The Crystal Structure of the 1:1 Adduct of Germacratriene with Silver Nitrate ($C_{15}H_{24}$,$AgNO_3$)

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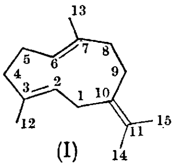
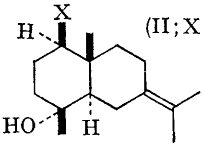
THE monocyclic triene (I) has recently been prepared[1] from the naturally occurring ketone, germacrone; we designate it germacratriene. An all-*trans*-configuration was suggested[1] for the molecule, partly from degradative and spectroscopic studies, and partly from a number of cyclisation reactions all suggesting that the 6–7 double bond is the more susceptible to electrophilic attack. Typical was the formation of the selinane derivative (II) by reaction with *N*-bromosuccinimide in aqueous acetone. In view of such cyclisations, and following Barton and de Mayo,[2] and Hendrickson,[3] the triene was postulated as a possible intermediate in sesquiterpene biosynthesis.

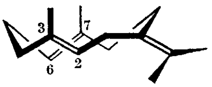


(I)



(II; X=H or Br)

In order to ascertain its conformation and to examine the molecular geometry about the double bonds we have performed a three-dimensional X-ray crystallographic study of the 1 : 1



(Ia)

adduct of germacratriene with silver nitrate ($C_{15}H_{24},AgNO_3 : M = 374{\cdot}2$). Crystal data: monoclinic, space group $P2_1/c$; $a = 7{\cdot}53_2$, $b = 10{\cdot}01_0$, $c = 20{\cdot}90_5$ Å, $\beta = 101{\cdot}75°$ (from Weissenberg data and least-square calculation), $V = 1543$ Å^3, $D_m = 1{\cdot}59 \pm 0{\cdot}05$ g.cm.$^{-3}$, $D_c = 1{\cdot}61$ g.cm.$^{-3}$ for $Z = 4$ formula units per cell. Absorption coefficient, $\mu = 106{\cdot}1$ cm.$^{-1}$ (Cu-K_α radiation).

1192 reflections were estimated visually from Weissenberg photographs. The location of the silver atoms from the three-dimensional Patterson and the solution of the structure from Fourier syntheses were straightforward. Refinement has reduced R to 0·099.

The crystal structure found confirms the constitution (I) suggested by Sutherland *et al.*[1] The actual conformation [see Figure and (Ia)] shows that the planes of the cyclic double bonds are approximately perpendicular to the macrocycle as in humulene.[4] The cell contains two L- and two D-molecules lying between chains of silver and nitrate ions, which run parallel to b (see Figure). Each silver ion is co-ordinated to the 6–7 double bond of one molecule and to the 2–3 double bond of another at Ag–C distances ranging from 2·49 to 2·59 Å (average 2·53 Å). A somewhat similar arrangement occurs in the $AgNO_3$ 1 : 1 adduct with cyclo-octatetraene[5] where Ag–C distances range from 2·46 to 2·84 Å (average 2·65 Å). By contrast, in the $2AgNO_3$–humulene adduct[4] (where each silver ion co-ordinates to only one double bond) the Ag–C distances range from 2·33 to 2·43 Å (average 2·38 Å), indicative of stronger co-ordination.

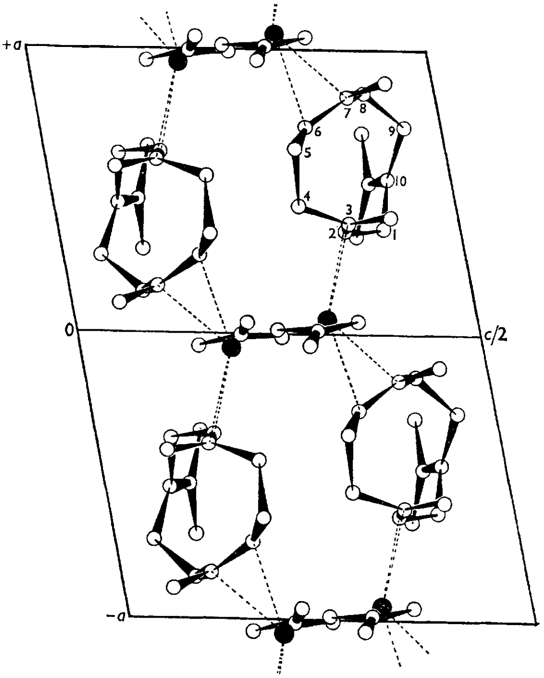


FIGURE. *The* [010] *projection of the crystal structure of the adduct, germacratriene*-$AgNO_3$.

The tensions exerted by the silver ions on the double bonds in the present structure (Figure), and some nonplanar deformation at each end of both cyclic double bonds, have combined to distend the ring much past what can be achieved with a Dreiding model. But there is nothing in the crystal structure to suggest that the double bond at 6–7 is more deformed (and therefore possibly more reactive) than that at 2–3. The conformation in solution is probably not so distended, but must obviously resemble (Ia) (at least immediately prior to cyclisation) and explains the ready formation and the stereochemistry of (II).

The co-ordination of the silver ion consists of 8 atoms, four oxygens (from two nitrate ions) very nearly coplanar (at distances ranging from 2·37 to

2·94 Å) and the four carbon atoms associated with the cyclic double bonds. The arrangement of the eight atoms is rather irregular, but one possible way of describing the co-ordination is to note that the vectors from Ag^+ to the midpoints of the double bonds and to the nitrogen atoms in the two chelated nitrate groups form an approximate tetrahedron as has been found for $[Hg(NO_3)_4]^{2-}$,[6] and for $[Ni(NO_3)_4]^{2-}$,[7] though in these cases the arrangement of the eight oxygen atoms is more regular.

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