crystallized on trituration with methanol. Recrystallization from ethanol–methanol gave 2.80 g of pure material.

2,3-Diphenyl-1,4-dipropylnaphthalene (3Pr).—By using 3.16 g (0.01 mole) of 3,4-diphenyl-2,5-dipropylcyclopentadienone and the procedure given for **3**, 2.51 g of pure material was obtained after recrystallization from methanol–water.

2,3-Diphenyl-1,4-dodecamethyleneanthracene (4).—To a refluxing solution of 15.9 g (0.04 mole) of 3,4-diphenyl-2,5-dodecamethylenecyclopentadienone in 100 ml of 1,2-dimethoxyethane were added, dropwise, solutions of 7.48 g (0.04 mole) of 3-amino-2-naphthoic acid in 80 ml of 1,2-dimethoxyethane and 12 ml of isoamyl nitrite in 80 ml of the same solvent. The mixture was refluxed for 2 hr, cooled, and made basic with 5% sodium hydroxide solution. The resulting scarlet solid was stirred in benzene and filtered to remove insoluble residue. After drying, the benzene solution was chromatographed on alumina. The effluent was stripped to yield an orange solid. Washing with methanol gave 6.83 g of yellow solid, mp 244–249°. Two recrystallizations from acetic acid provided an analytical sample as yellow needles.

The **tetracyanoethylene derivative** was prepared by reaction in tetrahydrofuran at room temperature overnight. After the solvent had been stripped, the residual solid was recrystallized from benzene–ligroin (bp 30–60°), mp 274–278°.

Anal. Calcd for $C_{44}H_{40}N_4$: C, 84.5; H, 6.4; N, 8.9. Found: C, 84.2; H, 6.4; N, 9.2.

2,3-Diphenyl-1,4-dodecamethylenetriptycene (5).—A solution of 4.0 g (0.008 mole) of 2,3-diphenyl-1,4-dodecamethyleneanthracene in 50 ml of 1,2-dimethoxyethane was refluxed. Solutions of 1.11 g (0.008 mole) of anthranilic acid in 50 ml of 1,2-dimethoxyethane and 0.92 g (0.008 mole) of isoamyl nitrite in 50 ml of the same solvent were added simultaneously over 0.5 hr. The mixture was refluxed a total of 1.5 hr, cooled, made basic with 5% sodium hydroxide solution, diluted with water, and refrigerated, and the solid was collected and dried. To remove anthracene, the solid was dissolved in tetrahydrofuran and treated with tetracyanoethylene in tetrahydrofuran. The solvent was then removed under vacuum and the residue was dissolved in benzene. The benzene solution was chromatographed on alumina; the benzene effluent was concentrated under vacuum. Two recrystallizations from acetic acid provided 2.0 g of an analytical sample.

2,3-Diphenyl-1,4-dipropyltriptycene (5Pr).—By using 1.98 g (0.0048 mole) of 2,3-diphenyl-1,4-dipropylanthracene (4Pr) and the procedure given for **5**, 0.78 g of pure material was obtained.

Nmr Spectra.—The nmr spectra were determined on a Varian A-60 spectrometer with the probe at the ambient operating temperature (~35°). Spectra were determined in deuteriochloroform solution at concentrations ranging from 1 to 10% (w/v).

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Acid- and Base-Catalyzed Hydrogen–Deuterium Exchange between Deuterium Oxide and Simple Ketones

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Recent communications by Warkentin and Tee[1] and by Rappe[2] prompt us to report the results of some measurements using proton nmr on the rate of acid- (KDSO₄) and base-catalyzed (NaOAc) enolization in D_2O solutions of acetone, methyl ethyl ketone, diethyl ketone, and methoxyacetone. These studies were made in order to explore the feasibility of measuring separately the rate of enolization into the two branches of an unsymmetrical ketone. While the matter of rate of enolization has been the subject of much theoretical discussion,[3-9] experimental investigations have been hampered by the difficulties and uncertainties in the experimental methods employed.[6-14]

The results of our measurements are displayed in Tables I (catalysis by sodium acetate) and II (catalysis by potassium bisulfate). In view of the uncertainties in the rates (±20%), detailed analysis is not warranted, but several interesting points can be made from the qualitative behavior exhibited. (1) The results of Warkentin and Tee[1] are supported. (2) Alkyl or methoxyl substitution affects the rate of enolization in *both branches* quite strongly. (3) The methoxyl substituent accelerates base-catalyzed and retards acid-catalyzed enolization in both branches. (4) Diethyl ketone enolizes more slowly then acetone both in acid and base, in accord with earlier reports[15] that alkyl substitution *retards* acid-catalyzed enolization. (5) The variations in relative rates with temperature are sufficiently great that conclusions drawn on the basis of observations at one temperature may easily be reversed by observations of data at other temperatures.

We agree with Warkentin and Tee[1] that "...the polar effect of an alkyl group on rate of base-promoted enolization in aqueous medium has been overemphasized or even misinterpreted...," and suggest that this statement is equally true of acid-catalyzed enolization.

Experimental Section

Materials.—Reagent grade ketones were used, except for methoxyacetone, which was obtained from K & K Chemical Co. This material was purified by glpc using a 6 ft × 0.25 in. column packed with 20% Carbowax 20 M on Teflon 6, at 65–125° (2.9°/min) with a helium flow of 56 ml/min. The product collected was rechromatographed and had an indicated purity of 97–98%, as judged from peak areas.

Sample Preparation.—Stock solutions of sodium acetate and potassium bisulfate in D_2O were made up gravimetrically. The final solutions were made by pipetting together suitable quantities (9–9.75 ml) of stock acid or base and (0.25–1.00 ml) ketone. After thorough mixing, aliquots were sealed into 5-mm nmr sample cells, which had previously been steamed out and dried. The sample cells were immersed in a thermostat and removed periodically for measurement, at which time they were cooled in ice. Reaction time was accumulated only during the time the tube was in the thermostated bath. Control samples, kept at ice temperature, showed no measurable exchange in 24 hr, in which time the kinetic runs were usually complete.

Measurement.—Measurements were performed on a Varian A-60 spectrometer. Peak integrations were recorded, sweeping the field three times in each direction, for all visible peaks. Dur-

(1) J. Warkentin and O. S. Tee, *Chem. Commun.*, 190 (1966).
(2) C. Rappe, *Acta Chem. Scand.*, **19**, 276 (1965).

(3) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp 198, 199.
(4) J. M. Conia, *Bull. Soc. Chim. France*, 1040 (1956).
(5) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp 374, 375.
(6) R. C. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953).
(7) G. Archer and R. P. Bell, *J. Chem. Soc.*, 3228 (1959).
(8) J. M. Conia, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **24**, 43 (1963).
(9) H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963).
(10) A. Lapworth, *J. Chem. Soc.*, 30 (1904).
(11) J. R. Catch, D. F. Elliott, P. H. Hey, and E. R. H. Jones, *ibid.*, 272 (1948).
(12) J. R. Catch, D. H. Hey, E. R. H. Jones, and W. Wilson, *ibid.*, 276 (1948).
(13) H. M. E. Cardwell and A. E. H. Kilner, *ibid.*, 2430 (1951).
(14) H. M. E. Cardwell, *ibid.*, 2442 (1951).
(15) H. M. Dawson and R. Wheatley, *ibid.*, 2048 (1910); H. M. Dawson and H. Ark, *ibid.*, 1740 (1911); D. P. Evans, *ibid.*, 785 (1936).

TABLE I
RATES OF ENOLIZATION. BASE CATALYSIS

R_1 R_2	Vol. % of ketone	[NaOAc], moles/l.	—50°— k_{R1}, mole⁻¹ sec⁻¹	k_{R2}, mole⁻¹ sec⁻¹	—70°— k_{R1}, mole⁻¹ sec⁻¹	k_{R2}, mole⁻¹ sec⁻¹
CH_3COCH_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}
$CH_3CH_2COCH_3$	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}
$CH_3CH_2COCH_2CH_3$	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}
$CH_3OCH_2COCH_3$	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	[KHSO₄], mole/l.	—50°— k_{R1}, mole⁻¹ sec⁻¹	k_{R2}, mole⁻¹ sec⁻¹	—70°— k_{R1}, mole⁻¹ sec⁻¹	k_{R2}, mole⁻¹ sec⁻¹
CH_3COCH_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}
$CH_3CH_2COCH_3$	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}
$CH_3CH_2COCH_2CH_3$	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}
$CH_3OCH_2COCH_3$	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 $\pm 10\%$. 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 Guggenheim[17] 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 [ketone] ≪ [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).