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REACTIONS OF CYCLOOCTATETRAENE AND ITS DERIVATIVES - XI.[1] NOVEL ACID-CATALYZED REARRANGEMENT OF A 7,8-DIAZATRICYCLO$[4.2.2.0^{2,5}]$ DECA-3,9-DIENE

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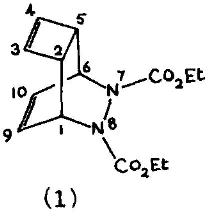
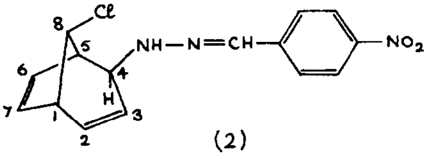
Treatment of the diaza-diester (1) with concentrated hydrochloric acid in glacial acetic acid, followed by alkaline hydrolysis and decarboxylation, gave 8(anti)-chloro-4(exo)-hydrazino-bicyclo[3.2.1]octa-2,6-diene (4), characterized as the p-nitrobenzaldehyde hydrazone.

When the cyclooctatetraene derivative (1)[2] was treated with glacial acetic acid containing ca. 10% concentrated hydrochloric acid, and the ester groups were subsequently removed by hydrolysis and decarboxylation (using potassium hydroxide in ethanol under nitrogen), the resulting crude hydrazino-compound formed a yellow crystalline derivative with p-nitrobenzaldehyde. This hydrazone, $C_{15}H_{14}ClN_3O_2$, m.p. 182-183°C (from $CHCl_3$-EtOH), was identified as the disubstituted bicyclo[3.2.1]octa-2,6-diene (2) on the basis of the spectral evidence, in particular the ^{1}H NMR spectrum. The proton-proton coupling pattern was established by double irradiation, and the values of those principal coupling constants which could be measured were found to be in close agreement with the reported values for bicyclo[3.2.1]octa-2,6-diene and various substituted derivatives.[3,4,5] The values for $J_{1,8}$ and $J_{5,8}$ (both 4.4 Hz) were fully in accord with the illustrated stereo-chemistry at C-8, whereas these coupling constants would be expected to be very small if H-8 were anti to the 6,7-double bond.[3,4] Moreover, the lack of observable coupling between H-4 and H-5 was consistent with an endo configuration for H-4, the dihedral angle between H-4(endo) and H-5 being near to 90° as judged from a molecular model.



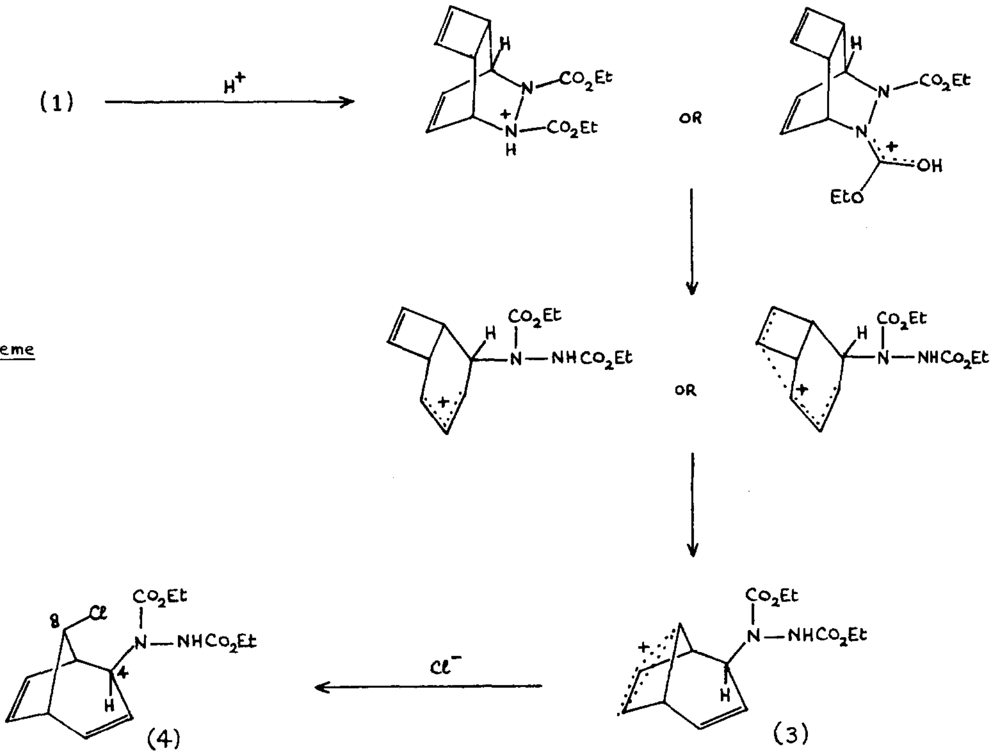
(1)

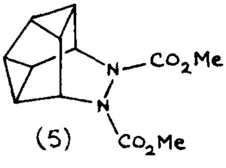


(2)

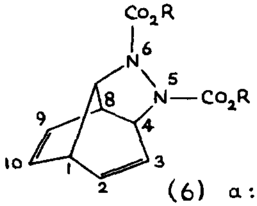
The rearrangement may be visualized as follows (see Scheme). N- (or O-) protonation of the diaza-diester (1), followed by cleavage of a C-N bond, would result in a bicyclic allyl (or homopentadienyl) cation which by a [1,2]-shift could give the bicyclo[3.2.1]octadienyl cation (3). This would be expected to undergo nucleophilic attack at C-8 selectively from the side anti to the participating π-bond. The stereochemistry at C-4 in the product (4) is of course predetermined by the structure of the diaza-bridged starting material (1). This sequence may be compared with the trifluoroacetic acid-catalyzed rearrangement of the 9,10-diazasnoutane(5) to the 5,6-diazatricyclo$[5.3.0.0^{4,8}]$deca-2,9-diene (6a), which would appear to involve, in the penultimate step, ring-closure of the cation (7).[6] When the diaza-diester (1) was treated similarly with trifluoroacetic acid, (6b) was formed [the ^{1}H NMR spectrum of the crude product, discounting signals due to impurities and the protons of the ester groups, was closely similar to that of (6a)[6]]. In the presence of hydrochloric acid, attack by chloride ion on the cation (3) evidently competes successfully with the cyclisation leading to (6b).

Scheme

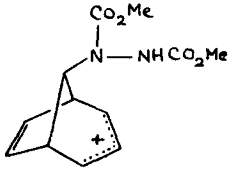




(5)



(6) a : R = Me
b : R = Et



(7)

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