# Polymer Modification and Synthesis using Sulphenyl Derivatives. Part 8.† Addition of Arylsulphenyl Chlorides to Polyisoprene

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Toluene-*p*-sulphenyl chloride reacts smoothly with *cis*-1,4-polyisoprene (PIP) in various proportions, but the resulting adducts decompose spontaneously *via* loss of hydrogen chloride. From an examination of model compounds and of the adducts of PIP with other sulphenyl chlorides, it is concluded that decomposition results from the saturation of successive double bonds along the polymer chain. The extent of decomposition indicates a high degree of regioselectivity in the original addition reaction. Some light is shed on the mechanisms of sulphenyl chloride additions to olefins and of the decomposition of aryl ω-halogenoalkyl sulphides.

PREVIOUS Parts [1-3] have described the ready addition of benzene- and toluene-*p*-sulphenyl chloride (1a and b) to
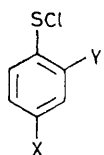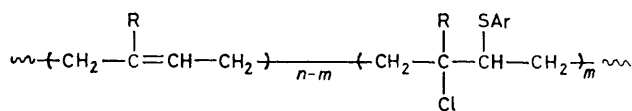

(1)

a; X = Y = H
b; X = CH$_3$, Y = H
c; X = OCH$_3$, Y = H
d; X = NO$_2$, Y = H
e; X = Y = NO$_2$
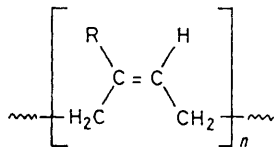
(2)

a; R = H
b; R = CH$_3$

cis-1,4-polybutadiene (PBD) (2a), 100% saturation of the double bonds being possible under mild conditions.


(3)

a; R = H
b; R = CH$_3$

Most important was the observation that the addition was regioselective; rather than reacting in a random fashion, there was a tendency for the sulphenyl chlorides to add to consecutive double bonds along the polymer chain, producing block copolymers (3a) when less than one equivalent of reagent was used. Regioselective addition was rationalised in terms of S_N1 type anchimeric assistance [4] from a neighbouring sulphide group (Scheme 1). Thus saturation of one double bond could activate the next towards electrophilic attack through overlap of the sulphur d orbitals with the adjacent π-system. This is analogous to the behaviour of cyclo-octa-1,5-diene towards methanesulphenyl chloride, good yields of di-adduct being produced in this reaction even when the diene is present in large excess.[5] This type of activation of an olefin towards sulphenyl chloride addition has
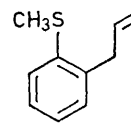
(4)

received little attention. Indeed, Kwart [4] doubts that it can occur in acylic systems, since no evidence of assistance was detected in the addition of 2,4-dinitro-benzenesulphenyl chloride (1f) to 2-allylthioanisole (4).

The formation of copolymers with blocky character from the reaction of polydienes with sulphenyl chlorides is therefore of some importance not only in the field of polymer chemistry, but also in the field of sulphur chemistry. Most of the evidence for regioselective

† Part 7, ref. 3.

[1] G. G. Cameron and R. B. Muir, *J. Polymer Sci. Polymer Letters*, 1976, **14**, 661.
[2] A. Brydon, G. G. Cameron, and R. B. Muir, *Makromol. Chem.*, 1977, **178**, 1739.
[3] G. M. Buchan, G. G. Cameron, and S. A. A. Chishti, *Makromol. Chem.*, in the press.
[4] H. Kwart and D. Drayer, *J. Org. Chem.*, 1974, **39**, 2157.
[5] W. H. Mueller, *J. Amer. Chem. Soc.*, 1969, **91**, 1223.

addition in these systems has come from studies of the physical properties of the product polymers. These include tensile strengths, glass transition temperatures (T_g),[2] and dielectric relaxation behaviour,[6] but the most

perature, the adducts quickly decomposed, discolouration and a strong odour of hydrogen chloride being apparent after 1—2 days' storage. Decomposition *via* loss of hydrogen chloride was confirmed by elemental
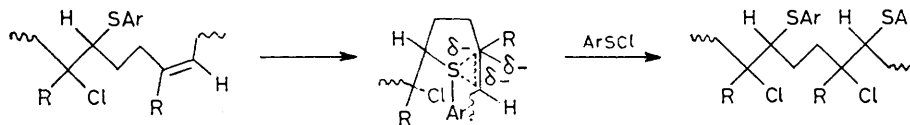
SCHEME 1

striking evidence comes from electron micrographs of stained sections of the 50% saturated adducts of (1a and b).[1,3] These clearly show a two-phase morphology,

analysis (Table). This instability contrasts sharply with the behaviour of the corresponding PBD adducts, which show good thermal stability;[1,2] the adducts of
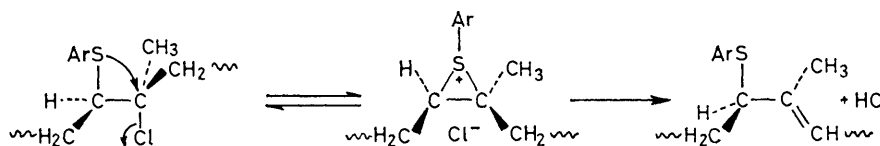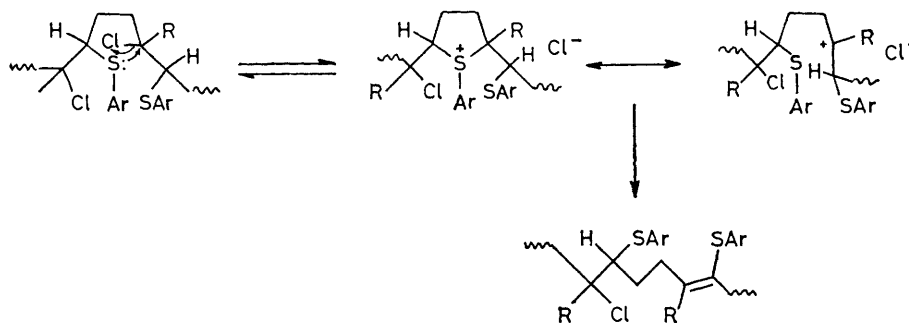

SCHEME 2

a phenomenon characteristic of block copolymers,[7] comprising domains of modified polymer in a matrix of unchanged polymer. Apart from some kinetic measurements, which have established that (1a) and other

PIP with other arenesulphenyl chlorides were therefore investigated.

The products of the reaction with 4-methoxybenzenesulphenyl chloride (1c) were extremely unstable, turning

SCHEME 3

sulphenyl chlorides have enhanced rates and reduced energies of activation of addition to polydienes compared with low-molecular weight mono-olefins,[1,3] little direct chemical evidence of the proposed regioselective addition has been obtained. We now describe the reactions of *cis*-1,4-polyisoprene (PIP) (2b) with arenesulphenyl chlorides, which provide such evidence and at the same time shed some light on the mechanism of addition of sulphenyl chlorides to olefins.

The addition of (1b) to (2b) in various proportions proceeded smoothly at room temperature in toluene solution (see Experimental section). However, the products were unstable, and rapidly turned brown with evolution of hydrogen chloride when dried at 50° under reduced pressure. Even when dried at room tem-

brown and evolving hydrogen chloride even more rapidly than the adducts with (1b). On the other hand,

Sulphur and chlorine analyses for adducts of PIP with (1b) (after *ca.* 2 weeks storage at room temperature)

Modification (%)	Calc. (%)	Found (%)	Cl lost (%)
25	S 6.8	7.0	47
	Cl 7.6	4.0	
50	S 10.9	11.2	19
	Cl 12.0	9.7	
75	S 13.0	12.9	25
	Cl 14.4	10.8	
100	S 14.1	14.6	19
	Cl 15.7	12.7	

the adducts with 4-nitrobenzenesulphenyl chloride (1d) were quite stable. Although slightly deficient in chlorine when isolated, they survived heating and prolonged storage without further loss of chlorine. Similarly, 2-nitrobenzenesulphenyl chloride (1e) reacted with
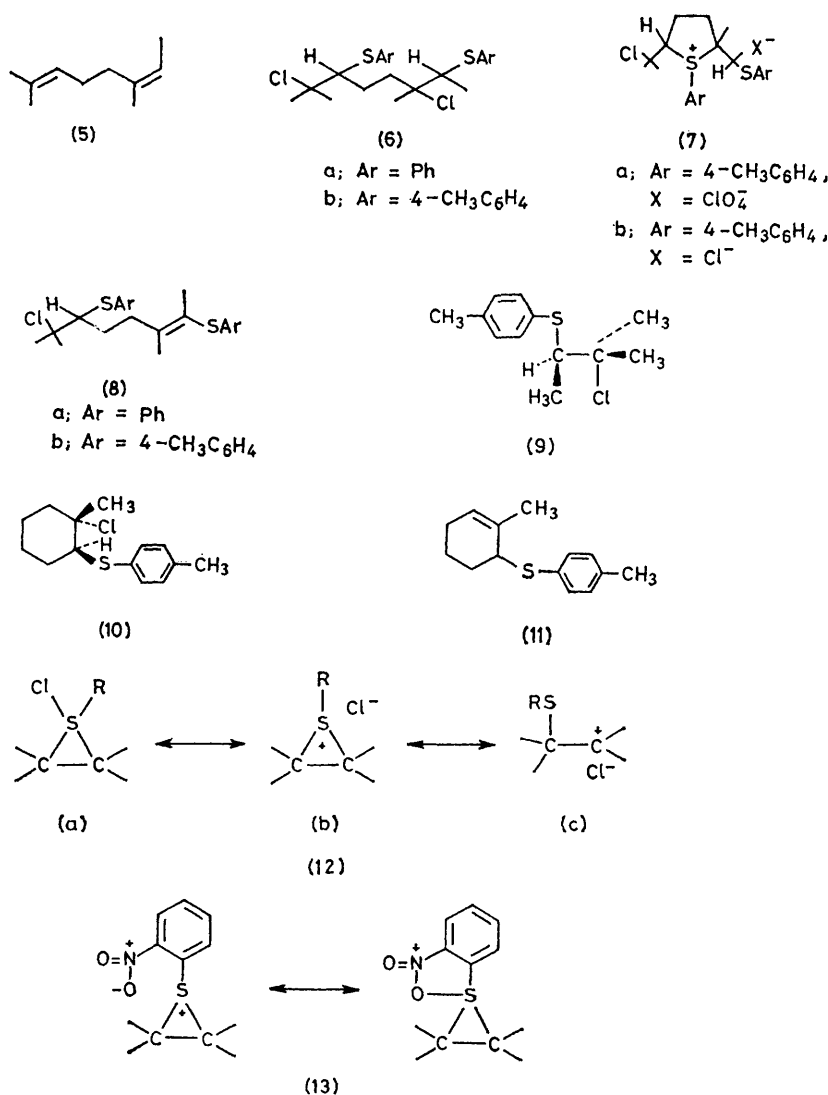
[6] A. T. Bullock, G. G. Cameron, and R. B. Muir, *Europ. Polymer J.*, 1977, **13**, 505.
[7] S. L. Aggarwal, *Polymer*, 1976, **17**, 938.

PIP, albeit very slowly, to give stable products. This time the adducts contained the theoretical amount of chlorine. The significance of the loss of chlorine during the course of the reaction of (1d) with PIP will be discussed later.

Markownikoff addition of sulphenyl chloride to PIP produces tertiary alkyl chloride groups, and hence elimination of hydrogen chloride from the adducts

(Scheme 3; R = CH$_3$) is also a possibility. Indeed, decomposition by the latter route, when possible, should occur more readily, since in the formation of cyclic sulphonium salts from aryl ω-halogenoalkyl sulphides, the equilibrium constant for five- is much greater than that for three-membered ring formation.[8] Steric constraints imposed by the polymer chain might also promote degradation *via* Scheme 3 rather than Scheme 2.[9]

(5)

(6)

a; Ar = Ph
b; Ar = 4-CH$_3$C$_6$H$_4$

(7)

a; Ar = 4-CH$_3$C$_6$H$_4$,
X = ClO$_4^-$
b; Ar = 4-CH$_3$C$_6$H$_4$,
X = Cl$^-$

(8)

a; Ar = Ph
b; Ar = 4-CH$_3$C$_6$H$_4$

(9)

(10)

(11)

(12)

(a)   (b)   (c)

(13)

should occur more readily than from the corresponding PBD adducts. However, any proposed decomposition mechanism must also take account of the fact that electron-releasing groups on the sulphur atom accelerated the decomposition and electron-withdrawing groups retarded it. Participation of the sulphide group is clearly indicated and intramolecular displacement of chloride by a β-arylthio group is a possibility (Scheme 2). But saturation of successive double bonds would also have introduced sulphide and chloride groups with a 1,4-disposition (Scheme 1; R = CH$_3$), so that decomposition *via* a five-membered ring sulphonium ion

As a check, the stabilities of model compounds (6b), (9), and (10) were compared. Compound (6b) was prepared by addition of (1b) to 2,6-dimethylocta-2,*cis*-6-diene (5), a model for a PIP segment, but was too unstable to be isolated. When the solvent was removed under reduced pressure, fumes of hydrogen chloride were visibly evolved from the residual oil, and both n.m.r. spectroscopy and t.l.c. indicated a complex mixture of products. Compound (6a), the diadduct of

[8] R. Bird and C. J. M. Stirling, *J.C.S. Perkin II*, 1973, 1221.
[9] H. J. Harwood, Abstracts Papers Amer Chem. Soc. Centennial Meeting, 1976, Chem. Educ. Division, No. 38.

(5) with (1a), was more stable, but its decomposition to (8a) (or its geometrical isomer) could be monitored by the appearance of methyl signals at δ 1.84 and 1.94. When (5) was treated with (1b) at low temperature, and then with lithium perchlorate, the sulphonium salt (7a) was isolated. Thus the reaction sequence (6b) ⟶ (7b) ⟶ (8b) was indicated. In contrast compounds (9) and (10), prepared by addition of (1b) to 2-methylbut-2-ene and 1-methylcyclohexene respectively, showed no tendency to decompose at room temperature. In fact, compound (9) survived reflux for 24 h in carbon tetra-chloride with decomposition only barely detectable by n.m.r. Under the same conditions, compound (10) underwent ca. 25% conversion to (11), as evidenced by new peaks in the n.m.r. spectrum at δ 5.50 and 1.87. The greater reactivity of (10) was expected, since the chloride and sulphide groups are locked in the trans-configuration necessary for episulphonium ion formation.

The sluggish decomposition of (9) and (10) shows that Scheme 2 cannot account for the spontaneous degrad-ation of the modified polymers, while (6b), which decomposed via Scheme 3, reproduced exactly the behaviour of the polymers. Elimination of hydrogen chloride from the adducts of PIP with (1b) must there-fore be a direct consequence of a 1,4-disposition of chloride and sulphide groups along the polymer back-bone. If the addition of (1b) to PIP had occurred in a purely random manner then simple statistics show that, for the sample modified to 25% saturation of olefinic bonds, only 25% of the reacted monomer units could occur in sequences of two or more. This implies that the loss of chlorine from such a randomly modified polymer could never exceed 25% and this figure assumes that all chlorine is lost from modified sequences of two or more units. The Table shows, however, that the PIP sample modified to 25% saturation lost 47% of the original chlorine content and hence the addition reaction could not have occurred at random. It follows that addition of (1b) to PIP must be subject to some regio-selective influence, a conclusion in agreement with previous observations on sulphenyl chloride modific-ation of PBD. The 1,4-disposition of chloride and sulphide groups necessary for hydrogen chloride elimin-ation must occur even more frequently in PIP modified to higher extents and hence one might expect higher chlorine deficiencies from the other polymers listed in the Table. However, as the olefinic bonds are replaced by β-chloro-sulphide groups, the polymer backbone becomes progressively less flexible. This is amply demonstrated by the dramatic increases in T_g, tensile strength,[2] and temperature of maximum dielectric loss[6] which accompany increases in saturation. The decrease

in rotational mobility about the backbone bonds thus hinders the acquisition of the conformation required by Scheme 3, and so chlorine loss from the highly modified polymers occurs more slowly than from the 25% adduct.

Our conclusion, that anchimeric assistance operates during addition of (1b) to polyolefinic substrates, appears to be at odds with that of Kwart. Although the additions of formic acid, hydrogen bromide, and iodine to (4) were assisted by the methylthio group, he found no evidence for such an effect in the addition of (1f) to (4). The discrepancy suggests a difference in mechanism between the addition reactions of (1f) and those of other sulphenyl chlorides. Depending on the reaction conditions, the structure of the olefin, and the substituent on sulphur, the reaction intermediate has been assigned sulphurane,[10] episulphonium ion,[11] or carbonium ion[12] character [(12a—c) respectively]. It has been suggested, however,[10a] that arenesulphenyl chlorides with a nitro-group in the ortho-position form a separate class in that they react with olefins via an episulphonium ion (13) which is stabilised by interaction with the nitro-group. Such an arrangement would allow for very little charge development on carbon in the transition state. The assignment of an atypical mechanism to the addition reactions of 2-nitroarene-sulphenyl chlorides is supported by the abnormally high energies of activation involved. Thus, the energy of activation for addition of (1f) to simple olefins is ca. 50 kJ mol⁻¹ while the corresponding value[2] for (1a) is ca. 10 kJ mol⁻¹.

Our observation on the marked differences in the properties of 4- and 2-nitrobenzenesulphenyl chloride also support this theory. As mentioned above, during reaction of the former with PIP, loss of hydrogen chloride took place, indicating carbonium ion character (12c) in the intermediate.[12] Furthermore, the products were found to be cross-linked, suggesting nucleophilic attack on (12c) by an unchanged double bond on a neighbouring polymer chain. Formation of (12c) would be favoured by the 4-nitrophenyl group on sulphur and the methyl substituent on the polymer backbone. No such complications arose in the reaction of 2-nitro-benzenesulphenyl chloride with PIP, and so in this case, much less positive charge must be developed on carbon in the intermediate, even though the 2-nitro-phenyl group is comparable with the 4-nitrophenyl group in electron-withdrawing power. Other authors have commented on the differing rates[13] and orient-ation[14] of the additions of (1d and e) to unsaturated systems; our results give further evidence that these react by differing routes. Thus, Kwart's conclusions[4] concerning neighbouring group participation in sulphenyl chloride addition reactions are valid only for 2-nitro-arenesulphenyl chlorides; our findings and those of

[10] (a) D. C. Owsley, G. K. Helmkamp, and M. F. Rettig, J. Amer. Chem. Soc., 1969, 91, 5329; (b) V. R. Kartashov, I. V. Bodrikov, E. V. Skorobogatova, and N. S. Zefirov, J. Org. Chem. U.S.S.R., 1976, 12, 289.

[11] N. Kharasch, ' Organic Sulfur Compounds,' Pergamon, New York, 1967, vol. 1, p. 375.

[12] W. H. Mueller and P. E. Butler, J. Amer. Chem. Soc., 1968, 90, 2075.

[13] (a) N. Kharasch, Z. S. Ariyan, and A. J. Havlik, Quart. Rep. Sulphur Chem., 1966, 1, 177; (b) A. Dondoni, G. Modena, and G. Scorrano, Ricerca sci., 1964, 34, 665.

[14] (a) G. M. Beverley, D. R. Hogg, and J. H. Smith, Chem. and Ind., 1968, 1403; (b) V. Calo, G. Modena, and G. Scorrano, J. Chem. Soc. (C), 1968, 1339.

Mueller,[5] indicate that other arenesulphenyl chlorides behave differently.

The great difference in stability between the corresponding PBD and PIP adducts merits further comment. Substitution of R = CH_3 for R = H in Scheme 3 clearly displaces the equilibrium to the right, possibly as a result of stabilisation of the ionised form through an increased contribution from the carbonium ion. Another possible effect of introducing the methyl group is a reduction in the free energy of activation for formation of the cyclic sulphonium ion, since alkyl substituents reduce the rotational freedom of acyclic molecules, and the entropy loss on cyclisation is therefore reduced.[15] The dramatic change in behaviour suggests that both factors may be contributing.

Apart from the identity of R, the equilibrium in Scheme 3 also depends on the nature of the substituent on sulphur. Replacement of the arylthio with a more strongly bridging alkylthio group ought to increase the tendency both for regioselective addition and for decomposition of the products. Preliminary experiments with PBD and alkanesulphenyl chlorides confirm this view; in the future we shall report on this and the preparation of novel block copolymers by displacement of the labile chlorine atom by a variety of nucleophiles.

EXPERIMENTAL

I.r. spectra were recorded for KBr discs on a Perkin-Elmer model 177 grating spectrometer. N.m.r. spectra were recorded for $CDCl_3$ solutions on a Varian HA-100 instrument using tetramethylsilane as internal standard. The polyisoprene was Natsyn 2200 (Goodyear Chemical Company) consisting of 98% cis-1,4-linkages, and containing ca. 1% antioxidant. It was purified prior to use by two precipitations from toluene into methanol and drying at 50° under reduced pressure to constant weight. Benzene-,[16] toluene-p-,[16] 4-methoxybenzene-,[17] and 4-nitrobenzene-sulphenyl [18] chlorides were prepared by chlorination of the appropriate thiophenols, 2-nitrobenzenesulphenyl chloride [19] by chlorinolysis of the disulphide. 2-Methylbut-2-ene [20] was prepared by dehydration of 2-methylbutan-2-ol; 1-methylcyclohexene (Aldrich) and 2,6-dimethyl-octa-2,cis-6-diene (ICN Pharmaceuticals) were commercial samples used without further purification. AnalaR grade toluene and carbon tetrachloride were dried over sodium and phosphorus pentaoxide respectively, then distilled. Light petroleum refers to the fraction boiling at 60—80°.

Addition of Toluene-p-sulphenyl Chloride to PIP (General Method).—cis-1,4-Polyisoprene (1.70 g, 0.025 monomer mol) in toluene (200 ml) was treated dropwise at room temperature, with magnetic stirring, with the theoretical amount of toluene-p-sulphenyl chloride in toluene (20 ml). The colour was discharged within minutes, and after stirring a further 3—6 h (overnight in the case of 100% modification), the mixture was poured into methanol or methanol–light petroleum (4 : 1) (7—8 l). The product was collected and dried at room temperature on the vacuum grid to constant weight. After several days' storage at room temperature, a strong odour of hydrogen chloride was

detectable, and the products began to turn brown. The process was greatly accelerated by heating at 50° under reduced pressure. The analytical data in the Table were obtained for samples kept at room temperature for ca. 2 weeks.

Addition of 4-Methoxybenzenesulphenyl Chloride to PIP.— Using the same method, 50 and 100% adducts were prepared, the products being precipitated into methanol–light petroleum (1 : 3) and further purified by reprecipitation from benzene into methanol–light petroleum (1 : 3), followed by freeze-drying from benzene: 50% adduct (Found: S, 9.3; Cl, 2.9. Calc.: S, 10.4; Cl, 11.5%); 100% adduct (Found: S, 12.4; Cl, 1.1. Calc.: S, 13.2; Cl, 14.6%). Samples of material not subjected to reprecipitation and freeze-drying gave chlorine analyses of 4.9 and 4.0% respectively, for 50 and 100% modification.

Addition of 4-Nitrobenzenesulphenyl Chloride to PIP.— cis-1,4-Polyisoprene (0.57 g, 0.0084 monomer mol) in toluene (50 ml) was treated dropwise at room temperature with 4-nitrobenzenesulphenyl chloride (1.59 g, 0.0084 mol) in toluene (20 ml). The reaction was rapid, but before the addition was complete, the product began to separate as a pale yellow precipitate. After stirring overnight, the mixture was poured into methanol (3 l), the product collected, and dried at room temperature under reduced pressure to constant weight (1.91 g). The weight gain corresponded to 85% modification (Found: Cl, 11.4; S, 11.1. 85% Modification requires Cl, 13.2; S, 11.9%). The product swelled, but did not dissolve, in acetone, dioxan, chloroform, and dimethylformamide, indicating cross-linking. Samples were left in contact with the latter two solvents (in which swelling was most pronounced) for 3 weeks, then poured into methanol, the solids collected, and dried at 50° under reduced pressure. Each gave a chlorine analysis of 11.3%.

Addition of 2-Nitrobenzenesulphenyl Chloride to PIP.— cis-1,4-Polyisoprene (1.37 g, 0.02 monomer mol) in toluene (200 ml) was treated dropwise at room temperature with 2-nitrobenzenesulphenyl chloride (1.90 g, 0.01 mol) in toluene (30 ml), and the mixture stirred for 3 days. No change in colour was apparent, and the starch–iodide test remained positive. The solution was poured into methanol (7 l), the yellow precipitate collected, and dried at room temperature under reduced pressure to constant weight (2.535 g). The weight gain indicated 31% modification (Found: Cl, 8.6; S, 8.1. 31% Modification requires Cl, 8.7; S, 7.8%). After several months' storage at room temperature, the chlorine content was 8.3%. The product was readily soluble in a variety of solvents, and so no cross-linking had occurred.

Addition of Toluene-p-sulphenyl Chloride to 2,6-Dimethyl-octa-2,cis-6-diene (5).—Toluene-p-sulphenyl chloride (1.59 g, 0.01 mol) in carbon tetrachloride (20 ml) was added dropwise at room temperature to 2,6-dimethylocta-2,cis-6-diene (0.69 g, 0.005 mol) in carbon tetrachloride (15 ml). Reaction was instantaneous and exothermic, and an odour of hydrogen chloride soon developed. After 1 h, the solvent was removed under reduced pressure at room temperature, leaving a pale yellow oil, smelling of hydrogen chloride. Within a few hours, the product had darkened, and copious fumes of hydrogen chloride were visibly evolved. The [1]H

[15] B. Capon, *Quart. Rev.*, 1964, **18**, 45.
[16] H. Lecher, F. Holschneider, K. Köberle, W. Speer, and P. Stocklin, *Ber.*, 1925, **58**, 409.
[17] F. Montanari, *Gazzetta*, 1956, 406.
[18] H. Baganz and H. Peissker, *Arch. Pharm.*, 1956, **289**, 262.
[19] M. H. Hubacher, *Org. Synth.*, 1943, Coll. Vol. II, 455.
[20] J. F. Norris and R. Reuter, *J. Amer. Chem. Soc.*, 1927, **49**, 2624.

n.m.r. spectrum showed a series of complex, overlapping signals at δ 1.3—2.0, 2.2—2.6, and 3.0—3.4, in addition to the aromatic proton peaks at δ 7.0—7.35. The reaction was repeated using diene (0.345 g, 2.5 mmol) and sulphenyl chloride (0.79 g, 5.0 mmol) with ice–salt-bath cooling. The mixture was stirred for 10 min, then treated with lithium perchlorate (0.32 g, 3.0 mmol) in acetone (25 ml) and left at room temperature overnight. Removal of the solvent left a cloudy oil, which on trituration with ether afforded an oil. Further trituration with cold benzene left a solid, which was stirred with distilled water and filtered to yield crystals (40 mg) of 5-(2-*chloro*-1-*methyl-ethyl*)-2-*methyl*-1-(4-*tolylthio*)-2-[1-(4-*tolylthio*)*ethyl*]*tetra-hydrothiophenium perchlorate* (7b), m.p. 142—145° (decomp.) (Found: C, 55.5; H, 6.5; Cl, 13.7; S, 12.1. $C_{24}H_{32}Cl_2O_4S_2$ requires C, 55.5; H, 6.2; Cl, 13.6; S, 12.3%), $\nu_{max.}$ 2 980, 2 920, 1 590, 1 490, 1 440, 1 380, 1 085, and 810 cm^{-1}, δ 1.3 (3 H, d, ArSCHCH_3), 1.62 (3 H, s, ArŚCCH_3), 1.83 [6 H, d, (CH_3)$_2$CCl], 2.25 (3 H, s, CH_3ArS), 2.42 (3 H, s, CH_3ArŚ), 2.4—3.4 (5 H, m, CH_2 + CH$_3$CHSAr), 5.11 (1 H, t, ArŚCH), 6.59 (4 H, q, ArS), and 7.70br (4 H, d, ArŚ). The ether extract, on standing at room temperature overnight, deposited further crystals (70 mg), m.p. 120—125°, with i.r. and n.m.r. spectra identical with those above. Elemental analysis suggested this material was contaminated with LiClO$_4$.

Addition of Benzenesulphenyl Chloride to 2,6-Dimethyl-octa-2,cis-6-diene (5).—The diene (0.69 g, 0.005 mol) was treated with benzenesulphenyl chloride (1.49 g, 0.01 mol) in carbon tetrachloride solution as before. Removal of the solvent left an oil which evolved hydrogen chloride much more slowly than the corresponding toluenesulphenyl chloride adduct. The n.m.r. spectrum immediately after

reaction had a complex series of overlapping signals at δ 1.3—1.8, but over several days at room temperature, these were joined by new signals at δ 1.84 and 1.94, consistent with decomposition to (8a) or its geometrical isomer.

Addition of Toluene-p-*sulphenyl Chloride to 2-Methylbut-2-ene and 1-Methylcyclohexene.*—These additions were carried out at room temperature in carbon tetrachloride using an excess of olefin. Removal of the solvent and excess of olefin under reduced pressure gave the products as oils. Although unstable towards both distillation and chromatography on silica gel, neither showed any tendency to decompose at room temperature. The product from 2-methylbut-2-ene showed δ 1.46 (3 H, d), 1.62 (3 H, s), 1.68 (3 H, s), 2.31 (3 H, s), 3.30 (1 H, q), and 7.16 (4 H, q) consistent with Markownikoff addition. Peaks at δ 1.30 (d) and 3.91 (q) indicated [21] roughly 30% anti-Markownikoff product. After reflux for 24 h in carbon tetrachloride, the proportion of the latter had decreased, and methyl and olefinic signals at δ 2.0 and δ 4.6 and 5.2 respectively, were just detectable, indicating a few percent elimination of hydrogen chloride. The adduct from 1-methylcyclohexene gave signals at δ 1.40—2.00 (11 H, s superimposed on m), 2.30 (3 H, s), 3.17 (1 H, m), and 7.16 (4 H, q), consistent with structure (10). A singlet at δ 1.26 indicated a few percent anti-Markownikoff product. The latter disappeared after reflux for 24 h in carbon tetrachloride, while new signals appeared at δ 1.87 and 5.50, indicating ca. 25% conversion to (11).

[21] G. H. Schmid, C. L. Dean, and D. G. Garratt, *Canad. J. Chem.*, 1976, **54**, 1253.