Reaction of Chlorosulphonyl Isocyanate with Cyclic Trienes. Stepwise Conjugate Addition

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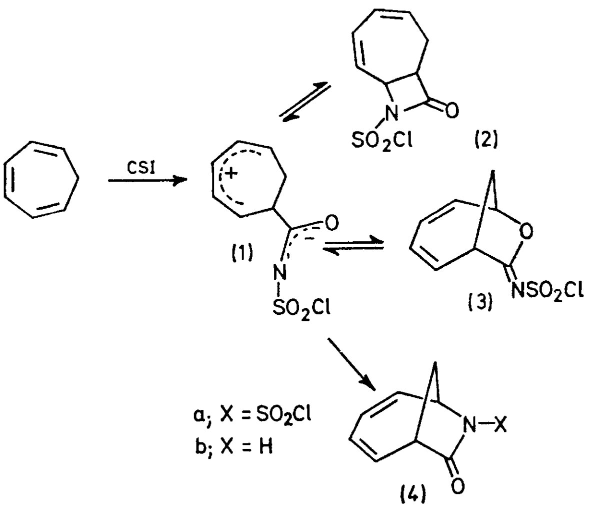
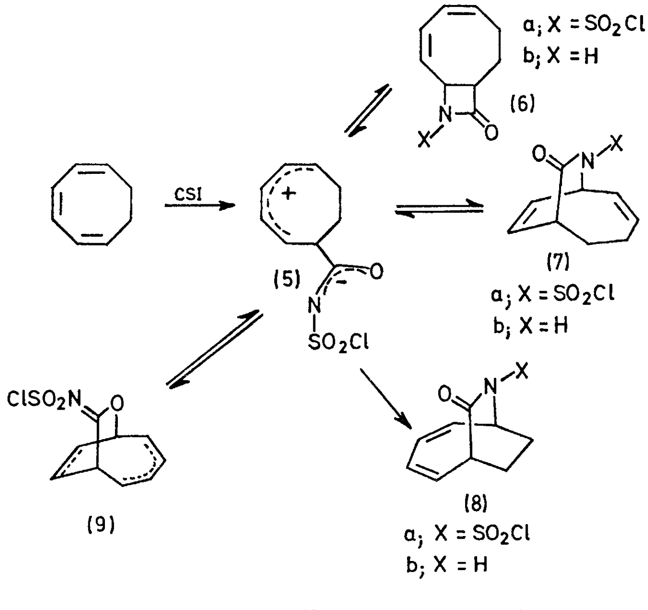
Summary Chlorosulphonyl isocyanate undergoes dipolar reactions with cyclohepta-1,3,5-triene and cyclo-octa-1,3,5-triene which proceed along a stepwise path culminating in the formation of *N*-chlorosulphonyl lactams *via* 1,6-addition; concerted ${}_{\pi}6_{s} + {}_{\pi}2_{a}$ cycloadditions are discounted.

Addition of chlorosulphonyl isocyanate (CSI) to cycloheptatriene in CH_2Cl_2 has been rationalised[1] as a near synchronous process leading to hypothetical 1,2- and/or 1,6-cycloaddition products (**2**) and (**4**a), followed by thermal and irreversible ring-opening to the dipolar intermediate (**1**). The observed product, imino-lactone (**3**), was thought to be the thermodynamically controlled product of cyclisation of (**1**).

Whilst reaction of equimolar quantities of cycloheptatriene and CSI proceeds in a matter of hours in CH_2Cl_2 at 25° to give 90% of (**3**),[1] the reaction in CCl_4 was much slower. An i.r. absorption at 1610 cm^{-1} (**3**) appeared over a period of days, accompanied by a small and apparently stationary concentration of *N*-chlorosulphonyl β-lactam (as shown by a peak at 1818 cm^{-1}). A new peak at 1772 cm^{-1} [assigned to (**4a**)] grew with time and ultimately became the major component. Consumption of CSI was complete after 2 weeks, when the absorption due to (**2**) disappeared. After a further 2 weeks, the ratio (**3**) : (**4a**) was 30 : 70 and still changing slowly in favour of (**4a**). Reaction in CCl_4 at reflux for 7 days yielded crude (**4a**) as a dark oil (*ca.* 50%) but conversion of (**3**) into (**4a**) was achieved most efficiently by the use of a polar solvent. Reaction in nitromethane for 2 days at 25° yielded (**4a**) [uncontaminated with (**3**)] which after hydrolysis with NaOH in aqueous Me_2CO at pH 7 ± 1 gave pure (**4b**), (50%), m.p. 107—108·5°, ν_{max} (CH_2Cl_2) 3420 and 1690 cm^{-1}; λ_{max} (EtOH) 262·5 (ϵ 4400) and 270·0 nm (4350).† A dipolar addition of CSI seems reasonable in view of the considerable stabilisation available to the cationic centre in (**1**). Whether (**2**) and (**3**) are formed consecutively or concurrently will not easily be determined. Clearly, (**4a**) is the ultimate product of thermodynamic control and is not an unstable precursor of (**3**) formed *via* a concerted ${}_{\pi}6_{s} + {}_{\pi}2_{a}$ cycloaddition.

On reaction of pure cyclo-octatriene[2] with CSI in CH_2Cl_2, absorption appeared at 1730 cm^{-1} together with small peaks at 1818 and 1570 cm^{-1} both of which disappeared when the CSI was consumed after 20 h. The remaining absorption at 1730 cm^{-1} was due to the products of 1,4- and 1,6-addition, (**7a**) and (**8a**), which were characterised as the lactams (**7b**) and (**8b**) after hydrolysis at pH 7, chromatography and sublimation: (**7b**), m.p. 108—109°, ν_{max} (CH_2Cl_2) 3400 and 1672 cm^{-1}, λ_{max} (EtOH), end absorption† and (**8b**), m.p. 112—113°, ν_{max} (CH_2Cl_2) 3400 and 1670 cm^{-1}, λ_{max} (EtOH) 258 nm (ϵ 4400) and 264·5 nm (4500),† each of which gave 7-azabicyclo[4,2,2]decan-8-one[3] on catalytic hydrogenation. The peak at 1570 cm^{-1} is ascribed to the *N*-chlorosulphonylimino-lactone(s) (**9**) formed by the alternative cyclisation through oxygen. Attempts to isolate derivatives of these unstable species are in hand.





Whilst the evidence for (**2**) depends on i.r. absorption at 1818 cm^{-1}, (**6a**) was isolated as the stable derivative (**6b**). After partial reaction (4 h), a mixture of triene and CSI in CH_2Cl_2 was cooled to −78° followed by treatment with benzenethiol-pyridine at the same temperature.[4] After work-up and chromatography, the first lactam to be eluted was (**6b**) (2%) which, after sublimation, gave a sample with

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† Proposed structures were fully substantiated by n.m.r. spectroscopy including double resonance studies, mass spectra, and by elemental analysis where stability allowed.

m.p. 118—119·5°; ν_{max} (CH_2Cl_2) 3400 and 1758 cm^{-1}; λ_{max} (EtOH) 228 nm (5800).† The second lactam fraction consisted of 86% of (**7b**) and only 14% of (**8b**). In parallel reactions, the ratios shown in the Table were obtained. Thus, formation of (**7a**) largely precedes formation of (**8a**). The reverse reaction (**6a**) → (**5**) again occurs readily, but (**7a**) → (**5**) is much slower and the most stable conjugated diene (**8a**) is obtained quickly only under polar conditions.

TABLE. *Variation in the ratio* (**7b**) : (**8b**) (*n.m.r. spectroscopy*) *with solvent, temperature, and time*

	(**7b**)	(**8b**)	Yield
CH_2Cl_2, 25° (4 h)	86	14	Incomplete reaction
CH_2Cl_2, 25° (36 h)	71	29	63%
CH_2Cl_2, 25° (200 h)	63	37	64%
$MeNO_2$, 85° (4 h)	50	50	61%
$MeNO_2$, 85° (24 h)	28	72	65%

Reaction of CSI with cyclo-octatriene did not occur to a measurable degree in non-polar solvents, in accord with a dipolar mechanism. On heating, preferential isomerisation occurred to bicyclo[4,2,0]octa-2,4-diene whose ready reaction with CSI has led to a further range of isomeric adducts.[5]

The dipolar species (**5**) may thus be pictured as undergoing 1,2-addition through nitrogen in the ambident anion followed (or partly accompanied) by 1,4-addition through nitrogen (with rather short-lived attempts to derive stabilisation *via* 1,4-and/or 1,6-cyclisation through oxygen) before finally coming to rest at the lowest point on the energy profile by achieving 1,6-addition through nitrogen.

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[3] L. A. Paquette, J. R. Malpass, and T. J. Barton, *J. Amer. Chem. Soc.*, 1969, **91**, 4714.
[4] J. R. Malpass and N. J. Tweddle, preceding communication.
[5] J. R. Malpass and N. J. Tweddle, following communication.