Stereoselective Synthesis of Homoallylic Bromides and Iodides

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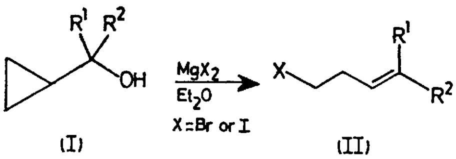
Summary The high-yield, stereoselective conversion of secondary and tertiary cyclopropylmethanols into homoallylic bromides or iodides by treatment with magnesium bromide or iodide is described.

There are many methods for the synthesis of olefins:[1] *e.g.* the procedure of Julia *et al.*,[2,3a] treatment of cyclopropylmethanols with conc. HBr or HCl to afford the ring-opened halides [(I) → (II)], and the procedure of Johnson *et al.*[4] involving prior conversion of the alcohols into bromides followed by treatment with $ZnBr_2$, which can allow high stereoselectivity. We report here the direct, high-yield conversion of (I) into (II) under mild, homogeneous conditions, with high stereoselectivity.



(I) (II)

a; $R^1=R^2=Me$
b; $R^1 = Me, R^2 = H$
c; $R^1 = R^2 = H$
d; $R = Ph, R^2 = H$
e; $R = Me, R^2 = Et$

Treatment of cyclopropyl methyl ketone with MeMgI gave a substantial amount of the homoallylic iodide (IIa; X = I), along with the expected tertiary alcohol (Ia). Further, treatment of (Ia) with MgI_2 in refluxing ether smoothly generated (IIa) in high yield.[5] This method was found to be generally applicable to secondary and tertiary alcohols of this type, affording high yields of the corresponding homoallylic iodides (see Table). In particular, although high yields also are obtained from secondary alcohols, reaction rates are substantially slower, even with a benzylic system (Id). The primary alcohol (Ic) was unaffected by these conditions after 72 h. When disubstituted olefins are formed, a high degree of stereoselectivity is observed, with the *E*-isomers predominating. The stereoselectivity during the generation of trisubstituted

TABLE

Alcohol	Reagent	Time/h	%Yield[b]	Product	E:Z ratio
(Ia)	MgI_2	4	100	(IIa; X=I)	—
(Ib)	MgI_2	91	95	(IIb; X=I)	94:6
(Ic)	MgI_2	72	0	None	—
(Id)	MgI_2	13	100	(IId; X=I)	95:5
(Ie)	MgI_2	4	100	(IIe; X=I)	3:1
MeCH(Ph)OH	MgI_2	13	0	None	—
(Ia)	$MgBr_2$	8	100	(IIa; X=Br)	—
(Ib)	$MgBr_2$	205	70	(IIb; X=Br)	93:7
(Id)	$MgBr_2$	3	100	(IId; X=Br)	98:2

[a] All reactions in refluxing Et_2O. [b] Yields determined by g.l.c. Products characterized by t.l.c., ^1H n.m.r., and mass spectrometry

olefins is apparently not as high; the one case examined, (Ie), afforded both E- and Z-isomers (IIe) (*ca.* 3:1 by g.l.c. and n.m.r.).

Bromides are also readily generated, using $MgBr_2$ in ether, in excellent yields (see Table). Not all activated alcohol systems are susceptible to MgI_2 in ether, however. The benzylic alcohol MeCH(Ph)OH (III) was unchanged after treatment with MgI_2 in refluxing ether for 13 h. The use of tetrahydrofuran (THF) as solvent to allow higher reaction temperatures was not successful; apparently MgI_2 is either insoluble or forms an insoluble complex.

This synthesis of homoallylic iodides and bromides has the advantages over previous methods of high yields, direct conversion of alcohols, homogeneous conditions, low temperatures, and use of relatively mild Lewis acids to which the olefinic linkage generated is less sensitive. Iodides can also be prepared, which otherwise require more circuitous routes.[3,4,6]

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[1] For reviews see J. Reucroft and P. G. Sammes, *Quart. Rev.*, 1971, 135; D. J. Faulkner; *Synthesis*, 1971, 175.

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[4] S. F. Brady, M. A. Ilton, and W. S. Johnson, *J. Amer. Chem. Soc.*, 1968, **90**, 2882.

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