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.

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 CCl₄ to provide pyrolysis mixture (A) containing (2) (10%), (3a) (80%), and indene (4) (10%) (estimated from ¹H 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%),


(5)

(6)

(7)

(9)
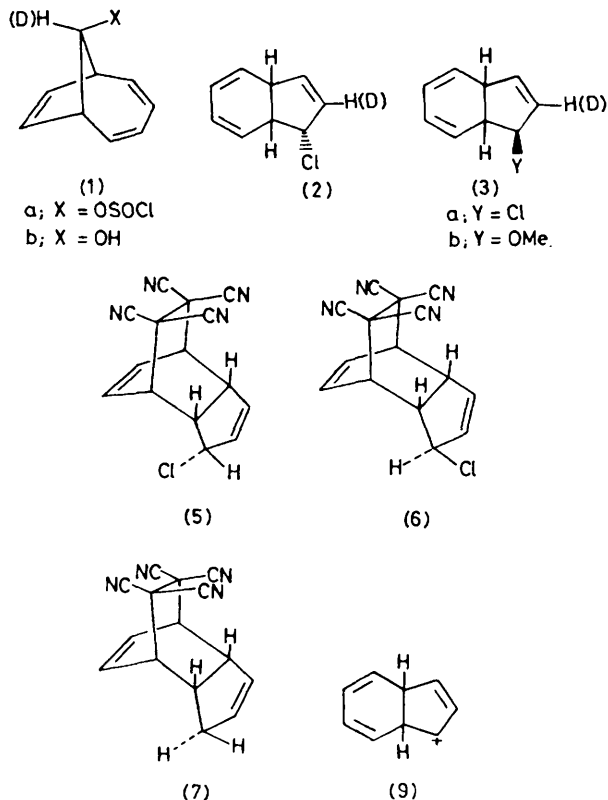
and (4) (5%) with no other products; no polymeric materials were detected in this pyrolysis mixture (estimated from [1]H n.m.r. spectrum). This strongly indicates that (2) is primary product of the thermal decomposition of (1a).

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]
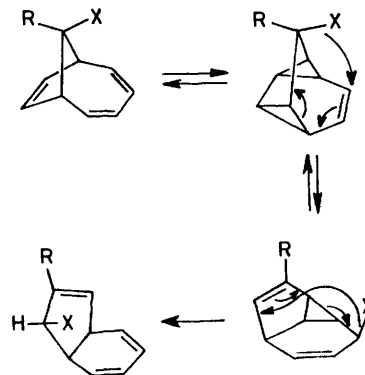
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Other thermodynamically acceptable precursors of cationic intermediates include the 9-substituted cyclonona-1Z,3E,5Z,7Z-tetraenes and the 4-substituted bicyclo[5.2.0]-nona-2,5,8-trienes.[9] Whatever the mechanistic details, it would appear increasingly 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.

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