The Thermal Rearrangement of a 4-Thia-1-azabicyclo[4,1,0]hept-2-ene

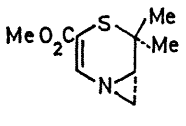
By A. R. DUNN and R. J. STOODLEY*

(*Department of Organic Chemistry, The University, Newcastle upon Tyne* NE1 7RU)

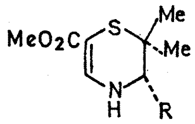
Summary (6*S*)-3-Methoxycarbonyl-5,5-dimethyl-4-thia-1-azabicyclo[4,1,0]hept-2-ene is converted into 2,3-dihydro-(3*R*)-(2-propenyl)-6-methoxycarbonyl-1,4-thiazine in boiling toluene.

IN connection with some work aimed at evaluating the nature of the u.v. absorption of some conjugated aziridines,[1] we required (6*S*)-3-methoxycarbonyl-5,5-dimethyl-4-thia-1-azabicyclo[4,1,0]hept-2-ene (I). The ester (II), available from another study,[2] was reduced with $LiBH_4$ in tetrahydrofuran to give the alcohol (III), m.p. 86—89°, $[\alpha]_D$ − 235° ($CHCl_3$), which was converted into the tolyl-*p*-sulphonate (IV), m.p. 126—127°, $[\alpha]_D$ − 314° ($CHCl_3$). When (IV) was treated with NaH in tetrahydrofuran, the bicyclic aziridine (I), $[\alpha]_D$ − 220° ($CHCl_3$), was formed in excellent yield. We now report a novel, thermally-induced rearrangement of (I).

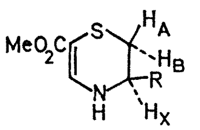
The aziridine was heated under reflux in toluene and the reaction was monitored by t.l.c. After 4 days no starting material remained and a number of slower-moving components were detected. The major fraction (54%), m.p. 132—133°, $[\alpha]_D$ + 38° ($CHCl_3$), which was isolated after silica gel chromatography, is formulated as 2,3-dihydro-(3*R*)-(2-propenyl)-6-methoxycarbonyl-1,4-thiazine (V) on the following evidence.



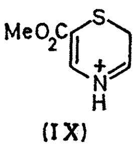
(I)



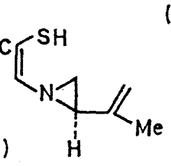
(II) R = CO_2Me
(III) R = CH_2OH
(IV) R = CH_2OTs



(V) R = $CMe{:}CH_2$
(VI) R = $CHMe_2$
(VII) R = Me
(VIII) R = CH_2I



(IX)



(X)

Micro-analysis and mass spectrometry indicated that the compound was isomeric with the starting material. The mass spectrum also exhibited a prominent peak at *m/e* 158, believed to be due to the ion (IX), which is characteristic of 3-substituted 2,3-dihydro-6-methoxycarbonyl-1,4-thiazines. I.r. spectroscopy (KBr) revealed absorptions at 3330 (NH), 1645 (unsaturated ester CO), and 1590 (C=C) cm.$^{-1}$, typical of the vinylgous urethan group; a u.v. maximum (EtOH) at 314 nm. (ϵ 11,200) corroborated this interpretation.[3] The 90 MHz n.m.r. spectrum ($CDCl_3$) showed singlets at τ 8·18 (vinylic Me), 6·24 (CO_2Me), 5·2 (br, NH), and 5·06 and 4·97 ($C{=}CH_2$); the C-2 methylene group appeared as an octet with τ_A 7·27 (J_{AB} 12·9, J_{AX} 6·9 Hz) and τ_B 7·15 (J_{AB} 12·9, J_{AX} 2·8 Hz), the C-3 proton as a multiplet at 5·92, and the vinylic proton as a doublet at 2·28 (*J* 7 Hz). After the deuteriochloroform solution was shaken with deuterium oxide the NH signal disappeared, the multiplet at 5·92 simplified to a quartet, and the doublet collapsed to a single line. Catalytic hydrogenation of (V) afforded 2,3-dihydro-6-methoxycarbonyl-(3*R*)-(2-propyl)-1,4-thiazine (VI), m.p. 114—116°, $[\alpha]_D$ + 123° ($CHCl_3$), in quantitative yield. Since (VI) possesses an optical rotation which is similar in sign and magnitude to that of 2,3-dihydro-6-methoxycarbonyl-(3*R*)-methyl-1,4-thiazine[4] (VII) {$[\alpha]_D$ + 159° ($CHCl_3$)}, we conclude that (V) possesses the *R*-configuration at position 3 and that the rearrangement of (I) probably occurs in high optical yield.

This result is of some mechanistic interest since an unusual 1,3-migration of sulphur† must occur. Recently

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† Paquette and his co-workers have recently shown that 1,4-sulphur participation is important in the solvolysis of some caged toluene-*p*-sulphonates.[5]

we have reported a similar, but degenerate, thermally-induced rearrangement in which 2,3-dihydro-(3*R*)-iodomethyl-6-methoxycarbonyl-1,4-thiazine (VIII) undergoes racemisation, and we have shown that a 1σ, 3σ-bond switch is involved.[6] In the present case two mechanisms, which have different stereochemical outcomes, warrant consideration for the sulphur-migration step. An intermediate such as (X), derivable from (I) by rupture of the S-4–C-5 bond, may undergo an intramolecular reaction in which the thiol group attacks the aziridine primary carbon, and, after proton transfer, (V) may be formed. This pathway requires an inversion of configuration at the aziridine methylene group. Alternatively, (I) may react in its thermodynamically unfavourable conformation[1] and undergo a concerted reorganisation in which the new S–C bond is formed with retention of configuration. As yet the stereospecific introduction of a single deuterium atom into the 7-methylene group of (I), which would enable these routes to be distinguished, has not been accomplished.

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