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## 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:<sup>1</sup> e.g. the procedure of Julia *et al.*,<sup>2,3a</sup> treatment of cyclopropylmethanols with conc. HBr or HCl to afford the ringopened halides  $[(I) \rightarrow (II)]$ , and the procedure of Johnson *et al.*<sup>4</sup> involving prior conversion of the alcohols into bromides followed by treatment with ZnBr<sub>2</sub>, which can allow high stereoselectivity. We report here the direct, highyield conversion of (I) into (II) under mild, homogeneous conditions, with high stereoselectivity.

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<sub>2</sub> in refluxing ether smoothly generated (IIa) in high yield.<sup>5</sup> This method was found to be generally applicable to secondary and tertiary alcohols of this type, affording high yields of the corre-

sponding 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 <sup>b</sup>	Product
(Ia)	$MgI_{2}$	4	100	(IIa; X=I)
(Ib)	MgI <sub>2</sub>	91	95	(IIb; X=I)
(Ic)	MgI <sub>2</sub>	72	0	None
(Iď)	$MgI_2$	13	100	(IId; X=I)
(Ie)	MgI <sub>2</sub>	4	100	(IIe; X=I)
MeCH(Ph)OH	$MgI_2$	13	0	None
(Ia)	MgBr <sub>2</sub>	8	100	(IIa; X=Br)
(Ib)	$MgBr_2$	205	70	(IIb; X = Br)
(Id)	$MgBr_2$	3	100	(IId; X=Br)

<sup>a</sup> All reactions in refluxing Et<sub>2</sub>O. <sup>b</sup> Yields determined by g.l.c. Products characterized by t.l.c., <sup>1</sup>H 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<sub>2</sub> in ether, in excellent yields (see Table). Not all activated alcohol systems are susceptible to MgI<sub>2</sub> in ether, however. The benzylic alcohol MeCH(Ph)OH (III) was unchanged after treatment with MgI<sub>2</sub> in refluxing ether for 13 h. The use of tetrahydrofuran (THF) as solvent to allow higher reaction temperatures was not successful; apparently MgI, is either insoluble or forms an insoluble complex.

E:Z ratio 94:6 95:53:1

> -----93:7

> 98:2

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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<sup>1</sup> For reviews see J. Reucroft and P. G. Sammes, Quart. Rev., 1971, 135; D. J. Faulkner; Synthesis, 1971, 175.

<sup>2</sup> (a) M. Julia, S. Julia, and R. Guegan; Bull. Soc. chim. France, 1960, 1072; (b) M. Julia and J.-M. Paris; Tetrahedron Letters, 1974, 244**Š**.

<sup>3</sup> E.g., E. J. Corey, R. Hartmann, and P. A. Vatakencherry, J. Amer. Chem. Soc., 1962, 84, 2611; E. J. Corey and M. Jautelat, Tetrahedron Letters, 1968, 5782.
<sup>4</sup> S. F. Brady, M. A. Ilton, and W. S. Johnson, J. Amer. Chem. Soc., 1968, 90, 2882.
<sup>5</sup> A recent report describes the transformation of tosylates into the corresponding iodides by treatment with MgI<sub>2</sub> in ether; J. Gore, P. Place, and M. L. Roumestant, J.C.S. Chem. Comm., 1973, 821.
<sup>6</sup> M. G. Johnson, T. Li, D. J. Berlinger, and S. E. Companylou, J. Amer. Chem. Soc., 1968, 90, 6326.

<sup>6</sup> W. S. Johnson, T. Li, D. J. Faulkner, and S. F. Campbell, J. Amer. Chem. Soc., 1968, 90, 6226.