Intramolecular Cycloadditions of α- and β-Allylthioalkyl Diazoalkanes

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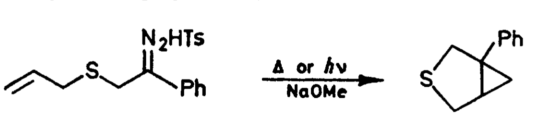
Summary 3-Thiabicyclo[3,1,0]hexanes and 4-thiabicyclo-[4,1,0]heptanes were obtained by the intramolecular cycloadditions of α- and β-allylthioalkyl diazoalkanes.

Thermal cycloaddition of diazoalkanes to the simple non-conjugated olefins is known to be a very slow and difficult reaction.[1,2] On the other hand, the thermal or photochemical formation of cyclopropanes from diazoalkanes and non-conjugated olefins is believed to be a carbenic process.[3] Certain diazoalkanes bearing an allylthio-substituent have been found, however, to undergo a ready intramolecular cycloaddition to produce pyrazolines, which are further transformed into cyclopropanes under the reaction conditions. The reaction may open a novel route to thiabicyclic ring systems.†



(I) (II)

α-Allylthioacetophenone tosylhydrazone (I) was thermally decomposed in diglyme in the presence of sodium methoxide at 150°. Distillation of the reaction mixture under reduced pressure afforded 1-phenyl-3-thiabicyclo-[3,1,0]hexane (II) as the sole isolable product in 68·5% yield; no olefins arising from a carbenic process could be detected in the product by g.l.p.c. analyses.[4] Photodecomposition of the sodium salt of the tosylhydrazone (I) in monoglyme at 10° also afforded (II) in 87·5% yield.‡ The carbenic process could be observed in this α-allylthio-system when the photolysis was carried out at −70°.[4] Thus, the formation of 3-thiabicyclo[3,1,0]hexane may mean that an intramolecular cycloaddition of the diazoalkane moiety to the double bond of allylthio-group and subsequent elimination of molecular nitrogen do really occur under the reaction conditions.

In a similar way, 3,3-dimethyl-1-phenyl-4-thiabicyclo-[4,1,0]heptane (IVa) was obtained in 45% yield by the thermal decomposition of β-allylthio-β-methylbutyrophenone tosylhydrazone (IIIa). The thermolysis of β-crotylthio-β-methylbutyrophenone tosylhydrazone produced 3,3,7-trimethyl-1-phenyl-4-thiabicyclo[4,1,0]heptane (IVb) in 44% yield. The n.m.r. spectrum and g.l.p.c. analyses of the product revealed that (IVb) is a mixture of *endo*- and *exo*-isomers in the ratio of 25·5:74·5. Photolysis of these

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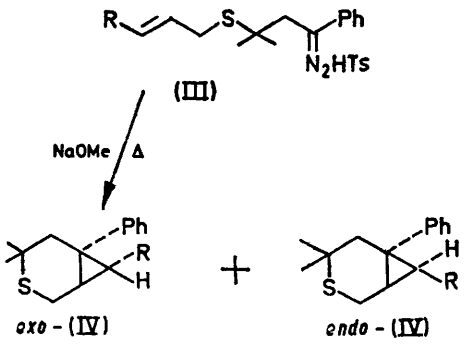
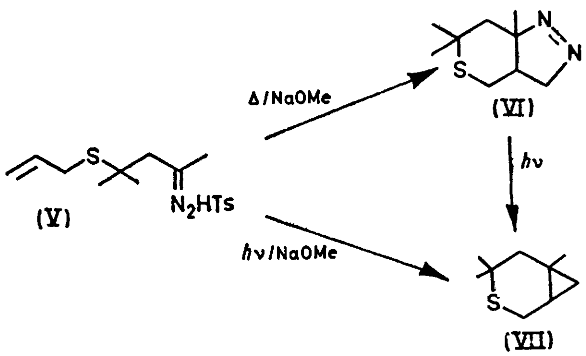
† The n.m.r. and mass spectra and elemental analyses of all new compounds were consistent with the structures assigned.

‡ Photolyses were performed with 450 w high-pressure Hg lamp using a Pyrex filter.

β-allylthio-systems at 10° afforded entirely different products.[4]



Conclusive evidence for the intramolecular thermal cycloaddition of the diazoalkane was obtained when 4-allylthio-4-methylpentan-2-one tosylhydrazone (V) was used as a substrate. Thus, the thermal decomposition of (V) in the presence of sodium methoxide at 150° afforded the bicyclic pyrazoline (VI) in 33% yield. On the other hand, photolysis of the sodium salt of (V) at 10° for 2 h yielded 1,3,3-trimethyl-4-thiabicyclo[4,1,0]heptane (VII) in 48% yield. Moreover, when the Δ-^{1}pyrazoline (VI) was irradiated under the same conditions, the same product (VII) was obtained in good yield. The photochemical generation of carbenes *via* diazo-compounds from tosylhydrazones under basic conditions is a known reaction.[5] Therefore, it can be concluded that the intramolecular thermal cycloaddition is a ready process even at 10°, and that the subsequent elimination of nitrogen is also an effective process under the photolytic conditions.



The unusually high efficiency of this intramolecular cycloaddition to the isolated double bond might be due to some kind of activating effect of the sulphur atom in the allylthio-group, but at present we have no convincing explanation.

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