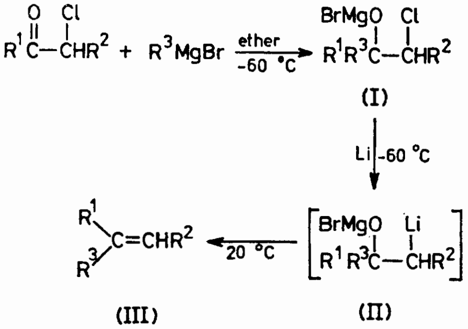
Convenient 'One-flask' Synthesis of Olefins. Reaction of α-Chloroketones with Grignard Reagents and Lithium

By JOSÉ BARLUENGA,* MIGUEL YUS, and PABLO BERNAD
(*Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Oviedo, Spain*)

Summary Olefins and diolefins with the double bonds in predetermined positions are prepared in a one-step process in moderate to good yields by the reaction of α-chloroketones with Grignard reagents and then with lithium.

NEARLY all olefin-forming elimination reactions of any theoretical or synthetic importance are β-eliminations. One of the groups eliminated is usually hydrogen. Eliminations from β-substituted organomercury(II) compounds[1] and 1,2-dihalides[2] may be brought about by metals or by metals or iodide ion, respectively. They are of little practical interest since the resulting olefin itself is the usual precursor for those compounds.

We now report a 'one-flask' synthesis of olefins and diolefins (III), with the double bonds in predetermined positions, by the reaction of α-chloroketones with Grignard reagents and then with lithium (Scheme).



SCHEME.

Compounds of type (I) could be isolated; they gave chlorohydrins on hydrolysis.[3] Compounds of type (II) could not be isolated; however, analogous compounds of the type $R^1R^3C(YLi)CHR^2Li(Y = O,PhN)$ have recently been characterized.[1]

TABLE. Synthesis of the olefins (III) from the α-chloroketones $R^1C(:O)CHClR^2$ and the alkylmagnesium bromides R^3MgBr

α-Chloroketones R¹	R²	Alkylmagnesium bromides R³	% Yield of (III)[a]
Me	H	C_6H_{11}	33
Me	H	$PhCH_2$	41
Me	Me	$CH_2{=}CHCH_2$	85[b]
Me	Me	Pr^n	56[b]
Me	Me	$PhCH_2$	74[b]
$-[CH_2]_3-$		Et	71
$-[CH_2]_3$		$CH_2{=}CHCH_2$	99
$-[CH_2]_3-$		Pr^n	78
$-[CH_2]_3-$		$PhCH_2$	62
$-[CH_2]_4-$		Et	87
$-[CH_2]_4-$		$CH_2{=}CHCH_2$	78
$-[CH_2]_4-$		Pr^n	43
$-[CH_2]_4-$		$PhCH_2$	62

[a] Based on α-chloroketone. Yields have not been optimized.
[b] Mixture of *Z*- and *E*-isomers.

In a typical reaction, to a well stirred ethereal solution under argon of a Grignard reagent (40 mmol) at −60 °C, the appropriate α-chloroketone (40 mmol) in dry ether (10 ml) was slowly added. After 0·5 h dry tetrahydrofuran (50 ml) and lithium powder (100 mmol) were added. After 4 h at −60 °C the temperature was raised to 20 °C and the mixture was hydrolysed with water and then dilute hydrochloric acid. The resulting solution was extracted with ether and the ethereal layer dried with anhydrous sodium sulphate. Solvents were removed and the residue distilled to yield the olefin. The olefin can alternatively be distilled from the reaction mixture prior to the hydrolysis but in lower yield.

(*Received*, 26*th June* 1978; *Com.* 675.)

---

[1] J. Barluenga, F. J. Fañanás, M. Yus, and G. Asensio, *Tetrahedron Letters*, 1978, 2015.
[2] W. H. Saunders, Jr. in 'The Chemistry of Alkenes,' ed. S. Patai, Wiley-Interscience, New York, 1964, p. 149.
[3] J. W. Cornforth, R. H. Cornforth, and K. K. Mathew, *J. Chem. Soc.*, 1959, 112.