

954. *Chlorine-activation by Redox-transfer. Part IV.¹ The Addition of Sulphonyl Chlorides to Vinylic Monomers and Other Olefins.*

By M. ASSCHER and D. VOFSI.

The copper chloride-catalysed addition of sulphonylchlorides to vinylic monomers and other olefins provides a general and convenient synthesis of β -chloro-sulphones. Telomer formation is not observed.

A free-radical chain-mechanism is suggested for the reaction, which is similar to that of addition of carbon tetrachloride and chloroform to olefins, and in which the catalyst participates in the propagation as a chlorine-atom transfer agent (redox-transfer).

The reversibility of addition of sulphonyl radicals to unconjugated olefins is demonstrated for the case of but-2-ene, where *cis-trans*-isomerisation of the olefin accompanies addition. With increasing catalyst concentrations, the rate of isomerisation falls, while that of adduct formation is increased, which is in accord with the suggested mechanism. An uncatalysed, slower *cis-trans*-isomerisation of but-2-ene takes place concurrently.

Chloromethanesulphonyl chloride, in the presence of excess of oct-1-ene and one mole-% of cupric chloride, is largely decomposed into methylene chloride and sulphur dioxide. With styrene, on the other hand, an adduct with undecomposed sulphonyl chloride is formed.

It is suggested that copper chloride will generally catalyse the decomposition of sulphonyl chloride into alkyl or aryl chloride and sulphur dioxide, thereby allowing a more selective reaction than the uncatalysed, purely thermal process. A redox-transfer mechanism for this decomposition is suggested.

WHILE the addition of sulphonyl chlorides to olefins by a free-radical mechanism has been described occasionally, the reaction appears to be far from general.² *p*-Chlorobenzene-sulphonyl chloride reacts with aliphatic terminal olefins.³ With ethylene at 100 atmospheres,³ both 1:1 adducts and telomers are obtained. Benzenesulphonyl chloride is reported to be less reactive, giving much smaller conversions, and only a trace of 1:1 adduct.³ *N*-Chlorosulphonylphthalimide also gives an adduct with terminal olefins.⁴ *p*-Toluenesulphonyl chloride can be added to norbornene and norbornadiene; the latter gives a nortricyclene derivative as the adduct.⁵ Trichloromethanesulphonyl chloride reacts through elimination of sulphur dioxide, adding the elements of carbon tetrachloride across the double bond. It is highly reactive, yielding 1:1 adducts even with styrene.⁶ Recently it was reported that chloro- and dichloro-methanesulphonyl chloride behave similarly, their reactivity decreasing with the number of chlorine atoms.⁷ Methanesulphonyl chloride⁷ and ethanesulphonyl chloride⁸ do not react with olefins. The reactions²⁻⁸ mentioned are induced by conventional sources of free radicals, *e.g.*, peroxides, azo-compounds, or ultraviolet light.

We have now⁹ found that the addition of substituted and unsubstituted aliphatic and aromatic sulphonyl chlorides to unconjugated olefins and vinylic monomers can be brought about smoothly with copper(I or II) chloride as the catalyst (see Table I). Iron(II or III) chloride is much less effective, giving only very poor yields of adduct.

¹ Part III, Asscher and Vofsi, *J.*, 1963, 3921.

² Walling, "Free Radicals in Solution," Wiley, New York, p. 330.

³ Ladd, U.S.P. 2,521,068/1950, 2,573,580/1951.

⁴ Kharasch and Mosher, *J. Org. Chem.*, 1952, 17, 453.

⁵ Cristol and Reeder, *J. Org. Chem.*, 1961, 26, 2182.

⁶ Ladd and Kiley, U.S.P. 2,606,213/1952.

⁷ Goldwhite and Harris, *Chem. and Ind.*, 1962, 172.

⁸ Kharasch and Zavist, *J. Amer. Chem. Soc.*, 1951, 73, 964.

⁹ Asscher, *Chem. and Ind.*, 1964, 32.

TABLE 1.

Reaction of sulphonyl chlorides (0.1 mole) with olefins, with cupric chloride as the catalyst (1.5 equivalent triethylammonium chloride is added on each eq. cupric chloride). Cuprous chloride gives identical results.

Run no.	Olefin	Molar ratio *	CuCl ₂ (mole %) †	Solvent (g.)	Temp.	Hr.	Product	Yield (%) †	Note
Benzenesulphonyl Chloride									
1	Styrene	1.1	1	MeCN, 4	95—110	2	PhSO ₂ CH ₂ ·CHClPh	86	1
2	Butadiene	2	1	CH ₂ Cl ₂ , 15; MeCN, 2	100	4	PhSO ₂ CH ₂ ·CH:CH·CH ₂ Cl	94	
3	Acrylonitrile	2	1	—	85—112	16	PhSO ₂ CH ₂ ·CHCl·CN	90	1, 2
4	Ethylene	7	3	CH ₂ Cl ₂ , 20; MeCN, 2	100	24	PhSO ₂ CH ₂ ·CH ₂ Cl	97	3
5	But-1-ene	2	2	CH ₂ Cl ₂ , 25; MeCN, 2	100	23	PhSO ₂ CH ₂ ·CHCl·C ₂ H ₅	86	4
6	But-2-ene:	see Table 2.							
<i>p</i> -Chlorobenzenesulphonyl Chloride									
7	Styrene	1.1	1	MeCN, 4	95—110	2	<i>p</i> -ClC ₆ H ₄ SO ₂ CH ₂ ·CHClPh	87	1
8	Acrylonitrile	2	1	—	85—112	16	<i>p</i> -ClC ₆ H ₄ SO ₂ CH ₂ ·CHClCN	76	1, 2
<i>p</i> -Nitrobenzenesulphonyl Chloride									
9	Ethylene	7	3	CHCl ₃ , 30; MeCN, 1	110	20	<i>p</i> -NO ₂ C ₆ H ₄ SO ₂ CH ₂ ·CH ₂ Cl	66	3
Methanesulphonyl Chloride									
10	Butadiene	2	1	CH ₂ Cl ₂ , 15; MeCN, 2	100	4	MeSO ₂ CH ₂ ·CH:CH·CH ₂ Cl	94	
11	Acrylonitrile	4	1	—	100	24	MeSO ₂ CH ₂ ·CHCl·CN	70	2
12	Me Acrylate	4	1	MeCN, 3	110	40	MeSO ₂ CH ₂ ·CHCl·CO ₂ Me	71	
Chloromethanesulphonyl Chloride									
13	Styrene	2	1	MeCN, 4	105	2	CH ₂ ClSO ₂ CH ₂ ·CHClPh	60	1, 3
14	Oct-1-ene	2	1	MeCN, 4	~80	8	CH ₂ Cl ₂	86	1, 3

* Molar ratio olefin : sulphonyl chloride. † Calculated on sulphonyl chloride charged.

Notes: (1) Reaction under reflux. (2) Catalyst dissolved in acrylonitrile. (3) See Experimental section. (4) Yield calculated on converted sulphonyl chloride: 97%.

TABLE 2.

Reaction between but-2-ene (0.05 mole) and benzenesulphonyl chloride (0.025 mole) in methylene chloride (10 g.) and acetonitrile (2 g.), at 100°, with anhydrous cupric chloride * as the catalyst.

Run no.	But-2-ene charged	CuCl ₂ (mole %) †	Hr.	Conversion (%) ‡	<i>trans</i> -But-2-ene after reaction (%) §	Remarks
1	<i>cis</i>	1	24	14	68	
2	<i>trans</i>	1	24	12	67	
3	<i>cis</i>	5	24	51	66	
4	<i>cis</i>	1	8	trace	56	
5	<i>cis</i>	5	8	22	44	
6	<i>cis</i>	10	8	30	38	
7	<i>cis</i>	—	24	—	44	
8	<i>cis</i>	—	24	—	48	1.5 mole % NET ₃ ·HCl (calc. on PhSO ₂ Cl) added
9	<i>cis</i>	—	8	—	22	1.5 " " "
10	<i>cis</i>	—	8	—	25	7.5 " " "
11	<i>cis</i>	—	8	—	21	15 " " "
12	<i>cis</i>	—	24	—	48	1 mole % styrene (calc. on PhSO ₂ Cl) added
13	<i>cis</i>	—	24	—	36	10 " " "
14	<i>cis</i>	—	24	—	18	100 " " "

Runs nos. 9—11 are the blanks of nos. 4—6.

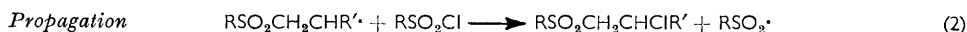
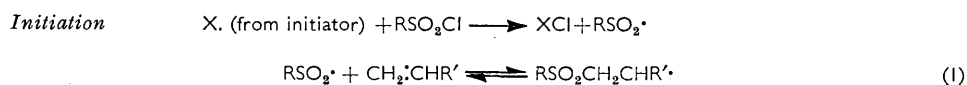
* A 50% molar excess of NET₃·HCl with respect to cupric chloride is added. † Calculated on sulphonyl chloride. ‡ Yield of adduct (mixture of diastereoisomers), calculated on PhSO₂Cl charged. Unconverted PhSO₂Cl is recovered. § The balance is *cis*-but-2-ene; determined by v.p.c., on a 5 m. column, packed with 15% *NN*-dimethylformamide on Chromosorb W, and cooled at -20°. This column adequately separates the three butenes. (Dr. J. Manassen, private communication.)

If the addition of sulphonyl chlorides to vinylic monomers is attempted with ordinary catalysts, polymers are formed, even in the presence of a large excess of sulphonyl chloride. With copper chloride-catalysis, on the other hand, only 1 : 1 adducts are obtained, at monomer : sulphonyl chloride molar ratios of 2 or even higher. Ethylene and the butenes also react readily, though more slowly (see Table 1).

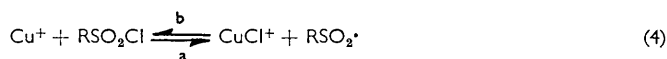
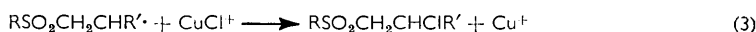
The copper chloride-catalysed addition of sulphonyl chlorides thus provides a general and convenient synthesis of β -chloro-sulphones, and, by dehydrohalogenation, of $\alpha\beta$ -unsaturated sulphones. Most of the adducts and their dehydrohalogenates listed in Table 3 have been prepared before, but invariably by more elaborate syntheses.

Both with styrene and with acrylonitrile or methyl acrylate (Table 1, nos. 1, 3, 7, 8, 11, 12, and 13) the sulphonyl group attaches itself to the terminal methylene. This clearly indicates that sulphonyl radicals are involved. The corresponding cation would give a reversed orientation with acrylonitrile.

For those sulphonyl chlorides which can be added to olefins with the aid of conventional radical-sources the following mechanism is operative:⁴

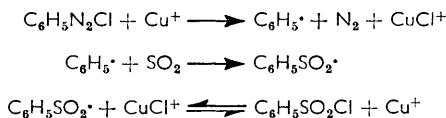


For a copper chloride-catalysed system we suggest a redox-transfer mechanism¹⁰ in which the transfer step (2) is completely superseded by the following reduction-oxidation steps, which together have formally the net result of (2):



The failure of unsubstituted aliphatic sulphonyl chlorides to react with olefins in the presence of the usual initiators can be attributed⁷ to their low reactivity in step (2). Their ready addition under copper chloride-catalysis represents, then, another instance in which covalently bound chlorine is activated by redox-transfer.^{1,10}

Step (3) is an example of a radical-destroying ligand-transfer reaction.¹¹ Normally, the formed cuprous ion is an inert product. Here, however, as in similar reactions of peroxy-compounds,^{11a} diazonium chlorides,^{11c} carbon tetrachloride,^{10,12} and chloroform,¹ it is chain-sustaining, owing to its ability to reduce sulphonyl chloride (step 4a). The back-reaction (4b) can be inferred from the fact that sulphonyl chlorides are formed from diazonium chlorides and sulphur dioxide, in the presence of copper chloride, according to the following mechanism:¹³



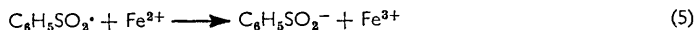
¹⁰ Asscher and Vofsi, *J.*, 1963, 1887.

¹¹ (a) Minisci, Galli, and Pallini, *Gazzetta*, 1961, **91**, 1023; Minisci and Galli, *Tetrahedron Letters*, 1962, 533; Kochi and Rust, *J. Amer. Chem. Soc.*, 1962, **84**, 3946; Kochi, *Tetrahedron*, 1962, **18**, 483; *J. Amer. Chem. Soc.*, 1962, **84**, 2785, 3271; Walling and Zavitsas, *ibid.*, 1963, **85**, 2084; (b) Kumamoto, de la Mare, and Rust, *ibid.*, 1960, **82**, 1935; Collinson, Dainton, Tayuke, Smith, and Mile, *J. Polymer Sci.*, 1962, **58**, 118; Watanabe and Kiuchi, *ibid.*, 1962, **58**, 103; (c) Nonhebel and Waters, *Proc. Roy. Soc.*, 1957, *A*, **242**, 16.

¹² Asscher and Vofsi, *J.*, 1961, 2261.

¹³ Meerwein, Dittmar, Göllner, Hafner, Mensch, and Steinfort, *Chem. Ber.*, 1957, **90**, 841.

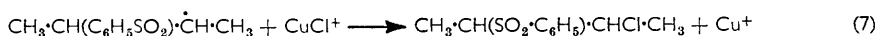
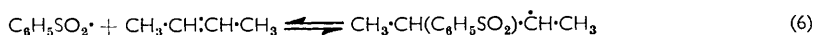
With stoichiometric amounts of ferrous salts, on the other hand, sulphinic acids are formed:¹⁴



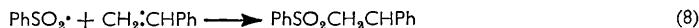
This last step probably explains the poor performance of iron chloride as a catalyst in our reactions; in a redox-transfer system, a reaction like (5), in which sulphonyl radicals are being destroyed without a simultaneous regeneration of ferrous ions, must be regarded as a chain-breaking step. (See also Walling and Zavitsas,^{11a} equations 7 and 21d there.)

Step (3) is very fast, and as a result, no polymer- or telomer-formation is observed, even when monomers of the electron-acceptor type (like acrylonitrile or methyl acrylate, Table 1, nos. 3, 8, 11, and 12) are involved.

In scope and mechanism, the addition of sulphonyl chlorides to conjugated or unconjugated olefins much resembles the copper chloride- or iron chloride-catalysed additions of carbon tetrachloride.¹⁰ In one important respect, however, there is a difference; with unconjugated olefins, step (1) is reversible for the case of sulphonyl, but not for trichloromethyl, radicals. This point, already commented upon by others,¹⁵ manifests itself in the reaction between but-2-ene and benzenesulphonyl chloride (see Table 2). Here, *cis-trans*-isomerisation of the olefin *via* equilibrium (6) appears to be much faster than adduct-formation *via* reaction (7):



With 1 mole-% of cupric chloride as the catalyst, both *cis*- and *trans*-but-2-ene are completely equilibrated after 24 hours at 100°, but only about 12% of the butenes is converted into adduct (Table 2, nos. 1 and 2). Unchanged benzenesulphonyl chloride is recovered. An increased initial concentration of cupric chloride produces an *increase* in the rate of adduct-formation, and a *decrease* in the rate of *cis-trans*-isomerisation (Table 2, nos. 4, 5, and 6). This result is a direct outcome of an increased rate of reaction (7), which, in turn, displaces equilibrium (6) to the right. The overall picture is somewhat complicated, however, by the fact, that at 100° a slower, uncatalysed * *cis-trans*-isomerisation takes place concurrently. This cannot be due to a thermal homolysis of the sulphonyl chloride,¹⁶ (followed by equilibrium (6)), since the presence of up to 100 mole-% of styrene (on sulphonyl chloride) does not entirely suppress the isomerisation (Table 2, nos. 12–14). Styrene can be expected to compete successfully with but-2-ene for benzenesulphonyl radicals:



The result of the catalysed reaction between chloromethanesulphonyl chloride and styrene on the one hand, and with oct-1-ene on the other, justifies this assumption (see below). Moreover, step (8), which contrary to equilibrium (6) yields a resonance-stabilised radical, is not appreciably reversible under the prevailing conditions.¹⁵ If nevertheless even large amounts of styrene do not completely inhibit the uncatalysed *cis-trans*-isomerisation, some other kind of reversible interaction between sulphonyl chloride and butene, the nature of which is not understood at present, must be assumed. Also, the isomerisation cannot be due to proton-catalysis, since but-1-ene, which should have been present in a mixture,

* By "uncatalysed *cis-trans*-isomerisation" is meant isomerisation in the presence of sulphonyl chloride, but *without* copper chloride.

¹⁴ Meerwein, Dittmar, Raue, and Lange, cited by Muth in Houben-Weyl, "Methoden der Organischen Chemie," Georg Thieme, Stuttgart, Vol. 9, p. 323.

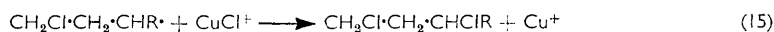
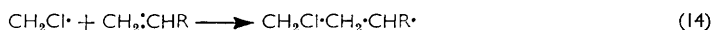
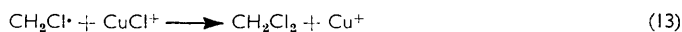
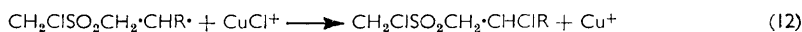
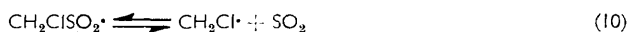
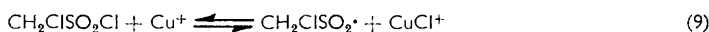
¹⁵ Walling, "Free Radicals in Solution," John Wiley and Sons Incorp., New York, 1957, pp. 223–228; *J. Polymer Sci.*, 1953, **10**, 49; Dainton and Ivin, *Proc. Roy. Soc.*, 1952, *A*, **212**, 96, 202; Dainton and Bristow, *ibid.*, 1955, *A*, **229**, 509, 525; *Nature*, 1953, **172**, 804.

¹⁶ Bain, Blackman, Cummings, Hughes, Lynch, McCall, and Roberts, *Proc. Chem. Soc.*, 1962, 186.

equilibrated in the presence of an acid catalyst (8% of but-1-ene, 61% of *trans*-, and 31% of *cis*-but-2-ene at 100°),¹⁷ was never detected. Further, but-1-ene is not isomerised in the presence of sulphonyl chloride at 100°, with or without catalyst (Table 1, no. 5).

The reversibility of steps (1) and (6) in the case of unconjugated olefins is most probably the main reason for their slower reaction with sulphonyl chlorides (compare in Table 1, nos. 1, 2, and 3 with 4, 5, and 6). Another factor is a faster initiation with conjugated olefins. If cupric chloride is the catalyst, we consider as an initiating process any reaction which reduces cupric chloride to cuprous chloride, even if no free radicals are simultaneously formed. The reduction by styrene and butadiene, giving chlorinated hydrocarbons,^{10,18} is much faster than that by acrylonitrile, and the latter reduces cupric chloride more rapidly than do unconjugated olefins (unpublished results; see also Watanabe and Kiuchi, ref. 11b). The same considerations apply to redox-transfer additions of carbon tetrachloride¹⁰ to olefins.

An interesting comparison can be made between styrene and oct-1-ene in their behaviour towards chloromethanesulphonyl chloride. This compound has been reported to react with olefins through elimination of sulphur dioxide, as the result of a reversible decomposition of the sulphonyl radical⁷ (step 10). If oct-1-ene is refluxed with the sulphonyl chloride in the presence of cupric chloride, sulphur dioxide is indeed evolved. After 8 hours, no sulphonyl chloride remains (Table 1, no. 14). Nearly all of the octene is recovered unchanged, and the main product appears to be methylene chloride. A very small amount of 1,3-dichlorononane, formed *via* steps (9), (10), (14), and (15) (R = hexyl), is found (under peroxide-catalysis, this is the main product⁷), and possibly also a trace of sulphone *via* steps (9), (11), and (12).



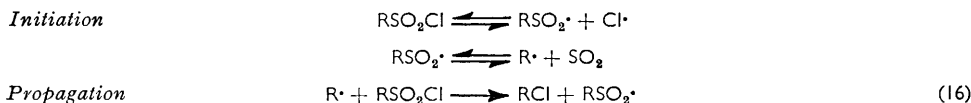
Methylene chloride accounts for 86 mole-% of the sulphonyl chloride. Apparently, cupric chloride competes successfully with oct-1-ene for the chloromethyl radicals formed in (10) (step 13)). Octene thus acts as an initiator, by reducing cupric chloride, but further remains largely inert, and does not interfere in the course of the reaction. This must be due to a comparatively slow, reversible addition (see above) of the sulphonyl radical to octene (step 11), which allows it to decompose nearly completely (step 10). Styrene, on the other hand, efficiently and irreversibly captures sulphonyl radicals generated *via* step (9), thereby largely suppressing their decomposition. As a result, a chloromethyl chlorophenylethyl sulphone is obtained in 60% yield (Table 1, no. 13). Some sulphur dioxide is nevertheless evolved. Methylene chloride found accounts for 12 mole-%, and 1,3-dichloropropylbenzene (formed *via* steps (9), (10), (14), and (15), R = phenyl) for 14 mole-%, of the sulphonyl chloride.

The sequence (9), (10), (13) represents a mechanism for the copper chloride-catalysed decomposition of chloromethanesulphonyl chloride, which can no doubt be applied to other sulphonyl chlorides as well. At 200—250°, aromatic sulphonyl chlorides undergo homolysis, and cuprous chloride is reported to catalyse this process.¹⁶ The uncatalysed decomposition of aliphatic sulphonyl chlorides higher than methyl- occurs at lower temperatures.

¹⁷ Kilpatrick, Prosen, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 559.

¹⁸ Kochi, *J. Amer. Chem. Soc.*, 1962, **84**, 2121.

A free-radical chain mechanism, involving the following main steps, has been suggested (see ref. 19 and literature cited there):



Step (16) of this decomposition chain is analogous to reaction (2) of the addition chain, and likewise is rather inefficient. As a result, extensive chlorination takes place concurrently in many cases.^{19,20} The redox-transfer decomposition of sulphonyl chlorides, in which

TABLE 3.
Adducts and their derivatives.

No.	Compound	M. p.*	Remarks
1	PhSO ₂ CH ₂ :CHClPh	89—90°	Ref. 21, m. p. 88—89°
2	PhSO ₂ CH:CHPh	75—76	Ref. 21, m. p. 74—75°
3	PhSO ₂ CH ₂ :CH:CH ₂ Cl		B. p. 120°/2·10 ⁻⁵ mm. <i>n</i> _D ²⁵ 1·5594
4	PhSO ₂ CH ₂ :CHCl·CN	104—105	Ref. 22, m. p. 105—106°
5	PhSO ₂ CH:CH·CN	104—105	Ref. 22, m. p. 102—103°
6	PhSO ₂ CH ₂ :CH ₂ Cl	53—54	Ref. 23, m. p. 54—55°
7	PhSO ₂ CH ₂ :CHEtCl	39	B. p. 132—133°/0·15 mm.
8	PhSO ₂ CHMe·CHMeCl		B. p. 123°/0·1 mm. <i>n</i> _D ²⁰ 1·5453
9	<i>p</i> -ClC ₆ H ₄ SO ₂ :CH ₂ :CHClPh	85	
10	<i>p</i> -ClC ₆ H ₄ SO ₂ :CH:CH·Ph	84	
11	<i>p</i> -ClC ₆ H ₄ SO ₂ :CH ₂ :CHCl·CN	93—94	Ref. 22, m. p. 90·5—91·5°
12	<i>p</i> -ClC ₆ H ₄ SO ₂ :CH:CH·CN	144—145	Ref. 22, m. p. 138—139°
13	<i>p</i> -NO ₂ C ₆ H ₄ SO ₂ :CH ₂ :CH ₂ Cl	132—133	Ref. 23, m. p. 129—130°
14	MeSO ₂ CH ₂ :CH:CH·CH ₂ Cl	46—47	B. p. 125°/0·1 mm. <i>n</i> _D ²⁵ 1·5087
15	MeSO ₂ CH ₂ :CHCl·CN	74—75	
16	MeSO ₂ CH:CH·CN	109—110	
17	MeSO ₂ CH ₂ :CHCl·CO ₂ Me	60—61	Ref. 24, m. p. 58—60°
18	MeSO ₂ CHCl:CH ₂ :CO ₂ Me	133—134	Ref. 24, m. p. 129—131°
19	MeSO ₂ :CH:CH·CO ₂ Me	83—84	
20	CH ₃ ClSO ₂ :CH ₂ :CHClPh	84—85	
21	CH ₃ ClSO ₂ :CH:CHPh	103—104	

* The listed products are recrystallised from methanol, except nos. 13 (toluene), 16 and 18 (water), and 19 (benzene).

No.	Found (%)					Formula	Required (%)				
	C	H	Cl	S	N		C	H	Cl	S	N
1	59·9	4·6	12·6	11·2	—	C ₁₄ H ₁₃ ClO ₂ S	59·9	4·7	12·6	11·4	—
3	52·2	4·9	15·2	13·8	—	C ₁₀ H ₁₁ ClO ₂ S	52·1	4·8	15·4	13·9	—
4	47·1	3·5	15·1	13·6	6·1	C ₉ H ₈ ClNO ₂ S	47·1	3·5	15·4	14·0	6·1
5	55·9	3·55	—	16·8	7·0	C ₉ H ₇ NO ₂ S	56·0	3·65	—	16·6	7·25
6	47·1	4·3	17·1	15·6	—	C ₉ H ₉ ClO ₂ S	46·9	4·4	17·3	15·7	—
7	51·85	5·8	15·35	14·1	—	C ₁₀ H ₁₃ ClO ₂ S	51·6	5·6	15·2	13·8	—
8	52·0	5·5	14·6	13·8	—	C ₁₀ H ₁₃ ClO ₂ S	51·6	5·6	15·2	13·8	—
9	53·4	3·85	22·4	10·2	—	C ₁₄ H ₁₂ Cl ₂ O ₂ S	53·3	3·8	22·5	10·2	—
10	60·4	3·85	12·75	11·5	—	C ₁₄ H ₁₁ ClO ₂ S	60·3	4·0	12·7	11·5	—
11	41·0	2·7	26·8	12·4	5·2	C ₉ H ₇ Cl ₂ NO ₂ S	40·9	2·7	26·85	12·1	5·3
12	47·6	2·4	15·9	14·2	6·3	C ₉ H ₆ ClNO ₂ S	47·9	2·7	15·6	14·1	6·15
13	38·5	3·4	13·8	13·1	5·5	C ₉ H ₆ ClNO ₄ S	38·5	3·2	14·2	12·8	5·6
14	35·95	5·3	20·6	18·7	—	C ₈ H ₉ ClO ₂ S	35·6	5·4	21·0	19·0	—
15	29·1	3·9	20·9	19·6	8·7	C ₈ H ₆ ClNO ₂ S	28·7	3·6	21·15	19·1	8·35
16	36·8	3·9	—	24·6	10·4	C ₈ H ₆ NO ₂ S	36·65	3·8	—	24·4	10·7
17	30·3	4·9	17·2	15·9	—	C ₈ H ₉ ClO ₄ S	29·9	4·5	17·7	16·0	—
18	29·8	4·45	17·5	16·2	—	C ₈ H ₉ ClO ₄ S	29·9	4·5	17·7	16·0	—
19	36·7	4·7	—	19·4	—	C ₈ H ₈ O ₄ S	36·6	4·9	—	19·5	—
20	42·8	3·8	28·1	12·6	—	C ₈ H ₁₀ Cl ₂ O ₂ S	42·7	4·0	28·0	12·7	—
21	49·9	4·25	17·2	14·9	—	C ₈ H ₉ ClO ₂ S	49·9	4·2	16·4	14·8	—

¹⁹ Geiseler and Kuschniers, *Z. phys. Chem. (Frankfurt)*, 1961, **23**, 33.

²⁰ Asinger, Fell, and Scherb, *Chem. Ber.*, 1963, **96**, 2837.

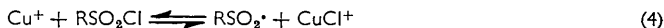
²¹ Field, *J. Amer. Chem. Soc.*, 1952, **74**, 3919.

²² B.P. 881,332/1958.

²³ Heyna and Riemenschneider, G.P. 887,505/1953.

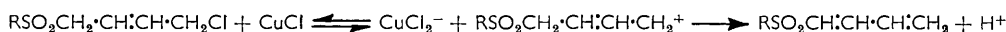
²⁴ Gundermann and Huchting, *Chem. Ber.*, 1962, **93**, 2191.

step (16) is being replaced by steps (17) and (4), may be expected to take place by much longer kinetic chains,¹⁰ giving rise to less side-reaction:



The thermal decomposition of higher aliphatic sulphonyl chlorides to the corresponding alkyl chlorides has been used, in order to analyse mixtures obtained in sulphochlorinations.²⁰ Hydrochloric acid was always evolved, for reasons outlined above, and corrections had to be made accordingly. We suggest that the reaction be carried out in the presence of copper chloride, at a lower temperature, in order to get a cleaner decomposition.

In the present work, cupric chloride was used invariably in conjunction with triethylammonium chloride. This was found to have a marked influence, most probably due to the following effects: (a) Alkylammonium chlorocuprates are formed. These are much more soluble than cupric chloride alone in solvents like chloroform or methylene chloride. Likewise, cuprous chloride, which is formed during the reaction, is kept in solution. In this respect, the choice of the cation is of obvious importance. In the presence of higher aliphatic alkylammonium chlorides, cupric chloride can be made to dissolve even in benzene. (b) The elimination of hydrochloric acid from styrene- and especially from butadiene-adducts is prevented. This reaction is catalysed by cuprous chloride,²⁵ which abstracts a chloride ion from the adduct, forming a complex:



Excess of chloride ion will suppress this process. (c) At least one chloride ion must remain in the cupric co-ordination-sphere, in order to make the product-forming ligand-transfer step possible:



but higher halide complexes of cupric ion may be expected to react faster, owing to their enhanced oxidising power.²⁶ It was found accordingly, that, as in additions of sulphonyl chlorides, excess of chloride ion completely suppresses telomerisation in the copper chloride-catalysed addition of carbon tetrachloride to vinylic monomers.¹⁰ (d) Excess of chloride ion suppresses the solvolysis of cupric chloride by solvent (*e.g.*, acetonitrile; see also refs. 10 and 21) or substrate. Thus, in the copper chloride-catalysed addition of sulphonyl chloride to acrylonitrile, omission of triethylammonium chloride causes a drastic drop in the yield. Acrylonitrile (AN) forms complexes with cupric ion,²⁷ and the marked effect of excess chloride must in this case be due to a displacement of the solvolysis-equilibrium to the left:



(CuCl_2 stands here also for higher halide complexes of cupric ion). (e) The chlorination of olefins by cupric chloride (the initiation reaction), which is formally a reduction of cupric ion, was observed to be faster in the presence of excess of halide, for the reasons outlined in (c) (unpublished results).

The behaviour of ferric chloride with respect to both stability against solvolysis, and the influence of excess of chloride ion on oxidation potential, differs much from that of cupric chloride.²⁶ Moreover, it is not reduced by olefin, and thus does not initiate reaction-chains in this way. Consequently, the effect of excess of chloride ion on iron chloride-catalysed additions of carbon tetrachloride to olefins (this reaction is, contrary to additions of

²⁵ Hatch and Estes, *J. Amer. Chem. Soc.*, 1945, **67**, 1730.

²⁶ Bailar, "The Chemistry of the Coordination Compounds," Reinhold Publ. Corp., New York, 1956, p. 403; Schneider and v. Zelewsky, *Helv. Chim. Acta*, 1963, **46**, 1848; Whealy, Bier, and McCormick, *J. Amer. Chem. Soc.*, 1959, **81**, 5900; Connick and Coppel, *ibid.*, 1959, **81**, 6389; Hathaway and Underhill, *J.*, 1962, 2258; Morris and Short, *J.*, 1962, 2672.

²⁷ Schrauzer, *Chem. Ber.*, 1961, **94**, 1893; Schrauzer and Eichler, *ibid.*, 1962, **95**, 260.

sulphonyl chloride, subject to both iron chloride- and copper chloride-catalysis) has been found to be very slight.¹⁰

Triethylammonium chloride alone has no catalytic activity.

Infrared absorption spectra indicate that from butadiene and methanesulphonyl chloride, the 1 : 4 *trans*-adduct is formed exclusively. The adduct of methanesulphonyl chloride to acrylonitrile, α -chloro- β -methylsulphonylpropionitrile, which had been previously prepared but not characterised,²⁴ could be converted⁹ into the known²⁴ methyl α -chloro- β -methylsulphonylpropionate. The same nitrile, after dehydrohalogenation (to β -methylsulphonylacrylonitrile), followed by hydrolysis in concentrated aqueous hydrochloric acid and esterification by methanol, gave the known²⁴ methyl- β -chloro- β -methylsulphonylpropionate.⁹

EXPERIMENTAL

Materials.—Olefins, vinylic monomers and solvents were used as in ref. 10. Cupric chloride dihydrate and triethylammonium chloride were B.D.H. reagent-grade products, as was benzenesulphonyl chloride. *p*-Chlorobenzenesulphonyl chloride was prepared according to Ullmann and Korselt,²⁸ and recrystallised from pentane, m. p. 52—53°. *p*-Nitrobenzenesulphonyl chloride was an Eastman Kodak White Label product, freshly recrystallised before use, and methanesulphonyl chloride was from Fluka A.G. (puriss.). Chloromethanesulphonyl chloride was prepared from trithiane, by chlorinolysis in water,²⁹ b. p. 80—82°/25 mm.

Although cupric chloride dihydrate, anhydrous cupric chloride and cuprous chloride gave identical results, anhydrous cupric chloride was preferred for solubility reasons. It was made by heating the dihydrate at 120° to constant weight.

Addition of Benzenesulphonyl Chloride and Methanesulphonyl Chloride to Butadiene and to the Butenes (Table 1, nos. 2, 5, 6, and 10).—The gaseous olefin was passed into a cooled (ice-salt) mixture of the specified amounts (Table 1) of methylene chloride and the sulphonyl chloride. The resulting solution was introduced into a pre-cooled Carius tube. A solution of cupric chloride and triethylammonium chloride (the latter in 50% molar excess over cupric chloride) in acetonitrile was added. After being cooled in liquid air, the tube was evacuated to 0.1 mm., sealed and heated to the indicated temperature. After the reaction, the tube was cooled in ice, opened, and excess olefin cautiously boiled off by dropping a boiling-chip into the tube, and gradually warming to about 40°. The catalyst was washed out by 1*N*-aqueous hydrochloric acid. This does not completely remove cuprous chloride, which is formed during the reaction, and is tenaciously held in the organic layer. Cuprous chloride does not interfere with the subsequent work-up of adducts to the butenes, ethylene, acrylonitrile or methyl acrylate. With adducts to styrene, and especially to butadiene, however, it causes a rapid decomposition of the product, and also a catalysed solvolysis, if the adduct is to be recrystallised from methanol. It must therefore be completely removed in these cases. This was effected by washing twice with an aqueous solution of disodium ethylenediaminetetra-acetate (Versenate). Subsequent drying on calcium chloride and evaporation of the solvent *in vacuo* in a rotating film-evaporator, at up to 50°, left a nearly colourless, oily residue, free from sulphonyl chloride, which in the case of addition of methanesulphonyl chloride to butadiene solidified on seeding to a hard mass. Yield of crude product, 94%. After twice recrystallising from methanol, m. p. 46—47° (Table 3, no. 14).

The adducts of benzenesulphonyl chloride to the butenes and to butadiene were isolated by distillation. Unconverted sulphonyl chloride was distilled through a 10 cm. Vigreux column (b. p. 70—120°/0.1 mm., bath up to 180°), and distillation continued without a column, at 0.1 mm. until dryness (bath up to 200°). (For purified products see Table 3, nos. 3, 7, and 8.)

Addition of Benzenesulphonyl Chloride and p-Chlorobenzenesulphonyl Chloride to Styrene and to Acrylonitrile (Table 1, nos. 1, 3, 7, and 8, Table 3, nos. 1, 4, 9, and 11).—The reactants were refluxed as specified in Table 1. The flask was fitted with a condenser of small diameter, and was filled to at least three-quarters, in order to minimise exposure to air. This was found to

²⁸ Ullmann and Korselt, *Ber.*, 1907, **40**, 642; Houben-Weyl, "Methoden der Organischen Chemie," Georg Thieme, Stuttgart, Vol. 9, p. 573.

²⁹ Douglas, Simpson, and Sawyer, *J. Org. Chem.*, 1949, **14**, 273.

affect the reaction. After cooling, 40 ml. (Table 1, nos. 1 and 7) or 25 ml. methanol (Table 1, nos. 3 and 8) was added, and the mixture left to crystallise. After standing for one hour in ice, the formed precipitate was filtered off under vacuum and washed with cold methanol. The products so obtained were substantially pure, not changing their melting points on recrystallisation.

Addition of Methanesulphonyl Chloride to Acrylonitrile and to Methyl Acrylate (Table 1, nos. 11 and 12).—The reaction was carried out in a sealed tube. The adduct to methyl acrylate was isolated by distillation (without prior removal of the catalyst, in order to prevent polymerisation of excess monomer) as a viscous oil, b. p. 120—145°/0.1 mm. (bath up to 200°), solidifying completely. After twice recrystallising from methanol, m. p. 60—61° (Table 3, no. 17).

The adduct to acrylonitrile was isolated by evaporating excess monomer *in vacuo* in a film-evaporator (bath up to 80°). The residue, which on cooling solidified completely, was ground under 20 ml. methylene chloride, filtered off under vacuum, and washed with 10 ml. methylene chloride. The crude product (70% yield, m. p. 70—73°, sintering from 68°) was recrystallised twice from methanol (m. p. 74—75°, Table 3, no. 15).

Addition of Benzenesulphonyl Chloride to Ethylene (Table 1, no. 4).—Catalyst and triethylammonium chloride were dissolved in the specified amount of solvents. Sulphonyl chloride was added, and the mixture introduced into a silver-lined autoclave of 200 ml., fitted with a Teflon-coated iron bar for magnetic stirring. The autoclave was kept under an ethylene pressure of 70 atm. during 1.5 min., while stirring. Excess ethylene was released to 35 atm.; about 20 g. ethylene remained. At reaction temperature (110°) the initial pressure was 72 atm., after 24 hr., 68 atm. After the autoclave had been cooled, ethylene was slowly released, and the reaction mixture washed once with 1N-aqueous hydrochloric acid, dried on calcium chloride, and freed from solvent in a film-evaporator, *in vacuo*, finally at 100°. The residue solidified to a hard grey mass (m. p. 45—51°. Yield of crude product, 97%). After once recrystallising from methanol, m. p. 53—54° (Table 3, no. 6).

The product is a vesicant, and should be handled with due care.

Addition of p-Nitrobenzenesulphonyl Chloride to Ethylene.—The reaction was carried out as above, with reagents as specified in Table 1, no. 9. The precipitate which formed in the autoclave on cooling was filtered off at the pump and washed with ice-cold ethanol; the mother-liquors were evaporated and the residue on the filter washed again, to give a 66% yield of crude product (m. p. 124—129°). After two recrystallisations from toluene, m. p. 132—133° (Table 3, no. 13).

Reaction of Chloromethanesulphonyl Chloride with Styrene (Table 1, no. 13).—Styrene was refluxed with sulphonyl chloride and solvent as indicated in Table 1, no. 13. The condenser was connected with a trap, cooled at -70°. The trap was fitted with a calcium chloride tube. A vigorous initial reaction was avoided by cautious heating, and occasionally lifting the flask from the heating mantle, during the first five minutes. After 2 hr., no sulphonyl chloride remained. In the trap, 2.6 g. sulphur dioxide had accumulated. The flask was now fitted with a 10 cm., thermally insulated Vigreux column, and its contents distilled slowly at atmospheric pressure. Distillate (6.8 g.) was collected, b. p. 48—83°, according to v.p.c. containing 12 mmoles methylene chloride. The balance was acetonitrile (solvent) and a small amount of styrene. (A 4 m. column was used, at 70°, packed with polyadipate on Chromosorb, as indicated in ref. 10, Table 2, asterisked footnote.) The residue was diluted with 10 ml. benzene, washed once with an aqueous solution of disodium versenate, dried on calcium chloride and, after decantation, diluted with 400 ml. pentane. The formed precipitate was filtered off at the pump, washed with pentane and dried. Crude sulphone (15.2 g.) was obtained (yield 60%), m. p. 82—83°, after recrystallisation from methanol 84—85° (Table 3, no. 20). The mother-liquor from the first precipitation was freed from pentane and benzene, and distilled *in vacuo* through a 10 cm. Vigreux column; 7 g., b. p. 40—47°/25 mm. (bath up to 100°) was collected, consisting of styrene. Continued distillation without a column gave 3.4 g. distillate, b. p. 72—104°/0.1 mm., containing according to v.p.c. 14 mmoles 1',3'-dichloropropylbenzene (on a 1.5 m. column, packed with 5% silicone oil on Haloport at 160°, 110 ml. helium per min.), identified by v.p.c. with an authentic sample.³⁰ Together, sulphone, methylene chloride, and 1',3'-dichloropropylbenzene account for 86% of charged sulphonyl chloride.

Reaction of Chloromethanesulphonyl Chloride with Oct-1-ene.—The reaction was carried out as above, styrene being replaced by oct-1-ene. No vigorous initial reaction was observed.

³⁰ Shorygina, *Zhur. obshchei Khim.*, 1956, **26**, 1460.

After 8 hr. reflux, no sulphonyl chloride remained. In the cold trap, 7.8 g. distillate accumulated, 1.4 g. in excess of the theoretical amount of sulphur dioxide to be evolved. This excess was considered to be methylene chloride (16 mmoles). The contents of the flask were distilled at atmospheric pressure through a 10 cm., thermally insulated Vigreux column. A fraction of b. p. 48—110° (17.4 g.) was collected, according to v.p.c. (on polyadipate, as above) consisting of 32% oct-1-ene, 34% methylene chloride, and 34% acetonitrile (solvent) = 70 mmoles methylene chloride (octene is eluted before methylene chloride and acetonitrile). Continued distillation gave a fraction (15 g.) of b. p. 30—32°/20 mm., consisting of oct-1-ene, and one of b. p. 100—130°/0.1 mm. (0.5 g., distilled without column, bath up to 185°); 0.2 g. residue remained. The last fraction contained some 1,3-dichlorononane (identified with an authentic sample, see below) and had a sulphur content of 11.5%. Methylene chloride accounts for 86% of charged sulphonyl chloride.

Dehydrohalogenation of Sulphonyl Chloride Adducts.—The reactions were carried out at room temperature, with a 50% molar excess of triethylamine, in benzene (for adducts listed in Table 3, nos. 1, 4, 9, 11, and 20), ethyl acetate (no. 15) or tetrahydrofuran (nos. 17 and 18). Saturated solutions in these solvents were mixed with a solution of triethylamine in the same solvent. The reaction, which was exothermic and virtually instantaneous, was quenched immediately by acidifying with 1N-aqueous hydrochloric acid.

Delayed acidification caused coloured and impure products to be formed from acrylonitrile and methyl acrylate adducts. The compound of Table 3, no. 18, on the other hand, was allowed to react during one hour before acidification. The organic layer was separated, dried on calcium chloride, and after decantation, diluted with pentane until precipitation of the unsaturated sulphone was complete. The yields were 70—90% in all cases.

Methyl β -Methylsulphonyl- β -chloropropionate and Methyl β -Methylsulphonyl- α -chloropropionate.— β -Methylsulphonyl acrylonitrile (4 g., m. p. 109—110°) was hydrolysed by heating at 100° during 7 hr. with 40 ml. concentrated hydrochloric acid, in a sealed tube. Water and hydrochloric acid were evaporated at 25 mm., and the residue kept at 100° during 1.5 hr. Extraction with acetone and evaporation of the solvent gave a residue, which was refluxed with 30 ml. methanol during 7 hr., while a slow stream of dry gaseous hydrochloric acid was passed through. (The inlet-tube became occasionally clogged with crystals.) The methanol was evaporated at 25 mm., and the residue recrystallised once from water, with a small amount of charcoal. Pure methyl β -methylsulphonyl- β -chloropropionate⁹ was obtained in 80% yield (4.9 g., m. p. 133—134°, Table 3, no. 18).

The same sequence, carried out on β -methylsulphonyl- α -chloropropionitrile (m. p. 74—75°), afforded methyl β -methylsulphonyl- α -chloropropionate (m. p. 60—61°, Table 3, no. 17).

*1,3-Dichlorononane.*⁷—Oct-1-ene (11.2 g.), chloromethanesulphonyl chloride (7.5 g.), and benzoyl peroxide (0.5 g.) dissolved in acetonitrile (3 g.) were refluxed during 2 hr. Benzoyl peroxide (0.5 g.) was added, and reflux continued for another 2 hr. Sulphonyl chloride was no longer present. In the cold trap connected with the reflux condenser, 3.1 g. liquid sulphur dioxide had accumulated (Theor. amount, 3.2 g.). Distillation through a 10 cm. Vigreux column afforded a fraction of b. p. 48—53°/0.1 mm. (6.8 g., bath up to 180°); 2.7 g. residue remained.

After rectification, pure 1,3-dichlorononane was obtained, b. p. 48°/0.1 mm., n_D^{20} 1.4568 (Found: C, 54.7; H, 9.1; Cl, 36.0. Calc. for $C_9H_{18}Cl_2$: C, 54.8; H, 9.2; Cl, 36.0%).