Tetrahedron Letters,Vol.26,No.22,pp 2717-2720,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

SODIUM IODIDE/BORON TRIFLUORIDE ETHERATE: A MILD REAGENT SYSTEM FOR THE CONVERSION OF ALLYLIC AND BENZYLIC ALCOHOLS INTO CORRESPONDING IODIDES AND SULFOXIDES INTO SULFIDES

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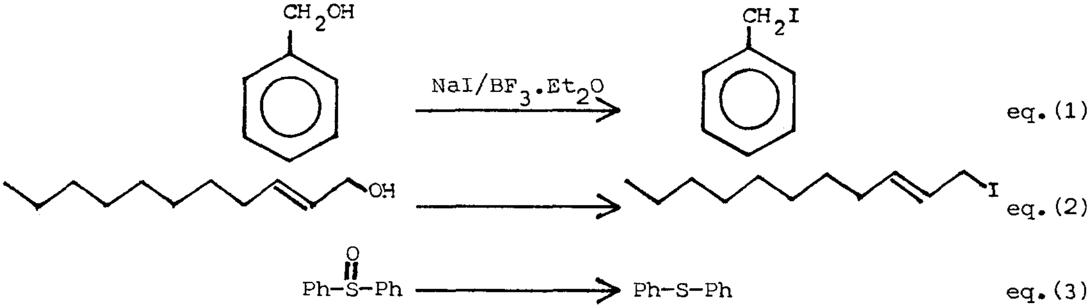
Summary: A variety of allylic and benzylic alcohols have been converted into the corresponding iodides using NaI/$BF_3.Et_2O$. Selective conversion of allylic and benzylic alcohols in preference to primary saturated alcohols has also been demonstrated. Further, the same reagent system has been used to convert sulfoxides into sulfides under mild conditions.

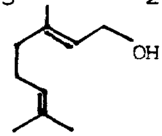
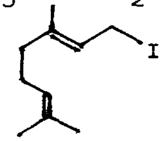
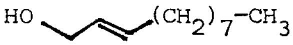
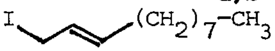
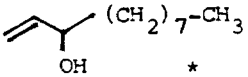
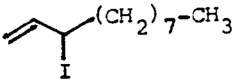
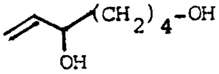
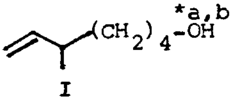
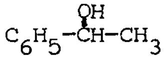
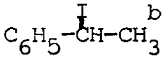
The utility of boron trifluoride etherate ($BF_3.Et_2O$) as a versatile reagent in organic chemistry is well documented[1]. An easy release of the BF_3 component (a Lewis acid) from this complex and its further coordination with either oxygen atom or other hetero atoms of the substrates and thereby bringing about specific transformations has also been well exploited[1(b)] in organic reactions. In this communication we wish to report the utility of $BF_3.Et_2O$ alongwith sodium iodide (NaI) in bringing about two important transformations viz. Alcohols ⟶ Iodides and Sulfoxides ⟶ Sulfides. In both these conversions the moiety $-\overset{\ominus}{O}BF_3$ was found to act as an excellent leaving group in conjuction with $I^{\ominus}$ as a nucleophile (Scheme 1).



Scheme 1

In case of alcohols it was observed that only allylic and benzylic alcohols underwent conversions to the corresponding iodides. This is apparent from entires (5), and (12) (see table 1) where primary saturated alcohols (marked with asterisk) are untouched whereas allylic or benzylic alcohols in the same molecule are converted into the corresponding iodides. Furthermore, the products from allylic alcohols (see entries 1-5) indicate that the attack of iodide ion does not involve allylic rearrangement. In view of the above observed selectivity and mildness of the reaction conditions

Table 1

Entry	Alcohol	Iodide	Time	Temperature (°C)	Yield %
1	$C_6H_5\text{-}CH{=}CH\text{-}CH_2OH$	$C_6H_5\text{-}CH{=}CHCH_2I$	15 mins 15 mins	0 RT	74
2			25 mins	0	70
3		 [a,b]	35 mins	0	95
4			45 mins	0	90
5	 *	 *[a,b]	30 mins	0	71
6	$C_6H_5CH_2OH$	$C_6H_5CH_2I$	25 mins	RT	94
7	$(m\text{-}Cl)C_6H_4\text{-}CH_2OH$	$(m\text{-}Cl)C_6H_4\text{-}CH_2\text{-}I$	15 mins 15 mins	10 RT	92
8	$(p\text{-}Cl)C_6H_4\text{-}CH_2OH$	$(p\text{-}Cl)C_6H_4CH_2I$	10 mins 15 mins	10 RT	91
9	$(m\text{-}OCH_3)C_6H_4\text{-}CH_2OH$	$(m\text{-}OCH_3)C_6H_4CH_2I$	20 mins 20 mins	10 RT	92
10	 $C_6H_5\text{-}\overset{OH}{C}H\text{-}CH_3$	 $C_6H_5\text{-}\overset{I}{C}H\text{-}CH_3$ [b]	15 mins 15 mins	0 RT	93
11	$(o\text{-}SCH_3)\text{-}C_6H_4CH_2OH$	$(o\text{-}SCH_3)C_6H_4CH_2I$ [a,c]	4 hrs	0	98
12	$[m\text{-}O(CH_2)_2\overset{*}{O}H]C_6H_4CH_2OH$	$[m\text{-}O(CH_2)_2\overset{*}{O}H]C_6H_4CH_2I$ [a,b]	35 mins	0	91

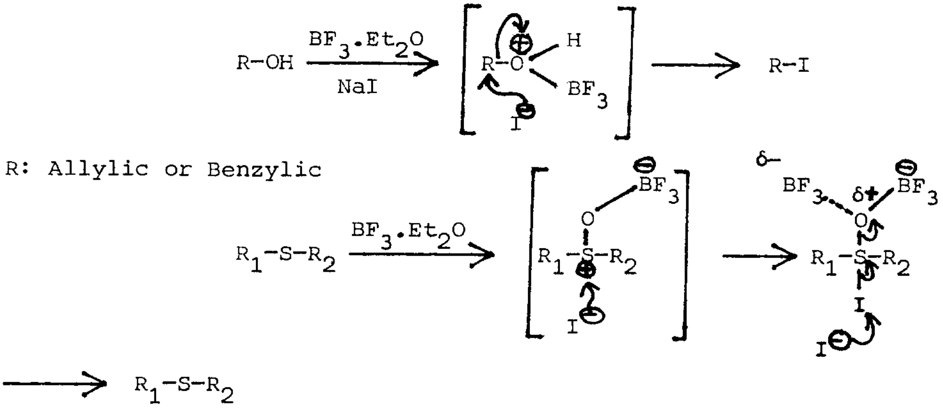
a: To our knowledge these compounds are not known in the literature

b: Isolated as thick oil which decompose during distillation c: m.p.63°C

d: m.p. 74°C.

we believe that the present method should find much use in organic synthesis. Interestingly all the reagents reported in literature, to our knowledge, for the conversion[2] of alcohols into iodides do not show any selectivity for benzylic and allylic alcohols instead they convert almost all types of alcohols into corresponding iodides[3].

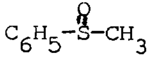
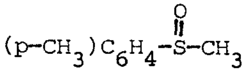
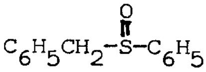
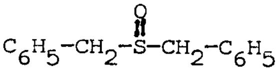
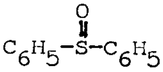
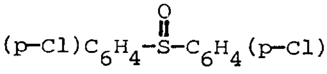
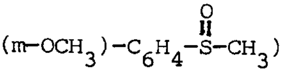
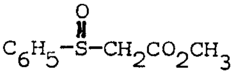
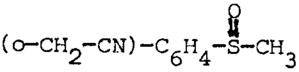
We have further utilized this reagent system for the conversion of sulfoxides into corresponding sulfides (equation 3, scheme 1). Accordingly we have found that a variety of sulfoxides undergo smooth conversion into sulfides in high yield (see table 2). Clearly here also $-\overset{\ominus}{O}BF_3$ acts as a leaving group and $I^{\ominus}$ as a nucleophile. Plausible mechanisms for both the conversions are shown in scheme 2.



Scheme 2

Although there exist[2,4] a number of methods for the above conversions in literature we consider present methods to be useful additions to them.

Table 2

Entry	Sulfoxide	Sulfide	Time	Yield %
1	 $C_6H_5-\overset{O}{\overset{\Vert}{S}}-CH_3$	$C_6H_5-S-CH_3$	40 mins	90
2	 $(p-CH_3)C_6H_4-\overset{O}{\overset{\Vert}{S}}-CH_3$	$(p-CH_3)C_6H_4-S-CH_3$	40 mins	90
3	 $C_6H_5CH_2-\overset{O}{\overset{\Vert}{S}}-C_6H_5$	$C_6H_5-CH_2-S-C_6H_5$	40 mins	98
4	 $C_6H_5-CH_2-\overset{O}{\overset{\Vert}{S}}-CH_2-C_6H_5$	$C_6H_5-CH_2-S-CH_2-C_6H_5$	20 mins	98
5	 $C_6H_5-\overset{O}{\overset{\Vert}{S}}-C_6H_5$	$C_6H_5-S-C_6H_5$	5 hrs	96
6	 $(p-Cl)C_6H_4-\overset{O}{\overset{\Vert}{S}}-C_6H_4(p-Cl)$	$(p-Cl)C_6H_4-S-(C_6H_4)$ $(p-Cl)$	5 hrs	98
7	 $(m-OCH_3)-C_6H_4-\overset{O}{\overset{\Vert}{S}}-CH_3)$	$(m-OCH_3)-C_6H_4-S-CH_3$	1 hr	90
8	 $C_6H_5-\overset{O}{\overset{\Vert}{S}}-CH_2CO_2CH_3$	$C_6H_5-S-CH_2CO_2CH_3$	2 hrs	95
9	 $(o-CH_2-CN)-C_6H_4-\overset{O}{\overset{\Vert}{S}}-CH_3$	$(o-CH_2CN)C_6H_4-S-CH_3$[a,b]	1.5 hrs	95

a: Not known in literature b. m.p. 35°C.

Experimental

A: General Procedure for the Conversion of Alcohols into Iodides

To a stirred mixture of the alcohol (2.5 mmol) and sodium iodide (5 mmol) in 8 ml dry acetonitrile (dried over P_2O_5) was added a solution of freshly distilled $BF_3.Et_2O$ (5 mmol) in 2 ml acetonitrile during 15 mins. period at temperature as indicated in table 1. The reaction mixture was poured into ice cold water (20 ml), treated with aq. solution (15%) of sodium thiosulfate and then extracted with ether (3x15 ml). The combined ether extracts were washed with water (2x5 ml), brine (10 ml) and then dried over anhydrous sodium sulfate. Evaporation of the solvent gave a residue which was purified by column chromatography over silica gel (with petroleum ether 60-80 as eluent) to obtain pure iodides corresponding to entires 2-7 and 10. In case of iodides corresponding to entires 1,8,9 and 11 solid compounds immediately separated out upon pouring the reaction mixture into ice cold water. These were washed with aqueous (15%) sodium thiosulfate solution, then with cold water and filtered to collect almost pure iodides. They were further purified by recrystallization.

B: General Procedure for the conversion of sulfoxides into sulfides

To a stirred solution of sulfoxide (2.5 mmol) and sodium iodide (8.75 mmol) in 8 ml dry acetonitrile (dried over P_2O_5) at 0^oC was added a solution of freshly distilled $BF_3.Et_2O$ (7.5 mmol) in 2 ml acetonitrile during 15 mins. The reaction mixture was then brought to room temperature and stirred for a period as indicated in table 2. The reaction mixture was poured into ice cold water (20 ml), treated with an aq. solution of sodium thiosulfate (15%) and extracted with ether (3x15 ml). The combined ether extracts were washed with water (2x5 ml) and with brine (15 ml) and dried over anhydrous sodium sulfate. Evaporation of the solvent gave almost pure sulfide which was further purified by distillation (or recrystallisation).

Acknowledgement

We are grateful to the Department of Science and Technology, Government of India for financial support.

References

1.(a) M. Fieser and L. Fieser, Reagents for organic synthesis, John Wiley and Sons, New York, Vols (1-10).

(b) H.O. House, Modern Synthetic Reactions, W.A. Benzamin Inc. Menlo Park, California, 1972, pp.533,654,718,772-777,781,782.

2.(a) G.A. Olah, S.C. Narang, B.G.B. Gupta and R. Malhotra, J. Org. Chem., 44, 1247 (1979).

(b) T. Mosita, S. Yohida, Y. Okamoto and H. Sakurai, Synthesis, 379 (1979) and references cited therein.

3. For selective converśion of allylic alcohols into corresponding chlorides (and bromides) see R.M. Magid, O.S. Fruchey and W.L. Johnson, Tetrahedron Lett., 2659 (1977) and references cited therein.

4. A.H. Schmidt and M. Russ, Chem. Ber., 114, 822 (1981) and references cited therein.

(Received in UK 10 April 1985)