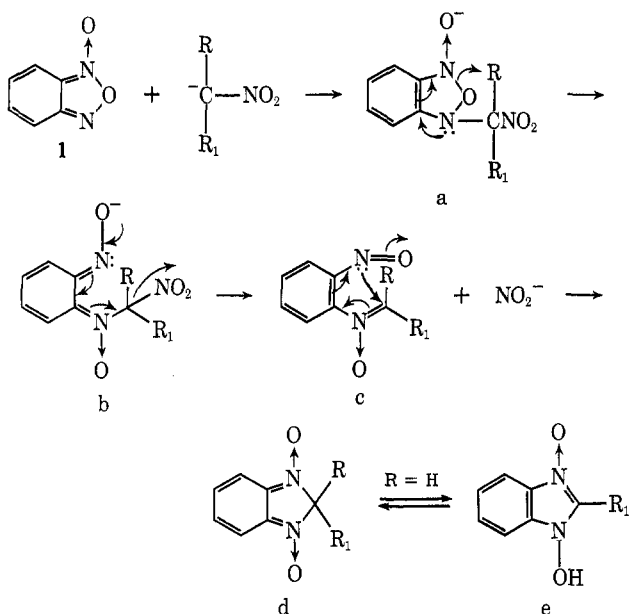
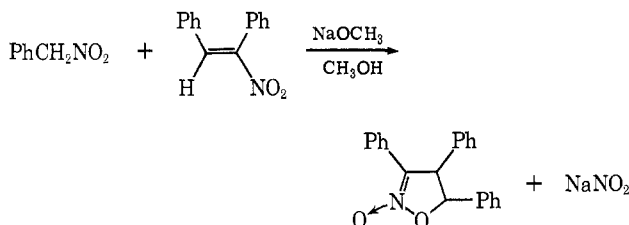


yield from 2-nitropropane. The ir spectrum (KBr) exhibited strong absorption bands for the $N \rightarrow O$ at 1399, 1361, and 1307 cm^{-1} ; the uv spectrum (MeOH) exhibited maxima at 510 $\text{m}\mu$ (ϵ 7.25×10^3) and 245 (2.34×10^4). The nmr spectrum (CDCl_3) showed absorption at δ 1.7 (s, 6 H) due to the dimethyl grouping and two A_2B_2 quartets for the aromatic protons at δ 6.9 ($J = 3$ Hz) and 7.25 ($J = 3$ Hz). The spiro compound **9** was obtained by allowing **1** to react with nitrocyclohexane in the presence of DBN.

A possible mechanism for the formation of the above products from **1** and the nitroalkanes is outlined below. The nitroanion probably adds to the N-3 nitrogen to



give **a**, which can tautomerize to **b**. Elimination of NO_2^- would give **c**, which could rearrange to **d**. The latter is the final product where R and R_1 are alkyl, whereas if $\text{R} = \text{H}$, the product tautomerizes to form **e**. A similar displacement of a nitro group was reported during the formation of 3,4,5-triphenylisoxazoline 2-oxide from phenylnitromethane and *cis*- α -nitrostilbene in the presence of base, as shown below.⁸



The first observation of the displacement of a nitro group from a tertiary carbon atom (by thiophenoxide and malonate anions) was reported by Kornblum, *et al.*⁹

Another route from benzofurazan oxides to 1-hydroxy-1H-benzimidazole 3-oxides, using β -keto sulfonides, has recently been reported.¹⁰

Registry No.—**2**, 15966-49-1; **3**, 15966-52-6; **4**, 31980-09-3; **5**, 34759-59-6; **6**, 31980-11-7; **7**, 31980-12-8; **8**, 34789-56-5; **9**, 31983-86-5.

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(10) D. P. Claypool and D. R. Sidani, *J. Org. Chem.*, in press.

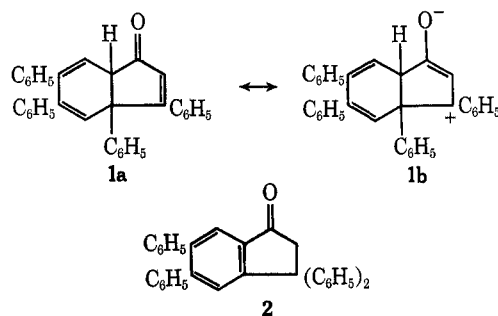
The Rearrangement of 3a,7a-Dihydro-3,3a,5,6-tetraphenylinden-1-one

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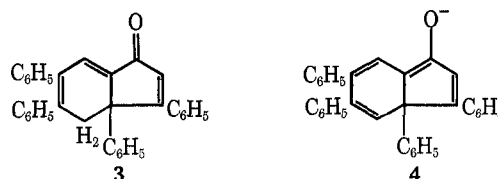
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The thermal rearrangement of 3a,7a-dihydro-3,3a,5,6-tetraphenylinden-1-one (**1a**) to 3,3,5,6-tetraphenyl-



indan-1-one (**2**), which has been considered to proceed through the polarized form **1b**,¹ has now been found to be catalyzed by base and acid. Addition of catalytic amounts of sodium methoxide to an alcohol solution of **1a** forms a purple enolate ion which on heating for a short time gives mainly the less acidic 3a,4-dihydro-3,3a,5,6-tetraphenylinden-1-one (**3**) and a small amount



of **2**. Further heating of this solution converts **3** to **2**. These results preclude the participation of **1b** in this rearrangement and indicates that the enolate ion **4**, which can be formed from both **1a** and **3**, is involved and would allow the rearrangement to proceed by a 1,5-suprafacial sigmatropic shift of the phenyl group.

The behavior of **1a** with acid is similar. Treatment with hydrogen bromide in acetic acid at 100° for 30 min gives **3**.² Prolonged heating of **1a** with hydrochloric acid in ethanol gave mainly **2**. This sequence of reactions favors the enol form of **1a** as a precursor of **2**.

The uncatalyzed thermal rearrangement of **1a** may proceed through the enol form even though this form could not be detected by either infrared or nmr spectroscopy. Studies of **1a** using the first technique were carried out at temperatures varying from 25 to 175°. At the melting point **1a**, when present as a film, was found to rearrange to **2**.

Nmr studies of **1a** found no evidence for the enol form; similar peak heights were observed in polar (DCCl_3) and nonpolar (C_6D_6) solvents.

The uncatalyzed thermal rearrangement² of **3** to **2** would involve first a 1,5 shift of hydrogen and the formation of **1a**. The possibility of a 1,7 shift of

(1) C. F. H. Allen and J. A. VanAllan, *J. Org. Chem.*, **20**, 315 (1955).

(2) C. F. H. Allen and J. W. Gates, Jr., *J. Amer. Chem. Soc.*, **64**, 2120 (1942).

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

Experimental Section³

Action of Sodium Methoxide on 3a,7a-Dihydro-3,3a,5,6-tetraphenylinden-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:² ir (Nujol) 1670 (C=O), 1650 cm⁻¹ (C=C); nmr (DCCl₃) 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:⁴ ir (Nujol) 1720 cm⁻¹ (C=O); nmr (DCCl₃) δ 3.51 (s, CH₂), 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*₆ were identical with respect to integration. Chemical shifts for the vinyl hydrogen differed: nmr (DCCl₃) 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 (C₆D₆) 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⁻¹ (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 Japp⁵ 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 Permanganate¹

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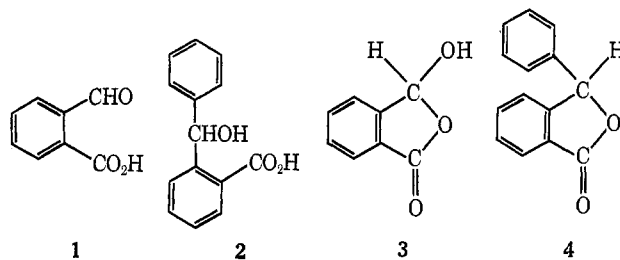
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The permanganate oxidation of both benzhydrol and benzaldehyde is much faster in alkaline solution than at neutral pH. The activation of alcohols toward *external* base is due to formation of alkoxide ion.² We have in-

(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.³ 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.⁴

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**,⁵ 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**,⁶ 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.⁴

Experimental Section

The rate measurements were made by both iodometric and spectrophotometric means, essentially as previously described.^{2a,3}

(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).