

washed with 15 ml. of ethanol. The combined ethanol solutions were distilled through a short column until ammonia ceased to collect in the distillate. The distillate was acidified and the alcohol removed by distillation. From the residual solution the benzoyl and benzenesulfonyl derivatives of ammonia were prepared by the Schotten-Baumann reaction.¹⁸ The derivatives were identical with authentic samples of benzamide and benzenesulfonamide.

The alcoholic distillation residue was diluted with water and distilled until the b.p. of water was reached. From the distillate the benzoyl and benzenesulfonyl derivatives of aniline were prepared.¹⁸

An aqueous solution of the colorless crystalline solid product was distilled to remove alcohol, ammonia and aniline. Acidification of the residue with sulfuric acid and extraction with ether gave trimellitic acid (XII), m.p. 211–214° (uncor.).¹⁹ Sublimation of XII at 12 mm. and 200–220° con-

(18) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 47.

(19) Beilstein, "Handbuch der organischen Chemie," IX, 977 (428). The reported m.p.s. of trimellitic acid range from 215–221°.

verted it to its anhydride¹⁰; m.p. 166.8–167.9° from toluene. A mixed m.p. determination with an authentic specimen of XII anhydride, m.p. 166.8–167.9° from toluene, showed no depression. The reported m.p. of XII anhydride is 162.5–163°.¹⁰

Oxidation of IV.—A solution of 90.6 g. (0.860 equiv.) of potassium permanganate in 1750 ml. of water was added portionwise with shaking over a 4-hour period to 10.7 g. (0.0861 mole) of IV and 1 l. of water. The resulting mixture was allowed to stand at room temperature for 21 hours. After destroying excess permanganate with bisulfite and adding aqueous potassium carbonate until the mixture was definitely basic, it was filtered. The concentrated filtrate (500 ml.) was acidified and steam distilled until 130 ml. of distillate had collected. This distillate, after being made basic, was steam distilled to remove neutral insoluble material. Ether extraction of the acidified distillate gave 1.52 g. (15%) of crude *t*-butylacetic acid; b.p. 170–185°. The acid was characterized as its amide¹¹ (m.p. 129.6–130.6°), its anilide¹¹ (m.p. 130.7–131.7°) and its *p*-bromophenacyl ester¹² (m.p. 81.6–82.1°).

ITHACA, N. Y.

[CONTRIBUTION FROM SOCONY-VACUUM LABORATORIES, A DIVISION OF SOCONY-VACUUM OIL CO., INC., RESEARCH AND DEVELOPMENT DEPARTMENT]

The Condensation of 2-Hydroxyethyl Sulfides with Alcohols and Phenols¹

BY FREDERICK RICHTER, FREDERICK B. AUGUSTINE, EMIL KOFT, JR., AND E. EMMET REID

RECEIVED NOVEMBER 19, 1951

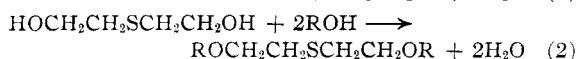
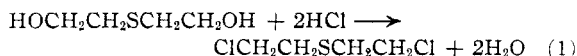
The high rate of reaction of thiodiglycol with aqueous hydrochloric acid suggests that it will readily condense with alcohols in the presence of an acid catalyst to form ethers. This anticipated activation of the hydroxyl group is demonstrated for thiodiglycol and for several other compounds containing the 2-hydroxyethyl sulfide grouping. The reaction appears to be general and when extended to glycols is useful for the preparation of linear and cross-linked polyethers. A mechanism for the condensation reaction is suggested.

In his study of the reactivity of atoms and groups in organic compounds Norris² demonstrated that a definite correlation exists between the reactivity of an alcohol with aqueous hydrochloric acid and its tendency to condense with ethyl alcohol to form a mixed ether. Thus, *t*-butyl alcohol, which "reacts with concentrated aqueous hydrochloric acid over 200,000 times as rapidly as *n*-butyl alcohol," could be condensed with ethyl alcohol in the presence of 15% aqueous sulfuric acid to produce *t*-butyl ethyl ether in 95% yield. *n*-Butyl alcohol under the same conditions yielded no mixed ether at all. *s*-Butyl alcohol, which is intermediate in its reactivity with aqueous hydrochloric acid, required a much higher sulfuric acid concentration to effect condensation with ethyl alcohol and since all three possible ethers were formed in this case the yield of mixed ether was much lower than that obtained in the condensation of *t*-butyl alcohol with ethyl alcohol.

On the basis of this correlation it seemed that thiodiglycol, (HOCH₂CH₂)₂S, which is known to react readily with hydrochloric acid according to equation 1, should condense with alcohols in the presence of an acid catalyst to form ethers according to equation 2.

(1) F. P. Richter and E. E. Reid (to Socony-Vacuum Oil Co., Inc.), U. S. Patent 2,582,605, January 15, 1952.

(2) J. F. Norris and G. W. Rigby, THIS JOURNAL, **54**, 2088 (1932).



The reaction suggested by equation 2 was studied, using all the normal alcohols from methyl to octadecyl alcohol, and condensation was found to proceed smoothly in each case to form the corresponding diether in good yield. Dilute aqueous sulfuric acid, *p*-toluenesulfonic acid and phosphoric acid served as effective catalysts. The physical properties of the diethers of thiodiglycol are listed in Table I. An interesting alternation of melting point with chain length is apparent.

The use of glycols or polyols such as pentaerythritol instead of the simple alcohols in equation 2 leads to the formation of polymeric ethers. The glycols yield linear polymers of which the average chain length (viscosity) may be regulated by introducing a monofunctional alcohol. Pentaerythritol when condensed with thiodiglycol rapidly forms a highly cross-linked polyether.

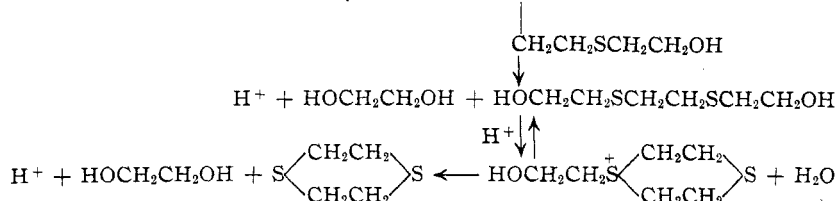
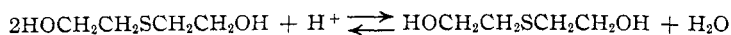
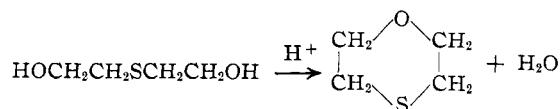
The condensation of thiodiglycol with glycols was found to proceed somewhat more slowly than in the case of the simple alcohols and required a higher reaction temperature. Under these conditions the formation of dithiane (m.p. 112° with sublimation) in minor amounts was observed in several instances. The mechanism of its formation prob-

TABLE I
DIALKYL ETHERS DERIVED FROM THIODIGLYCOL

Alkyl group	M.p., °C.	°C.	B.p., Mm.	Procedure	Yield, %	Sulfur, % Calcd.	Found
Methyl	-78 to -77	202.2-202.6	763 ^a	A	33	21.34	21.50
Ethyl	-32 to -31.5	127-128	35	A	50	17.98	18.10
<i>n</i> -Propyl	-48 to -47.5	156-157	43	A	51	15.54	15.71
<i>n</i> -Butyl	-38.5 to -38	162-164	20	B	81	13.68	14.08
<i>n</i> -Pentyl	-33.5 to -33	180.5-181	16	B	62	12.21	12.49
3-Methylbutyl	175-177	20	B	83	12.21	12.60
<i>n</i> -Hexyl	- 9.5 to -9	199.5-200.5	14.5	B	76	11.04	11.21
<i>n</i> -Heptyl	- 5.5 to -5	217.5-218	15.5	B	81	10.07	9.70
<i>n</i> -Octyl	15-15.5	184-188	0.8	B	78	9.25	9.45
2-Ethylhexyl	160-165	0.2	B	83	9.25	9.70
<i>n</i> -Nonyl	16.5-17	C	62	8.56	9.00
<i>n</i> -Decyl	32-32.3	206-210	0.3	B	84	7.96	8.06
<i>n</i> -Undecyl	32-32.5	C	70	7.44	7.80
<i>n</i> -Dodecyl	44-44.5	C	78	6.99	7.10
<i>n</i> -Tridecyl	43.5-44	C	81	6.59	7.08
<i>n</i> -Tetradecyl	53.5-54	C	74	6.23	6.65
<i>n</i> -Pentadecyl	52.5-53	C	78	5.90	6.60
<i>n</i> -Hexadecyl	59.5-60.3	C	74	5.61	6.42
<i>n</i> -Heptadecyl	59.5-60	C	72	5.34	6.24
<i>n</i> -Octadecyl	66-66.5	C	68	5.11	5.80

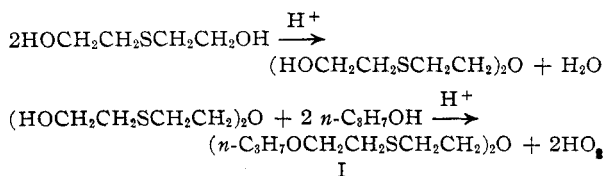
^a A. E. Kretov, *J. Russ. Phys. Chem. Soc.*, **61**, 2346 (1929), reported b.p. 201-203.5° for bis-(2-methoxyethyl) sulfide.

ably involves the intermediate formation of a sulfonium ion as suggested by Fuson and co-workers³ for the formation of 1,4-dithiane from mustard gas.



Since the amount of dithiane formed in any case was rather small and the ethylene glycol postulated would readily condense with thiodiglycol it was not possible to identify the ethylene glycol as a product of the reaction.

In all of the condensation reactions involving thiodiglycol the chief side reaction appears to be intermolecular condensation to form linear polymeric ethers. This can be minimized by employing an excess of the alcohol. In one experiment involving the condensation of *n*-propyl alcohol with thiodiglycol it was possible to isolate and identify the dipropyl ether of the "dimer," *i.e.*, bis-(*n*-propoxyethylmercaptoethyl) ether (I).



A third, although less important, side reaction is the intramolecular condensation of thiodiglycol

(3) R. C. Fuson, R. D. Lipscomb, B. C. McKusick and L. J. Reed, *J. Org. Chem.*, **11**, 513 (1946).

Because of these side reactions the method is not readily adaptable to the synthesis of monoethers of thiodiglycol in good yield. Thus, when one mole of *n*-butyl alcohol was heated under pressure with one mole of thiodiglycol in the presence of *p*-toluenesulfonic acid the products isolated were *p*-oxathiane (9.6%), monobutyl ether (12.90%), the dibutyl ether (14.1%) and higher polymeric ethers (61.4%). In interpreting these data it should, of course, be pointed out that equilibrium conditions prevailed, *i.e.*, no attempt was made to remove the water formed in the reaction.

The reaction of phenols with thiodiglycol in the presence of an acid catalyst is of particular interest because there exists the possibility of a nuclear hydrogen atom being involved in the condensation. The chief product, in the case of phenol itself, was found to be the diphenyl ether of thiodiglycol. Both *o*- and *p*-nitrophenol failed to undergo a similar condensation with thiodiglycol.

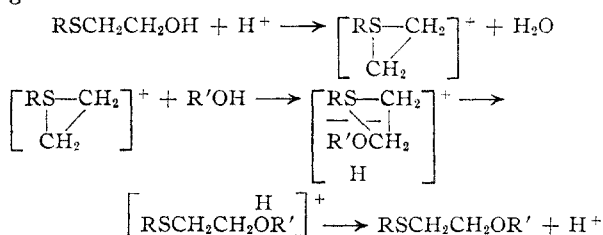
It was of interest to determine whether the condensation reaction would be generally applicable to 2-hydroxyethyl sulfides. Several of these were tried and the condensation was effected as anticipated. Thus, 2-hydroxyethyl 2-phenylethyl sulfide (from styrene and mercaptoethanol) was found to condense with *n*-amyl alcohol to form 2-*n*-amoxyethyl 2-phenylethyl sulfide in 80% yield and with phenol to form the corresponding phenyl ether in 62% yield. Other examples are listed in Table II.

TABLE II
 ETHERS PREPARED BY THE CONDENSATION OF ALCOHOLS AND PHENOLS WITH 2-HYDROXYETHYL SULFIDES

Compound, sulfide	°C. B.p.,	Mm.	M.p., °C.	Preparation Method	Yield, %	Analyses sulfur, % Calcd.	Found
2- <i>n</i> -Amoxyethyl 2-phenylethyl	142-148	3	<i>a</i>	80	12.7	13.1
2- <i>n</i> -Octyloxyethyl octyl	170-171	1.7	<i>b</i>	83	10.6	11.1
2-Isoamoxyethyl pinyll	136	0.8	<i>c</i>	49	11.3	11.8
2-Isoamoxyethyl phenyl	146-150	7	<i>d</i>	74	14.3	14.3
2-Phenoxyethyl 2-phenylethyl	165-169	0.9	<i>e</i>	62	12.4	12.9
Bis-(2-phenoxyethyl) ^f	182-185	0.9	54.3-54.4	<i>f</i>	40	11.7	11.8

^a Condensation (Procedure B) of *n*-amyl alcohol and 2-hydroxyethyl 2-phenylethyl sulfide (from styrene and mercaptoethanol). ^b Condensation (B) of *n*-octyl alcohol and 2-hydroxyethyl *n*-octyl sulfide (from octene-1 and mercaptoethanol). ^c Condensation (B) of isoamyl alcohol and the addition product of β -pinene and mercaptoethanol, boiling at 141-147° (4 mm.). ^d Condensation (B) of isoamyl alcohol and 2-hydroxyethyl phenyl sulfide (from ethylene chlorohydrin and sodium phenyl mercaptide). ^e Condensation (B) of phenol and 2-hydroxyethyl 2-phenylethyl sulfide. ^f Condensation (B) of phenol and thiodiglycol. ^g O. B. Helfrich and E. E. Reid, THIS JOURNAL, 42, 1208 (1920), report m.p. 54.2°.

The theory of a cyclic sulfonium ion has been postulated in many instances to explain the anomalous behavior of β -substituted sulfides. A possible mechanism for this condensation reaction involves the intermediate formation of a sulfonium ion. This then adds the alcohol, and the resulting adduct undergoes ring rupture. Loss of the proton gives the ether



Experimental

Materials.—The thiodiglycol used in these experiments was obtained by fractionally distilling the commercial product, "Kromfax Solvent," furnished by the Carbide and Carbon Chemicals Corp. A fraction boiling at 130-131° (2.5 mm.) or one of comparable boiling range was used in studying the condensation reactions. The alcohols employed for the synthesis of ethers were of Eastman grade except in the case of methanol where a technical grade synthetic product was used. The C₁₁- to C₁₈-alcohols were very highly purified prior to use.

Most of the 2-hydroxyethyl sulfides other than thiodiglycol were prepared by adding commercial mercaptoethanol to the appropriate olefins and then carefully fractionating the crude products.

Reaction Conditions.—Although the condensation was found to proceed at temperatures as low as 78-80° in the case of ethyl alcohol, a temperature range of about 140-150° was generally most expedient. The reaction time was usually 3 to 4 hours when operating within this temperature range. No condensation was observed in any case in the absence of an acid catalyst. *p*-Toluenesulfonic acid, added as the monohydrate, was very convenient and about 0.03-0.04 mole of this catalyst per equivalent of 2-hydroxyethyl sulfide was generally satisfactory. An equivalent amount of sulfuric acid, added as a 6 *N* aqueous solution, was found to be comparable in activity to the toluenesulfonic acid. Phosphoric acid, although effective, was generally less active.

Three different procedures were employed for carrying out the condensation reactions, the particular procedure depending upon the properties of the reactants and products involved. These are illustrated by typical examples:

Procedure A. Bis-(2-*n*-propoxyethyl) Sulfide.—A mixture consisting of 183 g. of thiodiglycol, 270 g. of *n*-propyl alcohol and 18.3 g. of *p*-toluenesulfonic acid monohydrate was held at 140-145° for 3.5 hours in a stainless steel bomb. After cooling, the reaction product was added to an equal volume of benzene, washed with 5% aqueous sodium carbonate and with water until neutral and the benzene solution was subjected to fractional distillation *in vacuo*. The fraction boiling at 75-81° (0.4 mm.), 160 g., represented a

yield of 51%. It was purified by refractionation, *n*_D²⁰ 1.4596.

Bis-(*n*-propoxyethylmercaptoethyl) Ether (I).—A second fraction, 46 g., b.p. 81-160° (0.4 mm.), was obtained from the reaction product mixture in the preparation of bis-(2-*n*-propoxyethyl) sulfide above. This was redistilled yielding 25 g., b.p. 228-230° (20 mm.), *n*_D²⁰ 1.4898; *d*₄²⁰ 1.0226. Calculated for (C₄H₉OCH₂CH₂SC₂H₅)₂O: *M*_{Rd} (Eisenlohr's values), 87.74. Found: *M*_{Rd}, 87.78.

Anal. Calcd.: S, 20.7. Found: S, 21.4.

Procedure B. Bis-(2-isoamoxyethyl) Sulfide.—A mixture of 122 g. of thiodiglycol (1 mole), 352 g. of isoamyl alcohol (4 moles, 100% excess) and 12 g. of *p*-toluenesulfonic acid monohydrate was heated under reflux with stirring in a one-liter flask equipped with a water trap which returned the alcohol to the flask but retained the water formed in the reaction. After 1.5 hr. 31 ml. of water had been collected and an additional one ml. was obtained after 2.5 hr. more. The mixture was allowed to cool to room temperature, washed with 150 ml. of 5% aqueous sodium carbonate and with water until neutral to litmus and finally fractionally distilled *in vacuo*, *n*_D²⁰ 1.4558.

In this procedure, if the alcohol boils above 150° it is convenient to add just enough xylene to the reaction mixture to assist in distilling out the water formed in the reaction. A large excess of xylene is to be avoided because its presence may retard the desired condensation.

Procedure C. Bis-(2-*n*-dodecyloxyethyl) Sulfide.—A mixture of 1.22 g. of thiodiglycol (0.01 mole), 4.10 g. of *n*-dodecyl alcohol (0.022 mole, 10% excess) and 0.12 g. of *p*-toluenesulfonic acid monohydrate was heated in a test-tube immersed in an oil-bath at 145° for four hours. The solid cake formed on cooling was broken up and digested with 20 ml. of water and filtered. It was recrystallized from a mixed ethyl-isopropyl alcohol solvent until the melting point was constant.

Condensation Polymerization of Thiodiglycol and Ethylene Glycol in the Presence of Isoamyl Alcohol.—A solution of 18 g. of *p*-toluenesulfonic acid monohydrate in 220 g. of isoamyl alcohol was added over a period of one hour to a mixture of 365 g. of thiodiglycol and 124 g. of ethylene glycol at 140-145°. In the next five hours the temperature was raised gradually to 190°, and 95 g. of aqueous distillate was collected. The reaction product was washed with 5% aqueous sodium carbonate and with water until neutral and the unreacted thiodiglycol was removed by distillation *in vacuo*. The polymeric product was finally held at 225° at 0.5 mm. pressure to remove the more volatile constituents. The finished product was a viscous oil. The kinematic viscosity at 100°F. was 53.1 cs. and at 210°F. was 10.33 cs. The product contained 19.6% sulfur.

Polymerization of Pentaerythritol with Excess Thiodiglycol.—To the clear solution obtained by heating 68 g. (0.4 mole) of pentaerythritol with 366 g. (3 moles) of thiodiglycol to 145° was added 12 g. of *p*-toluenesulfonic acid monohydrate. The reaction was stopped after 25 min. when 38 ml. of water had been collected. The product was neutralized with solid barium carbonate and filtered while hot. The viscous, pale yellow filtrate was subjected to distillation *in vacuo* to remove the excess thiodiglycol. The product was a gelatinous resin containing 24.3% sulfur. The polyether was insoluble in the usual solvents including chloroform, dioxane, benzene, ethanol and acetone.

Reaction of Thiodiglycol with *n*-Butyl Alcohol in Equimolecular Proportions.—A mixture consisting of thiodiglycol (122.2 g., 1 mole), *n*-butyl alcohol (74.1 g., 1 mole) and *p*-toluenesulfonic acid monohydrate (5.7 g., 0.03 mole) was held at 145–150° for three hours in a stainless steel tube. The reaction mixture was dissolved in 500 cc. of ether, the aqueous layer discarded and the ether solution washed with 2% sodium carbonate and finally with water until neutral. After removal of the ether and unreacted alcohol the residue was distilled and the following fractions were collected: *p*-oxathiane,⁴ 10 g. (9.6% based on the thiodiglycol), b.p. 147–149° (760 mm.).

(4) H. T. Clarke, *J. Chem. Soc.*, **101**, 1805 (1912), reported 147° 755 mm.) for the boiling point of 1,4-thioxane.

2-Hydroxyethyl 2-*n*-butoxyethyl sulfide, 23 g. (12.9% based on the thiodiglycol), b.p. 152–154° (20 mm.).

Anal. Calcd. for $C_{12}H_{26}O_2S$: S, 17.98; *MRD*, 50.29. Found: S, 18.0; n_D^{20} 1.4744; d_{20}^{25} 0.9919; *MRD*, 50.59.

Bis-(2-*n*-butoxyethyl) sulfide, 33 g. (14.1% based on the thiodiglycol), b.p. 162–164° (20 mm.).

Anal. Calcd. for $C_{18}H_{38}O_2S$: S, 13.68; *MRD*, 68.89. Found: S, 14.08; n_D^{20} 1.4560; d_{20}^{25} 0.9308; *MRD*, 68.46.

Residue, 64 g., consisting of polymeric ethers (61.4% calculated as $(OCH_2CH_2SCH_2CH_2)_n$ and based on the thiodiglycol).

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[CONTRIBUTION FROM THE BUREAU OF MINES, SYNTHETIC FUELS RESEARCH BRANCH]

Chemistry of the Oxo and Related Reactions. VI. Experiments with Meta- and Para-Substituted Benzyl Alcohols

BY IRVING WENDER, HAROLD GREENFIELD, SOL METLIN AND MILTON ORCHIN

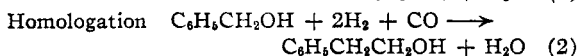
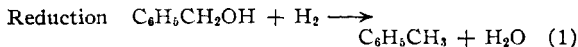
RECEIVED FEBRUARY 25, 1952

Nuclear-substituted benzyl alcohols react with synthesis gas ($2H_2:1CO$) in the presence of a cobalt catalyst to give a mixture containing a substituted toluene derived from the hydrogenolysis of the hydroxyl group (reduction) in addition to a substituted 2-phenylethanol (homologation). The effect of the substituent on the over-all rate of the reaction and on the product distribution was studied in a series of semi-quantitative experiments. The rate of reaction decreased in the following order: $p-OCH_3 \gg p-CH_3 > m-CH_3, p-t-butyl > H > p-Cl > m-OCH_3 \gg m-CF_3$. The proportion of homologation product as compared to reduction product also increased in the order in which the substituent is capable of releasing electrons but this effect was not nearly as pronounced as the effect on the reaction rate.

Treatment of benzyl alcohol with synthesis gas ($2H_2:1CO$) and a cobalt catalyst gives a mixture consisting of the hydrocarbon, toluene and the homologous alcohol, 2-phenylethanol, in a ratio of about 2:1.^{1,2} When substituted benzyl alcohols of the type $C_6H_5CR'R''OH$ (where R' and R'' are alkyl and/or aryl groups) are similarly treated, the corresponding hydrocarbons are formed almost exclusively.² The study has now been extended to nuclear-substituted benzyl alcohols to determine (a) the relative proportions of the hydrogenated and homologated products, and (b) the effect of different substituent groups on the speed of the two reactions. All reactions were conducted at 185–190° with an initial pressure of 238 atm. of 2:1 synthesis gas ($2H_2:1CO$).

The alcohols, solvent benzene and dicobalt octacarbonyl catalyst were placed in an autoclave which was heated from room temperature to 190° in 110 minutes. The rates with which the various substituted alcohols reacted with synthesis gas were followed by observing the drop in pressure recorded on a Bourdon gage (680 atm.) attached to the autoclave. The results are shown in Tables I and II.

Although the stoichiometry of the reduction reaction (equation 1) is quite different from that of the homologation reaction (equation 2), both reactions



usually proceed simultaneously, and the rate of gas absorption can be used as a rough measure of the speed of the over-all reaction.

(1) I. Wender, R. Levine and M. Orchin, *THIS JOURNAL*, **71**, 4160 (1949).

(2) I. Wender, H. Greenfield and M. Orchin, *ibid.*, **73**, 2656 (1951).

The time interval required to absorb one mole of gas per mole of starting alcohol was used qualitatively to compare reaction rates. The temperatures at which this absorption occurred varied; Table II gives time and temperature data. Thus, *p*-methoxybenzyl alcohol had absorbed one mole-equivalent of gas six minutes after the temperature reached 80°; the temperature at the end of this time interval was only 92°. *p*-Methylbenzyl alcohol absorbed this amount of gas between 80 and 166° in 44 minutes. Table II also shows that the rates of uptake of gas were in the following order: $p-OCH_3 \gg p-CH_3 > m-CH_3, p-t-butyl > H > p-Cl > m-OCH_3 \gg m-CF_3$. This sequence of substituents is in the order of their ability to release electrons. All the benzyl alcohols having electron-releasing substituents started to react between 80 and 166°. Benzyl alcohol started to absorb gas at 180°. The alcohols having electron-attracting substituents reacted so slowly at 190° that starting alcohol was recovered after 5 hours; some dehydrogenation of the starting alcohol occurred, and significant quantities of the corresponding aldehydes were identified in the reaction products from these experiments.

Table I shows that, in general, as the relative speed of the reaction decreased, the quantity of product derived from homologation decreased as compared to that from hydrogenolysis. For example, after 5 hours at 190° more than half of the original *m*-methoxybenzyl alcohol was recovered unchanged, and nearly all of the reacted portion was reduced. However, *p*-methoxybenzyl alcohol reacted more than 10^4 times as fast as *m*-methoxybenzyl alcohol; and the major part of the *p*-methoxy compound reacted by homologation, although considerable *p*-methoxytoluene (hydrogenation) was secured.