yielded 1.40 g. (95%) of solid *anti*-7-norbornenol (IX), m.p. after vapor phase chromatographic purification, 117–118°; reported[3a] m.p. is 117–118°. This material was hydrogenated to 7-norborneol, identical with the 7-norborneol obtained from VII and VIII above.

Pyrolysis of the acetate (VII). Pyrolysis of the acetate (VII) was effected by injecting a sample into the sample inlet of a Beckman GC-2 heated at 225° with a column temperature of 130°. No benzene could be detected among the many volatile products. The chief product, as shown by vapor phase chromatography, infrared and ultraviolet comparison with an authentic sample, was benzyl acetate.

The acetate (VII) could also be pyrolyzed at 375° in a 9 in. column packed with glass helices to give good yields of benzyl acetate. With this apparatus the acetate (VII) was not pyrolyzed at 275°. Pyrolysis at a lower temperature in the gas chromatograph was probably promoted by carbonized materials known to be present in the inlet tube.

Hydrolysis of 7-norbornadienyl acetate (VII). Hydrolysis of the acetate (VII) was attempted under the following conditions with uniformly negative results. In every instance the acetate was hydrolyzed but did not give the alcohol (VIII). In most cases infrared analysis indicated ring opening.

(1) 1*N* hydrochloric acid/50% aqueous methanol at room temperature for 3 hr.

(2) 2*N* hydrochloric acid/H_2O at room temperature overnight.

(3) 1*N* potassium hydroxide/75% aqueous methanol overnight at room temperature under nitrogen.

(4) 1*N* sodium methoxide/methanol at room temperature for 2 hr. under nitrogen.

Acid hydrolysis of the ether (VI) A solution of 0.5 g. (0.003 mole) of ether (VI) in 1 ml. of 50% sulfuric acid (0.018 mole) was allowed to stand at room temperature for 1 hr. Ice and water were added and the product was extracted with dichloromethane. None of the alcohol (VIII) could be detected in the product which appeared to consist chiefly of a saturated diol.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SOUTHERN ILLINOIS UNIVERSITY]

Mechanism of the Meerwein-Ponndorf-Verley Reduction[1]

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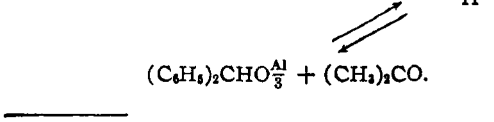
The rate of reduction of benzophenone by aluminum isopropoxide in isopropyl alcohol has been measured at three temperatures and three catalyst concentrations. The reaction is first order in benzophenone and approximately 1.5 order in aluminum isopropoxide. It is suggested that the reaction may proceed by two mechanisms, one the accepted mechanism which involves a cyclic transition state and one mole of aluminum isopropoxide, and a second mechanism which involves a noncyclic transition state and two moles of alkoxide.

The metal alkoxide-catalyzed equilibration of an alcohol and a carbonyl compound (Meerwein-Ponndorf-Verley reduction,[2] Oppenhauer oxidation[3]) has been generally thought to involve a cyclic transition,[4,5] which in the case of benzophenone and isopropyl alcohol can be formulated in the following way:



In support of this mechanism deuterium tracer studies indicate that hydrogen transferred to the carbonyl does come from the carbinol carbon.[6,7] Pickkart and Hancock[8] found a Hammett *rho* constant of 1.296 for the equilibrium between substituted benzophenone and diethylcarbinol. Thus increased positive character of the carbonyl group facilitates the reaction, which is evidence for hydride ion transfer. Doering and Young[9] have used the cyclic transition state to explain their observation that an optically active reductant gives a partially active product.

The evidence to date does not preclude a mechanism in which two molecules of aluminum isopropoxide would be involved, one to complex with the carbonyl oxygen and a second to serve as hydride ion donor. A choice between these two mechanisms should be possible on the basis of kinetic

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[1] Taken in part from the M.A. thesis of R. R. Ruch. This work was supported by grants from the Research Corporation and the Graduate School of Southern Illinois University.

[2] H. Meerwein and R. Schmidt, *Ann.*, **444**, 221 (1925); W. Ponndorf, *Z. angew. Chem.*, **39**, 138 (1926); M. Verley, *Bull. soc. chim.*, [4] **37**, 537 (1925).

[3] R. V. Oppenauer, *Rec. trav. chim.*, **56**, 137 (1937).

[4] R. E. Lutz and J. S. Gillespie, Jr., *J. Am. Chem. Soc.*, 72, 344 (1950).

[5] R. B. Woodward, N. L. Wendler, and F. J. Brutschy, *J. Am. Chem. Soc.*, **67**, 1425 (1945).

[6] W. von E. Doering and T. C. Ashner, *J. Am. Chem. Soc.*, **75**, 393 (1953).

[7] E. D. Williams, K. A. Krieger, and A. R. Day, *J. Am. Chem. Soc.*, **75**, 2404 (1953).

[8] D. E. Pickkart and C. K. Hancock, *J. Am. Chem. Soc.*, **77**, 4642 (1955).

[9] W. von E. Doering and R. W. Young, *J. Am. Chem. Soc.*, **72**, 631 (1950).

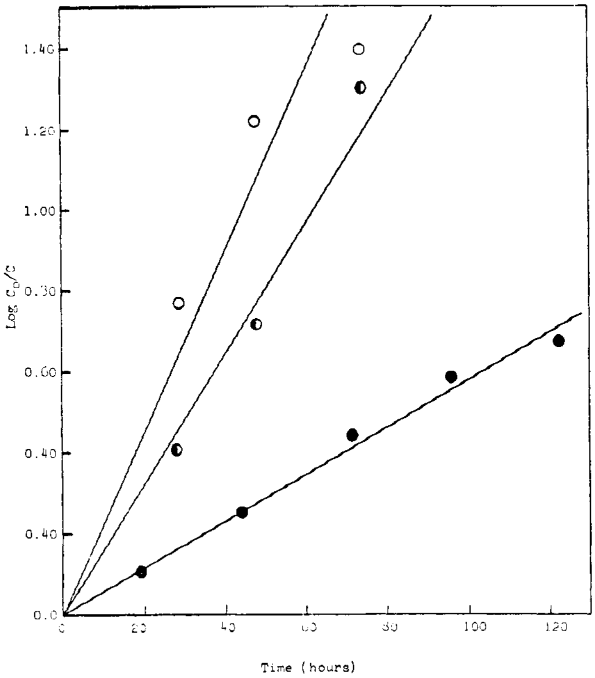


Fig. 1. Pseudo first-order rate plots for the reduction of 0.100*M* benzophenone with 0.110*M* aluminum isopropoxide in isopropyl alcohol; at three temperatures: ●, 25°; ◐, 35°; ○, 45°

experiments, for the accepted mechanism would be expected to be first order in ketone and first order in catalyst, while the second mechanism would be first order in ketone and second order in catalyst. In order to make this decision we have measured the rate of reduction of benzophenone in isopropyl alcohol solution, using aluminum isopropoxide as a catalyst.

A dilute solution of benzophenone and aluminum isopropoxide in isopropyl alcohol was allowed to react at constant temperature. The course of the reaction was followed by removing aliquot samples at convenient intervals, hydrolyzing the aluminum isopropoxide to stop the reaction, and measuring benzophenone and acetone concentrations polarographically. The temperatures and initial concentrations of benzophenone and aluminum isopropoxide are shown in Table I together with the rate constants obtained by calculations described subsequently. Kinetic data are shown in Figs. 1 and 2. Plots shown are for the pseudo first-order reaction of benzophenone, the concentrations of isopropyl alcohol and catalyst being essentially constant in any single run. Fig. 1 shows the results for reactions run at varying temperatures with the initial concentrations of reactants constant. Fig. 2 shows the results for reactions using varying concentrations of catalyst at a constant temperature of 35°.

TABLE I

Rate of Reduction of Benzophenone with Aluminum Isopropoxide in Isopropyl Alcohol[a]

Temp.	Aluminum Isopropoxide Moles/l.	k_1[b] hr.$^{-1}$	k_2[c] l./mole hr.$^{-1}$	$k_{2.5}$[d] (l./mole)$^{1.5}$ hr.$^{-1}$
25	0.110	0.013	0.11	0.36
35	0.022	0.0034	0.15	1.04
	0.055	0.011	0.20	0.85
	0.110	0.034	0.31	0.93
45	0.110	0.062	0.56	0.64

[a] Initial concentration of benzophenone, 0.100*M*. [b] Pseudo first-order rate constants. [c] Calculated rate constants assuming the reaction is first order in benzophenone and first order in aluminum isopropoxide. [d] Calculated rate constants assuming the reaction is first order in benzophenone and 1.5 order in aluminum isopropoxide.

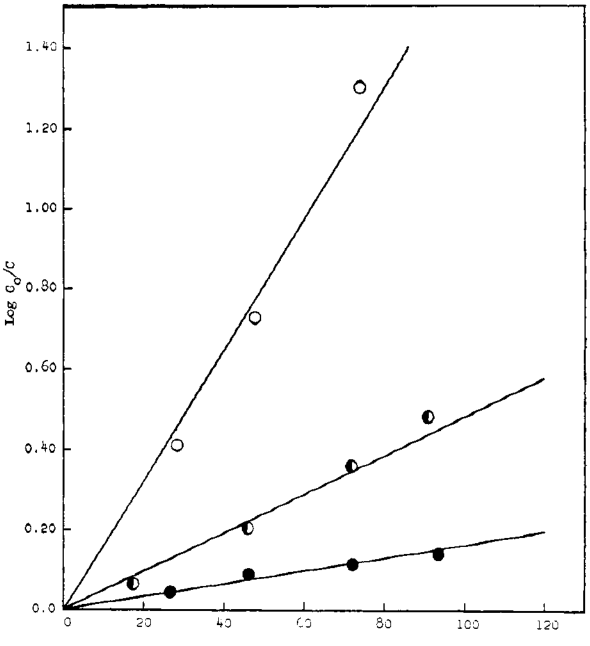
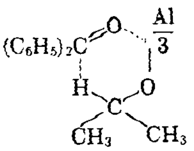


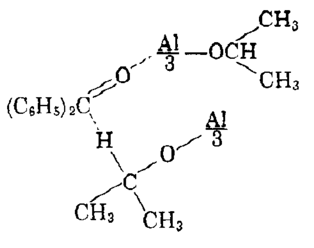
Fig. 2. Pseudo first-order rate plots for the reduction of 0.100*M* benzophenone in isopropyl alcohol at 35° at three catalyst concentrations: ●, 0.022*M*; ◐, 0.055*M*; ○, 0.110*M*

On the basis of the limited number of measurements made, the first order plots were generally linear with some deviation when the reaction was nearly complete and the benzophenone concentration was very low. The pseudo first-order rate constants are given in Table I. The experiments made at 35° with varying concentrations of catalyst showed the rate of the reaction to be dependent on the concentration of aluminum isopropoxide. Introduction of catalyst concentration to the first power into the rate equation failed to give satisfactory second order rate constants. Satisfactory rate constants were obtained when the catalyst concentration was raised to the 1.5 power. The results of these calculations are shown in Table I.

The rate data plotted according to the Arrhenius equation deviate to a small extent from a straight line. Graphical evaluation of the energy of activation leads to a value of 14 kcal., as does an analytical evaluation based on the reaction rates at 25° and 45°. Analytical evaluation based on reaction rates at 25° and 35° and at 35° and 45° lead to energies of activation of 11 and 17 kcal. respectively. The entropies of activation corresponding to the energies of activation are: ΔH^*, 17 kcal., ΔS^*, -20 e.u.; ΔH^* 14 kcal., ΔS^*, -31e.u.; ΔH^*11kcal., ΔS^*, -42e.u. It is evident that while exact numerical values may be questionable, qualitatively, the energy of activation is relatively small and the entropy of activation is large and negative.

The kinetic data would seem to suggest that the reduction process proceeds by two different mechanisms simultaneously. One of these is the accepted mechanism involving a cyclic transition state made up of one molecule of benzophenone and one molecule of aluminum isopropoxide. The second mechanism must involve two molecules of catalyst to fit the kinetic data. A process in which the hydride ion is transferred to the carbonyl carbon from a molecule of aluminum isopropoxide other than the one coordinated through aluminum to the carbonyl oxygen would meet this condition. In an analogous situation Swain and Boyles[10] have proposed that in the addition of Grignard reagents to ketones one molecule of Grignard coordinates with the carbonyl oxygen, while a second supplies the alkyl group to the carbonyl carbon atom. The two transition states can be written:





In both cases it is assumed that the complex formation that precedes the reduction step and alkoxide interchange reactions that follow the reduction are fast reactions and do not effect the overall rate of reduction. Although the reaction is reversible the rapid alkoxide interchange with solvent isopropyl alcohol keeps the concentration of benzhydrol present as alkoxide at a very low concentration, and hence makes the back reaction insignificant. Benzhydrol can be isolated in greater than 95% yield when the reaction is carried out on a synthetic scale.

Both of these mechanisms are consistent with the data of other investigators which has been summarized previously. The large negative entropy of activation is also consistent with both of these mechanisms. In one case there is one large group coordinated to the carbonyl group and the formation of a rigid sixmembered ring in the transition state. In the second case two bulky groups have become attached to the carbonyl group in the transition state. The failure of the reaction to give an exactly linear Arrhenius plot, and the lack of constancy of ΔH^* and ΔS^* may be due to a shift in the relative proportion of the reaction proceeding by each mechanism with change in temperature. Studies on the effect of catalyst concentration at various temperatures should help to clarify this point. These and other kinetic studies are being continued in this laboratory.

EXPERIMENTAL

Materials. The benzophenone was Eastman Kodak, White Label, recrystallized from isopropyl alcohol, m.p. 47.5–48.5°. The isopropyl alcohol was Fisher Scientific Company, Certified Reagent. The aluminum isopropoxide was obtained from Matheson Coleman and Bell, and was distilled under vacuum into the flask in which the catalyst solution was prepared. The *n*-butylamine was Eastman Kodak, White Label.

Kinetic procedure. A 0.200*M* solution of benzophenone was prepared. A solution *ca.* 0.2*M* in aluminum isopropoxide was prepared and the clear solution decanted from a small amount of insoluble aluminum oxide. The exact concentration of catalyst was determined by analysis for total aluminum by the method of Willard and Tang[11] and found to be 0.220*M*. A 50-ml. aliquot of benzophenone solution was transferred to a dry 100-ml. volumetric flask and filled to the mark with catalyst solution, care being taken to observe anhydrous conditions. The catalyst solution was diluted with the required amount of dry isopropyl alcohol for experiments with lower catalyst concentrations. A 5-ml. aliquot was removed at once for zero time analysis, the remainder placed in a constant temperature bath. From time to time 5-ml. aliquots were removed for analysis.

Analytical procedure. Benzophenone and acetone were determined simultaneously by a polarographic technique. Benzophenone is directly reducible and acetone was determined as its *n*-butylimine.[12] The 5-ml. aliquots removed from the reaction solution were added to 50 ml. of 5.0*M* ammonium chloride, 50 ml. of *n*-butylamine, and about 140 ml. of water in a 250-ml. volumetric flask. When the solution was cool the final volume was brought to 250 ml. by addition of water. The solution was allowed to stand overnight and filtered before the polarographic measurement was made. Polarographic analyses were made with a Leeds and Northrup Electrochemograph, Type E, using a water-jacketed H-cell with a saturated calomel electrode. The temperature was maintained at 25°. The benzophenone gave a wave at -1.2 volts, and the acetone gave an imine wave at -1.6 volts. The decrease in benzophenone concentration was directly proportional to the decrease in diffusion current for any solution to the diffusion current of solution prepared from the aliquot taken at zero time at which time the benzophenone concentration was known. Acetone concentrations were determined by comparison of diffusion currents of a given solution with calibration curves prepared using solutions of known concentration. The rate of acetone formation was at all points equal to the rate of benzophenone disappearance. The acetone analyses served to check the benzophenone analyses, but were otherwise superfluous.

CARBONDALE, ILL.

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(11) H. H. Willard and N. G. Tang, *Ind. Eng. Chem., Anal. Ed.*, **9,** 357 (1937).

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