46.2; H, 5.50; N, 18.0. The infrared spectrum showed, apart from carbonyl peaks at 1942 and 1857 cm^{-1}, the NH band at 3398 cm^{-1}. The nmr spectrum clearly demonstrated presence of the $Et_2B(pz)_2$ ligand and of one additional pyrazole: s (broad) τ 1.30, d (unresolved) 2.02, d (J = 2.0 cps) 2.21, d (J = 2.4) 2.31, d (unresolved) 2.94, t (J = 2.2) 3.83, m 5.8, d (J = 7.0) 6.62, d (J = 9.5) 8.43, m ~9.1, and "d" at 9.66 in a 1:1:2:2:1:3:1:2:2:5:5 ratio. These were assigned to the NH, 3-H of pyrazole, 3-H's of ligand, 5-H's of ligand, 5-H of pyrazole, 4-H's of pyrazole and ligand, allylic 1-H, allylic 2-H, allylic 3-H, pseudoaxial ethyl, and pseudoequatorial ethyl, respectively. Compound IV could be obtained directly by treatment of IIIb with pyrazole.

Compound IIIb formed yellow complexes possessing inert-gas electronic configuration with other nucleophiles as well, as could be anticipated from its coordinate unsaturation. Failure of IIIa to form comparable complexes may be rationalized on steric grounds. A variety of other stereochemically nonrigid and coordinately unsaturated, yet surprisingly stable, compounds of the general structure III (*e.g.*, R = H, R′ = R″ = CH_3, mp 179–180°; R = H, R′ = CH_3, R″ = C_6H_5, mp 156–157°; R = H, R′ = C_2H_5, R″ = H, mp 104–105°; R = H, R′ = C_2H_5, R″ = C_6H_5, mp 91–92°) has been synthesized and identified similarly. Details of this work and the chemistry of such compounds will be the subject of subsequent publications.

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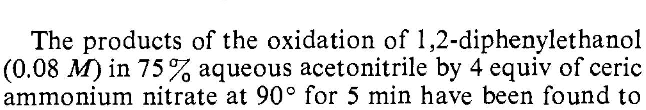
Oxidation of Organic Compounds with Cerium(IV). V. The Substituent Effect on the Rate of the One-Electron Oxidative Cleavage of 2-Aryl-1-phenylethanols[1]

Sir:

We have found that cerium(IV) quantitatively cleaves 1,2-diarylethanols to a benzaldehyde and products derived from the cleaved benzyl moiety. In this communication, we report results that show that this cleavage is a one-electron oxidation and establish the effect of substituted 2-phenyls on the rate of the cleavage reaction. We believe that this reaction is an excellent prototype for one-electron oxidation cleavages of alcohols.



The products of the oxidation of 1,2-diphenylethanol (0.08 *M*) in 75% aqueous acetonitrile by 4 equiv of ceric ammonium nitrate at 90° for 5 min have been found to be 60% benzaldehyde, 30% benzyl alcohol, and 10% benzyl nitrate by nmr and glpc analysis. Oxidation in the presence of 10% acrylamide leads to exclusive formation of benzaldehyde and a polymer with no benzyl alcohol or nitrate. Since acrylamide has been shown to be an effective radical trap,[2,3] these experiments clearly establish that the benzyl alcohol and nitrate arise from a cleaved benzyl radical.

The most reasonable mechanism for the cerium(IV) oxidation of 1,2-diarylethanols is that proposed for the cerium(IV) oxidation of other alcohols, namely the rapid formation of a 1:1 complex followed by slow decomposition of this complex.[4] The fact that the orange cerium(IV) solution turns red when mixed with a 1,2-diarylethanol supports the formation of a 1:1 complex.

$$\mathrm{Ce^{IV}} + \mathrm{ROH} \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} \text{complex} \xrightarrow[\substack{\text{rate}\\\text{determining}}]{k} \text{products} \qquad (1)$$

Competition experiments were carried out by oxidizing two 2-aryl-1-phenylethanols with ceric ammonium nitrate in 75% aqueous acetonitrile. The initial concentration of each alcohol was 0.08 *M* and that of the ceric ammonium nitrate was 0.16 *M*. After the oxidation, the amounts of unreacted alcohols were measured by glpc analysis.[5] With the assumptions that the mechanism of the cerium(IV) oxidation of 1,2-diarylethanols is that given by eq 1 and the equilibrium constants for complex formation are the same for all 1,2-diarylethanols, the relative rates of the decomposition of the complexes are given by eq 2[6] where X_0 and X_f are

$$k_X/k_Y = \frac{\log (X_0/X_f)}{\log (Y_0/Y_f)} \qquad (2)$$

the initial and final concentrations of alcohol X and Y_0 and Y_f are the initial and final concentrations of alcohol Y. The assumption that the equilibrium constants for complex formation are the same for all 1,2-diarylethanols is quite reasonable since we have found[7] that the equilibrium constants for complex formation between cerium(IV) and substituted benzyl alcohols are not very sensitive to electronic effects.

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[1] (a) Part IV: W. S. Trahanovsky, L. B. Young, and G. L. Brown, *J. Org. Chem.*, **32**, 3865 (1967); (b) this work was partially supported by Public Health Service Grant GM 13799 from the National Institute of General Medical Sciences; (c) based on work by P. M. N. in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University.

[2] G. Mino, S. Kaizerman, and E. Rasmussen, *J. Am. Chem. Soc.*, **81**, 1494 (1959). These workers quantitatively analyzed for acetone by an involved spectrophotometric method and carried out no control experiments to ascertain whether or not the high concentration of an amide affected the reaction. We essentially repeated their study[3] using bicyclohexyl-1,1′-diol which produced cyclohexanone which could be accurately analyzed directly by glpc methods that are now available and also carried out the oxidation in the presence of 10% acetamide. Our results agreed with their results, and the acetamide had no significant effect on the reaction.

[3] Unpublished work of W. S. Trahanovsky, L. H. Young, and M. H. Bierman.

[4] (a) W. H. Richardson in "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, pp 247–255, and references therein; (b) K. V. Rao and S. S. Muhammad, *Bull. Chem. Soc. Japan*, **36**, 943 (1963); (c) S. S. Muhammad and K. V. Rao, *ibid.*, **36**, 949 (1963); (d) M. Rangaswamy and M. Santappa, *Current Sci.* (India), **34**, 282 (1965); (e) B. Sethuram and S. S. Muhammed, *Acta Chim. Acad. Sci. Hung.*, **46**, 115, 125 (1965); (f) B. Sethuram, *Current Sci.* (India), **35**, 254 (1966); (g) M. Rangaswamy and M. Santappa, *ibid.*, **35**, 332 (1966); (h) H. L. Hintz and D. C. Johnson, *J. Org. Chem.*, **32**, 556 (1967).

[5] Benzophenone was used as an internal standard. Relative extraction and thermal conductivity ratios were corrected for by extracting and analyzing known amounts of 2-aryl-1-phenylethanols and standard from an artificial reaction mixture that had been prepared by the reduction of ceric ammonium nitrate in 75% aqueous acetonitrile by pinacol hydrate. All analyses were based on at least three independent runs.

[6] G. A. Russell and R. C. Williamson, Jr., *J. Am. Chem. Soc.*, **86**, 2357 (1964).

[7] Unpublished work of L. B. Young and W. S. Trahanovsky.

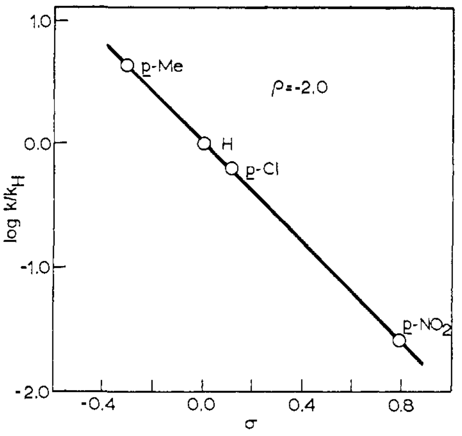

Figure 1. Plot of the logarithm of the relative rate of the cerium(IV) oxidation of 2-aryl-1-phenylethanols *vs.* σ^+ of the substituent of the 2-phenyl ring.

In Table I are presented the relative rates of cerium(IV) oxidation for four alcohols. Figure 1, which is a plot of the log of these rates against σ^+,[8] clearly shows that an excellent Hammett relationship with $\rho = -2.0$ exists for this reaction. Most radical reactions correlate better with σ^+ than with σ and give ρ's in the range of -0.69 to -1.46.[6,9] The relatively large negative ρ of -2.0 for the cerium(IV) oxidative cleavage of 2-aryl-1-phenylethanols indicates that a fair amount of positive charge is developed on the β carbon in the transition state that leads to cleavage. Nevertheless, a ρ of -2.0 is closer to those reported for radical reactions than the -5.0 range reported for cationic processes.[10]

Table I. Relative Rates of Cerium(IV) Oxidation of 2-Aryl-1-phenylethanols, $C_6H_5CHOHCH_2C_6H_5Z$, in 75% Aqueous Acetonitrile

Z	$k_{rel}{}^a$
p-CH_3	4.2 ± 0.4
H	(1.00)
p-Cl	0.63 ± 0.05
p-NO_2	0.027 ± 0.010

[a] Based on at least three runs. See ref 5 for method of analysis.

Competition experiments with 2-(*p*-methoxyphenyl)-, 2-(*m*-methoxyphenyl)-, and the 2-(*p*-acetamidophenyl)-1-phenylethanols were also carried out, but it was found that all of these alcohols were oxidized at least 100–1000 times faster than 2-(*p*-methylphenyl)-1-phenylethanol. Since the σ^+ for *m*-methoxy is close to that of hydrogen and *p*-chloro,[8] it is concluded that methoxy and acetamido substituents so activate the aromatic ring that a different mechanism must operate. A good possibility is the initial oxidation of the substituted benzene ring to a radical cation.[11]

Oxidative cleavages of alcohols by oxidants such as chromic acid and lead(IV) in addition to cerium(IV) have been reported.[12] A major question is whether these cleavages are one- or two-electron oxidations. For example, two-thirds of the products from the oxidation of secondary alcohols by chromic acid are cleavage products which are thought to result from a two-electron oxidation by chromium(V) or a one-electron oxidation by chromium(IV).[12a–d,g] Although cleavage by chromium(V) has been the favored mechanism,[12a–d] Roček and Radkowsky[12g] have recently presented firm evidence that the cleavage of cyclobutanol is a one-electron oxidation by chromium(IV) and suggest that all cleavages by chromic acid are one-electron oxidations by chromium(IV). The relative rate of oxidative cleavage of 2-aryl-1-phenylethanols that possess well-behaved substituents by oxidants other than cerium(IV) should provide a means of characterizing these cleavages as one- or two-electron processes. A one-electron oxidative cleavage should give a ρ of -2, but a two-electron process should give a more negative ρ. Experiments designed to establish this postulate and investigate other aspects of the cerium(IV) oxidation of 1,2-diarylethanols are in progress.

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(8) Values of σ^+ were obtained from H. C. Brown and Y. Okamota, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

(9) (a) P. D. Bartlett, *ibid.*, 82, 1756 (1960); (b) R. L. Huang and K. H. Lee, *J. Chem. Soc., C*, 935 (1966).

(10) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(11) (a) D. L. Allara, B. C. Gilbert, and R. O. C. Norman, *Chem. Commun.*, 319 (1965); (b) P. J. Andrulis, Jr., M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Am. Chem. Soc.*, **88**, 5473 (1966); (c) T. Aratani and M. J. S. Dewar, *ibid.*, **88**, 5479 (1966).

(12) (a) W. Watanabe and F. H. Westheimer, *J. Chem. Phys.*, **17**, 61 (1949); (b) R. Stewart, "Oxidation Mechanisms: Application to Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964; (c) K. B. Wiberg, Ed., "Oxidation in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965; (d) W. A. Mosher, W. H. Clement, and R. L. Hilliard in "Selective Oxidation Processes," Advances in Chemistry Series, No. 51, American Chemical Society, Washington, D. C., 1965, pp 81–88; (e) S. E. Schaafsma, H. Steinberg, and T. J. deBoer, *Rec. Trav. Chim.*, **85**, 73 (1966); (f) W. S. Trahanovsky, L. M. Smith, and P. J. Flash, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, No. S166; (g) J. Roček and A. E. Radkowsky, *J. Am. Chem. Soc.*, **90**, 2987 (1968).

(13) National Aeronautics and Space Administration Trainee, 1967–1968.

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Optical Properties of the *cis*-Vinyl Amide Chromophore

Sir:

Recent studies in these laboratories, concerned with the spectroscopic properties of tautomeric equilibria, have revealed a conjugated chromophoric system of unusual properties. We wish to report optical rotatory dispersion (ORD) and circular dichroic (CD) studies of Schiff base derivatives of 1-(*o*-hydroxylaryl)-butane-1,3-diones, **1** and **2**.[1,2] Large molecular rotations are observed for these derivatives, which may approach values comparable to the classic inherently dissymmetric chromophores.[3] For instance, **2b** exhibits $[\Phi]_D$ 4.3° × 10^3 (Table I) while hexahelicene[4]

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(1) Satisfactory elemental analyses and pmr, ultraviolet, and infrared spectral properties suitable for the assigned structures were obtained for all compounds. Ultraviolet spectra were taken on a Cary Model 14 UV-VIS spectrometer; ORD and CD curves were obtained on a Cary Model 60 spectropolarimeter equipped with a Cary Model 6001 CD accessory. Rotations at 589 mμ were determined on a Perkin-Elmer Model 141 automatic polarimeter. Compound **1a** has been previously characterized.[2]

(2) G. O. Dudek and E. P. Dudek, *Tetrahedron*, **23**, 3245 (1967).

(3) K. Mislow in "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," G. Snatzke, Ed., Heyden and Sons, Ltd., London, 1967, Chapter 10.

(4) M. S. Newman and D. Lednicer, *J. Am. Chem. Soc.*, **78**, 4765 (1956).