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ORGANIC SYNTHESIS WITH SULPHONES—XVII†

THE ANTI-MARKOWNIKOFF HALOSULPHONYLATION OF OLEFINS VIA AN IONIC PATHWAY. AND A NEW METHOD OF PREPARING BENZENESULPHONYL IODIDE

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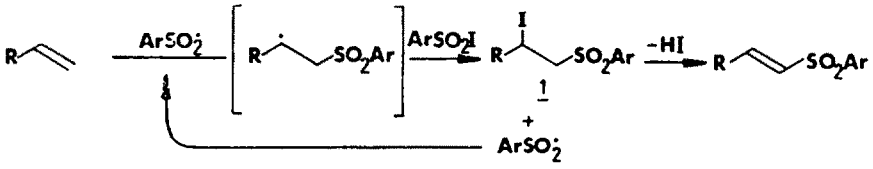
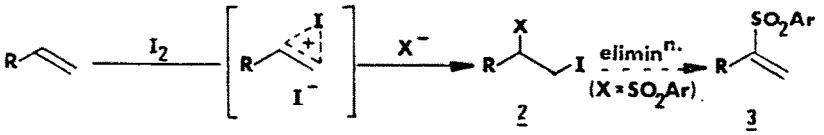
Abstract Iodine and bromine in the presence of sodium benzenesulphinate react with olefins in acetone solution to give halosulphones resulting from an apparent steric direction of attack at the intermediate halonium ion. A straightforward preparation of benzenesulphonyl iodide from benzenesulphonyl chloride and sodium iodide is also described.

Arenesulphonyl iodides under the influence of U.V. light[1a,b] or heat react with olefins by a radical pathway to give anti-Markownikoff products **1** from which elimination leads to ω-sulphonylated olefins (Scheme A). It has been shown that iodine in the presence of certain salts (e.g. azides,[2] acetates[3] and thiocyanates[4]) and also iodine azide[5] and iodine isocyanate[6] react with olefins to generally give Markownikoff addition products **2** via attack of the nucleophile on an intermediate iodonium species (Scheme B). Exceptions have been observed however with severely sterically hindered olefins such as t-butylethylene.[6] It was reasoned that iodination of olefins in the presence of sodium arenesulphinates might similarly lead to Markownikoff iodosulphonylation of olefins (**2**, X = SO_2Ar). This would lead, after dehydroiodination, to vinylsulphones **3** isomeric with the products formed from the olefin/arenesulphonyl iodide route. The electron deficient double bond of vinylic sulphones undergoes a variety of nucleophilic addition reactions[7] and this modification therefore appeared to be a suitable method of reversing the polarity of terminal olefins (Scheme C). The sulphonyl group could then be readily removed by hydrogenolysis.[8]

Reaction of olefins with a suspension of sodium benzenesulphinate in a solution of iodine in acetone in the dark at room temperature indeed led to the formation of β-iodosulphones. The direction of



Scheme A



Scheme B

Scheme C

†Part XVI: M. Julia, M. Nel and L. Saussine, *J. Organometallic Chem.*, 181, C 17 (1979).

addition, as demonstrated by dehydroiodination was however found to be anti-Markownikoff (Table I). Control experiments showed that under these conditions formation of benzenesulphonyl iodide did not take place, nor did benzenesulphonyl iodide add to olefins. These results cannot therefore be explained by *in situ* formation of benzenesulphonyl iodide.

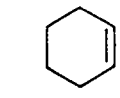
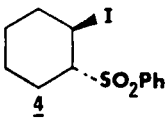
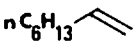
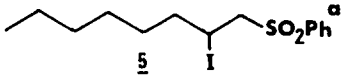
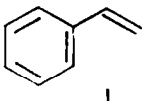
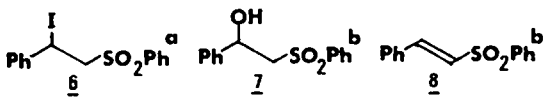
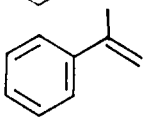
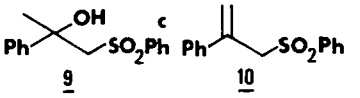
With styrenes, hydroxysulphones and dehydroiodination products were also observed. Their formation is readily explained by further reaction of the reactive benzylic iodides. The structure of the β-hydroxysulphone **9** obtained from α-methyl styrene was demonstrated by its spectral properties and its stability to oxidising agents, whereas **7**, obtained from styrene, was identical with an authentic sample.[9]

Treatment of the iodosulphones **5** and **6** with triethylamine in methylene chloride at room temperature[10] led to the corresponding terminal vinyl sulphones in good yield.

A similar reaction with bromine instead of iodine gave the corresponding β-bromosulphones (again the products of anti-Markownikoff addition, Table II) accompanied by variable amounts of bromohydrins (Markownikoff) and dibromides. The latter products, being stable under the reaction conditions, must therefore be true reaction products and not precursors to the bromosulphones.

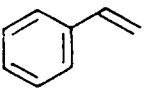
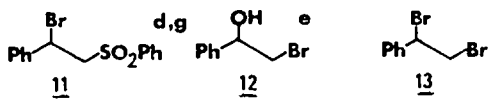
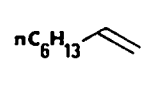
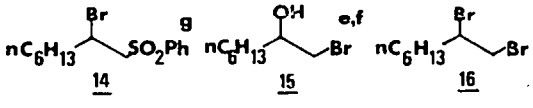
The β-bromosulphones **11** and **14** were readily dehydrobrominated with triethylamine to give the terminally sulphonylated olefins. Oxidation of the bromohydrins **12** and **15** with pyridinium chlorochromate led to α-bromoketones. In the case of bromohydrin **15** the crude 1-bromo-2-octanone obtained was contaminated with a small amount (~1% by N.M.R.) of 2-bromooctanal. This shows that the oxidation products of the anti-Markownikoff bromohydrins, being stable under the reaction conditions, would be detected if present. Regular formation of the anti-Markownikoff halosulphones is probably best explained by steric reasons. Owing to its large size the sulphinate anion would not be able to reach the inner side of the iodonium ion and would thus have to attack at the terminal carbon atom. A similar argument has been invoked to account for the "abnormal" addition of iodine isocyanate[6] and iodonium nitrate[14] to t-butylethylene. Analogously

Table I.

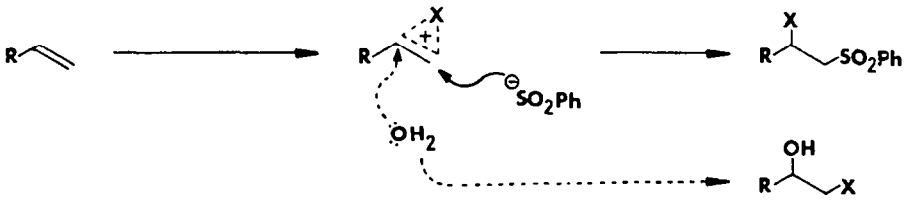
olefin	addition product	isolated yield (%)		
	 **4**	20		
	 **5**	48		
	 **6** **7** **8**	24	14	13
	 **9** **10**		19	20

a) Gives trans RCH=CHSO$_2$Ph with base b) Previously reported[9] c) Resists oxidation

Table II.

olefin	addition product	isolated yield (%)		
	 **11** **12** **13**	27	22	5
	 **14** **15** **16**	27	32	9

d) Previously reported[11,13] e) Oxidised to α-bromoketone f) Previously reported[12]
g) Gives trans RCH=CHSO$_2$Ph with base



Scheme D

arylsulphenyl chlorides add in an anti-Markownikoff fashion to t-butylethylene[15] and bulky nucleophiles are known to attack styrene oxide at the terminal carbon atom.[16] There are apparently no such restrictions on attack of the bromonium species by water as evidenced by the constitution of the bromohydrins obtained. (Scheme D).

From a preparative point of view the above results show no advantage over the very efficient U.V. catalysed addition of benzenesulphonyl iodide to olefins. This reagent is readily available through the reaction of sodium benzenesulphinate with iodine.[17] As the former is usually prepared by reduction of benzenesulphonyl chloride[18] and the latter by oxidation of iodides, the possibility of preparing benzenesulphonyl iodide directly by reaction of benzenesulphonyl chloride with an inorganic iodide, appeared to be worthy of investigation.

Early reports[19a,b] mention the formation of sodium benzenesulphinate and iodine when benzenesulphonyl chloride is added to a solution of sodium iodide in acetone (Scheme E). This appeared to be a suitable way of securing both reagents necessary for the preparation of benzenesulphonyl iodide.

$$PhSO_2Cl + 2NaI \rightarrow \underset{7}{PhSO_2Na} + I_2 + NaCl$$

Scheme E

Attempts to treat olefins directly with the reaction mixture did not lead to the formation of β-iodosulphones: a surprising result in view of the fact that iodine and sodium benzenesulphinate have been shown to react readily with olefins. We therefore reinvestigated the benzenesulphonyl chloride/sodium iodide system. The white solid which separated slowly from the initially homogenous reaction mixture was found to consist only of sodium benzenesulphinate and the use of slightly more than 3 equivalents of sodium iodide was necessary for 100% yield of the salt (Table III). The dark solution obtained after filtration and addition of pentane yielded a black solid which was filtered and extracted with chloroform. Removal of the chloroform gave a dark solid which was recrystallised from acetone giving black hygroscopic lustrous needles. The product readily evolved acetone on gentle heating. N.M.R. dosage of the freshly prepared product indicated six moles of acetone to be contained in each mole of complex. On stronger heating iodine monochloride was evolved, characterised by its boiling point (found 97–100°, Lit.[20] 97·4°), and demonstration of the presence of chloride and iodide in an aqueous solution. These facts have led us to formulate the crystalline product as **17**: the stoichiometry of the reaction is indicated in Scheme F. The complex proved to be too unstable to obtain an acceptable elemental analysis.

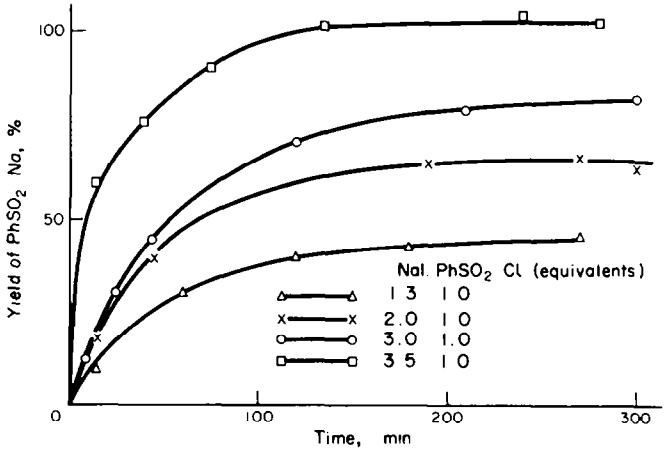
$$PhSO_2Cl + 3NaI \xrightarrow{\text{acetone}} (NaI)_2ICl(C_3H_6O)_6.$$

17

Scheme F

An aqueous solution of **17** is rapidly decolourised by thiosulphate hence providing an explanation of the previous erroneous assumption of the presence of iodine.[19a] Compound **17**, unlike iodine monochloride is not reactive towards olefins. A nucleophilic species I_2Cl^- [21] might be responsible for this. Admixture of aqueous solutions of **17** and sodium benzenesulphinate leads to instantaneous formation of

Table III.



benzenesulphonyl iodide, isolated as the pure product in 79% yield. Reactions F and G open the way to an economical synthesis of benzenesulphonyl iodide starting from benzenesulphonyl chloride and sodium iodide. The overall reaction is thus as represented in Scheme H. Complex **17** is a convenient precursor to benzenesulphonyl iodide being stable for periods of several months at 0°C in a sealed container. Although the rate of acetone loss is appreciable at room temperature this does not appear to effect the efficiency of the complex.

$$\mathbf{17} + PhSO_2Na \longrightarrow PhSO_2I$$

Scheme G

$$PhSO_2Cl + NaI \longrightarrow PhSO_2I + NaCl$$

Scheme H

EXPERIMENTAL

I.R. spectra were recorded with a Perkin Elmer 599 spectrometer either as the neat liquid or in chloroform solution, as stated. Mass spectra were recorded using a Varian Mat C.H.7. mass spectrometer. ^1H N.M.R. spectra were obtained using a Varian E.M. 390 model operating at 90 MHz. Chemical shifts were measured in deuterochloroform solution relative to TMS as internal standard. Melting points were taken using a Büchi capillary melting point apparatus and are uncorrected. Microanalyses were carried out by the staff of the Service Central de Microanalyse: I.C.S.N., 91190 Gif-sur-Yvette. (C, H, N, S, Br, Cl) and 43 boulevard du 11 novembre 1918, 69621 Villeurbanne (I). Acetone was dried before use by passage through a column of neutral alumina. All solvents were distilled before use. Sodium benzenesulphinate (Aldrich, Europe Division) and benzenesulphonyl chloride (Prolabo) were used without prior purification.

General technique for olefin halosulphonylation

To a solution of the olefin (10 mmoles) in acetone (75 ml) containing sodium benzenesulphinate (1.64 g, 10 mmoles, maintained in suspension by vigorous stirring) was added the halogen (10 mmoles) over a period of 20 mins. The mixture was stirred for 24 h. with protection from light at ambient temperature. The acetone was removed at reduced pressure and the residue extracted with ether (3 × 25 ml). The combined organic extracts were washed with 5% aqueous sodium metabisulphite (15 ml), 5% aqueous sodium bicarbonate (15 ml) distilled water (15 ml) and dried over anhydrous magnesium sulphate. Filtration and removal of the solvent under reduced pressure gave the crude product mixture from which the pure components were obtained by column chromatography on silica with protection from light (for yields see Tables I and II.)

Trans-1-*Benzenesulphonyl-2-iodocyclohexane* **4**. Colourless needles, mpt 63–6° (ether/pentane). (Found: C, 41.10; H, 4.34; S, 9.01; Calc.: C, 41.16; H, 4.32; S, 9.15%.) ν_{max}(neat): 1445, 1310, 1150, 1080 cm^{-1}. *m/e*: 350(M^+), 223, 209, 156, 143. ^1H NMR: 1.25–2.55 (m, 8H), 3.40 (broadened quartet, J = 5.0 Hz, 1H), 5.10 (broadened quartet, J = 5.0 Hz, 1H), 7.40–8.05 (m, 5H).

1-*Benzenesulphonyl-2-iodooctane* **5**. Pale yellow unstable oil. ν_{max}(neat): 1445, 1310, 1150, 1085 cm^{-1}. *m/e*: 380 (M^+), 253, 239, 143, 125, 111. ^1H NMR.: 0.90 (distorted triplet, J = 5.0 Hz, 3H), 1.05–2.15 (m, 10H), 3.50–4.00 (m, 2H), 4.30–4.65 (m, 1H), 7.45–7.80 (m, 3H), 7.85–8.10 (m, 2H).

1-*Benzenesulphonyl-2-iodo-2-phenylethane* **6**. Colourless needles, mpt. 128–30° decomp. (ether). (Found: C, 45.26; H, 3.52; I, 33.70; S, 8.50; Calc.: C, 45.18, H, 3.52; I, 34.09; S, 8.61%.). ν_{max}($CHCl_3$): 1445, 1315, 1135, 1075 cm^{-1}. *m/e*: 245 ($M^+ - 1$), 181, 141, 104. ^1H NMR: 3.90–4.60 (m, 2H), 5.60 (dd, J = 10.5 Hz, J′ = 5.0 Hz, 1H), 7.00–7.70 (m, 10H).

1-*Benzenesulphonyl-2-phenyl-2-propanol* **9**. Colourless needles, mpt. 97–100° (ether). (Found: C, 65.09; H, 5.81; S, 11.69: Calc.: C, 65.19; H, 5.83; S, 11.60%.) ν_{max}($CHCl_3$): 3580, 3300, 1300, 1150, 1075 cm^{-1}. *m/e*: 276 (M^+), 261, 183, 141. ^1H NMR: 1.70 (s, 3H), 3.60–(d, J = 13.5 Hz, 1H), 3.80 (d, J = 13.5 Hz, 1H), 4.60 (s, removable with D_2O, 1H), 7.05–7.70 (m, 10H).

2-*Phenyl-3-benzenesulphonyl-1-propene* **10**. Colourless rods, mpt. 107–8° (ether). (Found: C, 69.77, H, 5.53; S, 12.49; Calc.: C, 69.74, H, 5.46; S, 12.41%.) ν_{max}($CHCl_3$): 3015, 1640, 1300, 1140 cm^{-1}. *m/e*: 258 (M^+), 194, 179, 117. ^1H NMR.: 4.25 (s, 2H), 5.25 (s, 1H), 5.60 (s, 1H), 7.25 (s, 5H), 7.30–7.70 (m3H), 7.80 (dd, J = 8.0 Hz, J′ = 2.0 Hz-, 2H).

1-*Benzenesulphonyl-2-bromo-2-phenylethane* **11**. Long colourless needles, mpt. 90, 5–91.5° (ether) (lit.[13] 98–101°). (Found: C, 51.73; H, 4.04; Br, 24.38, S, 9.80; Calc.: C, 51.70; H, 4.03; Br, 24.57; S, 9.86%.) ν_{max}($CHCl_3$): 1445, 1320, 1140, 1075, 680 cm^{-1}. *m/e*: 326, 324 (M^+), 245, 181, 141, 104. ^1H NMR.: 4.10 (distorted doublet, J = 7.5 Hz, 2H), 5.40 (t, J = 7.5 Hz, 1H), 7.10–7.80 (m, 10H).

1-*Benzenesulphonyl-2-bromooctane* **14**. Colourless oil. ν_{max}(neat): 1445, 1310, 1145, 1085, 685 cm^{-1}. *m/e*: 253 (M^+ − Br), 191, 193, 115, 97. ^1H NMR: 0.75–1.05 (distorted triplet, 3H), 1.10–2.30 (m, 10H), 3.40–3.90 (m, 2H), 4.15–4.50 (m, 1H), 7.20–8.00 (m, 10H).

General technique for dehydrohalogenation of β-halosulphones **5, 6, 11, 14**

Triethylamine (100 mg, excess) was added to a solution of the β-halosulphone (1 mmole) in methylene chloride (10 ml) and the mixture allowed to stand at ambient temperature for 24 h. Washing the mixture with 5% aqueous hydrochloric acid (10 ml), distilled water (10 ml) and 5% aqueous sodium bicarbonate followed by drying, filtration and removal of the solvent under reduced pressure gave the *trans*-vinylsulphones, pure by NMR (yield: R = Ph, X = I 92%, X = Br 99%; R = n-hexyl, X = I 99%, X = Br 75%).

trans-*Benzenesulphonylstyrene* **8**. mpt 75–6° (lit.[10] 75–6°)

trans-*Benzenesulphonyl-1-octene*. Colourless oil. ν_{max}(neat): 3060, 1645, 1320, 1145, 965 cm^{-1}. *m/e*: 252 (M^+), 250, 195, 169, 143, 125, 110. NMR: 0.65–1.00 (distorted triplet, 3H), 1.10–1.75 (m, 8H), 2.05–2.45 (m, 2H), 6.20–6.50 (broadened doublet, J = 16.0 Hz, 1H), 8.00 (dt, J = 16.0 Hz, J′ = 7.0 Hz, 1H), 8.50–8.65 (m, 3H), 9.00–9.25 (m, 2H).

General technique for oxidation of bromohydrins **12, 15**

To a solution of the pure bromohydrin (0.80 mmole) in methylene chloride (20 ml) was added anhydrous sodium acetate (400 mg) and pyridinium chlorochromate (400 mg, excess) and the mixture stirred at ambient temperature for 6 h. After addition of ether (40 ml) and filtration of the black mixture through a short pad of silica followed by washing the residue with ether (40 ml) the crude product was obtained by removal of solvent at reduced pressure. Preparative thick layer chromatography gave the pure α-bromoketone (yield: R = Ph, 43%) or the α-bromoketone contaminated by roughly 1% (NMR) of the isomeric α-bromoaldehyde (yield: R = n-hexyl, 22%). No other identifiable products were obtained.

α-*Bromoacetophenone* identical with an authentic sample

1-*Bromo-2-octanone*[12] colourless oil. ν_{max}($CHCl_3$): 1740, 750 cm^{-1}. *m/e*: 191, 193 ($M^+ - 15$), 114. ^1H NMR: 9.90 (distorted triplet, J = 6.0 Hz, 3H), 1.10–1.85 (m, 8H), 2.70 (t, J = 7.0 Hz, 2H), 3.85 (s, 2H) 9.45 (d, J = 3.0 Hz – very small absorption corresponding to 2-bromooctanal contaminating sample.

Preparation of complex **17**

Rapid addition of benzenesulphonyl chloride (6.90 g, 39 mmoles) to a stirred solution of sodium iodide (20.50 g, 137 mmoles) in acetone (200 ml) resulted in an immediate

reddish brown colouration and the slower formation of a white precipitate. After 3 h at ambient temperature the mixture was filtered, washing the residue with acetone (2 × 30 ml), to give pure sodium benzenesulphinate (6.60 g, Yield: quantitative). Pentane (400 ml) was added to the filtrate and the resultant voluminous black precipitate filtered and triturated with methylene chloride (3 × 75 ml) to give a brown solution leaving behind a grey residue (2.90 g) shown to be crude sodium iodide. Evaporation of the solution at reduced pressure gave a dark powdery solid which was recrystallised rapidly from acetone under a nitrogen atmosphere to give the complex **17** as hygroscopic lustrous black needles (19.40 g, yield: 61%.)) Gentle heating caused loss of acetone from the solid which was best stored at 0°C under a slight positive pressure of dry nitrogen. The spectral data of this complex are identical with those of acetone.

Preparation of benzenesulphonyl iodide using complex **17**

A solution of complex **17** (5.38 g, 6.7 mmoles) in distilled water (20 ml) was added rapidly to a solution of sodium benzenesulphinate (1.31 g) in distilled water (20 ml). The instantaneously formed precipitate was filtered and the cream solid thus obtained dried *in vacuo* in darkness (1.41 g, yield: 79%). One recrystallisation from carbon tetrachloride gave large yellow needles mpt. 45–6° (Lit.[22] 44–5°).

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