

## Redox-transfer. Part VII.<sup>1</sup> Addition of Ethylene and Butadiene to Functionally Substituted Aromatic Sulphonyl Chlorides

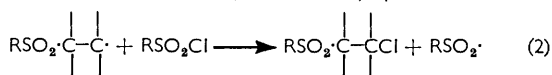
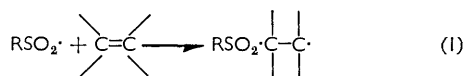
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Application of the copper chloride-catalysed addition of substituted aromatic sulphonyl chlorides to ethylene and butadiene is extended to sulphonyl chlorides carrying bromine, carboxy-, chloromethyl, chlorosulphonyl, and 2-chloroethylsulphonyl substituents. Several ethylene adducts are further transformed by chlorosulphonation, dehydrochlorination, and oxidation of a methyl to a carboxy-group.

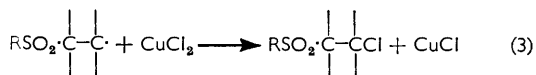
The *cis-trans*-isomerisation of but-2-ene by toluene-*p*-sulphonyl chloride at 100° is discussed. The isomerisation has a radical-chain character, is strongly retarded by chloride ions, and is completely inhibited by norbornadiene.

THE redox-transfer addition of sulphonyl chlorides to vinylic monomers and other olefins has proved to be a convenient method for the preparation of 2-chloroalkyl sulphones and their dehydrohalogeno-derivatives.<sup>2</sup> We here report an extension of this reaction to functionally substituted sulphonyl chlorides. At the same time, some observations are made about an earlier reported sulphonyl chloride-catalysed *cis-trans* isomerisation of but-2-ene which demonstrates its chain character.

**Reversibility of Sulphonyl Radical Addition.**—The addition of unactivated sulphonyl chlorides to olefins under conventional (*e.g.* peroxide) catalysis is successful only in the case of strained olefins such as norbornene, norbornadiene,<sup>3</sup> and  $\alpha$ - or  $\beta$ -pinene.<sup>4</sup> Because of the strained double bond, sulphonyl radicals are added largely irreversibly, resulting in this case in reactive compound radicals, which sustain the reaction chain by a fast abstraction of chlorine from sulphonyl chloride:



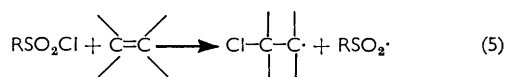
Addition to unstrained olefins proceeds less readily,<sup>5</sup> for now reaction (1) is reversible, and (2) is not fast enough to shift the highly unfavourable equilibrium.



Redox-transfer replaces reaction (2) by reactions (3) and (4); reaction (3), which is a very fast process, is apparently capable of shifting equilibrium (1) more to the right. Nevertheless, it cannot prevent the *cis-trans*-isomerisation of but-2-ene during its copper chloride-catalysed additions to sulphonyl chlorides.

If but-2-ene is heated with a sulphonyl chloride in the absence of any metal salt, extensive *cis-trans*-isomerisation also takes place, although no adduct is being formed. Even large quantities of styrene, which is a much better scavenger for sulphonyl radicals than but-2-ene, do not inhibit this isomerisation,<sup>2a</sup> although small amounts of butadiene were reported to do for the analogous thiyl radical-sensitised process.<sup>6</sup> Huyser and Kellogg<sup>7</sup> have presented evidence for a largely irreversible addition of thiyl radicals to norbornene. Furthermore, the same olefin copolymerises with sulphur dioxide in a way which indicates an irreversible addition of sulphonyl radicals to the double bond.<sup>8</sup> We found accordingly that norbornadiene was a very good inhibitor for the *cis-trans*-isomerisation, obviously owing to its very fast and irreversible capture of sulphonyl radicals. The isomerisation has thus the characteristics of a radical-chain reaction.

Sulphonyl radicals are possibly generated *via* a very slow thermal decomposition of sulphonyl chloride, or, alternatively, by a reaction with olefin, in much the same way as the spontaneous generation of radicals in olefin chlorinations:<sup>9</sup>



In the presence of norbornadiene, sulphonyl radicals are subsequently irreversibly scavenged, which precludes isomerisation *via* reaction (6). We have found that,



unexpectedly, chloride ions also suppress the isomerisation to a large extent (see Table 1). At this stage, we can only speculate about this strong inhibitory effect. Anions are known to combine with strongly electro-negative radicals to give anion-radicals,<sup>10</sup> and it is possible that chloride ions act in the same way with

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<sup>2</sup> E. S. Huyser and R. M. Kellogg, *J. Org. Chem.*, 1965, **30**, 3003.

<sup>3</sup> N. L. Zutty and C. W. Wilson, *Tetrahedron Letters*, 1963, 2181.

<sup>4</sup> M. L. Poutsma, *J. Amer. Chem. Soc.*, 1963, **85**, 3511; 1965, **87**, 2161, 2172; F. S. Dyachkovskii and A. E. Shilov, *Russ. Chem. Rev.*, 1966, **35**, 300.

<sup>5</sup> D. E. Bartak, W. C. Danen, and M. D. Hawley, *J. Org. Chem.*, 1970, **35**, 1206.

<sup>1</sup> Part VI, A. Orochov, M. Asscher, and D. Vofsi, *J. Chem. Soc. (B)*, 1969, 255.

<sup>2</sup> (a) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 1964, 4962; (b) W. E. Truce, C. T. Goralski, L. W. Christensen, and R. H. Bavry, *J. Org. Chem.*, 1970, **35**, 4217.

<sup>3</sup> S. J. Cristol and J. A. Reeder, *J. Org. Chem.*, 1961, **26**, 2182.

<sup>4</sup> M. Asscher, unpublished results.

<sup>5</sup> E. C. Ladd, U.S.P. 2,521,068/1950; 2,573,580/1951; M. S. Kharasch and R. A. Mosher, *J. Org. Chem.*, 1952, **17**, 453.

TABLE 1

Isomerisation of *cis*-but-2-ene by sulphonyl chloride \*

	CuCl <sub>2</sub> (mol %) <sup>a</sup>	Triethyl- ammonium chloride (mol %) <sup>a</sup>	Norbornadiene (mol %) <sup>a</sup>	% <i>trans</i> - But-2-ene after reaction <sup>b</sup>
1				60
2	2			40
3	2	3		27
4	2	6		9
5	2	12		8
6			4	0
7			2	0
8		6		4

\* *cis*-But-2-ene (25 mmol) and toluene-*p*-sulphonyl chloride (25 mmol) in methylene chloride (2.8 ml) and acetonitrile (1.9 ml) sealed in tubes after degassing; 7 h at 100°.

<sup>a</sup> Based on sulphonyl chloride. <sup>b</sup> The balance is *cis*-but-2-ene.

sulphonyl radicals ( $\text{Cl}^- + \text{RSO}_2\cdot \rightleftharpoons \text{RSO}_2\text{Cl}^-$ ), thus deactivating them towards addition to an electron-rich olefinic centre.

*Addition of Sulphonyl Chlorides to Ethylene and Butadiene.*—Some additions of ethylene and butadiene to aromatic sulphonyl chlorides under copper chloride catalysis have been described earlier.<sup>2a</sup> An extension of this reaction to functionally substituted sulphonyl chlorides gave generally high yields (see Tables 2 and 3). In many cases the crude product could be used for subsequent transformations without any further purification.

## EXPERIMENTAL

*Materials.*—Anhydrous copper(II) chloride, triethylammonium chloride, and acetonitrile were as specified in

TABLE 2

Addition of sulphonyl chlorides  $\text{RC}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$  (0.5 mol) to ethylene (2 mol)

No.	R	CuCl <sub>2</sub> *	Wt. of solvent (g)		T/°C	t/h	Yield (%) (crude)	M.p. (°C) (pure)
			MeCN	CH <sub>2</sub> Cl <sub>2</sub>				
1	<i>p</i> -Br	1.5	20	80	140	12	94 <sup>a</sup>	109—111 (from Pr <sup>o</sup> OH) (lit. <sup>b</sup> 113°)
2	<i>p</i> -Me	1.5	20	80	140	12	95 <sup>a</sup>	80—81 (from Pr <sup>o</sup> OH) (lit. <sup>c</sup> 77—78°)
3	<i>p</i> -CH <sub>2</sub> Cl	1.5	20	80	140	12	90 <sup>a</sup>	85
4	2,4,5-Br <sub>3</sub>	1.5	20	80	140	16	80 <sup>a</sup>	125—126
5	<i>m</i> -SO <sub>2</sub> Cl †	3	40	160	120	8	80 <sup>d</sup> ‡	121—122 (from MeOH) (lit. <sup>e</sup> 119°)
6	<i>m</i> -CO <sub>2</sub> H	3	150	100	120	12	55 <sup>d</sup>	193—195 (from MeCN) (lit. <sup>e</sup> 189—190°)

\* Based on sulphonyl chloride (1.5 mol triethylammonium chloride for each mol of CuCl<sub>2</sub>). † Molar ratio of sulphonyl chloride to ethylene 1 : 8. ‡ The adduct is *m*-C<sub>6</sub>H<sub>4</sub>(SO<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>·Cl)<sub>2</sub>.

<sup>a</sup> Ref. 2a. <sup>b</sup> T. Nambara and N. Matsuhisa, *Yagaku Zasshi*, 1963, **83**, 642 (*Chem. Abs.*, 1963, **59**, 7411h). <sup>c</sup> J. Heyna and W. Riemenschneider, Ger.P. 887,505/1953. <sup>d</sup> This work.

TABLE 3

Addition of sulphonyl chlorides  $\text{RC}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$  (0.1 mol) to butadiene (0.11 mol) at 100°

No.	R	CuCl <sub>2</sub> (mole %) <sup>*</sup>	Wt. of solvent (g)		t/h	Yield (%) (crude)	M.p. (°C) (pure)	Recryst. solvent
			MeCN	CH <sub>2</sub> Cl <sub>2</sub>				
1	<i>p</i> -Br <sup>a</sup>	1	1	20	1.5	79	85—86	Me <sub>2</sub> CO-C <sub>6</sub> H <sub>14</sub>
2	<i>p</i> -Me <sup>a</sup>	1	1	20	1.5	95	69—70	Pr <sup>o</sup> OH
3	<i>p</i> -CH <sub>2</sub> Cl <sup>a</sup>	1	1	20	2.4	92	78—79	Me <sub>2</sub> CO-C <sub>6</sub> H <sub>14</sub>
4	<i>m</i> -SO <sub>2</sub> Cl † ‡ <sup>b</sup>	4	10	30	1.5	92	187—188	MeCN
5	<i>m</i> -CO <sub>2</sub> H <sup>b</sup>	2	30	10	7	80	190—192	MeCN
6	<i>p</i> -CO <sub>2</sub> H § <sup>b</sup>	2	12	20	7	79	213—217	MeCN
7	<i>p</i> -NO <sub>2</sub> <sup>b</sup>	1	40	2	2	89	150—152	EtOH
8	<i>m</i> -SO <sub>2</sub> ·CH <sub>2</sub> ·CH <sub>2</sub> Cl <sup>b</sup>	1	30	5	5	70	123	EtOH

\* Based on sulphonyl chloride (1.5 mol triethylammonium chloride for each mol of CuCl<sub>2</sub>). † Molar ratio of sulphonyl chloride to butadiene 1 : 2.2. ‡ The adduct is *m*-C<sub>6</sub>H<sub>4</sub>(SO<sub>2</sub>·CH<sub>2</sub>·CH·CH·CH<sub>2</sub>·Cl)<sub>2</sub>. § Dissolved in bis-(2-methoxyethyl) ether (60 ml).

<sup>a</sup> Ref. 2a. <sup>b</sup> This work.

TABLE 4

Vinyl sulphones by dehydrochlorination of 2-chloroethylsulphones  $\text{RC}_6\text{H}_4\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$  (0.1 mol) in methylene chloride at 0° with triethylamine (0.15 mol)

No.	R	t/h	Yield (%)	
1	<i>p</i> -Br	6	95 <sup>*</sup>	B.p. (0.2 mmHg) 120—121° †
2	<i>p</i> -CH <sub>2</sub> Cl	1	94 <sup>*</sup>	B.p. (0.1 mmHg) 130°
3	2,4,5-Br <sub>3</sub>	1	95 <sup>*</sup>	M.p. 116—117°
4	<i>m</i> -SO <sub>2</sub> Cl ‡	1	83 ‡	†

\* After acidification and evaporation of solvent. † Lit.<sup>14</sup> 153—154° at 4 mmHg. ‡ See Experimental section.

ref. 2a. Methylene chloride was distilled and dried over calcium chloride. Ethylene and butadiene were Matheson C.P. products. Chlorosulphonic acid was freshly distilled before use. *p*-Chloromethylbenzenesulphonyl chloride, *p*-bromobenzenesulphonyl chloride, and *m*- and *p*-carboxybenzenesulphonyl chlorides were made according to refs. 11—14.

<sup>11</sup> J. Houben and T. Weyl, 'Methoden der Organischen Chemie,' Georg Thieme, Stuttgart, 1962, vol. 5/3, p. 746.

<sup>12</sup> F. Ullmann and J. Korselt, *Ber.*, 1907, **40**, 642.

<sup>13</sup> B. A. Everard and J. A. Mills, *J. Chem. Soc.*, 1950, 3386.

<sup>14</sup> S. Smiles and J. Stewart, *J. Chem. Soc.*, 1921, **119**, 1795.

N.m.r. spectra (Table 5) were taken for solutions in deuteriochloroform (tetramethylsilane as the internal standard) with a Varian HA 60 instrument. All products gave satisfactory analytical figures which are listed in Supplementary Publication No. SUP. 20445 (3pp., 1 microfiche).\*

**Sulphonyl Chlorides.**—(a) *m*-(2-Chloroethylsulphonyl)benzenesulphonyl chloride. 2-Chloroethyl phenyl sulphone (20.4 g) (for preparation see Table 2, no. 2), chlorosulphonic acid (60 g), and phosphorus pentoxide (8.5 g) were heated for 4 h at 110°. The cooled solution was then poured on crushed ice and extracted with methylene chloride. The extract was washed with water until free of sulphate, dried (CaCl<sub>2</sub>), and evaporated *in vacuo*. The residue, crystallised from acetone-hexane, gave crude *product*, which was recrystallised from benzene; m.p. 64–65°,  $\tau$  1.3–2.3 (4H, m, aromatic) and 7.2 (4H, m, SO<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>Cl).

(b) 2,4,5-Tribromobenzenesulphonyl chloride.<sup>15</sup> Chlorosulphonic acid (30 g) and 1,2,4-tribromobenzene (31.5 g)

**Additions of Butadiene.**—These are summarised in Table 3. An example follows.

**Bis-(4-chlorobut-2-enyl) *m*-phenylene disulphone.** Benzene-1,3-disulphonylchloride (27.6 g, 0.1 mol) in methylene chloride (30 g) was heated in an ampoule in the absence of air with butadiene (11.9 g, 0.22 mol) after addition of a solution of copper(II) chloride (536 mg) and triethylammonium chloride (824 mg) in acetonitrile (10 g), at 100° for 1.5 h. The ampoule was cooled in ice and the contents were diluted with cold ethanol (50 ml). The precipitate was filtered off, washed with cold ethanol, and dried; yield 30.4 g (92%).

**Vinyl Sulphones.**—Preparations are summarised in Table 4. An example follows.

***m*-Vinylsulphonylbenzenesulphonylchloride.** *m*-(2-Chloroethylsulphonyl)benzenesulphonyl chloride (30.4 g, 0.1 mol) was dissolved in benzene (150 ml) and treated with triethylamine (15 g, 0.15 mol) at 0° for 1 h. The amine hydrochloride formed was filtered off, and the filtrate freed from

TABLE 5

N.m.r. spectra ( $\tau$  values)

2-Chloroethyl sulphones (Table 2)

No.	Aromatic protons	SO <sub>2</sub> ·CH <sub>2</sub> ·CH <sub>2</sub> Cl	CH <sub>2</sub> Cl
1	2.18 (4H, s)	$\tau$ 6.0–6.7 (4H, m)	
3	2.2 (4H, q)	6.3 (4H, m)	5.3 (2H, s)
4	1.6 (1H, s), 1.9 (1H, s)	6.15 (4H, s)	

4-Chlorobut-2-enyl sulphones (Table 3)

	SO <sub>2</sub> ·CH <sub>2</sub> ·CH·CH·CH <sub>2</sub> Cl	SO <sub>2</sub> ·CH <sub>2</sub> ·CH·CH·CH <sub>2</sub> Cl	
1	6.03 (4H, m)	4.2 (2H, m)	
2	6.05 (4H, m)	4.2 (2H, m)	Me 7.6 (3H, s)
3	6.07 (4H, m)	4.23 (2H, m)	–CH <sub>2</sub> –Cl 5.33 (2H, s)

Vinyl sulphones (Table 4)

	SO <sub>2</sub> ·CH·CH <sub>2</sub>	
1	2.26 (4H, s)	3.0–4.0 (3H, m)
2	2.25 (4H, s)	3.0–4.0 (3H, q)
3	1.6 (1H, s), 1.9 (1H, s)	3.05–3.8 (3H, m)
4	1.3–2.2 (4H, m)	2.8–3.8 (3H, m)

were heated at 100° for 6 h. The cooled mixture was filtered through a glass sinter and the filtrate was poured on crushed ice. A solution of the precipitate in benzene was dried (CaCl<sub>2</sub>), and evaporated, leaving the *product* (34 g), m.p. 80–83°,  $\tau$  1.6 (1H, s) and 1.9 (1H, s).

**Additions of Ethylene.**—These are summarised in Table 2. An example follows.

**Bis-2-chloroethyl *m*-phenylene disulphone.** Benzene-1,3-disulphonyl chloride (69 g, 0.25 mol) in methylene chloride (80 g) was treated with ethylene (56 g, 2 mol) in the absence of air and in the presence of a solution of anhydrous copper(II) chloride (1 g, 7.5 mmol) and triethylammonium chloride (1.55 g, 11.25 mmol) in acetonitrile (20 g) for 8 h at 120°. After cooling and venting of unconverted ethylene, methanol (200 ml) was added. The mixture was cooled in ice and the precipitate was filtered off, washed with ice-cold methanol, and dried to give a white, crystalline powder (67 g, 81%).

\* See note about Supplementary Publications in Notice to Authors, No. 7, in *J. Chem. Soc. (A)*, 1970, Issue No. 20 (items less than 10 pp. will be supplied as full page copies).

benzene and excess of amine *in vacuo*. The remaining oil (22.2 g, 83%) could not be distilled *in vacuo* without decomposition.

**Oxidation of 2-Chloroethyl *p*-Tolyl Sulphone:** *p*-(2-Chloroethylsulphonyl)benzoic Acid.—Recrystallised 2-chloroethyl *p*-tolyl sulphone (21.8 g) was stirred vigorously with a solution of sodium dichromate (41 g) in water (90 ml). The mixture was heated to 80° and conc. sulphuric acid (100 g) was dropped slowly in, so that the temperature did not exceed 100°. After 1 h at 100° the suspension was cooled and poured into water (500 ml). The solid product was filtered off and washed with water and methanol to give the acid (23.1 g, 93%) as a white powder, m.p. 221–225° (lit.,<sup>16</sup> 219–220°).

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<sup>15</sup> M. V. Farrar, *J. Chem. Soc.*, 1960, 3063.<sup>16</sup> N. Shuriki and T. Nambara, *Chem. and Pharm. Bull. (Japan)*, 1963, **11**, 178.