1, COOH); ^{1}H nmr of separated 2 δ 0.90 (t, 6, J = 7 Hz, CH_3-CH_2–), 1.12 (s, 3, CH_3C–), 1.55 (m, 4, CH_3CH_2–), 10.9 (br, s, 1, COOH).

Anal. Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.34; H, 11.05.

***tert*-C_8 carboxylic acids** were obtained by the carbonylation of 1-heptene. The products were the mixtures of 2,2-dimethylhexanoic acid (A) and 2-methyl-2-ethylpentanoic acid (B): bp 214°; n^{25}D 1.4310; d^{25}_4 0.9154; ir 2950, 1700 (C=O), 1470, 1280, 1180 cm^{-1}; ^{1}H nmr of separated A δ 0.95 (t, 3, J = 6 Hz, CH_3CH_2–), 1.20 (s, 6, CH_3C–), 1.36 (m, 6, $-CH_2-$), 11.5 (br, s, 1, COOH); ^{1}H nmr of separated B δ 0.92 (t, 6, J = 7 Hz, CH_3CH_2–), 1.13 (s, 3, CH_3C–), 1.44 (m, 6, $-CH_2-$), 11.40 (br s, 1, COOH).

Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.19; H, 11.11.

***tert*-C_9 carboxylic acids** were obtained by the carbonylation of 1-octene and 2-octene. The products were the mixtures of 2,2-dimethylheptanoic acid, 2-methyl-2-ethylhexanoic acid, and 2-methyl-2-propylpentanoic acid with the ratio of 4:2:1: bp 132–133° (15 mm); n^{25}D 1.4291; d^{25}_4 0.9037; ir 2950, 1705 (C=O), 1470, 1205 cm^{-1}; ^{1}H nmr δ 1.12, 1.19 (s, CH_3CCOOH), 10.9 (br, 2, -COOH).

Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 67.93; H, 11.78.

***tert*-C_{11} carboxylic acids** were obtained by the carbonylation of 1-decene. The products were the mixtures of 2,2-dimethylnonanoic acid, 2-methyl-2-ethyloctanoic acid, 2-methyl-2-propylheptanoic acid, and 2-butylhexanoic acid with the ratio of 8:4:3:1: bp 142–143° (7 mm); n^{25}D 1.4368 [lit.[10] bp 139–148.5° (20 mm), n^{20}D 1.4363]; d^{25}_4 0.8976; ir 2950, 1700 (C=O), 1470, 1260 cm^{-1}; ^{1}H nmr δ 1.12, 1.18 (s, CH_3CCOOH), 9.80 (br, s, -COOH).

Anal. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90. Found: C, 71.01; H, 12.22.

1-Methylcyclopentanecarboxylic acid was obtained by the carbonylation of cyclohexene: ir 2980, 1705 (C=O), 1460, 1280, 1200 cm^{-1}; ^{1}H nmr δ 1.28 (s, 3, CH_3C–), 1.70 (m, 6, $-CH_2-$), 2.16 (m, 2, –HCHCCOOH), 11.78 (br, s, -COOH).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 66.02; H, 9.57.

α-Ethyl-γ-valerolactone was obtained by the carbonylation of 1,5-hexadiene: ir 2950, 1760 (C=O), 1460, 1175 cm^{-1}; ^{1}H nmr δ 1.00 (t, 3, J = 7 Hz, CH_3CH_2–), 1.40 (d, 3, J = 7 Hz, CH_3-CH–), 1.70 (m, 2, $-CH_2-$), 2.05 (m, 1, $-CHC_2H_5$), 2.50 (m, 2, $-CH_2-$), 4.50 (m, 1, –CHO–); mass spectrum (70 eV) m/e (rel intensity) 128 (10, M$^+$), 113 (12), 100 (62), 56 (90), 55 (100), 41 (88).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.15; H, 9.42.

Bicyclo[3.3.0]octanecarboxylic acid was obtained by the carbonylation of 1,5-cyclooctadiene: ^{1}H nmr δ 2.70 (m, 1, –CH–), 1.00–2.30 (m, 12, $-CH_2-$), 10.8 (br, s, -COOH); mass spectrum (70 eV) m/e (rel intensity) 154 (32, M$^+$), 126 (73), 113 (93), 109 (75), 67 (100).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.24; H, 8.76.

Registry No.—Carbon monoxide, 630-08-0; Cu_2O, 1317-39-1; H_2SO_4, 7664-93-9.

Steric Effects in the Cupric Ion Oxidation of α-Ketols[1]

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The kinetics of the oxidation of a series of α-ketols by copper(II) in buffered aqueous pyridine have been studied spectrophotometrically. At concentrations of cupric ion greater than 0.025 M the reaction exhibits first-order dependence with respect to copper(II), which is typical of a mechanism involving a rate-determining enolization of a copper(II)–ketol complex. The following order of reactivities was observed: α-hydroxyacetophenone > 2-hydroxycyclohexanone = benzoin > 4,4′-dimethoxybenzoin > 3-hydroxy-2-butanol > 2-hydroxycyclopentanone > 4-hydroxy-3-hexanone > 4-hydroxy-2,5-dimethyl-3-hexanone ≫ 4-hydroxy-2,2,5,5-tetramethyl-3-hexanone. In the cases of benzoin, 4,4′-dimethoxybenzoin, and 2-hydroxycyclopentanone large negative entropies of activation and large deviations from first-order kinetics were observed. These kinetic results are interpreted in terms of an intermediate copper(II)–ketol complex possessing a chelate structure.

Although the copper(II) oxidation of reducing sugars in alkaline aqueous media has been known for a very long time,[2] it has only been more recently that the mechanism of the reaction has been investigated.[3–7] The reaction is quite general for primary and secondary alcohols which possess an α-carbonyl group and is synthetically useful for the oxidation of acyloins to the corresponding diketones.[8] Weissberger, Schwarze, and Mainz[3] found that the oxidation of benzoin to benzil by ethanolic Fehling's solution was first order with respect to both the concentration of ketol and hydroxide ion, but was zero order with respect to copper(II) as shown by eq 1. In addition, it was found that the rates of

$$C_6H_5C(=O)CH(OH)C_6H_5 + 2OH^- + 2Cu^{2+} \longrightarrow C_6H_5C(=O)C(=O)C_6H_5 + 2H_2O + 2Cu^+$$

$$-\frac{d[Cu(II)]}{dt} = k[C_6H_5C(=O)CH(OH)C_6H_5][OH^-] \qquad (1)$$

autoxidation and racemization of benzoin, under identical conditions, obeyed the same rate law and proceeded at the same rate as the copper(II) oxidation.[9] Kinetic behavior of this type is indicative of an initial rate-determining enolization. Marshall and Waters[6] observed a similar behavior when they investigated the oxidation of acetoin and benzoin with Benedict's solution.

(1) This work was supported by grants from the Research Corporation and the University of Puget Sound Research Council.

(2) Trommer, *Ann. Chem. Pharm.*, **39**, 360 (1841); *Chem. Zentr.*, **12**, 762 (1841).

(3) A. Weissberger, W. Schwarze, and H. Mainz, *Justus Liebigs Ann. Chem.*, **481**, 68 (1930).

(4) J. Parrod, *C. R. Acad. Sci.*, **212**, 610 (1941).

(5) M. P. Singh, *et al.*, *Z. Phys. Chem. (Leipzig)*, **204**, 1 (1955); **205**, 285, 294 (1956); **207**, 187, 198 (1957); **208**, 265, 273 (1958); **216**, 13 (1961); **240**, 400 (1969); *J. Amer. Chem. Soc.*, **92**, 537 (1970).

(6) B. A. Marshall and W. A. Waters, *J. Chem. Soc.*, 2392 (1960); 1579 (1961).

(7) K. B. Wiberg and W. G. Nigh, *J. Amer. Chem. Soc.*, **87**, 3849 (1965).

(8) W. G. Nigh in "Oxidation in Organic Chemistry," part B, W. S. Trahanovsky, Ed., Academic Press, New York, N. Y., 1973, Chapter 1.

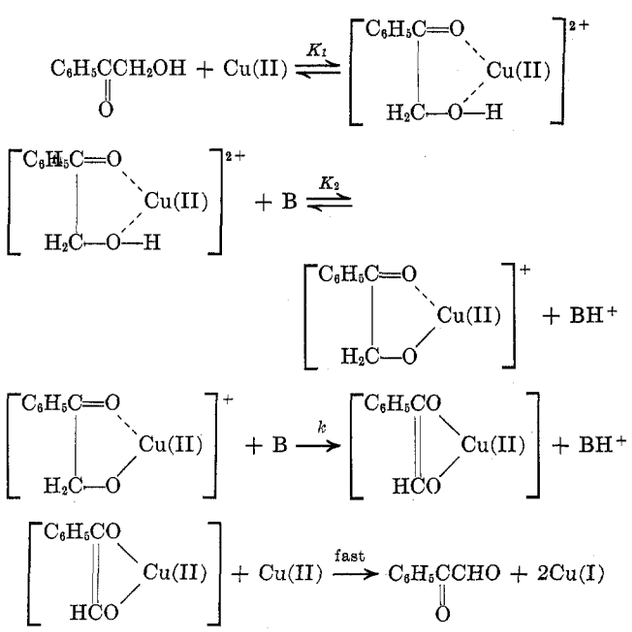
(9) A. Weissberger, H. Mainz, and E. Strasser, *Chem. Ber.*, **62**, 1942 (1929); A. Weissberger, A. Dorken, and E. Strasser, *ibid.*, **64**, 1200 (1931).

Somewhat different results were obtained by Wiberg and Nigh[7] when they investigated the oxidation of α-hydroxyacetophenone with cupric acetate in buffered aqueous pyridine. This reaction was found to obey the rate law of eq 2, where the second term exhibits a β-order dependence on base.

$$-\frac{d[Cu(II)]}{dt} = k_1[C_6H_5CCH_2OH][B] + k_2[C_6H_5CCH_2OH][B][Cu(II)] \quad (2)$$

Since the basicity of the reaction media may be held essentially constant, it was possible to demonstrate a base catalysis (*i.e.*, $\beta > 0$). However, a quantitative evaluation of β was prohibited by the complexity of the media. Thus the media contain four different bases (*i.e.*, OH^-, $CH_3CO_2^-$, C_5H_5N, and H_2O) each of which might catalyze the reaction. In addition, pyridine and acetate ion are potential complexing agents for cupric ion.

At low concentrations of cupric ion (*i.e.*, $k_1 \gg k_2$[Cu(II)]) the first term in eq 2 predominates and becomes identical with the rate of deuterium exchange (*i.e.*, enolization) under the same reaction conditions. Thus, under these conditions, eq 2 becomes identical with eq 1 and represents the same reaction pathway which operates in aqueous media. At higher concentrations of cupric ion (*i.e.*, $k_2[Cu(II)] \gg k_1$) the second term in eq 2 predominates and was found to exhibit a kinetic isotope effect of 7.4 (25°) and a Hammett reaction constant, ρ, of +1.24. This is strong evidence for a second reaction pathway involving a rate-determining proton removal from the α-methylene position of a copper(II)–ketol complex. The following mechanism[8] has been proposed for this copper(II)-catalyzed reaction.



This paper offers additional experimental data which further support the chelate structure of the copper(II)–ketol intermediate proposed in the above mechanism.

Results

The copper(II) oxidation of a series of α-ketols was investigated in buffered (0.10 *M* pyridinium acetate) 50 mol % aqueous pyridine. Oxygen was excluded during the reaction by degassing the reactants prior to sealing the reaction cells under vacuum or under an atmosphere of purified nitrogen. Under these conditions, tetrapyridinecopper(I) is stable in solution, allowing the reaction to be studied under homogeneous conditions.

The rate of disappearance of copper(II) was followed spectrophotometrically (800–900 nm) under pseudo-first-order conditions. The initial concentration of cupric acetate was always in excess of 0.025 *M* in order to ensure that only the copper(II)-catalyzed mechanism was kinetically observable. All of the kinetic results reported in this paper pertain only to the second term of the rate law (eq 2). Even under these reaction conditions benzoin, 4,4′-dimethoxybenzoin, and 2-hydroxycyclopentanone exhibited deviations from first-order behavior during the second half-life. The other ketols gave linear plots of ln $(A_t - A_\infty)$ *vs.* time well beyond 75% reaction. The slope of these plots yields the pseudo-first-order rate constant, k_{obsd}. The apparent second-order rate constant, k_2, is obtained by dividing k_{obsd} by the corresponding initial concentration of the ketol. The raw kinetic data were also computer analyzed by a least squares program.[10] These refined data are presented in Table I. The reported second-order rate constants (through the second half-life, except where indicated) are numerical averages of from two to five separate kinetic runs and the uncertainties are average deviations.

TABLE I
RATES OF REDUCTION OF COPPER(II) BY α-KETOLS IN 50 MOL % PYRIDINE–WATER

Ketol	[Cu(II)]	[Ketol]	Temp, °C	10^3k_2, l. mol^{-1} min^{-1}
3-Hydroxy-2-butanone	0.100	1.00	30.1	2.70 ± 0.03
	0.025	1.00	31.1	2.83 ± 0.01
	0.025	1.00	39.4	6.35 ± 0.02
	0.025	1.00	40.3	6.62 ± 0.02
	0.025	0.50	40.3	6.92 ± 0.08
	0.025	1.00	48.6	17.4 ± 0.3
	0.025	1.00	50.0	19.1 ± 0.5
	0.025	1.00	50.3	18.2 ± 0.3
4-Hydroxy-3-hexanone	0.100	1.00	30.0	1.53 ± 0.01
	0.100	1.00	40.0	4.63 ± 0.10
	0.100	1.00	50.0	12.3 ± 0.1
4-Hydroxy-2,5-dimethyl-3-hexanone	0.100	1.00	30.0	1.21 ± 0.01
	0.100	1.00	40.0	3.43 ± 0.04
	0.100	1.00	50.0	10.0 ± 0.3
4-Hydroxy-2,2,5,5-tetramethyl-3-hexanone	0.100	1.00	50.0	$<10^{-2}$
2-Hydroxycyclopentanone	0.025	1.00	35.0	4.40 ± 0.02[a]
	0.025	1.00	45.0	8.71 ± 0.17[a]
	0.025	1.00	55.0	23.3 ± 1.0[a]
2-Hydroxycyclohexanone	0.025	0.50	20.0	7.96 ± 0.09
	0.025	0.50	30.1	26.6 ± 0.2
	0.025	0.50	41.0	86.3 ± 1.3
Benzoin	0.025	0.30	25.4	22.7 ± 0.2[a]
	0.025	0.30	34.35	42.4 ± 3.3[a]
	0.025	0.30	44.0	124 ± 17[a]
4,4′-Dimethoxybenzoin	0.025	0.40	24.9	6.43 ± 0.40[a]
	0.025	0.40	35.0	18.7 ± 0.70[a]
	0.025	0.40	45.2	45.8 ± 0.25[a]

[a] Rate constants calculated for the first half-life.

(10) K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, p 554.

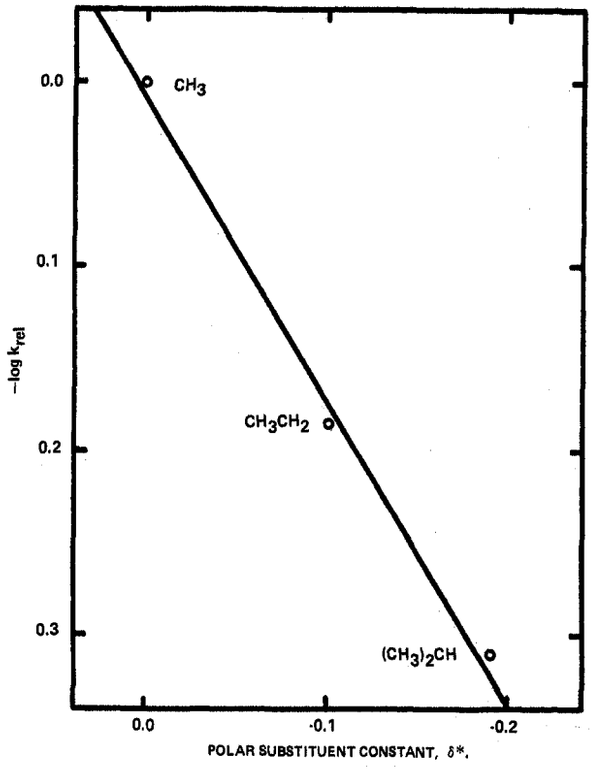


Figure 1.—Linear free energy plot for the oxidation of α-ketols by copper(II).

The relative rates of oxidation and the activation parameters are presented in Table II. The enthalpies

TABLE II

SUMMARY OF KINETIC PARAMETERS FOR THE COPPER(II)-CATALYZED OXIDATION OF α-KETOLS IN 50 MOL % PYRIDINE–WATER

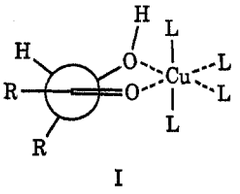
Ketol	k_{rel} (40°)	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
3-Hydroxy-2-butanone	1.0	18.6 ± 0.6	−18
4-Hydroxy-3-hexanone	0.65	19.4 ± 0.6	−16
4-Hydroxy-2,5-dimethyl-3-hexanone	0.49	19.6 ± 0.6	−15
4-Hydroxy-2,2,5,5-tetramethyl-3-hexanone	$<10^{-3}$		
2-Hydroxycyclopentanone	0.86	14 ± 1.5	−31
2-Hydroxycyclohexanone	11	19.2 ± 0.4	−11
Benzoin	11	15 ± 1.5	−24
4,4′-Dimethoxybenzoin	4.0	17.4 ± 0.6	−18
α-Hydroxyacetophenone[a]	49[b]	18.9 ± 0.4	−9

[a] From ref 7. [b] Corrected for statistical factor.

of activation were calculated from the slope of plots of log (k/T) *vs.* $1/T$ and the relative rates and entropies of activation were calculated at 40°.

Discussion

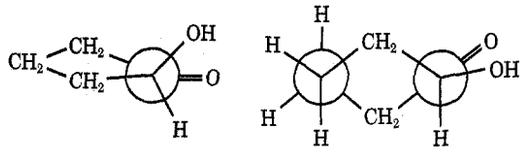
The most dramatic rate effect in Table II involves 4-hydroxy-2,2,5,5-tetramethyl-3-hexanone (pivaloin). This ketol does not exhibit any detectable oxidation by cupric ion even after 1 week at 50°. Under identical conditions, the oxidation of 4-hydroxy-2,5-dimethyl-3-hexanone (isobutyroin) was 50% complete after about 1 hr. The 1,2-nonbonding interactions associated with two skewed *tert*-butyl groups completely excludes any possibility of a planar chelate structure such as I.



I

The tremendous steric strain involved in such a chelate is best demonstrated with space-filled molecular models. When R is isopropyl the methyl groups can rotate to the outside (*i.e.*, away from one another), thereby reducing the steric hindrance. This mechanism for the relief of steric strain is also supported by the similarity of the activation parameters for 3-hydroxy-2-butanone (acetoin, R = methyl), 4-hydroxy-3-hexanone (propionoin, R = ethyl), and isobutyroin (R = isopropyl). The observed rate differences for these three ketols are consistent with the value of +1.24 previously reported for the Hammett reaction constant, ρ.[7] This is demonstrated by the linearity (within experimental error) of a plot (Figure 1) of log k_{rel} *vs.* the polar substituent constant, σ^*. A value of +1.3 for the polar reaction constant, ρ^*, was obtained from the slope of Figure 1. A similar sensitivity to electronic effects is observed in the case of benzoin and 4,4′-dimethoxybenzoin. The electron-releasing effect of the methoxy groups decreases the rate of reaction.

The sensitivity of the reaction to steric effects is also encountered in the case of the alicyclic α-ketols, 2-hydroxycyclopentanone (II) and 2-hydroxycyclo-



II III

hexanone (III). In structure II the carbonyl oxygen must be skewed between the hydroxy group and the enolizable hydrogen, whereas in structure III the carbonyl group is eclipsed by the hydroxy group. Therefore the internuclear oxygen–oxygen distance must be greater in II than in III. Crude measurements of molecular models indicate that this distance is approximately 30% greater in II. Thus, II cannot readily achieve the nearly planar conformation which is required for the maximum stability of the chelate, I. In contrast, III is perfectly aligned for the formation of the chelate ring. This large difference in the stability of the alicyclic chelates is reflected in the very large negative entropy of activation exhibited by II and the relatively small negative value obtained for III. In addition to this entropy effect, III is oxidized 13 times faster than II under identical reaction conditions. This difference in the rate of reaction cannot be due to some inherent ability of III to enolize, since cyclopentanone undergoes base-catalyzed enolization about seven times faster than cyclohexanone.[11] The more facile enolization of the five-membered ring is further demonstrated by the lower enthalpy of activation exhibited by II.

(11) H. Shechter, M. J. Collis, R. Dessy, Y. Okuzumi, and A. Chen, *J. Amer. Chem. Soc.*, **84**, 2905 (1962).

A comparison of the entropies of activation for benzoin and α-hydroxyacetophenone further supports the chelate structure of the reaction intermediate. The presence of a single aryl group in structure I does not produce any appreciable steric interaction. If a second aryl group is present, however, considerable steric strain is introduced, resulting in the larger negative entropy of activation for benzoin.

Although the application of eq 2 for all of the α-ketols investigated has not been rigorously demonstrated, such an assumption seems justified by the general kinetic results obtained. In addition, the kinetic data have been interpreted in terms of steric hindrance to the formation of an intermediate chelate, but there should also be a corresponding effect on the enolization step. Thus, as the steric bulk around the enolizable proton increases, the ability of a base to attack the proton must decrease (*i.e.*, the rate of enolization decreases). In summary, therefore, a mechanism for the copper(II)-catalyzed oxidation of α-ketol in aqueous pyridine which involves an initial rate-determining proton removal from the α position of a copper(II)–ketol chelate is compatible with all of the available experimental evidence.

Experimental Section

Reagents.—Cupric acetate monohydrate (J. T. Baker, reagent grade), pyridine (Aldrich, reagent grade), and acetic acid (Du Pont, reagent grade) were used as obtained from commercial sources. Benzoin and 4,4′-dimethoxybenzoin (Matheson Coleman and Bell) were recrystallized several times from ethanol. The 3-hydroxy-2-butanone (Aldrich) was purified by the method of Marshall and Waters,[6] while 4-hydroxy-3-hexanone, 4-hydroxy-2,5-dimethyl-3-hexanone, and 4-hydroxy-2,2,5,5-tetramethyl-3-hexanone were prepared and purified by the method of Snell and McElvain.[12] The 2-hydroxycyclohexanone and 2-hydroxycyclopentanone were prepared and purified by the method of Schrapler and Ruhlmann.[13] In these last two reactions, the ester was slowly added through a Soxhlet extractor instead of the usual diluting head.

Kinetic Method.—Solutions of cupric acetate and the α-ketol were prepared in 50 mol % aqueous pyridine containing acetic acid to buffer the solutions. In the case of the less reactive systems, equal amounts of each solution were placed in a special Pyrex reaction cell which had previously been cooled to Dry Ice–acetone temperature. The reaction mixture was carefully degassed on a vacuum line by successive freezing and melting. The cell was sealed under vacuum (or under an atmosphere of purified nitrogen) and stored at the Dry Ice temperature until ready for use. The run was initiated by quickly bringing the reaction cell to the desired reaction temperature in a constant-temperature bath. At appropriate time intervals the cells were removed from the bath and placed in a thermostated cell compartment of a Beckman DU spectrophotometer. After the absorption of the reaction mixture was measured, the cell was returned to the bath. In the case of the more reactive reaction systems, the copper(II) solution was isolated from the ketol solution during the degassing using reaction cells similar to those described by Wiberg and Lepse.[14]

Registry No.—Copper, 7440-50-8.

(12) J. M. Snell and S. M. McElvain, "Organic Syntheses," Collect. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1943, p 114.
(13) U. Schrapler and K. Ruhlmann, *Chem. Ber.*, **97**, 1383 (1964).
(14) K. B. Wiberg and P. A. Lepse, *J. Amer. Chem. Soc.*, **86**, 2612 (1964)

Reactions of Polyarylated Carbinols. III.[1] Base-Catalyzed Rearrangement of 1,2,3,4,5-Pentaphenyl-2,4-cyclopentadien-1-ol[2]

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The base-catalyzed rearrangement of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (1) to 2,3,4,5,5-pentaphenyl-2-cyclopenten-1-one (4) has been observed and its mechanism has been investigated. This rearrangement has been found to occur with a wide variety of bases [sodium hydroxide, sodium carbonate, sodium bicarbonate, sodium amide, hexamethylphosphoramide (HMPA), and *N*,*N*-diethylformamide (*N*,*N*-DEF)], at various temperatures (173 and 95°), and after various reaction periods (3 and 8 hr). Mechanistic investigations established that the completely delocalized carbanion **7** is formed during the reaction and that 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (**3**) is an intermediate in this rearrangement. It was further established that ketone **3** is the kinetically controlled product of this rearrangement while ketone **4** is the thermodynamically controlled product.

We have previously reported[1a] that 2,3,4,5,5-pentaphenyl-2-cyclopenten-1-one (**4**) could be prepared from 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (**1**) *via* the following sequence of reactions: a thermally induced [1,5] sigmatropic phenyl rearrangement to give 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (**3**), *via* the keto–enol tautomerization of the dienol intermediate **2**, followed by treatment of the ketone **3** with acid (HBr/HOAc) (Scheme I).

We now wish to report the direct base-catalyzed rearrangement of the dienol **1** to the ketone **4**. In addition to the interesting mechanistic aspects of this rearrangement, it also affords a simpler one-step preparative procedure for ketone **4** in greater yields than the preparative sequence represented in Scheme I.

Initial treatment of dienol **1** with base followed by aqueous quench and work-up afforded only one product, ketone **4**. Based upon these results the initial mechanism postulated for this rearrangement involved formation of the alcoholate **5**, followed by phenyl migration to produce the enolate **6**, which was then protonated upon aqueous quenching to give the final product, ketone **4** (Scheme II). However, one objection to the above mechanism which arises is that ketone **4** is the only product obtained from this reaction. This objection arises because if the anion **6** is indeed formed it should not exist as a localized carbanion but as a com-

(1) For previous papers in this series see (a) A. K. Youssef and M. A. Ogliaruso, *J. Org. Chem.*, **37**, 2601 (1972); (b) *ibid.*, **38**, 487 (1973).
(2) Presented at the 24th Southeastern Regional Meeting of the American Chemical Society, Birmingham, Ala., Nov 3, 1972.
(3) Taken from the Ph.D. Thesis of A. K. Y. submitted to the faculty of the Department of Chemistry, VPI and SU, in partial fulfillment of the requirements for the Ph.D., July 8, 1972.