

TABLE I
 RATES OF ENOLIZATION. BASE CATALYSIS

R ₁	R ₂	Vol. % of ketone	[NaOAc], moles/l.	50°		70°	
				k _{R1} , mole ⁻¹ sec ⁻¹	k _{R2} , mole ⁻¹ sec ⁻¹	k _{R1} , mole ⁻¹ sec ⁻¹	k _{R2} , mole ⁻¹ sec ⁻¹
CH ₃ COCH ₃		10	5	0.15 × 10 ⁻⁵	0.15 × 10 ⁻⁵	1.4 × 10 ⁻⁵	1.4 × 10 ⁻⁵
		5	5	0.15 × 10 ⁻⁵	0.15 × 10 ⁻⁵	1.5 × 10 ⁻⁵	1.5 × 10 ⁻⁵
		10	2.5	0.18 × 10 ⁻⁵	0.18 × 10 ⁻⁵	1.6 × 10 ⁻⁵	1.6 × 10 ⁻⁵
		5	2.5	0.18 × 10 ⁻⁵	0.18 × 10 ⁻⁵	1.9 × 10 ⁻⁵	1.9 × 10 ⁻⁵
CH ₃ CH ₂ COCH ₃		10	5	0.14 × 10 ⁻⁵	0.13 × 10 ⁻⁵	0.78 × 10 ⁻⁵	0.72 × 10 ⁻⁵
		5	5	0.14 × 10 ⁻⁵	0.16 × 10 ⁻⁵	0.83 × 10 ⁻⁵	0.85 × 10 ⁻⁵
		10	2.5	0.13 × 10 ⁻⁵	0.14 × 10 ⁻⁵	0.84 × 10 ⁻⁵	0.80 × 10 ⁻⁵
		5	2.5	0.14 × 10 ⁻⁵	0.15 × 10 ⁻⁵	0.80 × 10 ⁻⁵	0.98 × 10 ⁻⁵
CH ₃ CH ₂ COCH ₂ CH ₃		5	5	0.090 × 10 ⁻⁵	0.09 × 10 ⁻⁵	0.65 × 10 ⁻⁵	0.65 × 10 ⁻⁵
		2.5	5	0.095 × 10 ⁻⁵	0.095 × 10 ⁻⁵	0.75 × 10 ⁻⁵	0.75 × 10 ⁻⁵
		5	2.5	0.095 × 10 ⁻⁵	0.095 × 10 ⁻⁵	0.65 × 10 ⁻⁵	0.65 × 10 ⁻⁵
		2.5	2.5	0.095 × 10 ⁻⁵	0.095 × 10 ⁻⁵	0.55 × 10 ⁻⁵	0.55 × 10 ⁻⁵
CH ₃ OCH ₂ COCH ₃		10	5	0.57 × 10 ⁻⁵	1.3 × 10 ⁻⁵	4.7 × 10 ⁻⁵	8.5 × 10 ⁻⁵
		5	5	0.55 × 10 ⁻⁵	1.3 × 10 ⁻⁵	5.0 × 10 ⁻⁵	9.7 × 10 ⁻⁵
		10	2.5	0.52 × 10 ⁻⁵	1.3 × 10 ⁻⁵	4.0 × 10 ⁻⁵	10.4 × 10 ⁻⁵
		5	2.5	0.50 × 10 ⁻⁵	1.2 × 10 ⁻⁵	4.0 × 10 ⁻⁵	9.7 × 10 ⁻⁵

 TABLE II
 RATES OF ENOLIZATION. ACID CATALYSIS

R ₁	R ₂	Vol. % of ketone	[KHSO ₄], mole/l.	50°		70°	
				k _{R1} , mole ⁻¹ sec ⁻¹	k _{R2} , mole ⁻¹ sec ⁻¹	k _{R1} , mole ⁻¹ sec ⁻¹	k _{R2} , mole ⁻¹ sec ⁻¹
CH ₃ COCH ₃		10	1	1.0 × 10 ⁻⁴	1.0 × 10 ⁻⁴	4.9 × 10 ⁻⁴	4.9 × 10 ⁻⁴
		5	1	1.3 × 10 ⁻⁴	1.3 × 10 ⁻⁴	6.5 × 10 ⁻⁴	6.5 × 10 ⁻⁴
		10	0.5	1.2 × 10 ⁻⁴	1.2 × 10 ⁻⁴	4.8 × 10 ⁻⁴	4.8 × 10 ⁻⁴
		5	0.5	1.4 × 10 ⁻⁴	1.4 × 10 ⁻⁴	6.0 × 10 ⁻⁴	6.0 × 10 ⁻⁴
CH ₃ CH ₂ COCH ₃		10	1	1.9 × 10 ⁻⁴	0.92 × 10 ⁻⁴	5.0 × 10 ⁻⁴	3.8 × 10 ⁻⁴
		5	1	1.8 × 10 ⁻⁴	0.96 × 10 ⁻⁴	5.0 × 10 ⁻⁴	4.1 × 10 ⁻⁴
		10	0.5	1.7 × 10 ⁻⁴	0.87 × 10 ⁻⁴	5.8 × 10 ⁻⁴	3.9 × 10 ⁻⁴
		5	0.5	2.4 × 10 ⁻⁴	1.1 × 10 ⁻⁴	6.6 × 10 ⁻⁴	4.6 × 10 ⁻⁴
CH ₃ CH ₂ COCH ₂ CH ₃		5	1	0.6 × 10 ⁻⁴	0.6 × 10 ⁻⁴	1.7 × 10 ⁻⁴	1.7 × 10 ⁻⁴
		2.5	1	0.6 × 10 ⁻⁴	0.6 × 10 ⁻⁴	1.8 × 10 ⁻⁴	1.8 × 10 ⁻⁴
		5	0.5	0.65 × 10 ⁻⁴	0.65 × 10 ⁻⁴	1.0 × 10 ⁻⁴	1.0 × 10 ⁻⁴
		2.5	0.5	0.55 × 10 ⁻⁴	0.55 × 10 ⁻⁴	1.0 × 10 ⁻⁴	1.0 × 10 ⁻⁴
CH ₃ OCH ₂ COCH ₃		10	1	0.072 × 10 ⁻⁴	0.12 × 10 ⁻⁴	0.44 × 10 ⁻⁴	0.68 × 10 ⁻⁴
		5	1	0.080 × 10 ⁻⁴	0.12 × 10 ⁻⁴	0.49 × 10 ⁻⁴	0.74 × 10 ⁻⁴
		10	0.5	0.079 × 10 ⁻⁴	0.13 × 10 ⁻⁴	0.47 × 10 ⁻⁴	0.74 × 10 ⁻⁴
		5	0.5	0.10 × 10 ⁻⁴	0.15 × 10 ⁻⁴	0.56 × 10 ⁻⁴	0.81 × 10 ⁻⁴

ing a single series of measurements, integral values varied by ±10%. Exchange was followed to about 80%, each run consisting of a series of about ten observations.

Treatment of Data.—The exchange approximates the first-order McKay law,¹⁶ though deviations are expected (1) because of the isotope effect on the equilibrium constant for the exchange reaction, and (2) because of the presence of two sites exchanging at different rates. For these reasons the infinity value for H remaining in a particular branch of the ketone could not be calculated. The following method was therefore adopted. A series of values, $V_1(t) = I_{B1}/(I_{B1} + I_{B2} + I_W)$, was obtained, where I_{B1} was the integrated area at reaction time t of the proton signal from branch one of the ketone, I_{B2} was that from branch two of the ketone, and I_W was that from the water. The $V(t)$ was then treated by the Guggenheim¹⁷ procedure, to get $t_{1/2}$, the half-life for exchange. From the McKay law

$$R = \frac{[\text{water}][\text{ketone}]}{[\text{water}] + [\text{ketone}]} \frac{0.693}{t_{1/2}} n$$

where n = number of protons in the exchanging group, and since

$$R = k[\text{ketone}][\text{catalyst}]$$

and since $[\text{ketone}] \ll [\text{water}]$

$$k = \frac{0.693}{t_{1/2}} \frac{n}{[\text{catalyst}]}$$

Duplicate and repeat determinations agreed to about 20% in k . The values in Table I represent averages of at least two determinations.

(16) H. McKay, *Nature*, **142**, 997 (1938).

(17) E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1966).

Synthesis through Oxyplumbation. Reaction of Styrene with Acetylacetone in the Presence of Lead Tetraacetate

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In a previous paper, it was demonstrated that the substitution of active methylene compounds with alkyl or aralkyl groups containing mercury took place by the reaction of oxymercurial of olefin in the presence of perchloric acid.¹ Oxythallate reacted in a similar way. The resulting organothallium compounds, however, were unstable and reacted further under the conditions. For example, the reaction of styrene with acetylacetone in the presence of thallic acetate and the acid gave 3-acetyl-2-methyl-4-phenyl-4,5-dihydrofuran. This result was explained by a series of reaction steps involving oxythallation of styrene, reaction with acetylacetone, and dethallation.² It is desirable to check the possi-

(1) K. Ichikawa, O. Itoh, T. Kawamura, M. Fujiwara, and T. Ueno, *J. Org. Chem.*, **31**, 447 (1966).

(2) K. Ichikawa, S. Uemura, and T. Sugita, *Tetrahedron*, **22**, 407 (1966).

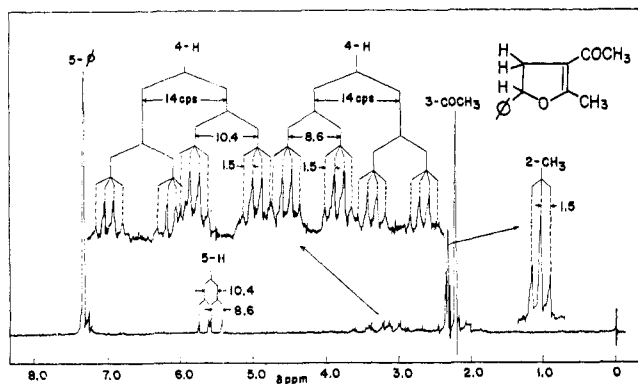


Figure 1.—Nmr spectrum of 3-acetyl-2-methyl-5-phenyl-4,5-dihydrofuran in deuteriochloroform at 60 Mc.

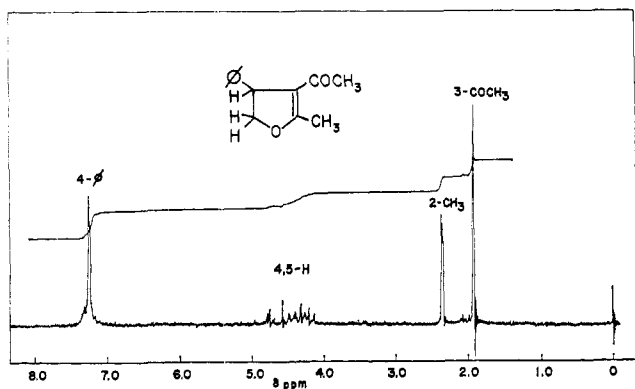


Figure 2.—Nmr spectrum of 3-acetyl-2-methyl-4-phenyl-4,5-dihydrofuran in deuteriochloroform at 60 Mc.

bility of extending this reaction to other oxymetalates. Lead tetraacetate is another metal salt for which the possibility of oxymetallation has been suggested. In connection with the mechanism of oxidation of olefins, several authors proposed oxyplumbation as the intermediate step of the reaction without isolating the oxyplumbates.³ Our results on the kinetic study of lead tetraacetate oxidation of anethole suggested that an addition compound, probably an oxyplumbate, was formed in appreciably high concentrations.⁴ Thus, assuming that oxyplumbation takes place, the question has been raised as to whether or not the reaction of styrene with acetylacetone will proceed in the presence of lead tetraacetate as in the case with thallic acetate.²

When acetylacetone was added to a solution of styrene in benzene containing 10% acetic acid, 0.5 M perchloric acid, and lead tetraacetate with stirring at 0–3°, a deep orange color developed at first and disappeared gradually with a simultaneous formation of a large amount of white crystals of lead acetate. Work-up of the resulting solution gave acetoxyacetylacetone (I) and 3-acetyl-2-methyl-5-phenyl-4,5-dihydrofuran (II) as the main products. The yields of I and II were 12–23 and 12–25%, respectively, in several experiments. Since a small amount of unidentified product could not be removed by distillation, the yield of the latter was calculated from the gas chromatographic tracings of the distillates, and the pure product for spectra and analysis was obtained by column chromatography.

(3) See, for example, K. Alder, F. H. Flock, and H. Wirtz, *Chem. Ber.*, **91**, 609 (1958); H. J. Kabbe, *Ann.*, **656**, 204 (1962).

(4) K. Ichikawa, Y. Takeuchi, and O. Itoh, *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 317 (1962).

The structure of II was determined on the basis of the results of elementary analysis and spectral data. Infrared and ultraviolet spectra were very similar to those of 3-acetyl-2-methyl-4-phenyl-4,5-dihydrofuran (III) which was obtained by the reaction of styrene with acetylacetone in the presence of thallic acetate.² However, the nmr spectrum (shown in Figure 1) was different from that of the 4-phenyl compound (III, Figure 2) and showed that II was the 5-phenyl isomer. The signals were observed at δ 7.32 (multiplet, phenyl protons), 5.59 (multiplet, proton at C₅), 3.42 (multiplet, methylene proton at C₄), 2.92 (multiplet, methylene proton at C₄), 2.31 (triplet, 2-methyl protons), and 2.20 (singlet, acetyl protons) with relative intensities of 5:1:1:1:3:3. Two multiplets centered at δ 2.92 and 3.42 and a multiplet centered at 5.59 can be assigned to the signals owing to ABX system splitting⁵ of C₄-methylene protons and C₅ proton. Because of a long-range coupling with the two protons at C₄, 2-methyl protons gave a triplet, while the same methyl protons of the 4-phenyl isomer (III) showed a doublet signal.² The coupling constants were 1.5 and 1.0 cps in II and III, respectively.

When the reaction was carried out in acetic acid solvent, the product was a mixture of I, II, and III. The ratio of II and III was roughly 2:1, and the total yield of the dihydrofurans was much lower (7–13%) than in the case of benzene solvent. The yield of I was also lower (4–5%).

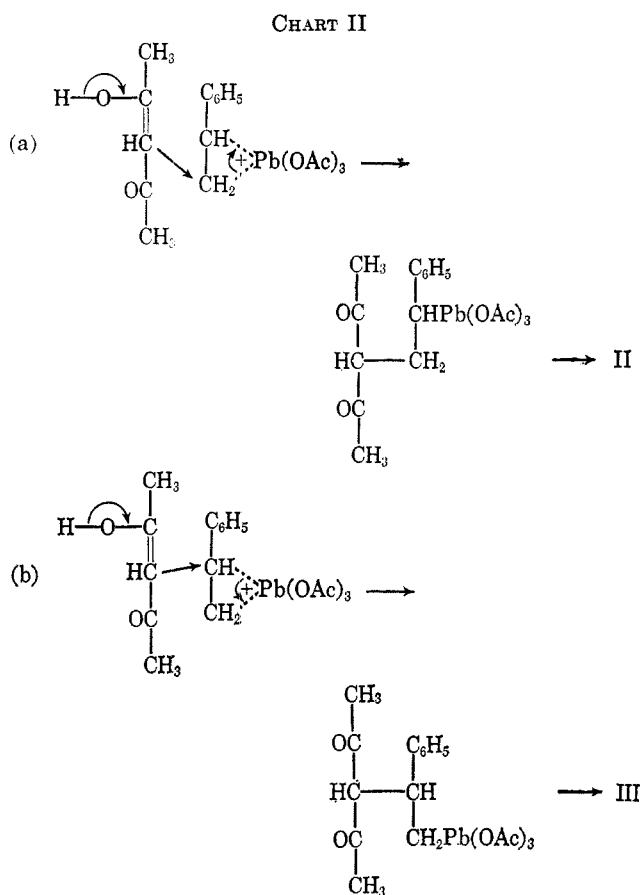
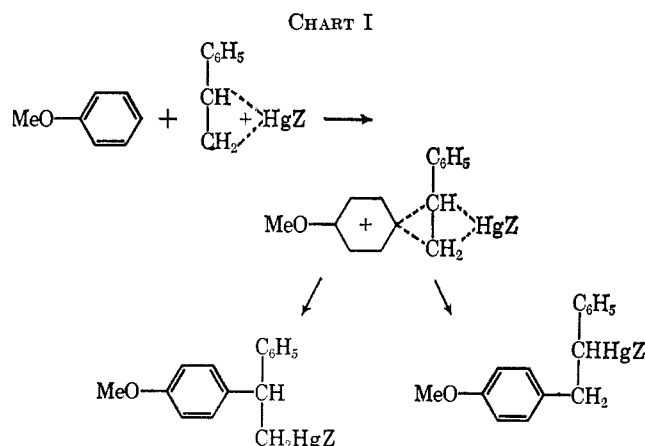
Since Cocker and Schwarz obtained I by the oxidation of acetylacetone with lead tetraacetate in dry benzene,⁶ it is clear that the same reaction proceeded in the present experiments. As far as the formation of II or III is concerned, the reaction conditions and the results are almost the same as those of the same reaction with thallic acetate except that the isomer distributions in the products are different. It appears, therefore, that II and III were formed by the reaction of styrene oxyplumbate with acetylacetone through a mechanism similar to that of the case with thallic acetate. The reason for the difference in isomer distributions is not yet clear. The migration of phenyl group in the product by acid catalysis does not explain the results because of the following fact. In the same reaction with thallic acetate, only the 4-phenyl isomer was obtained and no formation of the 5-phenyl derivative could be detected.² If the isomerization of the 4-phenyl to the 5-phenyl isomer proceeds in the present conditions, the latter should be found in the product with thallic acetate. A possible explanation would be found in the analogy with the reaction of mercurinium ion.⁷ The formation of two isomers in the reaction of anisole with the oxymethylmercurial of styrene has been explained by the mercurinium ion mechanism in Chart I. Assuming that the plumbinium ion from oxyplumbate is the reacting species and the analogy with the reaction of mercurinium ion mentioned above can be applied, two kinds of the product are expected by the mechanism in Chart II. It appears that the reaction proceeds through path a in benzene and

(5) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 132.

(6) W. Cocker and J. C. P. Schwarz, *Chem. Ind. (London)*, 390 (1951).

(7) K. Ichikawa, S. Fukushima, H. Ouchi, and M. Tsuchida, *J. Am. Chem. Soc.*, **81**, 3401 (1959).

through both paths a and b in acetic acid solution, respectively. However, the question of which is the controlling factor of the possible two reaction paths remains unexplained.



The results mentioned above show that the oxyplumbation of styrene does occur and the oxyplumbate reacts with active methylene as oxymercurial and oxythallate, although the applicability might be limited because of the strong oxidative nature of lead tetraacetate.

Experimental Section

Materials.—All reagents were commercial products. Organic reagents were used after distillation.

Spectral Measurements.—Infrared and ultraviolet spectra were determined by JASCO IR-S and Hitachi EPS-2U, respec-

tively. The nmr spectrum was obtained on a Varian A-60 using tetramethylsilane as the internal standard in deuteriochloroform.

Reaction of Styrene with Acetylacetone in the Presence of Lead Tetraacetate.—The following example shows a typical experimental procedure. Into a suspension of 50 g of lead tetraacetate in 70 ml of benzene containing 7 ml of acetic acid, 25 g of styrene was added with stirring. After 3 hr, 8 g of 70% perchloric acid was added during 1 hr, followed by 20 g of acetylacetone during 0.5 hr under careful cooling. Throughout the additions, the reaction mixture was maintained at 0–3°. After 6 hr of stirring, the lead acetate formed was filtered off. The filtrate was washed with 200 ml of water, then with saturated sodium bicarbonate solution. Distillation *in vacuo* gave the following fractions: 40–50° (10 mm) (D₁); 50–60° (1 mm), 3 g (D₂); 60–114° (1 mm), 1.3 g (D₃); 114–124° (1 mm), 2.4 g (D₄); 124–154° (1 mm), 3.2 g (D₅); 5.1 g of residue. These fractions were analyzed by gas chromatography. D₁ was a mixture of unreacted styrene and acetylacetone. D₂ was acetoxyacetylacetone (I). D₅ was a mixture of II (more than 80%) and unidentified products (less than 20%). D₃ and D₄ were the mixtures of I, II, and small amounts of unidentified products. Calculation on the basis of gas chromatograms showed that the yields of I and II were 4.3 g (22.5%) and 3.5 g (14.2%), respectively.

D₂ was redistilled, bp 79–80° (5.5 mm), *n*_D²⁰ 1.4361. The ultraviolet spectra in hexane showed λ_{max} 283 mμ (ε 2900) and 190 mμ (ε 18,000). A grayish green copper salt was obtained, mp 250° dec.

Anal. Calcd for (C₇H₉O₄)₂Cu: C, 44.50; H, 4.80. Found: C, 44.56; H, 4.95.

D₅ was chromatographed (alumina-hexane) and distilled, bp 137–142° (2 mm), *n*_D²⁰ 1.5566.

Anal. Calcd for C₁₃H₁₄O₂: C, 77.20; H, 6.98. Found: C, 77.25; H, 7.20.

The semicarbazone melted at 182–184°.

Anal. Calcd for C₁₄H₁₇N₃O₂: C, 64.84; H, 6.61; N, 16.21. Found: C, 64.66; H, 6.82; N, 15.96.

Ultraviolet absorption maxima were found at 270 mμ (ε 10,600), 191.5 (40,000), and 190 (38,000) in hexane; 280 (12,500) and 204 (12,500) in ethanol. Infrared maxima were located at 2950 (w), 2850 (w), 1740 (w), 1670 (s), 1605 (s), 1485 (w), 1440 (w), 1415 (w), 1380 (m), 1360 (m), 1320 (w), 1225 (s), 1140 (w), 1060 (w), 1025 (w), 985 (w), 965 (w), 940 (m), 765 (m), 700 (s), 630 (m), and 605 (w) cm⁻¹.

Acknowledgment.—The authors are indebted to Dr. T. Shingu, Department of Pharmacy, for determining the nmr spectra.

Reactions of Methyl β-Naphthyl Sulfides with N-Halosuccinimides

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We have previously reported the efficacy of N-chlorosuccinimide (NCS) for the preparation of α-chloro sulfides.¹ It seemed of interest, as part of a program examining the reactions of sulfides with various halogenating agents, to compare the behavior of representative sulfides toward NCS and N-bromosuccinimide (NBS).

Sulfides 1 in carbon tetrachloride at 25° have been cleanly converted by NCS to α-chloro sulfides (2). Isolation of the chloro sulfides was not attempted; their identification was made using nmr. The downfield shifts of the methylene singlets of 2a,b compared with the methyl singlets of 1a,b are 2.43 and 2.50 ppm.

(1) D. L. Tuleen and T. B. Stephens, *Chem. Ind. (London)*, 1555 (1966).