ane and addition product) was obtained. With these solubility data, the partial pressures of the olefins above the reaction mixture could be converted to the weight of dissolved unreacted olefins: 3.01 g. of *cis*-2-butene and 5.30 g. of *trans*-2-butene. Distillation of the reaction mixture sepa-

rated 63 g. of addition product. Since there is a volume decrease during the reaction, the final concentration of olefin was arbitrarily corrected for a 5% volume decrease, resulting in a 4% decrease of k_γ/k_t.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE A. AND M. COLLEGE OF TEXAS]

Equilibrium Constants of Substituted Benzophenones in the Meerwein–Ponndorf Reaction[1]

BY DON E. PICKART[2] AND C. KINNEY HANCOCK

Equilibrium constants in toluene at 100° for benzophenone and seven *p*-substituted benzophenones in the Meerwein–Ponndorf reaction have been determined. log $K^{100°}$ values show a good linear relationship with Hammett's σ-values, the σ-values being additive for disubstituted derivatives. Statistical treatment of the data yields the following results: (1) equation of the regression line, log $K^{100°}$ = 1.296 σ − 0.355, where 1.296 is the reaction constant ρ; (2) standard deviation from the regression line, 0.0605; (3) correlation coefficient, 0.992. The positive sign of ρ supports a mechanism previously proposed by others for the reaction.

Introduction

The history and nature of the Meerwein–Ponndorf reaction have been reviewed by Wilds.[3] The generally accepted mechanism,[4] shown in Fig. 1, involves the formation of a coördination complex A which assumes the cyclic transition state B and facilitates the direct transfer of the hydride ion, leading to C, which breaks down to yield acetone and the aluminum alkoxide product.
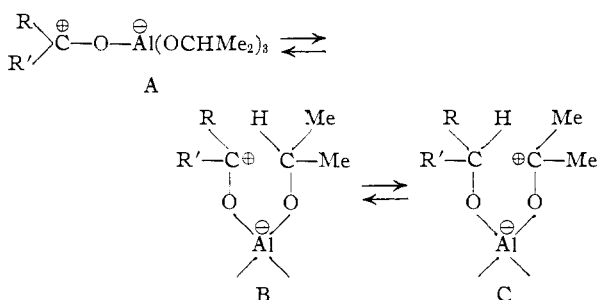
Fig. 1.—Mechanism of the Meerwein–Ponndorf reaction.

Baker and Adkins[5] determined polarographically the equilibrium positions and relative oxidation–reduction potentials of various alcohol–ketone systems. They also developed a method for synthesizing the aluminum alkoxide reductant *in situ* by the use of aluminum *t*-butoxide.

Brockman and Pearson[6] found a linear relationship between half-wave potentials of substituted benzophenones and Hammett's[7] substituent constants which indicates that electron-withdrawing groups favor reduction at the dropping mercury electrode.

The present study was undertaken with the objects of studying the effect of structure on equilib-

(1) Abstracted from the Ph.D. Dissertation of Don E. Pickart, The A. and M. College of Texas, 1954.

(2) Celanese Corporation of America, Clarkwood, Texas.

(3) A. L. Wilds in R. Adams, "Organic Reactions," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1944, chapter 5.

(4) L. M. Jackman and J. A. Mills, *Nature*, **164**, 789 (1949).

(5) R. H. Baker and H. Adkins, THIS JOURNAL, **62**, 3305 (1940).

(6) R. W. Brockman and D. E. Pearson, *ibid.*, **74**, 4128 (1952).

(7) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 184.

rium constants of substituted benzophenones in the Meerwein–Ponndorf reaction and of applying the results to a further consideration of the reaction mechanism.

Experimental

Materials.—The materials used in this work either were synthesized by well known methods or procured commercially. Physical constants of the purified materials were in good agreement with values reported in the literature.

Apparatus.—A Sargent model XXI polarograph was used. The 10-ml. electrolysis vessel was of the Heyrovsky–Erlenmeyer style (Sargent No. S-29370). Reaction mixtures were equilibrated at 100 ± 0.1° in an oven (Precision No. 504).

Determination of Equilibrium Constants.—The experimental procedure was similar to that of Cox and Adkins.[8] In some cases, diethyl ketone, diethylcarbinol, a substituted benzophenone, and the correspondingly substituted benzhydrol were equilibrated. In the remaining cases, only diethylcarbinol and a substituted benzophenone were used. Experiments proved that either method gave satisfactory results, but mixtures of the latter type required more time to reach equilibrium.

The solutions were made 0.05 M in total ketone and 0.05 M in total carbinol with toluene used as solvent. The reaction mixture contained 10 ml. of the above solution along with 1 ml. of catalyst (0.70 M solution of aluminum *t*-butoxide in toluene). Immediately after adding the catalyst and mixing, four 2-ml. aliquots were removed. The first of these was diluted with 10 ml. of 92% isopropyl alcohol to hydrolyze the catalyst and give a sample at zero time which was used for the polarographic standard. Three other aliquots were pipetted into constricted, nitrogen-filled, Pyrex test-tubes which then were sealed off and placed in the oven at 100°. At the specified times, the tubes were opened, and the contents diluted with 10 ml. of 92% isopropyl alcohol.

Polarographic cells were made of standard and test samples alike by diluting 2 ml. of the clear liquid with an equal volume of isopropyl alcohol and 1 ml. of 0.84 N tetramethylammonium hydroxide.

When all four components were originally present in the reaction mixture, the first tube was analyzed after one week. The second tube was analyzed one week later and, if identical analyses were obtained, the mixture was assumed to have reached equilibrium. When only two components were originally present, tubes were analyzed after three and four weeks. In all cases, equilibrium was attained after these periods.

Polarograms were run at 35 ± 0.01°. The equilibrium concentration of aryl ketone, determined from the polarogram by the Borcherdt[9] "b" method, was sufficient to de-

(8) F. W. Cox and H. Adkins, THIS JOURNAL, **61**, 3364 (1939).

(9) G. T. Borcherdt, V. W. Meloche and H. Adkins, *ibid.*, **59**, 2171 (1937).

termine the equilibrium concentrations of the other three components. Duplicate measurements were made on each system. The maximum deviation from the average of duplicate values was 0.8%.

Results and Discussion

Values of $K^{100°}$ and σ are presented in Table I. The σ-values listed for di-p-substituted benzophenones were obtained by adding the σ-values of the two substituents.[10] A plot of log $K^{100°}$ vs. σ is shown in Fig. 2.

TABLE I

EQUILIBRIUM CONSTANTS FOR SUBSTITUTED BENZOPHENONES IN THE MEERWEIN–PONNDORF REACTION

	Compound	$K^{100°}$	σ
1	Benzophenone	0.3779	0.000
2	4-Bromobenzophenone	1.057	.232
3	4-Chlorobenzophenone	0.9980	.227
4	4,4'-Dichlorobenzophenone	1.501	.454
5	4-Methylbenzophenone	0.2555	− .170
6	4,4'-Dimethylbenzophenone	.1433	− .340
7	4-Methoxybenzophenone	.2071	− .268
8	4,4'-Dimethoxybenzophenone	.09731	− .536

Statistical treatment[11] of the data of Table I yields the following results: (1) equation of the regression line, log $K^{100°} = -0.355 + 1.296\sigma$, where −0.355 is the value of (log $K°$)$_{calcd}$ and 1.296 is the slope (ρ) of the regression line; (2) standard deviation from the regression line, 0.0605; (3) correlation coefficient, 0.992. The regression line is shown in Fig. 2.

From an examination of the Hammett equation,[7] log k − log $k° = \rho\sigma$, it is obvious that ρ must be positive for reactions that are facilitated by substituents of positive σ-values, i.e., for reactions which are favored by low electron densities at the reaction site. That the Meerwein–Ponndorf reaction is of this sort can be seen from an examination of the mechanism illustrated in Fig. 1. The equilibrium

(10) H. H. Jaffé, Chem. Revs., 53, 191 (1953).

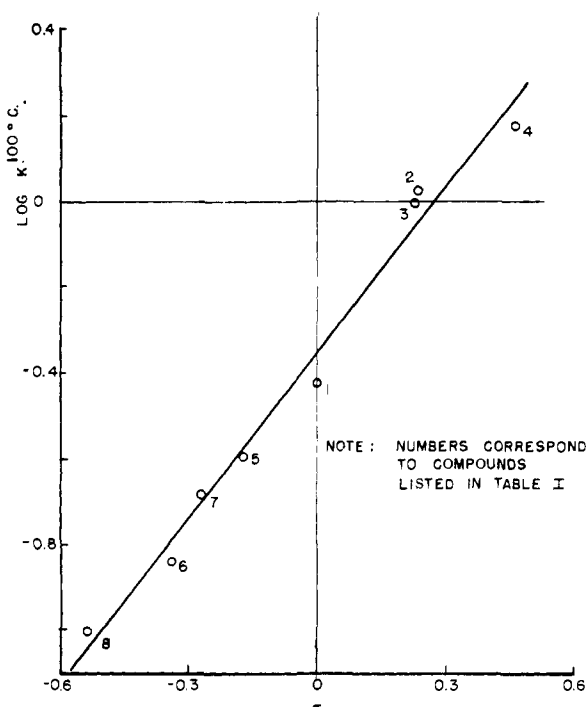(11) G. W. Snedecor, "Statistical Methods," 4th ed., The Collegiate Press, Inc., Ames, Iowa, 1946, Chaps. 6 and 7.

Fig. 2.—log $K^{100°}$ versus σ for Meerwein–Ponndorf reductions of substituted benzophenones.

between (B) and (C) controls the over-all equilibrium constant of the reaction. As the positive charge on the indicated carbon atom in (B) is increased, the hydride ion transfer is facilitated and the forward reaction proceeds more readily. Electron-withdrawing substituents on R and R' increase the positive charge on the central carbon atom and thus increase the over-all equilibrium constant of the reaction.

The positive value for ρ obtained in this research is, therefore, in agreement with the mechanism proposed by Jackman and Mills.[4]

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Kinetics of the Beckmann Rearrangement of Cyclohexanone Oxime

BY YOSHIRO OGATA, MASAYA OKANO AND KUNIO MATSUMOTO

The rates of the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam in aqueous sulfuric or perchloric acid have been measured at 60 and 90° by employing the 2,4-dinitrophenylhydrazone method. The rate was found to be first order with respect to the stoichiometric concentration of the oxime. An approximately linear relationship between the logarithm of rate constant and the acidity function (H_0 or J_0) was observed. Based on the experimental data, some probable reaction mechanisms for this reaction are discussed.

Many studies on the probable mechanism of the Beckmann rearrangement have been carried out with oxime esters,[1] but there seems to be little kinetic evidence at least with free oximes in strong aqueous acids. Recently, Pearson and Ball[2]

(1) Cf. B. Jones, Chem. Revs., 35, 335 (1944); G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 340; C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, p. 496.

(2) D. E. Pearson and F. Ball, J. Org. Chem., 14, 118 (1949).

studied the kinetics of this reaction with acetophenone oxime in sulfuric acid, and Roček, et al.,[3] measured the rate of rearrangement of cyclohexanone oxime to ε-caprolactam in oleum, but neither gave a detailed discussion of the correlation between the rate and the acidity in terms of mechanism. The present kinetic studies provide information

(3) (a) O. Wichtele and J. Roček, C. A., 46, 10809 (1952); (b) G. Roček and Z. Bergl, ibid., 48, 3279 (1954).