Redox-transfer. Part VII.¹ 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.² 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,³ and α - or β -pinene.⁴ 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:

$$RSO_{2} \cdot + C = C \longrightarrow RSO_{2} \cdot C - C \cdot (1)$$

$$RSO_{2} \cdot C - C \cdot + RSO_{2}C I \longrightarrow RSO_{2} \cdot C - CC I + RSO_{2} \cdot (2)$$

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

$$RSO_2 \cdot C - C \cdot + CuCl_2 \longrightarrow RSO_2 \cdot C - CCl + CuCl \qquad (3)$$

$$CuCl + RSO_2Cl - CuCl_2 + RSO_2^{\bullet}$$
(4)

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-transisomerisation of but-2-ene during its copper chloridecatalysed additions to sulphonyl chlorides.

¹ Part VI, A. Orochov, M. Asscher, and D. Vofsi, J. Chem.

Part V1, A. Orocnov, M. Assenter, and D. Vola, J. Cons., Soc. (B), 1969, 255.
² (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.
³ S. J. Cristol and J. A. Reeder, J. Org. Chem., 1961, 26, 2182.
⁴ M. Asscher, unpublished results.
⁵ E. C. Ladd, U.S.P. 2,521,068/1950; 2,573,580/1951;
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M. S. Kharasch and R. A. Mosher, J. Org. Chem., 1952, 17, 453.

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,^{2a} although small amounts of butadiene were reported to do for the analogous thivl radical-sensitised process.⁶ Huyser and Kellogg⁷ 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.⁸ 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: 9

$$RSO_{2}CI + C = C \longrightarrow CI - C - C + RSO_{2}$$
 (5)

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

$$RSO_2 + MeCH:CHMe \Longrightarrow RSO_2 + CHMe + CHMe$$
 (6)

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 electronegative radicals to give anion-radicals,¹⁰ and it is possible that chloride ions act in the same way with

⁶ D. M. Graham, L. L. Mieville, and C. Sivertz, Canad. J. Chem., 1964, 42, 2339.

7 E. S. Huyser and R. M. Kellogg, J. Org. Chem., 1965, 30, 3003.

⁸ N. L. Zutty and C. W. Wilson, Tetrahedron Letters, 1963, 2181.

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.
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Chem., 1970, 35, 1206.

J.C.S. Perkin I

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2 3 4

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TABLE 1

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

CuCl ₂ (mol %) ^a	Triethyl- ammonium chloride (mol %) ^a	Norbornadiene (mol %) ª	% trans- But-2-ene after reaction ^b
			60
2			40
2	3		27
2	6		9
2	12		8
		4	0
		2	0
	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°.

" Based on sulphonyl chloride. " The balance is cis-but-2ene.

sulphonyl radicals $(Cl^- + RSO_2 \rightarrow RSO_2Cl^-)$, 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.2a. 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 RC_6H_4 ·SO₂Cl (0.5 mol) to ethylene (2 mol)

			Wt. of se	olvent (g)			Viold (0/)	
No.	R	CuCl ₂ *	MeCN	CH ₂ Cl ₂	T/°C	t/h	(crude)	M.p. ($^{\circ}$ C) (pure)
1	p-Br	1.5	20	80	140	12	94 ª	109—111 (from Pr ⁱ OH) (lit. ⁵ 113°)
2	∕p-Me	1.2	20	80	140	12	95 a	80-81 (from Pr ⁱ OH) (lit., ° 77-78°)
3	p-CH,Cl	1.5	20	80	140	12	90 a	85
4	2,4,5-Br ₃	1.5	20	80	140	16	80 a	125 - 126
5	m-SO,Cl †	3	40	160	120	8	80 ª ±	121—122 (from MeOH) (lit., e 119°)
6	$m-CO_{2}H$	3	150	100	120	12	55 ª '	193—195 (from MeCN) (lit., 189—
	-							190°)

* Based on sulphonyl chloride (1.5 mol triethylammonium chloride for each mol of CuCl₂). † Molar ratio of sulphonyl chloride to ethylene 1:8. \ddagger The adduct is $m-C_6H_4(SO_2 \cdot CH_2 \cdot CH_2 \cdot CI)_2$.

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

TABLE 3

Addition of sulphonyl chlorides RC_6H_4 ·SO₂Cl (0·1 mol) to butadiene (0·11 mol) at 100°

		CuCl.	Wt. of s	olvent (g)		Yield (%)	M.p. (°C)	Recryst.
No.	\mathbf{R}	(mole %) *	MeCN	CH ₂ Cl ₂	t/h	(crude)	(pure)	solvent
1	p-Br ª	1	1	20	1.5	79	8586	Me ₂ CO-C ₆ H ₁₄
2	<i>p</i> -Me	1	1	20	1.5	95	6970	Pr ⁱ ÕH
3	· p-CH₂Cl ª	1	1	20	$2 \cdot 4$	92	78-79	Me ₂ CO-C ₆ H ₁₄
4	$m-SO_2Cl \dagger \ddagger b$	4	10	30	1.5	92	187	MeCN
5	$m - CO_2 H^{b}$	2	30	10	7	80	190 - 192	MeCN
6	p-CO₂H § ^b	2	12	20	7	79	213 - 217	MeCN
7	p-NO2 b	1		40	2	89	150 - 152	EtOH
8	m-SO2·CH2·CH2Cl b	1		30	5	70	123	EtOH

* Based on sulphonyl chloride (1.5 mol triethylammonium chloride for each mol of $CuCl_2$). \dagger Molar ratio of sulphonyl chloride to butadiene $1:2\cdot2$. \ddagger The adduct is $m-C_6H_4(SO_2\cdot CH_2\cdot CH\cdot CH_2Cl)_2$. § Dissolved in bis-(2-methoxyethyl) ether (60 ml).

^a Ref. 2a. ^b This work.

TABLE 4

Vinyl sulphones by dehydrochlorination of 2-chloroethylsulphones RC_6H_4 ·SO₂·CH₂·CH₂Cl (0·1 mol) in methylene chloride at 0° with triethylamine (0.15 mol)

			Yield	
No.		t/h	(%)	
1	p-Br	6	95 *	B.p. (0·2 mmHg) 120—
				121° †
2	p-CH₂Cl	1	94 *	B.p. (0·1 mmHg) 130°
3	2,4,5-Br ₃	1	95 *	M.p. 116—117°
4	m-SO₂Cl t	1	83 ‡	‡ ⁻

* After acidification and evaporation of solvent. † Lit.,¹⁶ 153—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, pbromobenzenesulphonyl chloride, and m- and p-carboxybenzenesulphonyl chlorides were made according to refs. 11-14.

¹¹ J. Houben and T. Weyl, 'Methoden der Organischen Chemie,' Georg Thieme, Stuttgart, 1962, vol. 5/3, p. 746. ¹² F. Ullmann and J. Korselt, *Ber.*, 1907, **40**, 642. ¹³ B. A. Everard and J. A. Mills, *J. Chem. Soc.*, 1950, 3386.

- 14 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 (CaCl₂), and evaporated in vacuo. The residue, crystallised from acetone-hexane, gave crude product, which was recrystallised from benzene; m.p. 64-65°, 7 1.3-2.3 (4H, m, aromatic) and 7.2 (4H, m, SO₂·CH₂·CH₂Cl).

(b) 2,4,5-Tribromobenzenesulphonyl chloride.¹⁵ 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-envl) 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 (τ	values)	
		2-Chloroethyl sulphones (Table 2)	
No.	Aromatic protons	$SO_2 \cdot CH_2 \cdot CH_2 Cl$		
1	2·18 (4H, s)	τ 6·0—6·7 (4H, m)		
3 4	2·2 (4H, q) 1·6 (1H, s), 1·9 (1H, s)	6·3 (4H, m) 6·15 (4H, s)	CH ₂ Cl 5·3 (2H, s)	
		4-Chlorobut-2-enyl sulphone	s (Table 3)	
		SO ₂ ·CH ₂ ·CH:CH·CH ₂ Cl	SO ₂ ·CH ₂ ·CH:CH·CH ₂ Cl	
1		6.03 (4H, m)	4·2 (2H, m)	
2	2·4 (4H, q)	6.05 (4H, m)	4.2 (2H, m)	Me 7.6 (3H, s)
3	2·23 (4H, q)	6·07 (4H, m)	4·23 (2H, m)	$-CH_2$ -Cl 5·33 (2H, s)
		Vinyl sulphones (Tabl	le 4)	
		SO ₂ ·CH:CH ₂		
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)	$2 \cdot 8 - 3 \cdot 8 (3H m)$		

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 (CaCl₂), and evaporated, leaving the product (34 g), m.p. 80-83°, τ 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-1,3disulphonyl 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(11) 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-Chloro- $\it ethyl sulphonyl) benzoic \ Acid. --- Recrystallised \ 2-chloroethyl$ 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.,16 219-220°).

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