# Oxidation of Organic Compounds with Cerium(IV). XV. Electronic and Steric Effects on the Oxidative Cleavage of 1,2-Glycols by Cerium(IV) and Lead(IV)[1a-c]

WALTER S. TRAHANOVSKY,*[1d] JOHN R. GILMORE, AND PAUL C. HEATON

*Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50010*

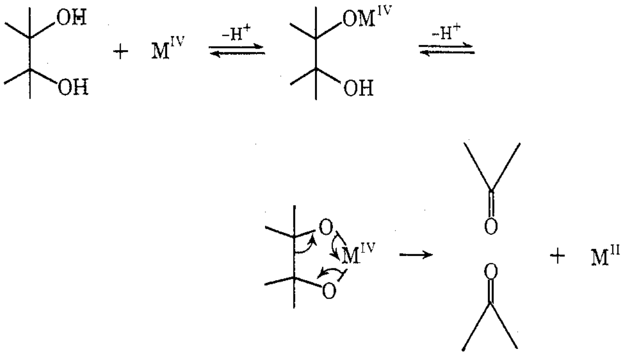
*Received October 17, 1972*

The relative rates of oxidative cleavage of a series of substituted *meso*-hydrobenzoins, *dl*-hydrobenzoin, and *erythro-O*-methylhydrobenzoin by cerium(IV) and lead(IV) were measured by competition studies. The relative rates of oxidative cleavage by periodate of some of these hydrobenzoins were also measured. All oxidations were carried out at 50° in 85% aqueous acetic acid. From these data $\rho$ values of $+0.016$ for the lead(IV) and $-1.53$ for the cerium(IV) oxidations of *meso*-hydrobenzoins were calculated using $\sigma^+$ values. With lead(IV) *dl*-hydrobenzoin is oxidized nine times faster than the meso isomer, but with cerium(IV) these rates are equal. The relative rates of oxidation of *meso*-hydrobenzoin and its monomethyl ether are more similar with cerium(IV) than with lead(IV). These results support the intermediate formation of a bidentate complex with lead(IV) but not with cerium(IV) and are consistent with the mechanism for the cleavage of cerium(IV), which involves the formation of a monodentate complex followed by a one-electron cleavage to give an intermediate radical which is then further oxidized.

The cleavage of 1,2-glycols by periodic acid[2] and lead tetracetate[3] has been known for some time. Although these two oxidants seem to be the most widely used ones to bring about 1,2-glycol cleavages,[4] several other oxidants such as sodium bismuthate,[4a,5] manganese(III) pyrophosphate,[6] phenyl iodosoacetate,[4,7] cerium(IV) salts,[4b,8] vanadium(V) salts,[4b,9] chromic acid,[10] and nickel peroxide[11] also readily cleave 1,2-glycols. A catalytic system, the silver(I)-catalyzed oxidative cleavage of 1,2-glycols by peroxy disulfate, has been reported.[12]

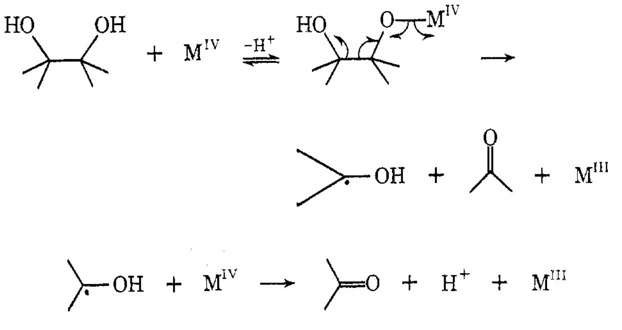
The mechanism for the cleavage of 1,2-glycols by lead(IV) is thought to involve the formation of a bidentate metal–glycol complex which then breaks down to products *via* a two-electron process[4a] (mechanism I). The main support for this mechanism comes from the fact that cis diols are more rapidly oxidized than the corresponding trans diols and threo diols are more rapidly oxidized than the corresponding erythro diols.[4a,13] Although there is no direct evidence for these cyclic lead complexes, their existence has been made more reasonable by the isolation of cyclic osmates.[14] Mechanism I is further supported by the failure to trap radical intermediates.[8e]

MECHANISM I



Other mechanisms for the cleavage of 1,2-glycols can be written, and indeed the cleavage of 1,2-glycols by cerium(IV) seems to involve coordination to only one hydroxy group followed by a one-electron oxidation to give an intermediate radical (mechanism II).[8] The main support for this mechanism is the similar rates of oxidation of 1,2-glycols and their monomethyl ethers,[8d,8j] and the successful trapping experiments[8c,8e] which indicate that an intermediate radical is formed. Some support for the intermediacy of a bidentate cerium(IV)–glycol complex has been given,[8f] but other results,[8d] including formation constants for cerium(IV) complexes

MECHANISM II



---

[1] (a) Part XIV: W. S. Trahanovsky and M. D. Robbins, *J. Amer. Chem. Soc.* **93**, 5256 (1971). (b) This work was partially supported by Public Health Service Grant No. GM 13799 from the National Institute of General Medical Sciences and Grant No. GP-18031 from the National Science Foundation. We are grateful for this support. (c) Preliminary communication: Abstracts, 162nd National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, ORGN 13. (d) Alfred P. Sloan Research Fellow, 1970–1972.

[2] L. Malaprade, *C. R. Acad. Sci.*, **186**, 382 (1928); *Bull. Soc. Chim. Fr.*, [4], **43**, 683 (1928); [5], **1**, 833 (1934).

[3] R. Criegee, *Justus Liebigs Ann. Chem.*, **481**, 275 (1930).

[4] (a) C. A. Bunton in "Oxidation in Organic Chemistry," part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, Chapter VI; (b) A. S. Perlin in "Oxidation," Vol. 1, R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter IV.

[5] W. Rigby, *J. Chem. Soc.*, 1907 (1950).

[6] (a) A. Y. Drummond and W. A. Waters, *ibid.*, 3119 (1953); (b) P. Levesley, W. A. Waters, and A. N. Wright, *ibid.*, 840 (1956).

[7] H. Beucker and R. Criegee, *Justus Liebigs Ann. Chem.*, **541**, 218 (1939).

[8] (a) F. R. Duke and A. A. Forist, *J. Amer. Chem. Soc.*, **71**, 2790 (1949); (b) F. R. Duke and R. F. Bremer, *ibid.*, **73**, 5179 (1951); (c) G. Mino, S. Kaizerman, and E. Rasmussen, *ibid.*, **81**, 1494 (1959); (d) J. S. Littler and W. A. Waters, *J. Chem. Soc.*, 2767 (1960); (e) W. S. Trahanovsky, L. H. Young, and M. H. Bierman, *J. Org. Chem.*, **34**, 869 (1969); (f) H. L. Hintz and D. C. Johnson, *ibid.*, **32**, 556 (1967).

[9] J. S. Littler, A. I. Mallet, and W. A. Waters, *J. Chem. Soc.*, 2761 (1960).

[10] (a) R. Slack and W. A. Waters, *ibid.*, 594 (1949); (b) K. B. Wiberg in "Oxidation in Organic Chemistry," part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., Chapter II.

[11] R. Konaka and K. Kuruma, *J. Org. Chem.*, **36**, 1703 (1971), and references cited therein.

[12] E. S. Huyser and L. G. Rose, *ibid.*, **37**, 851 (1972), and references cited therein.

[13] R. Criegee, E. Höger, G. Huber, P. Kruck, F. Marktscheffel, and H. Schellenberger, *Justus Liebigs Ann. Chem.*, **599**, 81 (1956).

[14] (a) R. Criegee, *Angew. Chem.*, **50**, 153 (1937); (b) R. Criegee, B. Marchand, and H. Wannowins, *Justus Liebigs Ann. Chem.*, **550**, 99 (1942).

TABLE I

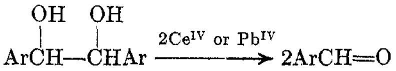
RELATIVE RATES OF OXIDATIVE CLEAVAGE OF SUBSTITUTED *meso*-HYDROBENZOINS, $(ZC_6H_4CHOH\text{-})_2$, WITH CERIC AMMONIUM NITRATE (CAN), LEAD TETRAACETATE (LTA), AND POTASSIUM PERIODATE $(KIO_4)$[a]

| Registry no. | Z | CAN $k_{rel}$ | LTA $k_{rel}$ | $KIO_4$ $k_{rel}$ |
|---|---|---|---|---|
| 5173-29-5 | $p$-$CH_3$ | 2.62 ± 0.36 | 1.023 ± 0.071 | 1.15 |
| 37580-80-6 | $m$-$CH_3$ | 1.80 ± 0.09 | 1.84 ± 0.10 | |
| 655-48-1 | H | (1.00) | (1.00) | (1.00) |
| 37580-81-7 | $p$-Cl | 0.395 ± 0.017 | 1.79 ± 0.14 | |
| 37580-82-8 | $p$-Br | 0.446 ± 0.010 | 1.09 ± 0.11 | |
| 37580-83-9 | $m$-Cl | 0.244 ± 0.012 | 1.37 ± 0.12 | 1.13 |
| 37580-84-0 | $p$-$NO_2$ | 0.0619 ± 0.0039 | 1.205 | |

[a] In 85% aqueous acetic acid at 50°. The numbers with standard deviations are based on three runs and those without are based on one run.

with glycols and their monomethyl ethers,[15] give no indication that a bidentate complex is formed.

In order to gain further support for the validity of these mechanisms and to establish the electronic effects on these mechanisms, a study of the relative rates of oxidative cleavage by cerium(IV) and lead(IV) of substituted *meso*-hydrobenzoins was undertaken. Also, the relative rates of oxidation by these oxidants of *meso*- and *dl*-hydrobenzoin were measured in order to determine if there were any steric differences between these two oxidants. A small amount of data was collected using periodate as the oxidant. All oxidations were carried out at 50° in 85% acetic acid to ensure a direct comparison of the relative rate constants.



$$\underset{}{\overset{OH}{ArCH}}-\overset{OH}{CHAr} \xrightarrow{2Ce^{IV}\text{ or }Pb^{IV}} 2ArCH{=}O$$

## Results

The substituted hydrobenzoins were synthesized *via* the benzoin condensation of the corresponding aldehyde.[16] The benzoin was further reduced with sodium borohydride to the hydrobenzoin.[16] The meso isomer was isolated by fractional recrystallization; the *dl* isomer, being more soluble, stayed in solution and usually one or two recrystallizations sufficed. The purity of the isomers was checked by melting point and nmr spectroscopy since the signals for the benzylic protons of the meso and *dl* isomers have large chemical-shift differences. 4,4′-Dinitrohydrobenzoin was synthesized by a different route.[17] *dl*-Hydrobenzoin was prepared by a modification of the method of Fieser.[16] The *erythro*-monomethyl ether of hydrobenzoin was prepared by methylating benzoin with methyl iodide–silver oxide in acetone[18] and reducing the methyl benzoin to the required compound with sodium borohydride.

The kinetic study was carried out by competitively oxidizing equimolar quantities of a substituted hydrobenzoin and the unsubstituted hydrobenzoin with the required oxidant. The amount of oxidant used was such that only a maximum of 5% of either of the substrates would be consumed. Since the substrate concentration at the beginning of the reaction was approximately equal to substrate concentration at the end of the reaction, the relative rate constants are given by eq 1. The ratio of the two aldehydes produced were

$$k(X)/k'(H) = [X\text{ products}]/[H\text{ products}] \quad (1)$$

determined by glpc, making corrections for relative extraction and thermal conductivity ratios. The relative rates for *dl*-hydrobenzoin were determined against *meso*-4,4′-dimethylhydrobenzoin and the relative rates for the *erythro*-monomethyl ether of hydrobenzoin were determined against *meso*-3,3′-dichlorohydrobenzoin. The results are summarized in Tables I–III. Plots of the logarithms of the relative rate of each substrate by ceric ammonium nitrate (CAN) *vs.* the Hammett $\sigma$ and $\sigma^+$ values[19] gave about equally good correlations with $\sigma$ and $\sigma^+$ values. A least squares treatment of these data using $\sigma^+$ values gave a $\rho$ of $-1.53 \pm 0.15$ and using $\sigma$ values gave a $\rho$ of $-1.72 \pm 0.09$. Similar treatment of the relative rates obtained with lead tetraacetate (LTA) using $\sigma^+$ values gave a $\rho$ of $0.016 \pm 0.14$ and $\sigma$ values gave a $\rho$ of $0.010 \pm 0.015$.[20] Plots of the logarithms of the relative rates of each substrate by CAN and LTA *vs.* $\sigma^+$ values are shown in Figure 1. Use of the $\sigma^+$ values are

TABLE II

RELATIVE RATES OF OXIDATIVE CLEAVAGE OF *dl*- TO *meso*-HYDROBENZOIN WITH VARIOUS OXIDANTS[a]

| Oxidant | $k_{dl}/k_{meso}$ |
|---|---|
| CAN | 0.90 ± 0.28[b] |
| LTA | 8.29 ± 0.58[c] |
| $KIO_4$ | 5.16[d] |

[a] In 85% aqueous acetic acid at 50°. [b] Based on three runs. [c] Based on two runs. [d] Based on one run.

TABLE III

RELATIVE RATES OF OXIDATIVE CLEAVAGE OF *meso*-HYDROBENZOIN TO ITS MONOMETHYL ETHER AND WITH VARIOUS OXIDANTS[a]

| Oxidant | $k_{diol}/k_{monoether}$ |
|---|---|
| CAN | 6 |
| LTA | 20 |

[a] See footnote *a*, Table I.

---

[15] L. B. Young and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **91**, 5060 (1969).

[16] L. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath, Boston, Mass., 1957.

[17] T. Ukita and R. Takeshita, *Chem. Pharm. Bull.*, **9**, 600 (1961).

[18] H. Wren, *J. Chem. Soc.*, **95**, 1584 (1909).

[19] H. C. Brown and Y. Okamota, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

[20] When the two abnormally high rate constants for the LTA oxidations were omitted, a $\rho$ of $0.097 \pm 0.055$ using $\sigma^+$ and a $\rho$ of $0.086 \pm 0.070$ using $\sigma$ were calculated. We have no good explanation for the slightly higher rate constants for the *m*-methyl and *p*-chloro compounds. Possibly these compounds were slightly contaminated with their *dl* isomer, which would have been oxidized more rapidly. In any case, it is clear that there is no correlation with the rate constants for the LTA oxidations and the electronic effects of the substituents and even the abnormally high rate constants (*ca.* 1.8) are fairly close to 1.0.

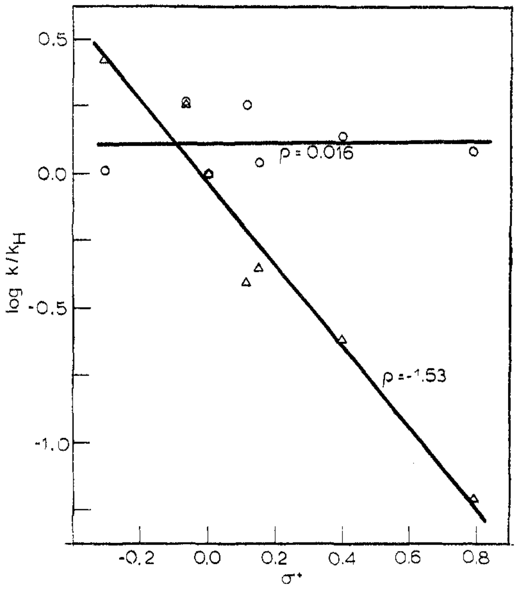


Figure 1.—Plots of the logarithms of the relative rates of oxidative cleavage of *meso*-hydrobenzoins by CAN (△) and LTA (○) *vs.* $\sigma^+$ for the substituent.

favored since oxidative cleavages have generally correlated better with $\sigma^+$ than $\sigma$.[21]

## Discussion

The results of this study strongly support mechanism I for the cleavage of 1,2-glycols by lead(IV) and mechanism II for the cleavage of 1,2-glycols by cerium(IV). The contrasting results obtained for these two oxidants under comparable reaction conditions make these conclusions all the more firm.

The lack of a substituent effect (a $\rho$ of +0.02) for the 1,2-glycol cleavage by lead(IV) indicates that the formation of the bidentate complex is rate determining, or that the decomposition of this complex is rate determining but little charge develops on the benzylic carbon atoms in the cyclic transition state. Additional support for the intermediacy of this bidentate complex comes from the observation that the *dl* isomer of hydrobenzoin was oxidized 8.3 times faster than the meso isomer by lead(IV) whereas these isomers were oxidized at comparable rates by cerium(IV), which evidently does not form a cyclic intermediate. The lead(IV) and cerium(IV) results considered together mean that the rate difference for the oxidation of these two isomers by lead(IV) must result from a difference in transition-state energies, not groundstate energies. This difference in energy is no doubt a result of the increased steric interaction between the cis phenyl groups of the meso transition state compared to the trans phenyl groups of the *dl* transition state. The more similar relative rates of oxidation of *meso*-hydrobenzoin and its monomethyl ether with cerium(IV) ($k_{\text{diol}}/k_{\text{monoether}}$ = 6) compared to the corresponding relative rates with lead(IV) ($k_{\text{diol}}/k_{\text{monoether}}$ = 20) also support the two different mechanisms for the two oxidants.

The relative rates of oxidation by LTA of a small number of tetrasubstituted benzpinacols (unsubstituted, 4-methoxy, 4-methyl, and 4-chloro) show a slight rate increase as the substituent becomes more electron donating.[22] From these results, it was concluded that the formation of the monodentate complex is rate determining. Although this conclusion is in disagreement with the results in this article and other data,[4a,13] it may be true for more hindered glycols such as the benzpinacols.[23] Because only a limited number of examples were studied and the benzpinacols possess special features which make them atypical 1,2-glycols, this study is of little use in defining a mechanism for the LTA oxidation of most 1,2-glycols.

The $\rho$ value of −1.5 found for the cerium(IV) oxidative cleavage of substituted *meso*-hydrobenzoins is consistent with mechanism II and requires that the rate-determining step must be the decomposition of the monodentate complex to the intermediate radical and carbonyl compound. The $\rho$ value of −1.5 is comparable to the one observed (−2.0) for the oxidative cleavage of 1,2-diarylethanols.[21] It is reasonable that the formation of benzylic radicals should be a little more sensitive to substituents than the formation of $\alpha$-hydroxybenzyl radicals.

It is interesting to note that, based on orbital symmetry considerations, the cyclic mechanism, mechanism I, is a forbidden process for one-electron oxidants such as cerium(IV).[25]

The cleavage of 1,2-glycols by cerium(IV) is just a special case of the general oxidative cleavage of alcohols by cerium(IV).[21,26] The same mechanism seems to operate for all of these oxidative cleavages and as expected the $\alpha$-hydroxy radicals are stable enough that alcohols which can form them (1,2-glycols) undergo rapid cleavage. The polar nature of the transition state for the cleavage reaction[21] also favors the cleavage of $\alpha$-hydroxy radicals.

The favored mode of oxidative cleavages seems to be a one-electron process,[21,26,27] but the facile cleavage of 1,2-glycols by LTA is clearly a two-electron process. Most likely a facile two-electron cleavage will occur only if a special situation exists such as the possibility of forming a bidentate complex and going directly from this complex to stable organic products and a stable oxidation state of the oxidant.[12] The fact that alcohols which cannot meet these requirements undergo two-electron cleavages reluctantly[21,27] suggests that the slow oxidative cleavages by LTA of 1,2-glycols which cannot form bidentate complexes, such as *trans*-decalin-9,10-diol,[4a,13] are one-electron processes involving the intermediate formation of lead(III).

The limited results obtained with potassium periodate as oxidant are comparable to those obtained with LTA and indicate that periodate cleavage of 1,2-glycols proceeds by a mechanism similar to mechanism I, *i.e.*, one which involves a bidentate complex as an intermediate. This is in agreement with previous conclusions.[4a]

Recently the silver(I)-catalyzed cleavage of 1,2-glycols by peroxy disulfate was reported to be accomplished

---

[21] (a) P. M. Nave and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **90**, 4755 (1968); (b) *ibid.*, **93**, 4536 (1971).

[22] J. P. Cordner and K. H. Pausacker, *J. Chem. Soc.*, 102 (1953).

[23] Such a change in mechanism has been observed for the periodate oxidation of ethylene glycol and a series of methylated ethylene glycols.[24]

[24] F. R. Duke and V. G. Bulgrin, *J. Amer. Chem. Soc.*, **76**, 3803 (1954).

[25] J. S. Littler, *Tetrahedron*, **27**, 81 (1971).

[26] (a) W. S. Trahanovsky, P. J. Flash, and L. M. Smith, *J. Amer. Chem. Soc.* **91**, 5068 (1969); (b) W. S. Trahanovsky and J. Cramer, *J. Org. Chem.*, **36**, 1890 (1971).

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

by two paths.[12] It was proposed that one path involves silver(II) which cleaves by mechanism II.

Utilization of the above-mentioned techniques should provide a useful tool for determining the mechanism of other glycol cleaving reagents as well as giving some indication as to the stereochemistry of appropriate substrates.

## Experimental Section

**Methods and Materials.**—Most equipment and methods have been previously described.[28] Glpc analysis was carried out on a Varian Aerograph 1700 gas chromatograph using a thermal conductivity detector and a 5 ft × 0.25 in. 20% SE-30 on Chromosorb W column.

CAN (Baker) was used as a solution in 85% aqueous acetic acid (1.0705 g/25 ml). The LTA (Analabs) solution was freshly prepared for each reaction by dissolving the solid (0.0375 g) in 85% aqueous acetic acid (5 ml). The solution was warmed to 50° before addition to the substrate mixture. The potassium periodate (Matheson Coleman and Bell) solution was freshly prepared for each reaction by dissolving the solid (0.0195 g) in water (7.5 ml). The aqueous solution, warmed to 50°, was then added to the mixture of substrates in glacial acetic acid (22.5 ml).

*meso*-**Hydrobenzoin** was prepared by the method of Fieser:[16] mp 135–136° (lit.[16] mp 136–137°); nmr ($CDCl_3$) $\delta$ 7.26 (s, 10), 4.81 (s, 2), and 2.70 (broad s, 2, $D_2O \rightarrow 0$).

*meso*-**4,4′-Dimethylhydrobenzoin** was prepared by the method of Fieser:[16] mp 143–145° (lit.[29] mp 145–146°); nmr (DMSO-$d_6$) $\delta$ 7.06 (s, 8), 4.96 (m, 2, $D_2O \rightarrow 0$), 4.54 (m, 2, $D_2O \rightarrow$ s), and 2.26 (s, 6).

*meso*-**4,4′-Dinitrohydrobenzoin** was prepared by the nitration of *meso*-diacetylhydrobenzoin[17] followed by hydrolysis of the diacetate: mp 232° (lit.[17] mp 231°); nmr (DMSO-$d_6$) $\delta$ 7.85 (AA′BB′ pattern, $\nu_a \sim 8.15$, $\nu_b \sim 7.52$, 8), 5.70 (broad s, 2, $D_2O \rightarrow 0$), and 4.79 (s, 2).

*meso*-**4,4′-Dichlorohydrobenzoin.**—4,4′-Dichlorobenzoin was prepared by the method of Lutz and Murphy[30] and reduced to the hydrobenzoin by the method of Fieser:[16] mp 109–110° (lit.[31] mp 151°); nmr ($CDCl_3$) $\delta$ 7.4 (AA′BB′ pattern, $\nu_a \sim 7.18$, $\nu_b \sim 6.95$, 8), 4.68 (s, 2), and 2.59 (s, 2).

*meso*-**4,4′-Dibromohydrobenzoin** was prepared by the method used to prepare the dichloro compound: mp (from 95% ethanol) 137–138°; nmr (DMSO-$d_6$) $\delta$ 7.29 (AA′BB′ pattern, $\nu_a \sim 7.62$, $\nu_b \sim 7.16$, 8), 5.38 (m, 2), and 4.53 (m, 2).

*Anal.* Calcd for $C_{14}H_{12}O_2Br_2$: C, 45.19; H, 3.25; Br, 42.95. Found: C, 45.10; H, 3.27; Br, 43.01.

*meso*-**3,3′-Dimethylhydrobenzoin** was prepared by the method used to prepare 4,4′-dichlorohydrobenzoin and purified by chromatography on a silica column, mp (from petroleum ether, bp 60–70°) 87–88°; nmr ($CDCl_3$) $\delta$ 7.05 (m, 8), 4.63 (broad s, 2), 2.29 (s, 6), and 2.17 (m, 2, $D_2O \rightarrow 0$). *Anal.* Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.41; H, 7.67.

*meso*-**3,3′-Dichlorohydrobenzoin** was prepared by the method used to prepare the 4,4′ isomer: mp (from benzene) 96–98° (lit.[31] mp 95°); nmr ($CDCl_3$) $\delta$ 7.07 (m, 8), 4.65 (s, 2), and 2.69 (broad s, 2).

*dl*-**Hydrobenzoin** was prepared by a modification of the method of Fieser.[16] Instead of purifying the crude diacetate by chromatography, it (*ca.* 2 g) was dissolved in 20 ml of carbon tetrachloride and 200 ml of petroleum ether and this solution was held at 0° for 24 hr, during which the diacetate crystallized from the solution: mp 119–120° (lit.[16] 120°); nmr ($CDCl_3$) $\delta$ 7.1 (m, 10), 4.6 (s, 2), and 3.21 (s, 2).

*erythro-O*-**Methylhydrobenzoin.**—*O*-Methylbenzoin was prepared by the method of Wren[18] and reduced to the monomethyl ether of hydrobenzoin with sodium borohydride, mp (from aqueous ethanol) 100° (lit.[32] 100–102°).

**Procedure for Competition Experiments.**—The two hydrobenzoins ($5 \times 10^{-4}$ mol of each) were dissolved in 85% aqueous acetic acid (28 ml for CAN, 25 ml for LTA, and 22.5 ml of glacial acetic acid for $KIO_4$) at 50°. To the rapidly stirred solution was added an aliquot (2 ml for CAN, 5 ml for LTA, and 7.5 ml for $KIO_4$) of the oxidant. The mixture was stirred at 50° for 20 min. All mixtures remained homogeneous throughout the reaction; the pale yellow color of Ce(IV) disappeared in about 1 min.

The reaction mixture was poured into water (25 ml) and extracted with benzene (2 × 25 ml). The conbined benzene extracts were washed with water (25 ml), saturated sodium bicarbonate (25 ml), and finally water (25 ml). The benzene layer was dried ($MgSO_4$) for 18 hr and filtered, and the benzene was removed on a rotary evaporator. To the residue was added 1 ml of benzene and the resultant solution was analyzed by glpc (three injections per run). The areas of the glpc peaks were determined by Xeroxing the traces and cutting and weighing the peaks. The thermal conductivity and extraction ratios were determined by preparing weighed mixtures of the authentic aldehydes in 85% aqueous acetic acid (30 ml) and performing identical extraction and area-determination procedure. At least three determinations were carried out for each standard.

**Registry No.**—CAN 12125-48-3; LTA, 546-67-8; $KIO_4$, 7790-21-8; *erythro-O*-methylhydrobenzoin, 6941-71-5.

**Acknowledgment.**—We wish to thank John E. Fulkrod for his procedure for preparing *dl*-hydrobenzoin and Darryl W. Brixius for carrying out the least squares calculations.

---

(28) W. S. Trahanovsky and M. P. Doyle, *J. Org. Chem.*, **32**, 146 (1967).

(29) J. Grimshaw and J. S. Ramsey, *J. Chem. Soc. C*, 653 (1966).

(30) R. E. Lutz and R. S. Murphy, *J. Amer. Chem. Soc.*, **71**, 480 (1949).

(31) H. D. Law, *J. Chem. Soc.*, **99**, 1115 (1911).

(32) J. C. Irvine and J. Weir, *ibid.*, **91**, 1390 (1907).