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NOVEL STEREOSPECIFIC SYN ADDITION OF IODINE AZIDE TO A STRAINED CYCLOBUTENE (TRICYCLO[4.2.2.0^{2,5}] DECA-3,7-DIENE DERIVATIVE)

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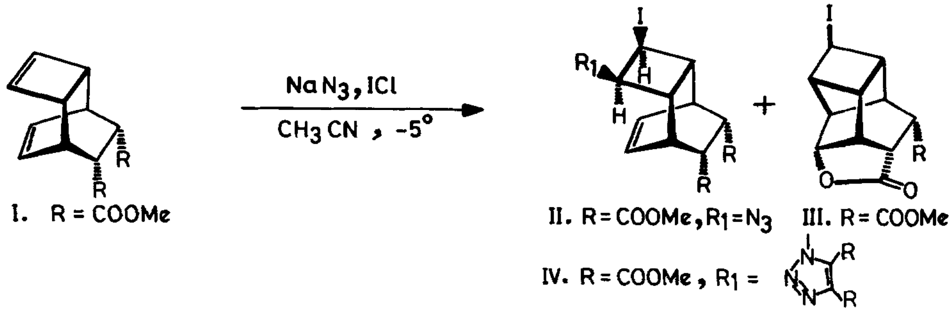
The addition of iodine azide (IN_3) to olefins provides a versatile route for the synthesis of organic azides.[1a] These reactions have been shown to be highly stereospecific anti additions, leading to trans products via the iodonium ion intermediates.[1a,b] In pursuit of certain synthetic aims the reaction of IN_3 with 9,10-dicarbomethoxytricyclo[4.2.2.0^{2,5}] deca-3,7-diene (I) has been investigated. We wish to report here the first example[2] of exclusive syn addition of IN_3 to the strained cyclobutene ring of (I). The syn addition of IN_3 to the cyclobutene double bond of (I) is in contrast to the usually observed anti addition of electrophiles to cyclobutene[3,4] and highlights the dominant role of twist strain[4] in electrophilic additions to strained olefins.



I. R = COOMe

II. R = COOMe, R$_1$ = N$_3$

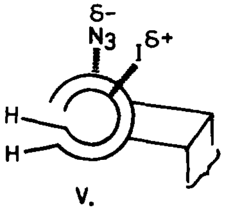
III. R = COOMe

IV. R = COOMe, R$_1$ =

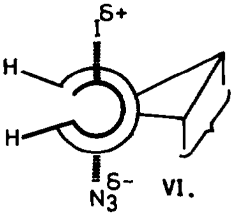
The reaction of (I) with IN_3 solution prepared in situ from excess sodium azide and iodine monochloride in acetonitrile (-5°) furnished a mixture of (II) & (III) in 80 and 10% yield. The minor compound (III), mp 161°, was clearly a product of transannular cyclisation and was identical with the product obtained[5] by the addition of ICl to (I). The major product (II), mp 137°, $C_{14}H_{16}O_4IN_3$, exhibited the diagonistic azide absorption at 2120 cm^{-1}

and the ester bands at 1740 & 1210 cm^{-1} in the ir spectrum. The pmr spectrum showed two quartets at δ 4.32 and 3.12 due to *H*-C-I and *H*-C-N_3 type protons along with a clean triplet at δ 6.51 due to the two olefinic protons. The *cis* orientation of I and N_3 on the cyclobutene ring follows from the relatively sharp triplet for the two olefinic protons at C_7 and C_8 arising from the equivalence of the vinyl hydrogens and the fortuitous near equivalence of their coupling constants.[6] Furthermore, the 1,3-dipolar addition product (IV), mp 192-4°, of (II) with dimethylacetylenedicarboxylate also displayed, as expected, a sharp triplet at δ 6.61 for the olefinic protons at C_7 and C_8.

The formation of *cis* products in the IN_3 addition and oxymercuration[7] of (I), as against the formation of both *cis* and *trans* products in the addition[8] of halogens, is reminiscent of the analogous behaviour of norbornene and bicyclo [2.1.1] hex-2-ene.[9] These results are best explained on the basis of the twist strain theory[4] and the *syn* transition state (V) is favoured over the strained *anti*-coplanar transition state (VI).



V.



VI.

REFERENCES

1. A. Hassner, Acc. Chem. Res., **4**, 9 (1971); F.W. Fowler, A. Hassner, and L.A. Levy, J. Amer. Chem. Soc., **89**, 2077 (1967).
2. This *syn* addition of IN_3 to (I) has also been independently observed by Professor T. Sasaki, Nagoya University. We wish to thank him for a preprint of his publication, T. Sasaki, K. Kanematsu and A. Kondo, Tetrahedron, In Press.
3. M. Avram, E. Marcia and C.D. Nenitzescu, Chem. Abstrs. **54**, 8664f (1960).
4. T.G. Traylor, Acc. Chem. Res., **2**, 152 (1969); T.G. Traylor and A.W. Baker, J. Amer. Chem. Soc., **85**, 2746 (1963).
5. We find that addition of many electrophiles to (I) proceeds via a cross type cyclisation followed by lactonisation. G. Mehta, P.K. Dutta and P.N. Pandey, Unpublished results; also see, T. Sasaki, K. Kanematsu and A. Kondo, J. Org. Chem., **39**, 2246 (1974).
6. The appearance of a symmetrical triplet for the vinyl protons at C_7 and C_8 in tricyclo [4.2.2.0^{2,5}] dec-7-enes is diagonistic of symmetrical *endo* substitution at C_3 and C_4 and has been used for the determination of configuration at C_3 and C_4. J.P. Snyder and D.G. Farnum, J. Org. Chem., **31**, 1699 (1966).
7. G. Mehta, P. K. Dutta and P. N. Pandey, Unpublished results.
8. D. G. Farnum and J. P. Snyder, Tetrahedron Letters, 3861 (1965).
9. F. T. Bond, J. Amer. Chem. Soc., **90**, 5326 (1968).