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ADDITION OF IODINE AZIDE TO C-9 AND C-10 MEDIUM-RING DIENES

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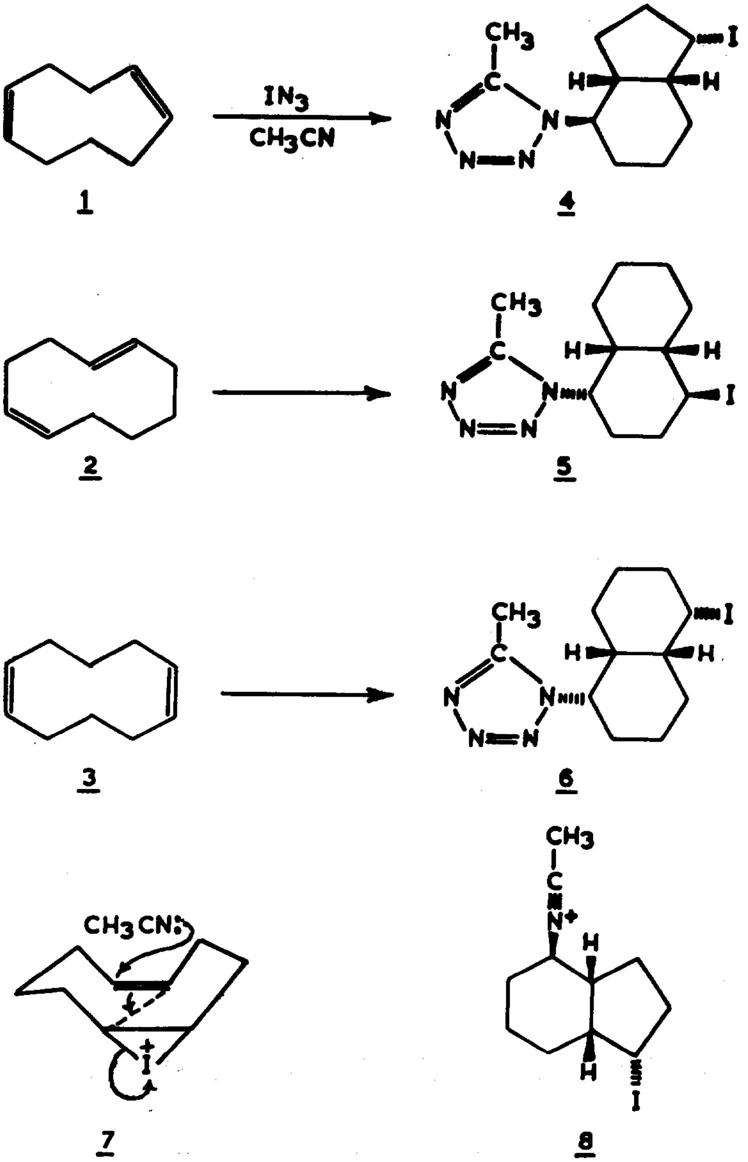
It is well known that the medium-ring dienes C-8, C-9 and C-10 show many transannular cyclization reactions with electrophilic reagents[1,2]. Therefore, we considered it interesting to ascertain whether C-9 and C-10 dienes, cis,cis-1,5-cyclononadiene (1), cis,trans-1,5-cyclodecadiene (2) and cis,cis-1,6-cyclodecadiene (3) behave like cis,cis-1,5-cyclooctadiene with IN_3. It has been shown recently that cis,cis-1,5-cyclooctadiene reacts with IN_3 in 1:1 mole ratio to form monocyclic unsaturated 1,2-adduct which suggests the non-participation of the π-electrons in the ring opening of the three-membered iodonium ion intermediate[3,4].

Iodine azide was prepared in situ in the manner described by Hassner and co-workers[5] by addition of ICl (0.11 mole) to a stirred suspension of NaN_3 (0.25 mole) in CH_3CN (25 ml) at ca. 0°. The diene (0.10 mole) in CH_3CN (20 ml) was added slowly at 0° over a period of 30 min and stirred overnight at room temperature. The usual work-up procedure followed by chromatography over neutral alumina using petroleum ether (40-60°) gave 1:1 pure solid adduct.

The addition of 1 to IN_3 proceeded to yield a tetrazole derivative (4) in 80% yield (Scheme 1). The solid adduct 4 decomposed on heating. The

Scheme 1



elemental analysis was in accord with that calculated for $C_{11}H_{17}IN_4$. The IR spectrum had no absorption at 2100 cm^{-1}, but a series of peaks at 1600-1400 cm^{-1} characteristic of N-N double bond. The NMR spectrum showed absorptions at δ 4.95 (q, 1H, iodomethine), 4,35 (m, 1H, tetrzoyl-methine), 2.50 (s, 3H, tetrazoyl-methyl) and 3.00-1.10 (m, 12H, ring methine and methylene). The MS of 4 had a molecular ion peak at m/e 331, and other peaks at 205 (M^+-I), 127 (I) and 121 ($M-C_2H_3N_4I$) in agreement with the assigned structure for 4. The stereochemistry of 4 was assigned based on the known transannular reactions of 1[6]. Similarly, the addition of 2 to IN_3 yielded 5, whereas the addition of 3 to IN_3 gave 6 whose structural assignments were deduced by elemental analysis, IR, NMR, MS and known reactions of 2[7,8] and 3[9].

Our results are consistent with an electrophilic transannular addition reaction involving the intervention of a cyclic iodonium ion. The formation of the tetrazole derivative (4) from 1 is rationalized on the basis of the solvent assisted opening of the initially formed iodonium ion (7) to give the Ritter reaction intermediate (8) which undergoes cycloaddition with azide ion to form 4 as shown in the Scheme 1. Although the participation of solvent has not been observed by Hassner and co-workers[10] among the innumerable olefins examined with IN_3, it has been shown recently that such a participation takes place with α- and β-pinene[11,12]. However, the exact reason for such a participation followed by cycloaddition by the azide ion to form tetrazole derivative in specific cases, is not clear. Furthermore, we have observed that the reaction of 1 with IN_3 in methylene dichloride gives the expected transannular product, and also confirmed the results reported regarding the addition of IN_3 to cis,cis-1,5-cyclooctadiene.

In conclusion, our results with C-9,and C-10 medium-ring dienes indicate the different behaviour of these dienes as compared with C-8 diene. The present reactions shed light on the diverse behaviour of unsaturated three-membered ring iodonium ion intermediates in C-8, C-9 and C-10 medium-ring dienes and the conformational factors governing ionic additions.

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