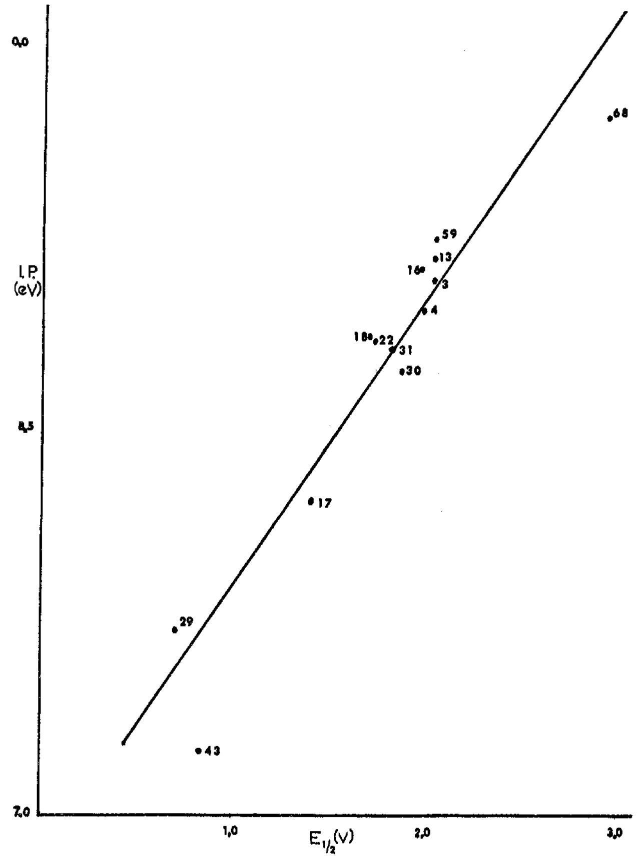

Figure 2.—Plot of selected vertical IP *vs.* $E_{1/2}$. Numbers refer to Table I.

cation radical decays much more rapidly than the time required for the measurement $E_{1/2}$ is a kinetic parameter for the overall oxidation process. If one considers this fact in addition to the possible incursion of specific surface effects and differential solvation, this simple correlation is fascinatingly accurate. The correlation results because the energy of the highest occupied molecular orbital (HOMO) primarily determines both potentials. Several groups have described correlations of IP or $E_{1/2}$ with the HOMO energy[2,11] and it is clear that either potential should be calculable. It does appear that phenol and butyl mercaptan have abnormally low $E_{1/2}$ values because of special solvation. The cation radicals of these species will be strong acids stabilized by hydrogen bonding to the basic solvent, acetonitrile. This will, of course, lower the $E_{1/2}$. Other solvation effects and specific surface effects might be uncovered by a careful study of $E_{1/2}$ variations as a function of solvent and electrode material.

This correlation should have interesting ramifications in organic electrochemistry. As indicated, decisions about synthetic feasibility can be made with some confidence based upon oxidation potential predictions for reactants and products. In a similar manner, electrooxidation can be applied selectively to the most easily oxidized functionality of a complex molecule. Photoelectron spectroscopy is of interest in this regard since it not only provides IP data but reveals the nature of the HOMO.[4] Finally, it is noted that homogeneous electron-transfer oxidation rates and the $E_{1/2}$ of radicals[12] and inorganic complexes may be amenable to a similar treatment.

Acknowledgment.—We thank the Petroleum Research Fund and the National Science Foundation for support.

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[11] An extensive and modern treatment with references is M. J. S. Dewar, J. A. Hashmall, and N. Trinajstic, *J. Amer. Chem. Soc.*, **92**, 5555 (1970).

[12] H. Volz and W. Lotsch, *Tetrahedron Lett.*, 2275 (1969) report −0.47 V for the reduction $E_{1/2}$ of tropylium perchlorate on mercury. Since this couple is probably fully reversible and therefore independent of electrode, we would calculate the IP as 6.25. The reported[1] spectroscopic IP is 6.24!

Oxidative Coupling of Aldehydes and the Rearrangement of Dioxa-1,5-hexadienes

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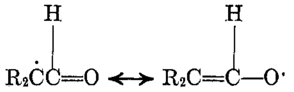
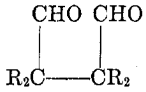
The oxidation[2] of aldehydes of the form R_2CHCHO by active manganese dioxide gives products which can be formulated as dimers of the free radical a. These are **1** and **2**. The other symmetrical coupling product, the divinyl peroxide, $R_2C{=}C(H)OOC(H){=}CR_2$, **3**, has not been observed. We have been interested in dioxa-1,5-hexadienes and their rearrangements in connection with our studies[3] of allylic carboxylates, which are 1,3-dioxa-1,5-hexadienes. Compounds **1**, **2**, and **3** are respectively substituted 1,6-, 1,4-, and 3,4-dioxa-1,5-hexadienes.



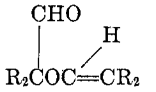
$R_2\dot{C}C(H){=}O \longleftrightarrow R_2C{=}C(H){-}O^{\cdot}$

a



$R_2C(CHO){-}C(CHO)R_2$

1



$R_2C(CHO)OC(H){=}CR_2$

2

The Cope rearrangement would lead to the rearrangements **2** ⇄ **2** and **1** ⇄ **3**. The first is a degenerate rearrangement which could be revealed by labeling as has been done in one cyclic case;[4] in the open-chain case the completely methylated compound **2a** does not show any nmr line broadening at 150°,[2] showing by this method no degenerate rearrangement. In this note we present evidence supporting in some detail the free-radical coupling mechanism and observe some of the proposed rearrangements.

There was a possibility that the active manganese dioxide oxidation could be exploited to give products allowing a study of the rearrangement whether or not the radical coupling mechanism is correct. If the mechanism is incorrect, then oxidation of optically active α-methylbutylraldehyde might give an optically active form of the oxidation product in either of the geometrically isomeric form **2b** or **2c**. On the other hand, if the mechanism is correct, **2b** and **2c** will be optically inactive, but cross products **2d**, **2e**, and **2f** might result from the oxidation of a mixture of isobutyraldehyde and α-methylbutyraldehyde. The Cope rearrangement would be expected to be accom-

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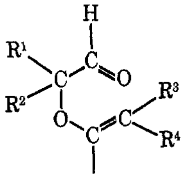
[1] National Science Foundation Predoctoral Fellow, 1968–1971.

[2] J. C. Leffingwell, *Chem. Commun.*, 357 (1970).

[3] E. S. Lewis, J. T. Hill, and E. R. Newman, *J. Amer. Chem. Soc.*, **90**, 662 (1968).

[4] J. D. Roberts and R. P. Lutz, *ibid.*, **83**, 2198 (1961).

panied by the racemization of optically active **2b** or **2c**, and by the interconversions **2b** ⇄ **2c**, **2f** ⇄ **2e**, and **2f** ⇄ **2d**.



2a, $R^1 = R^2 = R^3 = R^4 = CH_3$
b, $R^1 = R^3 = CH_3$; $R^2 = R^4 = C_2H_5$
c, $R^1 = R^4 = CH_3$; $R^2 = R^3 = C_2H_5$
d, $R^1 = R^2 = R^3 = CH_3$; $R^4 = C_2H_5$
e, $R^1 = R^2 = R^4 = CH_3$; $R^3 = C_2H_5$
f, $R^1 = R^3 = R^4 = CH_3$; $R^2 = C_2H_5$

We find that the manganese dioxide oxidation of optically active α-methylbutyraldehyde (from the oxidation of *sec*-butylcarbinol from fusel oil) gave in agreement with the previous report a mixture of **2b** and **2c**, as shown by the nmr,[5] with no detectable rotation (<0.01° neat in a 1-dm tube). The oxidation of a mixture of isobutyraldehyde and α-methylbutyraldehyde gave a complex mixture. After steam distillation, the volatile fraction showed upon gas chromatographic analysis peaks of retention time corresponding to **2a**, the mixture of **2d**, **2e**, and **2f**, and the mixture of **2b** and **2c**. It was possible by preparative gas chromatography to further isolate and characterize **2f** and the mixture of olefinic stereoisomers **2d** and **2e**. All of these results are consistent with the proposed free-radical mechanism.

It did prove possible to separate partially the cis and trans isomers, **2b** and **2c**, by gas chromatography. From the roughly 1:1 mixture given by oxidation, a fraction containing a 3.8:1 ratio was obtained. This fraction on heating to 200° in a capillary tube for 95 min was converted to a mixture of 1.8:1 ratio, together with a good deal of polymer. If we assume an equilibrium constant of unity and equal rates of polymerization, this gives a rate constant for **2b** → **2c** (or the reverse) of roughly 6×10^{-5} sec^{-1}. Assuming an A factor of 10^{11} sec^{-1}, we calculate an activation energy of roughly 33 kcal/mol. Furthermore, we have observed that **2f** → **2d** and **2e** at 200° at about the same rate as the cis–trans isomerization.

A simple estimate of ΔH for the **3** → **1** process using average bond energies shows it to be exothermic by more than 100 kcal/mol. The activation energy for this reaction would be probably no more than half that for the symmetric **2** → **2** process. This low an activation energy would make the reaction **3** → **1** very fast and account for the failure to observe **3** even if formed, and the slower rate of the **2** → **2** process accounts for the temperature-independent nmr spectrum of **2a**.

Registry No.—**2d**, 33066-03-4; **2e**, 33066-04-5; **2f**, 33061-15-3; isobutyraldehyde, 78-84-2; α-methylbutyraldehyde, 96-17-3.

Acknowledgment.—We acknowledge gratefully the support of this research by a grant from the National Science Foundation. We also thank Dr. J. C. Leffingwell for telling us of an improved technique for the oxidation.

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[5] J. C. Leffingwell, French Patent 1,544,604 (1968).

Reduction of Sulfoxides with Sodium Hydrogen Sulfite[1]

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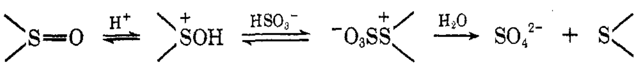
Sulfoxides can be reduced to sulfides under a variety of conditions.[2] The sulfoxide group is capable of oxidizing a carbon atom, but more typical are reactions in which heteroatoms are oxidized. Thiols are oxidized to disulfides,[3] phosphines to phosphine oxides,[4] phosphorus thioacids to phosphorus oxyacids,[5] halide ions to halogens,[6] and silanes to silicon–oxygen derivatives[7] with the concomitant reduction of a sulfoxide to the corresponding sulfide.

The sulfoxides of *dl*-methionine and α-ethyl thioglucoside were reported in 1939 to be reduced by aqueous sulfite.[8] More recently, aqueous solutions of sodium "metabisulfite" have been employed in the selective reduction of the sulfoxide group in α-methylsulfinylacetophenone and derived compounds.[9] Our interest in this method of reduction of sulfoxides was fostered by a fortuitous observation that brief treatment of a mixture of *cis*- and *trans*-2-methylthiolane 1-oxide[10] with aqueous sodium hydrogen sulfite results in the preferential destruction of the cis isomer. This experiment provided an easy method for the preparation of pure *trans*-2-methylthiolane 1-oxide. The more rapid consumption of the cis isomer immediately suggests to us that this reduction reaction involves a nucleophilic attack at sulfur. The "back-side" of the sulfoxide group is less sterically encumbered in the cis diastereomer. Similarly, we find that the *cis*-4-*tert*-butylthiane 1-oxide[11] is reduced somewhat faster than *trans*-4-*tert*-butylthiane 1-oxide. As a working hypothesis we propose the following mechanistic scheme



$$>S{=}O \xrightleftharpoons{H^+} >\overset{+}{S}OH \xrightleftharpoons{HSO_3^-} {}^-O_3S\overset{+}{S}< \xrightarrow{H_2O} SO_4^{2-} + S<$$

Analysis of reaction of thiolane 1-oxide and sodium hydrogen sulfite revealed that sulfate was formed in amounts equimolar with the consumption of the sulfoxide. As predicted from the scheme, aqueous sodium sulfite is not an effective reducing reagent for sulfoxides; the pH of the solution is not low enough to result in a significant concentration of protonated sulfoxide. On the other hand, aqueous solutions of

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[1] Part XXXVII in the series "Chemistry of Sulfoxides and Related Compounds." We gratefully acknowledge support by the National Science Foundation (GP 8648).

[2] For recent leading references see D. W. Chasar, *J. Org. Chem.*, **36**, 613 (1971).

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[9] G. A. Russell and E. T. Sabourin, *J. Org. Chem.*, **34**, 2336 (1969).

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[11] C. R. Johnson and D. McCants, Jr., *J. Amer. Chem. Soc.*, **87**, 1109 (1965).