tetrachlorobutane (3 g) at 86–88° (50 mm) and the residue solidified. The solid was recrystallized from a $CCl_4$–*n*-hexane mixture to give 4,4,4-trichloro-2-methylbutyramide (11 g). The amide (9 g) was dissolved in ethanolic HCl (40%, 50 ml) and refluxed for 3 hr. The solution was neutralized with ammonia and ethanol was evaporated. $NH_4Cl$ was removed by filtration and the filtrate was subjected to distillation to give ethyl 4,4,4-trichloro-2-methylbutyrate at 95–97° (12 mm, 7.5 g).

Following derivatives of succinic acids were obtained by the hydrolysis of the trichloro esters formed from various olefins in concentrated $H_2SO_4$ and their melting points are shown (reported melting points): $CH_3$–, 111–112° (111°); $C_2H_5$–, 97° (98°); *n*-$C_4H_9$–, 80° (81°); *n*-$C_6H_{13}$–, 83° (83–84°).

Properties of the other reaction products and their derivatives are shown in Tables III and IV.

**Registry No.**—Carbon tetrachloride, 56-23-5; carbon monoxide, 630-08-0; I, 10210-68-1; II, 12087-10-4; III, 12091-64-4; Table III—a, 13275-19-9; b, 19967-19-2; c, 20518-70-1; d, 13375-88-7; e, 1070-27-5; Table IV—a, 25236-71-9; b, 20101-80-8; c, 25236-73-1; d, 25236-74-2; e, 25236-75-3; f, 25236-76-4; g, 25236-77-5; h, 25236-78-6; i, 25236-79-7; j, 25236-80-0; k, 25236-81-1; l, 25236-82-2; ethylene, 74-85-1; propylene, 115-07-1; 1-butene, 106-98-9; 1-hexene, 592-41-6; 1-octene, 111-66-0; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 2-hexene, 592-43-8; isobutene, 115-11-7; 1,3-butadiene, 106-99-0.

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# Zinc Reduction of γ Diketones

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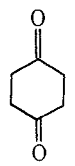
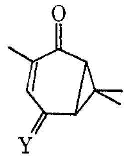
The reduction of cyclic γ diketones with amalgamated zinc and hydrochloric acid has been studied. While the eight- and seven-ring systems yield 1,2-glycols, cyclohexane-1,4-dione fragments into acyclic hexane-2,5-dione. Reduction of the latter produces 2-hexanol. The ease of reduction of 1,2-diacylethylenes, -cyclopropanes, and -cyclobutane is compared. A seven-membered-ring analog of the quinone–hydroquinone reduction–oxidation system is described.

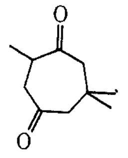
In continuation of a study of the Clemmensen reduction of diketones,[1] an investigation of the reaction of some cyclic γ diketones with amalgamated zinc in hydrochloric acid was undertaken. Diketones **1**, **3**, and **5** were chosen as six-, seven-, and eight-membered cyclic 1,4-dione representatives. The latter two substances were prepared by reduction of ketones **2a**[2] and **4**,[3] respectively, with zinc in acetic acid.



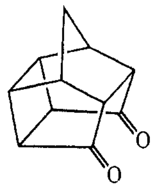
**1**



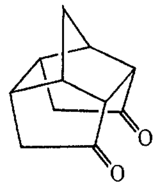
**2a**, Y = O
**b**, Y = H, OH



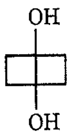
**3**



**4**

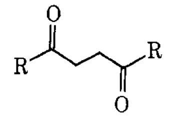


**5**

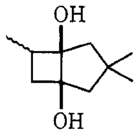


**6**

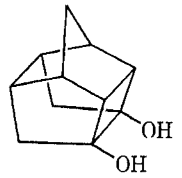
The Clemmensen products were expected to be pinacols, although the high strain of potential pinacolic product **6** from **1** suggested that the reduction of the six-membered cyclic diketone might take a different course from that of its homologs. The Clemmensen reduction of cyclohexane-1,4-dione (**1**) yielded acetonylacetone (**7a**), while the reduction of 2,6,6-trimethylcycloheptane-1,4-dione (**3**) gave the pinacol isomer pair **8** and that of **5** led to pinacol **9**. Periodate oxidation of the diols reverted them to their diketonic precursors.



**7a**, R = Me
**b**, R = *t*-Bu

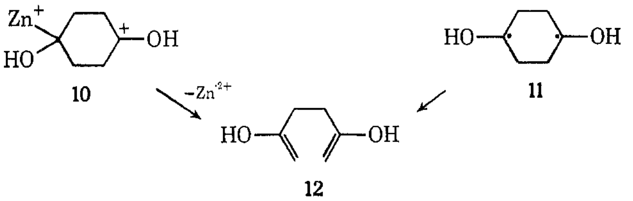


**8**



**9**

The fragmentation of **1** is reminiscent of the conversion of 1,4-dibromocyclohexane or 1,4-diiodocyclohexane into diallyl on zinc reduction[4] and can be envisaged to involve the breakup of the reduction intermediate(s) (**10**, **11**, or organozinc equivalents) into the dienol (**12**) of **7a**.[5]



**10** **11** **12**

The formation of products besides **7a** on reduction of **1** at elevated temperature led to a study of the Clemmensen reduction of acetonylacetone (**7a**). The sole isolable product of a reaction at room temperature was 2-hexanol, while the latter and a mixture of stereoisomeric 2,5-dimethyltetrahydrofurans (**13a**) were obtained from a reaction at slightly elevated temperature and proved to be the products of overreduction of cyclohexane-1,4-dione (**1**).[6] In view of the possibility of the

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[1] E. Wenkert and E. Kariv, *Chem. Commun.*, 570 (1965).

[2] E. J. Corey and H. J. Burke, *J. Amer. Chem. Soc.*, **78**, 174 (1956).

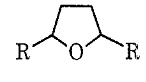
[3] R. C. Cookson, E. Crundwell, and J. Hudec, *Chem. Ind. (London)*, 1003 (1958).

[4] C. A. Grob and W. Baumann, *Helv. Chim. Acta*, **38**, 594 (1955).

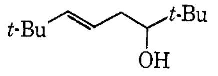
[5] (a) For a general discussion of heterolyses of this type, *cf.* C. A. Grob and P. W. Schiess, *Angew. Chem.*, **79**, 1 (1967). (b) For examples of homolyses of this type, *cf.* S. G. Cohen and R. Zand, *J. Amer. Chem. Soc.*, **84**, 586 (1962); W. R. Roth and M. Martin, *Tetrahedron Lett.*, 3865 (1967).

[6] An independent study of the Clemmensen reduction of acetonylacetone and cyclohexane-1,4-dione under somewhat different conditions by J. G. St. C. Buchanan and B. R. Davis, *J. Chem. Soc. C*, 1340 (1967), has yielded related results. The authors are indebted to Dr. Davis for furnishing them information on this work prior to publication.

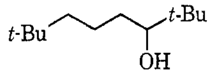
product of fragmentation of acetonylacetone (**7a**), *i.e.*, acetone, having been missed on work-up, another acyclic diketone, **7b**,[7] was exposed to the Clemmensen reaction. The reduction products consisted of a mixture of 2,5-di-*t*-butyltetrahydrofuran (**13b**) stereoisomers, *trans*-2,2,7,7-tetramethyl-5-octen-3-ol (**14**), and 2,2,7,7-tetramethyl-3-octanol (**15**). The acyclic $\gamma$ diketones thus had undergone their own mode of reduction, yielding neither pinacols nor scission products.



**13a**, R = Me
b, R = *t*-Bu

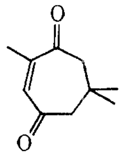


**14**

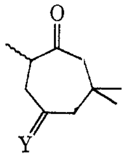


**15**

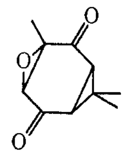
Alongside the above investigation a qualitative study of the ease of reduction of 1,2-diacylethylene, 1,2-diacylcyclopropane, and 1,2-diacylcyclobutane derivatives by zinc in acetic acid was undertaken. Several of the following substances were prepared for this endeavor. Selenium dioxide oxidation of diketone **3** yielded 2,6,6-trimethyl-2-cycloheptene-1,4-dione (**16**). Hydrogenation of enolone **2b**[2] gave ketol **17b**, whose Jones oxidation afforded diketone **17a**. An alternate attempt of transformation of **2b** into **17a**, by base-catalyzed isomerization, went awry. Exposure of either **2b** or **17a** to hydroxide without precaution of exclusion of air led to diketoepoxide **18**. The initial enolate apparently trapped oxygen from the air and the intermediate hydroperoxide, *e.g.*, **19**, suffered oxygen-oxygen bond cleavage by intramolecular displacement by the second enolate.



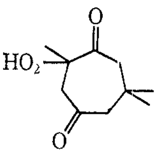
**16**



**17a**, Y = O
b, Y = H, OH



**18**

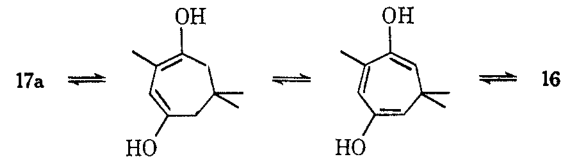


**19**

**20**

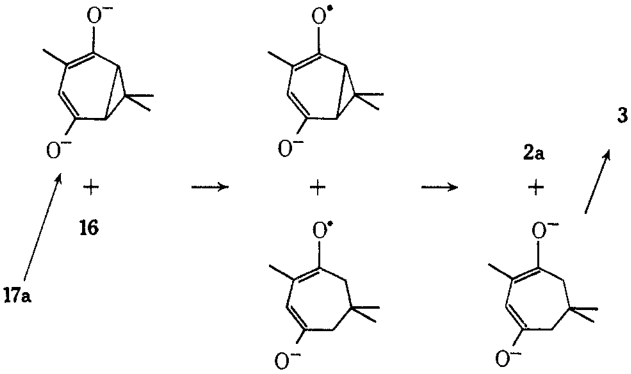
**21**

Zinc reduction of **16**, **17a**, and **18** in acetic acid yielded **3**. While, however, the reduction of enedione **16** was extraordinarily facile, the reductions of the diacylcyclopropanes **17a** and **18** and the transformation of diacylcyclobutane **4** into **5** under the same reaction conditions (*vide supra*) required extended time or/and elevated temperature. Thus the ability of an enedione to form a highly delocalized anion radical (or its conjugate acid) on electron acceptance (**20** → **21**) facilitates the reduction. This conclusion indicated that the easy conversion of **2a** into **3** on reduction with zinc in acetic acid (*vide supra*) had occurred in an indirect manner. While the double-bond system of **2a** had to be the site of initial reduction, diketone **17a** could not have been a reduction intermediate. If, however, it be assumed that after the initial one- or two-electron transfer stage a norcaradiene–cycloheptatriene rearrangement takes place, **16** would have become the reduction intermediate (*vide infra*) and, being an enedione, could have been expected to undergo further reduction rapidly.



To gain more insight into the rearrangement of the ring systems, a base-catalyzed isomerization of **17a** into **16** was attempted. Surprisingly, however, exposure of **17a** to potassium hydroxide in methanol at 0° under nitrogen produced the diketones **2a** and **3** in equimolar quantity. Thus the desired transformation had occurred but had been followed by an unprecedented oxidation–reduction process involving **16** and **17a** dienol, reminiscent of quinone–hydroquinone interactions.[8] The likely reduction–oxidation sequence is portrayed in Scheme I.

SCHEME I



## Experimental Section

Melting points were determined on a Reichert micro hot stage and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer. Proton magnetic resonance spectra of deuteriochloroform solutions containing tetramethylsilane as internal standard were taken on a Varian Associates A-60 spectrometer.

**Clemmensen Reductions.**—A mixture of 95 mg of cyclohexane-1,4-dione (**1**) and 10 g of amalgamated zinc in 55 ml of 6.5 *N* hydrochloric acid was stirred at room temperature for 2 hr. The solution was decanted off the remaining zinc; the latter was washed with water; and the combined aqueous solutions were saturated with sodium chloride and extracted with methylene chloride. The extract was treated with solid sodium bicarbonate and thereafter dried over anhydrous magnesium sulfate. Filtration and solvent evaporation yielded 68 mg of a liquid whose gas phase chromatographic analysis (Carbowax column at 205°) revealed it to consist of over 95% of one component and less than 2% of starting material. Preparative gpc collection (SE30 column at 150°) gave acetonylacetone (**7a**) identical with an authentic sample by ir and pmr analyses and gpc retention time. Clemmensen reduction of **1** at elevated temperature led to products of similar reductions of **7a** (*vide infra*).

A mixture of 125 mg of 2,6,6-trimethylcycloheptane-1,4-dione (**3**) and 10 g of amalgamated zinc in 55 ml of 6.5 *N* hydrochloric acid was stirred at room temperature for 2 hr. Work-up as above gave 97 mg of liquid diol **8** (no carbonyl absorption in the ir spectrum).

*Anal.* Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.27; H, 10.62.

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[7] R. Ramasseul and A. Rassat, *Bull. Soc. Chim. Fr.*, 2214 (1963).

[8] L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold, New York, N. Y., 1961, pp 845–878.

Fractional sublimation of **8** yielded two isomers: mp 34–35°, pmr δ 1.06 (d, 3, $J = 7$ Hz, cyclobutyl Me), 1.08 (s, 3, Me), 1.11 (s, 3, Me); mp 96–98°, pmr δ 1.09 (d, 3, $J = 7$ Hz, cyclobutyl Me), 1.08 (s, 3, Me), 1.13 (s, 3, Me). Periodate oxidation of either isomer of **8** in a manner analogous to the oxidation of **9** (*vide infra*) afforded **3**, identical with an authentic sample by ir, pmr, and gpc comparison, in over 95% yield.

A mixture of 500 mg of dione **5** and 10 g of amalgamated zinc in 31 ml of concentrated hydrochloric acid, 23 ml of water, and 4 ml of methanol was heated at 80° for 10 min. Work-up as above gave 500 mg of a white solid whose sublimation at 40° (0.05 Torr) led to diol **9**: mp 202° dec; ir (KBr) OH 2.90 (m) μ, no C=O.

*Anal.* Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.44; H, 8.13.

A mixture of 50 mg of diol **9** and 3 ml of a 5% sodium periodate solution in 2 ml of water and 1 ml of methanol was stirred at room temperature for 30 min and then extracted with methylene chloride. The extract was washed with sodium bicarbonate solution, dried, and evaporated, leaving 35 mg of dione **5**, mp and mmp 255° dec, ir spectrum identical with that of authentic **5**.

A mixture of 670 mg of acetonylacetone (**7a**) and 10 mg of amalgamated zinc in 55 ml of 6.5 *N* hydrochloric acid was stirred at room temperature for 13 hr. (An extra 15 ml of concentrated hydrochloric acid was added in intervals during this period.) Work-up as above gave 470 mg of a liquid whose gpc analysis showed it to contain no starting material and greater than 97% a single compound. Chromatography of the product on silica gel and elution with 7:3 petroleum ether (bp 30–60°)–ether yielded 450 mg of 2-hexanol identical with an authentic sample by ir and pmr analyses and gpc retention time.

A mixture of 2.0 g of acetonylacetone (**7a**), 20 g of amalgamated zinc, and 60 ml of concentrated hydrochloric acid in 46 ml of water was refluxed for 15 min. Work-up as above gave 1.1 g of a liquid whose gpc analysis indicated the presence of *ca.* 60% 2-hexanol, 35% starting dione, and 5% another substance. Isolation of the latter by preparative gpc and comparison of the material with authentic 2,5-dimethyltetrahydrofuran (**13a**) stereoisomers[9] (ir, pmr, gpc) showed it to be **13a**.

A mixture of 180 mg of 2,2,7,7-tetramethyloctane-3,6-dione (**7b**), 15 g of amalgamated zinc, and 60 ml of 6.5 *N* hydrochloric acid in 15 ml of methanol was stirred at room temperature for 5.5 hr. Work-up as above gave 154 mg of liquid whose gpc analysis showed the absence of starting compound and the presence of four components in 11, 65, 14, and 12% yields. Their isolation by preparative gpc gave respectively 2,5-di-*t*-butylfuran [ir and pmr spectra identical with those cited in the literature];[7] liquid 2,5-di-*t*-butyltetrahydrofuran (**13b**) stereoisomers [pmr δ 0.88 (s, 9, *t*-butyl H's), 0.89 (s, 9, *t*-butyl H's of other isomer), 1.62 (m, 4, methylenes), 3.45 (m, 2, methines); *m/e* 184 (M), 183 (M − 1, base peak)]; *trans*-2,2,7,7-tetramethyl-5-octen-3-ol (**14**) [mp 53–55°; pmr δ 0.92 (s, 9, methyls), 1.01 (s, 9, methyls), 2.1 (m, 2, methylene), 3.20 (q, 1, $J = 10.0$, 2.5 Hz, oxymethine), 5.43 (q, 1, $J = 7.5$, 6.0 Hz, olefinic H), 5.52 (s, 1, olefinic H), double resonance (the 2.1 signal coupled with the 3.20 and 5.43 signals)].

*Anal.* Calcd for $C_{12}H_{24}O$: C, 78.20; H, 13.12. Found: C, 78.26; H, 13.02.

The fourth substance was 2,2,7,7-tetramethyl-3-octanol (**15**): mp 80–81°; pmr δ 0.90 (s, 18, methyls), 1.1–1.5 (m, 6, methylenes), 3.2 (m, 1, methine).

*Anal.* Calcd for $C_{12}H_{26}O$: C, 77.35; H, 14.06. Found: C, 77.06; H, 13.75.

**Diketones 16, 17a, and 18.**—A mixture of 75 mg of dione **3** and 200 mg of selenium dioxide in 24 ml of methanol was refluxed for 44 hr.[10] It was then decanted from precipitated selenium, diluted with water, and extracted with methylene chloride. The extract was washed with water, dried, and evaporated. Chromatography of the residue on 2 g of silica gel topped by a layer of precipitated silver yielded a 25-mg fraction whose gpc analysis showed the presence of one component and a 50-mg fraction containing more than 90% (by gpc) starting material. Distillation of the product gave yellow, liquid 2,6,6-trimethyl-2-cycloheptene-1,4-dione (**16**): pmr δ 1.12 (s, 6, saturated methyls), 2.01 (d, 3, $J = 2.0$ Hz, olefinic Me), 2.62 (s, 2, methylene), 2.69 (s, 2, methylene), 6.42 (d, 1, $J = 2.0$ Hz, olefinic H).

*Anal.* Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.94; H, 8.56.

A mixture of 166 mg of enolone **2b**[2] [pmr δ 1.06 (s, 3, Me), 1.22 (s, 3, Me), 1.77 (d, 3, $J = 2.0$ Hz, olefinic Me), 4.35 (d, 1, $J = 3.0$ Hz, oxymethine), 6.51 (q, 1, $J = 3.0$, 2.0 Hz, olefinic H)] and 60 mg of 10% palladium–charcoal in 40 ml of ethanol was hydrogenated at atmospheric pressure and room temperature. After an uptake of one hydrogen equivalent the mixture was filtered and the filtrate evaporated. Chromatography of the residue, 135 mg, on silica gel and elution with 1:1 petroleum ether–ether gave 45 mg of a liquid whose distillation led to ketol **17b**: ir (neat), OH 2.90 (m), C=O 5.92 (s) μ; pmr δ 1.04 (d, 3, $J = 6.5$ Hz, Me), 1.11 (s, 3, cyclopropyl Me), 1.19 (s, 3, cyclopropyl Me), 2.49 (septet, 1, $J = 6.5$ Hz, α-ketomethine), 3.48 (m, 1, oxymethine).

*Anal.* Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.31; H, 9.56.

Jones reagent,[11] 1.5 ml, was added over a 30-min period to a solution of 250 mg of ketol **17b** in 40 ml of acetone at −50°. After an additional 15 min 2 ml of methanol was added and the mixture allowed to come to room temperature slowly. Methylene chloride, 50 ml, and solid sodium bicarbonate were added, and the mixture was shaken and filtered. The filtrate was dried and evaporated and the residue chromatographed on silica gel. Elution with 4:1 petroleum ether–ether gave 197 mg of an oil [ir (neat) C=O 5.92 (s) μ] whose distillation yielded diketone **17a**: mp 49–50°; pmr δ 1.10 (d, 3, $J = 6.5$ Hz, Me), 1.28 (s, 6, cyclopropyl methyls), 2.1–2.7 (m, 3, α-ketomethylene, α-ketomethine).[12]

*Anal.* Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.56; H, 8.68.

A solution of 100 mg of enolone **2b** in 25 ml of 0.07 *N* sodium hydroxide solution was stirred at room temperature for 5 hr. Upon neutralization with hydrochloric acid it was extracted with methylene chloride. The extract was dried and evaporated. Chromatography of the residue, 74 mg, on silica gel and elution with 10:1 petroleum ether–ether yielded 27 mg of a colorless oil whose distillation gave liquid epoxy diketone **18**: ir (neat) C=O 5.87 (s) μ; pmr δ 1.10 (s, 3, cyclopropyl Me), 1.31 (s, 3, cyclopropyl Me), 1.51 (s, 3, epoxy Me), 1.98 (s, 2, cyclopropyl Hs), 3.37 (s, 1, epoxy H).

*Anal.* Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.60; H, 6.71.

A solution of 25 mg of **17a** and 30 mg of potassium hydroxide in 21 ml of methanol was kept at 0–5° for 1.5 hr. Work-up as above gave 18 mg of **18**.

**Reductions by Zinc in Acetic Acid.**—A mixture of 0.40 g of dione **4**[3] and 1 g of zinc dust in 20 ml of glacial acetic acid was stirred at room temperature for 5 hr. It then was poured into ice water and extracted with methylene chloride. The extract was washed with dilute sodium hydroxide solution, dried, and evaporated. Sublimation of the solid residue, 0.40 g, gave diketone **5**: mp 255° dec; ir ($CCl_4$) C=O 5.72 (s) μ; pmr δ 1.8–2.0 (m, 2, methylene), 2.1–2.3 (broad s, 4, methines), 2.6–2.8 (broad s, 4, α-ketomethylenes), 2.7–2.9 (m, 2, α-ketomethines).

*Anal.* Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.87. Found: C, 74.84; H, 6.79.

A mixture of 2.00 g of diketone **2a**[2] [pmr δ 1.32 (s, 6, cyclopropyl methyls), 1.96 (d, 3, $J = 2.0$ Hz, olefinic Me), 2.31 (s, 2, cyclopropyl H's), 6.49 (d, 1, $J = 2.0$ Hz, olefinic H)] and 4 g of zinc dust in 30 ml of glacial acetic acid was stirred at room temperature for 10 min. Work-up as above gave 1.75 g of gpc pure product whose distillation yielded liquid diketone **3**: ir (neat) C=O 5.85 (s) μ; pmr δ 0.99 (s, 3, Me), 1.08 (s, 3, Me), 1.12 (d, 3, $J = 7.0$ Hz, Me), 2.2–2.9 (m, 7, methylenes, methine).

*Anal.* Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.57; H, 9.50.

A mixture of 9.5 mg of **16** and 0.5 g of zinc dust in 15 ml of glacial acetic acid was stirred at room temperature for 5 min. Work-up as above gave 8 mg of a liquid identified by gpc and ir as diketone **3**.

A mixture of 60 mg of **17a** and 1 g of zinc dust in 20 ml of glacial acetic acid was refluxed for 12 hr. During this time 3 g of zinc dust and 10 ml of glacial acetic acid were added. Work-up as above gave 35 mg of a liquid identified by gpc, ir, and pmr as diketone **3**.

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(12) Jones oxidation of **17b** at room temperature led to enedione **2a**.

A mixture of 6 mg of **18** and 0.5 g of zinc dust in 20 ml of glacial acetic acid was refluxed for 1.5 hr. During this time 1.5 g of more zinc dust was added in portions. Work-up as above gave 5 mg of a liquid identified by gpc and ir as diketone **3**.

**Disproportionation of Diketone 17a.**—A solution of 25 mg of **17a** and 30 mg of potassium hydroxide in 28 ml of methanol was kept at 0° under nitrogen for 1 hr. It was neutralized with 6.5 *N* hydrochloric acid, diluted with 30 ml of water, and extracted with methylene chloride. The extract was dried and evaporated. Chromatography of the residue, 23 mg, on silica gel and elution with 6:1 petroleum ether–ether yielded 8 mg of a solid identified by gpc and ir as diketone **2a**, while elution with 3:1 petroleum ether–ether gave 7 mg of a liquid identified as dione **3** by gpc and ir.

**Registry No.**—**1,** 637-88-7; **3,** 25237-81-4; **5,** 25282-60-4; **8,** 25237-82-5; **9,** 25237-83-6; **14,** 25237-84-7; **15,** 25237-85-8; **16,** 25282-56-8; **17a,** 25237-86-9; **17b,** 25237-87-0; **18,** 25237-88-1.

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# Permanganate Oxidations. V. Kinetics and Mechanisms of the Oxidation of Mandelate Anions[1,2]

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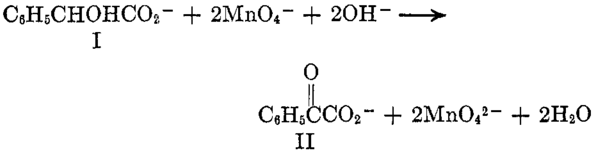
The kinetics of the permanganate oxidation of mandelic acid were examined over the pH range of 7.3 to 13.65 *via* spectrophotometric stopped-flow techniques. The reaction appears to proceed through three different paths. Presumably oxidative decarboxylation, to give benzaldehyde and carbon dioxide, and a reaction independent of hydroxide ion concentration occur between pH 7.3 and 12.7. Above pH 12.7, where phenylglyoxylic acid is formed, the reaction shows a first-order dependence on hydroxyl ion concentration and the rate expression is $\nu = k[\text{mandelate anion}][OH^-][MnO_4^-]$. The mandelate anion exhibits a kinetic isotope effect of 3.15 and 5.45 at pH 13.3 and 13.6, respectively. A positive salt effect is observed at pH 13.3. Correlation of the second-order rate constants with $\sigma^n$ and $\sigma^0$ substituent constants gives $\rho$ values of 1.0 and 0.97, respectively. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for four different mandelate anions varied from 6.6 to 7.7 kcal/mol and −33.3 to −38.2 eu. The kinetic data, at pH greater than 12.7, is consistent with either a hydride transfer from the mandelate dianion to permanganate or a hydrogen atom abstraction from the mandelate dianion by permanganate in the rate-determining step.

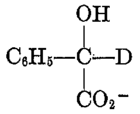
Although the kinetics and mechanisms of the permanganate oxidation of malic acid,[3] tartaric acid,[4,5] citric acid,[6] mandelic acid,[7] and lactic acid[8,9] have been investigated in neutral and acid media, no mechanistic studies have been reported concerning the permanganate oxidation of hydroxy acids in alkaline media. Permanganate oxidizes the mandelate anion (I) to phenylglyoxylic acid (II) under basic conditions (eq 1).[10] In contrast, when mandelic acid is oxidized



$$\underset{\text{I}}{C_6H_5CHOHCO_2^-} + 2MnO_4^- + 2OH^- \longrightarrow \underset{\text{II}}{C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}CO_2^-} + 2MnO_4^{2-} + 2H_2O \quad (1)$$

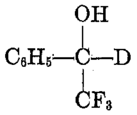
in acid solution, oxidative decarboxylation occurs to give benzaldehyde and carbon dioxide.[7] In order to obtain a more detailed mechanistic picture of the permanganate oxidation of the mandelate anion (I), we have examined the kinetics of the reaction from pH 7.3 to 13.65 *via* spectrophotometric stopped-flow techniques.

The permanganate oxidation of α-deuteriomandelate anion (III) is also of interest because of its close structural similarity to IV which gives a remarkably



$$C_6H_5\text{—}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CO_2^-}{|}}{C}}\text{—}D$$

III



$$C_6H_5\text{—}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CF_3}{|}}{C}}\text{—}D$$

IV

large $k_H/k_D$ of 16.1 in alkaline permanganate oxidations.[11-13]

## Experimental Section

**Reagents.**—Distilled water was purified by passing through two type R-2 ion-exchange columns.[14] Standard volumetric (Acculute) sodium hydroxide ($CO_2$ free) concentrate was diluted to the specified volume for the desired pH. Potassium permanganate stock solutions were also prepared from standard volumetric solutions (Acculute). The stock solution was stored under nitrogen, and the absorbancy index was checked before each set of kinetic runs. Reagent grade sodium chloride (Mallinckrodt), potassium nitrate (Mallinckrodt), and potassium sulfate (Mallinckrodt) were used without further purification to adjust ionic strength. All solutions were prepared immediately before use, and the pH was measured potentiometrically.

**Mandelic Acid** (Matheson Coleman and Bell) was recrystallized from benzene before use, mp 118–119° (lit.[15] mp 119.5–120.5°).

**Substituted Mandelic Acids.**—Mandelic acid derivatives were prepared *via* the imido ester (eq 2),[16] the cyanohydrin (eq 3),[17]

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