

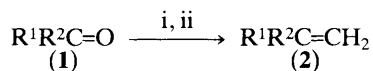
Methylenation of Carbonyl Compounds Using Chloromethyl-lithium; a New Method for Terminal and Exocyclic Olefins

José Barluenga,* José L. Fernández-Simón, José M. Concellón, and Miguel Yus

Departamento de Química Orgánica, Facultad de Química, Universidad de Oviedo, 33071 Oviedo, Spain

The *in situ* generated chloromethyl-lithium reacts at -78°C with different aldehydes and ketones to afford, after lithiation with lithium powder, terminal and exocyclic olefins.

The use of methylenetriphenylphosphorane in the Wittig reaction¹ remains the most generally useful method for the conversion of carbonyl compounds into terminal olefins. Since this discovery² many alternative procedures have been intro-



Scheme 1. Reagents and conditions: i, $\text{ClCH}_2\text{I}-\text{MeLi}$, -78 to -60°C ; ii, Li, -60 to 20°C .



Table 1. Olefins (2) from carbonyl compounds (1).

(1)	(2)		% Yield ^a
		(2a) ^b	43 ^b
		(2b)	80
		(2c)	55
		(2d)	80
		(2e)	80
		(2f)	80
		(2g)	95
		(2h)	60
		(2i)	50

^a Isolated yield based on the starting carbonyl compound (1).

^b Isolated as its 1,2-dibromo derivative.

duced to expand the utility of this reaction.³ We report here a new method for the direct methylenation of aldehydes and ketones using chloromethyl-lithium.⁴

The reaction of different aldehydes and ketones (1) with chloromethyl-lithium (generated *in situ* by reaction of chloriodomethane with methyl-lithium) at -78°C followed by lithiation with lithium powder led to the corresponding terminal or exocyclic olefins (2)[†] (Scheme 1 and Table 1).

The first step in the reaction is the addition of the carbenoid to the carbonyl group⁴ leading to the intermediate (3), which after lithiation gives the β -substituted organolithium compound (4);⁵ the final decomposition of this system through a β -elimination process⁶ yields the olefin (2). *Typical procedure:* to a solution of chloriodomethane (11 mmol) and the starting carbonyl compound (1) (10 mmol) in tetrahydrofuran (25 ml) was added a 1 M diethyl ether solution of methyl-lithium (11 mmol) over 15 min at -78°C under argon. The mixture was stirred for 45 min allowing the temperature to rise to -60°C . Then lithium powder (45 mmol) was added; the resulting suspension was stirred for 6 h at the same temperature and then overnight allowing it to warm to room temperature. The mixture was hydrolysed with aqueous HCl, extracted with diethyl ether, the ethereal layer dried (Na_2SO_4), and the resulting residue distilled to afford the olefin (2). In the case of the product (2a) it was isolated as its 1,2-dibromo derivative following the literature method.⁷

We think that the method described in this communication represents a reasonable alternative to the Wittig reaction.

Received, 14th July 1986; Com. 987

References

- See, for instance, D. J. H. Smith, in 'Comprehensive Organic Chemistry,' Vol. 2, ed. I. O. Sutherland, Pergamon, Oxford, 1979, pp. 1316–1325.
- G. Wittig and G. Geissler, *Liebigs Ann. Chem.*, 1953, **580**, 44.
- See, for instance, R. Greenwald, U. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, 1963, **28**, 1128; E. J. Corey and J. Kang, *J. Am. Chem. Soc.*, 1982, **104**, 4724; L. Clawson, S. L. Buchwald, and R. H. Grubbs, *Tetrahedron Lett.*, 1984, **25**, 5733.
- R. Tarhouni, B. Kirschleger, M. Rambaud, and J. Villieras, *Tetrahedron Lett.*, 1984, **25**, 835; K. M. Sadhu and D. S. Matteson, *ibid.*, 1986, **27**, 795.
- For stabilized intermediates of this type see, for instance, J. Barluenga, J. Flórez, and M. Yus, *J. Chem. Soc., Chem. Commun.*, 1982, 1153.
- See, for instance, J. Barluenga, M. Yus, and P. Bernad, *J. Chem. Soc., Chem. Commun.*, 1978, 847.
- J. Barluenga, M. Yus, J. M. Concellón, and P. Bernad, *J. Org. Chem.*, 1981, **46**, 2721.

[†] All compounds (2) gave satisfactory spectral data (i.r., ^1H and ^{13}C n.m.r., and mass spectra).