# Metal-Ion Oxidative Decarboxylations. 10.[1] Substituent Effects in the Cerium(IV)–Benzilic Acids Reaction

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*Received July 27, 1976*

The rates of oxidation by cerium(IV) of several substituted benzilic acids (unsubstituted, 2,2′-dichloro, 4,4′-dichloro, 4,4′-dimethyl, 4,4′-dimethoxy, and 4,4′-dinitro) to the corresponding benzophenones have been studied spectrophotometrically in aqueous $H_2SO_4$, aqueous $HClO_4$–HOAc, and acetonitrile. The rates are much slower in $H_2SO_4$ than in the other two media, probably because of heavy sulfato complexation of cerium(IV). The p$K_a$s of the various acids were determined potentiometrically. The Hammett $\rho$ values in acetonitrile and $HClO_4$–HOAc media, derived from correlations with several sets of $\sigma$ constants and with the newly determined p$K_a$s, are about −0.7 and −0.35 in the two media, respectively. These values rule out the possibility of positive charge development at the benzhydrilic carbon, at or prior to the rate-determining step. Instead, a mechanism involving free (?) radicals is proposed.

Many substituted benzilic acids and their esters are known for their analgesic and physiological activities and have, accordingly, been subjected to detailed pharmacological studies.[2] The ethyl and isopropyl esters of 4,4′-dichlorobenzilic acid are used as pesticides and their degradation products are believed to contribute to water pollution and to increasing environmental hazards.[3,4] Aside from these and similar studies, the literature on the chemistry of substituted benzilic acids is scarce. On the other hand, unsubstituted benzilic acid itself has been, alone or included with other $\alpha$-hydroxy acids, the subject of several studies involving metal-ion oxidations.[5–7] In the preceding paper, we reported on the cerium(IV) oxidation of benzilic acid in acidic perchlorate and sulfate media,[8] and realized the need for information regarding the effect of substituents on the oxidative decarboxylations of substituted benzilic acids. Such information is expected to yield valuable clues pertaining to the structure of the transition state (free-radical vs. carbocationic character) and to the mode of action of the oxidizing agent (one-electron vs. two-electron oxidation).[9] In this paper, we report the results of a kinetic and mechanistic study of the cerium(IV) oxidation of benzilic, 2,2′-dichloro-, 4,4′-dichloro-, 4,4′-dimethyl-, 4,4′-dimethoxy-, and 4,4′-dinitrobenzilic acids in several media.

## Experimental Section

**Materials.** Aniline, 4,4′-dimethylbenzil, 4,4′-dimethoxybenzil (anisil), and 4,4′-dichlorobenzophenone were obtained from Aldrich Chemical Co. Benzil was from Matheson Coleman and Bell Co. Benzilic acid, *p*-chlorobenzaldehyde, and bis(*p*-nitrophenyl)methane were Eastman White Label; 2,2′-dichlorobenzilic acid was from ICN-K & K Laboratories; nitric acid (90%, *d* 1.5) was from J. T. Baker Chemical Co. Cerium(IV) perchlorate (0.5 M in 6 M perchloric acid), iron(II) ammonium sulfate, perchloric acid (70%, lead-free, double vacuum distilled) and sodium perchlorate were from G. Frederick Smith Chemical Co. Cerium(IV) sulfate was from Merck, and cerium(IV) ammonium nitrate (CAN) was from Fisher Scientific Co. Glacial acetic acid was from Mallinckrodt.

**Syntheses.** 4,4′-Dimethylbenzilic acid was prepared by reacting the corresponding benzil with potassium ethoxide (metallic potassium in ethanol) in $EtOH–Et_2O$ mixture for 24 h at 0 °C with exclusion of air.[10] Acidification of the reaction mixture to pH 4 gave a precipitate which, after recrystallization from benzene–petroleum ether, was identified as *p*-toluic acid, mp 177–179 °C, $\lambda_{max}$ (MeOH) 237 nm.[11] Lowering the acidity of the filtrate to pH 2 brought about a second precipitate which, after recrystallization from hot water and drying under vacuum, had mp 132–134 °C.[12] 4,4′-Dimethoxybenzilic (anisilic) acid was prepared by the benzilic acid rearrangement of anisil effected by potassium hydroxide in refluxing *n*-butyl alcohol[13] After purification and recrystallization from *n*-heptane–ethyl acetate, anisilic acid had mp 156–158 °C[14] 4,4′-Dichlorobenzilic acid was prepared from *p*-chlorobenzaldehyde via the benzoin condensation. The corresponding benzil, obtained by oxidation of the benzoin with nitric acid (*d* 1.38) in glacial acetic acid and recrystallized from benzene, had mp 198–199 °C.[15] The benzilic acid rearrangement was effected by a refluxing solution of KOH in *n*-butyl alcohol. The potassium salt of the acid was acidified; redissolution in $NaHCO_3$ solution and reprecipitation gave the desired acid which, after recrystallization from *n*-heptane, had mp 101–102 °C.[16] 4,4′-Dinitrobenzilic acid was prepared by nitration of benzilic acid with white fuming nitric acid (*d* 1.5).[17] The material was purified through the formation of the anilinium salt (mp 140–142 °C dec) and reliberation of the acid which, after recrystallization from *n*-heptane–ethyl acetate, gave colorless crystals, mp 170–173 °C dec.[18]

Spectral analyses of the benzilic acids were conducted on a JEOL-D100 mass spectrometer, Perkin-Elmer 180 and 137 infrared spectrometers, Varian EM-360 NMR, and Beckman DK-2A UV-visible spectrophotometer. The spectral characteristics are summarized in Table I.

**p$K_a$ Measurements.** These were done by potentiometric titrations of the benzilic acids (mostly in 1% $EtOH–H_2O$) with $Ba(OH)_2$ which had been standardized against potassium hydrogen phthalate. A Corning Digital-112 research pH meter equipped with a Fisher combination electrode was used for the determinations which were carried out at 25 °C. Neutralization equivalents and p$K_a$ values were first evaluated graphically. The p$K_a$ values were further checked by computation using the equation[19]

$$\mathrm{p}K_a = \mathrm{pH} + \log\frac{C_a - C_s - [\mathrm{H}^+]}{C_s + [\mathrm{H}^+]} + \frac{0.509\sqrt{C_a}}{1 + \sqrt{C_a}}$$

where

$$C_a = n_A/(V_A + X)$$
$$C_s = XC_b/(V_A + X)$$
$$[\mathrm{H}^+] = 10^{-\mathrm{pH}}$$

$n_A$: moles of benzilic acid
$V_A$: initial volume of the benzilic acid solution
$X$: volume of added base solution
$C_b$: initial normality of base
$C_a$: concentration of acid
$C_s$: concentration of base

A summary of the p$K_a$ values and the neutralization equivalents appears in Table II.

**Solutions.** Electrolytically prepared cerium(IV) perchlorate solutions were prepared as described previously.[8,20] They were mixed with the appropriate amounts of glacial acetic to obtain 49.5% (wt) solutions. The Ce(IV) concentration was determined by titration with iron(II) ammonium sulfate. The benzilic acids were first dissolved in glacial acetic acid and then diluted with water to 49.5% (wt) acetic acid.

In experiments where CAN was used, the oxidizing agent and the benzilic acids were dissolved separately in acetonitrile. Only freshly prepared solutions were used for rate measurements.

**Kinetics.** Rate measurements were conducted spectrophotometrically under conditions where the benzilic acid's concentration was in excess of the cerium(IV) concentration. With the exception of a few slow runs which were carried out on a Beckman DK-2A most of the kinetic runs were performed on a Durrum-Gibson stopped-flow apparatus equipped with a photometric log amplifier and interfaced with

**Table I. Spectral Data for Benzilic Acids**

| Registry no. | Acid | UV λ, nm[a] | UV Medium | UV $\epsilon_{max}$ | Mass spectrum, *m/e* | Infrared[b] Wavenumbers, $cm^{-1}$ | NMR[b] ArH chem shift, δ |
|---|---|---|---|---|---|---|---|
| 76-93-7 | Benzilic | 252, *258*, 264 | $OH^-/H_2O$ | 540 | 184, 183, 105, 77, 76, 51, 44 | 3340, 3100–2400 (b), 1720, 133, 1240, 1050 | 7.36 |
| 3152-12-3 | 2,2′-Di-Cl | *263*, *267*, 274 | $OH^-/H_2O$ | 460 | 253, 251, 141, 139, 111, 76, 75 | 3500–2400 (b), 1720, 760 | 7.35 |
| 23851-49-9 | 4,4′-Di-Cl | *259*, 266, 275<br>259, *266*, 275 | $OH^-/H_2O$<br>MeOH | 680<br>605 | 253, 251, 141, 139, 111, 76, 75, 44, 40 | 3450–2400 (b), 1720, 825, 760 | 7.44 |
| 2695-79-6 | 4,4′-Di-Me | 257, *264*, 273<br>257, *264*, 273 | $OH^-/H_2O$<br>MeOH | 880 | 211, 119, 91, 65, 44 | 3350, 3100–2400 (b), 1720, 820 | 7.24 |
| 639-61-2 | 4,4′-Di-OMe | *273*, 280 | $OH^-/H_2O$ | 2950 | 243, 135, 119,107, 77, 45, 44 | 3600–2700 (b), 1725, 835 | 7.12 |
| 62058-71-3 | 4,4′-Di-$NO_2$ | *282*<br>*280* | $OH^-/H_2O$<br>MeOH | 16 200 | 272, 256, 150, 120, 104, 76, 44 | 3350, 3100–2400 (b), 1720, 1510, 1345, 855, 845 | 8.01 |

[a] Wavelength in italics denotes peak of maximum absorbance. [b] Full spectra are available from the authors upon request.

**Table II. p$K_a$ Values and Neutralization Equivalents for Benzilic Acids**

| Acid | Mol wt (calcd) | Neut equiv, potentiometric | p$K_a$ |
|---|---|---|---|
| Benzilic | 228.24 | 225.03 | 3.04 |
| 2,2′-Dichloro- | 297.13 | 291.68 | 2.54 |
| 4,4′-Dichloro- | 297.13 | 302.02 | 2.96 |
| 4,4′-Dimethyl- | 256.30 | 259.92 | 3.30 |
| 4,4′-Dimethoxy- | 288.30 | 287.41 | 3.93 |
| 4,4′-Dinitro- | 318.23 | 317.72 | 2.47 |

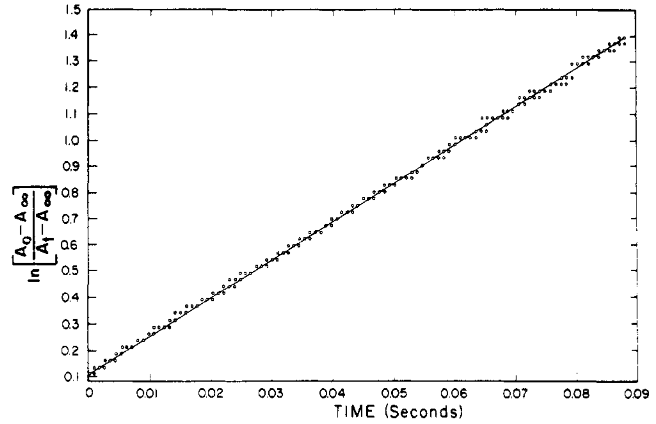
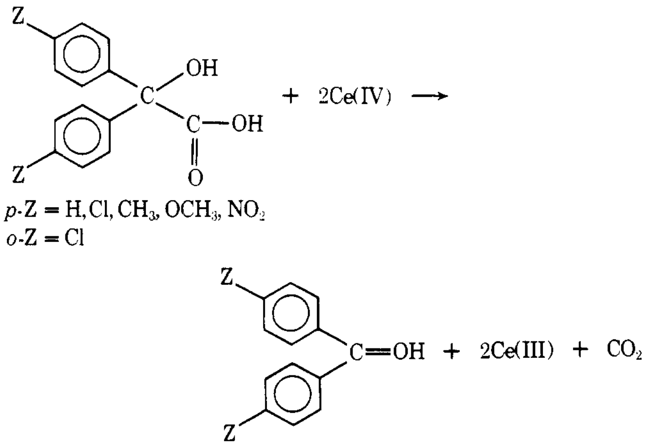


**Figure 1.** Plot of first-order kinetics of benzilic acid oxidation with Ce(IV).

a Tektronix storage oscilloscope, a Bausch and Lomb recorder, and a Data Cap tape perforator Model 820, through a Biomation transient recorder, Model 802. The digitized data were processed by a linear least-squares program of polynomial fit on an IBM 370/168. A typical computer-drawn plot of data processed as first-order kinetics (uncertainty in slope is less than 0.5%) showing linearity over 80% of reaction appears as Figure 1. The rate constants were reproducible to ±3%.

## Results and Discussion

**Stoichiometry and Products.** The oxidation of each of the benzilic acids by cerium(IV) leads to the formation of the corresponding benzophenone in quantitative yield. From a comparison of the decrease in absorbance at 300–320 nm, characteristic of cerium(IV), with increase in absorbance at the wavelength characteristic of the benzophenone produced on oxidation, the following stoichiometry was established:



The products' identities were established by comparison with the characteristics of benzophenones produced by other routes. The results are summarized in Table III.

**p$K_a$ Values.** The influence of substituents on the dissociation of benzilic acids was evaluated by measuring the p$K_a$s by potentiometric titration. The results are shown in Table II. The trends are as expected; the dinitro compound is the strongest acid whereas the dimethoxy is the weakest in the series. However, the p$K_a$ values determined in this work do not agree with those already reported in the literature for benzilic and the 4,4′-dichloro acid.[30a] We, therefore, determined the p$K_a$ for another α-hydroxy acid, viz., mandelic acid, to assess the dependability of our measurements. Our value of 3.41 for mandelic acid agrees within 0.02 p$K_a$ units of literature values.[30b] This strengthens the credibility of our measurements and we will, accordingly, use our own p$K_a$ values in preference to the literature values for benzilic acid and 4,4′-dichlorobenzilic acids.[30a]

**Relative Reactivities.** The rates of oxidation of the benzilic acids were conducted with the concentration of the α-hydroxy acid in excess. Pseudo-first-order kinetics were observed for the consumption of cerium(IV). Preliminary measurements were conducted with cerium(IV) sulfate in aqueous sulfuric acid solutions where the disappearance of Ce(IV) could be followed at 319 nm. It was realized, however, that because of solubility problems, particularly with the produced benzophenones, a different medium is needed. The results in $H_2SO_4$ solutions were limited accordingly to those benzilic acids which did not pose solubility problems. The results, summarized in Table IV, for four different $H_2SO_4$ concentrations, reveal two features. First, anisilic acid is far more reactive than benzilic acid which, in turn, is more reactive than 2,2′-dichlorobenzilic acid. At 1 N $H_2SO_4$, for example, $k_{benzilic}$:$k_{anisilic}$:$k_{2,2'\text{-diCl}}$ = 1:9:0.4. It seems that high

**Table III. Characteristics of Benzophenones Produced on Oxidation of Benzilic Acids**

| Registry no. | Benzilic acid | Mp of benzophenone derived from benzilic acid oxidation, °C | Ref for other routes of benzophenone production and mp, °C |
|---|---|---|---|
| 5293-97-0 | 2,2′-Dichloro- | 45 | 45–46,[21] 50–51.5[22] |
| 90-98-2 | 4,4′-Dichloro- | 147–148 | 144–145[23] |
| 611-97-2 | 4,4′-Dimethyl- | 94–95 | 97,[24] 90–91[25] |
| 90-96-0 | 4,4′-Dimethoxy- | 145–146 | 144–145[26] |
| 1033-26-7 | 4,4′-Dinitro- | 188–191 | 189,[27] 190–191,[28]<br>188.6–189.4[29] |

**Table IV. Observed Pseudo-First-Order Rate Constants[a] for the Oxidation of Benzilic Acids[b] with Cerium(IV)[c] in $H_2SO_4$ Solutions**

| $H_2SO_4$, N | $10^2k_1$, $s^{-1}$<br>Benzilic | <br>Anisilic | <br>2,2′-Dichlorobenzilic |
|---|---|---|---|
| 0.5 | 1.84 | | 0.804 |
| 1.0 | 0.55 | 4.95 | 0.235 |
| 1.5 | 0.22 | 3.88 | 0.124 |
| 2.0 | 0.15 | 3.52 | 0.064 |

[a] Measured at 319 nm. [b] [Benzilic acid] = 5 × $10^{-4}$ M. [c] [Ce(IV)] = 5 × $10^{-5}$ M.

**Table V. Rate Constants[a] for the Reaction of CAN[b] with Substituted Benzilic Acids[c] in Acetonitrile at 25 °C**

| Hydroxy acid | $k_1$, $s^{-1}$ | $k_1$ (rel) |
|---|---|---|
| Benzilic | 29.6 | 1.00 |
| 2,2′-Dichlorobenzilic | 10.3 | 0.35 |
| 4,4′-Dichlorobenzilic | 28.8 | 0.97 |
| 4,4′-Dimethylbenzilic | 37.5 | 1.27 |
| 4,4′-Dimethoxybenzilic | 53.1 | 1.79 |
| 4,4′-Dinitrobenzilic[d] | 7.57 | 0.26 |

[a] Measured at 325 nm. [b] [CAN] = 2.5 × $10^{-4}$ M. [c] [Benzilic acid] = 2 × $10^{-3}$ M. [d] Measured at 400 nm.

**Table VI. Rate Constants[a] for the Reaction of Cerium(IV)[b] with Substituted Benzilic Acids[c] in Perchloric Acid[d]-Acetic Acid (49.5 wt %) at 25 °C**

| Hydroxy acid | $k_1$, $s^{-1}$ | $k_1$ (rel) |
|---|---|---|
| Benzilic | 14.9 | 1.00 |
| 2,2′-Dichlorobenzilic | 11.6 | 0.78 |
| 4,4′-Dichlorobenzilic | 15.2 | 1.03 |
| 4,4′-Dimethylbenzilic | 21.0 | 1.41 |
| 4,4′-Dimethoxybenzilic[e] | 41.0 | 2.76 |
| 4,4′-Dinitrobenzilic[f] | 12.7 | 0.85 |

[a] Measured at 305 nm. [b] [Ce(IV)] = 2.5 × $10^{-4}$ M. [c] [Benzilic acid] = 5 × $10^{-3}$ M. [d] [$HClO_4$] = 0.195 M. [e] Measured at 390 nm. [f] Measured at 400 nm.

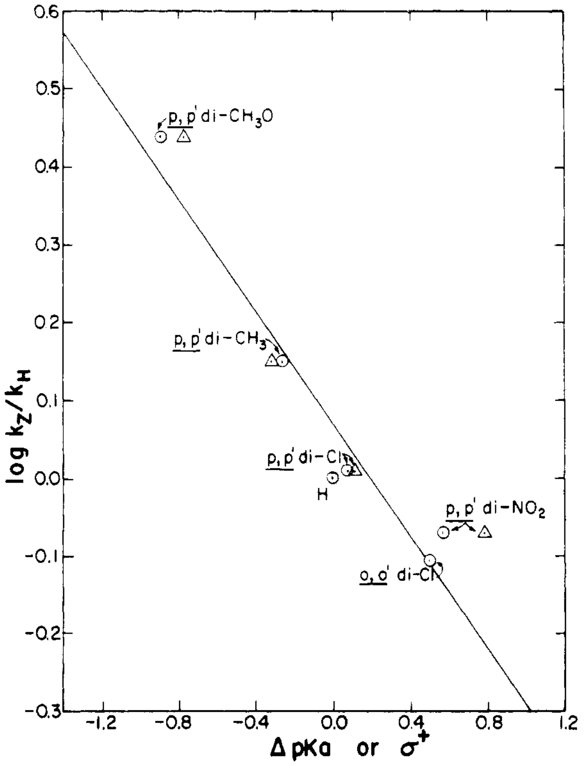


**Figure 2.** Hammett plot for the substituent effects on the Ce(IV) oxidation of benzilic acids in $HClO_4$–HOAc.

electron density facilitates oxidative decarboxylation by Ce(IV). This is to be expected for a reaction of an electrophile with the reductant. Among the various cerium(IV)–sulfato species,[31] $CeSO_4^{2+}$, $Ce(SO_4)_2$, $Ce(SO_4)_3^{2-}$, only the monosulfato species qualifies as an electrophile and is expected to be the most reactive species.[8,32] Second, for any of the three benzilic acids studied in $H_2SO_4$, the rate decreases with increasing acidity. However, whereas the decrease in $k_{\text{benzilic}}$ parallels the decrease in $k_{2,2'\text{-di-Cl}}$ (about 12-fold for a 4-fold increase in acidity), anisilic acid is far less sensitive to changing the concentration of $H_2SO_4$ in the range studied. It is possible that anisilic acid, because of the electron-supplying $OCH_3$ groups, is already so heavily protonated at 1 N $H_2SO_4$ when compared to the other two α-hydroxy acids that further increases in acidity are not effective in bringing about a significant change in the amount of protonated species.

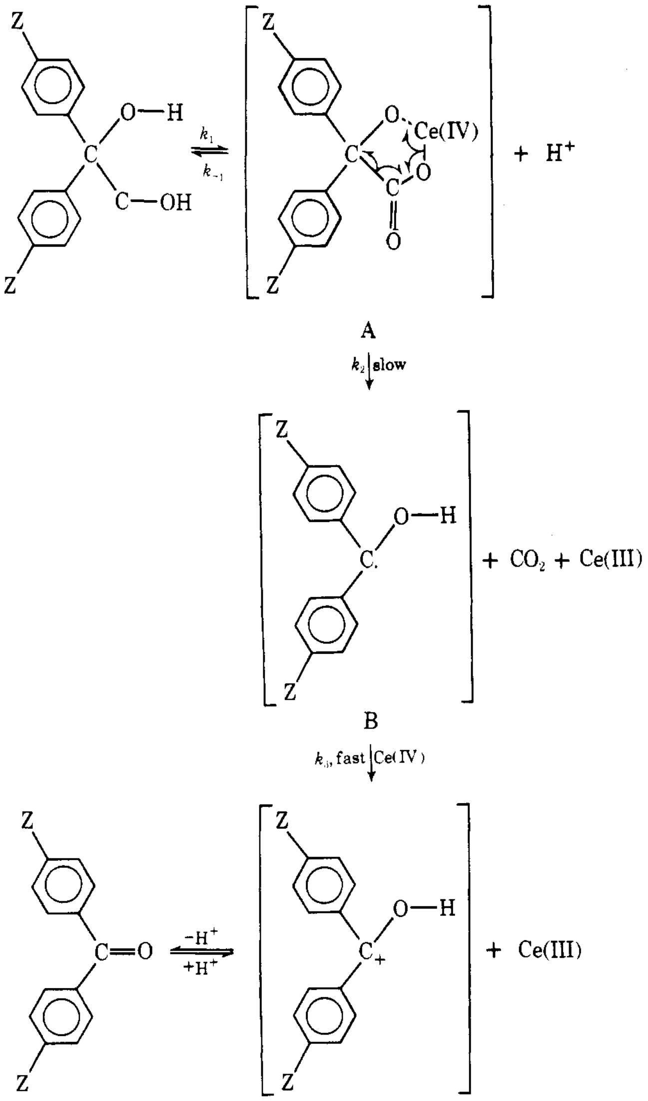
In Tables V and VI are presented the rate constants for the oxidation of substituted benzilic acids by cerium(IV) in acetonitrile and in perchloric–acetic acids mixtures, respectively. The relative rates indicate that in both media, electron-supplying groups facilitate the reaction whereas electron-withdrawing groups slow down the rate of oxidation. This may be taken as an indication of development of some carbocationic character in the transition state which would be stabilized by electron-releasing groups and hence the enhancement of rate by $CH_3$ and $OCH_3$ groups. To test for the development of charge at the reaction site, various Hammett substituent correlations were tried. Different sets of $\sigma^{33-35}$ and $\sigma^{+\,36,37}$ were used. The Hammett correlation, obtained with the $\sigma_p^+$ values of Brown and Okamoto,[36] gave $\rho = -0.317$ (±0.100) in the acetic–perchloric acids medium (Figure 2). With the $\sigma_p^+$ values, calculated by Swain and Lupton,[37] $\rho = -0.617$ (±0.084) in acetonitrile. A summary of the ρ values obtained in the Hammett correlations of the observed rate constants with different sets of literature-available substituent constants appears in Table VII. Inspection reveals several features. (1) The ρ values for either medium are negative but less than 1. (2) The ρs for the reaction in acetonitrile are approximately twice as negative as the corresponding ρs for the reaction in $HClO_4$–HOAc. (3) The magnitude of ρ is not very sensitive to the set of σ values used. These features are to be viewed in the light of the following information. The ρ values reported for reactions which involve cationic character at benzylic or benzhydrilic center lie in the vicinity of −5.0.[38] On the other hand, whereas most radical reactions display better correla-

**Table VII. Substituent Constants' Correlations in Acetonitrile and in Perchloric-Acetic Acids Media**

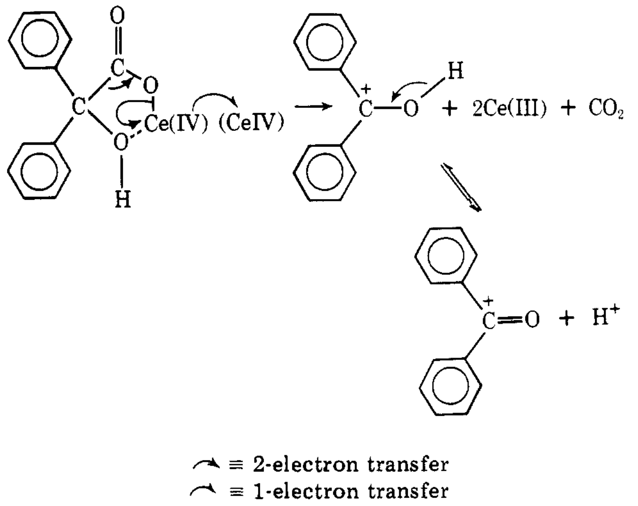
| Origin of σ values | ρ in acetonitrile | ρ in $HClO_4$-HOAc |
|---|---|---|
| Brown and Okamoto[36] $\sigma^+$ | −0.541 (±0.091) | −0.317 (±0.100) |
| Swain and Lupton[37] $\sigma^+$ | −0.617 (±0.084) | −0.350 (±0.113) |
| Sjostrom and Wold[34] $\sigma$ | −0.779 (±0.100) | −0.337 (±0.176) |
| McDaniel and Brown[35] $\sigma$ | −0.752 (±0.086) | −0.368 (±0.153) |
| Taft[30] $\sigma^0$ | −0.763 (±0.115) | −0.341 (±0.174) |

tions with $\sigma^+$ than with $\sigma$,[39] the ρs lie in the range of −0.3 to −1.5.[40] In some cases, ρ is as high as −2.0, or even −2.9.[9a] In the oxidative decarboxylation of benzilic acids (Scheme I), one might expect little, if any, development of cationic charge at the benzhydrilic carbon. For the development of positive charge character at that carbon, which would interact with substituents in the aromatic rings, the decarboxylation will have to have proceeded to such an extent that the incipient free radical is already interacting with a second Ce(IV). This would necessitate second-order kinetics with respect to Ce(IV), which is not the case. An alternative mechanism (Scheme II) which portrays development of carbocationic character in the rate-determining step would, again, necessitate second-order kinetics in Ce(IV). This alternative, however, is termolecular in nature because a divalent cerium species, Ce(II), which would result from a two-electron transfer, is highly unlikely.

Scheme I



Scheme II



Because the σ constants developed by Sjostrom and Wold,[31] in connection with phenylacetic and phenylpropionic acids, are different from the generally used Hammett σ values (benzoic acids), we sought a correlation with $\Delta pK_a$ determined in this work for the investigated benzilic acids. The plot of log $k_{rel}$ vs. $\Delta pK_a$ [$pK_a$ (benzilic) − $pK_a$ (substituted benzilic)] is shown in Figure 2; ρ = −0.362 (±0.056) for the reaction in acetic acid.

In summary, the ρs are negative and lie within the range characteristic of free-radical reactions. The higher sensitivity of the reaction to substituent effects in acetonitrile as compared to $HClO_4$-HOAc may very well reflect the difference in the solvation abilities of the two media. The developing charge, or the change in electron density, at the benzhydrilic carbon which accompanies the C-C bond cleavage is expected to be better dispersed with $HClO_4$-HOAc than with acetonitrile. This would lead to a greater interaction between substituent and reaction site in acetonitrile (higher ρ) than in $HClO_4$-HOAc.

Although we have no direct evidence for the intermediacy of free radicals, the substituent effects reported in this work are compatible with the mechanism proposed in Scheme I. The mechanism involves the rapid formation of a coordination complex (A) between Ce(IV) and the benzilic acid characterized by the equilibrium constant K. This disproportionates unimolecularly in the rate-determining step ($k_d$) by a one-electron transfer from the carboxyl group to Ce(IV), thereby generating the benzophenone ketyl radical (B) and Ce(III). The free radical is rapidly oxidized by a second Ce(IV).

**Registry No.**—Cerium(IV) perchlorate, 14338-93-3; cerium(IV) sulfate, 13590-82-4; cerium(IV) ammonium nitrate, 16593-75-2; 4,4′-benzil, 3457-48-5; potassium ethoxide, 917-58-8; *p*-toluic acid, 99-94-5; *p*-chlorobenzaldehyde, 104-88-1; 4,4′-dinitrobenzilic acid anilinium salt, 62058-72-4.

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# Asymmetric Reduction of Acetophenone with Lithium Aluminum Hydride Complexes of Terpenic Glycols[†]

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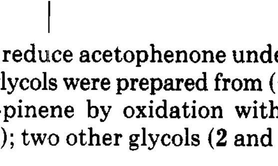
*Received November 8, 1976*

Optically active 1,2-glycols derived from (+)-1-menthene, (+)-$\alpha$-terpineol, and (+)-$\alpha$- and (−)-$\beta$-pinene formed chiral complexes with lithium aluminum hydride. The complexes were used to reduce acetophenone in different solvents and at various temperatures. The solvents included dioxane, diethyl ether, ethylene glycol dimethyl ether, and tetrahydrofuran, and temperatures ranged from −50 to 66 °C. Enantiomeric excess was maximum when the solvent was diethyl ether and the temperature was 15–20 °C. Various glycol complexes reduced the ketone in enantiomeric excesses ranging from 15% negative rotation to 30% positive rotation.

Conversion of abundant optically active terpenes such as limonene and pinene to useful optically active products has been the focus of much research effort. One approach is to synthesize asymmetric reagents from the terpenes.

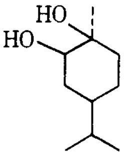
In previous studies,[1] glycol–lithium aluminum hydride complexes were prepared from monosaccharide derivatives[2] and diol derivatives of tartaric acid[3] and $\alpha$-pinene.[4,5] In one case, use of a monosaccharide derivative resulted in an enantiomeric excess (optical yield) of 70%.[2c] Enantiomeric excess has been found to depend on the glycol structure, whether ethanol or benzyl alcohol is added to the complex, and other variables, such as temperature and solvent.[1]

We converted glycols 1–7 to hydride complexes



$$\begin{array}{l} \quad | \\ -\mathrm{C}-\mathrm{O} \\ \quad | \qquad \rangle \mathrm{AlH_2}^- \quad \mathrm{Li}^+ \\ -\mathrm{C}-\mathrm{O} \\ \quad | \end{array}$$

and used them to reduce acetophenone under various conditions. Five of the glycols were prepared from (+)-limonene and (+)-$\alpha$ and (−)-$\beta$-pinene by oxidation with $KMnO_4$ (compounds 1 and 4–7); two other glycols (2 and 3) were donated



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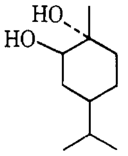

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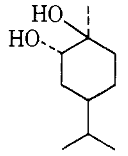

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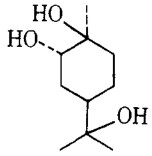

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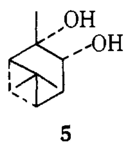

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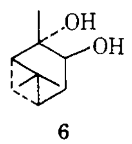

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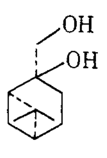

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to us. Since (+)-limonene could not be converted directly to a simple 1,2-glycol, it was first converted to (+)-1-menthene and (+)-$\alpha$-terpineol by procedures which preserved the optical activity.[6,12] The respective products were then oxidized to the 1,2-glycol **1**, and the 1,2,8-triol **4**. The pinane glycols (**5**, **6**, and **7**) were synthesized by the oxidation of $\alpha$- or $\beta$-pinene according to published procedures.[3–6] Acetophenone was chosen as the test ketone because it is frequently so used in the evaluation of asymmetric hydride reducing agents.[1]

## Results and Discussion

Tables I and II show that the yields of $\alpha$-methylbenzyl alcohol from the reduction of acetophenone under various conditions were generally high but that the optical yields were

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[†] Mention of a brand name is for identification only and does not imply its endorsement by the U.S. Department of Agriculture over others which may also be suitable.

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