their conjugation. However, they could all be kept indefinitely under nitrogen at 5°.

Hydrogenation of the isobutylamides in ethanol solution using platinum oxide catalyst, gave in each case N-isobutylstearamide, m.p. 77–78°, undepressed by admixture with an authentic sample, m.p. 77–78°.[2]

The properties of the isobutylamides are summarized in Table II.

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The Alkaline and Neutral Hydrolysis of 2-Methoxyethyl Iodide

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This work was undertaken to determine whether or not the Hinshelwood, Laidler and Timm theory[1] would again[2] predict the correct qualitative trend in activation energy for the neutral hydrolysis of another organic iodide. The alkaline hydrolysis was studied in order to show that the formation of ethylene iodohydrin by reaction in basic solution is associated with the fact that there is a hydrogen which is easily ionizable[3] in the iodohydrin, whereas, when this hydrogen is replaced by methyl, the ordinary replacement of OH for I is obtained.

Experimental

The 2-methoxyethyl iodide was prepared from 2-methoxyethyl chloride. This latter compound was obtained by the reaction of methyl cellosolve with thionyl chloride in dimethylaniline.[4] The 2-methoxyethyl iodide was obtained by treating the corresponding chloride, obtained above, with sodium iodide in 95% ethanol.[5] The product of this reaction was purified by vacuum distillation. The boiling point at 35 mm. pressure was 53.5°. Pressure fluctuations caused the constancy of boiling point not to be indicative of purity. Powdered silver was used to keep iodine from distilling over. An analysis of the final product was made by completely hydrolyzing a weighed sample and titrating iodide by a potentiometric method described below. The analysis showed the product was 99% pure.

The 1,4-dioxane was Eastman Kodak Co. Best Grade. It was further purified by refluxing over metallic sodium, followed by distillation. The final product was not appreciably alkaline, as shown by titration with standard acid.

The neutral hydrolysis kinetics experiments were carried out in sealed tubes immersed in an oil thermostat which held to ± 0.05°. An approximately 0.02 *N* stock solution of 2-methoxyethyl iodide was made up before each run. A magnetic stirrer was employed to quicken the solution. Reaction tubes of about 25-cc. capacity were filled with this solution, sealed off, and placed in the thermostat for known lengths of time. Care was exercised to make the gas space above the solution as low as possible (~ 1 cc.) since appreciable amounts of the organic iodide would have accumulated there. Reproducible results were obtained even though the small gas space was varied by a factor of 2 or 3. The tubes were removed from the thermostat, cooled quickly, and a 20.00-ml. sample was titrated with silver nitrate to determine the amount of I^- formed. This was assumed to equal the amount of 2-methoxyethyl iodide which had been hydrolyzed. The end-point was obtained potentiometrically, using a silver electrode, sealed in the tip of the buret containing the silver nitrate, *vs.* a silver-silver iodide electrode in the solution being titrated.[6] The concentration of the 2-methoxyethyl iodide stock solution was obtained by letting a sample stay in the thermostat or, in some cases, boiling water, until the reaction was at least 99.9% completed.

The temperatures were determined by an N.B.S. platinum resistance thermometer and a Mueller bridge.

The alkaline hydrolysis was carried out in polyethylene bottles, since considerable difficulty with silica formation was experienced in Pyrex tubes when the temperature was above 60°.

The product of the alkaline hydrolysis of 2-methoxyethyl iodide in pure water was established as methyl cellosolve by extraction of the product from the aqueous phase by chloroform. The chloroform layer was dried with potassium carbonate, followed by magnesium sulfate. Comparison of the infrared spectrum of this solution and that of a synthetic solution of methyl cellosolve showed the same strong absorption at 9.1 microns. The general shape of the absorption band was sufficient to identify the reaction product as methyl cellosolve. A Baird Infrared Spectrophotometer was used for the analysis.

Experimental Results

The Neutral Hydrolysis.—The neutral hydrolysis in all cases followed the usual first order plot of concentration of 2-methoxyethyl iodide *vs.* time, showing the absence of appreciable salt effects and giving confidence that the starting reactant was pure and that the reaction was not catalyzed by the presence of small amounts of I_2 which appeared during the course of the reaction from the air oxidation of I^-.

The velocity constants were determined from the slope of the line obtained by plotting the log of the concentration of the 2-methoxyethyl iodide in the various tubes withdrawn at different times as a function of the time withdrawn. Duplicate runs gave satisfactory checks as seen in Table I. The percentages are given by weight.

TABLE I

Temp., °C.	Solvent	k(hr.$^{-1}$)	k(average)
91.06	Water	2.99×10^{-2}	2.98×10^{-2}
91.06	Water	2.97×10^{-2}	
91.06	20.8% EtOH	1.90×10^{-2}	1.91×10^{-2}
91.06	20.8% EtOH	1.92×10^{-2}	
91.06	44.1% EtOH	1.21×10^{-2}	1.23×10^{-2}
91.06	44.1% EtOH	1.25×10^{-2}	
99.76	Water	7.19×10^{-2}	7.22×10^{-2}
99.76	Water	7.25×10^{-2}	
107.89	Water	1.50×10^{-1}	1.58×10^{-1}
107.89	Water	1.66×10^{-1}	

The Alkaline Hydrolysis.—The alkaline hydrolysis showed second order kinetics as shown by linearity of the plot of $\log b - x/a - x$ *vs.* t. From the slope of this line the velocity constant was calculated from, slope $= 2.303/k(a - b)$.[7] At the low temperatures the reaction was followed to about 30% completion, while at the higher temperatures to about 80% completion. The kinetic results are summarized in Table II. Preliminary experiments in ethanol–water mixtures are not reported in the table because the precision of the results does not warrant it. However, it was found that in a 33.3% by volume ethanol–water solution at 70°, the k was 1.2, while k was 0.8 in a

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[1] C. N. Hinshelwood, H. J. Laidler and E. W. Timm, *J. Chem. Soc.*, 848 (1938).

[2] H. D. Cowan, C. L. McCabe and J. C. Warner, THIS JOURNAL, **72**, 1194 (1950).

[3] C. L. McCabe and J. C. Warner, *ibid.*, **70**, 4031 (1948).

[4] G. M. Bennett and F. Heathcoat, *J. Chem. Soc.*, 270 (1929).

[5] L. C. Swallen and C. E. Boord, THIS JOURNAL, **52**, 665 (1930).

[6] H. H. Willard and A. W. Boldyreff, *ibid.*, **51**, 471 (1929).

[7] Samuel Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., p. 1056.

20% ethanol–water mixture at the same temperature.

TABLE II

Temp., °C.	Solvent % by volume	k in liters/mole-hr.
62.36	60% dioxane–water	1.64
62.36	60% dioxane–water	1.75
54.09	60% dioxane–water	0.69
53.90	60% dioxane–water	.58
46.4	60% dioxane–water	.31
62.36	40% dioxane–water	.24
62.36	20% dioxane–water	.03

The Neutral Hydrolysis.—Table III shows that the Hinshelwood, Laidler and Timm theory, as applied in a previous paper,[2] again is applicable. It should be especially noted in this table that the qualitative trends in the activation energy can be successfully correlated with the inductive effect of the group attached to the carbon undergoing substitution, but the rate constant itself cannot. This shows that the entropy of activation is the factor which does not vary in a systematic manner and also shows the inadequacy of the statement by Hughes and Ingold[8] that "rate constant itself is more truly related to the chemical conditions than is the measured temperature coefficient."

TABLE III

Alkyl halide	k in days^{-1} at 60.0° in pure water	E (kcal.)
CH_2OHCH_2I[2]	0.0330	28.9
$CH_3OCH_2CH_2I$	.0094 (extrap.)	27.4
CH_3I[9]	.00720	25.8
CH_3CH_2I[10]	1.46	21.2

The variation of the rate constant with different ethanol–water mixtures, summarized in Table IV, shows that the neutral hydrolysis of 2-methoxyethyl iodide falls into the S_N2 type of reaction by the empirical method given in a previous paper.[2]

TABLE IV

Wt. % C_2H_5OH	$D - 1/2D + 1$[6]	$k \times 10^{-2}$ at 91.06° in hr.$^{-1}$
0	0.4870	2.98
20.8	.4845	1.91
44.1	.4795	1.23

The Alkaline Hydrolysis.—In a previous paper[3] the kinetics of the reaction between ethylene iodohydrin and hydroxyl ion in dioxane–water and ethanol–water mixtures was studied. It was shown that the mechanism involves the loss of a hydrogen ion from the iodohydrin, followed by an S_N2 intramolecular displacement of I^- by the O^- to form ethylene oxide. One would predict that on going to the reaction of OH^- and 2-methoxyethyl iodide, the above mechanism would not be able to be operative in view of the stability of the C–O bond to ionization. The ordinary S_N2 reaction of the OH^- on C–I would be expected to take place. This is borne out by the product analysis showing the formation of methyl cellosolve.

Table II shows that the velocity constant increases with increasing dioxane concentration in the solvent. The enormous increase in velocity of reaction of the alkaline over the neutral hydrolysis shows that the alkaline reaction is an S_N2 reaction by the Hughes–Ingold criterion.[12] They further predict[13] for this type of reaction that the rate will be higher in media of lower dielectric constant. This is indeed the case.

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(8) E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 672 (1941).

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(13) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 252 (1935).

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1,3-Bis-(p-hydroxyphenyl)-cyclopentane[1]

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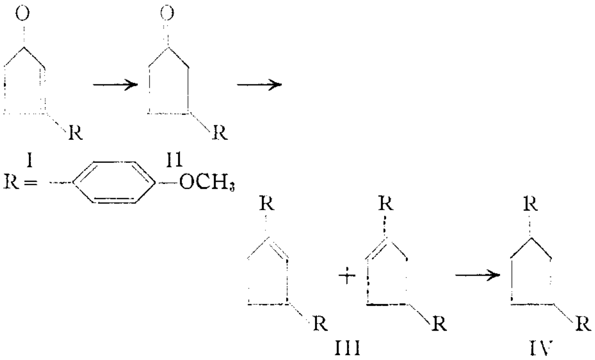
In preparing this member of the diarylcycloalkane group by the series of reactions outlined in our previous papers we were fortunate in having available the excellent directions of Wilds and Johnson[2] for the preparation of 3-(p-methoxyphenyl)-cyclopenten-2-one. These authors also described the hydrogenation of I to 3-(p-methoxyphenyl)-cyclopentanone over a palladium–charcoal catalyst in dioxane in fair yield, with the comment that further hydrogenation seemed to occur. Although we were able to isolate the saturated ketone from this reaction, the yields were unsatisfactorily low, the main product being an oily mixture. Apparently, the hydrogenation does not proceed with initial attack at the double bond but under these conditions gives rise to a mixture of products by the scheme described by Weidlich[3] for hydrogenation of α,β-unsaturated ketones in neutral or acid media. We found that application of Weidlich's alkaline conditions with the palladium oxide catalyst gave II in excellent yields.



p-Methoxyphenylmagnesium bromide reacted readily with the ketone, II, to yield a mixture of 1,3- and 1,4-bis-(p-methoxyphenyl)-cyclopentenes (III). In accord with previous experience none of the carbinol intermediate could be isolated, even under mild conditions. On the other hand both unsaturated isomers were expected, and although a definite separation on an alumina column was indicated, the products in the various fractions were indistinguishable either by their melting points or absorption

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(1) Abstracted from a thesis presented by Joseph A. Meredith in partial fulfillment of requirements for the M.Sc. Degree.

(2) A. L. Wilds and T. L. Johnson, THIS JOURNAL, **67**, 286 (1945).

(3) H. Weidlich, *Die Chemie*, **58**, 30 (1945).