

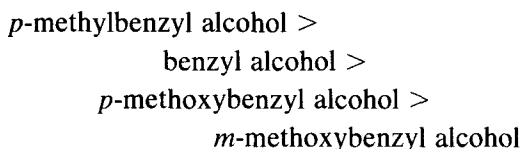
Hydride Transfer Reactions: Part IX. Effect of Substitution on the Disproportionation of Benzyl Alcohol over Alumina¹

In an earlier paper in this series (1), it was reported that diphenylcarbinol underwent quantitative disproportionation to diphenylmethane, benzophenone, and water when passed over alumina at 300°C. Adkins and Folkers (2) and later Landis and Heiba (3) had reported disproportionation of benzyl alcohol to benzaldehyde, toluene, and water over alumina in addition to the expected ether formation. In an earlier communication (4), we had reported that by suitably modifying the reaction conditions and the method of preparation of the catalyst it was possible to bring about the disproportionation of benzyl alcohol with more than 95% selectivity. The present paper deals with the influence of substituents on the disproportionation of benzyl alcohol.

Alumina catalyst was prepared by the controlled hydrolysis of aluminum isopropoxide. Catalyst 3 (Ref. (4)) was used for these studies. Experimental procedure for the catalytic reaction and product analysis have been reported elsewhere (5).

¹ For Part VIII see Ref. (4).

Results of the reaction of benzyl alcohol and substituted benzyl alcohols are shown in Table 1. From these results one can infer a reactivity order for benzyl alcohols as shown below.



This order is not as expected from the electronic effects of the substituents and cannot be rationalized on the basis of available data.

However, the results of the reaction between benzyl alcohols (1:1) molar ratio, given in Table 2, are interesting. It is seen from the data in Table 1 that the ratio of toluene to benzaldehyde is 1 for all alcohols studied. However, in the mixed alcohol studies (Table 2) toluene/benzaldehyde ratio pertaining to any one of the reactants is not 1.

The significance of these data can be seen when we consider that disproportionation of benzyl alcohol, by analogy with the cor-

TABLE 1
Reactions of Benzyl Alcohols over Alumina

No.	Reactant	Mole percentage of products ^a			Others ^b
		Substituted toluene	Substituted benzaldehyde	Substituted benzyl alcohol	
1	Benzyl alcohol	40	41	17	2
2	<i>p</i> -Methylbenzyl alcohol	49	48	0.5	2.5
3	<i>p</i> -Methoxybenzyl alcohol	22	23	53	4
4	<i>m</i> -Methoxybenzyl alcohol	9	10	77	4

Note. Temperature: 390°C. Weight of alumina: 3 g. Flow rate: 20 ml/h. Reactant: 0.125 mol made up to 10 ml in benzene.

^a The product distribution refers to composition of total product collected for entire period of reaction.

^b Diphenyl ethers, diphenylmethanes, and 1,2-diphenylethanes were identified. In addition, trace quantities of unidentified products were also present.

TABLE 2

Reaction of Benzyl Alcohol, and Substituted Benzyl Alcohol over Alumina

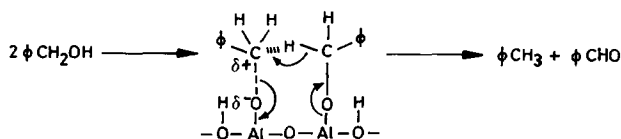
No.	Reactants	% Reaction of benzylalcohol	Ratio of toluene/benzaldehyde	% Reaction of substituted benzyl alcohol	Ratio of substituted toluene/substituted benzaldehyde
1	Benzyl alcohol/ <i>p</i> -methylbenzyl alcohol	44	0.45	58	1.9
2	Benzyl alcohol/ <i>p</i> -methoxybenzyl alcohol	43	0.49	27	2
3	Benzyl alcohol/ <i>m</i> -methoxybenzyl alcohol	28	1.2	15	0.7

Note. Temperature: 390°C. Weight of alumina: 0.36 g. Flow rate: 20 ml/h. Reactants: 0.5 mol of 1:1 molar ratio of benzyl alcohol and substituted benzyl alcohol, made up to 10 ml in benzene.

responding reaction of diphenylcarbinol, involves a hydride transfer mechanism. The hydride donor ends up as the aldehyde and the acceptor ends up as the hydrocarbon. In the reaction of benzyl alcohol with *p*-methylbenzyl alcohol the ratio *p*-methyltoluene/*p*-methylbenzaldehyde is larger than 1, (about 2 in the present study) showing that *p*-methylbenzyl alcohol acts as a better acceptor of hydride than donor compared to benzyl alcohol. As expected, the ratio of toluene/benzaldehyde arising from benzyl alcohol in the reaction is less than 1 (about 0.4). The same trend is observed in the reaction between *p*-methoxybenzyl alcohol and benzyl alcohol. Both *p*-methyl

and *p*-methoxy groups are electron-releasing. In contrast the electron-withdrawing *m*-methoxy group in *m*-methoxybenzyl alcohol has made it a poor hydride acceptor than benzyl alcohol (ratio *m*-methoxytoluene/*m*-methoxybenzaldehyde = 0.7). The limited data available indicate that electron-releasing substituents enhance the hydride acceptor ability of benzyl alcohol. Similar substituent effect has been reported by Kieboom, DeKreuk and Van Bekkum (6) in the hydrogenolysis of benzyl alcohols in the presence of palladium catalyst.

These observations are in favor of a surface mechanism represented below.



The substituent effect is best accounted for by a transition state in which the C—O bond polarization and consequent creation of a residual positive charge on the benzylic carbon atom of the hydride acceptor takes

place ahead of the rest of the bond changes.

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