

The Selective Monoaddition of Sulphenyl Chlorides to Conjugated Dienes

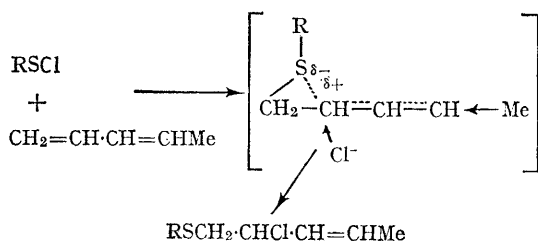
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In contrast to previous work¹ reporting 1,4-addition of sulphenyl chlorides to cyclopentadiene and cyclo-octatetraene, we find exclusive 1,2-Markovnikov addition to a variety of 1,3-dienes (see Table).

Our recent re-interpretation of the mechanism of sulphenyl chloride additions to olefins² has now been further substantiated and been given a wider scope by the present results.

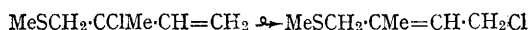
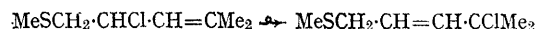
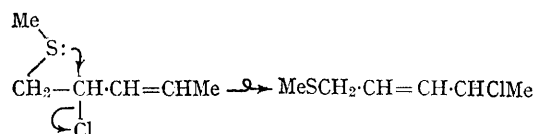
Contrary to the sterically-controlled ring opening observed with alkyl-substituted episulphonium-ion intermediates, a partial positive charge is developed on the allylic carbon (C-2) due to stabilization by the adjacent vinylic substituent. This stabilization by electronically more biased substituents allows the formation of an unsymmetrical episulphonium ion and leads to electronic control of the ring opening with the formation of Markovnikov-oriented products, *e.g.*,



The lack of 1,4-adducts excludes concomitant development of a carbonium ion. From the data in the Table it becomes evident that attack on the terminal position of double bonds in substituted butadienes is preferred. It may be argued that


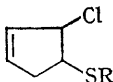
terminal methyl substituents stabilize the positively charged intermediate of the preferred product. However, based on similar considerations, a larger isomer ratio would be expected with isoprene. Thus, steric effects cannot be eliminated.

Post-isomerization of the following 1,2-adducts to the thermodynamically more stable 1,4-adducts occurred on standing at ambient temperatures:



The equilibrium mixtures contained > 90% of the 1,4-adducts as determined by n.m.r. and i.r. analysis. All other 1,2-adducts are stable under these conditions. It is particularly noteworthy that none of the benzenesulphenyl chloride adducts rearranged. Apparently the smaller availability of the unshared electrons on the phenyl-substituted sulphur atom prevents their participation in S_Ni displacement of the chlorine. This indicates that the episulphonium ion is also an intermediate in the rearrangement to 1,4-adducts.

TABLE
Methane- and benzene-sulphenyl chloride-1,3-diene adducts^a

Diene	Adducts	Mole % ^b	
		R = Me	R = Ph
$\text{CH}_2=\text{CH}\cdot\text{CH}=\text{CH}_2$	$\text{RSCH}_2\cdot\text{CHCl}\cdot\text{CH}=\text{CH}_2$	93	98
	$\text{ClCH}_2\cdot\text{CHSR}\cdot\text{CH}=\text{CH}_2$	7	—
$\text{CH}_2=\text{CH}\cdot\text{CH}=\text{CHMe}$	$\text{RSCH}_2\cdot\text{CHCl}\cdot\text{CH}=\text{CHMe}$	86	82
	$\text{CH}_2=\text{CH}\cdot\text{CHCl}\cdot\text{CHMe}$	14	18
$\text{CH}_2=\text{CH}\cdot\text{CH}=\text{CMe}_2$	$\text{RSCH}_2\cdot\text{CHCl}\cdot\text{CH}=\text{CMe}_2$	88	—
	$\text{RSCH}_2\cdot\text{CH}=\text{CH}\cdot\text{CClMe}_2$	[12] ^c	—
$\text{CH}_2=\text{CMe}\cdot\text{CH}=\text{CH}_2$	$\text{RSCH}_2\cdot\text{CClMe}\cdot\text{CH}=\text{CH}_2$	57	60
	$\text{CH}_2=\text{CMe}\cdot\text{CHCl}\cdot\text{CH}_2\text{SR}$	43	40
		85	—

^a All additions were carried out at -20 to -25° using methylene chloride as a solvent. Distillation *in vacuo* provided samples which gave satisfactory elemental analyses. ^b The adduct ratio was calculated from the relative intensity of their characteristic n.m.r. signals. ^c Most likely the result of post-isomerization.

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¹ H. Brintzinger and H. Ellwanger, *Chem. Ber.*, 1954, **87**, 300.

² W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, 1966, **88**, 2866, and references therein.