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# A FACILE CONVERSION OF TETRAHYDROPYRANYL ETHERS TO THE CORRESPONDING BROMIDES AND IODIDES

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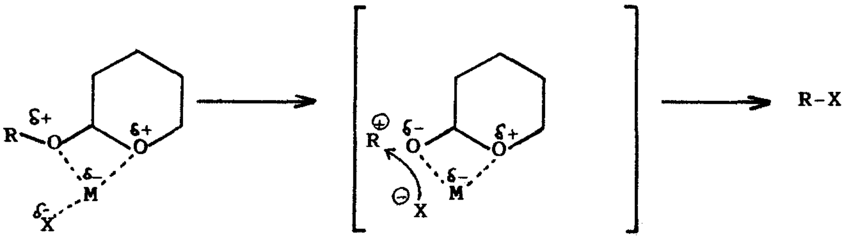
*Abstract :* Tetrahydropyranyl ethers are converted to the corresponding bromides and iodides upon reaction with NaI (or LiBr) and $BF_3.Et_2O$ (or $ClSiMe_3$).

Protection of alcohols as tetrahydropyranyl ethers (THP ethers) is well utilised[1] in organic synthesis. Transformation of the protected ethers directly into different functionalities has also been reported in the literature. For example, THP ethers have been converted into acetates[2], chlorides[3], bromides[4] and iodides[5] without passing through the deprotected alcohols. One of the recent reports involves the use of $Ph_3P-CBr_4$ by Mioskowski et al[6] for the conversion of THP ethers into bromides. They have also reported that THP protected (-)- menthol gave neomenthyl bromide with complete inversion and thus concluded this reaction to be of $SN^2$ type. In addition to this, Oreta et al[7] have recently converted THP ethers into a variety of functionalities proceeding via their alkoxy stannanes by using $Bu_3SnMe$ and $BF_3.Et_2O$. Prompted by these reports we wish to delineate ,in this letter, our results in this area.

Sodium iodide-boron trifluoride etherate has been reported by us as a mild reagent system in the conversion of alcohols to iodides and sulfoxides to sulfides[8], selective cleavage of benzyl ethers[9], conversion of conjugated ene-diones into 1,4-diketones[10] and $\alpha$-nitroepoxides into $\alpha$-iodoketones[11]. Mandal et al[12] have also reported independently non aqueous conversion of acetals into carbonyl compounds and reduction of 2-keto-oxiranes into $\alpha,\beta$-unsaturated ketones. We have now found that this as well as three similar reagent systems viz. $LiBr-BF_3.Et_2O$, $NaI-ClSiMe_3$ and $LiBr-ClSiMe_3$ convert THP ethers into corresponding halides[13] in moderate yields (cf. Table). THP ether derived from (-)-menthol [obtained from Fluka; rotation$[\alpha]_D^{25}$ = -50, C= 10, EtOH] gave the corresponding bromides and iodides with retention[14] of configurations (cf. Table for rotation values). It is possible that the present conversions proceed via $S_Ni$ type of mechanism involving a tight ion pair as shown in the scheme.



where M = $-SiMe_3$ or $-BF_3$
and X = Br or I

Scheme

We hope that the present methodology could be useful in converting alcohols[15] via their THP ethers into corresponding bromides and iodides with retention of configurations.

## General Procedure

To a stirred solution of a THP ether (1 mmol) and NaI (or LiBr) (1 mmol) in 1 ml acetonitrile was added freshly distilled $BF_3.Et_2O$ (1.1 mmol) under nitrogen atmosphere at 0°c. Reaction mixture was then brought to room temperature and stirred for 24 hr. Solvent was removed under vacuum and the residue was dissolved in ether (20 ml). It was then washed successively with 10% aq. thiosulfate, water and brine. Drying ($Na_2SO_4$) and evaporation of ether gave the crude halide which was purified by chromatography($SiO_2$).

With $ClSiMe_3$, the THP ether was added after metal halides and $ClSiMe_3$ were mixed and stirred for 5 min. Rest of the procedure was same as above.

## Acknowledgement

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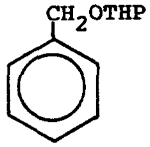
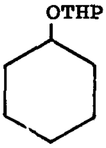
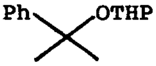
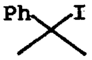
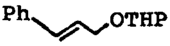
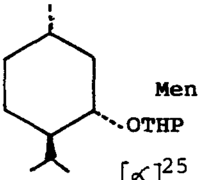
## Table

| THP ether | Reaction Products with<br>$NaI-BF_3.Et_2O$ | <br>$LiBr-BF_3.Et_2O$ | (% yield)<br>$NaI - ClSiMe_3$ | <br>$LiBr - ClSiMe_3$ |
|---|---|---|---|---|
|  | Benzyl iodide<br>(95) 1 | Benzyl bromide<br>(89) 2 | 1(92) | 2(84) |
|  | Iodocyclohexane<br>(63) 3 | Bromocyclohexane<br>(61) 4 | 3(58) | 4(53) |
|  | <br>(59)$^{(i)}$ 5 | <br>(53)$^{(i)}$ 6 | 5(57)$^{(i)}$ | 6(51)$^{(i)}$ |
|  | Cinnamyl iodide<br>(77) 7 | Cinnamyl bromide<br>(78) 8 | 7(71) | 8(70) |
|  | Menthyl iodide<br>(55) 9 | Menthyl bromide<br>(54) 10 | 9(48) | 10(42) |
| $[\alpha]_D^{25}$ in $CHCl_3$ | (-50.6, c 0.85) | (-45.4, c 1) | (-48, c 1.8) | (-60, c 0.5) |

(i) Yield based on recovered starting material. The reaction was carried out for 48 hr.

## References and notes

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(ii)Mandal, A.K. and Mahajan, S.W. Tetrhedron **1988**, 44, 2293.

(13) Use of LiCl in place of LiBr or NaI did not give any chloride.

(14) For the conversion of secondary alcohols to chlorides with retention of configuration see Kozikowski, A.P. and Lee, J. Tetrahedron Lett. **1988**, 29, 3053.

(15) THP ethers of primary alcohols reacted very sluggishly and harsh conditions gave no desired halides.

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