm; 25°; nitrogen atmosphere; 0.02 M solution; 18 hr) gave an acidic solution from which an oil was isolated by ether extraction. Chromatography of the oil on silica gel gave four main products, 2, 3a, 3b, and 4, in yields of 4, 15, 2, and 6%, respectively. Under
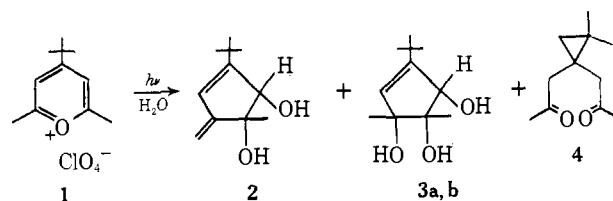
the conditions described, ca. 70–80% of the pyrylium salt was destroyed. The structural assignments are based on the following evidence.

The diol 2, mp 71–72°, $C_{11}H_{18}O_2$, had τ (CDCl₃)[1] 4.06, 5.08, 5.13 (each 1 H, apparent s), 5.94 (1 H, d, $J = 7$ Hz; collapsed to s on D₂O exchange), 7.33 (OH, d, $J = 7$ Hz), 7.4 (OH, s), 8.75 (3 H, s), and 8.84 (9 H, s).

Triol 3a crystallized as the hemihydrate $C_{11}H_{20}O_3 \cdot 0.5H_2O$, mp 60–61°, which had τ (CDCl₃)[1] 4.39 (1 H, s), 5.97 (1 H, d, $J = 6$ Hz; collapsed to s on D₂O exchange), 6.53 (OH, s), 7.58 (OH, d, $J = 6$ Hz), 7.69 (OH, s), 8.41 (OH, s), 8.79 (3 H, s), and 8.88 (12 H, s).

Triol 3b mp 150.5–151°, $C_{11}H_{20}O_3$, had nmr (CDCl₃)[1] τ 4.47 (1 H, s), 5.62 (1 H, d, $J = 7$ Hz; collapsed to s on D₂O exchange), 7.49 (OH, s), 7.82 (OH, d, $J = 7$ Hz), 8.39 (OH, broad), 8.62 (3 H, s), 8.72 (3 H, s), and 8.86 (9 H, s).

3a and 3b were both converted into 2, identical in all

(1) The chemical shifts for the OH signals in 2, 3a, and 3b were concentration dependent. The quoted values are for ca. 1% solutions. At higher concentrations, the OH resonances collapsed to a single broad peak.

respects with the diol 2 isolated from the photolysate, upon acid-catalyzed dehydration with toluene-*p*-sulfonic acid in boiling benzene. Catalytic hydrogenation (5% Rh on alumina) of 3a and 3b gave isomeric saturated triols 5, both of which showed doublet C*H*-OH splitting patterns in the nmr after D_2O exchange. This experiment eliminated the possibility that 3a and 3b (and 2 as well) had carbon skeletons as shown in 6. The exact stereochemistry of the triols 3a and 3b remains to be determined, though it may be relevant that both underwent oxidative fission with sodium periodate.

1,1-Diacetonyl-2,2-dimethylcyclopropane (4) was obtained as an oil, bp 50–55° (0.1 mm), which had ν_{max} (liquid film) 1710 cm^{-1}; τ (CCl$_4$) 7.47 (4 H, s), 7.99 (6 H, s), 8.93 (6 H, s), and 9.72 (2 H, s). The compound gave a bis-2,4-dinitrophenylhydrazone of the appropriate spectroscopic and analytical properties and cyclized upon alumina chromatography to the oily spirocyclohexenone 7, C$_{11}$H$_{16}$O: λ_{max} (ethanol) 233

5   6   7
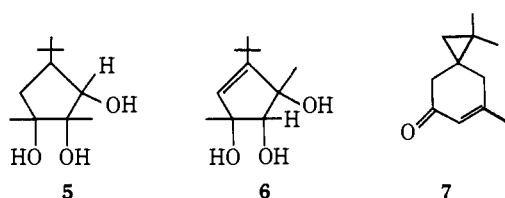
nm (ϵ 9900); ν_{max} (liquid film) 1670 cm^{-1}; τ (CCl$_4$) 4.21 (1 H, m), 7.5–8.0 (4 H, m), 8.19 (3 H, s), 8.90 (6 H, s; resolved into two equal intensity singlets, τ 9.11 and 9.15, in benzene solution), 9.68 (1 H, d, $J = 5$ Hz), and 9.79 (1 H, d, $J = 5$ Hz).

The formation of 2–4 can most simply be rationalized as shown in Scheme I. Excitation of the pyrylium

Scheme I
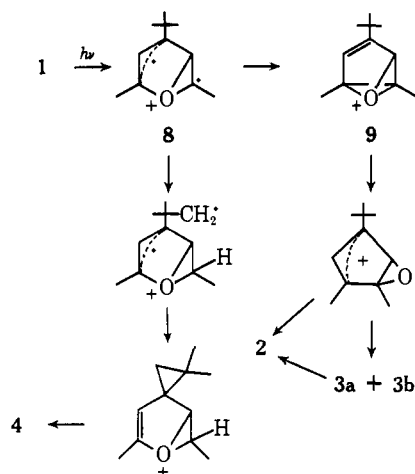
salt, probably to a π–π* state,[2] gives rise to the "prevalene" 8 and then the oxoniabenzvalene 9 analogous to the intermediates formed from excited states of isoelectronic species such as benzene[3] and pyridinium salts.[4] The hydrolytic behavior of the azoniabenzvalenes postulated[4] in the latter case resembles closely that depicted in Scheme I for the valene 9. A novel feature of the present work is the formation of the cyclo-

(2) A. T. Balaban, V. E. Sahini, and E. Keplinger, *Tetrahedron*, **9**, 163 (1960).

(3) D. Bryce-Smith, *Pure Appl. Chem.*, **16**, 47 (1968).

(4) L. Kaplan, J. W. Pavlik, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, **94**, 3283 (1972).

propane 4. It is primarily the isolation of this compound that leads us to suggest prevalene 8, rather than its isomer 10, as the precursor of the oxoniabenzvalene 9, for there exists no obvious simple mechanism for deriving 4 from 10. Stereochemically, intramolecular hydrogen abstraction of a *tert*-butyl hydrogen atom appears feasible in 8 but virtually impossible in 10.

10   11
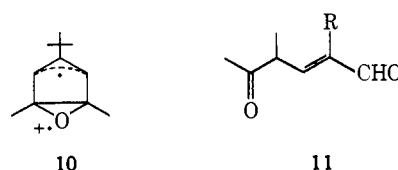
No products of type 11 (R = *t*-Bu) could be detected in the irradiation of 1, in marked contrast to the case of 2,4,6-trimethyl-[5] and 2,6-dimethyl-4-ethylpyrylium[6] perchlorate, where compounds (11; R = Me and Et, respectively) were formed, presumably by skeletal atom transposition *via* valene intermediates analogous to 9. No reason can yet be given for the difference in behavior of 1 and the other two pyrylium salts.

In the light of our results, published reports[7,8] on the monomeric photochemistry of γ-pyrones can be reinterpreted as proceeding *via* valene-type species, *e.g.*, the conversion of the hydroxy-γ-pyrone 12 into 13 and 14[7] and of 2,6-dimethyl-γ-pyrone (15) into the 2-furaldehyde (16)[8] could well occur as depicted in Schemes II

Scheme II

12   14   13
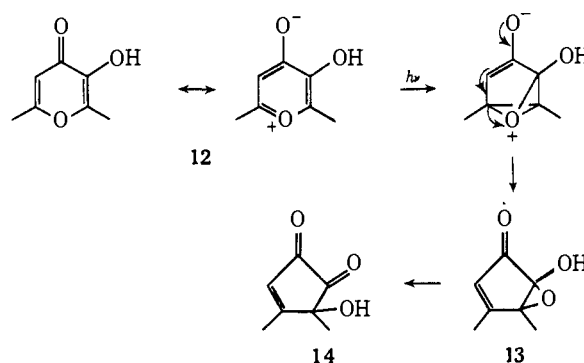
and III. Scheme II is strictly analogous to our present

Scheme III

15   16
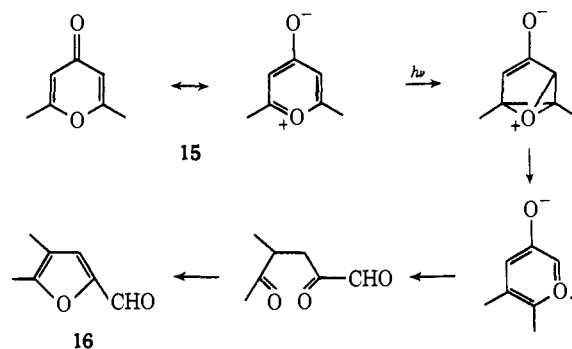
work while Scheme III is analogous to our proposed mechanism for the photohydrolysis of 2,4,6-trimethylpyrylium perchlorate.[5]

(5) J. A. Barltrop, K. Dawes, A. C. Day, and A. J. H. Summers, *J. Chem. Soc., Chem. Commun.*, 1240 (1972).

(6) J. A. Barltrop, K. Dawes, A. C. Day, S. J. Nuttall, and A. J. H. Summers, unpublished work.

(7) M. Shiozaki and T. Hiraoka, *Tetrahedron Lett.*, 4655 (1972).

(8) P. Yates and I. W. J. Still, *J. Amer. Chem. Soc.*, **85**, 1208 (1963); *cf.* A. Padwa, *Tetrahedron Lett.*, 813 (1964).

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The Reductive Degradation of Nitrogen-Containing Ligands in the Presence of Cobalt Ions

Sir:

We have observed the reductive degradation of various cobalt complexes of organic ligands in aqueous borate buffer. Upon reduction by sodium borohydride the complexes break up with deposition, apparently, of metallic cobalt, degradation of the ligand, and evolution of ammonia when the ligand initially contains nitrogen. In at least one system, based on trisodium *meso*-tetra-(*p*-sulfonatophenyl)porphinatocobalt(III), [Co^{III}(tpps)], dioxygen significantly affects the course of the degradation and there is a claim that this system reduces dinitrogen to ammonia.[1] Our results are summarized in Table I.

Table I. Degradative Reduction of Cobalt Complexes

System	Yield of ammonia,[a] mol/ atom Co
$Na_3[Co^{III}(tpps)]$	0.6
$[Co^{III}(bipy)_3](ClO_4)_3$	0.4
Hexamethyltetraethyltetradehydrocorrin-cobalt(II)	0.5
$[Co^{III}(dmg)_2(H_2O)Cl]$	0.7
$[Co^{II}(o\text{-}NH_2C_6H_4COO)_2]$	0.1
$[Co^{II}(4\text{-}C_5H_4NCOO)_2]$	Nil
$[Co^{III}(acac)_3] + 2\text{-}C_4H_3NHCOOH$	Nil
Dimethylglyoxime (dmg)	Nil
2,2'-Bipyridyl (bipy)	Nil

[a] Borohydride reductions in borate buffer with passage of air at room temperature during 2 days.

We have investigated the reduction of [Co^{III}(tpps)][2] electrochemically, to gain some insight into the route of the degradation. The porphyrin complex was electrolyzed in a three-electrode cell during the passage of purified gas. The gases were purified by acid and alkali scrubbing followed by passage through a trap at $-80°$. In addition the Ar was passed over hot copper catalyst (Badische Anilin und Soda Fabrik). The working electrode was maintained at a preset potential relative to a saturated calomel electrode within the range -0.5 to -1.5 V. This approximates to the spread of potentials produced by the sodium borohydride during its decomposition in the reaction mixture. Polarography was used to characterize and determine the constituents of the solution (Table II). In addition, the concentrations of free porphyrin (tpps) and [Co^{III}-tpps)] were monitored during the reduction by their visible spectra. The cobalt concentration and the ammonia swept out of the system were determined by

(1) E. B. Fleischer and M. Krishnamurthy, *J. Amer. Chem. Soc.*, **94**, 1382 (1972).
(2) Elemental analysis of the cobalt porphyrin indicated that the compound was pure and free from nitrogen-containing impurities.

Table II. Polarographic Half-Wave Potentials

	$E_{1/2},^a$ V		$E_{1/2},^a$ V
$[Co^{III}(tpps)]$	-0.65^b	O_2	-0.03
$[Co^{II}(tpps)]$	-1.10^b	H_2O_2	-0.97
(tpps)	-0.87^b	Borate buffer (pH 9.7)	-1.9
(tpps)$^-$	-1.63^b		

[a] Half-wave potentials were measured in borate buffer and are in volts relative to the potassium chloride saturated calomel electrode. [b] The number of electrons involved in the reduction process is assumed to be *one* in agreement with the ratio of wave heights and with published work: H. W. Whitlock and B. K. Bower, *Tetrahedron Lett.*, **32**, 4827 (1965); D. W. Clack and N. S. Hush, *J. Amer. Chem. Soc.*, **87**, 4238 (1965).

atomic absorption spectroscopy and by the indophenol test, respectively.

Electrolysis at -0.5 V of [Co^{III}(tpps)] in the presence of Ar or air neither produced ammonia nor reduced the complex. However, a reduction at -1.3 V with passage of Ar during 20 hr produced [Co^{II}(tpps)], a 20% decrease in total porphyrin and cobalt concentration, and 0.3 mol of ammonia per atom Co. Under air or Ar:O_2 (4:1), the decrease in total porphyrin and cobalt concentrations was now 80%, but the yield of ammonia was 0.2 mol/atom Co. The major product of reduction under these conditions was a reduced nonmetallated derivative of the porphyrin (A) which absorbed at 322 nm and had a $E_{1/2}$ of -1.45 V. The free base (tpps) was also reduced at -1.3 V for 20 hr under both Ar and an Ar–O_2 mixture; however, A was not produced even though there was some degradation of the porphyrin and ammonia was detected (approximately 1 mol/mol porphyrin).

The cobalt(III) porphyrin was also electrolyzed at -1.5 V. Reduction of [Co^{III}(tpps)] with the passage of Ar during 20 hr produced [Co^{II}(tpps)], a 60% decrease in porphyrin and cobalt concentrations, and a negligible amount of NH_3 (0.01 mol/atom Co). When these reductions were carried out both under air or an Ar–O_2 mixture, the final solution did not contain any electroactive species; the degradation of the porphyrin and loss of cobalt from solution were 98% complete, and the yield of NH_3 increased to 0.05 mol/atom Co. During these last electrolyses it was observed that, after the initial 4–5 hr of reduction, another reduced species (B) was formed which, unlike A, did not have a characteristic spectrum but which could be reduced ($E_{1/2}$) at -1.45 V. Species B could not be formed by reducing (tpps) in the presence of Ar–O_2 at -1.5 V. This electrolysis did, however, completely degrade the porphyrin and produced three times more ammonia than the comparable reduction of [Co^{III}(tpps)].·

To confirm that A and B are partially reduced porphyrin derivatives, they were prepared by the electrolysis of [Co^{III}(tpps)] under Ar–O_2 mixture at -1.3 and -1.5 V, respectively. Then a second electrolysis was performed with the passage of Ar at -1.5 V which completely reduced A and B and produced ammonia in excess of the amount derived from the reduction of [Co^{III}(tpps)] under Ar at -1.5 V.

The degradation of the porphyrin does not appear to involve removal of cobalt from [Co^I(tpps)] by O_2 or a peroxo species, followed by reduction of the free porphyrin, since reduction of (tpps) in the presence of O_2 fails to produce either A or B. Furthermore, since