[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Reaction Rates by Distillation. VI. The Etherification of Benzyl and Related Alcohols

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Benzyl alcohols have been converted to a variety of ethers in good yield by a modification of the distillation method previously applied to the etherification of triphenylcarbinol and benzhydrol. An increase in the electron-releasing ability of the *para* substituent of a benzyl alcohol markedly increases the rate at which it etherifies *n*-butyl alcohol, but apparently because of increased "deactivation" of the catalyst the rate at which it etherifies anisyl alcohol is decreased. Etherification of *n*-butyl alcohol by benzyl alcohol may be suppressed completely in favor of benzylation of the benzene solvent by converting the butyl alcohol to its coördination complex with *p*-toluenesulfonic acid. A refined procedure for carrying out and following the etherification of triphenylcarbinol and benzhydrol by *n*-butyl alcohol gave kinetics which are accurately first order in the polyphenylcarbinol at a variety of reactant ratios and catalyst concentrations.

A number of ethers of triphenylcarbinol and benzhydrol were prepared smoothly by the distillation method described in the first paper of this series, but the results of attempts to etherify benzyl alcohol were unsatisfactory.[2,3] The data of Table I show, however, that a variety of benzyl butyl ethers are obtained in fair yield when a 1:3 molar ratio of the benzyl to the butyl alcohol in benzene is employed (*cf.* expts. 2 and 9). The rate of reaction, as shown primarily by the increasing catalyst concentration, and the yield of ether tend to decrease sharply as the electron-releasing ability of the *para* substituent of the benzyl alcohol decreases (expts. 1 to 5) or as the butyl alcohol is changed from primary to secondary to tertiary (expts. 2, 7 and 8).

TABLE I

ETHERIFICATIONS WITH A 1:3 RATIO OF p-$RC_6H_4CH_2OH$ TO n-BUTYL ALCOHOL[a]

Expt.	R	Cat.,[b] mole	$t_{50\%}$, min.	Yield, %
1	$(CH_3)_2N$	0.000125	158	76
2	CH_3O	.002	184	87
3	CH_3	.064	254	72
4	H	.128	1210	59
5	Cl	.256	347	40[c]
6[d]	Cl	.256	279	40[d]
7[e]	CH_3O	.002	287	84
8[f]	CH_3O	.002	426	48[f]
9[g]	CH_3O	.002	96	47

[a] Solution of 0.125 mole of p-$RC_6H_4CH_2OH$ in sufficient benzene to give one liter of solution used in all cases unless otherwise noted. In all experiments the yield of water was 94 to 101%. [b] *p*-Toluenesulfonic acid. [c] A 30% yield of *p*-chlorodiphenylmethane was also obtained. [d] A 3:1 by volume mixture of cyclohexane:nitrobenzene replaced the benzene solvent. An 11% yield of bis-*p*-chlorobenzyl ether was also obtained. [e] *sec*-Butyl alcohol replaced the *n*-butyl alcohol. [f] *t*-Butyl alcohol replaced the *n*-butyl alcohol. A 29% yield of dianisyl ether was also obtained. [g] An equivalent amount of *n*-butyl alcohol was used here.

Dianisyl ether was readily prepared in 80% yield at the catalyst concentration of expt. 2.[4] It was also found that upon refluxing (160 to 175°) a solution of *p*-toluenesulfonic acid in *n*-hexyl alcohol until a 75% yield of water collected, self-etherification of the alcohol proceeded in high yield.[5,6]

The etherifications of Table I doubtless proceed *via* cleavage of the carbon-oxygen bond of the various benzyl alcohols while the etherifications of Table II would be expected to proceed primarily *via* cleavage of the carbon-oxygen bond of the anisyl alcohol. The increasing rate as the electron-releasing ability of the substituent decreases can reasonably be attributed to decreasing "deactivation" of the catalyst and a qualitative measure of the relative basicities of these alcohols[7] is thereby afforded.

TABLE II

ETHERIFICATIONS WITH A 3:1 RATIO OF p-$RC_6H_4CH_2OH$ TO ANISYL ALCOHOL[a]

Expt.	R	$t_{50\%}$, min.	Yield, %
10	CH_3	181	73
11	H	98	93
12	Cl	43	94
13	O_2N	14	87

[a] A solution of 0.125 mole of anisyl alcohol, 0.001 mole of catalyst and sufficient benzene to give one liter of solution used in all cases. The yield of water was 97 to 98% except for expt. 10 for which the yield was only 88%.

It is felt that the data of Tables I and II enable one to estimate the approximate catalyst concentration required and the yield to be expected in the formation of any of the fifteen unsymmetrical dibenzyl ethers derived from the six benzyl alcohols. From the results of expts. 1 and 2, for example, it would be expected[8] that a good yield of *p*-dimethylamino-*p*'-methoxydibenzyl ether would be obtained with a 3:1 ratio of methoxy to amino alcohol at the catalyst concentration of expt. 1; a 74% yield was obtained in 5 hours under these conditions. Concurrent formation of the two possible symmetrical esters would tend to decrease as the difference in ease of cleavage of the carbon-oxygen bonds of the two benzyl alcohols increased and as the excess of the alcohol undergoing this cleavage less readily was increased.

Anisyl *n*-butyl ether was prepared in 94% yield by the transetherification of dianisyl ether by *n*-butyl alcohol. An 83% yield of anisyl benzyl ether

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[1] From the Ph.D. thesis of P. W. Erickson, October, 1951.

[2] E. F. Pratt and J. D. Draper, THIS JOURNAL, **71**, 2846 (1949).

[3] For valuable related studies, see M. P. Balfe, J. Kenyon and E. M. Thain, *J. Chem. Soc.*, 790 (1952), and earlier papers from their laboratories.

[4] R. Quelet and J. Allard, *Bull. soc. chim.*, **4**, 1468 (1937), obtained this ether in good yield by the action of concentrated hydrochloric acid on anisyl alcohol.

[5] Mrs. Gloria Weiss carried out the first successful experiment of this type in our laboratories.

[6] R. Vernimmen, *Bull. soc. chim. Belg.*, **33**, 96 (1924), obtained a 20% yield of ether upon refluxing *sec*-hexyl alcohol with 5% of *p*-toluenesulfonic acid without removal of the by-product water.

[7] E. F. Pratt and K. Matsuda, THIS JOURNAL, **75**, 3739 (1953).

[8] Revised values for the electron-releasing abilities of these *para* substituents are given by H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

TABLE III

ETHERIFICATIONS OF POLYPHENYLCARBINOLS BY *n*-BUTYL ALCOHOL

Expt.	*n*-BuOH,[a] mole	Cat. concn. $\times 10^4$, moles/l.	$t_{1/2}$,[c] min.	$k \times 10^4$, minutes^{-1}						
				30%	40%	50%	60%	70%	80%	Av.[b]
				Etherification of triphenylcarbinol						
14	0.25[a]	0.625	40	61.5	61.0	61.6	63.0	63.8	65.2	62.7 ± 1.33
15	.25	.625	120	50.4	52.4	55.0	57.5	59.7	63.2	.........[d]
16	.50	.625	189	37.1	36.2	36.6	36.6	36.2	36.7	36.6 ± .26
17	.75	.625	200	34.1	34.5	34.3	34.6	34.6	34.3	34.4 ± .20
18	1.00	.625	241	28.9	29.1	28.8	28.7	28.0	28.2	28.6 ± .30
19	0.75	2(0.625)	104	67.1	67.8	67.3	66.4	66.2	64.8	66.6 ± .80
20	0.75	0.5(0.625)	451	15.1	15.3	15.5	15.4	15.1	14.7	15.2 ± .23
				Etherification of benzhydrol						
21	0.25	20.0	102	56.8	58.6	64.0	67.9	71.1	..	.........[d]
22	.50	20.0	295	21.9	22.4	23.2	23.5	23.6	..	22.9 ± 0.62
23	.75	20.0	518	13.9	13.5	13.5	13.4	13.2	..	13.5 ± .16
24	1.00	20.0	707	10.2	10.2	10.0	9.81	9.52	..	9.95 ± .22
25	0.75	40.0	181	37.1	37.4	38.1	38.3	38.5	..	37.9 ± .50
26	0.75	10.0	1348	5.40	5.22	5.13	5.14	5.03	..	5.18 ± .10

[a] One-fourth mole of polyphenylcarbinol was used in all expts. except in expt. 14 in which 0.5 mole was used. [b] These are the arithmetic mean of the separate values plus or minus the average deviation of a single value from this mean. [c] These values read from the graph. [d] Average values here would have little meaning.

was obtained when dianisyl ether was prepared and, without isolation, transetherified by the stoichiometric amount of benzyl alcohol.[9]

It was of considerable interest to find that the yield of benzyl *n*-butyl ether decreased from 80 to 0% while the yield of diphenylmethane increased from 0 to 74% as the amount of *n*-butyl alcohol was decreased to the stoichiometric amount for etherification. In the experiment with the stoichiometric amount of butyl alcohol the amount of *p*-toluenesulfonic acid exceeded the amount of both alcohols. The apparent result is that the *n*-butyl alcohol is completely converted to a complex with the acid so that its etherification is blocked while the alkylation of the benzene solvent is not hindered.

Satisfactory rate constants were not obtained for the experiments of Tables I and II. This was at least in part due to the occurrence of side reactions such as self-etherification and alkylation of the solvent to a significant extent. It is shown in Table III, however, that highly satisfactory constants are obtained for the etherification of triphenylcarbinol and benzhydrol by *n*-butyl alcohol when the ratio of butyl alcohol to phenylcarbinol is at least 2:1. All rate constants were calculated on the assumption that the reactions are first order in the polyphenylcarbinol. These studies are an extension of a previous one[2] with chief emphasis on determining the effects of varying the reactant ratio and catalyst concentration and on more completely defining the limits of accuracy of the distillation method. Improved accuracy was obtained by doubling the amount of polyphenylcarbinol thereby doubling the volume of water being measured and by increasing fourfold the volume of the reaction mixture so that changes in the medium as the reaction progressed were minimized.

The upward drifts in the rate constants when not more than the stoichiometric amount of butyl alcohol is present (expts. 14, 15 and 21) may well be due to an increase in catalyst activity as the butyl alcohol, which is much the most basic constituent of the mixture[7] is converted to the less basic ether. Increased "deactivation" of the catalyst apparently causes the decrease in rate as the starting concentration of butyl alcohol is increased. In the etherification of triphenylcarbinol doubling the catalyst concentration approximately doubled the rate of reaction (expts. 20, 17 and 19) while doubling the higher catalyst concentrations required with benzhydrol nearly tripled the rate (expts. 26, 23 and 25). Related disproportionate effects have frequently been encountered in aprotic solvents.[10]

It is felt that the data of Table III adequately demonstrate the kinetics of the etherification of these polyphenylcarbinols by *n*-butyl alcohol. Since, largely because of the rapid and imperfectly understood equilibria which precede the rate-controlling reactions, the results are to a major extent consistent with alternative mechanisms of etherification a choice between them will not be attempted at this time.

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Experimental[11]

Starting Materials.—All constituents of the reaction mixtures were carefully purified by standard methods until the refractive indices or melting points agreed closely with literature values.

Experiments of Tables I and II.—The standard procedure given below for the experiments of Table III was used except for the following changes and certain other obvious modifications. Here instead of using 0.250 mole of polyphenylcarbinol only 0.125 mole of the alcohol present in the smaller proportion was used so that the amount of by-product water was halved. The total volume of solution was decreased to 1 liter and when more than 0.004 mole of catalyst was used the solid *p*-toluenesulfonic acid monohydrate was dissolved in benzene and the water of hydration distilled off as previously described.[2]

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[9] We wish to thank Dr. Jack Lasky for carrying out this experiment.

[10] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 290.

[11] We wish to thank Prof. Mary Aldridge and Mr. Byron Baer for the microanalyses. The values given are the average of duplicates.

The most significant data for the new compounds follow. *p*-**Dimethylaminobenzyl** *n*-**butyl ether** distilled at 131° (0.4 mm.), $n^{25}\text{D}$ 1.5230. *Anal.* Calcd. for $C_{13}H_{21}NO$: C, 75.31; H, 10.21. Found: C, 75.33; H, 10.22. *p*-**Methoxybenzyl** *n*-**butyl ether** distilled at 93–96° (0.1 mm.), $n^{20}\text{D}$ 1.4978. *Anal.* Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.54; H, 9.53. *p*-**Methylbenzyl** *n*-**butyl ether** distilled at 55° (0.15 mm.), $n^{25}\text{D}$ 1.4871. *Anal.* Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.17. Found: C, 81.17; H, 10.21. *p*-**Chlorobenzyl** *n*-**butyl ether** distilled at 121–123° (9.5 mm.), $n^{25}\text{D}$ 1.5010. *Anal.* Calcd. for $C_{11}H_{15}ClO$: C, 66.50; H, 7.61; Cl, 17.86. Found: C, 66.75; H, 7.74; Cl, 17.84. *p*-**Methoxybenzyl** *sec*-**butyl ether** distilled at 67–69° (0.1 mm.), $n^{25}\text{D}$ 1.4933. *Anal.* Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.05; H, 9.46. *p*-**Methoxybenzyl** *t*-**butyl ether** distilled at 61–65° (0.1 mm.), $n^{25}\text{D}$ 1.4943. *Anal.* Calcd. for $C_{12}H_{18}O_2$: C, 74.18; H, 9.34. Found: C, 74.35; H, 9.30. *p*-**Methyl**-*p*′-methoxy**dibenzyl ether** distilled from a Hickman still at 152–158° (0.4 mm.), $n^{25}\text{D}$ 1.5572. *Anal.* Calcd. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.49. Found: C, 79.7; H, 7.61. *p*-**Methoxydibenzyl ether** distilled at 100–106° (0.1 mm.), $n^{25}\text{D}$ 1.5619. *Anal.* Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.07. Found: C, 79.22; H, 7.19. *p*-**Chloro**-*p*′-methoxy-**dibenzyl ether** distilled at 122–126° (0.9 mm.), $n^{25}\text{D}$ 1.5689. *Anal.* Calcd. for $C_{15}H_{15}ClO_2$: C, 68.57; H, 5.75; Cl, 13.50. Found: C, 68.40; H, 6.07; Cl, 13.50. *p*-**Nitro**-*p*′-methoxy-**dibenzyl** ether distilled at 179–185° (0.2 mm.), $n^{25}\text{D}$ 1.5830. *Anal.* Calcd. for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 66.39; H, 6.01; N, 5.35. *p*-Di**methylamino**-*p*′-meth**oxydibenzyl** ether distilled from a Hickman still at 135–136° (gage pressure 0.001 mm.), $n^{25}\text{D}$ 1.5842. *Anal.* Calcd. for $C_{17}H_{21}NO_2$: C, 75.24; H, 7.79; N, 5.16. Found: C, 75.35; H, 8.03; N, 5.53.

Standard Procedure for Experiments of Table III.—Except for obvious modifications the following procedure was used in all cases. One-fourth mole of the polyphenylcarbinol and the stipulated amount of *n*-butyl alcohol were dissolved in about 800 ml. of benzene. This solution was diluted at 25° (thermostat) with benzene to a volume of 1885 ml. less the volume of catalyst solution to be added later. A recalibrated 2 liter volumetric flask was used here. This volume expanded to 2 liters at the reflux temperature. The solution was placed in a 3-liter round-bottom flask fitted with a thermometer well and a modified Bidwell and Sterling water trap[12] which was attached to a reflux condenser. All connections were ground glass. Boiling chips were added and a voltage was applied to the hemispherical heating mantle just below that at which flooding would occur. After refluxing the solution for a half-hour to remove any traces of water the proper amount of a previously prepared and standardized solution of *p*-toluenesulfonic acid in benzene was added from a buret. This catalyst solution had been dried previously by distillation as above. Before each reading of the water volume any droplets adhering to the tip of the condenser were displaced by means of a Chromel wire inserted through the top of the condenser.

With triphenylcarbinol the yield of water was 98 to 100% and the yield of ether about 94%; the corresponding values with benzhydrol were 93 to 97% and 88%.

A careful plot of the volume of water collected *vs.* time was made and rate constants calculated for the 20 to 30% portion of the reaction, then for the 20 to 40% portion and so on as previously described.[2] The temperatures for the 20 to 80% portion among all the experiments of the first section of Table III were 80.0 ± 0.5° while for the second section they were 81.3 ± 0.5°. Within a given experiment the maximum variation was ±0.1°. Numerous check runs showed that the rate constants for the experiments of Table III were readily reproducible to ±2%. In typical cases after completion of the reaction the catalyst was extracted into water and titrated; 99% recovery was obtained.

Self-etherifications.—Dianisyl ether was prepared by a procedure identical with that for expt. 2 except that 0.250 mole of anisyl alcohol and no second alcohol was used. A 50% yield of water collected in 80 min. and the total yield of water was 97%.

It has not been established whether the *n*-hexyl group underwent any rearrangement in the self-etherification of *n*-hexyl alcohol. A solution of 0.250 mole of *p*-toluenesulfonic acid in 4 moles of hexyl alcohol was employed.[5] It was found that if the reaction was stopped when the yield of water was 75% (12 hours) the yield of ether, allowing for the 24% of alcohol recovered, was 94% while if the reaction was allowed to proceed until the yield of water was 100% (25 hours) only about a 75% yield of ether was obtained. The product distilled at 80–83° (5.0 mm.), $n^{25}\text{D}$ 1.4190. *Anal.* Calcd. for $C_{12}H_{26}O$: C, 77.34; H, 14.06. Found: C, 77.66; H, 14.20.

Transetherification.—Under the conditions of expt. 2 except that 0.0625 mole of dianisyl ether replaced the 0.125 mole of anisyl alcohol no significant amount of water was evolved until the catalyst concentration was doubled. Transetherification then proceeded slowly to give a 94% yield of anisyl *n*-butyl ether and a 97% yield of water in 48 hours. The slight evolution of water at the lower catalyst concentration indicates that in expt. 2 little of the product was formed *via* transetherification.

Under the conditions of expt. 11, except with the amount of benzyl alcohol decreased to 0.125 mole, water evolution practically stopped after 4 hours at about 70% yield (calculated for unsymmetrical ether formation) indicating complete conversion of the anisyl alcohol to anisyl benzyl ether and dianisyl ether; the catalyst concentration was then quadrupled whereupon water evolution proceeded giving a 98% yield of water and an 83% yield of anisyl benzyl ether in a total time of 6 hours.[9]

Etherification *vs.* **Alkylation.**—In a series of three experiments the amount of *n*-butyl alcohol was decreased from 1.125 to 0.375 to 0.125 mole while holding the amount of benzyl alcohol at 0.125 mole and the amount of *p*-toluenesulfonic acid at 0.256 mole. Sufficient benzene to give 1 liter of solution was used and the yield of water was 100 ± 1% in all cases. The yields of benzyl *n*-butyl ether, in the same order, were 80, 47 and 0% while the yields of diphenylmethane were 0, 32 and 74%. The evolution of a 50% yield of water required 36, 3.2 and 0.36 hours, respectively. Upon repetition of the experiment with 0.125 mole of *n*-butyl alcohol, but with only half as much acid, the time required for the evolution of a 50% yield of water rose nearly tenfold to 3.5 hours and the yield of ether rose to 23% while the yield of hydrocarbon fell to 57%.

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(12) Ace Glass Inc., cat. no. 7735, 5-ml. capacity.