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UNUSUAL REDUCTIVE CONDENSATIONS IN THE REACTION OF DIIODODIMETHYLSILANE WITH KETONES

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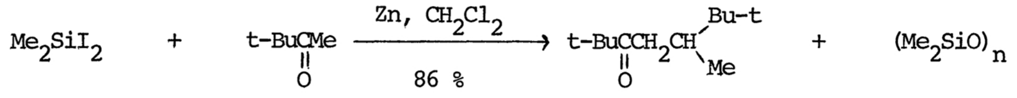
Diiododimethylsilane reacts with various ketones in the presence of zinc to give the corresponding reductive condensation products in good yields.

We recently reported the unusual ability of diiododimethylsilane for the reduction of α-arylalkanols[1]. With this ability in mind, we have extended the studies on the utility of diiododimethylsilane as special reducing reagent for the selected organic substrates. We now wish to report that diiododimethylsilane reacts easily with ketones in the presence of zinc to give the corresponding reductive condensation products in good yields. Recently, Calas et al. reported double silylation of a saturated ketone with trimethylchlorosilane and lithium in THF[2]. Motherwell has reported that ketones can be deoxygenated to olefins by treatment with an excess of trimethylchlorosilane and zinc in ether[3]. However, under our reaction conditions, double silylation and deoxygenation were not observed.



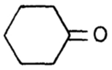
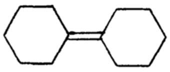
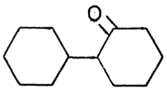
$$\mathrm{Me_2SiI_2} + \text{t-Bu}\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{Me} \xrightarrow[86\ \%]{\mathrm{Zn,\ CH_2Cl_2}} \text{t-Bu}\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_2CH}\begin{smallmatrix}\text{Bu-t}\\ \mathrm{Me}\end{smallmatrix} + (\mathrm{Me_2SiO})_n$$

The typical procedure is described for the reaction of diiododimethylsilane with pinacolone; To a mixture of zinc dust(3 mmol) and pinacolone(1 mmol) in CH_2Cl_2 was added a CH_2Cl_2 solution of diiododimethylsilane(1 mmol). The exothermic reaction occurred immediately. After the mixture stood at room temperature for 10 min., direct analysis by GLC showed the formation of 2,2,5,6,6-pentamethyl-3-heptanone(86%), octamethylcyclotetrasiloxane(60%) and decamethylcyclopentasiloxane (18%). But under similar conditions, dichlorodimethylsilane did not show any reaction with ketones. In a similar manner, the reaction of diiododimethylsilane with various ketones was examined and the results are listed in the Table.

These reductive condensations occurred neither by a trace amount of hydrogen iodide contained in diiododimethylsilane nor in the absence of zinc. These results indicate that the reaction may proceed through a nucleophilic attack of the oxygen of carbonyl group polarized partially by some zinc salts on the silicon atom of diiododimethylsilane. But the definitive reaction mechanism is yet not understood.

On the other hand, under above conditions, the reaction with aryl ketone, for example acetophenone gave two type products; one is the reductive condensation product ($\mathrm{PhCOCH_2CHMePh}$ 16%)[4] as seen above, and the other is C-C bond formation products on carbonyl carbon ($\mathrm{MeCOCMePh_2}$ 40% and PhMeC=CMePh 10%). The C-C bond formation may be explained by dimerization of a ketyl radical anion via one electron transfer from zinc to ketone. The reaction of diiododimethylsilane with

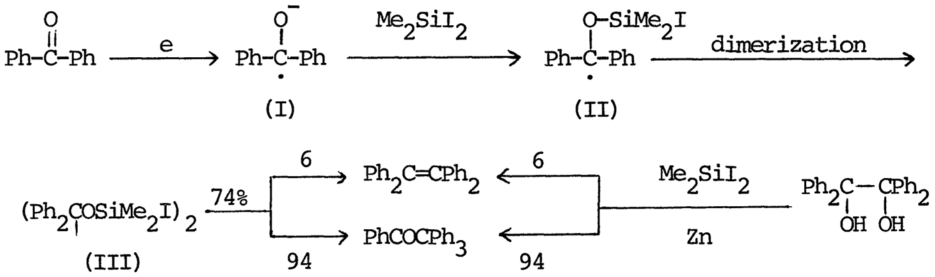
Table The reaction of diiododimethylsilane with ketones in the presence of zinc

Ketone	Product			
MeCOMe	$MeCOCH_2CHMe_2$	25%		
EtCOEt	$EtCOCH(Me)CHEt_2$	70%		
t-BuCOMe	$t\text{-}BuCOCH_2CHMeBu\text{-}t$	86%		
		12%,		28%

Products confirmed by comparisons of I.R. and N.M.R. with authentic samples.

benzophenone in the presence of zinc gave benzopinacolone in 70% yield and tetraphenylethylene in 4% yield.

This reaction can be explained by an initial formation of a ketyl radical anion(I) which reacts with diiododimethylsilane to give a silyl pinacolate(III) via dimerization of a siloxyalkyl radical (II). The decomposition of III afforded benzopinacolone and tetraphenylethylene. In order to confirm the final step, we studied the reaction of diiododimethylsilane with benzopinacol in the presence of zinc and found that benzopinalolone and tetraphenylethylene were formed in the same molar ratio as the case of benzophenone. These results suggest that these two products are produced via silyl pinacolate(III).



Subsequently, the reaction of diiododimethylsilane with 2-adamantanone in the presence of zinc gave only adamantylideneadamantane in 30% yield.

It is noted that diiododimethylsilane is a unique reducing reagent for various ketones in the presence of zinc. Definitive mechanistic studies are now in progress.

References

1) W.Ando and M.Ikeno, Tetrahedron Lett., 1979, 4941.
2) J.Dunoques, A.Ekouya, R.Calas and N.Duffaut, J. Organometal. Chem., 87 (1975) 151.
3) W.B.Motherwell, Chem. Commun., 935 (1973).
4) The reductive condensation product was obtained in 76% yield in the absence of zinc, probably via silyl enol ether.

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