

The photochemical reaction involves the lowest energy TPE excited singlet state whereas the more energetic carbonium ion(s) intermediates are involved in the electrochemical oxidation. Despite different intermediates there were no differences apparent in the overall stoichiometry for the major TPE reaction. However, intramolecular coupling reactions are much

less important (and in some cases did not occur) when similar compounds giving carbonium ion radicals that are less stable than TPE⁺, e.g., triphenyl- and diphenylethylenes, were electrolyzed under the same conditions described above.⁸⁸

(38) J. D. Stuart and W. E. Ohnesorge, Abstract 128, The Electrochemical Society, New York, N. Y., May 1969.

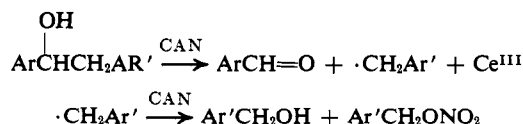
Oxidation of Organic Compounds with Cerium(IV). XI. Oxidative Cleavage of 1,2-Diarylethanols and 1-Aryl-2,3-diphenylpropan-2-ols by Cerium(IV) and Chromic Acid^{1,2}

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Abstract: The cerium(IV) oxidation of 1,2-diarylethanols in 75% aqueous acetonitrile and 85% aqueous acetic acid is shown to give only products of oxidative cleavage. Relative rates of oxidation of a series of 2-aryl-1-phenylethanols which were determined by competition experiments are reported. Plots of the log of these rates against σ^+ for the substituent of the 2-aryl group give ρ values of -2.00 ± 0.02 in 75% aqueous acetonitrile and -2.01 ± 0.04 in 85% aqueous acetic acid. Radical trapping experiments show that the benzyl radical is an intermediate in the reaction, and these results and the ρ values characterize the oxidative cleavage as a one-electron oxidation. Oxidations of 1-aryl-2,3-diphenylpropan-2-ols with either cerium(IV) or chromic acid are shown to give benzyl phenyl ketone and the substituted benzyl phenyl ketone, the expected products of oxidative cleavage. From the relative yields of the two ketones, the relative rates of cleavage of substituted benzyl radicals were obtained. These rates are correlated with the σ^+ for the substituent and give ρ values of -1.91 ± 0.01 and -1.01 ± 0.01 for the cerium(IV) and chromic acid oxidations, respectively. The latter ρ value compares well with the previously reported ρ value of -0.96 for the oxidative cleavage of 2-aryl-1-phenylethanols by chromic acid. These results indicate that these oxidative cleavages are one-electron oxidations and are consistent with our assumptions for the 2-aryl-1-phenylethanol series that the substituent effect on the equilibrium of alcohol-metal complex formation is very small and that for both oxidants, equilibrium complex formation is attained. That a free alkoxy radical is not formed in these oxidations is shown by the magnitude of the ρ values and their difference for the two oxidants. The different ρ values for the two oxidants must reflect differences in the transition state of the decomposition of the alcohol-metal complexes. Analysis of existing data suggests that for secondary alcohols the oxidative cleavage reaction is normally a one-electron oxidation and ketone formation is normally a two-electron oxidation.

In a preliminary communication^{2a} we have shown that the oxidative cleavage of 1,2-diarylethanols by ceric ammonium nitrate (CAN) is a one-electron process since the intermediate benzyl radical could be trapped, and the ρ for the reaction was -2.0 , which is closer to



(1) (a) Part X: W. S. Trahanovsky, L. B. Young, and M. D. Robbins, *J. Amer. Chem. Soc.*, **91**, 7084 (1969); (b) this work was partially supported by Public Health Service Grant GM 13799 from the National Institute of General Medical Sciences and Grant GP-18031 from the National Science Foundation. We thank these organizations for their support; (c) based on work by P. M. N. in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Iowa State University; (d) National Aeronautics and Space Administration Trainee, 1967-1969; (e) Alfred P. Sloan Research Fellow, 1970-1972.

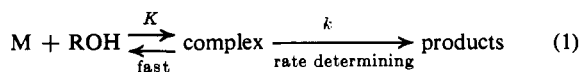
(2) Preliminary communications: (a) P. M. Nave and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **90**, 4755 (1968); (b) Abstracts of the Joint Chemical Institute of Canada-American Chemical Society Conference, Toronto, May 1970, PHYS 31.

the range of ρ 's reported for benzyl radical reactions, -0.3 to -1.5 ,³ than the -4.5 to -6.5 range⁴ reported for benzyl cation processes. Part of this publication is devoted to further details of this study. From a similar study of the oxidation of 1,2-diarylethanols by chromic acid, we concluded that the oxidative cleavage reaction brought about by chromic acid is also a one-

(3) (a) P. D. Bartlett and C. Ruchardt, *J. Amer. Chem. Soc.*, **82**, 1756 (1960); (b) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963); (c) G. A. Russell and R. C. Williamson, Jr., *J. Amer. Chem. Soc.*, **86**, 2357 (1964); (d) R. P. Gilliom and B. F. Ward, Jr., *ibid.*, **87**, 3944 (1965); (e) L. Huang and K. H. Lee, *J. Chem. Soc. C*, 935 (1966); (f) H. Sakurai and A. Hosomi, *J. Amer. Chem. Soc.*, **89**, 458 (1967); (g) H. Sakurai, A. Hosomi, and M. Kumada, *J. Org. Chem.*, **35**, 993 (1970).

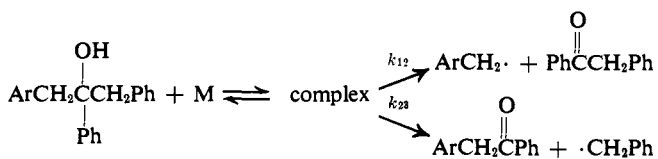
(4) (a) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); H. C. Brown and Y. Okamoto; (b) *J. Org. Chem.*, **22**, 485 (1957); (c) *J. Amer. Chem. Soc.*, **80**, 4979 (1958); (d) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *ibid.*, **89**, 370 (1967); (e) V. J. Shiner, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *ibid.*, **90**, 418 (1968); (f) D. S. Noyce and G. V. Kaiser, *J. Org. Chem.*, **34**, 1008 (1969); (g) E. A. Hill, M. L. Gross, M. Stasiewicz, and M. Manion, *J. Amer. Chem. Soc.*, **91**, 7381 (1969); (h) P. G. Gassman and A. F. Feniman, Jr., *ibid.*, **92**, 2549 (1970).

electron process which strongly supports chromium(IV) as the chromium species which leads to cleavage.⁵ As in the cerium(IV) oxidation, the intermediate benzyl radical could be trapped; however, the ρ for the oxidative cleavage was -1.06 instead of -2.0 . In both studies, the relative rates of cleavage of the various 2-aryl-1-phenylethanols were determined by competition studies which involve equations derived with the assumption that the mechanism of the oxidative cleavage involves formation of a complex followed by rate-



determining reaction of that complex as given by eq 1, and the assumption that the equilibrium constants for complex formation are the same for all 2-aryl-1-phenylethanols for a given metal ion. The latter assumption is quite reasonable since we have found⁶ that the formation constants for complexes between cerium(IV) and substituted benzyl alcohols are not very sensitive to electronic effects. A more serious question about using our equations to calculate relative rates is whether or not an equilibrium exists for complex formation. If this were not the case, the values for the calculated relative rates would reflect, to some extent, the first step of the reaction. Since the substituent effect for this first step would be smaller than that for the second step, the result would be that the calculated ρ value would be closer to zero. Thus one possible explanation of the fact that a smaller negative ρ value is obtained for cleavage with chromic acid than with cerium(IV) is that in the case of chromic acid, equilibrium is not obtained in complex formation. Another possible explanation is that the expression for relative rates derived with the assumption that 1:1 complexes are formed may not be valid due to complications introduced by chromate diesters.⁷ In order to determine whether or not these complications were affecting the results, a system was chosen for oxidation in which the competition involved two modes of cleavage within the same molecule, the 1-aryl-2,3-diphenylpropan-2-ol system (Scheme I). This publication reports the results

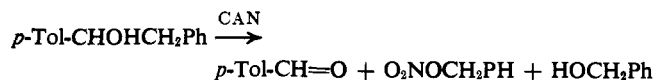
Scheme I



of this study in which both cerium(IV) and chromic acid were used as oxidants.

Results

The facile oxidation of 1-*p*-tolyl-2-phenylethanol with CAN in aqueous acetonitrile produces a high yield of *p*-tolualdehyde, benzyl nitrate, benzyl alcohol, and benzaldehyde. When the oxidation is carried out under nitrogen, no benzaldehyde is produced. None of the corresponding ketone, benzyl *p*-tolyl ketone, was detected either by nmr or glpc analysis. That the



ketone could not have been a transient intermediate was shown by the fact that the oxidation of deoxybenzoin was very slow and gave a large amount of product which was not found in the oxidation of 1,2-diphenylethanol. The glpc peak of this product was enhanced by the addition of benzil, but no other attempts to identify the product were made. Thus, the CAN oxidation of 1,2-diarylethanols gives exclusively cleavage products.

In order to help establish the intermediacy of the benzyl radical, the oxidation of 1-*p*-tolyl-2-phenylethanol was carried out in the presence of known radical traps, acrylamide and oxygen.⁸ The relative yields of the products of these reactions based on nmr analysis are given in Table I. It is seen that in the

Table I. Relative Yields of Products for Radical Trapping Experiments in the CAN Oxidation of 1-*p*-Tolyl-2-phenylethanol^a

| Additive | Tolu-aldehyde | Benz-aldehyde | Benzyl nitrate | Benzyl alcohol |
|-------------------|---------------|---------------|----------------|----------------|
| None | 1.00 | | 0.89 | 0.16 |
| Acrylamide (5 g) | 1.00 | | 0.58 | 0.15 |
| Acrylamide (25 g) | 1.00 | | 0.54 | 0.13 |
| Oxygen | 1.00 | 1.00 | | 0.13 |

^a In 40 ml of a 75% aqueous acetonitrile solution at 85°.

presence of acrylamide, the yield of products from the benzyl moiety is significantly reduced relative to the *p*-tolualdehyde produced. Oxygen was found to be a more effective trap. No benzyl nitrate was found, but a high yield of benzaldehyde and a small amount of benzyl alcohol were recovered. Both of these products could be expected as decomposition products of the benzylperoxy radical.⁹ The benzaldehydes could have been partially converted by the oxygen to the corresponding benzoic acids which would not have been detected since acidic materials were removed from the products during work-up.

Competition experiments were carried out by oxidizing two 2-aryl-1-phenylethanols with a limited amount of CAN. The initial concentration of each alcohol was 0.08 *M* and that of the CAN was 0.16 *M*. After the oxidation, the amounts of unreacted alcohols were measured by glpc analysis using an internal standard. With the assumptions that the mechanism of the cerium(IV) oxidation of 1,2-diarylethanols is that given by eq 1 and that there is a negligible effect on the equilibrium constants for complex formation by a substituent on the 2-aryl ring, the relative rates of the decomposition of the complexes are given by eq 2 where

$$k_x/k_y = \frac{\log(X_0/X_f)}{\log(Y_0/Y_f)} \quad (2)$$

X_0 and X_f are the initial and final concentrations of alcohol X and Y_0 and Y_f are the initial and final concentrations of alcohol Y.

Aqueous acetonitrile was used as the solvent for the initial competition studies with CAN, but could not be

(5) P. M. Nave and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **92**, 1120 (1970).

(6) L. B. Young and W. S. Trahanovsky, *ibid.*, **91**, 5060 (1969).

(7) K. B. Wiberg and H. Schäfer, *ibid.*, **91**, 933 (1969).

(8) See ref 5 and references cited therein.

(9) G. A. Russell, *J. Amer. Chem. Soc.*, **79**, 3871 (1957).

used with chromic acid since chromic acid is unstable in acetonitrile solutions. Consequently, the relative rates of cerium(IV) oxidation of most of the 2-aryl-1-phenylethanols were redetermined in 85% aqueous acetic acid. In Table II, the relative rates of oxidation

Table II. Relative Rates of Cerium(IV) Oxidation of 2-Aryl-1-phenylethanols, $C_6H_5CHOHCH_2C_6H_4Z$, in 75% Aqueous Acetonitrile and 85% Aqueous Acetic Acid

| Z | k_{rel} , 75% aq acetonitrile | k_{rel} , 85% aq acetic acid |
|---------------------------|------------------------------------|-----------------------------------|
| <i>p</i> -CH ₃ | 4.2 ± 0.4 | 4.1 ± 0.2 |
| H | (1.00) | (1.00) |
| <i>p</i> -Cl | 0.63 ± 0.05 | 0.57 ± 0.005 |
| <i>p</i> -NO ₂ | 0.027 ± 0.010 | |

of 2-aryl-1-phenylethanol by CAN in the two solvent systems are presented. Plots¹⁰ of the log of the relative rates against σ^+ ¹¹ for the substituent of the 2-phenyl ring give a ρ of -2.00 ± 0.02 for the 75% aqueous acetonitrile data and -2.01 ± 0.04 for the 85% aqueous acetic acid data. Thus, there was no significant solvent effect on the substituent affect.

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,¹¹ it is concluded that methoxy and acetamido substituents so activate the aromatic ring that a different mechanism must operate. In a study of the chromic acid oxidation of substituted toluenes, the methoxy group could not be used as a substituent since it facilitates attack of the aromatic nucleus.¹² One possibility for the mode of attack of the aromatic ring is an electron-transfer oxidation to give a radical cation. Such a process has been proposed for the lead tetraacetate–boron trifluoride oxidation of anisole and *N,N*-dimethylaniline¹³ and for the manganese(III) oxidation of alkoxytoluenes.¹⁴

Oxidations of 1-aryl-2,3-diphenylpropan-2-ols with both cerium(IV) and chromic acid were carried out in 85% aqueous acetic acid. Oxidation by cerium(IV) appeared to be slower than for the 1,2-diarylethanols. Oxidative cleavage of a tertiary alcohol by chromic acid requires the presence of a primary or secondary alcohol to produce the lower oxidation state of chromium which is responsible for cleavage. Secondary alcohols were found to react so much more rapidly than the 1-aryl-2,3-diphenylpropan-2-ols that they were completely oxidized without any concurrent oxidation of the 1-aryl-2,3-diphenylpropan-2-ols. Oxidation of 1-aryl-2,3-diphenylpropan-2-ols was achieved by inducing oxidation with an excess of 1-propanol along with a proportional amount of chromic acid.

Based on the mechanism given in Scheme I, where k_{12} and k_{23} are the rate constants of C₁–C₂ and C₂–C₃

cleavage, respectively, the relative rate of these constants, k_{12}/k_{23} , is equal to the ratio of the two ketones produced, $[Kt_{12}]/[Kt_{23}]$, where Kt_{12} represents the ketone produced from C₁–C₂ cleavage, and Kt_{23} represents the ketone produced from C₂–C₃ cleavage. The relative yields of the two ketones were easily and accurately determined by measuring the areas of the nmr signals of the methylenes of the two ketones. The relative rates of C₁–C₂ and C₂–C₃ cleavage by cerium(IV) and chromic acid for the *p*-methyl- and *p*-chloro-1-aryl-2,3-diphenylpropan-2-ols are given in Table III.

Table III. Relative Rates of C₁–C₂ and C₂–C₃ Cleavage in the Oxidation of 1-Aryl-2,3-diphenylpropan-2-ols, $ZC_6H_4CH_2C(C_6H_5)_2OH$, by Cerium(IV) and Chromic Acid^a

| Z | k_{12}/k_{23} for cerium(IV) | k_{12}/k_{23} for chromic acid |
|---------------------------|-----------------------------------|-------------------------------------|
| <i>p</i> -CH ₃ | 3.93 | 2.00 |
| | 3.85 | 2.02 |
| <i>p</i> -Cl | 0.614 | 0.769 |
| | 0.616 | 0.757 |

^a In 85% aqueous acetic acid at 85°.

Plots of the log of these relative rates against σ^+ for the substituent of the 1-aryl ring give ρ values of -1.91 ± 0.01 and -1.01 ± 0.01 for the cerium(IV) and chromic acid oxidations, respectively.

Discussion

The trapping experiments and substituent effects show that the oxidative cleavage of 1,2-diarylethanols and 1-aryl-2,3-diphenylpropan-2-ols by cerium(IV) and chromic acid are one-electron oxidations. As previously noted⁵ chromium(IV) is the chromium species most likely responsible for the cleavage reaction.

The ρ values for the cerium(IV) oxidation of 2-aryl-1-phenylethanols and 1-aryl-2,3-diphenylpropan-2-ols, -2.01 and -1.91 , respectively, compare quite well as do the ρ values for the chromic acid oxidation of these alcohols, which are -0.96 and -1.01 , respectively. These results are consistent with our assumptions for the 2-aryl-1-phenylethanol series that the substituent effect on the equilibrium complex formation is very small and that in both cases, equilibrium complex formation is attained. That a free alkoxy radical is not formed in these oxidations is shown by the magnitude of the ρ values and their difference for the two oxidants.

In all cases, except the chromic acid oxidation of 2-aryl-1-phenylethanols,⁵ better correlations with σ^+ than with σ were obtained. In the chromic acid oxidation of 2-aryl-1-phenylethanols, the correlations with both constants were about equally good.⁵ The relative rates of the 1-aryl-2,3-diphenylpropan-2-ols are no doubt more accurate since they are based on a single measurement. Thus, the rates of metal ion oxidative cleavages seem to be correlated better by σ^+ than σ . The mechanism of the cleavage of 1,2-diarylethanols by both oxidants can be represented by Scheme II. The negative ρ and the better correlations with σ^+ suggest that a fairly large amount of positive character develops on the benzylic carbon atom.³ This is reasonable since the metal ion should be able to polarize the electron distribution of the transition state so that the benzylic carbon atom is partially positive.

(10) See Figure 1 of ref 2a.

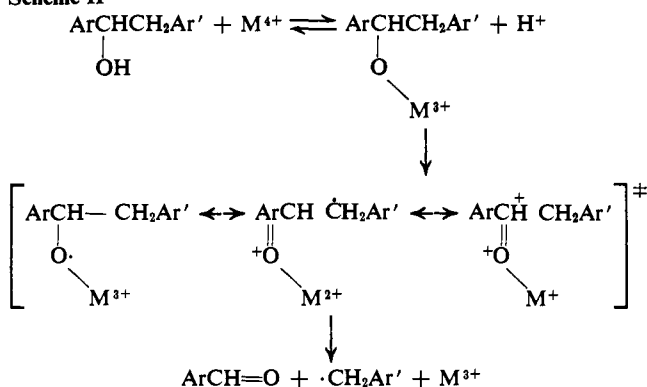
(11) Values of σ and σ^+ were obtained from ref 4c.

(12) H. C. Duffin and R. B. Tucker, *Tetrahedron*, **23**, 2803 (1967).

(13) D. L. Allara, B. C. Gilbert, and R. O. C. Norman, *Chem. Commun.*, 319 (1965).

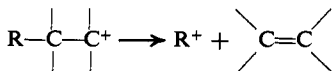
(14) (a) P. J. Andrusis, Jr., M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Amer. Chem. Soc.*, **88**, 5473 (1966); (b) J. R. Gilmore and J. M. Mellor, *Chem. Commun.*, 507 (1970).

Scheme II

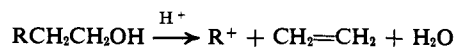


The different ρ values for the cerium(IV) cleavage and the chromic acid cleavage clearly indicate that the ρ of an oxidative cleavage reaction is a function of the specific oxidant used to bring about the cleavage. The different ρ values cannot be due to differences involving the complexation step since the same results were obtained by internal competitions. Thus, the differences in cleavage by the two oxidants must lie in the transition state of complex decomposition. Several interrelated factors may be important here, such as the oxidation potentials of the two metals under these conditions and the effective charge on the metal ion.

For both cerium(IV) and chromic acid, the oxidative cleavages are one-electron oxidations. The favored mode of reaction for cerium(IV) seems to be as a one-electron oxidant, and, indeed, oxidative cleavage is the exclusive pathway for the cerium(IV) oxidation of a variety of alcohols.¹⁵ In chromic acid oxidations, both one- and two-electron oxidations can occur. In the chromic acid oxidation of a secondary alcohol which can undergo a cleavage reaction to give a relatively stable radical, both ketone formation and cleavage occur with ketone formation being a two-electron process and cleavage a one-electron process.⁵ Thus, in the two-electron oxidation, proton elimination is so favored over cation fragmentation that the latter does not occur. Even in the case of tertiary alcohols, where there can be no competition from an α -proton elimination, the reaction proceeds *via* elimination of water followed by oxidation of the olefin.¹⁶ Thus, a two-electron cleavage seems to be a rather unfavored process. Fragmentations of cations have



been reported for reactions which proceed through "hot" carbonium ions¹⁷ or give extremely stable carbonium ions.¹⁸ However, cleavage is not a very facile reaction as illustrated by the fact that under given acidic conditions, 2-(9-xanthy)ethanol will fragment to give ethylene but 2-tritylethanol will not.¹⁹ Also,



(15) (a) W. S. Trahanovsky, L. H. Young, and M. H. Bierman, *J. Org. Chem.*, **34**, 869 (1969); (b) W. S. Trahanovsky, P. J. Flash, and L. M. Smith, *J. Amer. Chem. Soc.*, **91**, 5068 (1969).

(16) (a) W. F. Sager, *ibid.*, **78**, 4970 (1956); (b) J. Roček, *Collect. Czech. Chem. Commun.*, **25**, 375 (1960).

(17) P. S. Skell and P. H. Reichenbacher, *J. Amer. Chem. Soc.*, **90**, 2309 (1968).

(18) D. Bethell and V. Gold, "Carbonium Ions," Academic Press, New York, N. Y., 1967, pp 200-204.

(19) N. C. Deno and E. Sacher, *J. Amer. Chem. Soc.*, **87**, 5120 (1965).

cleavages of carbonium ions of bicyclic systems which can release strain energy and go to a stable cation upon cleavage have been reported.^{18,20,21} Fragmentations to give cations which are stabilized by an adjacent atom such as nitrogen or oxygen, which has a non-bonding pair of electrons, are well known.^{18,22,23} Again, the unusual stability of the fragmented cations seems to be necessary for two-electron cleavage to occur.

Since the cleavage reaction seems to be the favored pathway for one-electron oxidations even if a free radical of only modest stability can be formed,^{15b} it is likely that metal ion oxidative cleavages for most monohydric alcohols are one-electron processes except in those cases which proceed *via* elimination of water followed by oxidation of the olefin. Thus, oxidative cleavage of phenyl-*tert*-butylcarbinol, which has been reported as one pathway for lead tetraacetate,²⁴ chromic acid,²⁵ and permanganate,²⁶ and is the only pathway for the known one-electron oxidants,²⁷ is most likely in all cases a one-electron process leading to the *tert*-butyl radical and benzaldehyde. In the case of permanganate the lower intermediate manganese ions may be responsible for cleavage.

The pathway of the oxidative cleavage of diols is less certain. A one-electron fragmentation has been established, but two-electron fragmentations may also occur.^{15a} The finding that a tertiary α -hydroxy cation, which would be the fragment of a two-electron oxidation, can be ejected from carbonium ions^{22,23} makes the two-electron fragmentation of diols a reasonable possibility.

Experimental Section

Methods and Materials. Most methods and materials have been previously reported.⁵ Ceric ammonium nitrate was obtained from G. F. Smith. For glpc analysis, a 5 ft \times 0.25 in. 20% SE-30 column was used.

1-Phenyl-2-*p*-methoxyphenylethanol. *p*-Methoxybenzyl phenyl ketone was prepared by the method of Jenkins:²⁸ mp 89-92° (lit.²⁸ mp 89-92°); nmr (CDCl₃) δ 7.9 (m, 2), 7.3 (m, 7), 4.08 (s, 2), and 3.7 (s, 3). To a 15% solution (0.5 g in 33 ml) of sodium borohydride in methanol was added 6 g of the ketone dissolved in 50 ml of methanol, and the solution was stirred at room temperature overnight. The reaction mixture was concentrated and extracted with ether. The ether extract was dried (MgSO₄) and concentrated, and the residue was recrystallized from hexane to give 5.4 g (90%) of 1-phenyl-2-*p*-methoxyphenylethanol: mp 60-61° (lit.²⁸ mp 61°); nmr (CDCl₃) δ 7.3 (s, 5), 6.9 (m, 4), 4.8 (t, 1, J = 6.5 Hz), 3.75 (s, 3), 2.93 (d, 2, J = 6.5 Hz), and 1.95 (broad s, 1).

1-Phenyl-2-*m*-methoxyphenylethanol. *m*-Methoxybenzaldehyde was converted to *m*-methoxybenzyl alcohol by reduction with lithium aluminum hydride. The alcohol was converted to the chloride by treatment with thionyl chloride.²⁹ The Grignard reagent was then prepared from 15 g of the *m*-methoxybenzyl

(20) P. G. Gassman and J. G. Macmillan, *ibid.*, **91**, 5527 (1969).

(21) R. Baker, T. J. Mason, and J. C. Salter, *Chem. Commun.*, 509 (1970).

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(28) S. S. Jenkins, *J. Amer. Chem. Soc.*, **54**, 1155 (1935).

(29) J. W. Cornforth and R. J. Robinson, *J. Chem. Soc.*, 686 (1942).

chloride and added to 9.0 g of benzaldehyde as described by Alderová and Protiva.³⁰ The mixture was hydrolyzed with 20% ammonium chloride solution and extracted with ether. The ether extract was dried (MgSO₄) and concentrated to give a yellow oil which was then separated into several fractions by distillation under vacuum. The fractions that contained the desired product as indicated by their nmr spectra were combined and chromatographed on a silica gel column using first benzene, then 10% ether in benzene as eluents. The fractions containing the alcohol were collected and concentrated to give 0.7 g of 1-phenyl-2-*m*-methoxyphenylethanol: nmr (CCl₄) δ 7.2–6.6 (m, 9), 4.67 (t, 1, *J* = 6.0 Hz), 3.63 (s, 3), 2.83 (d, 2, *J* = 6.0 Hz), and 2.15 (broad s, 1).

1-Phenyl-2-*p*-acetamidophenylethanol. *p*-Aminobenzyl phenyl ketone was prepared by the catalytic hydrogenation of *p*-nitrobenzyl phenyl ketone⁹ using platinum in 95% ethanol. The crude product was recrystallized from methylene chloride and ether: mp 98–100°; nmr (CDCl₃) δ 8.0–7.4 (broad m, 5), 6.8 (m, 4), 4.12 (s, 2), and 3.50 (s, 2). The amino compound was acetylated with acetic anhydride. To a suspension of 2 g of *p*-acetamidobenzyl phenyl ketone in 50 ml of ethanol was added 10 ml of 10% sodium borohydride in ethanol. The mixture was stirred for 2 hr in which time the color changed from violet to clear and the solution became homogeneous. The solution was concentrated and extracted with ether. The ether extract was concentrated and the residue recrystallized from ether to give 1.5 g of a white powdery precipitate: mp 134–136°; nmr (CDCl₃) δ 7.35–7.00 (broad m, 10), 4.82 (t, 1, *J* = 5.5 Hz), 2.97 (d, 2, *J* = 5.5 Hz), 2.13 (s, 3), and 2.07 (s, 1).

Anal. Calcd for C₁₆H₁₇NO₂: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.34; H, 6.74; N, 5.30.

***p*-Methylbenzyl phenyl ketone** was prepared by the method of Corey and Schaefer³¹ and recrystallized from methylene chloride and ether to give a 23.5% yield of *p*-methylbenzyl phenyl ketone: mp 95–96° (lit.³² mp 96.3–97.5°); nmr (CDCl₃) δ 8.1–7.2 (m, 4), 7.1 (s, 5), 4.1 (s, 2), and 2.1 (s, 3).

1-*p*-Chlorophenyl-2,3-diphenylpropan-2-ol. To a stirred mixture of 3.4 g of magnesium turnings in 200 ml of ether was added 10.6 g (0.066 mol) of α,*p*-dichlorotoluene. Some heating was necessary to initiate the reaction. To the Grignard reagent, a solution of 12.9 g (0.066 mol) of deoxybenzoin²⁸ in 50 ml of ether was added very slowly. At the point of entry of a drop of the ketone solution into the reaction mixture, a red color formed. When this red color no longer appeared, the addition of the ketone was ceased. The reaction mixture was stirred an additional 45 min, and hydrolyzed with 250 ml of 20% aqueous ammonium chloride solution. The ether layer was separated, washed with 50 ml of saturated sodium chloride (saturated NaCl) solution, dried (MgSO₄), and concentrated. The residue was recrystallized from methylene chloride and hexane to give 3.9 g (18.4%) of the alcohol: mp 76–77°; nmr (CDCl₃) δ 7.3–6.8 (broad m, 14), 3.2 (m, 4), and 1.8 (broad s, 1).

Anal. Calcd for C₂₁H₁₉ClO: C, 78.10; H, 5.93; Cl, 14.37. Found: C, 78.28; H, 6.08; Cl, 14.42.

1-*p*-Tolyl-2,3-diphenylpropan-2-ol. The same procedure was used as for 1-*p*-chlorophenyl-2,3-diphenylpropan-2-ol, using 9.9 g (0.066 mol) of α-chloro-*p*-xylene to give 2.0 g (10%) of product: mp 58–59°; nmr (CDCl₃) δ 7.4–6.8 (broad m, 14), 3.2 (m, 4), 2.4 (s, 3), and 1.8 (broad s, 1).

Anal. Calcd for C₂₂H₂₃O: C, 87.38; H, 7.33. Found: C, 87.05; H, 7.04.

Product Study of the CAN Oxidation of 1-*p*-Tolyl-2-phenylethanol. To 8 ml of a 0.25 *M* solution of CAN in 50% aqueous acetonitrile was added 0.212 g (1 mmol) of 1-*p*-tolyl-2-phenylethanol. The solution was heated on a steam bath for several minutes until the red color disappeared. To the cooled reaction mixture was added 8 ml of ether. The ether extract was dried (MgSO₄) and the products were analyzed by glpc with the column at 150°. The four product peaks were enhanced by samples of benzaldehyde, benzyl alcohol, *p*-tolualdehyde, and benzyl nitrate.

The only remaining glpc peak was enhanced with starting material. The ether extract was concentrated and the residue was dissolved in deuteriochloroform and analyzed by nmr. The new spectrum confirmed the presence of the four products and starting material. No acidic protons were observed by nmr. Neither the glpc nor nmr analysis showed the presence of benzyl *p*-tolyl ketone.

CAN Oxidation of Deoxybenzoin. Deoxybenzoin was oxidized in the same manner as was 1-*p*-tolyl-2-phenylethanol. The reaction proceeded very slowly relative to the alcohol oxidation. Analysis by glpc gave peaks which were enhanced by starting material and benzil and peaks corresponding to traces of cleavage products.

Competitive Oxidations of 2-Aryl-1-phenylethanols by CAN in Aqueous Acetonitrile. To 5 ml of 75% aqueous acetonitrile was added 0.40 mmol of one of the 2-aryl-1-phenylethanols, 0.40 mmol of 1,2-diphenylethanol, and 0.8 mmol of CAN. After the solution was heated on a steam bath for 20 min and cooled, 0.20 mmol of standard, benzophenone, was added. The solution was diluted with 10 ml of saturated NaCl solution and extracted with 10 ml of ether. The ether layer was dried (MgSO₄) and analyzed by glpc with the column initially at 180° and raised to 300° at a rate of 20°/min. The amount of each alcohol present in the reaction mixture was determined by making use of relative extraction ratios and thermal conductivities which were measured as follows. To an artificial reaction mixture that had been prepared by reducing 20 ml of a 75% aqueous acetonitrile solution that contained 0.40 mmol of CAN with 0.40 mmol of pinacol hydrate was added 0.20 mmol quantities of each alcohol and the standard. These solutions were worked up and analyzed by glpc in the same manner as the reaction mixtures. The relative extraction ratios and thermal conductivities ranged from 0.90 to 1.12.

Competitive Oxidations of 2-Aryl-1-phenylethanols by CAN in Aqueous Acetic Acid. The procedures for these studies in 85% aqueous acetic acid were the same as those for the studies in aqueous acetonitrile. The reaction mixtures were heated just long enough for the color to change since prolonged heating produced the acetates of the starting alcohols. The relative extraction ratios and thermal conductivities ranged from 0.94 to 1.06.

Radical Trapping Experiments. Acrylamide. Nitrogen was passed through 40 ml of a 75% aqueous acetonitrile solution that contained 0.212 g (1.0 mmol) of 1-*p*-tolyl-2-phenylethanol and 5 g of acrylamide. The mixture, under nitrogen, was heated on a steam bath and stirred as a solution of 0.877 g (1.6 mmol) of CAN in 10 ml of 75% aqueous acetonitrile was added slowly. A large amount of polymeric material was produced. After the oxidation, 150 ml of saturated NaCl solution was added and the mixture was extracted with 50 ml of ether. The ether extract was washed twice with 1 *M* sodium hydroxide solution, dried (MgSO₄), and concentrated. In a similar experiment, 25 g of acrylamide was used and the CAN solution was added rapidly. A control run was carried out in which conditions were identical except that no acrylamide was added.

Oxygen. This experiment was carried out under the same conditions as the acrylamide trapping control experiment except that oxygen was passed through the system during the reaction.

Oxidation of 1-Aryl-2,3-diphenylpropan-2-ols with CAN. To 7.5 ml of 85% aqueous acetic acid was added 0.8 mmol of the 1-aryl-2,3-diphenylpropan-2-ol and 0.877 g (1.6 mmol) of CAN. After the solution was heated on a steam bath for 10 min and cooled, it was made 0.5 *M* in sodium acetate by the addition of sodium acetate in order to obtain a medium similar to that for which extraction ratios for the substituted benzyl phenyl ketones had been determined.⁵ The work-up was as usual for the 85% aqueous acetic acid oxidations. The ratio of the two ketones produced was determined by the nmr expansion method used for the competitive chromic acid oxidations of 2-aryl-1-phenylethanols.⁵

Oxidation of 1-Aryl-2,3-diphenylpropan-2-ols with Chromic Acid. To a solution of 0.6 g (6 mmol) of chromium trioxide in 40 ml of 85% aqueous acetic acid was added 0.4 mmol of one of the 1-aryl-2,3-diphenylpropan-2-ols. The mixture was heated on a steam bath and to it was added dropwise a solution of 0.24 g (4 mmol) of 1-propanol in 10 ml of 85% aqueous acetic acid. The reaction mixture was green after all the propanol had been added. The solution was made 0.5 *M* in sodium acetate and worked up and analyzed by nmr as were the reaction mixtures from the CAN oxidations.

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