

A NOVEL REDUCTION OF α -ARYL ALKANOLS BY DIIODODIMETHYLSILANE

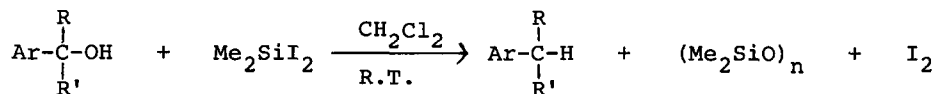
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Summary: An effective and convenient reduction of α -aryl alkanols has been developed with diiododimethylsilane to give the corresponding alkanes under mild conditions.

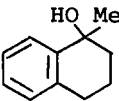
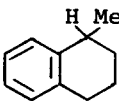
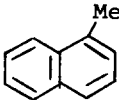
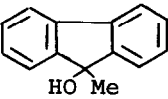
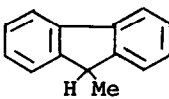
In recent years, organosilicon compounds became increasingly important reagents in synthetic organic chemistry. One such reagent is iodotrimethylsilane, which efficiently converts alcohols into iodides as well as in the cleavage of esters and ethers^{1,2,3}. In the course of a general investigation of the comparative reactivity of silicon halides, we have observed a novel reduction in which diiododimethylsilane has reduced α -aryl alkanols to the corresponding alkanes under extremely mild conditions. Although there are several reports for the reduction of alcohols by aluminum chloride-palladium⁴ and lithium-ammonia⁵, our method could be considered to be simple, mild and effective in contrast with above drastic conditions. The overall reduction by diiododimethylsilane can be represented as follows.



Typical reactions were normally conducted on equimolar amounts of alcohol and diiododimethylsilane at room temperature. A methylene chloride solution of 1,1-diphenyl ethanol(0.5 mmol) was added to the diiododimethylsilane in methylene chloride. The exothermic reaction occurred immediately to liberate iodine. After the mixture stood at room temperature for 10 min., direct analysis by gas liquid chromatography showed the formation of 1,1-diphenylethane(100%) with octamethylcyclotetrasiloxane(78%) and decamethylcyclopentasiloxane(22%).

Similarly, various α -aryl alkanols can be reduced by diiododimethylsilane to yield the corresponding alkanes in good yields (Table I). This method also permits the reduction in the presence of other functional group. A neighboring β -keto group is not reduced by diiododimethylsilane. However, benzyl alcohol was converted benzyl iodide, and non aryl-substituted alkanols did not give any hydrocarbon under these reaction conditions.

Table I. The reactions of diiododimethylsilane with α -aryl alkanols

Alcohol	Product ^a (%)	Alcohol	Product ^a (%)
$\begin{array}{c} \text{Ph} \\ \\ \text{Ph}-\text{C}-\text{OH} \\ \\ \text{Ph} \end{array}$	$\begin{array}{c} \text{Ph} \\ \\ \text{Ph}-\text{C}-\text{H} \\ \\ \text{Ph} \end{array} \quad (94)^b$	$\begin{array}{c} \text{Ph}-\text{C}-\text{CHPh} \\ \quad \\ \text{O} \quad \text{OH} \end{array}$	$\begin{array}{c} \text{Ph}-\text{C}-\text{CH}_2\text{Ph} \\ \\ \text{O} \end{array} \quad 45$
$\begin{array}{c} \text{Ph} \\ \\ \text{Ph}-\text{C}-\text{OH} \\ \\ \text{Me} \end{array}$	$\begin{array}{c} \text{Ph} \\ \\ \text{Ph}-\text{C}-\text{H} \\ \\ \text{Me} \end{array} \quad 100 \quad (98)^b$		 72
$\begin{array}{c} \text{Me} \\ \\ \text{Ph}-\text{C}-\text{OH} \\ \\ \text{Me} \end{array}$	$\begin{array}{c} \text{Me} \\ \\ \text{Ph}-\text{C}-\text{H} \\ \\ \text{Me} \end{array} \quad 50$		 17
$\begin{array}{c} \text{Ph} \\ \\ \text{Ph}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{Ph} \\ \\ \text{Ph}-\text{C}-\text{H} \\ \\ \text{H} \end{array} \quad 100 \quad (96)^b$		 79 (75) ^b

a: Products confirmed by comparison of I.R., N.M.R., and physical constant data with those reported. b: Isolated yield.

Reduction occurred best with secondary and tertiary α -aryl alkanols. Among the advantages of this new method are quite effective, mild conditions and rapid reaction rates. We are actively investigating the mechanism and synthetic utility of this reaction.

References

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(Received in Japan 6 September 1979)