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SHORT
COMMUNICATIONS

Lewis Acids as Co-reagents in Sulfenylation Reactions

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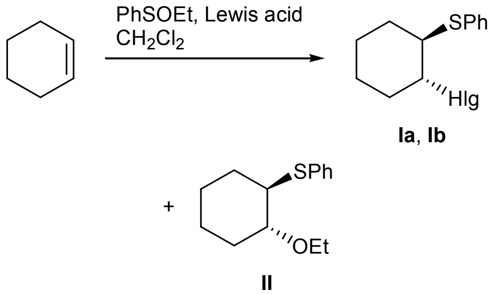
Sulfenic acid derivatives possess a versatile synthetic potential. However, up to now attention was given mainly to sulfenyl chlorides [1] and sulfenamides [2] as electrophilic reagents in electrophilic addition (Ad_E) reactions, whereas sulfenic acid esters were poorly studied in this respect. We previously developed a convenient procedure for chloro- and bromosulfenylation of alkenes and dienes using ethyl benzenesulfenate and phosphoryl halide [3] or thionyl halide [4]. In continuation of these studies we examined reactions of some alkenes with ethyl benzenesulfenate–Lewis acid systems.

The reaction of ethyl benzenesulfenate with cyclohexene in the presence of $AlCl_3$, $TiCl_4$, $SnCl_4$, or PBr_3 gave only the corresponding *trans*-1-halo-2-phenylsulfanylcyclohexanes **Ia** and **Ib** in good yields, whereas in the presence of $ZnCl_2$ the major product was *trans*-1-ethoxy-2-phenylsulfanylcyclohexane (**II**) (Scheme 1, see table).

Scheme 1.

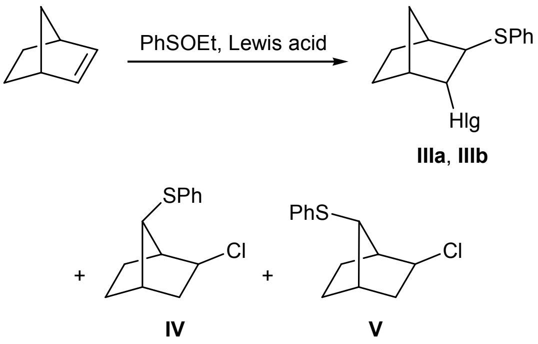


Hlg = Cl (**a**), Br (**b**).

In the reactions with norbornene, mixtures of isomeric haloalkyl phenyl sulfides were formed, and the yield and ratio of unrearranged (**IIIa**) and rearranged compounds **IV** and **V** depended on the nature of both Lewis acid and solvent (Scheme 2, see table).

Thus sulfenylation of alkenes with ethyl benzenesulfenate in the presence of Lewis acid makes it possible to control the product composition by varying the reaction conditions.

Scheme 2.



Hlg = Cl (**a**), Br (**b**).

Reactions of ethyl benzenesulfenate with alkenes in the presence of Lewis acids in methylene chloride (*general procedure*). A solution of 2.5 mmol of ethyl benzenesulfenate and 2.5 mmol of cyclohexene or norbornene in 10 ml of anhydrous methylene chloride was slowly added under vigorous stirring at 0°C in a dry argon atmosphere to a solution (or suspension) of Lewis acid (2.5 mmol of $TiCl_4$, $SnCl_4$, and $ZnCl_2$ or 5.0 mmol of $AlCl_3$) in 10 ml of the same solvent. The mixture was stirred until the reaction was complete and filtered through a column charged with silica gel, and the solvent was removed under reduced pressure. If necessary, the products were separated by column chromatography.

Reactions of ethyl benzenesulfenate with alkenes in the presence of Lewis acids in nitromethane (*general procedure*). A solution of 2.5 mmol of ethyl benzenesulfenate and 2.5 mmol of cyclohexene or norbor-

Reactions of ethyl benzenesulfenate with alkenes in the presence of Lewis acids

Initial compound	Reaction conditions		Products				
	Lewis acid	solvent	compound no.	yield, %	isomer ratio, %		
					III	**IV**	**V**
Cyclohexene	$AlCl_3$	CH_2Cl_2	**Ia**	81	–	–	–
	$TiCl_4$	CH_2Cl_2	**Ia**	76	–	–	–
	$SnCl_4$	CH_2Cl_2	**Ia**	70	–	–	–
	$ZnCl_2$	CH_2Cl_2	**Ia**	10	–	–	–
			II	34	–	–	–
	PBr_3	CH_2Cl_2	**Ib**	84	–	–	–
Norbornene	$AlCl_3$	CH_2Cl_2	**IIIa**	72	100	0	0
	$TiCl_4$	CH_2Cl_2	**IIIa**	86	100	0	0
		$MeNO_2$	**IIIa** + **IV** + **V**	90	21	49	30
	$SnCl_4$	CH_2Cl_2	**IIIa** + **IV** + **V**	84	18	23	59
		$MeNO_2$	**IV** + **V**	92	0	67	33
	$ZnCl_2$	CH_2Cl_2	**IIIa** + **IV** + **V**	46	26	41	33
	PBr_3	CH_2Cl_2	**IIIb**	67	100	0	0

nene in 10 ml of anhydrous nitromethane was slowly added under vigorous stirring at 0°C in a dry argon atmosphere to a solution of 2.5 mmol of Lewis acid in 5 ml of anhydrous nitromethane. The mixture was stirred until the reaction was complete, treated with an aqueous solution of sodium carbonate, and extracted with chloroform (2×25 ml). The extract was dried over Na_2SO_4, and the solvent was removed under reduced pressure.

Reactions of ethyl benzenesulfenate with alkenes in the presence of phosphorus(III) bromide (*general procedure***).** A solution of 2.5 mmol of ethyl benzenesulfenate and 2.5 mmol of cyclohexene or norbornene in 10 ml of anhydrous methylene chloride was cooled to –30°C, and a solution of 2.5 mmol PBr_3 in 10 ml of methylene chloride was slowly added under vigorous stirring in an argon atmosphere. The mixture was stirred for 1 h, allowed to warm up to 20°C, and passed through a column charged with silica gel, and the solvent was removed under reduced pressure.

The yields are given in table. Compounds **Ia**, **Ib**, **IIIa**, and **IIIb** were reported previously; their physical properties coincided with those given in [4].

***trans*-1-Ethoxy-2-phenylsulfanylcyclohexane (II).** R_f 0.69. ^{1}H NMR spectrum, δ, ppm: 1.18 t (3H, CH_3, $J = 7.0$ Hz), 1.22–1.48 m (4H, CH_2), 1.75 m (2H, CH_2), 2.06 m (2H, CH_2), 3.20 t.d and 3.24 t.d (1H each, 1-H, 2-H, $J = 8.4$, 3.7 Hz), 3.52 d.q and 3.65 d.q (1H each, OCH_2, $J = 9.2$, 7.0 Hz), 7.2–7.4 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 15.6 (CH_3), 24.3, 24.8, 30.9, 31.5 (CH_2), 51.3 (CHS), 64.3 (CH_2O), 80.4 (CHO), 126.5, 129.8, 132.6, 135.9 (C_{arom}). Found, %: C 71.38; H 8.54. $C_{14}H_{20}OS$. Calculated, %: C 71.18; H 8.52.

***exo*-2-Chloro-*syn*-7-phenylsulfanylbicyclo[2.2.1]-heptane (IV) and *exo*-2-chloro-*anti*-7-phenylsulfanylbicyclo[2.2.1]heptane (V) (**mixture of stereoisomers**).** R_f 0.60. ^{1}H NMR spectrum, δ, ppm: **IV**: 2.49 br.s (1H, 4-H), 2.64 br.s (1H, 1-H), 3.32 br.s (1H, HCS), 3.97 d.d.d (1H, CHCl, $J_{2,endo\text{-}3} = 7.7$, $J_{2,exo\text{-}3} = 3.2$, $J_{2,anti\text{-}7} = 1.0$ Hz); **V**: 2.39 br.s (1H, 4-H), 2.54 br.s (1H, 1-H), 3.85 br.s (1H, HCS), 4.03 d.d (1H, CHCl, $J_{2,endo\text{-}3} = 7.8$, $J_{2,exo\text{-}3} = 2.7$ Hz); signals from the C^3H_2, C^5H_2, C^6H_2 (1.36–2.00 ppm) and aromatic protons (7.20–7.40 ppm) of compounds **IV** and **V** overlapped each other. Mass spectrum, *m*/*z* (I_{rel}, %): **IV**: 240 (36) $[M + 2]^+$, 238 (100) $[M]^+$, 203 (40), 136 (36), 123 (56), 110 (41), 93 (49); **V**: 240 (33) $[M + 2]^+$, 238 (100) $[M]^+$, 203 (43), 136 (43), 123 (56), 110 (50), 93 (49). Found, %: C 65.53; H 6.42. $C_{13}H_{15}ClS$. Calculated, %: C 65.41; H 6.29. *M* 238.78.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 and 100 MHz, respectively, using hexamethyldisiloxane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT TSQ 7000

GC–MS instrument. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using petroleum ether–ethyl acetate (3 : 1) as eluent.

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