The Arenesulphonomercuriation of Alkenes—a Route to Vinyl Sulphones

Wojciech Sas

Department of Chemistry, Warsaw Technical University, 00-664 Warszawa, Noakowskiego 3, Poland

Vinyl sulphones were obtained from the reaction of alkenes with mercury(II) chloride and sodium arenesulphinate followed by base catalysed eliminative demercuriation.

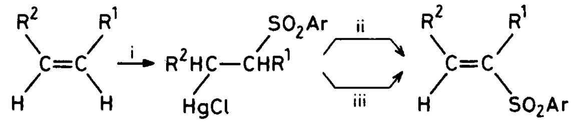
Solvatomercuriation–demercuriation and related processes are important methods of conversion of alkenes into alcohols, ethers, amines, azides, nitroalkenes, *etc.*[1,2] Surprisingly this sequence has not been adapted for the synthesis of sulphones. In the present communication the arenesulphonomercuriation of alkenes and the transformation of the sulphonyl mercury compounds (**1**) obtained to vinyl sulphones (**2**) (Scheme 1) is described.

In a typical experiment mercury(II) chloride (1 equiv.), sodium benzene- or toluene-*p*-sulphinate (1.25 equiv.), and

Table 1.

				(1)			(2)	
	R^1	R^2	Ar	Yield (%)[a]	M.p./°C[b]	Method	Yield (%)[b]	M.p.[b](Lit. m.p.)/°C
(a)	H	H	Ph	82	122—124	B[c]	77.5	66.5—68.5(68.5[3])
(b)	$-[CH_2]_3-$		Ph	73	134.5—137	A	79	64—66 (64.5—65[4])
(c)	$-[CH_2]_4-$		Ph	82	163—167 (decomp.)	A	79	47.5—49 (46—47[5])
(d)	$-[CH_2]_4-$		*p*-MeC_6H_4	83	192 (decomp.)	A	84	82.5—84.5 (81—82[6])
(e)	H	CO_2Me	Ph	85	163—167	B[d]	75	97.5—100 (97[7])
(f)	H	COMe	Ph	96	175—179 (decomp.)	B[d]	59.5	61—62.5 (61—62[8])

[a] The yield of crude (**1**), which was used in the next step. [b] These data are for the compounds obtained after crystallization. [c] Room temperature, 15 h. [d] 0 °C, 1 h.



(**1**) (**2**)

Scheme 1. *Reagents:* i, $HgCl_2$, $ArSO_2Na$, H_2O, room temp., 24—46 h; ii, 50% aq. NaOH–dioxane, room temp.; iii, (a) Br_2, benzene, room temp., (b) NEt_3 (3 equiv.).

an alkene (1.1 equiv.)† were vigorously stirred in water for 24—46 h at room temperature. The results obtained are given in Table 1. The structure of compounds (**1**) was supported by i.r. and n.m.r. spectra. The ^1H n.m.r. spectrum of (**1c**) showed that arenesulphonomercuriation had occurred in a *trans* fashion.

The sulphonylmercury compounds (**1**) were sufficiently pure to be used in the next step without purification. The base catalysed eliminative demercuriation described by Corey for 2-chloromercurionitroalkanes[2] was applied to compounds (**1**). However, the sulphonylmercury compounds were not efficiently converted into vinyl sulphones by dilute aqueous sodium hydroxide or organic bases *e.g.* triethylamine or tetramethylguanidine. The transformation of (**1**) to (**2**) was achieved by the treatment of (**1**) in dioxane with 50% aqueous sodium hydroxide for 15 h at room temperature (method A). The use of a concentrated solution of a strong inorganic base limited the application of this procedure and good yields were obtained for (**1b—d**) only. For the other compounds (**1**) this method failed. More effective was a two-step one-pot procedure (method B) as follows: reaction of (**1**) in benzene with a stoicheiometric quantity of bromine‡ and, when the bromine was consumed, treatment of the resulting mixture with triethylamine (3 equiv.). Both methods gave vinyl sulphones in good yields (Table 1).

The arenesulphonomercuriation–eliminative demercuriation appears to be quite a general and preparatively valuable method for the conversion of alkenes into vinyl sulphones.

Received, 2nd April 1984; Com. 453

References

1 R. C. Larock, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 27; H. C. Brown and G. J. Lynch, *J. Org. Chem.*, 1981, **46**, 531, 930; J. Barluenga, C. Jimenez, C. Najera, and M. Yus, *Synthesis*, 1981, 201; 1982, 414.

2 E. J. Corey and H. Estreicher, *J. Am. Chem. Soc.*, 1978, **100**, 6294.

3 A. H. Ford-Moore, R. A. Peters, and R. W. Wakelin, *J. Chem. Soc.*, 1949, 1754.

4 P. B. Hopkins and P. L. Fuchs, *J. Org. Chem.*, 1978, **43**, 1208.

5 H. E. Zimmerman and B. S. Thyagarajan, *J. Am. Chem. Soc.*, 1957, **80**, 3060.

6 L. K. Lin, Y. Chi, and K.-Y. Jen, *J. Org. Chem.*, 1980, **45**, 406.

7 E. A. Berdnikov, F. K. Mukhitova, F. R. Tantasheva, and E. G. Kataev, *Zh. Org. Khim.*, 1977, **13**, 1418.

8 N. K. Kochetkov and V. N. Vinogradova, *Zh. Obshch. Khim.*, 1957, **27**, 2745.

---

† For $R^1 = R^2 = H$ the alkene was slowly bubbled through the reaction mixture for 30 h.

‡ For (**1a**) the bromination was carried out with irradiation from a 200 W tungsten lamp.