[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Kinetics of the Chromic Acid Oxidation of Benzaldehyde

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RECEIVED JANUARY 29, 1958

The rate of the chromic acid oxidation of benzaldehyde, in water at 80°, increases with the first power of the concentration of benzaldehyde, with the first power of the concentration of acid chromate ion, and with a more complicated function of the concentration of acid. The data are consistent with a mechanism for the oxidation–reduction process which involves the chromic acid ester of hydrated benzaldehyde as intermediate.

The rate of the chromic acid oxidation of isopropyl alcohol increases with the first power of the concentration of the alcohol, and the first power of the concentration of the acid chromate ion[3] (as contrasted to the dichromate ion). The reaction induces the oxidation of manganous ion, and the induced oxidation is accompanied by a diminution of reaction rate.[4,5] These data have been interpreted to support the hypothesis that the reaction proceeds by abstracting a proton[6] from a chromic acid ester[7] of the alcohol. A comparable study now has been carried out for the chromic acid oxidation of benzaldehyde in aqueous solution; this work complements the investigation of Wiberg and Mill[8] of the chromic acid oxidation of benzaldehyde and of substituted benzaldehydes in aqueous acetic acid solution.

Experimental

Materials.—The chromic acid, and other standard reagents, were prepared as in previous studies.[3,4,6] Paragon brand "chlorine-free" benzaldehyde was distilled under vacuum, with purified nitrogen introduced through the capillary "bleeder." The material was stored in the dark under nitrogen. Prior to each experiment, a sample of this benzaldehyde was transferred, under nitrogen, to a separatory funnel, washed with alkali, saturated sodium sulfite and boiled distilled water. It was then dried over Drierite under nitrogen, and just prior to an experiment, distilled at 10^{-5} mm. at room temperature, In all experiments (except the rate determination in vacuum) this distilled aldehyde was transferred under nitrogen to the kinetic reaction mixture. Such aldehyde showed no peroxide by the starch-iodide test, and only a trace with the sensitive $FeSO_4$–NH_4CNS reagent.

Rate Determination in Vacuum.—A Corex Beckman cell was sealed to a 250-cc. round-bottom flask by means of a long side-arm; 100 cc. of reaction mixture (without benzaldehyde) was placed in the flask, degassed and frozen. Then a known quantity of benzaldehyde was distilled into the flask at 10^{-5} mm. pressure, and the reaction vessel was sealed. The contents of the flask were melted, and the flask introduced into the 80° thermostat. When the contents came to temperature, and at stated intervals thereafter, some of the solution was run into the Corex cell. The apparatus was so arranged that the flask remained in the thermostat bath while the Corex cell was in the Beckman spectrophotometer; the latter was thermostated by circulating bath fluid through a special cell compartment. After each measurement, the liquid in the Corex cell was returned to the flask in the thermostat bath by tipping the sealed container. The decrease in chromic acid concentration was followed spectrophotometrically.[6,7] The experiment in vacuum served to standardize those carried out under nitrogen.

Rate Determination under Nitrogen.—The reaction mixture was maintained under prepurified nitrogen, and aliquots were delivered through a thermostated, jacketed pipet (Fig. 1) by pressure from a stream of nitrogen. Forty odd experiments were carried out under nitrogen in this manner; and only in one instance was the rate anomalous by comparison with that in vacuum. In this one instance, the rate was high by a factor of 3.5. This anomalous result could not be duplicated, and the result was therefore discarded. In all the rate determinations, the ionic strength was maintained at 0.50 with sodium perchlorate.

Effect of Oxygen.—Since benzaldehyde is rapidly autoxidized, the effect of oxygen on the rate was investigated. When air was present over the solution in a reaction flask, it had very little effect upon the rate constant. When, however, oxygen was bubbled through a reaction mixture, the rate was increased by as much as a factor of three. Furthermore, when the stream of oxygen was cut off, and a stream of nitrogen substituted, the rate only slowly returned to that which had obtained originally. In one experiment, the reaction proceeded under nitrogen with a rate constant of 1.87 min.^{-1} $(\text{mole/l.})^{-3}$. When the reaction was about 35% complete, a stream of oxygen was introduced, and the rate constant rose to 5.9 min.^{-1} $(\text{mole/l.})^{-3}$. When nitrogen was again introduced, the rate constant gradually fell (at about 90% reaction) to 2.80 min.^{-1} $(\text{mole/l.})^{-3}$. Although these experiments show that some precautions must be taken to obtain reproducible rates, they do not suggest that the chromic acid oxidation of benzaldehyde in aqueous solution at 80° can be converted by oxygen into a free-radical chain process.

Effect of Light.—The reaction rate was unaffected by the light from a 150 watt lamp 1 cm. from the reaction flask. The rate was also the same in a Beckman cell with the light on continuously, and in a parallel experiment where the reaction proceeded in the dark, except for four 5-second intervals when readings were taken.

Product.—In the presence of an excess of chromic acid, peroxide-free benzaldehyde reacted under nitrogen to consume 98.5% of the calculated amount of chromic acid, and to yield a 97.5% yield of crude benzoic acid which melted (without recrystallization) at 121–122°.

Results

Chromic Acid.—The reaction rate was measured spectrophotometrically[6,7] as a function of the chromic acid concentration, the benzaldehyde concentration and the acid concentration. In most experiments, the chromic acid concentration was kept so low, relative to those of benzaldehyde and acid, that the latter remained essentially constant during any one run. Even under these conditions, the apparent first-order rate constant varies, with the concentration of chromic acid, much as it does for the chromic acid oxidation of isopropyl alcohol. The rate constant is greatest and the reaction most nearly first order for the most dilute solutions. The data are presented graphically in Fig. 2, where the integral[3] for a fourth-order rate is plotted

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[3] F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943).

[4] W. Watanabe and F. H. Westheimer, *ibid.*, **17**, 61 (1949); J. Hampton, A. Leo and F. H. Westheimer, THIS JOURNAL, **78**, 306 (1956).

[5] F. H. Westheimer, *Chem. Revs.*, **45**, 419 (1949), and Errata, June, 1950.

[6] N. Nicolaides and F. H. Westheimer, THIS JOURNAL, **71**, 25 (1949).

[7] F. Holloway, M. Cohen and F. H. Westheimer, *ibid.*, **73**, 65 (1951); A. Leo and F. H. Westheimer, *ibid.*, **74**, 4383 (1952).

[8] K. Wiberg and T. Mill, *ibid.*, **80**, 3022 (1958).

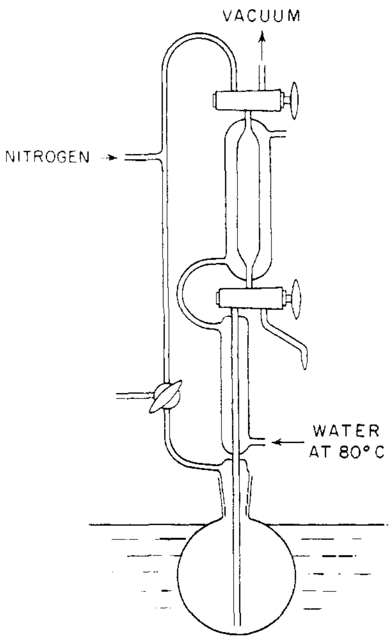

Fig. 1.—Sampling apparatus.

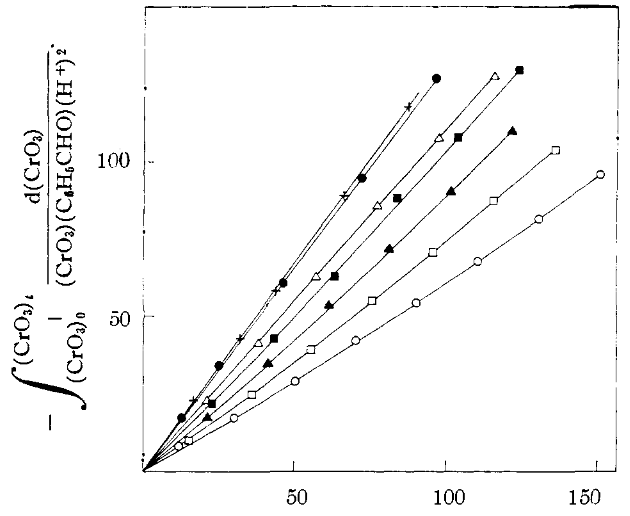

Fig. 2.—Rate integral *vs.* time: initial chromic acid concentrations: ○, 0.0480; □, 0.0240; ▲, 0.00961; +, 0.000483; ■, 0.00483; △, 0.002417; ●, 0.000967; initial (H^+) = 0.3935 mole/l.; initial (C_6H_5CHO) = 0.076 mole/l.

against time. These data are consistent with the assumption that the reaction rate is controlled by the concentration of acid chromate ion. The equilibrium

$$Cr_2O_7^= + H_2O \rightleftarrows 2HCrO_4^- \qquad (1)$$

is displaced to the right in dilute solutions, and only here will the reaction be first order in hexavalent chromium. The equilibrium constant for reaction 1 is known[9,10] at 25°; the data of Fig. 2, covering a hundred-fold variation in the concentration of chromic acid, were recalculated (Table I) on the assumption that the equilibrium constant for the hydration of dichromate ion is 0.015 mole/l.; this is the value formerly[3] used for this constant at high ionic strength at 25°. A different choice of this equilibrium constant within the range 0.01–0.02 mole/l. affects the absolute values of the rate constants, but does not change the qualitative conclusion that the rate varies with the first power of the acid chromate ion concentration.

TABLE I

VARIATION IN CHROMIC ACID CONCENTRATION

Initial (H^+) = 0.3935 mole/l.; initial (C_6H_5CHO) = 0.0764 mole/l.; K' = 0.015 mole/l.

Initial (CrO_3), mole/l.	k_4, (mole/l.)$^{-3}$ min.$^{-1}$
0.04805	1.72
.02403	1.57
.00961	1.40
.004834	1.34
.002417	1.30
.000967	1.43
.0004834	1.43

Benzaldehyde.—The rate data for a tenfold change in the concentration of benzaldehyde are presented in Table II.

TABLE II

VARIATION IN BENZALDEHYDE CONCENTRATION

Initial (H^+) = 0.436 mole/l.; initial (CrO_3) = 0.00263 mole/l; K' = 0.015 mole/l.

Initial (C_6H_5CHO), mole/l.	k_4, (mole/l.)$^{-3}$ min.$^{-1}$
0.095	1.35
.076	1.32
.057	1.34
.038	1.35
.028	1.23
.0190	1.17
.0095	1.18

Hydrogen Ion.—The fourth-order rate constants show a variation with hydrogen ion concentration; they are presented in Table III.

TABLE III

VARIATION IN HYDROGEN ION CONCENTRATION

Initial (C_6H_5CHO) = 0.0762 mole/l.; initial (CrO_3) = 0.001934 mole/l.; K' = 0.015 mole/l.

Initial (H^+), mole/l.	k_4 (mole/l.)$^{-3}$ min.$^{-1}$
0.4999	1.21
.3030	1.47
.1494	1.87
.0756	2.76
.0315	6.00

These data are consistent with the equation

$$-\,d(CrO_3)/dt = (H^+)(HCrO_4^-)(C_6H_5CHO)[0.147 + 0.95\,(H^+)]$$

Metal Ions.—Manganous and cerous ions decrease the reaction rate, whereas chromic ion is without effect on the reaction. In particular, 0.0005 molar Mn^{++} lowered the reaction rate by 40%, and 0.0008 molar Ce^{+++} by 35%.

Discussion

The kinetics for the chromic acid oxidation of benzaldehyde in aqueous solution closely resemble those for isopropyl alcohol. The reaction rate depends upon the first power of the acid chromate ion (as contrasted to the dichromate ion), the first

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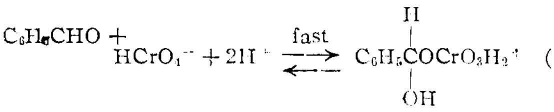
[9] E. King and J. Tong, THIS JOURNAL, **75**, 6180 (1953).

[10] J. D. Neuss and W. Rieman, *ibid.*, **56**, 2238 (1934).

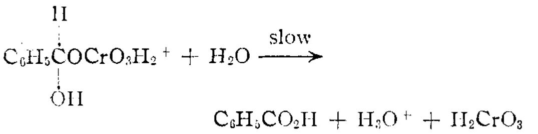
power of the benzaldehyde concentration; the dependence of the rate on acid concentration is complex. In concentrated acid solution, the activated complex consists of one molecule of benzaldehyde, one of undissociated chromic acid, and one proton; the dependence of the rate on the concentration of acid closely parallels that for isopropyl alcohol. The number of water molecules in the activated complex has not yet been determined.

Some further information about mechanism can be obtained from the data of Lucchi[11] on the effect of substituents on the reaction rate. Lucchi found that chlorine atoms in the *m*- and *p*-positions accelerate, and alkyl groups retard the oxidation of benzaldehyde. A Hammett[12] plot of Lucchi's data yields a good straight line with the slope $\rho = +1.06$ (for acetic acid solution).

These data suggest that the reaction proceeds by way of the chromic acid ester of hydrated benzaldehyde as intermediate.



$$C_6H_5CHO + HCrO_4^- + 2H^+ \underset{\longleftarrow}{\xrightarrow{\text{fast}}} C_6H_5\overset{\text{H}}{\underset{\text{OH}}{C}}OCrO_3H_2^+ \quad (2)$$



$$C_6H_5\overset{\text{H}}{\underset{\text{OH}}{C}}OCrO_3H_2^+ + H_2O \xrightarrow{\text{slow}} C_6H_5CO_2H + H_3O^+ + H_2CrO_3 \quad (3)$$

$$Cr^4 + Cr^6 \xrightarrow{\text{fast}} 2Cr^5 \quad (4)$$

$$Cr^5 + C_6H_5CHO \xrightarrow{\text{fast}} C_6H_5CO_2H + Cr^3 \quad (5)$$

In equation 3, the inorganic product is assumed to be a compound of tetravalent chromium; presumably the fate of this intermediate (as shown in equations 4 and 5) is similar to that previously[4,5] postulated.

Equations 2 and 3 account for the observed kinetics in the region of moderately concentrated (*e.g.*, 0.2 *M*) acid. The rate-controlling step (equation 3) postulates that the aldehydic hydrogen atom is lost as a proton. This formulation accounts for the positive value of rho; electron-withdrawing substituents increase the acidity of this hydrogen atom. If, alternatively, the reaction were one in which the hydrogen atom were removed as a hydride ion, one would expect a negative value of rho. (A much more complicated situation, which obtains for the chromic acid oxidation of substituted phenethyl alcohols, has been discussed by Kwart and Francis.[13])

Equation 3 has been written as if a water molecule abstracts the proton from the protonated hemiacetal ester. An alternate possibility, consistent with the ester mechanism, is that the proton is abstracted in a cyclic process by one of the chromate oxygen atoms.

In strong sulfuric acid solution, the rate of chromic acid oxidation of isopropyl alcohol[14] follows H_0.[15] Contrary to the interpretation put forward by Roček and Krupicka, this behavior is entirely consistent with the ester mechanism, and with the Hammett–Zucker hypothesis.[16] On the basis of the ester mechanism, the activated complex consists of a molecule of chromic acid ester and one of water; this is stoichiometrically equivalent to a molecule of alcohol, one of chromic acid, and a proton; a reaction which proceeds through such an activated complex should[16] follow H_0. The doubts[17,18] which have been raised recently concerning the strict validity of the Hammett–Zucker hypothesis, however, somewhat diminish its value as a diagnostic criterion. The number of water molecules in the benzaldehyde complex has not been established experimentally. Crude experiments show that the rate increases sharply with increasing acidity, but the effect of substituents, discussed above, makes it nevertheless likely that the reaction proceeds by way of the hydrated aldehyde. The ester mechanism appears the most probable for the oxidation of benzaldehyde, and is consistent with the available data (although unproved) for the oxidation of isopropyl alcohol. The mechanism cannot be the only one which occurs, since some oxidations (*e.g.*, those of hydrocarbons) necessarily follow another course. The ranges of validity of the various mechanisms remain to be elucidated.

The rate of oxidation of benzaldehyde in aqueous acetic acid[8], extrapolated to 80°, is faster than that in water at the same H_0 by less than a power of ten; the rate of oxidation of isopropyl alcohol in aqueous acetic acid[19] is greater than that in water at the same H_0 by several powers of ten. Furthermore, whereas the rate in water at about 0.2 *M* acid apparently requires the elements of chromic acid plus a proton, the rates in aqueous acetic acid solution[8,19] require only the elements of chromic acid. A possible explanation for this difference is that, in acetic acid solution, the dominant species may be the acetylchromic anion, $CH_3COOCrO_3^-$, rather than the acid chromate ion itself. Presumably, acetylchromic acid is a much stronger acid than is chromic acid, and therefore would be ionized even in aqueous acetic acid solutions. This hypothesis is consistent with the electrometric data of Watanabe[20] and the spectroscopic studies by Holloway,[21] but its validity has not yet been tested.

Finally, the decrease in the rate of oxidation of benzaldehyde caused by Mn^{++} and Ce^{+++} is analogous to that which obtains in the oxidation of isopropyl alcohol.[4,6] Since cerium has only two valence states (plus 3 and plus 4) its participation in the reaction almost certainly indicates that it has been oxidized from tri- to tetravalent in a one-electron step. This implicates tetravalent chromium

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[11] E. Lucchi, *Gazz. chim. ital.*, **71**, 729 (1941); **71**, 752 (1941); *C. A.*, **36**, 6880 (1942); **37**, 2252, 4293 (1943).

[12] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 186.

[13] H. Kwart and P. S. Francis, THIS JOURNAL, **77**, 4907 (1955).

[14] J. Roček and J. Krupicka, *Chemistry & Industry*, 1668 (1957).

[15] Reference 12, p. 267.

[16] L. Zucker and L. P. Hammett, THIS JOURNAL, **61**, 2779, 2785, 2791 (1939).

[17] N. C. Deno and C. Perizzolo, *ibid.*, **79**, 1345 (1957).

[18] F. A. Long and M. Paul, *Chem. Revs.*, **57**, 935 (1957).

[19] M. Cohen and F. H. Westheimer, THIS JOURNAL, **74**, 4387 (1952).

[20] W. Watanabe, Dissertation, University of Chicago, 1948.

[21] F. Holloway, Dissertation, University of Chicago, 1950.

as the oxidant, and suggests that the reaction sequence is

$$\mathrm{Cr^4 + Ce^3 \longrightarrow Cr^3 + Ce^4} \qquad (6)$$

When reaction 6 intervenes in place of reaction 4, the total rate of consumption of chromic acid is decreased. Although the study of the induced oxidation is very much less complete than that for the oxidation of isopropyl alcohol,[4] the result is similar, and suggests that the rate-controlling reaction produces tetravalent chromium. If this is so, then the chromic acid oxidation of benzaldehyde is a two-electron process, such as that shown in equations 2, 3, 4 and 5.

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[Contribution from the Department of Chemistry, University of Washington]

The Deuterium Isotope Effect in the Side Chain Halogenation of Toluene[1]

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Received December 12, 1957

The intramolecular deuterium isotope effect obtained in the side chain halogenation of toluene and some of its derivatives has been determined. Factors which decreased the energy of activation decrease the isotope effect. This observation may be interpreted by a consideration of the potential energy curves for the dissociation of reactants and products. The magnitude of the isotope effect is used as a criterion in considering the mechanisms of some halogenation reactions.

Introduction

The isotope effects obtained in the side chain halogenation of toluene and some of its derivatives have been examined previously.[2] The more extensive of these investigations gave, however, the value for a mixture of an inter- and an intramolecular isotope effect. In order to obtain data which may be consistently interpreted throughout a series, we have measured the pure intramolecular isotope effect for a number of these reactions. The method involved in this work was to carry out the halogenation to a known extent (usually about 50% of completion) and then to isolate the unchanged reactant and the product. Whenever possible, the product was converted back to the reactant by reduction. Mass spectrometric analysis of the starting material, the unchanged reactant and the product, along with the extent of reaction gave the data necessary for the calculation of the intramolecular isotope effect.

Experimental

Reactants.—Most of the α-deuteriotoluenes were prepared by the reduction of the appropriate side-chain halogenated compound. Three procedures were used: zinc and deuterioacetic acid reduction (method A),[3] treatment of the Grignard reagent with deuterium chloride (method B)[4] and treatment of the halide with lithium aluminum deuteride (method C).[5] The results are summarized in Table I.

Ethylbenzene-α-d_1 was kindly supplied by Drs. H. J. Dauben and L. L. McCoy and had a composition 1.37% d_0 and 98.63% d_1. The other compounds were prepared as follows.

***p*-Methylacetophenone-d_3.**—To a solution of 28.5 g. (0.35 mole) of toluene-d_3 in 120 ml. of dry carbon disulfide was added 89.6 g. (0.67 mole) of anhydrous aluminum chloride. The mixture was heated on the steam-bath to reflux and 24.5 g. (0.24 mole) of acetic anhydride was added slowly while stirring over a period of one hour. Heating was continued for an additional hour. The solvent was removed by distillation from a steam-bath. The reaction mixture was cooled and slowly poured into a well stirred ice–hydrochloric acid mixture. The mixture was extracted several times with 200–300-ml. portions of ether, and the combined extracts were washed twice with water, once with 10% sodium hydroxide and twice more with water. The extract was dried over calcium chloride, filtered and the solvent removed. Distillation gave 25.7 g. (63%) of *p*-methylacetophenone-d_3, b.p. 100–100.5° at 12–13 mm.

***p*-Cresyl Acetate-d_3.**—A solution of peroxytrifluoroacetic acid prepared by the addition of trifluoroacetic anhydride (0.36 mole, 50.8 ml.) to 8.3 ml. of 90% hydrogen peroxide in 50 ml. of methylene chloride at 0° was added slowly to a mixture of 130 g. of dibasic sodium phosphate and 25.7 g. (0.19 mole) of *p*-methylacetophenone-d_3 in 150 ml. of methylene chloride over a period of 30 minutes. The reaction mixture was heated to reflux for one hour, cooled, and filtered. The filtrate was washed once with 50 ml. of 10% sodium carbonate and dried over anhydrous magnesium sulfate. Upon filtering and distilling, 23.7 g. (83%) of *p*-cresyl acetate-d_3 was obtained, b.p. 90–91° at 10 mm.

***p*-Cresol-d_3.**—A solution of 23.7 g. of *p*-cresyl acetate-d_3 in 150 ml. of ether was added to a suspension of 0.2 mole (7.6 g.) of lithium aluminum hydride and 1.0 g. of lithium hydride in 400 ml. of anhydrous ether at such a rate as to cause gentle reflux. Heating was continued for one hour, the mixture was cooled and the excess reagent was destroyed by the dropwise addition of water. The mixture was added to a 10% sulfuric acid–ice mixture. After the aluminum salt had dissolved, the layers were separated and the ether was washed with water and dried over calcium sulfate. The ether was removed leaving an oil which was not purified before the next reaction.

***p*-Methoxytoluene-d_3.**—To a solution of 6.6 g. (0.16 mole) of sodium hydroxide and the crude *p*-cresol-d_3 prepared above in 65 ml. of water was added 0.19 mole of dimethyl sulfate over a period of one hour with the solution maintained at 5–10°. It was stirred an additional 45 minutes at 10° and 30 minutes at 50–60°. An additional 2.5 g. of sodium hydroxide was added in 15 ml. of water and the mixture was heated to reflux with stirring for 7 hours. After cooling the mixture, it was extracted several times with benzene. The benzene solution was dried over anhydrous calcium chloride and distilled giving 15.9 g. (85%) of *p*-methoxytoluene-d_3 b.p. 168–175°. Careful distillation through an efficient column gave the pure compound (14.5 g.), b.p. 177.0–177.1°, $n^{25}\mathrm{D}$ 1.5100.

Cumene-d_1.—To a solution of 15 g. of methyl 2-phenyl-2-propyl ether in 300 ml. of anhydrous ether was added 10 ml. of liquid sodium–potassium alloy (prepared under benzene from 3 parts potassium and 1 part of sodium). The mixture was stirred for four hours. After this time, a stream of warm, dry nitrogen which had been passed through deuterium oxide was passed into the reaction mixture until the red color of the carbanion had been discharged. Ethanol was then added to decompose the excess alloy. The solution was treated with water and the organic layer was sepa-

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(1) This is taken from a thesis submitted by L. H. Slaugh to the University of Washington in partial fulfillment of the requirements for the Ph.D. degree, 1956.

(2) H. C. Brown and G. A. Russell, This Journal, **74**, 3995 (1952); W. H. Urry, Abstracts Twelfth National Symposium, Denver, Colo., June, 1951, p. 30.

(3) R. Renaud and L. C. Leitch, *Can. J. Chem.*, **34**, 98 (1956).

(4) H. C. Brown and G. A. Russell, This Journal, **74**, 3995 (1952)

(5) E. Eliel, *ibid.*, **71**, 3970 (1949).