

hydrogen directly to the enol exists but would require more energy.

### Experimental Section<sup>3</sup>

**Action of Sodium Methoxide on 3a,7a-Dihydro-3,3a,5,6-tetra-phenylinden-1-one (1a).**—The indenone 1a (1 g) was refluxed with sodium methoxide (0.01 g) in 95% ethanol (60 ml) for 30 min. The resulting brownish yellow solution upon cooling gave **3** (0.48 g) which after successive crystallizations from ethyl acetate and benzene melted at 240–242°. This sample was identical with a sample prepared by the acid isomerization of 1a:<sup>2</sup> ir (Nujol) 1670 (C=O), 1650 cm<sup>-1</sup> (C=C); nmr (DCCl<sub>3</sub>) δ 3.29 (d, *J* = 16 Hz, H-4), 3.62 (d, *J* = 16 Hz, H-4), 6.7–7.4 ppm (m, 20 aromatic H and H-2).

The filtrate upon treatment with water and a trace of acid gave **2**, which after recrystallization two times from ethanol melted at 176°, yield 0.16 g. This sample was identical with that obtained by pyrolysis:<sup>4</sup> ir (Nujol) 1720 cm<sup>-1</sup> (C=O); nmr (DCCl<sub>3</sub>) δ 3.51 (s, CH<sub>2</sub>), 7.0–7.3 (m, 20 aromatic hydrogens), 7.4 (s, H-7), and 7.83 ppm (s, H-4).

Heating a solution of the indenone 1a (0.62 g) in 95% ethanol (35 ml) with sodium methoxide (0.01 g) for 8.5 hr gave 0.43 g of **2**.

**Action of Hydrochloric Acid on 3a,7a-Dihydro-3,3a,5,6-tetra-phenylinden-1-one (1a).**—The indenone 1a was heated in ethanol (50 ml) with concentrated hydrochloric acid (1 ml) for 17 hr. Addition of water gave a solid (0.40 g) which, based upon the ir spectrum, consisted mainly of **2** with a small amount of **3**.

**3a,7a-Dihydro-3,3a,5,6-tetra-phenylinden-1-one (1a).**—The nmr spectra in chloroform-*d* and benzene-*d*<sub>6</sub> were identical with respect to integration. Chemical shifts for the vinyl hydrogen differed: nmr (DCCl<sub>3</sub>) δ 3.54 (d, *J* = 5.5 Hz, H-7a), 5.98 (d, *J* = 5.5 Hz, H-7), 6.18 (s, H-4), 6.8–7.5 (m, 20 aromatic H and H-2); nmr (C<sub>6</sub>D<sub>6</sub>) δ 3.54 (d, *J* = 5.5 Hz, H-7a), 6.13 (d, *J* = 5.5 Hz, H-7), 6.40 (s, H-4), 6.8–7.5 ppm (m, 20 aromatic hydrogens and H-2); ir (Nujol) 1690 cm<sup>-1</sup> (C=O).

**Registry No.**—1a, 16643-52-0; **2**, 16643-46-2; **3**, 16643-45-1.

(3) Melting points are not corrected. Infrared spectra were determined on a Perkin-Elmer Infracord and Model 421 and nmr spectra were obtained with a Varian A-60 spectrometer.

(4) On occasion the ketone from the pyrolysis was obtained in a crystalline form which melted at 153.5–155°. This sample upon standing in ethanol slowly changed into the 176° melting form. The ir spectra were identical. This behavior explains the range of melting points reported by Japp<sup>5</sup> for this compound.

(5) F. R. Japp and C. I. Burton, *J. Chem. Soc.*, **51**, 420 (1887).

## Neighboring Carboxylate Groups and the Oxidation of Benzhydrol and Benzaldehyde by Permanganate<sup>1</sup>

J. ANTHONY MACPHEE AND ROSS STEWART\*

Department of Chemistry, University of British Columbia, Vancouver 8, Canada

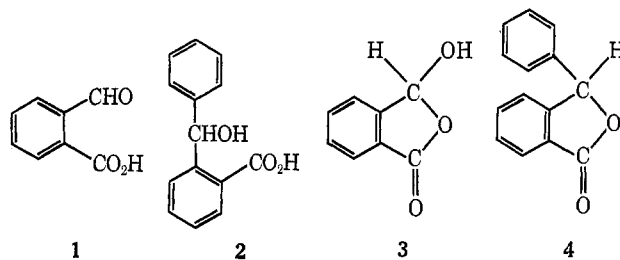
Received November 18, 1971

The permanganate oxidation of both benzhydrol and benzaldehyde is much faster in alkaline solution than at neutral pH. The activation of alcohols toward *external* base is due to formation of alkoxide ion.<sup>2</sup> We have in-

(1) The financial support of the National Research Council of Canada is gratefully acknowledged.

(2) (a) R. Stewart, *J. Amer. Chem. Soc.*, **79**, 3057 (1957); (b) R. Stewart and R. Van der Linden, *Discuss. Faraday Soc.*, **29**, 211 (1960); (c) R. Stewart, "Oxidation Mechanisms, Applications to Organic Chemistry," W. A. Benjamin, New York, N. Y., 1964, pp 63–70; (d) R. Stewart in "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965.

vestigated the effect of *internal* base (in the form of neighboring carboxylate) on the oxidation of alcohols and aldehydes and have reported elsewhere the existence of such catalysis in the case of *cis*-2-hydroxycyclohexanecarboxylic acid.<sup>3</sup> However, no such effect can be observed in the case of the anions of the ortho carboxy derivatives of benzaldehyde and benzhydrol, **1** and **2**, as will be seen from the subsequent discussion.



The present brief report is prompted by the appearance of a paper which reports the presence of such intramolecular catalysis in the oxidation of **1** by bromine.<sup>4</sup>

Comparison of the oxidation of the anions of **1** and **2** was made with the corresponding compounds lacking a carboxyl group and with those containing such a group in the para position. The results are summarized in Table I.

The effect of a carboxylate group on the oxidation of benzaldehyde in the neutral and mildly basic regions is small, whether the group is in the ortho or para position. As the medium is made more acidic than pH 5 the oxidation of all three compounds accelerates and becomes autocatalytic. The one striking effect of the ortho carboxyl group in phthalaldehydic acid is that at still higher acidities the oxidation rate for this compound decreases again and the autocatalysis vanishes. A clean second-order reaction is observed at pH 1.55 at a rate that is considerably less than that observed under neutral conditions. This is presumably due to **1** existing under these conditions almost completely in the ring-closed phthalide form, **3**,<sup>5</sup> a form whose oxidation behavior should resemble that of an alcohol rather than an aldehyde.

In the case of benzhydrol an ortho carboxy group has a pronounced *inhibiting* effect on the oxidation both in neutral and in basic solution. This effect cannot be due to the formation of the ring-closed phthalide compound, **4**,<sup>6</sup> since this form predominates only below pH 5, where, indeed, it precipitates from the reaction mixture and makes a study of its reaction with permanganate impossible. The inhibiting effect of adjacent carboxylate can be attributed to electrostatic repulsion between this group and permanganate ion. Evidently, a specific conformational relationship between alcoholic hydroxyl and neighboring carboxylate is required before intramolecular catalysis of the permanganate-alcohol reaction can be observed.<sup>4</sup>

### Experimental Section

The rate measurements were made by both iodometric and spectrophotometric means, essentially as previously described.<sup>2a,3</sup>

(3) R. Stewart and J. A. MacPhee, *J. Amer. Chem. Soc.*, **93**, 4271 (1971).

(4) B. G. Cox, *J. Chem. Soc. B*, **1971**, 1704.

(5) (a) P. R. Jones, *Chem. Rev.*, **63**, 461 (1963); (b) D. D. Wheeler, D. C. Young, and D. S. Erley, *J. Org. Chem.*, **22**, 547 (1957).

(6) G. E. Resinger and J. A. Thompson, *Recl. Trav. Chim. Pays-Bas*, **82**, 801 (1953).

TABLE I  
RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE PERMANGANATE OXIDATION  
OF VARIOUS COMPOUNDS IN WATER

Registry no.	Compd	$k$ , l. mol <sup>-1</sup> sec <sup>-1</sup> , at 25°			$\Delta H^\ddagger$ , kcal mol <sup>-1</sup>	$\Delta S^\ddagger$ , eu
		pH 8.1	pH 10.3	pH 12.7		
	Benzaldehyde <sup>a</sup>	0.37	0.42		10.3 <sup>b</sup>	-26.2 <sup>b</sup>
119-67-5	Phthalaldehydic acid (1)	0.18	0.17		10.4 <sup>c</sup>	-27.1 <sup>c</sup>
619-66-9	Terephthalaldehydic acid	0.28	0.39		11.2 <sup>c</sup>	-23.4 <sup>c</sup>
91-01-0	Benzhydrol <sup>d</sup>	0.070	0.10	3.7	<i>e</i>	<i>e</i>
34737-60-5	Benzhydrol-2-carboxylic acid (2)	0.006	0.004	0.19	8.8 <sup>f</sup>	-36.4 <sup>f</sup>
579-52-2	Benzhydrol-4-carboxylic acid	0.057	0.060	6.0	8.9 <sup>f</sup>	-32.4 <sup>f</sup>

<sup>a</sup> K. B. Wiberg and R. Stewart, *J. Amer. Chem. Soc.*, **77**, 1786 (1955). <sup>b</sup> At pH 6.5. <sup>c</sup> At pH 8.1. <sup>d</sup> Reference 2a. <sup>e</sup>  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for this compound are 5.7 and -38.4, respectively, at pH 12.3, a pH at which the oxidation proceeds almost entirely by way of the alkoxide ion. <sup>f</sup> At pH 5.45, for which  $k$  at 25° is 0.0237 and 0.139 l. mol<sup>-1</sup> sec<sup>-1</sup> for the 2- and 4-substituted compounds, respectively.

The oxidations of 1 and terephthalaldehydic acid in water were allowed to proceed to completion and the organic products were isolated. The only products were phthalic and terephthalic acids, each being formed in near quantitative yield. In the case of benzhydrol-2-carboxylic acid the reaction was quenched, at the point where the kinetic experiments showed the reaction to be 60% complete, by the addition of sodium bisulfite and acid. The organic product was taken up in ether and this solution was

extracted with aqueous bicarbonate. The two fractions yielded 3-phenylphthalide and 2-benzoylbenzoic acid in quantitative amount corresponding to 60% reaction. The physical properties of the phthalide,<sup>g</sup> 2-benzoylbenzoic acid, and 4-benzoylbenzoic acid (formed in 98% yield by oxidation of 4-benzhydroxycarboxylic acid) were identical with those of authentic samples.

**Registry No.**—Permanganate, 14333-13-2.