# Studies Related to Dihydro-1,4-thiazines. Part I. Rearrangements Involving 1,3-Sulphur Migrations [1]

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Methyl (3*S*)-3,4-Dihydro-3-iodomethyl-1,4-2*H*-thiazine-6-carboxylate (6) undergoes racemisation when heated under reflux in ethyl methyl ketone; deuterium-labelling experiments reveal that a 1,3-sulphur migration is involved. Under corresponding conditions, methyl (3*R*)-3,4-dihydro-3-iodomethyl-2,2-dimethyl-1,4-2*H*-thiazine-6-carboxylate (20) rearranges to methyl (3*R*)-3,4-dihydro-3-isopropenyl-1,4-2*H*-thiazine-6-carboxylate (8). Methyl (6*S*)-5,5-dimethyl-4-thia-1-azabicyclo[4,1,0]hept-2-ene-3-carboxylate (21) also affords compound (8) when heated in boiling toluene.

In connection with work related to the conformational behaviour of dihydro-1,4-thiazines,[2,3] methyl (3*S*)-3,4-dihydro-3-iodomethyl-1,4-2*H*-thiazine-6-carboxylate (6) was prepared (98%) by heating the methanesulphonate (4) with sodium iodide in ethyl methyl ketone for 22 h.[3] The iodide (6) was also obtained (93%) by treating the aziridine[3] (12) with hydriodic acid. Although the materials were identical, on the basis of m.p., chromatographic mobility, and i.r. and n.m.r. spectroscopy, the former sample possessed a significantly lower optical rotation {$[\alpha]_D$ +54° ($CHCl_3$)} than the latter {$[\alpha]_D$ +93° ($CHCl_3$)}. It therefore appeared that some racemisation had occurred in the former reaction; indeed, when the mixture was left for 9 days, the derived iodide was optically inactive. In a control experiment, the optically pure iodide was heated under reflux in ethyl methyl ketone for 10 days; complete loss of optical activity was observed, indicating that the racemisation is thermally induced.

In seeking an explanation for this behaviour, the possibility that the iodide equilibrates with the olefin (15), by a reversible elimination–addition of hydriodic acid, was considered. This pathway is not likely since the imino-group of the iodide (6) is not expected to be of sufficient basicity to induce the elimination and, furthermore, addition of hydriodic acid to intermediate (15) is not expected to regenerate the iodide (6). Nevertheless, the route was tested by racemising the iodide in ethyl methyl ketone saturated with deuterium oxide. The racemic iodide did not incorporate deuterium, on the basis of mass spectroscopy; consequently, the intervention of the olefin (15) is excluded.

A second possibility was that a 1,3-sulphur migration is involved in the iodide racemisation. In such an event the 2-methylene and exocyclic methylene groups become equivalent during the course of the reaction. The dideuteriated iodide (7) was required to test this proposal. Reduction of the ester[2] (1) with lithium borodeuteride afforded the alcohol (3), which was converted into the methanesulphonate (5) by methanesulphonyl chloride. Sodium hydride transformed the last-named derivative into the aziridine (13), which yielded the iodide (7), $[\alpha]_D$ +87° ($CHCl_3$), in the presence of hydriodic acid. Mass spectroscopy indicated that the

(1) R = $CO_2Me$
(2) R = $CH_2$·OH
(3) R = $CD_2$·OH
(4) R = $CH_2$·O·$SO_2Me$
(5) R = $CD_2$·O·$SO_2Me$
(6) R = $CH_2I$
(7) R = $CD_2I$
(8) R = CMe:$CH_2$
(9) R = $CHMe_2$
(10) R = Me
(11) R = $CIMe_2$

(12) R = H
(13) R = D
(14) R = Me

(15)

(16)

(17) R = $CO_2Me$
(18) R = $CH_2$·OH
(19) R = $CH_2$·OTs
(20) R = $CH_2I$

(21)

[1] Preliminary communications, A. R. Dunn and R. J. Stoodley, *Chem. Comm.*, 1969, 1169, 1368.

[2] A. R. Dunn, I. McMillan, and R. J. Stoodley, *Tetrahedron*, 1968, **24**, 2985.

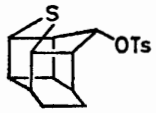
[3] A. R. Dunn and R. J. Stoodley, *Tetrahedron Letters*, 1969, 2979; *Tetrahedron*, 1972, **28**, 3315.

iodide (7) was *ca.* 85% dideuteriated, *ca.* 14% monodeuteriated, and *ca.* 1% undeuteriated; the presence of a prominent peak at *m/e* 158, also present in the mass spectrum of the undeuteriated iodide and believed to be due to the ion (16), confirmed that the isotope was confined to the exocyclic methylene group. N.m.r. spectroscopy substantiated this result since there was no octet centred at $\tau$ 6·7 ($CDCl_3$) for the iodomethyl protons.[3] When the dideuteriated iodide (7) was heated in ethyl methyl ketone for 9 days its optical rotation fell to zero and, on the basis of n.m.r. and mass spectroscopy, the deuterium was *ca.* equally distributed between the 2-methylene and exocyclic methylene groups of the product. Clearly, therefore, the racemisation occurs by a degenerate rearrangement involving a 1,3-sulphur migration.

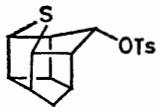
In an attempt to provide an example of a non-degenerate rearrangement, the thermal behaviour of methyl (3*R*)-3,4-dihydro-3-iodomethyl-2,2-dimethyl-1,4-2*H*-thiazine-6-carboxylate (20) was examined. The iodide was obtained quantitatively from hydriodic acid and the aziridine (21), which, in turn, was prepared from the ester [4] (17) by a route analogous to that employed in the synthesis of compound (12).[3] Thus, the ester (17) was quantitatively reduced by lithium borohydride in dioxan to the alcohol (18), which was converted into the toluene-*p*-sulphonate (19) (92%) by toluene-*p*-sulphonyl chloride in pyridine; the last-named derivative afforded the aziridine (21) (96%) in the presence of sodium hydride in tetrahydrofuran.

When heated in ethyl methyl ketone for 5 days the iodide (20) was converted mainly into material which ran more slowly on t.l.c. This component, which was isolated in 67% yield after silica gel fractionation, is considered to be methyl (3*R*)-3,4-dihydro-3-isopropenyl-1,4-2*H*-thiazine-6-carboxylate (8), on the basis of analytical and spectroscopic evidence. Catalytic hydrogenation of compound (8) afforded methyl (3*R*)-3,4-dihydro-3-isopropyl-1,4-2*H*-thiazine-6-carboxylate (9) in high yield. The absolute stereochemistry of the latter derivative is assigned on the basis of its optical rotation {$[\alpha]_D$ +123° ($CHCl_3$)}, which is similar in sign and magnitude to that of methyl (3*R*)-3,4-dihydro-3-methyl-1,4-2*H*-thiazine-6-carboxylate [3] (10) {$[\alpha]_D$ +159° ($CHCl_3$)}.

The foregoing rearrangements are significant since 1,3-sulphur migrations are involved. There appears to be little precedence for such shifts although Paquette and his co-workers have reported [5] that 1,4-sulphur participation is important in the solvolysis of the caged tosylate (22), in which the S(1)–C(4) bond distance is *ca.* 2·6 Å; there is also evidence for some participation in the case of compound (23). It has been previously shown that there is a marked tendency for the iodide (6) to adopt the conformation with the iodomethyl group in the axial position.[3] This behaviour was attributed to the presence of a dipolar attraction between the sulphur atom and the electrophilic carbon atom of the 3-substituent. It is of added interest, therefore, that these centres, which are *ca.* 2·8 Å apart according to Dreiding models, can participate in bond-making and -breaking processes.

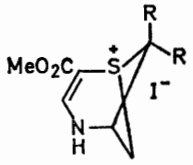



(22)

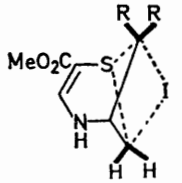



(23)

The possibility that the aziridines are intermediates in the iodide rearrangements can be excluded; thus, when heated in ethyl methyl ketone, compound (12) was not racemised and compound (21) did not afford (8). Two pathways, therefore, warrant consideration for the 1,3-sulphur shifts. The rearrangements may either involve the ion-pairs (24) and (25) or they may




(24) R = H
(25) R = Me




(26) R = H
(27) R = Me

occur in a concerted manner, possible *via* transition states (26) and (27). The stereochemical consequences of these mechanisms are distinct: the former requires a 1,3-sulphur migration with inversion of configuration at the exocyclic methylene group, whereas the latter demands retention of configuration at this site. Moreover, in the case of compound (20), the iodide (11) is an obligatory intermediate if the concerted reorganisation operates; a similar intermediate may intervene in the non-concerted process although the ion-pair (25) may also afford the product (8) by direct loss of a proton.

Although the aziridines were shown not to be involved in the iodide rearrangements, they did undergo thermal reactions at higher temperatures. Thus, compound (21) was slowly (*ca.* 4 days) converted into a mixture of products in boiling toluene (b.p. 110°). The main component, which was stable under the reaction conditions, was isolated in 53% yield after silica gel chromatography; it was the isopropenyl derivative (8). Aziridine (12) underwent little reaction when heated in boiling toluene for 7 days. However, in boiling xylene (b.p. 140°) it had been converted into a complex mixture of products after 3 days; the mixture was not effectively fractionated by silica gel chromatography and was not further investigated.

The isomerisation of the aziridine (21) to compound (8) is also of mechanistic interest since a 1,3-sulphur migration is again implicated. The migration may be concerted with the cleavage of the 1,7- and 4,5-bonds or it may occur after fission of these linkages.

[4] I. McMillan and R. J. Stoodley, *Tetrahedron Letters*, 1966, 1205; *J. Chem. Soc.* (*C*), 1968, 2533.

[5] L. A. Paquette, G. V. Meehan, and L. D. Wise, *J. Amer. Chem. Soc.*, 1969, **91**, 3231.

A study of the rearrangements of the iodides (6) and (20) and the aziridine (21), specifically monodeuteriated in the exocyclic methylene and 7-methylene groups, is expected to provide insight into these mechanistic details.

## EXPERIMENTAL

N.m.r. spectra were determined for *ca.* 0·2M-solutions with tetramethylsilane as internal standard; 60 MHz spectra were recorded with a Perkin-Elmer R10 spectrometer and 90 MHz spectra with a Brucker Spectrospin. Optical rotations were measured at room temperature (*ca.* 20°) with a Bendix–Ericson automatic polarimeter. I.r. spectra were recorded with a Hilger and Watts Infrascan. U.v. spectra were measured for solutions in ethanol with a Unicam SP 800. Mass spectra were determined with an A.E.I. MS9 spectrometer.

Adsorption chromatography was carried out on silica gel (Mallinckrodt) or aluminium oxide (Savoury and Moore). T.l.c. was performed with Gelman chromatography medium ITLC type SA in chloroform–ethyl acetate (9 : 1); compounds were detected with iodine vapour.

*Methyl* (3S)-3,4-*Dihydro*-3-*iodomethyl*-1,4-2*H*-*thiazine*-6-*carboxylate* (6).—(*a*) The iodide (6), m.p. 125—126° (from chloroform–light petroleum), $[\alpha]_D$ +54° (0·2% in $CHCl_3$), was obtained by heating the methanesulphonate (4) with sodium iodide in ethyl methyl ketone as described earlier.[3]

(*b*) The aziridine [3] (12) (1·00 g, 6 mmol) was dissolved in methanol (20 ml) and acidified with dilute hydriodic acid. The solution was extracted with chloroform and the extract dried ($MgSO_4$). Evaporation left the iodide (1·63 g, 93%), m.p. 125—126° (from chloroform–light petroleum), $[\alpha]_D$ +93° (0·2% in $CHCl_3$), identical (t.l.c. and i.r. and n.m.r. spectroscopy) with that obtained in method (*a*).

*The Dideuteriated Iodide* (7).—The dideuteriated aziridine (13) was obtained in a manner similar to that used to prepare the aziridine [3] (12) except that the ester (1) was reduced with lithium borodeuteride in place of lithium borohydride. Compound (13) (0·50 g, 3 mmol) was converted into the dideuteriated iodide (7) as described in procedure (*b*); m.p. 125—126° (from chloroform–light petroleum), $[\alpha]_D$ +87° (0·2% in $CHCl_3$). The i.r. spectrum of the material was similar to that of the undeuteriated iodide; the n.m.r. spectrum was also similar except that the octet centred at *ca.* τ 6·7, due to the exocyclic methylene group, was absent. Mass spectrometry indicated that the substance was *ca.* 85% dideuteriated, *ca.* 14% monodeuteriated, and *ca.* 1% undeuteriated; a prominent peak at *m/e* 158, probably due to the ion (16), was present but there were no peaks at *m/e* 159 and 160.

*Racemisation of the Iodides* (6) *and* (7).—(*a*) The optically pure iodide (6) (0·030 g, 0·1 mmol) was heated in boiling ethyl methyl ketone (2 ml) for 9 days. Evaporation left a crystalline residue, which possessed similar chromatographic mobility, m.p., and i.r. and n.m.r. spectra to those of the starting material; $[\alpha]_D$ 0° (0·2% in $CHCl_3$).

(*b*) The optically pure iodide (6) (0·030 g, 0·1 mmol) was heated under reflux in ethyl methyl ketone (2 ml) and deuterium oxide (0·2 ml). After 10 days the solution was diluted with chloroform and shaken with water. The dried ($MgSO_4$) organic layer was evaporated to give the iodide, $[\alpha]_D$ 0° (0·2% in $CHCl_3$). The m.p., and i.r., n.m.r., and mass spectra of the sample were identical with those of the starting material.

(*c*) The optically pure dideuteriated iodide (7) was racemised in ethyl methyl ketone as in procedure (*a*). Mass spectroscopy indicated that the optically inactive product possessed 52·7% of the total deuterium in the exocyclic methylene group and 47·3% in the 2-methylene group. The analysis was performed by comparing the peak heights at *m/e* 158 with the sum of those at *m/e* 159 and 160; the former represents unrearranged and the latter rearranged mono- and di-deuteriated iodide. N.m.r. spectroscopy corroborated this result and showed signals at τ 7·1 and 6·7 for the 2-methylene and exocyclic methylene groups, respectively; the combined signals integrated for 2 protons.

*Methyl* (3S)-3,4-*Dihydro*-3-*hydroxymethyl*-2,2-*dimethyl*-1,4-2*H*-*thiazine*-6-*carboxylate* (18).—The ester [4] (17) (2·45 g, 0·01 mol) was dissolved in dry dioxan (25 ml) and lithium borohydride (0·218 g, 0·01 mol) was added. The mixture was stirred at room temperature until starting material was not detected on t.l.c. (*ca.* 4 days) and water was then added. Metal ions were removed by IR-120 ($H^+$) resin and the solvent was evaporated off. The residue was dissolved in methanol and the solution concentrated (repeated 3 times) to leave the *alcohol* (18) (2·17 g, 100%), m.p. 86—89° (after sublimation under reduced pressure), $[\alpha]_D$ −235° (0·2% in $CHCl_3$), $\nu_{max.}$ (KBr) 3460 (OH), 3370 (NH), 1635 and 1625 (unsat. C=O), and 1605 (C=C) $cm^{-1}$, $\lambda_{max.}$ 259 (ε 1600) and 311 nm (9200), τ (60 MHz; $CDCl_3$) 8·70 (6H, s, *gem*-$Me_2$), 6·7—6·05 (4H, m, 3-H and $CH_2$·OH), 6·30 (3H, s, $CO_2Me$), 4·05br (1H, NH), and 2·35 (1H, d, *J* 7 Hz, 5-H) (addition of $D_2O$ to the solution caused the signal at τ 4·05 to disappear, that at 6·7—6·05 to sharpen slightly, and that at 2·35 to collapse to a singlet) [Found: C, 49·1; H, 6·85; N, 6·15%; *M* (mass spectrum), 217. $C_9H_{15}NSO_3$ requires C, 48·8; H, 6·9; N, 6·45%; *M*, 217].

*Methyl* (3S)-3,4-*Dihydro*-2,2-*dimethyl*-3-p-*tolylsulphonyloxymethyl*-1,4-2*H*-*thiazine*-6-*carboxylate* (19).—The alcohol (18) (2·17 g, 0·01 mol) was dissolved in pyridine (10 ml) and toluene-*p*-sulphonyl chloride (2·10 g, 0·011 mol) was added. The mixture was left overnight, acidified with dilute hydrochloric acid, and extracted with chloroform. The organic layer was washed with water, dried ($MgSO_4$), and evaporated to yield the *toluene*-p-*sulphonate* (19) (3·41 g, 92%), m.p. 126—127° (from chloroform–light petroleum ether), $[\alpha]_D$ −314° (0·2% in $CHCl_3$), $\nu_{max.}$ (KBr) 3320 (NH), 1655 (unsat. C=O), and 1600 (C=C) $cm^{-1}$, $\lambda_{max.}$ 226 (ε 13,800) and 308 nm (10,100), τ (60 MHz; $CDCl_3$) 8·73 (6H, s, *gem*-$Me_2$), 7·55 (3H, s, tolyl Me), 6·65 (1H, m, 3-H), 6·30 (3H, s, $CO_2Me$), 5·95 (2H, octet, *J* 8, *J'* 4 Hz, $CH_2O$), 4·9br (1H, NH), 2·65 and 2·21 (each 2H, d, *J* 8 Hz, aromatic protons), and 2·53 (1H, d, *J* 7 Hz, 5-H) (addition of $D_2O$ to the solution caused the signal at τ 4·9 to disappear, that at 6·65 to simplify to a quartet, and that at 2·53 to collapse to a singlet) (Found: C, 51·35; H, 5·8; N, 3·65. $C_{16}H_{21}NO_5S_2$ requires C, 51·7; H, 5·65; N, 3·75%).

*Methyl* (6S)-2,2-*Dimethyl*-4-*thia*-1-*azabicyclo*[4,1,0]*hept*-2-*ene*-3-*carboxylate* (21).—The toluene-*p*-sulphonate (19) (0·37 g, 1 mmol) was dissolved in dry tetrahydrofuran (10 ml) and sodium hydride (0·07 g, 3 mmol) was added. When the reaction was complete (t.l.c.; *ca.* 2·5 h), methanol (2 ml) was added and the solution was diluted with water and extracted with chloroform. The dried ($MgSO_4$) organic layer was evaporated to leave the *aziridine* (21) (0·19 g, 96%) as a syrup, $[\alpha]_D$ −220° (0·2% in $CHCl_3$), $\nu_{max.}$ (film) 1705 (unsat. C=O) and 1570 $cm^{-1}$, $\lambda_{max.}$ 230 (ε 5100) and 309 nm (6600), τ (90 MHz; $CDCl_3$) 8·98 and 8·39 (each 3H, s, *gem*-$Me_2$), 8·18 (1H, d, *J* 3·5 Hz, *exo* 7-H), 7·70 (1H, d, *J*

4·6 Hz, *endo* 7-H), 7·25 (1H, dd, separation 8 Hz, 6-H), 6·30 (3H, s, $CO_2Me$), and 2·24 (1H, s, 2-H) [Found: *M* (mass spectrum), 199·0662. $C_9H_{13}NO_2S$ requires *M*, 199·0667].

*Methyl* (3R)-3,4-*Dihydro*-3-*iodomethyl*-2,2-*dimethyl*-1,4-2*H*-*thiazine*-6-*carboxylate* (20).—The aziridine (21) (0·13 g, 0·65 mmol) was dissolved in chloroform and the solution was shaken with dilute hydriodic acid. The organic layer was washed with water, dried ($MgSO_4$), and evaporated to leave the *iodide* (20) (0·21 g, 100%), m.p. 109—110° (from chloroform–light petroleum), $[\alpha]_D$ −302° (0·2% in $CHCl_3$), $\nu_{max.}$ (KBr) 3300 (NH), 1655 (unsat. C=O), 1600 (C=C), and 1525 (amide II) $cm^{-1}$, $\lambda_{max.}$ 307 nm (ε 11,000), τ (60 MHz; $CDCl_3$) 8·60 (6H, s, *gem*-$Me_2$), 7·1—6·4 (3H, m, 3-H and $CH_2I$), 6·20 (3H, s, $CO_2Me$), 4·6br (1H, NH), and 2·38 (1H, d, *J* 7 Hz, 5-H) (addition of $D_2O$ to the solution caused the singlet at τ 4·6 to disappear and that at 2·38 to collapse to a singlet) (Found: C, 33·25; H, 4·15; I, 39·1; N, 4·15. $C_9H_{14}INO_2S$ requires C, 33·05; H, 4·3; I, 38·85; N, 4·3%).

*Pyrolysis of the Iodide* (20).—The iodide (20) (0·49 g, 1·5 mmol) was heated under reflux in ethyl methyl ketone (25 ml) for 5 days. The solvent was evaporated off and the residue was fractionated by silica gel chromatography to give the *isopropenyl derivative* (8) (0·20 g, 67%), m.p. 132—133° (from chloroform–light petroleum), $[\alpha]_D$ +35° (0·2% in $CHCl_3$), $\nu_{max.}$ (KBr) 3330 (NH), 1645 (unsat. C=O), 1590 (C=C), and 1515 (amide II) $cm^{-1}$, $\lambda_{max.}$ 265 (ε 3040) and 314 nm (11,200), τ (90 MHz; $CDCl_3$) 8·18 (3H, s, C-Me), 7·27 (1H, dd, *J* 12·8, *J′* 6·9 Hz, 2β-H), 7·15 (1H, dd, *J* 12·8, *J′* 2·8 Hz, 2α-H) 6·30 (3H, s, $CO_2Me$), 5·93 (1H, m, 3-H), 5·2br (1H, NH), 5·0 (2H, d, separation 8 Hz, $C=CH_2$), and 2·30 (1H, d, *J* 7 Hz, 5-H) (addition of $D_2O$ to the solution caused the signal at τ 5·2 to disappear and that at 2·30 to collapse to a singlet) [Found: C, 54·7; H, 6·85; N, 7·5%; *M* (mass spectrum), 199·0661. $C_9H_{13}NO_2S$ requires C, 54·3; H, 6·55; N, 7·05%; *M*, 199·0667].

(3R)-3,4-*Dihydro*-3-*isopropyl*-1,4-2*H*-*thiazine*-6-*carboxylate* (9).—Compound (8) (0·05 g, 0·25 mmol) was dissolved in methanol (10 ml) and hydrogenated over platinum (0·015 g). After 2 days the catalyst was filtered off and the solution concentrated to afford the *isopropyl derivative* (9) (0·05 g, 100%), m.p. 114—116° (from chloroform–light petroleum), $[\alpha]_D$ +123° (0·2% in $CHCl_3$), $\nu_{max.}$ (KBr) 3340 (NH), 1650 (unsat. C=O), 1595 (C=C), 1525 (amide II), and 1390 and 1370 (*gem*-$Me_2$) $cm^{-1}$, $\lambda_{max.}$ 261 (ε 2450) and 312 nm (10,800), τ (90 MHz; $CDCl_3$) 9·04 and 8·96 (each 3H, d, *J* 6·5 Hz, *gem*-$Me_2$), 8·15 (1H, m, C*H*$Me_2$), 7·30 (2H, d, separation 4·6 Hz, 2-$H_2$), 6·75 (1H, m, 3-H), 6·30 (3H, s, $CO_2Me$), 4·9br (1H, NH), and 2·37 (1H, d, *J* 7 Hz, 5-H) (addition of $D_2O$ to the solution caused the signal at τ 4·9 to disappear and that at 2·37 to collapse to a singlet) [Found: C, 53·85; H, 7·35; N, 6·9%; *M* (mass spectrum), 201. $C_9H_{15}NO_2S$ requires C, 53·7; H, 7·45; N, 6·95%; *M*, 201).

*Pyrolyses of the Aziridines* (21) *and* (12) (with J. Kitchin).—(*a*) The aziridine (21) (0·066 g, 0·33 mmol), $[\alpha]_D$ −220° (0·2% in $CHCl_3$), was heated under reflux in ethyl methyl ketone (5 ml) for 8 days. Since some decomposition occurred, the product was fractionated by alumina chromatography; the recovered aziridine (0·046 g, 70%), $[\alpha]_D$ −197° (0·9% in $CHCl_3$), was identical to the starting material (t.l.c., and i.r. and n.m.r. spectroscopy).

The aziridine (21) (0·6 g, 3 mmol) was heated under reflux in toluene (100 ml) until it had disappeared (t.l.c.; *ca.* 4 days). The solvent was evaporated off and the residue fractionated by silica gel chromatography to give the isopropenyl derivative (8) (0·32 g, 53%), m.p. 132—133° (from chloroform–light petroleum), $[\alpha]_D$ +38° (0·2% in $CHCl_3$). The i.r. and n.m.r. spectra of the sample were identical with those of the derivative obtained from the pyrolysis of the iodide (20).

(*b*) The aziridine (12) (0·138 g, 0·8 mmol) was heated in ethyl methyl ketone (10 ml) for 2 days. Since some decomposition occurred, the material was fractionated by alumina chromatography; the major product (0·07 g, 50%) was identical with the starting material (i.r. and n.m.r. spectroscopy). It was converted into the iodide (6), m.p. 124—126° (from chloroform–light petroleum), $[\alpha]_D$ +92° (0·7% in $CHCl_3$).

The aziridine (12) (0·238 g, 1·4 mmol), $[\alpha]_D$ +550° (0·24% in $CHCl_3$), was heated under reflux in toluene (30 ml) for 7 days. The product was fractionated by alumina chromatography and the major product (0·139 g, 58%), $[\alpha]_D$ +532° (0·5% in $CHCl_3$), was identical with the starting material (i.r. and n.m.r. spectroscopy).

The aziridine (12) (0·17 g, 1 mmol) was heated under reflux in xylene (15 ml). After 3 days no starting material remained and a complex mixture of products was present (t.l.c.). An attempt to fractionate the mixture by silica gel chromatography was unsuccessful.

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