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SELECTIVE REDUCTION WITH LITHIUM ALUMINUM HYDRIDE/DIPHOSPHORUS TETRAIODIDE. A MILD CONVERSION OF AROMATIC KETONES TO PARENT HYDROCARBONS

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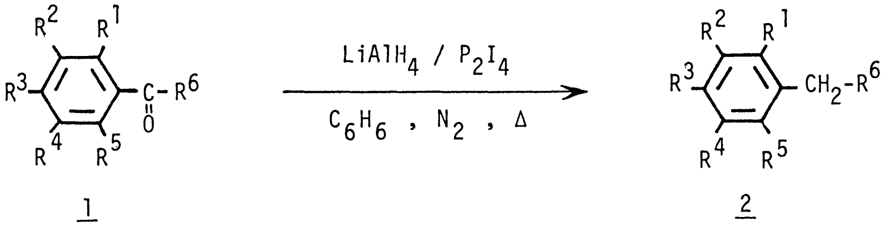
Treatment of aromatic ketones with the title reagent in boiling benzene gives parent hydrocarbons in good to moderate yields.

We have previously shown that benzyl alcohols are readily reduced to hydrocarbons by treatment with diphosphorus tetraiodide (P_2I_4)[1)] in boiling benzene.[2)] We now report an extension of this observation as a new mild method for the conversion of aromatic ketones to hydrocarbons.

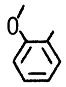


A general procedure is as follows: to a stirred solution of ketone (1; 0.5 mmol) in dry benzene (10 ml) under nitrogen, lithium aluminum hydride (0.5 mmol) followed by P_2I_4 (0.5 mmol) was added at several minutes interval, and the resulting mixture was gradually brought to gentle refluxing. The progress of the reaction was monitored by TLC. After appropriate time, water was added and the organic layer was separated, washed with dilute hydrochloric acid and water, dried, and evaporated to leave crude hydrocarbon 2, which was purified by passing on a short alumina column using hexane as eluant. Representative results are summarized in the Table.

Ease of reduction was found to be markedly dependent on the ring substituent groups; alkyl and alkoxyl groups facilitate the reaction while nitro, cyano, and carboxyl groups suppress it. Halogens, ester group, and conjugated olefinic bond remain unaffected during the reduction.

The Clemmensen[3)] and Wolff-Kishner reductions[4)] are classical laboratory procedures to convert aromatic ketones to hydrocarbons. Both methods, however, require highly acidic/alkaline media and prolonged heating at elevated temperatures, which often lead to undesirable transformations of other functional groups present. Aromatic ketones can also be reduced to hydrocarbons with complex metal hydrides such as chloroaluminum hydrides,[5)] or with alkali metal dissolved in liquid ammonia.[6)] Major drawbacks involved are concurrent formation of olefins and/or chlorides as side

Table 1. Reduction of aromatic ketones with $LiAlH_4/P_2I_4$

Aromatic ketone 1						Reaction time	Hydrocarbon 2[a,b]
R^1	R^2	R^3	R^4	R^5	R^6	(h)	Yield (%)
H	H	H	H	H	Me	2	~ 100[c]
H	H	Br	H	H	Me	3	87
H	H	I	H	H	Me	4	73
H	H	MeO	H	H	Me	6	65
H	H	Ph	H	H	Me	5	50
Me	H	Me	Me	H	Me	8	75
Et	Et	Et	Et	Et	Me	20	53
H	H	H	H	H	Ph	1	~ 100[c]
H	H	Cl	H	H	Ph	2	82
H	H	Br	H	H	Ph	2	76
H	H	MeO	H	H	Ph	6	65
H	H	CO_2Et	H	H	Ph	18	44
H	H	H	H	H	$PhCH_2$	6	62
H	H	H	H	H	PhCH=CH	4	61
H	H	H	H	$-(CH_2)_3-$		5	66
H	H	H	H			1	82
H	H	H	H			10	87

a) Yields based on unrecovered materials refer to the compounds isolated and are not optimized. b) Products were identified by direct comparison with authentic specimens. All compounds are known. c) GLC yields.

products in the former case and of diarylmethanes and/or pinacols in the latter. The present method is free from these disadvantages and may be applicable to the selective reduction of aromatic ketone function in the presence of other reducible or reductively removable functionarities. Manipulation is simple and the product is easily isolable in a state of high purity.

The actual intermediate species and the reaction mechanism involved are not clear at present.

References

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