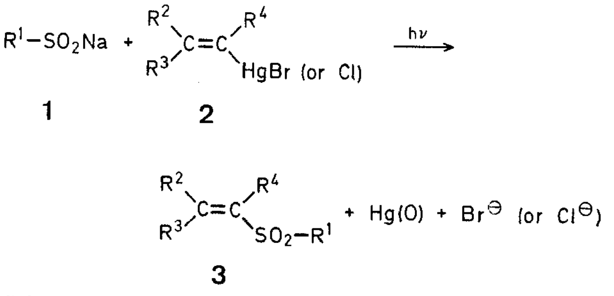
Reaction of 1-Alkenylmercury Halides with Sulfinate Anions to Form α,β-Unsaturated Sulfones[1]

James Hershberger, Glen A. Russell*

Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.

α,β-Unsaturated sulfones are of synthetic importance since they can be used as dienophiles, Michael acceptors, or in the case of aryl vinyl sulfones may be metallated at the α-vinylic position[2,3].

1-Alkenyl sulfones are generally synthesized by an elimination reaction of the β-halo sulfone which may be synthesized from the appropriate olefin[4,5]. We have found that α,β-unsaturated sulfones can also be conveniently prepared by a photostimulated coupling of 1-alkenylmercury halides **2** with the sodium salts of alkane- or arenesulfinic acids **1** (Scheme A).



Scheme **A**

The reaction was conveniently monitored by the precipitation of mercury metal upon sunlamp irradiation (Pyrex) under nitrogen in a suitable solvent mixture. The reaction temperatures employed were in the range 25°–50 °C depending upon the proximity of a 275 Watt sunlamp required for a convenient reaction rate (5–15 cm). A mixed solvent system (dimethyl sulfoxide/*t*-butyl alcohol/water) which is inert to free radical attack is preferred. The presence of water in the solvent causes the mercury to form small drops which facilitates filtration. Pure dimethyl sulfoxide as the solvent should be avoided since in dimethyl sulfoxide induced symmetrization of the organomercury halide (to yield R_2Hg) becomes a competing process.

Table 1 summarizes the yields of isolated product and those estimated by ^{1}H-N.M.R. for a variety of substituted vinylmercury halides. The reaction appears to be retarded by a bulky R^4 group (products **3g, h**), but occurs readily with R^2 and R^3 = alkyl or aryl. When steric hindrance is a problem (e.g. product **3g**) improved yields of the sulfone were obtained by use of a RPR-100 Rayonet reactor with 350 nm light source. Vinylmercury chloride fails to yield a coupling product possibly because of competing polymerization processes.

The reaction appears to be a vinylic $S_{RN}1$ process involving attack of the 1-alkenyl radical on the sulfinate anion (Scheme **B**)[6] or possibly an addition-elimination process.

$$[R{-}Hg{-}X]^{\ominus\bullet} \longrightarrow R^{\bullet} + Hg(0) + X^{\ominus}$$

$$R^{\bullet} + R^1{-}SO_2^{\ominus} \longrightarrow [R{-}SO_2{-}R^1]^{\ominus\bullet}$$

$$[R{-}SO_2{-}R^1]^{\ominus\bullet} + R{-}Hg{-}X \longrightarrow R{-}SO_2{-}R^1 + [R{-}Hg{-}X]^{\ominus\bullet}$$

Scheme **B**

Thus, not only is photostimulation required, but addition of 5 mol% of di-*t*-butylnitroxide to the reaction mixture for **3e** completely inhibited the photostimulated reaction for many hours. Alkylmercury halides undergo a similar $S_{RN}1$ reaction with nitronate anions[7], but fail to react with sulfinate anions when photostimulated. Arylmercury halides react sluggishly to yield the sulfones plus other products. The reactions occur with a high degree of stereoselectivity when $R^3 = R^4 = H$. With $R^2 = t\text{-}C_4H_9$ or C_6H_5 only the (*E*)-isomer has been observed, based on the I.R. spectrum and G.L.P.C. chromatography (usually 5% OV-3 on Chromosorb W at 160–200 °C).

Typical Procedure: (*E*)-3,3-Dimethyl-1-butenyl *p*-Tolyl Sulfone (3a):

(*E*)-1-Chloromercury-3,3-dimethyl-1-butene[8] (**2**, $R^2 = t\text{-}C_4H_9$, $R^3 = R^4 = H$; 1.0 g, 3.1 mmol) and sodium *p*-toluenesulfinate (**1**, $R = 4\text{-}H_3C{-}C_6H_4$; 1.6 g, 9 mmol) are dissolved in a mixture of *t*-butyl alcohol (40 ml) and water (10 ml). The solution is deoxygenated by nitrogen bubbling for 10 min and then stirred under a nitrogen atmosphere while irradiated with a 275 Watt sunlamp 8 cm from the Pyrex flask. After 21 h precipitation of mercury ceases. The mercury is removed by filtration through Celite (diatomaceous silica) and most of the solvent removed by vacuum distillation. The resulting product is extracted from brine with ether and the extract washed with aqueous sodium thiosulfate to remove organomercurial contaminants. After drying with magnesium sulfate, removal of the solvent from the ether extract under vacuum gives 81% (N.M.R.) of the crude sulfone, which upon distillation gives the pure sulfone as a colorless oil; yield: 0.5 g (68%); b.p. 105 °C/0.15 torr.

0039-7881/80/0632-0475 $ 03.00

Table. 1-Alkenyl Sulfones **3** from Alkenylmercury Halides **2**

Product	R[1]	R[2]	R[3]	R[4]	Halide in **2**	Reaction time/solvent	Yield [%][a] of **3**	Stereochemistry of **3**[b]
3a	4-H_3C—C_6H_4	t-C_4H_9	H	H	Cl	21 h/t-C_4H_9OH/H_2O	68 (81)	>95% (E)
3b	4-H_3C—C_6H_4	n-C_3H_7	H	H	Cl	22 h/DMSO/t-C_4H_9OH/H_2O	63 (71)	86% (E), 14% (Z)
3c[c]	4-H_3C—C_6H_4	H	n-C_8H_{17}	H	Cl	15 h/DMSO/t-C_4H_9OH/H_2O	55 (74)	89% (E), 11% (Z)
3d[c, 12]	4-H_3C—C_6H_4	H	CH_3	CH_3	Br	24 h/DMSO/t-C_4H_9OH/H_2O	67 (72)	—
3e[13]	4-H_3C—C_6H_4	C_6H_5	H	H	Cl	19 h/DMSO/t-C_4H_9OH	77 (81)	>95% (E)
3f	4-H_3C—C_6H_4	C_6H_5	C_6H_5	H	Br	40 h/DMSO/t-C_4H_9OH/H_2O	61 (80)	—
3g	4-H_3C—C_6H_4	C_6H_5	C_6H_5	CH_3	Br	69 h/DMSO/t-C_4H_9OH/H_2O	31 (66)[g]	—
3h	4-H_3C—C_6H_4	H	H	c-C_6H_{11}—CH_2	Br	51 h/DMSO/t-C_4H_9OH/H_2O	0[g]	—
3i	c-C_6H_{11}	t-C_4H_9	H	H	Cl	18 h/t-C_4H_9OH/H_2O	66 (71)	>95% (E)
3j	c-C_6H_{11}	C_6H_5	H	H	Cl	25 h/DMSO/t-C_4H_9OH	65 (68)	>95% (E)
3k	t-C_4H_9	C_6H_5	H	H	Cl	24 h/DMSO/t-C_4H_9OH	55 (56)	>95 (E)
3l[14]	n-C_3H_7	t-C_4H_9	H	H	Cl	30 h/DMSO/t-C_4H_9OH/H_2O	69 (75)	>95% (E)
3m	C_6H_5	t-C_4H_9	H	H	Cl	24 h/t-C_4H_9OH/H_2O	85 (88)	>95% (E)

[a] Yield of isolated product; value in brackets is yield estimated by ^{1}H-N.M.R.

[b] Determined by I.R. and G.L.C. (1.5 m, 5% OV-3).

[c] Satisfactory microanalyses (C ±0.34, H ±0.18%) and mass spectra (m/e for M^+ within ±0.001 units of the theoretical value; AEI MS 902 spectrometer).

[d] ^{1}H-N.M.R. of mixture.

[e] Compound **2** was a mixture of (E)- and (Z)-isomers.

[f] Recrystallized from ether/hexane.

[g] Irradiation at 350 nm through Pyrex; Rayonet RPR-100 reactor.

Alkenylmercury Halides (2):

2-Bromomercury-3-cyclohexyl-1-propene (see entry **3h**), m.p. 95–96 °C, is obtained in 62% yield by addition of excess mercury(II) bromide to the Grignard reagent in tetrahydrofuran at 25 °C, followed by recrystallization from ethanol. *2-Bromomercury-2-methyl-1,1-diphenylethene* (see entry **3g**), m.p. 163.5–164.5 °C, is prepared similarly in 60% yield. The other alkenylmercury halides are prepared by literature procedures[8–11]. Satisfactory microanalyses (C ±0.1%, H ±0.15%) for the organomercury halides **2** were obtained.

This work was supported by grant CHE-7823866 from the National Science Foundation.

Received: December 31, 1979

---

[1] Electron Transfer Processes; 22. Part 21: G. A. Russell, M. Jawdosink, F. Ros, *J. Am. Chem. Soc.* **101**, 3378 (1979).

[2] For a recent review see P. D. Magnus, *Tetrahedron* **33**, 2019 (1977).

[3] J. J. Eisch, J. E. Galle, *J. Org. Chem.* **44**, 3277, 3279 (1979).

b.p. [°C]/ torr	Molecular formula[c]	^{1}H-N.M.R. (CDCl$_3$) δ [ppm] of (*E*/*Z*)-mixture
105°/ 0.15	$C_{13}H_{18}O_2S$ (238.4)	7.8–7.2 (m, 4H); 6.88 (d, *J*=15 Hz, 1H); 6.16 (d, *J*=15 Hz, 1H); 2.42 (s, 3H); 1.09 (s, 9H)
120°/ 0.1	$C_{12}H_{16}O_2S$ (224.3)	7.8–7.2 (m, 4H); 7.2–6.7 (m, 1H); 6.45–6.1 (m, 1H); 2.4 (s, 3H); 2.4–1.95 (m, 2H); 1.8–1.15 (m, 2H); 0.88 (t, 3H, *J*=6.5 Hz)[d]
150°/ 0.15	$C_{17}H_{26}O_2S$ (294.4)	7.8–7.2 (m, 4H); 7.1–6.1 (m, 2H); 2.4 (s, 3H); 2.4–2.0 (m, 2H); 1.7–0.7 (m, 15H)[d]
115°/ 0.15	$C_{11}H_{14}O_2S$ (210.3)	7.75–7.2 (m, 4H); 7.1–6.1 (m, 1H); 2.4 (s, 3H); 2.1–1.7 (m, 6H)[d]
165°/ 0.2	$C_{15}H_{14}S$ (258.3)	7.8–7.2 (m, 9H); 7.63 (d, *J*=15 Hz, 1H); 6.82 (d, *J*=15 Hz, 1H); 2.39 (s, 3H)
m.p. 101.5–103°	$C_{21}H_{18}O_2S$ (334.4)	7.6–7.0 (m, 14H); 6.97 (s, 1H); 2.38 (s, 3H)
m.p.[f] 158.5–160°	$C_{22}H_{20}O_2S$ (348.5)	7.6–6.9 (m, 14H); 2.33 (s, 3H); 2.13 (s, 3H)
105°/ 0.15	$C_{12}H_{22}O_2S$ (230.4)	6.83 (d, *J*=15.5 Hz, 1H); 6.07 (d, *J*=15.5 Hz, 1H); 3.0–0.9 (m, 11H); 1.14 (s, 9H)
150°/ 0.15	$C_{14}H_{18}O_2S$ (250.4)	7.6 (d, *J*=15.5 Hz, 1H); 7.6–7.2 (m, 5H); 6.8 (d, *J*=15.5 Hz, 1H); 3.2–1.0 (m, 11H)
120°/0.1 m.p. 98–100°	$C_{12}H_{16}O_2S$ (224.3)	7.6–7.1 (m, 4H); 7.60 (d, *J*=16 Hz, 1H); 6.80 (d, *J*=16 Hz, 1H); 1.40 (s, 9H)
80°/ 0.08	$C_8H_{18}O_2S$ (190.3)	6.88 (d, *J*=15.5 Hz, 1H); 6.23 (d, *J*=15.5 Hz, 1H); 3.12–2.85 (m, 2H); 1.95–1.55 (m, 2H); 1.14 (m, 3H); 1.12 (s, 9H)
107°/ 0.09	$C_{12}H_{11}O_2S$ (224.3)	7.9–7.4 (m, 4H); 6.87 (d, *J*=16 Hz, 1H); 6.11 (d, *J*=16 Hz, 1H); 1.09 (s, 9H)

[4] M. Asscher, D. Vofsi, *J. Chem. Soc.* **1964**, 4962; *J. Chem. Soc. Perkin Trans. 1* **1972**, 1543.

[5] P. B. Hopkins, P. L. Fuchs, *J. Org. Chem.* **43**, 1208 (1978).

[6] It has been suggested that certain photostimulated reactions of vinyl halides with primary-enolate anions proceed by the $S_{RN}1$ scheme [J. F. Bunnett, X. Creary, J. C. Sundberg, *J. Org. Chem.* **41**, 1707 (1976)].

[7] G. A. Russell, J. Hershberger, K. Owens, *J. Am. Chem. Soc.* **101**, 1312 (1979).

[8] R. C. Larock, H. C. Brown, *J. Organomet. Chem.* **36**, 1 (1972).

[9] C. P. Casey, G. M. Whitesides, J. Kurth, *J. Org. Chem.* **38**, 3406 (1973).

[10] W. Schlenk, E. Bergmann, *Justus Liebigs Ann. Chem.* **463**, 98 (1928).

[11] R. C. Larock, *J. Org. Chem.* **40**, 3237 (1975).

[12] F. G. Bordwell, P. S. Landis, *J. Am. Chem. Soc.* **79**, 1596 (1957).

[13] E. P. Kohler, H. Potter, *J. Am. Chem. Soc.* **57**, 1316 (1935).

[14] E. P. Gracheva, V. I. Laba, N. R. Kul'bovskaya, M. F. Shostakovskii, *Zh. Obshch. Khim.* **33**, 2493 (1963); *C. A.* **60**, 399 (1964).

0039-7881/80/0632-0477 $ 03.00