Direct Deoxygenation of Alicyclic Ketones. A New Olefin Synthesis

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Summary A new synthesis of olefins by the reaction of alicyclic ketones with chlorotrimethylsilane and zinc is described; some mechanistic implications are discussed.

Conversions of the cyclohexanone–cyclohexene type have found widespread application in organic synthesis. This communication reports a convenient method for such transformations which involves treatment of an alicyclic ketone with chlorotrimethylsilane and zinc in ether solution.

Although optimum conditions for the reaction have yet to be established, the data in the Table reveal that preparatively useful yields can be obtained under exceptionally mild conditions. In particular, the successful conversion of the functionalised cyclohexanones highlights the selective nature of the process, Moreover, the reaction is easily carried out in a single reaction vessel, and thus is much more convenient than existing methods.[1]

From the mechanistic standpoint, this reaction poses several intriguing problems. In the first instance, the possibility of a silyl enol ether intermediate was dismissed by subjecting the silyl enol ether of cyclohexanone to standard reaction conditions; cyclohexene was not detected in this experiment. The isolation of bicyclo[3,3,0]octane from the reaction with cyclo-octanone, does however provide strong presumptive evidence for the penultimate intermediacy of an ylide-stabilised organozinc carbenoid which can then undergo insertion into a neighbouring C–H bond.[2] A similar type of carbenoid species has also been proposed in the reaction of benzaldehyde with boron trifluoride and zinc.[3] This mechanism is also consonant with the observed regioselectivity in the case of 2-methylcyclohexanone. The unexpected formation of the silylated pinacols from acetophenone is not without precedent, however, since the same products have been obtained under much more forcing conditions by the use of chlorotrimethylsilane and magnesium in hexamethylphosphoramide.[4] It is interesting that the proposed mechanism in this case was entirely carbanionic in nature.

Table

Compound	Time[a]	Temp. (t/°C)	Products	Yield (%)
Cyclohexanone	18 h	25	Cyclohexene	72
4-Bromocyclohexanone	18 h	25	4-Bromocyclohexene	48
4-Acetoxycyclohexanone	36 h	25	4-Acetoxycyclohexene	60
2-Methylcyclohexanone	7 days	40	Methylcyclohexene	62[b]
			3-Methylcyclohexene	19[b]
Bicyclo[3,3,1]nonan-2-one	72 h	40	Bicyclo[3,3,1]non-2-ene	56
Cyclo-octanone	5 days	80	*cis*-Cyclo-octene	37[c]
			Bicyclo[3,3,0]octane[d]	18[c]
Cyclopentanone	4 days	25	Cyclopentene	14[e]
Acetophenone	2 h	0	(±)- and *meso*-2,3-Diphenyl-2,3-Di(trimethylsiloxy)-butane (1 : 1)	82

[a] Not necessarily optimum time. [b] Yield and ratio determined by g.l.c. [c] Product ratio determined by g.l.c. [d] Isolated by preparative g.l.c. and identical with an authentic sample. [e] Isolated as the dibromide.

In a typical procedure, cyclohexanone (1 equiv.) in ether was added to a rapidly stirred suspension of zinc† (10 equiv.) in dry ether containing chlorotrimethylsilane (5 equiv.). After 18 h, the mixture was filtered, and the ethereal solution was washed with aqueous $NaHCO_3$ and dried. Careful fractionation gave cyclohexene (72%).

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† Although commercial zinc dust is satisfactory, uniformly consistent results were obtained with amalgamated zinc.

[1] I. T. Harrison and S. Harrison, in 'Compendium of Organic Synthetic Methods,' Wiley-Interscience, 1971, pp. 516—519.

[2] W. Kirmse, in 'Carbene Chemistry,' Academic Press, 1971, ch. 7.

[3] I. Elphimoff-Felkin and P. Sarda, *Chem. Comm.*, 1969, 1065.

[4] T. H. Chan and E. Vinokur, *Tetrahedron Letters*, 1972, 75.