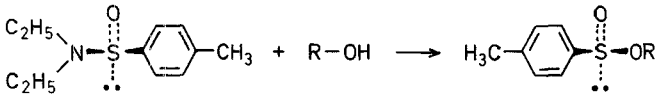
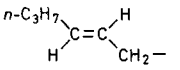
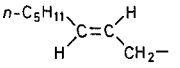
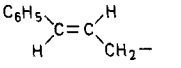
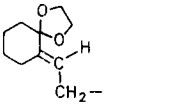
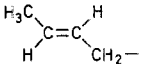
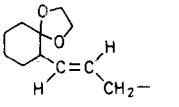


(S)-(+)-1 2a-l (S)-(-)-3a-l

2,3	R	2,3	R
a	H_3C	h	
b	C_2H_5	i	
c	$n\text{-}C_3H_7$	j	
d	$H_2C{=}CH{-}CH_2$	k	
e	$i\text{-}C_3H_7$		
f	$t\text{-}C_4H_9$		
g		l	

The absolute configuration and the optical rotations of the optically pure (−)-**3a–l** were determined by conversion of the resulting sulfinates (−)-**3a–l** into (*R*)-(+)-phenyl *p*-tolyl sulfoxide[3] of known configuration by means of treatment with phenylmagnesium bromide. The stereospecificity was calculated from the optical rotation of the produced sulfinates **3**, corrected for the optical purity of the starting sulfinamide **1** used, and the results are summarized in Table.

Thus, the results obtained here indicate that this esterification, catalyzed by boron trifluoride etherate proceeded, almost completely stereospecifically with inversion of configuration at the sulfinyl functions.

Hitherto, several methods have been reported for the preparation of optically active sulfinates[1,4–9]. In alcoholysis of sulfinamides catalyzed by strong acids[1] such as benzenesulfonic acid, trifluoromethanesulfonic acid, or trifluoroacetic acid, a rather low degree of stereospecificity was observed in the case of secondary and tertiary alcohols; however, the present method could circumvent these difficulties to provide a facile entry to optically active sulfinates with extremely high stereospecificity. Moreover, the mildness of the reagent, boron trifluoride etherate, enable us to apply this method to alcohols bearing acid-labile functions such as acetals.

To reveal the detailed mechanism of this transformation further studies are required, however this high stereospecificity could be explained by a stereospecific substitution, possibly via a direct back-side attack of alcohols to a boron trifluoride etherate-activated amide group of the sulfinamide, and a good retention of optical activity of the produced sulfinates without racemization under the reaction conditions in the presence of boron trifluoride etherate.

Compounds **3a–f** were identified by the spectral comparison with the authentic samples[1], and compounds **3g–l** were characterized by microanalyses, I.R., N.M.R., mass spectral data, and exact mass determination.

Thus, this boron trifluoride etherate-catalyzed esterification of sulfinamides is a practically useful method for the general preparation of optically active sulfinates, from the points of the chemical yields, the stereospecificity, the ready availability of the starting optically active sulfinamides, the mildness of the reagent, and the simplicity of the procedure.

A Highly Efficient and General Synthetic Route to Optically Active Sulfinates; Stereospecific Boron Trifluoride Etherate-Catalyzed Esterification of Sulfinamides

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One of the most important points, besides the chemical yield, in the preparation of chiral organo-sulfur compounds is the stereospecificity of the reactions utilized. We demonstrate herein a highly efficient and general synthetic way to optically active sulfinates, involving the boron trifluoride etherate-catalyzed alcoholysis of chiral sulfinamides.

Treatment of a readily obtainable optically active sulfinamide, (*S*)-(+)-*N*,*N*-diethyl-*p*-tolylsulfinamide (**1**)[1,2], with excess of alcohols **2a–l** in toluene in the presence of 1.5 equivs of boron trifluoride etherate at 0 °C resulted in the formation of the (*S*)-(−)-sulfinates **3a–l** in excellent yields.

Table. The Boron Trifluoride Etherate-Catalyzed Conversion of (*S*)-(+)-Sulfinamide **1** into (*S*)-(−)-Sulfinates **3a–l**

Product	e.e. [%] of **1**	equivs of **2**	Reaction time	Yield [%]	m.p. [°C] or b.p. [°C]/torr	Molecular formula[a] or Lit. m.p. or b.p.	$[\alpha]_D$ (C_2H_5OH)	e.e. [%] of **3**	Stereospecificity of **1**→**3** [%]	M.S. *m/e* (M^+) (calc. for M^+)
3a	78.0	3–30	3 h	99	102–104°/3	98–102°/3[10]	−170.7°	78.0	100	—
3b	87.0	37	3 h	91	105–108°/3	100°/1[11]	−178.8°	85.8	98.7	—
3c	87.0	28	3 h	92	128–130°/4	$C_{10}H_{14}SO_2$ (198.3)[b]	−169.9°	85.4	98.2	—
3d	58.0	39	3 h	93	120–122°/3	79–81°/0.002[12]	− 80.4°	55.1	95.0	—
3e	87.2	22	3 h	89	130–133°/3	$C_{10}H_{14}SO_2$ (198.3)[c]	−165.7°	82.9	96.3	—
3f	58.0	12	5.5–7.5 h	70	*oil*[d]	—	− 69.2°	53.4	91.9	—
3g	60.0	3	4 h	99	110–112°/1	$C_{11}H_{14}SO_2$ (210.3)	−124.6°	59.3	98.8	210.0679 (210.0644)
3h	63.4	3	4 h	95	140–143°/2	$C_{13}H_{18}SO_2$ (238.3)	−111.3°	57.5	90.7	238.1013 (238.1001)
3i	63.4	3	4 h	96	164°/2	$C_{15}H_{22}SO_2$ (266.4)	−103.1°	56.8	89.6	266.1315 (266.1290)
3j	63.4	3	4 h	94	42–45°	$C_{16}H_{16}SO_2$ (272.4)	− 40.7°	62.7	98.9	272.0863 (272.0857)
3k	61.0	3	4 h	69	oil	—	− 57.7°	59.0	96.7	322.1204 (322.1171)
3l	57.1	3	5 h	70	oil	—	− 65.6°	54.8	96.0	336.1379 (336.1364)

[a] Satisfactory microanalyses (C ±0.21, H ±0.11, S ±0.09) obtained **3c, 3e, 3g–j.**
[b] No b.p. given in Ref.[7].
[c] No b.p. given in Refs.[9,13].
[d] Decomposed on heating under vacuum (0.05 torr)[8].

(*S*)-(−)-Sulfinates 3a–l; General Procedure:
A dry, 25 ml two-necked flask with a septum inlet and a magnetic stirring bar is flushed with nitrogen and maintained under a positive pressure of nitrogen. A solution of (*S*)-(+)-*N,N*-diethyl-*p*-tolylsulfinamide (**1**; 260 mg, 1.23 mmol) and alcohol **2a–l** (equivs indicated in the Table) in toluene (2 ml) is added, followed by dropwise addition of a solution of boron trifluoride etherate (262 mg, 1.85 mmol) in toluene (1 ml) at 0 °C. The mixture is allowed to stir at 0 °C for the time listed in the Table, then quenched with saturated aqueous sodium hydrogen carbonate (5 ml), and extracted with ether (3 × 20 ml). The ether extracts are combined, washed with saturated aqueous sodium chloride (2 × 5 ml), dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The resulting crude products are subjected to preparative T.L.C. over silica gel 60PF-254 (Merck) (ether/hexane, 1:1) to give the (*S*)-(−)-sulfinates **3a–l**.

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[1] M. Mikołajczyk, J. Drabowicz, B. Bujnicki, *J. Chem. Soc. Chem. Commun.* **1976**, 568.
[2] S. Colonna, R. Giovini, F. Montanari, *J. Chem. Soc. Chem. Commun.* **1968**, 865.
[3] D. N. Harpp, S. M. Vines, J. P. Montillier, T. H. Chan, *J. Org. Chem.* **41**, 3987 (1976).
[4] H. Phillips, *J. Chem. Soc.* **1925**, 2552.
[5] L. Sogramora, P. Koch, A. Garbesi, A. Fava, *J. Chem. Soc. Chem. Commun.* **1967**, 985.
[6] M. Mikołajczyk, J. Drabowicz, *Tetrahedron Lett.* **1972**, 2379; *J. Am. Chem. Soc.* **100**, 2510 (1978).
[7] M. Mikołajczyk, J. Drabowicz, *J. Chem. Soc. Chem. Commun.* **1974**, 547.
[8] W. H. Pirkle, M. S. Hoekstra, *J. Am. Chem. Soc.* **98**, 1832 (1976).
[9] M. Mikołajczyk, J. Drabowicz, H. Slebocka-Tilk, *J. Am. Chem. Soc.* **101**, 1302 (1979).
[10] M. Kobayashi, *Bull. Chem. Soc. Jpn.* **39**, 1296 (1966).
[11] M. Kobayashi, M. Terao, *Bull. Chem. Soc. Jpn.* **39**, 1292 (1966).
[12] M. Kobayashi, H. Minato, Y. Miyaji, T. Yoshioka, K. Tanaka, K. Honda, *Bull. Chem. Soc. Jpn.* **45**, 2817 (1972).
[13] Y. Miyaji, H. Minato, M. Kobayashi, *Bull. Chem. Soc. Jpn.* **44**, 862 (1971).