Generation of *endo*-9-Chloro-*cis*-bicyclo[4.3.0]nona-2,4,7-triene by Flash Vacuum Pyrolysis of *syn*-9-Bicyclo[4.2.1]nona-2,4,7-trienyl Chlorosulphite

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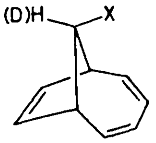
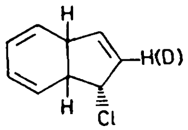
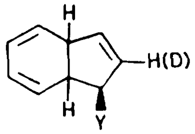
Summary Gas-phase pyrolysis of *syn*-9-bicyclo[4.2.1]-nona-2,4,7-trienyl chlorosulphite gave predominantly *endo*-9-chloro-*cis*-bicyclo[4.3.0]nona-2,4,7-triene, a new bicyclic C_9H_9Cl.



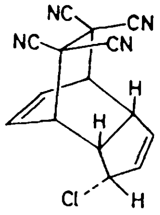
(1)
a; X = OSOCl
b; X = OH



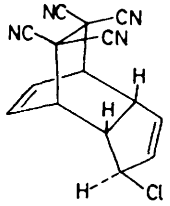
(2)



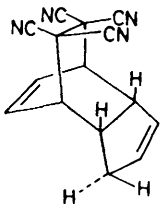
(3)
a; Y = Cl
b; Y = OMe.



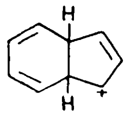
(5)



(6)



(7)



(9)

Gas-phase pyrolysis of chlorosulphites has not hitherto been used to prepare thermally labile organic chlorides.[1] We now report the flash vacuum pyrolysis of a new stable chlorosulphite, *syn*-9-bicyclo[4.2.1]nona-2,4,7-trienyl chlorosulphite (**1a**) and demonstrate that (**1a**) is initially transformed into *endo*-9-chloro-*cis*-bicyclo[4.3.0]nona-2,4,7-triene (**2**) which slowly epimerizes to the *exo*-isomer (**3a**)[2] at ambient temperature.

Although previous workers had obtained di-*syn*-9-bicyclo-[4·2·1]nona-2,4,7-trienyl sulphite from the reaction of *syn*-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (**1b**) with thionyl chloride,[3] we were able to isolate the moisture-sensitive (**1a**) in 100% yield by treating (**1b**) with a large excess of thionyl chloride in ether or chloroform at 0 °C followed by distillation under reduced pressure at 25 °C. The structure of (**1a**) was established by its reversion to (**1b**) upon treatment with water as well as by its spectroscopic properties.† The chlorosulphite (**1a**) was thermolysed at 45—75 °C in CCl_4 to provide pyrolysis mixture (A) containing (**2**) (10%), (**3a**) (80%), and indene (**4**) (10%) (estimated from ^{1}H n.m.r. spectrum). In sharp contrast, however, when (**1a**) was pyrolysed in a Pyrex tube at 270—330 °C and 10^{-6} Torr, the colourless product mixture (B), which was collected in a trap cooled at −196 °C, contained (**2**) (65%), (**3a**) (30%),

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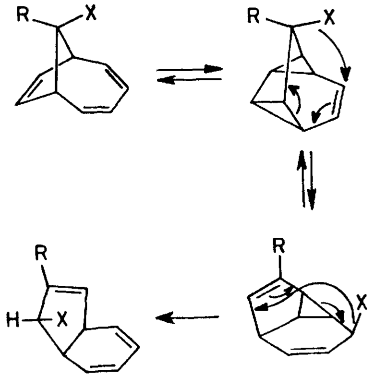
† ν (CCl_4) 1200 cm^{-1} (S=O); ^{1}H n.m.r. δ (CCl_4) 6·03 (m), 5·53 (t, *J* 6·7 Hz), and 5·28 (d, *J* 1·0 Hz) (total 7·06H), and 3·37 (t, *J* 6·7 Hz, 1·94H); ^{13}C n.m.r. δ ($CDCl_3$) 45·7, 71·5, 122·3, 127·1, and 131·3 p.p.m.

and (**4**) (5%) with no other products; no polymeric materials were detected in this pyrolysis mixture (estimated from ^{1}H n.m.r. spectrum). This strongly indicates that (**2**) is primary product of the thermal decomposition of (**1a**).

Purification of (**2**) could not be achieved because of its easy and clean epimerization into (**3a**) at room temperature. Nevertheless, its structural assignment is consistent with its chemical transformations and spectroscopic properties. The pyrolysis mixture (B) was cleanly converted into mixture (A) in CCl_4 at 25 °C within two days. Methanolysis of mixture (B) at 0 °C in the presence of $NaHCO_3$ afforded *exo*-9-methoxy-*cis*-bicyclo[4.3.0]nona-2,4,7-triene (**3b**) within 7 h in 92% yield. In the ^{1}H n.m.r. spectrum of mixture (B), signals due to (**2**) were assigned at δ 6·03—5·53 (m, 6·1H), 4·94 (dd, *J* 7 and 2 Hz, 0·9H), and 3·52—3·13 (m, 2·0 H). The ^{13}C n.m.r. spectrum of (**2**) showed six sp^2 (δ 137·1, 131·9, 124·6, 124·1, 123·9, and 121·0 p.p.m.), one chloromethylene (δ 69·4 p.p.m.), and two sp^3 (δ 43·0 and 39·6 p.p.m.) carbons, each of which was bound to one hydrogen atom as shown by off-resonance decoupling. Treatment of mixture (B) with tetracyanoethylene (TCNE) in tetrahydrofuran (THF) at 0 °C for 30 min provided adducts (**5**) (65%) [m.p. 232—233 °C (decomp.), satisfactory elemental analysis] and (**6**) (30%)[2] which were separated by fractional crystallization from ethanol. Exposure (10 min) of (**5**) or (**6**) to hydrogen over 10% Pd–C in THF at 0 °C gave (**7**) in high yield, which is the TCNE adduct of *cis*-bicyclo[4.3.0]nona-2,4,7-triene (**8**). Compound (**7**) was also independently prepared from TCNE and (**8**).

The ease with which (**2**) is obtained from (**1a**) is remarkable in view of its subsequent easy epimerization into (**3a**). In order to gain some mechanistic insight into the decomposition of (**1a**), its C-9 deuteriated derivative [^{2}H]-(**1a**) was pyrolysed both in solution and in the gas-phase. In both cases, the products, after methanolysis, showed a reduction in area of the vinyl proton signal to 5·06H. By analogy,[4] we assume the single deuterium to be located at C-8 of (**3b**). It is surprising that the covalent products, isolated from gas-phase pyrolysis of (**1a**), should so closely resemble those that were hitherto attributed to covalent capture of the bishomotropylium cation (**9**).[3,5–7]‡ Discovery of the easy (**2**) → (**3a**) isomerism now makes it possible to consider the adaptation of the Berson 'Hydrogen-Rebound mechanism' for this reaction (Scheme, X = chlorosulphite, chloride, or tosylate, rather than hydrogen).[8]



SCHEME

Other thermodynamically acceptable precursors of cationic intermediates include the 9-substituted cyclonona-1*Z*,3*E*,5*Z*,7*Z*-tetraenes and the 4-substituted bicyclo[5.2.0]-nona-2,5,8-trienes.[9] Whatever the mechanistic details, it would appear increasingly clear that many cationic processes can be initiated by a prior thermal rearrangement.

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‡ The ultimate products of *anti*-9-phenyl-*syn*-bicyclo[4.2.1]nona-2,4,7-trien-9-ol with thionyl chloride–pyridine (ref. 6) and of photolytic methanolysis of bicyclo[4.2.1]nona-2,4,7-trien-9-one tosylhydrazone (ref. 5b) represent anomalies in an otherwise uniform pattern.

[1] For thermal decomposition of chlorosulphites in solutions, see: E. S. Lewis and C. E. Boozer, *J. Amer. Chem. Soc.*, 1952, **74**, 308, C. E. Boozer and E. S. Lewis, *ibid.*, 1953, **75**, 3182; S. H. Sharman, F. F. Caserio, R. F. Nystrom, J. C. Leak, and W. G. Young, *ibid.*, 1958, **80**, 5965.
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[5] (a) D. C. Sanders and H. Shechter, *J. Amer. Chem. Soc.*, 1973, **95**, 6858; A. F. Diaz, J. Fulcher, M. Sakai, and S. Winstein, *ibid.*, 1974, **96**, 1294; (b) W. Kirmse and G. Voigt, *ibid.*, p. 7598.
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