Reaction of the Tetrahydrodicyclopentadien-9-*exo*-yl Chlorosuphinates*

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THE decomposition of alkyl chlorosulphinates giving alkyl chlorides and sulphur dioxide often exhibits characteristics of a carbonium-ion reaction. The relative stabilities of the chlorosulphinates, the molecular rearrangements which occur in their decomposition, the effects of variation of solvent on these rearrangements, on the rates of decomposition and on the epimerisation in the reaction, and the isotope effects on the rate of decomposition, suggest that a carbonium-ion intermediate is formed[1] although this may be very short lived. Sulphur dioxide and chloride are produced asymmetrically in the same solvent cage as the carbonium ion.

We have decomposed the tetrahydro-*endo*- and -*exo*-dicyclopentadien-9-*exo*-yl chlorosulphinates (I and II) with varying solvent and temperature. The chlorosulphinates were prepared *in situ* by the slow addition of the corresponding alcohol to thionyl chloride in solvent at the required temperature. After reaction, the solvents were removed by evaporation, except in the high-temperature experiments in mineral oil where the product was removed by distillation. The product chlorides (III and IV) were analysed by gas–liquid partition chromatography between helium and Ucon polar oil, and were identified by comparison with authentic samples.[2]

The *endo*-ring-fused chlorosulphinate (I) gave a mixture of the *endo*-(III) and *exo*-(IV) ring-fused chlorides (see Table 1), and two minor unidentified isomeric compounds. The *exo*-ring-fused chlorosulphinate (II) gave a mixture (III and IV) containing less of (III) (see Table 2).

TABLE 1

Decomposition products of chlorosulphinate (I)

Solvent	Temp.	% (III)*	% (IV)*
Cyclohexane ..	28°	34	47
Diethyl ether ..	28°	33	49
Toluene	110°	20	66
Thionyl chloride ..	28°	10	65
Thionyl chloride ..	78°	13	65

* Analyses were reproducible to within ±4%. Percentages are of total chloride product.

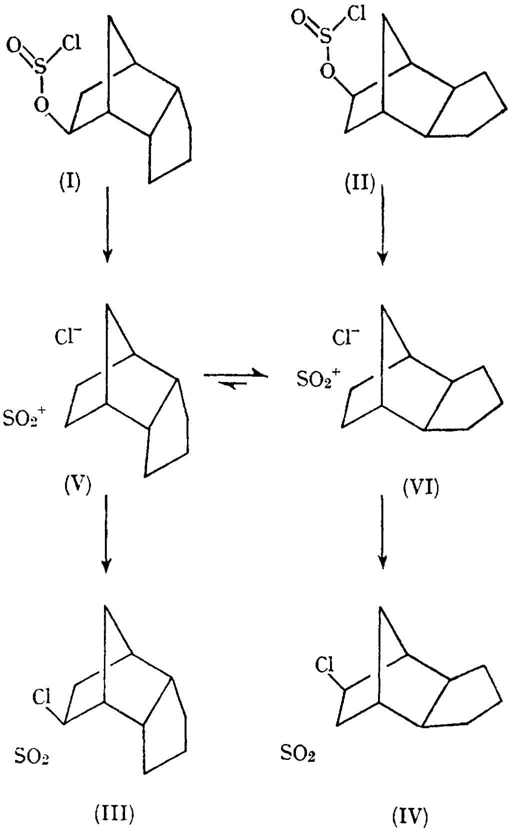
TABLE 2

Decomposition products of chlorosulphinate (II)

Solvent	Temp.	% (III)*	% (IV)*
Thionyl chloride ..	28°	2·4	97·6
Cyclohexane ..	28°	2·6	97·4
Chlorosulphinate ..	63°	3·2	96·8
Thionyl chloride ..	78°	4·3	95·7
Toluene	110°	4·0	96·0
Mineral oil	160°	6·8	93·2
Mineral oil	250°	10·0	90·0

* Analyses were reproducible to within ±0·5%.

Because (I) and (II) did not give identical product mixtures, a single common intermediate was not involved. The increasing rearrangement with temperature and solvent polarity in the decomposition of (I) is consistent with the scheme drawn. The tautomeric carbonium ions (V and VI) have been postulated to explain retention of configuration in other reactions.[3] The effect of temperature on the product mixture from (II) satisfied the Boltzman equation for the temperature-dependance of an equilibrium between two species with a free energy difference of $\Delta F = 2280$ cal./mole. This is a reasonable value for the energy difference between (V) and (VI).[4] The insignificant solvent effect in the decomposition of (II) supports the postulation that the tautomeric equilibrium between (V) and (VI) was achieved quickly relative to reaction of the ion pairs to form the alkyl chlorides.



The product mixture from (I) depended on the extent of rearrangement before neutralisation of the carbonium ions (kinetic control), while the product mixture from (II) reflects the equilibrium mixture of the carbonium ions (thermodynamic control). Thus decomposition of the chlorosulphinate (I) was a device to illustrate the kinetic control observable in this system.[3,4] Attempts to demonstrate kinetic control in reactions of other norbornyl derivatives have been unsuccessful.[5] It remains to be seen whether the tautomerism is faster for these other cations, or whether they have a bridged mesomeric structure.

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