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A MILD REDUCTION OF BENZYL ALCOHOLS WITH DIPHOSPHORUS TETRAIODIDE

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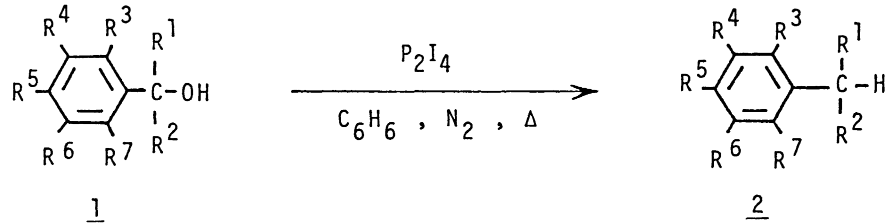
On treatment with diphosphorus tetraiodide in boiling benzene, benzyl alcohols are smoothly reduced to parent hydrocarbons in good to moderate yields.

A number of useful transformations have been carried out using diphosphorus tetraiodide (P_2I_4)[1)] due to its unique affinity for oxygen. These include the deoxygenation of epoxides,[2)] sulfoxides,[3,4)] selenoxides,[4)] and amine N-oxides[5)]; dehydration of aldoximes,[2,6)] amides,[7)] and nitroalkanes[4)] to nitriles; conversion of alcohols to olefins and iodides,[6,8)] and deprotection of acetals and ketals.[9)] We now wish to report a further new property of this compound as reducing agent; benzyl alcohols are readily deoxygenated with P_2I_4 to parent hydrocarbons. In this respect, P_2I_4 stands out in sharp contrast to phosphorus triiodide (PI_3) which reacts simply as an iodinating agent.



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Experimentally, the reaction involves stirring alcohol 1 with P_2I_4 in boiling benzene under nitrogen. After appropriate hours the mixture is quenched with aqueous sodium sulfite, and worked up as usual to afford the expected hydrocarbon 2 in good to moderate yields (Table 1). A variety of functional groups are compatible with these conditions. This mild non-aqueous procedure is particularly attractive for the reduction of crowded secondary benzyl alcohols, since these compounds cannot be satisfactorily reduced to hydrocarbons with other known methods. Thus the reduction with hydriodic acid/red phosphorus was often accompanied by the isomerization of branched side-chain, while alkali metal/ammonia reduction did not work well. Also the indirect methods based on the conversion of alcohols to halides or esters followed by treatment with common reducing agents failed and the metallic reduction led to the formation of 1,2-diarylethanes.

The extremely hindered benzyl alcohol 1k when heated with P_2I_4 suffered from the extensive isomerization of alcoholic side-chain, giving olefinic compound as major product. This undesired reaction could be suppressed when the reduction was carried out in the presence of triethylsilane as hydrogen source.

The mechanism of the reduction with P_2I_4 is not known to us at present. How-

Table 1 Reduction of Benzyl Alcohols with P_2I_4

	Alcohol 1							Reaction time (h)	Hydrocarbon 2 1)	Yield (%) 2)
	R^1	R^2	R^3	R^4	R^5	R^6	R^7		Mp (°C)	
a	H	H	Me	H	Me	H	Me	6	oil	59
b	Me	H	Me	H	Me	H	Me	6	oil	84
c	Ph	H	H	H	H	H	H	2	23-25	92
d	Ph	H	H	H	CO_2Et	H	H	4	oil	90
e	Ph	H	H	H	NO_2	H	H	5	oil	76
f	Me	Me	H	H	H	H	H	6	oil	92
g	Ph	Ph	H	H	H	H	H	2	93-94	98
h	Ph	Ph	H	H	Br	H	H	4	80-82	87
i	Ph	Ph	H	H	CN	H	H	9	97-99	71
j	Bu^t	H	Me	H	Me	Me	H	6	oil	64
k	Bu^t	H	Me	Me	Me	Me	Me	10	59-60	77 3)

1) Products were identified by direct comparison with authentic specimens. All compounds are known. *2)* Yields refer to the isolated compounds and are not optimized. *3)* The reaction was carried out in the presence of triethylsilane. Loss of alcoholic side-chain was observed to some extent.

ever, the origin of hydrogen atom which replaced the alcoholic function has been attributed to the hydroxyl group by deuterium labelling experiment; benzhydrol-O-*d* Ph_2CHOD gave diphenylmethane-α-*d* Ph_2CHD. This observation suggests potential uses of P_2I_4 as a reagent for the synthesis of some deuterated and tritiated compounds.

The general procedure is as follows: stirred suspension of P_2I_4 (0.6 mmol) in dry benzene (20 ml) was heated for several minutes under nitrogen to yield an orange-colored solution, to which a solution of benzyl alcohol (1.0 mmol) in the same solvent (10 ml) was added in one portion. The resulting mixture was heated under reflux for 5-10 h and then quenched with 10% aqueous sodium sulfite. The organic phase was extracted with ether and the extract was washed with water, dried over sodium sulfate, and evaporated. The residue was either chromatographed over alumina using hexane as the solvent, or crystallized from appropriate solvent, or distilled through a Kugelrohr apparatus.

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