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AZIRIDINE FORMATION BY LITHIUM ALUMINUM HYDRIDE REDUCTION OF OXIMES

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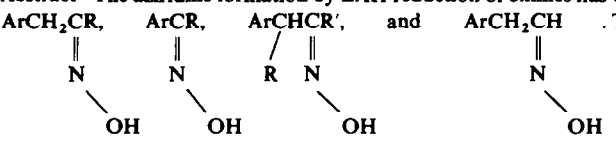
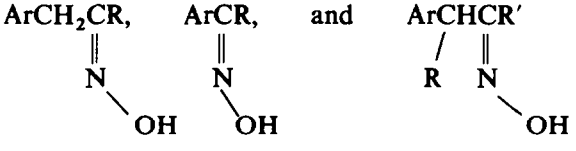
Abstract—The aziridine formation by LAH reduction of oximes has been extended to several types, such as  zation of this reaction.

THE LAH reduction of ketoximes usually gives the corresponding primary amines,[1] and the reduction of certain aryl ketoximes[2] and strained alicyclic oximes[3] yields rearranged secondary amines together with primary amines. On the other hand, the reaction of ketoximes with Grignard reagent[4] (the Hoch–Campbell synthesis), and treatment of ketoxime tosylates[5] (the Neber rearrangement), N-chloroketimines[6] or N-substituted hydrazones[7] with alkaline reagent give the corresponding aziridines.

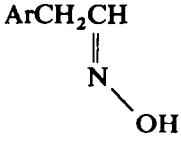
In our previous communication,[8] it was reported that LAH reduction of some ketoximes provided a new method for the synthesis of aziridines. At almost the same time, Waight *et al.* found a similar reaction in only one instance of phenyl vinyl ketoxime.[9]

For generalization of this reaction, a number of experimental data are accumulated and these are the subject of this paper.

On several types of ketoximes, i.e.



and on aldoximes such as



the LAH reduction was examined in refluxing tetrahydrofuran (THF).

(a) *Formation of aziridines from the ketoximes of the type:*

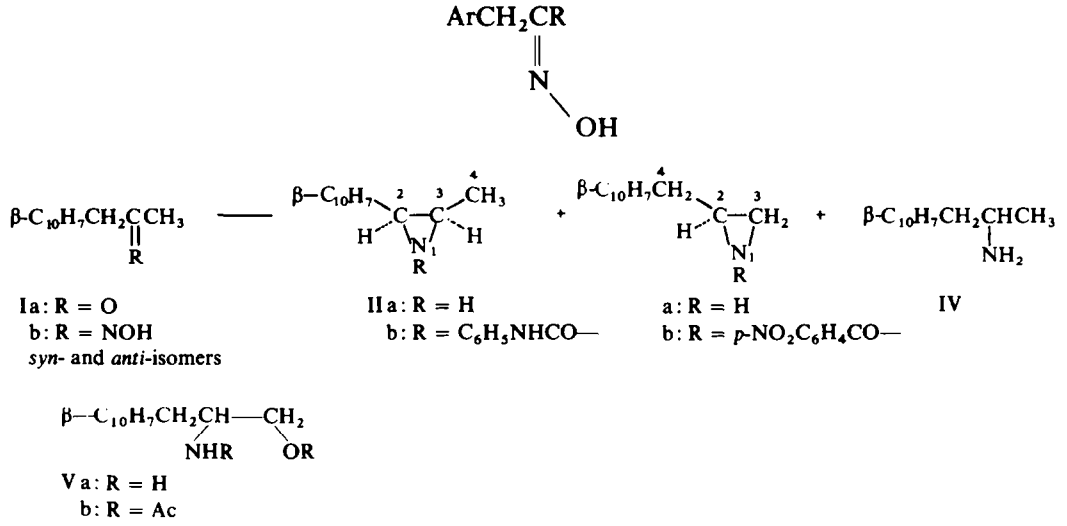


CHART 1

Treatment of 1-β-naphthylpropan-2-one[10] (Ia) with hydroxylamine–HCl and sodium acetate gave 1-β-naphthylpropan-2-one oxime (Ib) which had a m.p. of 108–117°, suggesting to be a mixture of *syn-* and *anti*-isomers. The NMR study (60 Mc, in benzene) indicated that the mixture is composed of *syn-* and *anti*-forms (about 1:4). The oxime Ib was reduced with 2 molar equivalents of LAH in refluxing THF for 1·5 hr. The products showed three spots (R_f-values, 0·55, 0·37 and 0·12) on TLC using SiO_2 and solvent system of Chf:MeOH (20:1). By column-chromatography on SiO_2, the three basic products corresponding to the TLC spots were isolated in 25, 7 and 47% yields, respectively. The first product (R_f 0·55) was proved to be *cis*-2-β-naphthyl-3-methylaziridine (IIa), m.p. 83–84°, which was characterized as its phenylcarbamoyl derivative IIb, m.p. 147–148°. The NMR spectrum (60 Mc, $CDCl_3$) of IIa shows the respective proton signals at 8·85 τ (s, >NH), 9·09 τ (d, $J_{3,4}$ = 5·6 c/s, —CH$_3$), 6·65 τ (d, $J_{2,3}$ = 6·7 c/s, C_2—H) and 7·57 τ (q–d, $J_{2,3}$ = 6·7 c/s, $J_{3,4}$ = 5·6 c/s, C_3—H). The coupling constant (6·7 c/s) between C_2- and C_3-protons indicates that this aziridine has *cis*-configuration.[11] The second oily product (R_f 0·37) was found to be another aziridine, 2-β-naphthylmethylaziridine (IIIa) cyclized towards the terminal Me group, which was characterized as the *p*-nitrobenzoyl derivative IIIb, m.p. 94·5–95·5°, ν_{max} 1667 cm^{-1} (>NCO—). In the NMR spectrum of IIIb, the proton signals of C_3-methylene group appear at 7·63 τ (d, $J_{2,3}$ = 2·7 c/s, C_3-*trans*-H) and at 7·40 τ (d, $J_{2,3}$ = 6·0 c/s, C_3-*cis*-H), and those of C_2—H and C_4—H$_2$ appear centered at 6·92 τ as an unresolving multiplet. The structure IIIa was also supported by the formation of an alkanolamine Va on treatment of IIIa with aqueous sulphuric acid. The third oily product (R_f 0·12) was a primary amine IV, characterized as the hydrochloride, m.p. 207–208°. In this connection, the stereochemistry of the aziridine formation was investigated using the

technique of TLC and a fairly suggestive result has been obtained from experiments using pure *anti*-isomers and a mixture of *syn*- and *anti*-isomers of 1-phenylpropan-2-one oxime and 1-α-naphthylpropan-2-one oxime,[12] and their purely separated oxime tosylates.[13] The detailed result will be reported elsewhere together with that of the kinetic study, which is being in progress. At any rate, the oximes of the following ketones (Chart 2) were reduced with LAH in refluxing THF to give aziridines and the results are summarized in Table 1.

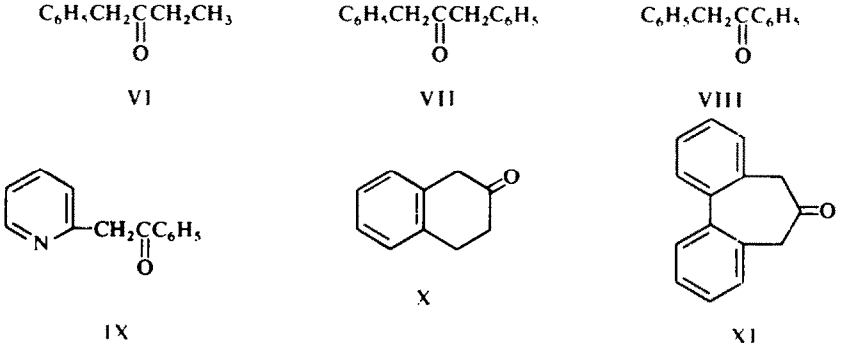
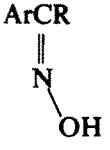


CHART 2

(b) *Formation of aziridines from the ketoximes of the type*:



As well as the oximes of the above-mentioned benzylketones, ketoximes of the acetophenone type also afforded the corresponding aziridines by treatment with LAH in refluxing THF. For instance, the LAH reduction of the oxime of α-acetylnaphthalene (XIV) gave 2-α-naphthylaziridine, m.p. 65–67°, in 63·7% yield. The

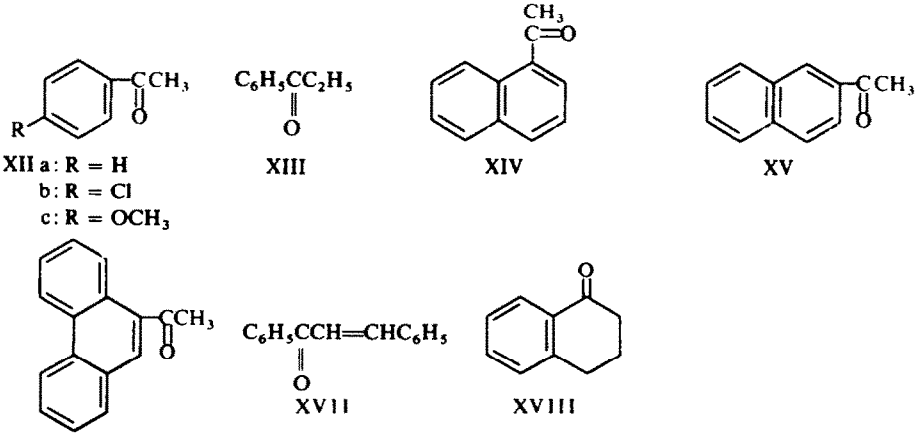
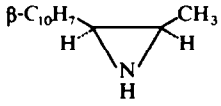
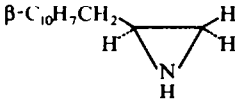
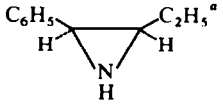
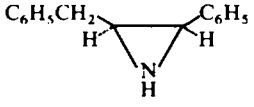
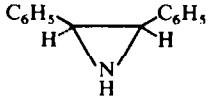
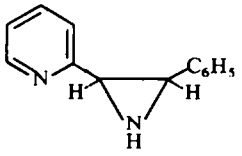
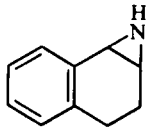
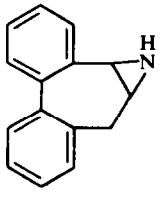


CHART 3

TABLE 1.

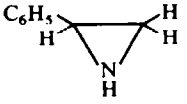
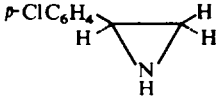
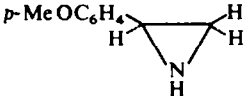
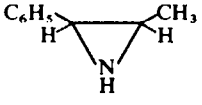
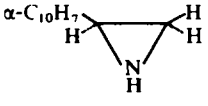
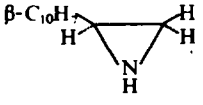
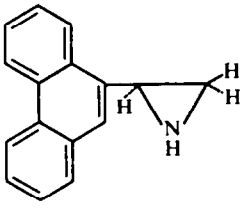
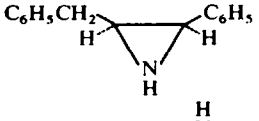
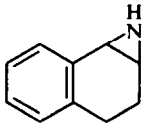
Parent ketone	Structure	Aziridine m.p., °C	Aziridine Yield, %[b]	C_6H_5NHCO- and p-$NO_2C_6H_4CO$-derivative, m.p., °C
		83–84	25·0	147–148
Ia		oil	7·0	94·5–95·5[c]
VI		45–46[14]	24·4	95–96 62–63[c]
VII		44–45[15]	77·0	123–125
VIII		83–84[5a]	25·0	163–164
IX		66–67	22·3	123–125
X		52–53·5[16]	40·0	157–158
XI		95–96[17]	70·0	152–153 193–194[c]

[a] Treatment of this aziridine with CS_2 gave 4-ethyl-5-phenyl-thiazolidine-2-thione, m.p. 130–131°.

[b] The theoretical yields of the isolated aziridines to the oximes were shown, unless otherwise stated. This is the same in the following Tables (2 and 4).

[c] p-Nitrobenzoyl derivatives.

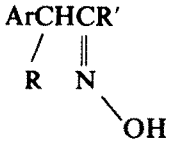
TABLE 2.

Parent ketone	Structure	Aziridine m.p., °C	Aziridine Yield, %	C_6H_5NHCO- deriv., m.p., °C	Thiazolidine-[b] 2-thione deriv., m.p., °C
XIIa		oil[14]	17·3[c]	96·5–97·5 120·5–122·5[a]	170–171
XIIb		oil	11·4[c]	—	157–158
XIIc		oil	15·8[c]	—	140–141
XIII		41–43	3·3[d]	92–94	—
XIV		66–67	63·7	133·5–135	235–237
XV		102·5–103·5	16·2	145–146	—
XVI		90–91	39·4	194–196	—
XVII		44–45	22·3[d]	123–125	—
XVIII		52–53·5	11·0	157–158	188·5–190·5

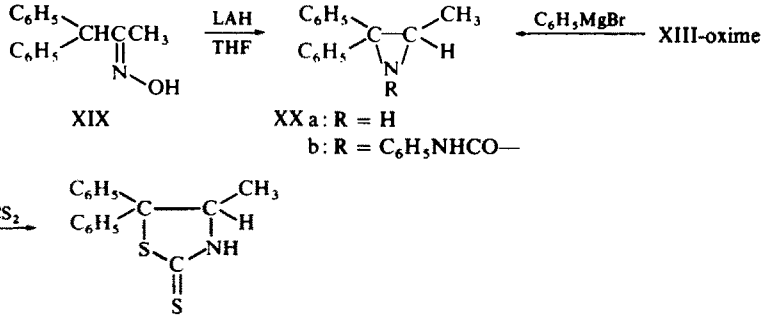
[a] *p*-Nitrobenzoyl derivative.
[b] 5-Arylthiazolidine-2-thione derivatives.
[c] From the yields of the corresponding thiazolidine-2-thione derivatives.
[d] From the yields of the phenylcarbamoyl derivatives obtained.

results obtained from the ketoximes (Chart 3) belonging to this type are recorded in Table 2.

(c) *Formation of aziridines from ketoximes of the type*:



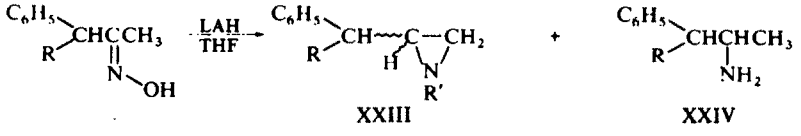
Treatment of 1,1-diphenylpropan-2-one oxime (XIX)[18] with LAH in refluxing THF afforded 2,2-diphenyl-3-methylaziridine (XXa), m.p. 73·5–74° in 40·5% yield, characterized as its phenyl carbamoyl derivative, XXb, m.p. 148·5–150°. The assigned



XIX XX a: R = H
b: R = C_6H_5NHCO—

XXI CHART 4

structure XXa was confirmed by identification with the product synthesized from propiophenone oxime and phenylmagnesium bromide according to the method of Campbell *et al.*[19] The reaction of XXa with CS_2 gave 3-methyl-5,5-diphenylthiazolidine-2-thione (XXI), m.p. 169–169·5°. On the other hand, the LAH reduction of 1-phenyl-1-alkylpropan-2-one oximes resulted in the formation of aziridines, cyclized reversely towards the terminal Me groups. For example, LAH reduction of 1-phenyl-1-methylpropan-2-one oxime (XXIIa) and 1-phenyl-1-ethylpropan-2-one oxime (XXIIb) in refluxing THF yielded the corresponding aziridines, XXIIIa and XXIIIc, in 38·3 and 31·2% yields, respectively, together with the corresponding primary amines, XXIVa and XXIVb. Although precise examination on the aziridines, XXIIIa



XXII a: R = CH_3
b: R = C_2H_5

XXIII
a: R = CH_3, R′ = H
b: R = CH_3, R′ = p-$NO_2C_6H_4CO$—
c: R = C_2H_5, R′ = H
d: R = C_2H_5, R′ = p-$NO_2C_6H_4CO$—

XXIV
a: R = CH_3
b: R = C_2H_5

CHART 5

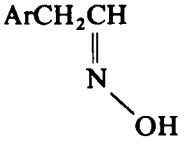
and XXIIIc, exhibited that each of the both consists of a mixture of stereosiomers, no formation of aziridines cyclized to the benzylic position was recognized at all. The preparative TLC using Al_2O_3 (GF_{254}, Merck) and solvent system of benzene : acetone (3 : 1) was especially useful for separation of the aziridine XXIIIa into the respective isomers. The derivatives obtained are shown in Table 3.*

TABLE 3.

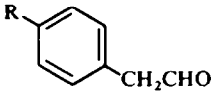
Aziridine[a]		p-$NO_2C_6H_4CO$— derivative, m.p., °C	Thiazolidine-2-thione[b] derivative, m.p., °C
XXIIIa	XXIIIb	65–66	96·5–97 (major)
		178–179	165·5–166 (minor)
XXIIIc	XXIIId	49–50	135–136 (major)
		132–133	125–126 (minor)

[a] Presumably isomers of erythro- and threo-types.
[b] Presumably 4-substituted thiazolidine-2-thione derivatives.

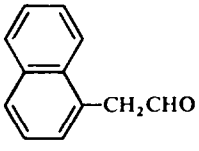
(d) *Formation of aziridines from aldoximes of the type*:



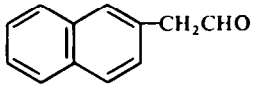
The application of our reaction on aldoximes gave an interesting finding, in contrast with the Neber reaction which did not proceed with tosylates of aldoximes.[20] For



XXV
a: R = H
b: R = Cl
c: R = OCH_3



XXVI



XXVII

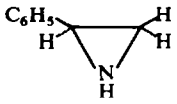
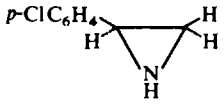
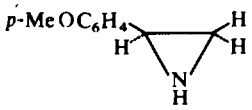
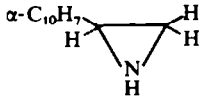
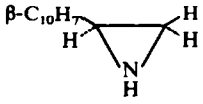
CHART 6

instance, the LAH reduction of phenylacetaldehyde oxime gave, in 34% yield, 2-phenylaziridine, identical with the product from acetophenone oxime. The results obtained from the instances so far examined are shown in Table 4.

This paper has described that several types of oximes gave the corresponding aziridines by the LAH reduction in refluxing THF. Further development of this reaction is expected to provide the more useful method for synthesis of aziridines.

* The detailed results for structure elucidation of these derivatives will be reported elsewhere in near future.

TABLE 4.

Parent aldehyde	Structure	Aziridine m.p., °C	Aziridine Yield, %	C_6H_5NHCO- deriv., m.p., °C	Thiazolidine-[b] 2-thione deriv., m.p., °C
XXVa		oil[14]	34·0[c]	96·5–97·5 120·5–122·5[a]	170–171
XXVb		oil	28·0[c]	—	157–158
XXVc		oil	23·0[c]	—	140–141
XXVI		66–67	20·4	133·5–135·0	237–240
XXVII		101·5–102·5	12·0	145–146	—

[a] *p*-Nitrobenzoyl derivative.

[b] 5-Arylthiazolidine-2-thione derivatives.

[c] From the yields of the isolated thiazolidine-2-thione derivatives.

EXPERIMENTAL

All m.ps determined in capillary tubes were uncorrected. NMR spectra were taken in $CDCl_3$ soln containing TMS as an internal standard using a Varian A-60 spectrophotometer. UV spectra were determined with a Hitachi EPS-2 recording spectrophotometer and IR spectra with a Nippon Bunko DS-201B spectrometer. Unless otherwise stated, solns were drived over Na_2SO_4.

LAH *reduction of* 1-β-*naphthylpropan*-2-*one oxime* (Ib). Compound Ib, m.p. of 108–117°, recrystallized as needles from benzene-n-hexane. NMR (in benzene): *anti*-isomer; 8·26 τ (3H, s, —CH_3), 6·50 τ (2H, s, —CH_2—), *syn*-isomer; 8·35 τ (3H, s, —CH_3), 6·18 τ (2H, s, —CH_2—). The NMR spectrum showed that Ib is composed of *syn*- and *anti*-isomers in a ratio of 1:4. (Found: C, 78·72; H, 6·90; N, 7·39. $C_{13}H_{13}ON$ requires: C, 78·36; H, 6·58; N, 7·63%). A soln of Ib (1·70 g) in THF (40 ml) was added with stirring to a suspension of LAH (750 mg) in THF (20 ml) at room temp over a period of 10 min. The mixture was refluxed with stirring for 1·5 hr. After cooling, a small amount of H_2O was added to the mixture to decompose excess LAH and inorganic substance spearated by filtration, washed with ether and benzene. The filtrate

was combined with the washings and evaporated to dryness *in vacuo* to give an oily residue (1·6 g), which was chromatographed on SiO_2 (50 g, Merck). Elution with benzene: Chf (1:1) gave a crude IIa (460 mg), which on vacuum-distillation followed by recrystallization from ether-n-hexane gave a pure IIa (410 mg), m.p. 83–84° as needles; $\nu_{max}^{CCl_4}$ 3306 cm^{-1} (>NH); NMR: 8·85 τ (1H, s, —NH—), 9·09 τ (3H, d, 5·6 c/s, —CH_3), 6·65 τ (1H, d, 6·7 c/s, C_2—H), 7·57 τ (1H, q-d, 5·6, 6·7 c/s, C_3—H). (Found: C, 85·47; H, 7·15; N, 7·54. $C_{13}H_{13}N$ requires: C, 85·20; H, 7·15; N, 7·64%). A soln of IIa (50 mg) and phenylisocyanate (33 mg) in dry ether (3 ml) was stirred at room temp for 30 min and the mixture evaporated to dryness to yield a crystalline residue (75 mg), which was recrystallized from acetone-n-hexane to give a pure IIb (52 mg), m.p. 147–149°; ν_{max}^{Nujol} 3275 cm^{-1} (—NH—), 1673 cm^{-1} (—NHCO—). (Found: C, 79·57; H, 6·16; N, 9·19. $C_{20}H_{18}ON_2$ requires: C, 79·44; H, 6·00; N, 9·27%).

Elution with Chf gave a crude IIIa (150 mg) as an oil which was characterized as the *p*-nitrobenzoyl derivative. *p*-Nitrobenzoyl chloride (78 mg) in dry benzene (1 ml) was added to a soln of crude IIIa (71 mg) and $(Et)_3N$ (52 mg) in dry benzene (1 ml) under cooling with ice and the mixture stirred for 2 hr. The ppt was removed by filtration and the filtrate evaporated to dryness to give a residue (105 mg), which was dissolved in benzene and passed through the layer of neutral Al_2O_3 (Woelm) to remove the impurity. On trituration with ether and recrystallization from ether, the eluate gave pure *p*-nitrobenzoyl derivative, IIIb, m.p. 94·5°, ν_{max}^{Nujol} 1667 cm^{-1} (>NCO—); NMR: 7·40 τ (1H, d, 6·0 c/s, C_3-*cis*-H), 7·63 τ (1H, d, 2·7 c/s, C_3-*trans*-H). (Found: C, 72·66; H, 4·73; N, 8·52. $C_{20}H_{16}O_3N_2$ requires: C, 72·28; H, 4·85; N, 8·43%).

Elution with Chf: MeOH (10:1) gave a crude primary amine IV (700 mg) as an oil which was distilled under reduced press. A portion of crude IV was converted to its hydrochloride, which on recrystallization from AcOEt–EtOH gave pure IV–HCl, m.p. 207–208° as needles. (Found: C, 70·33; H, 7·55; N, 6·48; Cl, 16·25. $C_{13}H_{15}N \cdot HCl$ requires: C, 70·42; H, 7·27; N, 6·32; Cl, 15·99%).

Action of 5% sulfuric acid on IIIa. Crude IIIa (120 mg) was refluxed with 5% H_2SO_4 (12 ml) for 1 hr. After cooling, the mixture was extracted with ether to remove neutral substance. The aqueous layer was made basic with Na_2CO_3, saturated with NaCl, extracted with AcOEt and the organic layer was dried and evaporated to dryness to leave an oily residue (110 mg), which was chromatographed on 5% H_2O containing neutral Al_2O_3 (3 g, Woelm). The fractions eluted with benzene were combined to give a crude Va (86 mg) as an oil, which was subjected to preparative TLC using SiO_2 (GF_{254}) and solvent system (Chf:MeOH, 1:1) yielding pure oily Va (47 mg). This was characterized as its O,N-diacetate. Compound Va (40 mg) was acetylated with Ac_2O (0·5 ml) and pyridine (1·5 ml) allowing to stand at room temp for 2 days. Working up in a usual manner, the residue (52 mg) was chromatographed on neutral Al_2O_3 (1·5 g, Woelm) to give a crude Vb (37 mg), which was eluted with AcOEt:benzene (2:1). Recrystallization from AcOEt–n-hexane gave pure Vb, m.p. 105–106° as needles; ν_{max}^{Nujol} 3275 cm^{-1} (>NH), 1722 cm^{-1} (—OAc), 1652 cm^{-1} (—NHAc); NMR: 8·10 τ (3H, s, —OCOCH_3), 7·95 τ (3H, s, —NHCOCH_3), 7·01 τ (1H, d, 7 c/s, β—$C_{10}H_7CH_2$—), 5·92 τ (2H, d, 4·7 c/s, —CH_2OAc), 5·47 τ (1H, d-d, 7, 4·7 c/s —CH(NHAc)—). (Found: C, 71·29; H, 6·63; N, 5·19. $C_{17}H_{19}O_3N$ requires: C, 71·56; H, 6·71; N, 4·91%).

LAH *reduction of the oxime of* 1-*phenylbutane*-2-*one* (VI). 1-Phenylbutane-2-one oxime had a b.p. of 120–121° at 5 mm Hg and its NMR spectrum suggested it to be a mixture of *syn*- and *anti*-isomers. Compound VI-oxime (1·0 g) in THF (30 ml) was added with stirring to a suspension of LAH (752 mg) in THF (16 ml) over a period of 10 min and the mixture refluxed for 3 hr. Working up gave an oily residue (1·1 g), which was chromatographed on SiO_2 (30 g, Merck) to give an eluate (390 mg) from the fractions eluted with Chf: benzene (1:1, 2:1). After a vacuum-distilation at 100–130° (bath-temp)/9 mm Hg, the eluate gave crude *cis*-2-phenyl-3-ethylaziridine (220 mg), m.p. 42–44° as prisms by crystallization from n-hexane. A pure sample for analysis had a m.p. of 45–46° by repeated recrystallization from the same solvent; ν_{max}^{Chf} 3314 cm^{-1} (>NH). NMR: 6·72 τ (1H, d, 6·5 c/s, C_2—H), 7·74 τ (1H, d-d, 6·5, 13·0 c/s, C_3—H), near 9·0 τ (5H, m, as A_3B_2 part of A_3B_2 system, CH_3CH_2—). (Found: C, 81·68; H, 8·77, N, 9·26. $C_{10}H_{13}N$ requires: C, 81·58; H, 8·90; N, 9·52%).

Elution with Chf: MeOH (10:1) gave a crude primary amine (520 mg), which was subjected to vacuum-distillation (9 mm Hg) at 110–140° (bath-temp) to give pure 1-phenylbutane-2-amine (430 mg). The amine was characterized as its hydrochloride, m.p. 139–140°, which was identical with that reported in the literature.[21]

The aziridine was characterized as its *p*-nitrobenzoyl and phenylcarbamoyl derivatives. Treatment of the aziridine with *p*-nitrobenzoyl chloride and $(Et)_3N$ gave the *p*-nitrobenzoyl derivative, m.p. 60–62° as silky needles by recrystallization from AcOEt–n-hexane. ν_{max}^{Nujol} 1681 cm^{-1} ($\rangle$NCO—). (Found: C, 68·97; H, 5·39; N, 9·52. $C_{17}H_{16}O_3N_2$ requires: C, 68·90; H, 5·44; N, 9·45%). The reaction of the aziridine with phenylisocyanate in ether gave the phenylcarbamoyl derivative, m.p. 95–96° as prisms from AcOEt–n-hexane; ν_{max}^{Chf} 3420 cm^{-1} (—NH—), 1701 cm^{-1} ($\rangle$NCNH—); NMR: 6·25 τ (1H, d, 7·0 c/s, C_2—H), 7·22 τ (1H, d-d, 7·0, 13·0 c/s, C_3—H). (Found: C, 76·87; H, 6·77; N, 10·88. $C_{17}H_{18}ON_2$ requires: C, 76·66; H, 6·81; N, 10·52%).

The aziridine was treated with CS_2 in a sealed tube in a boiling water-bath for 6 hr. Working up and recrystallization from ether–n-hexane gave 4-ethyl-5-phenylthiazolidine-2-thione, m.p. 130–131° as prisms. (Found: C, 58·97; H, 5·90; N, 6·48. $C_{11}H_{13}NS_2$ requires: C, 59·15; H, 5·87; N, 6·27%).

LAH *reduction of the oxime of deoxybenzoin* (VIII). Deoxybenzoin oxime, m.p. 95–96° (1·0 g) was reduced under reflux with LAH (317 mg) in THF (25 ml) for 3 hr. The mixture showed remarkable colour change: yellowish green → dark green → reddish violet. Working up gave an oily residue (895 mg), which was chromatographed on SiO_2 (25 g, Merck) to give crude *cis*-2-phenyl-3-phenylaziridine (300 mg) from the fractions eluted with benzene. Pure aziridine (225 mg), m.p. 83–84° as prisms was obtained by recrystallization from n-hexane; $\nu_{max}^{CCl_4}$ 3329 cm^{-1} ($\rangle$NH); UV (in cyclohexane): λ_{max} 251, 255 mμ (ε, 4990, 4630; NMR: 8·45 τ [1H, s (broad), $\rangle$NH], 6·45 τ (2H, s, C_2—H, C_3—H). (Found: C, 86·32; H, 6·82; N, 7·13. $C_{14}H_{13}N$ requires: C, 86·11; H, 6·71; N, 7·17%). The phenylcarbamoyl derivative on recrystallization from ether–n-hexane had a m.p. of 163–164° as needles; ν_{max}^{Nujol} 3198 cm^{-1} (—NH—), 1663 cm^{-1} ($\rangle$NCONH—). (Found: C, 80·39; H, 5·92; N, 9·07. $C_{21}H_{18}ON_2$ requires: C, 80·23; H, 5·77; N, 8·91%).

LAH *reduction of the oxime of 2-(2-pyridyl)-acetophenone* (IX). The oxime of 2-(2-pyridyl)-acetophenone synthesized according to Goldberg *et al.*[22] had a m.p. of 118–119°[23] (ref. 23, m.p. 120°). The oxime (500 mg) was refluxed with stirring with LAH (360 mg) in THF (22 ml) for 3·5 hr. Working up gave an oily residue (435 mg), which showed three spots (R_f-values, 0·81, 0·70 and 0·22) on TLC using Al_2O_3 and solvent system of Chf:MeOH (100:1). The preparative TLC using Al_2O_3 (GF_{254} 500 mμ) and solvent system of Chf:MeOH (100:1) gave the respective products as crude material. Of them, the second product (90 mg) was recrystallized from ether—n-hexane to give *cis*-2-(2-pyridyl)-3-phenylaziridine, m.p. 66–67° as prisms; ν_{max}^{Nujol} 3317 cm ($\rangle$NH); UV: λ_{max}^{EtOH} 265 mμ (ε, 4310); NMR: 8·08 τ(1H, s, —NH—), 6·30 τ (2H, s, C_2—H, C_3—H). (Found: C, 79·51; H, 6·35; N, 14·48. $C_{13}H_{12}N_2$ requires: C, 79·56; H, 6·16; N, 14·28%). Other products were not further examined. Treatment of the aziridine with phenylisocyanate in benzene gave the phenylcarbamoyl derivative, m.p. 161–162° as needles from acetone–n-hexane. ν_{max}^{Nujol} 3241 cm^{-1} (—NH—), 1668 cm^{-1} ($\rangle$NCO—); UV: λ_{max}^{EtOH} 243 mμ (ε, 21,500); NMR: 2·17 τ [1H, s (broad), —NH—], 5·84 τ (2H, s, C_2—H, C_3—H). (Found: C, 75·98; H, 5·47; N, 13·13. $C_{20}H_{17}ON_3$ requires: C, 76·17; H, 5·43; N, 13·33%).

LAH *reduction of the oxime of* β-*tetralone* (X). β-Tetralone oxime had a m.p. of 84–86°[24] (ref. 24, m.p. 89–90°). A soln of the oxime (1·27 g) in THF (40 ml) was added with stirring to a suspension of LAH (600 mg) in THF (25 ml) at room temp over a period of 5 min. The mixture was refluxed with stirring for 3 hr, indicating green colour. Working up gave a greenish-brown residue (1·2 g) as an oil, which was chromatographed on neutral Al_2O_3 (30 g, Woelm) to give crude crystalline 1,2-imino-tetralin (897 mg) from the fractions eluted with benzene and benzene: Chf (5:1, 3:1). The crude aziridine was distilled under reduced press (3 mm Hg) at 100–105° (bath-temp) to remove coloured impurity. The colourless aziridine (523 mg) thus obtained was crystallized from n-hexane yielding pure aziridine (474 mg), m.p. 50·5–51·5° as colourless needles. Recrystallization from the same solvent gave an analytical sample, m.p. 52–53·5°. ν_{max}^{Chf} 3306 cm^{-1} ($\rangle$NH). (Found: C, 82·81; H, 7·82; N, 9·66. $C_{10}H_{11}N$ requires: C, 82·71; H, 7·64; N, 9·38%). The N-phenylcarbamoyl derivative had a m.p. of 157–158° by recrystallization from ether; ν_{max}^{Chf} 3411 cm^{-1} ($\rangle$NH), 1697 cm^{-1} ($\rangle$NCO—). (Found: C, 77·10; H, 6·19; N, 10·27. $C_{17}H_{16}ON_2$ requires: C, 77·25; H, 6·05; N, 10·60%).

LAH *reduction of the oxime of acetophenone* (XIIa). A soln of acetophenone oxime (30 g) in THF (150 ml) was added with stirring to a suspension of LAH (25·2 g) in THF (500 ml) at 5–8° and the mixture refluxed with stirring for 3 hr. After cooling, H_2O was added to destroy excess LAH, inorganic material separated by filtration and washed with ether. The filtrate was combined with ethereal washings, dried over K_2CO_3 and evaporated to dryness to give a yellow oil (28·5 g), which was once distilled under reduced press to give a colourless oil (23·91 g), b.p. 60–82°/8 mm Hg. Of them, the oil (533 mg) was heated with CS_2 (676 mg) in a sealed tube in a boiling water-bath for 5 hr. After cooling, the mixture was warmed with 10% NaOH aq and extracted with ether to remove an alkali-insoluble substance. The aqueous alkaline layer was acidified with conc HCl under cooling to afford a crystalline precipitate (335 mg), which was separated by filtration and gave on two recrystallization from MeOH 5-phenyl-thiazolidine-2-thione (168 mg), m.p. 170–171°. (Found: C, 55·50; H, 4·89; N, 7·01; S, 32·41. $C_9H_9NS_2$ requires: C, 55·35; H, 4·64; N, 7·17; S, 32·84%). The reported m.ps of this product were 169–170°[25] and 167·8–168·0,[26] respectively. Repeated fractional distillation of the remaining oil (23·3 g, b.p. 60–82°/8 mm Hg) gave a pure primary amine (7·75 g), b.p. 64°/9 mm Hg. The residual oil (14·178 g), which was expected to include 2-phenylaziridine (main), ethylaniline and primary amine, etc, was subjected to the more precise fractional distillation, although the result was unsatisfactory, pure aziridine was obtained in a low yield from the fraction of b.p. 90·5–93°/10 mm Hg (ref. 14, b.p. 94–95°/10 mm Hg). The aziridine was converted with CS_2 into the identical thiazolidine-2-thione, m.p. 170–171° with that mentioned above. Furthermore, this was also confirmed from 2-phenylaziridine obtained by the addition of iodoisocyanate to styrene.[11] 2-Phenylaziridine thus obtained was characterized as its *p*-nitrobenzoyl and phenylcarbamoyl derivatives. The former had a m.p. of 120·5–122·5° by recrystallization from ether–n-hexane. (Found: C, 67·20; H, 4·38; N, 10·58. $C_{15}H_{12}O_3N_2$ requires: C, 67·16; H, 4·51; N, 10·44%). The latter was recrystallized from ether–n-hexane to give pure phenylcarbamoyl derivative, m.p. 96·5–97·5° as needles. (Found: C, 75·36; H, 6·05; N, 12·00. $C_{15}H_{14}ON_2$ requires: C, 75·60; H, 5·92; N, 11·76%).

LAH *reduction of the oxime of p-chloroacetophenone* (XIIb). Similarly to the case of acetophenone oxime, *p*-chloroacetophenone oxime (5·005 g) was reduced with LAH (4·495 g) in refluxing THF (120 ml) for 3 hr to yield a residual oil (4·433 g). Of them, the oil (512 mg) was converted with CS_2 (1·034 g) to its 5-(*p*-chlorophenyl)-thiazolidine-2-thione (90 mg), m.p. 157–158° from MeOH. (Found: C, 47·33; H, 3·74; N, 6·09. $C_9H_8NS_2Cl$ requires: C, 47·05; H, 3·51; N, 6·10%).

LAH *reduction of the oxime of p-methoxyacetophenone* (XIIc). *p*-Methoxyacetophenone oxime (3·637 g) was refluxed with stirring with LAH (3·406 g) in THF (250 ml) for 3·5 hr to give a brown oil (3·372 g), which gave on a vacuum-distillation a pale-yellow oil (2·963 g), b.p. 90–105°/3 mm Hg. The oil was converted with CS_2 (2·450 g) to its 5-(*p*-methoxyphenyl)-thiazolidine-2-thione (750 mg), m.p. 140–141° by chromatography on Al_2O_3 followed by recrystallization from MeOH. (Found: C, 53·45; H, 5·06; N, 6·48. $C_{10}H_{11}ONS_2$ requires: C, 53·30; H, 4·88; N, 6·22%).

LAH *reduction of the oxime of propiophenone* (XIII). Propiophenone oxime (1·016 g) was reduced with LAH (1·031 g) in refluxing THF (60 ml) for 3 hr. Working up gave a pale-yellow oil (953 mg), which was treated with phenylisocyanate (853 mg) to give a residue (1·699 g). Chromatography on neutral Al_2O_3 (51 g, Woelm) gave crystalline fractions (337 mg) eluted with petr-ether : benzene (9 : 1), which was recrystallized from ether–n-hexane to give N,N'-diphenyl-N'-(n-propyl)-urea (247 mg), m.p. 87–88°. (Found: C, 75·71; H, 7·12; N, 11·06. $C_{16}H_{18}ON_2$ requires: C, 75·56; H, 7·13; N, 11·02%). Further elution with pet-ether : benzene (4 : 1, 1 : 1) yielded N-phenylcarbamoyl-*cis*-2-phenyl-3-methylaziridine (57 mg), m.p. 95–97° from ether–n-hexane, which was identical with that from *cis*-2-phenyl-3-methylaziridine obtained by LAH reduction of 1-phenyl-propan-2-one oxime.[8]

LAH *reduction of the oxime of α-acetylnaphthalene* (XIV). α-Acetylnaphthalene oxime (3·0 g) was reduced with LAH (2·56 g) in refluxing THF (120 ml) for 2·5 hr. Working up gave a residual oil (2·75 g), which was allowed to stand overnight at room temp to give a crystalline residue. The crystals were separated and recrystallized from ether yielding 2-α-naphthylaziridine (1·417 g), m.p. 65–67°. The mother-liquor (1·31 g) was chromatographed over Al_2O_3 (30 g, Woelm) to yield additional crop of the aziridine (330 mg), m.p. 65–66° by recrystallization of the eluate with benzene and benzene : Chf (1 : 1) from ether; ν_{max}^{Nujol} 3185 cm^{-1} ( )NH); NMR : 6·68 τ (1H, d-d, C_2—H), 7·88 τ (1H, d, C_3—H), 8·33 τ (1H, d, C_3—H), 9·35 τ (1H, s, —NH—). (Found: C, 85·17; H, 6·66; N, 8·19. $C_{12}H_{11}N$ requires: C, 85·17; H, 6·55; N, 8·28%). The mother-liquor was combined with other fractions of the chromatography and the residue (798 mg) was treated with phenylisocyanate in benzene. On standing overnight at room temp, the mixture gave a crystalline ppt, which was separated by filtration and gave on recrystallization from acetone, N-phenyl-N'-

[2-(α-naphthyl)-ethyl]-urea (201 mg), m.p. 197–198° as needles. (Found: C, 78·53; H, 6·40; N, 9·74. $C_{19}H_{18}ON_2$ requires: C, 78·59; H, 6·25; N, 9·65%). The filtrate was evaporated to dryness giving an oily residue (1·23 g), which was chromatographed on Al_2O_3 (36 g, Woelm). Elution with pet-ether : benzene (1 : 4) and benzene gave a crystalline product (150 mg), m.p. 177–179° from acetone–MeOH, which afforded, on two recrystallization from the same solvent, pure product of unknown structure (105 mg), m.p. 182–183° as needles, [MW (observed), 379]. The fractions with Chf : MeOH (95 : 5) gave N-phenyl-N′-[2-hydroxy-2-(α-naphthyl)ethyl]-urea (40 mg), m.p. 169–170° from ether. (Found : C, 74·53; H, 5·98; N, 8·98. $C_{19}H_{18}O_2N_2$ requires: C, 74·49; H, 5·92; N, 9·15%). The phenylcarbamoyl derivative of 2-(α-naphthyl)aziridine and the reaction of the aziridine with CS_2 are described in the experimental section of the oxime of α-naphthyl-acetaldehyde (XXVI).

LAH *reduction of the oxime of* β-*acetylnaphthalene* (XV). β-Acetylnaphthalene oxime (2·09 g) was reduced with LAH (1·74 g) in refluxing THF (70 ml) for 2·5 hr. Working up gave a yellow oil (1·96 g), which was chromatographed on Al_2O_3 (60 g, Woelm). Elution with benzene : Chf (5 : 1–1 : 1) followed by crystallization from ether gave 2-(β-naphthyl)aziridine (310 mg), m.p. 102·5–103·5° as plates; ν_{max}^{Nujol} 3246 cm^{-1} ($\rangle$NH); NMR : 9·15 τ (1H, s, —NH), 8·23 τ (1H, d, C_3—H), 7·87 τ (1H, d, C_3—H), 6·97 τ (1H, d-d, C_2—H). (Found : C, 85·11; H, 6·77; N, 8·26. $C_{12}H_{11}N$ requires: C, 85·17; H, 6·55; N, 8·28%). The phenylcarbamoyl derivative had a m.p. of 145–146°; ν_{max}^{Nujol} 3260 cm^{-1} ($\rangle$NH), 1675 cm^{-1} ($\rangle$NCONH—). (Found : C, 79·23; H, 5·82; N, 9·53. $C_{19}H_{16}ON_2$ requires: C, 79·14; H, 5·59; N, 9·72%). Analogously to the case of α-acetyl-naphthalene oxime, when a mixture of reaction products was immediately treated with phenylisocyanate without the isolation of the aziridine and the reaction products were chromatographed over Al_2O_3, there were obtained N-phenyl-N′-[1-(β-naphthyl)ethyl]-urea and N-phenyl-N′-[2-hydroxy-2-(β-naphthyl)ethyl]-urea and a product of unknown structure, m.p. 168·5–169° [MW (observed), 439]. N-Phenyl-N′-[1-(β-naphthyl)ethyl]-urea had a m.p. of 188·5–189·5° (48·9%). (Found : C, 78·86; H, 6·46; N, 9·90. $C_{19}H_{18}ON_2$ requires: C, 78·59; H, 6·25; N, 9·65%). N-Phenyl-N′-[2-hydroxy-2-(β-naphthyl)-ethyl]-urea had a m.p. of 177–178° (11·1%), presumably arising from the phenyl-carbamoyl derivative of the aziridine. (Found : C, 74·47; H, 5·98; N, 9·13. $C_{19}H_{18}O_2N_2$ requires: C, 74·49; H, 5·92; N, 9·15%).

LAH *reduction of the oxime of* 9-*acetylphenanthrene* (XVI). 9-Acetylphenanthrene oxime (2·22 g) was reduced with LAH (1·46 g) in refluxing THF (50 ml) for 2 hr. Working up gave a yellow residue as an oil (2·06 g), which was chromatographed on Al_2O_3 (60 g, 3% Woelm). Elution with pet-ether : benzene (4 : 1) and benzene gave crude aziridine (1·05 g), which was crystallized from ether to give pure 2-(9-phenanthryl)-aziridine (815 mg), m.p. 90–91°; ν_{max}^{Nujol} 3291 cm^{-1} ($\rangle$NH); NMR : 9·32 τ (1H, s, —NH—), 8·30 τ (1H, d, 4 c/s, C_3-*trans*-H) 7·87 τ (1H, d, 6·5 c/s, C_3-*cis*-H), 6·67 τ (1H, d-d, 4, 6·5 c/s, C_2—H). (Found : C, 87·56; H, 5·98; N, 6·45. $C_{16}H_{13}N$ requires: C, 87·64; H, 5·98; N, 6·39%). The phenylcarbamoyl derivative had a m.p. of 194–196°. ν_{max}^{Nujol} 3290 cm^{-1} (—NH—), 1660 cm^{-1} ($\rangle$NCONH—). (Found : C, 81·36; H, 5·63; N, 8·45. $C_{23}H_{18}ON_2$ requires: C, 81·63; H, 5·36; N, 8·28%).

LAH *reduction of the oxime of chalcone* (XVII). Chalcone oxime (497 mg) was reduced with LAH (175 mg) in refluxing THF (25 ml) for 3 hr. Working up gave a yellow residual oil (441 mg), which was treated with phenylisocyanate in ether, and the residue (763 mg) was chromatographed on Al_2O_3 (23 g, 5% Woelm) to give the phenylcarbamoyl derivative (163 mg), m.p. 123–125° by elution with pet-ether : benzene (9 : 1) followed by recrystallization from ether–n-hexane. This was identical in all respects with that obtained from *cis*-2-benzyl-3-phenylaziridine.

LAH *reduction of the oxime of* α-*tetralone* (XVIII). α-Tetralone oxime, m.p. 103–104 , (1·0 g) was reduced with LAH (450 mg) in refluxing THF (60 ml) for 3·5 hr. Working up gave an orange oil (900 mg), which was chromatographed on neutral Al_2O_3 (40 g, Woelm). The fractions eluted with n-hexane : benzene (1 : 1, 1 : 2, 1 : 5), benzene and benzene : Chf (10 : 1, 5 : 1) were dissolved in dil HCl and extracted with ether to remove neutral products. The acid layer was evaporated to dryness under reduced press and the residue was crystallized from acetone–MeOH to give a crystal, m.p. 173–175° as prisms, which gave, on repeated recrystallization, 2,3,4,5-tetrahydro-1H-benz[b]azepine–HCl[27] (107 mg), m.p. 188–189° as prisms. (Found : C, 65·56; H, 7·37; N, 7·50; Cl, 19·55. $C_{10}H_{13}N \cdot HCl$ requires: C, 65·39; H, 7·68; N, 7·63; Cl, 19·30%).

The structure of this azepine was confirmed by the synthesis of the following reaction sequence. The lactam, 2,3,4,5-tetrahydro-1H-benz[b]azepine-2-one, which was obtained by the Schmidt reaction of α-tetralone, had a m.p. of 140–140·5°. (Found : C, 74·45; H, 6·93; N, 8·73. $C_{10}H_{11}ON$ requires: C, 74·51;

H, 6·88; N, 8·93%). The LAH reduction of the lactam gave identical azepine with that mentioned above, characterized as its hydrochloride, m.p. 188–190°.

The second fractions eluted with benzene:Chf (5:1), which chiefly involved crude aziridine (253 mg), gave 1,2-imino-tetralin (98 mg), m.p. 52–53·5° by a vacuum-distillation followed by recrystallization from pet-ether. Treatment of the aziridine with CS_2 gave the corresponding thiazolidine-2-thione derivative, m.p. 188·5–190·5° from acetone. (Found: C, 59·84; H, 5·07; N, 6·50; S, 29·26. $C_{11}H_{11}NS_2$ requires: C, 59·69; H, 5·01; N, 6·33; S, 28·97%).

Further elution with Chf and Chf:MeOH (30:1, 10:1) gave a brown oil (236 mg), which was dissolved in dil HCl and extracted with ether to remove neutral products. The HCl layer was evaporated to dryness to give a residue (136 mg), which was recrystallized from acetone–MeOH to yield tetralin-1-amine-HCl, m.p. 182·5–184° as needles. (Found: C, 64·99; H, 7·98; N, 7·60; Cl, 19·44. $C_{10}H_{13}N \cdot HCl$ requires: C, 65·39; H, 7·68; N, 7·63; Cl, 19·30%).

LAH *reduction of* 1,1-*diphenylpropan-2-one oxime* (XIX). 1,1-Diphenylpropan-2-one oxime (1·6 g), m.p. 165°, was reduced with LAH (550 mg) in refluxing THF (65 ml) for 1 hr. Working up gave a yellowish-green oil (1·5 g), which was chromatographed on SiO_2 (40 g, Merck). Crystalline fractions (812 mg) eluted with benzene and benzene:Chf (30:1, 15:1, 7:1, 3:1) were recrystallized from pet-ether to give 2,2-diphenyl-3-methylaziridine (611 mg), m.p. 73·5–74°; ν_{max}^{Chf} 3306 cm^{-1} ($\rangle$NH); NMR: 8·96 τ (1H, s, —NH—), 8·98 τ (3H, d, 5·3 c/s, —CH_3), 7·20 τ (1H, q, 5·3 c/s, C_3—H). (Found: C, 86·38; H, 7·07; N, 6·84. $C_{15}H_{15}N$ requires: C, 86·68; H, 7·19; N, 6·73%). The structure of this aziridine was confirmed by the independent synthesis from propiophenone oxime and phenylmagnesium bromide by the known method.[19] The phenylcarbamoyl derivative, recrystallized from n-hexane–ether, had a m.p. of 148·5–150° as fine needles; ν_{max}^{Nujol} 3267 cm^{-1} ($\rangle$NH), 1663 cm^{-1} ($\rangle$NCONH—). (Found: C, 80·15; H, 5·97; N, 8·80. $C_{22}H_{20}ON_2$ requires: C, 80·46; H, 6·14; N, 8·53%). Treatment of the aziridine with CS_2 in a sealed tube in a boiling water-bath for 7 hr gave 4-methyl-5,5-diphenylthiazolidine-2-thione, m.p. 169–169·5° as needles. (Found: C, 67·70; H, 5·38; N, 4·96; S, 22·33. $C_{16}H_{15}NS_2$ requires: C, 67·33; H, 5·20; N, 4·91; S, 22·47%).

LAH *reduction of* 1-*phenyl*-1-*methylpropan*-2-*one oxime* (XXIIa). The oxime of 1-phenyl-1-methylpropan-2-one, which was synthesized from 1-phenylpropan-2-one and MeI,[28] had a m.p. of 54·5–56° as prisms from pet-ether. (Found: C, 73·39; H, 8·12; N, 8·63. $C_{10}H_{13}ON$ requires: C, 73·59; H, 8·03; N, 8·58%). The oxime (2·0 g) was refluxed with LAH (1·0 g) in THF (120 ml) for 5 hr. Working up gave a residual oil (1·9 g), which was chromatographed on SiO_2 (50 g, Merck). The fractions (850 mg) eluted with Chf:benzene (2:1) were distilled under reduced press (10 mm Hg) at 110–130° (bath-temp) to yield a distillate (690 mg) as an oil, which was considered to be crude aziridine XXIIIa. The crude aziridine was subjected to the preparative TLC using Al_2O_3 (GF_{254} 250 mμ, Merck) and solvent system of benzene:acetone (3:1), resulting in comparably successful separation into a pair of stereoisomers. The upper part (major) on the preparative TLC could be separated as pure substance. Treatment of this aziridine with *p*-nitrobenzoyl chloride gave the corresponding *p*-nitrobenzoyl derivative, XXIIIb, m.p. 65–66° as rods; ν_{max}^{Chf} 1681 cm^{-1} ($\rangle$NCO—). (Found: C, 68·90; H, 5·43; N, 9·44. $C_{17}H_{16}O_3N_2$ requires: C, 68·90; H, 5·44; N, 9·45%). The cleavage reaction of the aziridine with CS_2 afforded the corresponding thiazolidine-2-thione, m.p. 96·5–97° as leaflets from ether. (Found: C, 59·28; H, 6·09; N, 6·26; S, 28·94. $C_{11}H_{13}NS_2$ requires: C, 59·15; H, 5·87; N, 6·27; S, 28·71%). The lower part (minor) was separated, accompanied with a small quantity of the upper part. Heating of this aziridine with CS_2 in a sealed tube gave another thiazolidine-2-thione, m.p. 165·5–166° as prisms from ether–MeOH, together with a small amount of the above thione, m.p. 96·5–97°, which were separated by the preparative TLC using SiO_2 (GF_{254}, 500 mμ). (Found: C, 59·69; H, 6·05; N, 6·47; S, 28·67. $C_{11}H_{13}NS_2$ requires: C, 59·15; H, 5·87; N, 6·26; S, 28·94%). The *p*-nitrobenzoyl derivative of the lower part was obtained as follows. Treatment of crude aziridine XXIIIa (760 mg) with *p*-nitrobenzoyl chloride (1·05 g) and $(Et)_3N$ (632 mg) in benzene (13 me) gave a residual oil (1·7 g), which was chromatographed on SiO_2 (30 g, Merck). Elution with benzene gave crude *p*-nitrobenzoyl derivative (870 mg) of the upper part, which was recrystallized from ether–n-hexane to give the product (450 mg), m.p. 63–65°. The fractions eluted with benzene and benzene:Chf (4:1) gave an oily residue (140 mg), which afforded, on crystallization from AcOEt–n-hexane, the *p*-nitrobenzoyl derivative (47 mg) XXIIIb of the lower part, m.p. 178–179° as plates; ν_{max}^{Nujol} 1650 cm^{-1} ($\rangle$NCO—). (Found: C, 68·73; H, 5·56; N, 9·41. $C_{17}H_{16}O_3N_2$ requires: C, 68·90; H, 5·44; N, 9·45%). The NMR spectra (60 Mc, $CDCl_3$) of these two *p*-nitrobenzol derivatives XXIIIb showed proton signals due to the corresponding only one methyl group near 8·7 τ as doublet.

LAH *reduction of* 1-*phenyl*-1-*ethylpropan*-2-*one oxime* (XXIIb). The oxime XXIIb, b.p_{20} 104–108°, (2·0 g) was reduced with LAH (1·36 g) in refluxing THF (120 ml) for 4·5 hr. Working up gave an oily residue (1·86 g), which was chromatographed on SiO_2 (50 g, Merck). Elution with Chf:benzene (3:1) gave an oily residue (780 mg), which was subjected to a vacuum-distillation (10 mm Hg) at 110–130° (bath-temp) to give an oily aziridine XXIIIc (570 mg). Separation of this aziridine on the preparative TLC under the same condition as mentioned above was unsatisfactory, differing from XXIIIa. The aziridine (770 mg) was treated with *p*-nitrobenzoyl chloride (977 mg) and $(Et)_3N$ (586 mg) in benzene (11 ml) at room temp for 2 hr. Working up gave a residue (1·8 g), which was chromatographed on SiO_2 (45 g, Merck). Four fractions eluted with benzene at an earlier stage gave an oily residue (1·01 g), which was rechromatographed on SiO_2 (33 g, Merck) to give a crystalline residue (652 mg) from the fractions eluted with benzene:n-hexane (2:1) and benzene. The crystals were recrystallized from ether–n-hexane to yield one of XXIIId (240 mg), m.p. 49–50° as rods; ν_{max}^{Nujol} 1686 cm^{-1} ($\rangle$NCO—). (Found: C, 69·86; H, 5·81; N, 8·98. $C_{18}H_{18}O_3N_2$ requires: C, 69·66; H, 5·85; N, 9·03%). Subsequent eluate of first chromatography with benzene gave a crystalline residue (169 mg), which on recrystallization from AcOEt–n-hexane gave another one of XXIIId (25 mg), m.p. 132–133° as rods; ν_{max}^{Nujol} 1656 cm^{-1} ($\rangle$NCO—). (Found: C, 69·59; H, 5·80; N, 9·08. $C_{18}H_{18}O_3N_2$ requires: C, 69·66; H, 5·85; N, 9·03%). The reaction of the aziridine (130 mg) with CS_2 (266 mg) gave a resulting residue (190 mg), which showed two spots on TLC using SiO_2 and solvent system of Chf. The preparative TLC using SiO_2 (GF_{254} 300 mμ) and Chf as solvent system gave the upper part (85 mg) and the lower part (36 mg) as crystals, respectively. The former was recrystallized from AcOEt–n-hexane giving one of thiazolidine-2-thiones (71 mg), m.p. 135–136° as plates. (Found: C, 61·08; H, 6·12; N, 6·01; S, 26·98. $C_{12}H_{15}NS_2$ requires: C, 60·71; H, 6·37; N, 5·90; S, 27·01%). The latter gave, on recrystallization from MeOH, another thione (10 mg), m.p. 125–126° as rods. (Found: C, 60·45; H, 6·19; N, 5·78. $C_{12}H_{15}NS_2$ requires: C, 60·71; H, 6·37; N, 5·90%).

LAH *reduction of the oxime of phenylacetaldehyde* (XXVa). Phenylacetaldehyde oxime (1·0 g) was reduced with LAH (1·10 g) in refluxing THF (45 ml) for 3 hr, yielding a residual oil (846 mg) after working up in an usual manner. The residue (423 mg) was treated with CS_2 (1·07 g) in a sealed tube in a boiling water-bath for 6 hr. The reaction mixture was evaporated to dryness, treated with 10% NaOH aq, extracted with ether and the ethereal layer was dried and evaporated to give a basic residue (245 mg) which was chromatographed on Al_2O_3 (8 g, 5% Woelm). The eluate (88 mg) with benzene gave, on recrystallization from benzene–n-hexane, N,N′-diphenethylthiourea (40 mg), m.p. 89–92° as plates, which could be also derived by the reaction of phenethylamine with CS_2. The 5% NaOH layer was acidified with 10% HCl aq to give a crystal (296 mg), which was recrystallized from MeOH yielding 5-phenyl-thiazolidine-2-thione, m.p. 170–171° as needles, identical with that obtained from acetophenone oxime.

LAH *reduction of the oxime of* p-*chlorophenylacetaldehyde* (XXVb). A soln of *p*-chlorophenylacetaldehyde oxime[29] (500 mg), m.p. 133–134° in THF (10 ml) was added with stirring to a suspension of LAH (448 mg) in THF (15 ml) at room temp over a period of 10 min and the mixture refluxed for 2 hr. Working up gave an oily residue (425 mg). The residue (420 mg) was treated with CS_2 (834 mg) in a sealed tube in a boiling water-bath for 6 hr. After cooling, the mixture was treated with 10% NaOH aq and extracted with ether. The organic layer was dried and evaporated to dryness yielding an oily residue (248 mg), which on chromatography and recrystallization of the eluate with benzene from benzene–n-hexane gave N,N′-di(*p*-chlorophenethyl)-thiourea (41 mg), m.p. 119–120° as plates. (Found: C, 57·98; H, 5·40; N, 7·84. $C_{17}H_{18}N_2SCl_2$ requires: C, 57·79; H, 5·14; N, 7·93%). The 10% NaOH layer was acidified with 10% HCl aq, extracted with AcOEt and the organic layer was dried, evaporated to dryness giving a residue (270 mg), which was treated with carbon in a MeOH soln. The resulting residue was recrystallized from MeOH to give 5-(*p*-chlorophenyl)-thiazolidine-2-thione (192 mg), m.p. 157–158° as prisms. (Found: C, 47·33; H, 3·74; N, 6·09. $C_9H_8NS_2Cl$ requires: C, 47·05; H, 3·51; N, 6·10%).

LAH *reduction of the oxime of* p-*methoxyphenylacetaldehyde* (XXVc). *p*-Methoxyphenylacetaldehyde oxime[30] (1·0 g), m.p. 113–114° was reduced with LAH (1·02 g) in refluxing THF (50 ml) for 3 hr. Working up gave a residual oil (930 mg). The residue (387 mg) was treated with CS_2 (790 mg) in a sealed tube in a boiling water-bath for 6 hr. The mixture was treated with 10% NaOH aq and extracted with ether. The ethereal layer gave an oily residue (247 mg), which afforded, by decolouration in MeOH with carbon followed by recrystallization from benzene–n-hexane, N,N′-di-(*p*-methoxyphenethyl)-thiourea (108 mg), m.p. 123–124° as prisms. (Found: C, 66·38; H, 7·19; N, 8·06. $C_{19}H_{24}O_2N_2S$ requires: C, 66·24; H, 7·02; N, 8·13%). The 10% NaOH layer was made acidic with 10% HCl to give a crystalline ppt (216 mg), which

was, after the treatment with carbon in a MeOH soln, recrystallized from MeOH yielding 5-(*p*-methoxyphenyl)-thiazolidine-2-thione (165 mg), m.p. 140–141° as prisms. (Found: C, 53·45; H, 5·06; N, 6·48. $C_{10}H_{11}ONS_2$ requires: C, 53·30; H, 4·89; N, 6·22%).

LAH *reduction of the oxime of α-naphthylacetaldehyde* (XXVI). α-Naphthylacetaldehyde oxime (500 mg), m.p. 127–129° was reduced with LAH (200 mg) in refluxing THF (20 ml) for 3 hr. Working up gave an oily residue (440 mg), which was chromatographed on Al_2O_3 (15 g, 3% Woelm). Elution with benzene gave a crystalline residue (230 mg), which was recrystallized from n-hexane–ether to give 2-(α-naphthyl)-aziridine (93 mg), m.p. 64–65°. The fractions eluted with benzene:Chf (5:1, 1:1) gave a residue (112 mg), which was converted to its hydrochloride (52 mg), m.p. 245–250°, identical with 2-(α-naphthyl)-ethylamine·HCl, m.p. 243–248°.

The phenylcarbamoyl derivative of the aziridine, which was obtained from the aziridine and phenylisocyanate, had a m.p. of 133·5–135° as needles from ether. (Found: C, 79·41; H, 5·46; N, 9·52. $C_{19}H_{16}ON_2$ requires: C, 79·14; H, 5·59; N, 9·72%). Cleavage reaction of the aziridine with CS_2 gave 5-(α-naphthyl)-thiazolidine-2-thione, m.p. 237–240° as needles from benzene. (Found: C, 63·89; H, 4·63; N, 5·43. $C_{13}H_{11}NS_2$ requires: C, 63·66; H, 4·52; N, 5·71%).

LAH *reduction of the oxime of β-naphthylacetaldehyde* (XXVII). β-Naphthylacetaldehyde oxime (300 mg), m.p. 115–116·5° was reduced with LAH (114 mg) in refluxing THF (9 ml) for 2·5 hr. Working up gave an oily residue (281 mg), which showed two spots (R_f values, 0·75 and 0·25) on TLC using Al_2O_3 and Chf:MeOH (10:1). Chromatography on Al_2O_3 (6 g, 1% Woelm) gave crude aziridine (R_f 0·75) (106 mg) from the eluate with pet-ether:benzene (1:3), which was distilled under reduced press (5 mm Hg) at 135–155° (bath-temp) to yield a distillate (41 mg). Crystallization of the distillate from ether afforded 2-β-naphthylaziridine (33 mg), m.p. 101–102°, which was identical in all respects with that from β-acetylnaphthalene oxime. The product corresponding to R_f 0·25 was proved to be 2-(β-naphthyl)-ethylamine.

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