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STEREOCHEMISTRY OF AZIRIDINE FORMATION FROM KETOXIMES OF BRIDGED RING SYSTEMS BY LITHIUM ALUMINUM HYDRIDE REDUCTION ON BENZOBICYLO[3.2.1]OCTENONE OXIMES*

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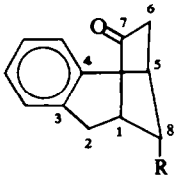
Abstract—In order to study further the applicability and stereochemistry of aziridine formation by LAH reduction of ketoximes of bridged ring systems, several ketones having the benzobicyclo[3.2.1]octene ring system have been synthesized by suitable methods. Separation of *syn*- and *anti*-isomers of the corresponding ketoximes and GLC analyses of reduction products have been performed. Although the effects of the benzene ring fused to the bridged rings on aziridine formation involving *endo* and *exo* ratio of the formed aziridines remain uncertain, the results clearly indicate that aziridine formation strongly depends upon the configurations of the oximes and occurs preponderantly from the *syn*-oximes.

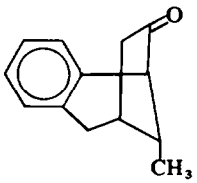
RECENTLY, our group reported a new method for the synthesis of aziridines by LAH reduction of ketoximes.[2] It was demonstrated that this reaction was also applicable for ketoximes having bridged ring systems.[2,3] As reported, LAH reduction of ketoximes having bridged ring systems fused to benzene ring afforded the respective aziridines in fair yields, but ketoximes having no benzene ring produce the expected aziridines in quite low yields. At that stage, these results could not be interpreted reasonably, although the effects of the benzene ring and/or the configurations of the oximes used might be considered as its factors. For the purpose of clarifying these unambiguities on the aziridine formation from oximes, the synthesis of benzobicyclo[3.2.1]octenones, I, II, and III, which have the respective ketonic functions at the different positions towards the fused benzene ring, were carried out. Separation of *syn*- and *anti*-isomers of the synthesized ketoximes and GLC analyses of the reduction products were accomplished. This paper deals with the results obtained.

CHART 1

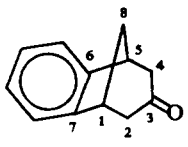


I

a: R = H
b: R = CH_3



II



III

* Bridged Ring Compounds: Part V. The outline of this paper was presented in our preliminary communication.[1]

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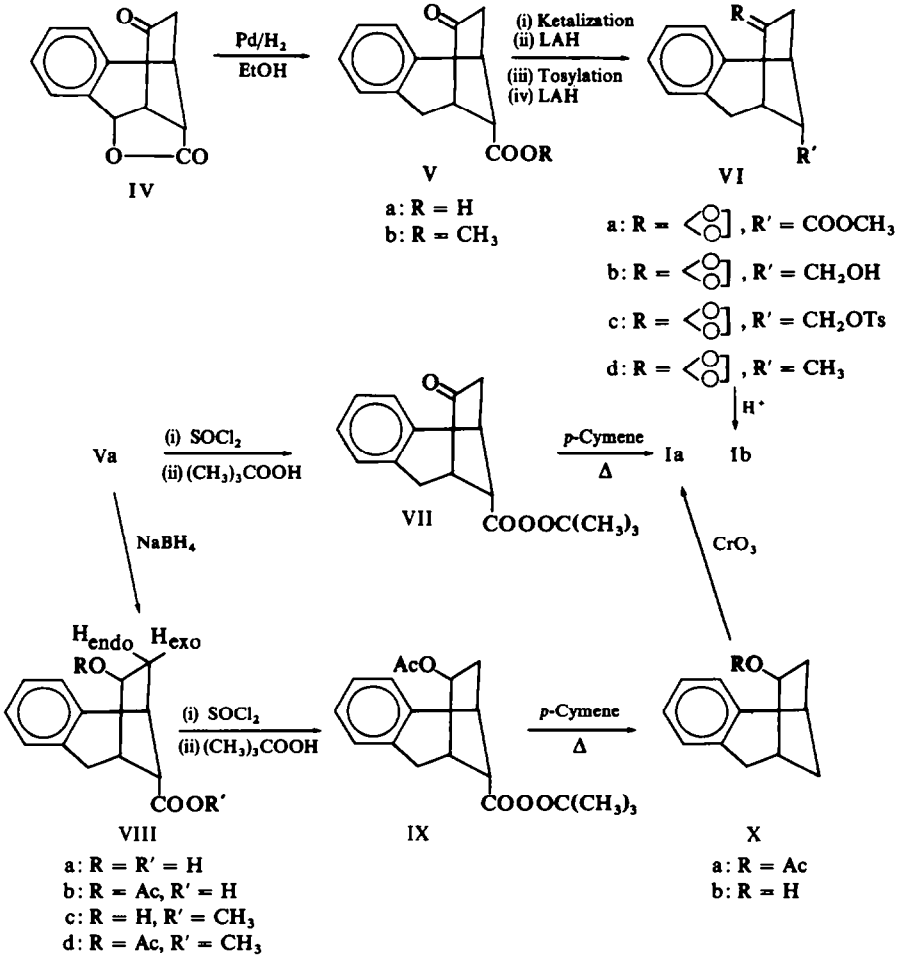
(a) *Syntheses of benzobicyclo*[3.2.1]*octenones*, Ia, Ib, II *and* III

Starting from the known keto-lactone IV,[4] 3,4-benzobicyclo[3.2.1]octen-7-one (Ia)* and its 8-*endo*-Me derivative Ib were synthesized as shown in Chart 2. The keto-carboxylic acid Va, m.p. 165–167°, which were obtained by hydrogenolysis of IV over Pd-carbon catalyst in 90% yield, was easily converted into Ib, m.p. 70–70·5° by a 6-step process. The synthesis of Ia was somewhat laborious in comparison with that of Ib. Decarboxylation of the keto-acid Va to Ia by the known method[5] was unsuccessful since refluxing of the keto-carboxylic acid perester VII in *p*-cymene resulted in the formation of complicated products with a small amount of the ketone Ia. Therefore, the following synthetic route was carried out. $NaBH_4$ reduction of Va gave 7-*endo*-hydroxy-8-*endo*-carboxylic acid VIIIa, which was acetylated to VIIIb. The perester IX obtained from VIIIb was subjected to decarboxylation reactions[5] affording the aimed product Xa in ca. 20% over-all yield from VIIIb. The deacetylated product Xb was oxidized to the oily ketone Ia.

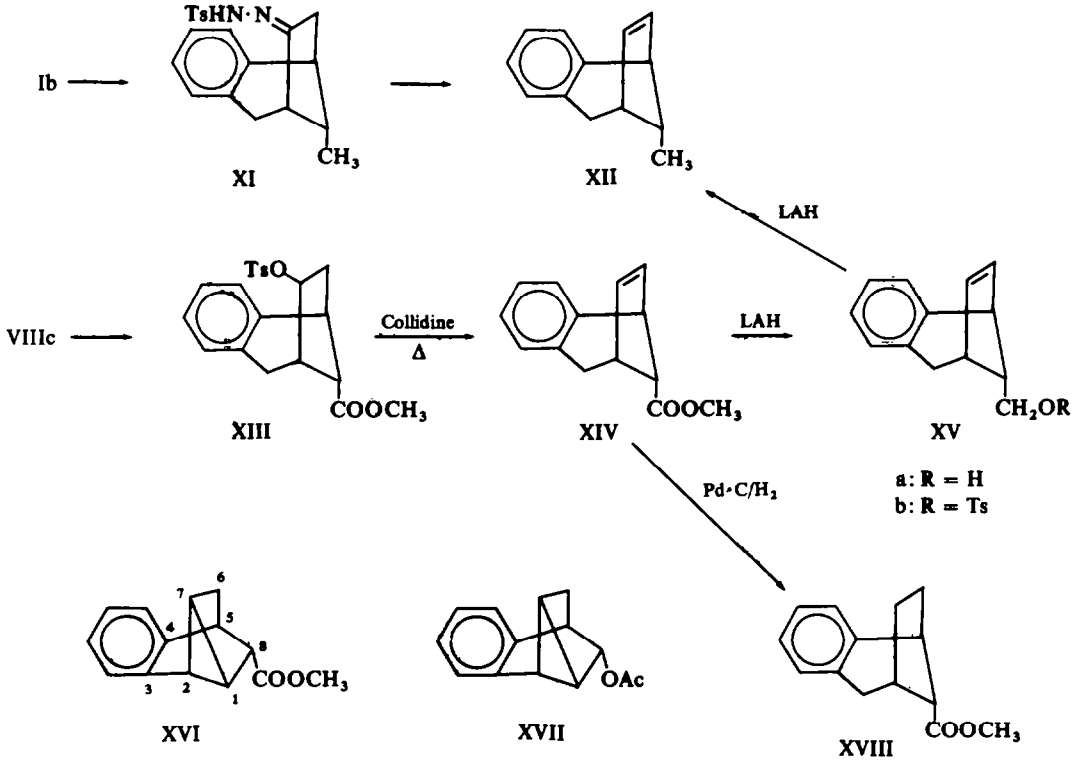
CHART 2



* The numbering used in this paper is shown in the Charts.

For the synthesis of II, migration of the C_7 ketonic function of Ib to the C_6 position is necessary. For this purpose, the unsaturated compound XII seemed to be a suitable intermediate. Treatment of the tosylhydrazone XI of the ketone Ib with alkaline reagent (Bamford reaction) gave a low yield of the aimed product XII. The key compound XII was successfully synthesized by refluxing the tosylate XIII, prepared from VIIIc, with collidine. When crude VIIIc was used as the starting material, the same reaction gave a small amount of a tricyclo-product XVI as a by-product.

CHART 3



This comes probably from the C_7-*exo*-hydroxy-isomer involved in the starting material. Structure elucidation of XVI was readily established from its NMR data analogous to those of the known tricyclo-compound XVII.[6] With the key intermediate XII thus synthesized, its transformation into II was achieved based on the results obtained by hydroboration,[7] epoxidation-LAH reduction and oxymercuration[8] of XII. The respective products by the three methods were analyzed by GLC and relative product ratios were obtained as indicated in Table 1. From the data, it was found that oxymercuration is the best process for the synthesis of II, since the reaction gave a mixture of only two products and hydroxylation to the C_6-position is superior to that to the C_7-position.

TABLE 1. RELATIVE PRODUCT RATIOS OBTAINED BY OXYMERCURATION, HYDROBORATION AND EPOXIDATION-LAH REDUCTION OF XII USING GLC[a]

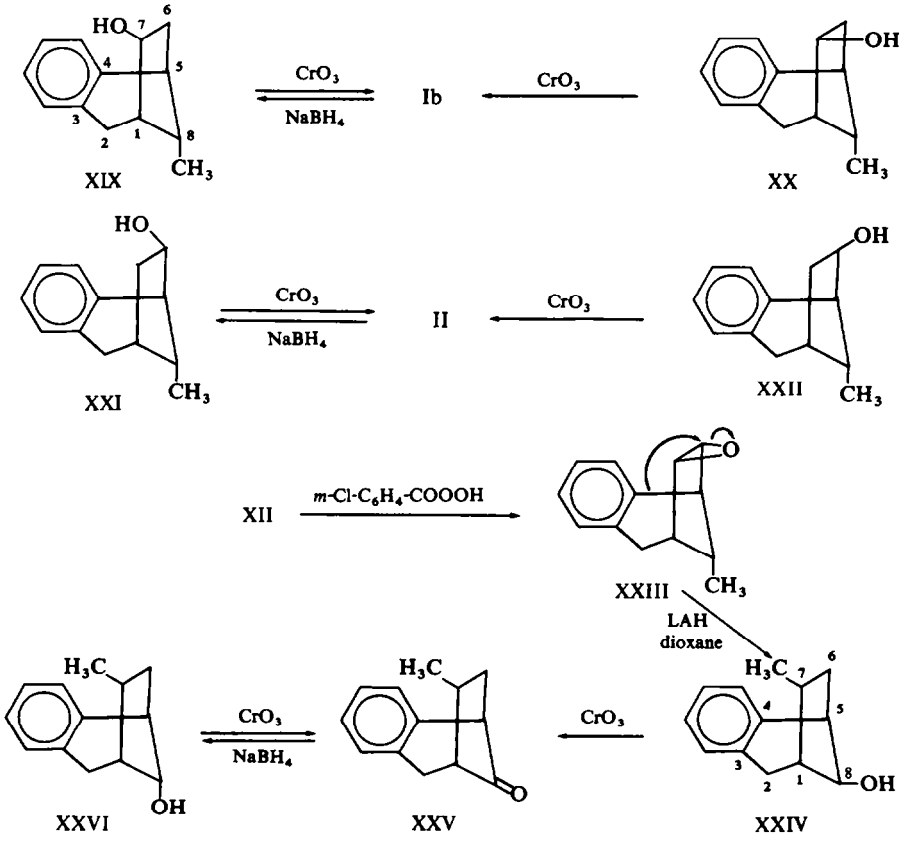
Procedure	Product %				
	7-OH		6-OH		8-OH
	XIX	XX	XXI	XXII	XXIV
Oxymercuration	32 (32)[b]	0	trace (68)[b]	68	0
Hydroboration	3 (59)	56	8 (41)	33	0
Epoxidation-LAH reduction	trace[c] (21)	21	3[c] (37)	34	42

[a] Details of GLC were described in the Experimental.

[b] Percentages of the total yield of 7-OH or 6-OH derivatives are shown in the parentheses.

[c] This suggests that the epoxide used here may involve a small amount of the *endo*-epoxide.

CHART 4



The structures of the hydroxylated products were elucidated by chemical evidence involving oxidation to the ketones and $NaBH_4$ reduction of the ketones as portrayed in Chart 4. In addition, the configurations of OH groups of reaction products were determined based on their NMR data, especially on the signal patterns of the protons attached to the carbons bearing the OH groups (Table 2).

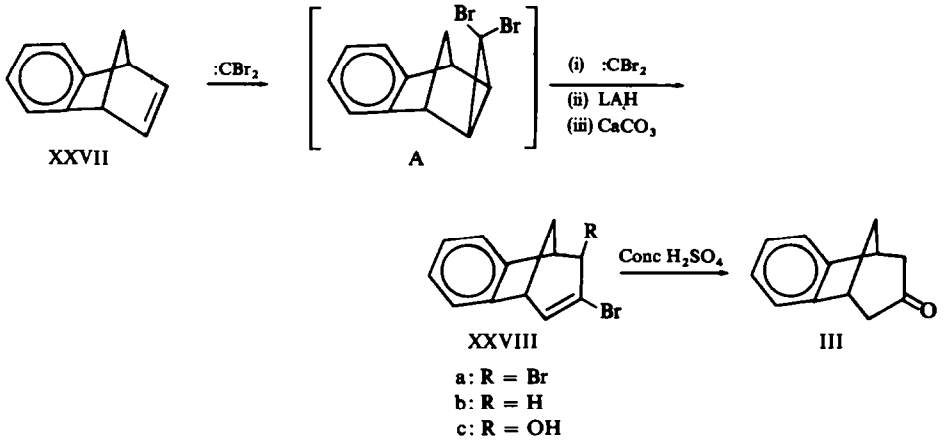
TABLE 2. NMR SPECTRAL DATA OF PROTON SIGNALS OF HYDROGENS ATTACHED TO THE CARBONS BEARING HYDROXYL GROUPS IN Xb, XIX, XX, XXI, XXII, XXVI AND XXIV (60 Mc, $CDCl_3$)

Compound	Chemical shift (τ)	
	endo-OH	*exo*-OH
Xb	C_7—H; 5·43 m	—
XIX and XX	XIX C_7—H; 5·53 m	XX C_7—H; 5·87 d-d
XXI and XXII	XXI C_6—H; 5·60 m	XXII C_6—H; 5·87 d-d
XXVI and XXIV	XXVI C_8—H; 5·68 t	XXIV C_8—H; presumably singlet

m: multiplet, d-d: doublets of doublet, t: triplet

In these examinations, epoxidation-LAH reduction afforded complicated products, i.e. the *exo*-epoxide XXIII was reduced with LAH largely to a rearranged product, the structure of which was assigned as XXIV based on the analogy to the LAH reduction products of *exo*-epoxides having bicyclo[2.2.1]heptane ring system.[9] Ultimately, the preparation of the ketone II was achieved by oxymercuration of XII. The reaction products were simply composed of a mixture of the 7-*endo*-isomer XIX and the 6-*exo*-isomer XXII in relative ratio of ca. 1:2 and the aimed ketone II, m.p. 78·5–80° was readily obtained by controlling the reaction condition of CrO_3 oxidation of the mixture, since the C_7-OH compound XIX remained intact and was easily removed.

CHART 5



XXVII A XXVIII III

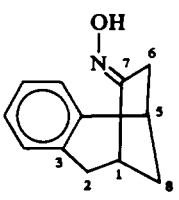
a: R = Br
b: R = H
c: R = OH

The synthesis of 6,7-benzobicyclo[3.2.1]octen-3-one (III), m.p. 64–66° was accomplished by application of the known method[10] on benzonorbornadiene as illustrated in Chart 5.

(b) *Stereochemistry of aziridine formation from the ketoximes* (XXIX, XXX, XXXI *and* XLVI)

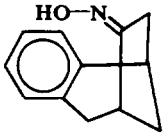
The oxime of 3,4-benzobicyclo[3.2.1]octen-7-one (Ia) showed two spots (R_f-values, 0·64 and 0·70) on TLC using SiO_2 and the solvent of ether–n-hexane (3:1, vol). By combination of column-chromatography and preparative TLC over SiO_2, the oxime was separated into the respective components, *syn*-isomer (R_f 0·64) XXIXa, m.p. 112–112·5° and *anti*-isomer (R_f 0·70) XXIXb, m.p. 115°. The stereochemistry of the separated oximes was established from the NMR data. The C_1-proton signal of XXIXa seems to appear near 7·00 τ as a multiplet obscured with those of C_5-hydrogen and C_2-hydrogens, while that of XXIXb appears near 6·43 τ as an isolated multiplet, which is shifted to low field owing to deshielding effect by the proximity of the OH group.[11] Similarly, the oxime XXX was successfully separated into the isomers, the *syn*-form XXXa (C_1-H, ~7·16 τ), m.p. 115–116° and the *anti*-form

CHART 6



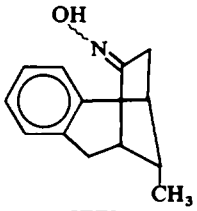
XXIXa

syn-isomer



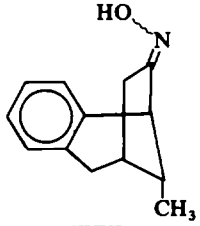
XXIXb

anti-isomer



XXX

a: *syn*-isomer
b: *anti*-isomer



XXXI

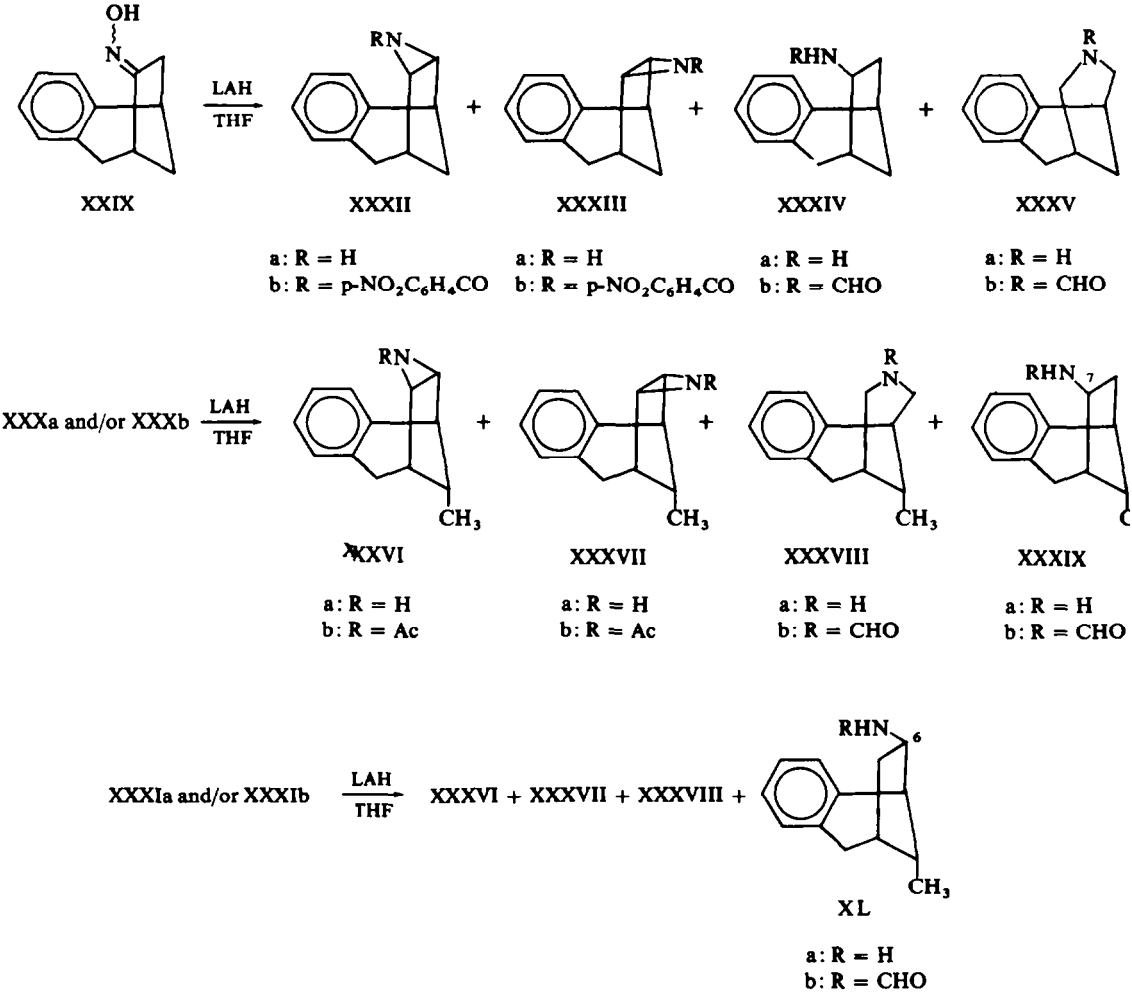
a: *syn*-isomer
(b: *anti*-isomer)

XXXb (C_1-H, ~6·70 τ), m.p. 149–151°. As to the oxime XXXI, only the *syn*-oxime XXXIa, m.p. 135·5–136°, could be isolated.* Separation of *syn*- and *anti*-ketoximes having bridged ring systems has been hitherto unreported.

In order to study the stereochemistry of aziridine formation, preliminary test was carried out with the oxime XXIX. The LAH reduction in boiling THF gave the *endo*-aziridine XXXIIa (*p*-nitrobenzoyl derivative XXXIIb, m.p. 139–140°), the *exo*-aziridine XXXIIIa (*p*-nitrobenzoyl derivative XXXIIIb, m.p. 159–160°), the *endo*-primary amine XXXIVa (N-formate XXXIVb, m.p. 141·5–142·5°) and a secondary amine XXXVa (N-formate XXXVb, m.p. 107–107·5°). Since structure elucidation of reduction products was made in a manner similar to the cases of XXX and XXXI

* The separated oximes were stable for isomerization during chromatography over SiO_2 and recrystallization from ether-n-hexane. The prefixes, *syn* and *anti*, were used in the sence that the oxime having the hydroxyl group directed to the C_6–methylene group is *syn* and the oxime with reverse orientation is *anti*, as shown in XXIXa and XXIXb, respectively. Analogous prefixes were employed on the oximes, XXX and XXXI.

CHART 7

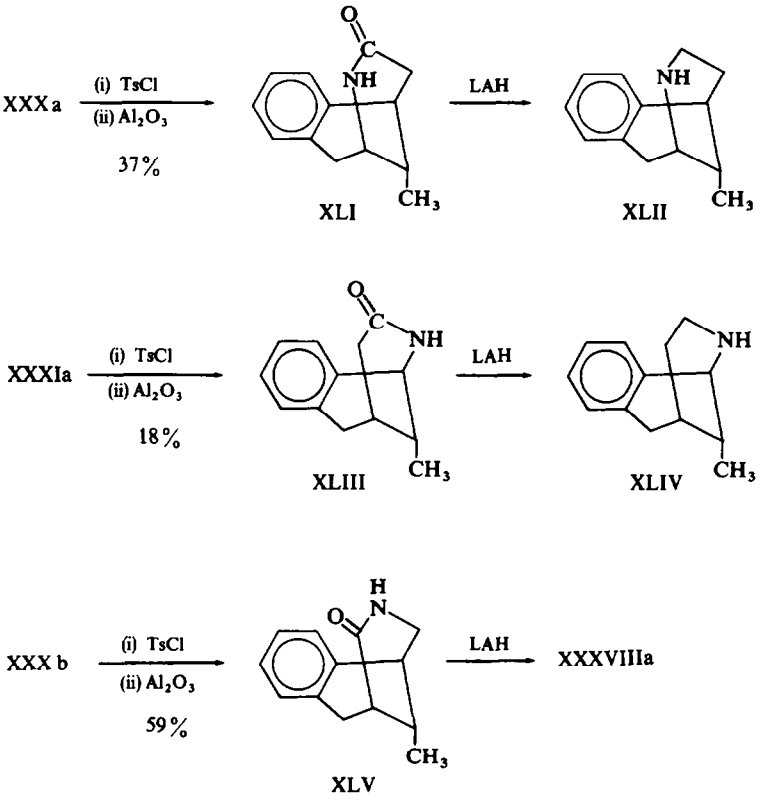


described later, it is omitted here. However, it is only mentioned that the use of pure *syn*-oxime XXIXa gave the primary amine XXXIVa and the aziridines (XXXIIa, *endo*, main) in 22 and 33% yields, respectively, whereas, the similar treatment of the *anti*-oxime XXIXb yielded the primary amine XXXIVa (59%) and a small amount of the aziridines (XXXIIa, *endo*, main, detected by TLC). These results distinctly indicate preponderant aziridine formation from the *syn*-form in comparison with the *anti*-form.

With the preliminary results from the isomers, XXIXa and XXIXb, in mind, LAH reduction of the oximes, XXX and XXXI was performed. By elution-chromatography over Al_2O_3, the respective reduction products were separated into the *endo*-aziridine XXXVIa, m.p. 92–92·5°, the *exo*-aziridine XXXVIIa, m.p. 89–89·5° and a secondary amine XXXVIIIa (N-formate XXXVIIIb, m.p. 105–106°), which were isolated as common products from both oximes, besides the C_7-*endo*-primary amine XXXIXa

(N-formate XXXIXb, 156–157°) from XXX and the C_6-*endo*-primary amine XLa (N-formate XLb, m.p. 74–75°) from XXXI. The structures and stereochemistry of the aziridines were determined based on the IR spectra involving interaction between the benzene ring and the secondary amine group, and on the NMR data of the respective N-acetates XXXVIb and XXXVIIb including the shielding effect of the benzene ring.[1] The *endo*-configuration of the primary amines was established by catalytic reduction of the *endo*-aziridine to XXXIXa and XLa in almost equal yields. The structure of a secondary amine XXXVIIIa was established based on the Beckmann rearrangements of the oximes, XXXa, XXXIa and XXXb, and on LAH reduction of the respective lactams, XLI, XLIII and XLV, to the corresponding secondary amines, XLII, XLIV and XXXVIIIa (Chart 8). In this case, it is noteworthy that the lactam

CHART 8



XLI and the secondary amine XLII have the same ring system as 9-Me-6,7-benzomorphan derivatives.[12] Therefore, this may provide the possibility of a new synthetic route to 6,7-benzomorphan derivatives.

Thus, the structures and stereochemistry of reduction products from XXX and XXXI were fully elucidated. Detailed quantitative study of aziridine formation was performed with the oxime isomers, XXXa and/or XXXb, and XXXIa and/or XXXIb,

changing content ratios of *syn*- and *anti*-isomers. The respective reduction products were quantitatively analyzed by GLC. The results are summarized in Table 3.

TABLE 3. GLC ANALYSES OF LAH REDUCTION PRODUCTS OF 8-*endo*-Me-3,4-BENZOBICYCLO-[3.2.1]OCTENONE OXIMES, XXX AND XXXI[a]

Isomer ratio of the oxime	Product %				Secondary amine XXXVIIIa
	Aziridine		Primary amine		
	XXXVIa	XXXVIIa	XXXIXa or XLa		
XXXa (*syn*)	42·2	12·0 (54·2)[b]	19·3 (XXXIXa)	(32·6)[c]	13·3
XXXa:XXXb = 1:1	23·5	9·1 (33·4)	22·7 (XXXIXa)	(39·9)	17·2
XXXb (*anti*)	7·7	5·2 (12·9)	39·4 (XXXIXa)	(63·0)	23·6
XXXIa (*syn*)	19·3	39·2 (58·5)	11·9 (XLa)	(20·4)	8·5
XXXIa:XXXIb = 1·1:1	10·5	20·9 (31·4)	44·1 (XLa)	(62·2)	18·1

[a] In each case, the oxime (50 mg) was reduced under heating at 90° with 4 molar equiv of LAH (37 mg) in THF (5 ml) in a sealed tube for 4 hr and the products were analyzed by GLC using diphenyl ether as internal reference.

[b] Total yield of the aziridines.

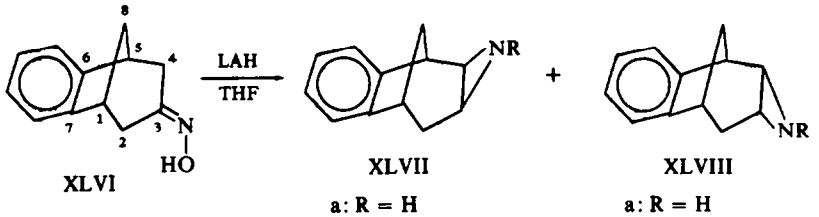
[c] Yield of the primary amine plus the secondary amine.

It was found that the aziridine isomers, XXXVIa and XXXVIIa, are preponderantly formed from the *syn*-oximes in comparison with those from the *anti*-oximes. For example, LAH reduction of the *syn*-oxime XXXa gave the aziridine isomers in 54·2% yield (XXXVIa and XXXVIIa in 42·2 and 12·0%, respectively). The increase of the *anti*-oxime XXXb results in reduced formation of the aziridine isomers. The use of the pure *anti*-oxime XXXb shows extremely decreased formation of the aziridine isomers (12·9%).* The similar tendency can be recognized on the LAH reduction of the oxime isomers, XXXIa and /or XXXIb. These results agree well with those from aralkyl alkyl ketoximes and their oxime tosylates.[13] The most interesting finding is that total yields of the aziridine isomers formed from both of the *syn*-oximes, are almost the same (ca. 55%), but product ratio between the *endo*- and *exo*-isomers varies reversely. This can not be interpreted only by the probably homobenzylic character of the methylene group adjacent to the oximino function and remains unsolved.

As mentioned above, it was distinctly proved that aziridine formation from benzobicyclo[3.2.1]octenone oximes is strongly influenced by configurations of oximes used, indicating overwhelming aziridine formation from the *syn*-oximes in comparison with from the *anti*-oximes. As an example where *syn*- and *anti*-isomers do not exist, 6,7-benzobicyclo[3.2.1]octen-3-one oxime (XLVI) was chosen. The LAH reduction

* The aziridine formation from the pure *anti*-oxime XXXb may be tentatively interpreted by supposing the equilibrium between the *anti*- and *syn*-oximes during the LAH reduction.

CHART 9



XLVI

XLVII
a: R = H
b: R = $COOCH_3$

XLVIII
a: R = H
b: R = $COOCH_3$
c: R = C_6H_5NHCO

gave two aziridines, XLVIIa, m.p. 45·5–46° (characterized as its N-carboxylate XLVIIb, m.p. 112·5–114°) and XLVIIIa as an oil (characterized as its N-carboxylate XLVIIIb, m.p. 119–119·5° and phenylcarbamoyl derivative XLVIIIc, m.p. 197°), of which the structures and stereochemistry were deduced from their IR data and the NMR data of XLVIIb and XLVIIIb in a manner similar to the cases mentioned above. The yields were quantitatively analyzed by GLC. These data are summarized in Table 4.

TABLE 4. IR DATA OF XLVIIa AND XLVIIIa, NMR DATA OF XLVIIb AND XLVIIIb, AND GLC ANALYSIS OF THE REDUCTION PRODUCTS

Product	XLVII	XLVIII
IR (cm^{-1}) (NH)	3318 (XLVIIa)	3286[a] (XLVIIIa)
NMR (τ) ($COOCH_3$)	6·32 (XLVIIb)	6·48[b] (XLVIIIb)
GLC[c] Yield (%)	36·8 (XLVIIa)	54·7 (XLVIIIa)

[a] Showing interaction between the benzene ring and the secondary amino group.

[b] Shifted owing to shielding effect of the benzene ring.

[c] The oxime (42 mg) was reduced with LAH (40 mg) in THF (5 ml) in a sealed tube under heating at 85° for 4 hr and the products were analyzed by GLC using diphenyl ether as internal reference.

As the GLC analytical data show, the aziridines were formed in extremely excellent yield (91·5%). This yield almost equals to the yields of the aziridines obtained from dibenzo[a.c]cycloheptadien-6-ketoxime[2,14] and dibenzylketoxime,[2,15] which are also free from the factors of configurations of oximes.

(c) *Conclusion*

Studies on aziridine formation with benzobicyclo[3.2.1]octenone oximes result

in the conclusion that our reaction is of different type from the Neber rearrangement[16] in the point that aziridine formation strongly depends upon the configurations of the oximes used. Usually, the *syn*-oximes afford the aziridines in fair yields, but the effects of the benzene ring fused to bridged ring systems on the aziridine formation remained to be solved.

EXPERIMENTAL

M.ps were taken by capillary tube and are uncorrected. B.ps are also uncorrected. The NMR spectra were determined at 60 Mc with a Varian A-60 spectrometer using TMS as internal standard in $CDCl_3$. The IR spectra were measured using a Koken Model D.S.-301 IR double-monochromatic spectrophotometer and interaction between the benzene ring and the secondary amino group was measured in CCl_4 (0·005M or less) and 20 mm cell using a Nihonbunkō Model D.S.-402G grating spectrometer. The UV spectra were measured using a Hitachi Model E.P.S.-2 UV spectrometer. Unless otherwise stated, solns were dried over Na_2SO_4.

Hydrogenolysis of IV *to* V. A soln of IV[4] (215 mg) in EtOH (50 ml) was shaken in the presence of H_2 over 10% Pd-charcoal catalyst (200 mg). After 1 molar equiv of H_2 had been absorbed, the reaction stopped. After removal of the catalyst, the mixture was evaporated to dryness *in vacuo* and the crystalline residue (199 mg) was twice recrystallized from CH_2Cl_2–benzene to give a pure sample (140 mg) of Va, m.p. 165·5–167°; ν_{max}^{Nujol} 3313, 1731, 1711, 1653 cm^{-1}. (Found: C, 72·01; H, 5·64. $C_{13}H_{12}O_3$ requires: C, 72·21; H, 5·59%). The *Me-ester* Vb prepared by treatment of Va with CH_2N_2 had a m.p. of 126·5–128° as plates from ether; ν_{max}^{Nujol} 1740, 1714 cm^{-1}. (Found: C, 72·95; H, 6·11. $C_{14}H_{14}O_3$ requires: C, 73·02; H, 6·13%).

Synthesis of 8-endo-Me-3,4-*benzobicyclo*[3.2.1]*octen-7-one* (Ib). A soln of Vb (1·041 g), ethylene glycol (2 ml) and *p*-toluenesulfonic acid (54 mg) in benzene (100 ml) was refluxed using a water-separator for 39 hr. The soln was washed with 5% $NaHCO_3$ aq and then H_2O, dried and evaporated to give quantitative yield of VIa (1·26 g), which was used for the next step. A soln of VIa (1·26 g) in THF (45 ml) was dropwise added with stirring at 10–15° to a suspension of LAH (0·35 g) in THF (35 ml) over a period of 10 min, and the mixture was refluxed for 4 hr. Under cooling in ice, excess LAH was decomposed with H_2O and the mixture was extracted with ether. Evaporation of the dried organic layer afforded a crystalline VIb (1·10 g), which was recrystallized from ether to yield the analytical sample, m.p. 97–98°, as needles; ν_{max}^{Nujol} 3286, 1101, 1018 cm^{-1}. (Found: C, 73·08; H, 7·33 $C_{15}H_{18}O_3$ requires: C, 73·14; H, 7·37%).

To a soln of VIb (1·10 g) in pyridine (20 ml), *p*-toluenesulfonyl chloride (1·28 g) was added and the mixture was left overnight at room temp. After addition of ice water, the mixture was extracted with ether. The extract was washed with 5% $NaHCO_3$ aq and H_2O, dried and evaporated to dryness leaving oily VIc (1·899 g), which was used for the next step. A soln of VIc (1·899 g) in THF (35 ml) was dropwise added with stirring at 13–15° to a suspension of LAH (0·43 g) in THF (30 ml) over a period of 15 min and the mixture was refluxed for 4 hr. Working up left oily crude VId (981 mg; 93·8%). A mixture of crude VId (981 mg), AcOH (10 ml), and H_2O (2 ml) was heated in a boiling water-bath for 1·5 hr. Evaporation of the solvent *in vacuo* left an oily residue, which was extracted with ether. The extract was washed with 5% $NaHCO_3$ aq and H_2O, dried and evaporated to give crude Ib (791 mg) which was chromatographed over neutral Al_2O_3 (24 g, Woelm, act. I). Elution with ether–pet. ether (1:9) gave a crystalline residue (409 mg), which was twice recrystallized from ether–pet. ether to give pure Ib, m.p. 70–70·5°; ν_{max}^{Nujol} 1731 cm^{-1}. $\lambda_{max}^{n\text{-heptane}}$ 260·0, 266·5, 273·9, 313·5 mμ (ε 322, 487, 538, 19); NMR: ~6·85 τ (1-H, m, C_1-H), 7·02 τ (1-H, d-d, C_6-H_{exo}), 7·08τ (1-H, d-d, C_6-H_{endo}). (Found: C, 83·77; H, 7·55. $C_{13}H_{14}O$ requires: C, 83·83; H, 7·58%).

Attempt to synthesize Ia *from* VII. The treatment of Va similar to the case of VIIIb described later gave the perester VII, m.p. 106–107°, as needles from ether–pet, ether; ν_{max}^{Nujol} 1763, 1746 cm^{-1}. (Found: C, 70·61; H, 7·07. $C_{17}H_{20}O_4$ requires: C, 70·81; H, 6·99%).

A soln of crude VII prepared from Va (300 mg) in *p*-cymene (6·0 ml) was heated at 118–130° for 2 hr. Evaporation of the solvent *in vacuo* gave a residue, which was chromatographed over neutral Al_2O_3 (40 g, Woelm, act. I). Elution with benzene–pet. ether (1:4) gave an oil, which showed several spots on TLC using SiO_2. Attempt to isolate the ketone Ia on further column-chromatography was not successful.

$NaBH_4$ *reduction of* Va *and its derivatives*, VIIIb, VIIIc and VIIId. To a soln of Va (21·51 g) in 2% NaOH aq (220 ml), Na BH_4 (3·76 g) was added in portions below 10° and the mixture was allowed to stand at room temp with stirring for 2 hr. The reaction mixture was acidified with 10% HCl aq and extracted with ether. The ethereal layer was washed with H_2O, dried and evaporated leaving a crystalline residue which was

twice recrystallized from benzene–acetone to give pure VIIIa (19·48 g; 89·7%), m.p. 133–134°, ν_{max}^{Nujol} 3462, 3244, 1681 cm^{-1}. (Found: C, 71·33; H, 6·58. $C_{13}H_{14}O_3$ requires: C, 71·54; H, 6·47%). A portion (143 mg) of the mother liquor of the recrystallization was evaporated, esterified with CH_2N_2 and acetylated with Ac_2O and pyridine. On column-chromatography of the mixture (123 mg) over SiO_2 (6 g, Woelm, act. II), elution with ether–n-hexane (3:7) left a residue (84 mg), which may involve *exo*-acetate besides *endo*-acetate VIIId from its NMR data; 6·53τ (s, $COOCH_3$ in VIIId and its *exo*-isomer), 8·05τ (s, $OCOCH_3$ in VIIId), 8·00τ (s, $OCOCH_3$ in *exo*-isomer), 4·75 τ (m, C_7-H in VIIId), 5·07 τ (d-d, C_7-H in *exo*-isomer). Separation of the isomers was unsuccessful.

The *Me-ester* VIIIc prepared by treatment of VIIIa with CH_2N_2, had a m.p. of 113–114° as needles from ether–pet. ether; ν_{max}^{Nujol} 3434, 1739 cm^{-1}. (Found: C, 72·36; H, 7·05. $C_{14}H_{16}O_3$ requires: C, 72·39; H, 6·94%). A mixture of VIIIa (17·93 g), Ac_2O (180 ml) and pyridine (160 ml) was kept overnight at room temp. After addition of ice–water, the mixture was extracted with ether. The extract was washed with 20% H_2SO_4aq and H_2O, dried and evaporated to dryness leaving a residue, which, on twice crystallization from benzene–acetone, gave pure VIIIb (20·83 g; 97·4%), m.p. 157–158° as needles; ν_{max}^{Nujol} 1723, 1692 cm^{-1}. (Found: C, 68·78; H, 6·16. $C_{15}H_{16}O_4$ requires: C, 69·21; H, 6·20%).

Treatment of VIIIb with CH_2N_2 afforded the *Me-ester*, VIIId, m.p. 111–112° as prisms from ether–pet. ether; ν_{max}^{Nujol} 1734, 1253 cm^{-1}. (Found: C, 70·19; H, 6·67. $C_{16}H_{18}O_4$ requires: C, 70·03; H, 6·61%). A mixture of VIIIa (243 mg) and KOH (1 g) in triethylene glycol (7 ml) was heated at 200° for 5 hr. The mixture was acidified with 5% HClaq and extracted with ether. The dried extract was evaporated and the residue (242 mg) was chromatographed over SiO_2 (7·2 g, Woelm, act. II). Elution with AcOEt and Chf–AcOEt (1:9) gave crude *exo*-OH isomer (138 mg) of VIIIa, which afforded, on thrice recrystallization from acetone–benzene, the pure sample, m.p. 160–161°; ν_{max}^{Nujol} 3310, 1699 cm^{-1}. (Found: C, 71·35; H, 6·48. $C_{13}H_{14}O_3$ requires: C, 71·45; H, 6·47%).

Synthesis of Ia *from* VIIIb. A mixture of VIIIb (15 g) and $SOCl_2$ (120 ml) was warmed at 70° for 1 hr. Evaporation left a crystalline residue which was dissolved in abs ether (225 ml). To the soln, a soln of t-butyl hydroperoxide (6·86 g) in pyridine (22·5 ml) was added dropwise with stirring at 3° over a 30 min period and the mixture was stirred at the same temp for further 3 hr. The ethereal layer was washed with 10% H_2SO_4aq, 5% $NaHCO_3$aq and with H_2O. Evaporation of the ether, which was dried over anhyd $MgSO_4$, gave crude IX (11·97 g; 62·5%) which was recrystallized from n-hexane–ether to yield the pure sample, m.p. 102–102·5°, as rods; ν_{max}^{Nujol} 1763, 1740 cm^{-1}. (Found: C, 68·05; H, 7·34. $C_{19}H_{24}O_5$ requires: C, 68·05; H, 7·28%). The $NaHCO_3$ layer was acidified with conc HCl, and extracted with ether. Evaporation of the extract showed the recovery of the starting VIIIb (4·99 g; 32·9%).

A soln of IX (1·234 g) in *p*-cymene (15 ml) was heated at 130° in an oil-bath for 3 hr. Evaporation of the solvent left a brown oil, which was extracted with ether. The extract was washed with 10% H_2SO_4aq, 5% $NaHCO_3$aq and then with H_2O, dried over anhyd $MgSO_4$ and evaporated to give an oil which was chromatographed over 1% H_2O-containing neutral Al_2O_3 (60 g, Woelm). Elution with benzene and Chf–benzene (1:1) followed by recrystallization of the eluate gave pure Xa (249 mg; 31·0%), m.p. 93–94°; ν_{max}^{Nujol} 1730, 1247 cm^{-1}. (Found: C, 77·84; H, 7·51. $C_{14}H_{16}O_2$ requires: C, 77·75; H, 7·46%). A mixture of Xa (44 mg) and 3% methanolic KOH (2 ml) was refluxed for 1 hr. Evaporation of the solvent gave a residue which was extracted with ether. The extract was washed with H_2O, dried and evaporated to dryness leaving almost quantitative yield of Xb, m.p. 92·5–93° as needles on recrystallization from ether–pet. ether; ν_{max}^{Nujol} 3306 cm^{-1}. (Found: C, 82·78; H, 8·24. $C_{12}H_{14}O$ requires: C, 82·78; H, 8·10%). A soln of Xb (99 mg) in pyridine (3 ml) was added under cooling in ice to the complex prepared from CrO_3 (300 mg) and pyridine (3 ml), and the mixture was left overnight at room temp. To the mixture, MeOH (4 ml) and H_2O (5 ml) were added and the mixture was extracted with ether. The extract was washed with 20% H_2SO_4aq, 5% $NaHCO_3$aq and with H_2O, dried and evaporated to dryness leaving an oil (98 mg), which was chromatographed over neutral Al_2O_3 (3·3 g, Woelm, act. I) to give oily pure Ia (83 mg; 84·4%) which was eluted with benzene–pet. ether (1:9); ν_{max}^{film} 1743 cm^{-1}; $\lambda_{max}^{n\text{-heptane}}$ 259·7, 266·3, 274·7, 313·0 mμ (ε 334, 477, 512, 31); NMR: ~6·62 τ (1-H, m, C_1-H), ~7·25 τ (1-H, m, C_5-H), 6·95 τ (1-H, d, C_6-H_{exo}) 7·00 τ (1-H, d-d, C_6-H_{endo}).

Bamford reaction of Ib. A soln of Ib (240 mg) and *p*-toluenesulfonylhydrazine (389 mg) in abs EtOH (8 ml) was refluxed for 1·5 hr. Evaporation of the solvent *in vacuo* gave an oil, which was extracted with ether. The extract was washed with 10% HClaq and then H_2O, dried and evaporated to give crude XI (475 mg), which was used for the next step. A mixture of XI (475 mg) Na (297 mg) and ethylene glycol (15 ml) was refluxed for 1·5 hr. After cooling, H_2O was added and the mixture was extracted with ether. The extract was washed with H_2O, dried and evaporated to give an oil (226 mg), which showed three peaks involving

the aimed XII on GLC using Apiezon J (column temp 180°, N_2 1·5 kg/cm^2). Attempt to separate the products into the three components by column-chromatography over Al_2O_3 was unsuccessful.

Synthesis of XIV *from* VIIIc. To a soln of VIIIc (5·26 g) in pyridine (100 ml), *p*-toluenesulfonyl chloride (1·3 molar equiv) was added and the mixture was left at room temp for 2 days. Working up and recrystallization of the residue from AcOEt gave the tosylate XIII (6·65 g), m.p. 130–133°; ν_{max}^{Nujol} 1778, 1597 cm^{-1}. (Found: C, 65·38; H, 5·80; S, 8·69. $C_{21}H_{22}O_5S$ requires: C, 65·27; H, 5·74; S, 8·30%). A soln of crude XIII (6·65 g), which may involve a small amount of *exo*-tosylate, in 2,4,6-collidine (100 ml) was refluxed for 18 hr, and H_2O was added to the cooled mixture, which was extracted with ether. The extract was washed with 10% HCl aq, 5% $NaHCO_3$ aq and then, dried over anhyd $MgSO_4$ and evaporated to give a crystalline residue (3·96 g), which was chromatographed on SiO_2 (87 g, Woelm, act. II). Elution with benzene–pet. ether (1:4–1:2) gave crude XIV (3·06 g; 83·0%) and elution with benzene–pet. ether (1:1) afforded crude tricyclo-compound XVI (0·201 g; 5·5%). A pure sample of XIV, m.p. 70–70·5° was obtained by recrystallization from pet. ether; ν_{max}^{Nujol} 1724 cm^{-1}; NMR: 3·78 τ and 4·20 τ (2-H, d-d, C_7- and C_6-H), 6·55 τ (3-H, s, —$COOCH_3$), 6·90 τ (1-H, t, C_8-H). (Found: C, 78·69; H, 6·79. $C_{14}H_{14}O_2$ requires: C, 78·48; H, 6·59%). A pure sample of XVI, m.p. 69–70°, was obtained by thrice recrystallization from pet. ether; ν_{max}^{Nujol} 1738 cm^{-1}; NMR: 6·62 τ (1-H, t, C_5-H), 6·68 τ (3-H, s, —$COOCH_3$), 6·95 τ (1-H, s, C_8-H), 7·70 τ (1-H, t, C_2-H), ~8·08 τ (3-H, m, C_1-H, C_6-H_{endo}, and C_7-H), 8·92 τ (1-H, d, C_6-H_{exo}). (Found: C, 78·48; H, 6·47. $C_{14}H_{14}O_2$ requires: C, 78·48; H, 6·59%).

Hydrogenation of XIV *to* XVIII. A soln of XIV (30 mg) in AcOEt (20 ml) was shaken in the presence of H_2 over 5% Pd–C (12 mg) until 1 molar equiv of H_2 was absorbed. After removal of the catalyst, the solvent was evaporated *in vacuo* giving a crystalline residue (30 mg), m.p. 66–70°, which afforded, on recrystallization from ether–pet. ether, a pure sample of XVIII, m.p. 71–73°; ν_{max}^{Nujol} 1733 cm^{-1}; NMR: 6·50 τ (3-H, s, —$COOCH_3$). (Found: C, 77·53; H, 7·39. $C_{14}H_{16}O_2$ requires: C, 77·75; H, 7·46%).

Synthesis of 8-endo-Me-3,4-*benzobicyclo*[3.2.1]*octa*-3,6-*diene* (XII) *from* XIV. A soln of XIV (3·053 g) in THF (40 ml) was dropwise added below 10° with stirring to a suspension of LAH (1·08 g) in THF (30 ml) over a period of 10 min and the mixture was refluxed for 4 hr. Working up left oily XVa (2·584 g; 93·8%), which was used for the next step. To a soln of XVa (2·409 g) in pyridine (40 ml), *p*-toluenesulfonyl chloride (3·84 g) was added and the mixture was allowed to stand at room temp for 19 hr. Working up and recrystallization of the residue (4·43 g) from acetone–AcOEt gave almost quantitative yield of XVb, m.p. 129·5–130°, as prisms. (Found: C, 70·67; H, 5·96; S, 9·38. $C_{20}H_{20}O_3S$ requires: C, 70·56; H, 5·92; S, 9·47%).

A soln of XVb (4·116 g) in THF (120 ml) was dropwise added below 10° with stirring to a suspension of LAH (0·968 g) in THF (30 ml) over a period of 10 min and the mixture was refluxed for 4·5 hr. Working up left crude XII (2·04 g; 99·1%), m.p. 30–35°, which was twice recrystallized from MeOH to furnish the analytical sample, m.p. 34·5–35·5°; $\lambda_{max}^{n\text{-heptane}}$ 192·5, 258·8, 266·0, 273·5 mμ (ε 3870, 467, 646, 710). (Found: C, 91·38; H, 8·35. $C_{13}H_{14}$ requires: C, 91·71; H, 8·29%).

Hydroboration of XII. Diborane was generated by addition of a soln of $NaBH_4$ (555 mg; 14·57 m mole) in diglyme (4 ml) to a soln of BF_3-etherate (4·725 g; 33·3 m mole) in diglyme (4 ml) according to the known method.[7] The gas was passed into a soln of XII (345 mg; 2 m mole) in THF (4 ml) during 4 hr at 5° by means of a slow stream of N_2. After stirring at 24° for 2·5 hr, H_2O (0·5 ml) was added to destroy excess diborane and the organoborane was oxidized at 25° by addition of 3N-NaOH aq (1 ml) and then 30% H_2O_2 (1 ml). The reaction mixture was stirred for further 1 hr and then extracted with ether. The extract was washed with H_2O, dried and evaporated to give a crystalline residue (382 mg), which was chromatographed on 5% H_2O-containing neutral Al_2O_3 (76 g, Woelm). Elution with ether–n-hexane (3:7) gave XXII (98 mg; 26·1%) and elution with ether–n-hexane (1:1) afforded XX (191 mg; 50·8%). A pure sample of XX, m.p. 88·5–90°, was obtained as needles by recrystallization from ether–pet. ether; ν_{max}^{Nujol} 3268 cm^{-1}. $\lambda_{max}^{95\%\ EtOH}$ 260·1, 266·5, 273·6 mμ (ε 394, 612, 717). (Found: C, 83·06; H, 8·40. $C_{13}H_{16}O$ requires: C, 82·93; H, 8·57%). A pure sample of XXII, m.p. 130–131°, was obtained as needles by recrystallization from ether–pet. ether; ν_{max}^{Nujol} 3250 cm^{-1}. $\lambda_{max}^{95\%\ EtOH}$ 259·9, 266·0, 273·2 mμ (ε 386, 583, 672). (Found: C, 82·85; H, 8·89. $C_{13}H_{16}O$ requires: C, 82·93; H, 8·57%).

Synthesis of II *through oxymercuration of* XII. A soln of XII (5·279 g) in THF (30 ml) was added with stirring to a soln of mercuric acetate (19·80 g) in H_2O (70 ml) and THF (40 ml), and the mixture was stirred at 24° for 2·5 hr and 3N NaOH aq (70 ml) and then, a soln of $NaBH_4$ (1·18 g) in 3N NaOH aq (70 ml) were added to the mixture. The mixture was extracted with ether. The extract was washed with H_2O, dried and evaporated to give a crystalline mixture (6·075 g), which was dissolved in pyridine (30 ml). The pyridine soln was added under cooling to the complex prepared from CrO_3 (11·2 g) and pyridine (30 ml), and the mixture was left at room temp for 17 hr. Working up gave an oily residue (5·457 g), which was

chromatographed over neutral Al_2O_3 (162 g, Woelm, act. II). Elution with ether–pet. ether (1:19) afforded an oil, which was saponified with 3% methanolic–KOH to give the recovered XII (730 mg; 12·5%). Further elution with ether–pet. ether (1:9) gave the aimed ketone II (2·92 g; 50·6%), which was recrystallized from ether–pet. ether to furnish the pure sample, m.p. 78·5–80°; ν_{max}^{Nujol} 1734 cm^{-1}; $\lambda_{max}^{n\text{-heptane}}$ 263·7, 268·7, 276·3, 289·1, 298·1, 308·7, 320·0 mμ (ε 373, 433, 445, 418, 542, 526, 280); NMR: 6·78 τ (1-H, m, C_5-H), ~7·53 τ (1 H, m, C_1-H). (Found: C, 83·68; H, 7·44. $C_{13}H_{14}O$ requires: C, 83·83; H, 7·58%). Elution with ether gave crude XIX, which was repeatedly recrystallized from ether–pet. ether affording its pure sample (247 mg), m.p. 119·5–120° as needles; ν_{max}^{Nujol} 3260 cm^{-1}; $\lambda_{max}^{95\%\ EtOH}$ 260·8, 267·2, 274·3 mμ (ε 417, 656, 772). (Found: C, 82·84; H, 8·52. $C_{13}H_{16}O$ requires: C, 82·93; H, 8·57%).

Conversion of XII *to ketones* (Ib, II *and* XXV) *through epoxidation*-LAH *reduction*. To a soln of *m*-chloroperbenzoic acid (282 mg) in CH_2Cl_2 (10 ml), a soln of XII (215 mg) in CH_2Cl_2 (5 ml) was added under cooling in ice, and the mixture was allowed to stand at room temp for 17 hr. The reaction mixture was washed with 10% NaOH aq and then H_2O, dried and evaporated to give an oily residue (232 mg), which was chromatographed on Merck standardized Al_2O_3 (9·5 g). Elution with benzene–pet. ether (1:4) gave XXIII (175 mg), m.p. 57–58°, which was twice recrystallized from n-hexane to afford the pure sample, m.p. 59–59·5°; ν_{max}^{Nujol} 1238, 1196, 842, 748 cm^{-1}; NMR: 6·65 τ (2-H, d-d, C_6- and C_7-H), 7·05 τ (1-H, d-m, C_5-H), ~7·70 τ (1-H, m, C_1-H). 7·16 τ and 7·38 τ (2-H, d-d, C_2-H), ~7·90 τ (1-H, m, C_8-H), 9·20 τ (3-H, d, CH_3). (Found: C, 84·10; H, 7·65. $C_{13}H_{14}O$ requires: C, 83·83; H, 7·58%).

A soln of XXIII (533 mg) in dioxane (25 ml) was dropwise added below 12° with stirring to a suspension of LAH (543 mg) in dioxane (120 ml) over a period of 5 min and the mixture was refluxed for 25 hr. Working up left a mixture of alcohols (500 mg), of which GLC examination revealed the presence of XX, XXII and XXIV as main products. Attempt to separate the products into the components on column-chromatography over 5% H_2O containing SiO_2 (100 g, Woelm) was unsuccessful. A soln of above mixture (404 mg) in pyridine (20 ml) was added under cooling in ice to the complex prepared from CrO_3 (1·80 g) and pyridine (3 ml) and the mixture was allowed to stand at room temp for 2 days. Working up left an oil (331 mg) which was chromatographed over 1% H_2O-containing neutral Al_2O_3 (66 g, Woelm). Elution with pet. ether–benzene (1:1) left a crystalline residue which gave pure II (55 mg), m.p. 78·5–80°, on recrystallization from ether–pet. ether, and elution with benzene left a crystalline residue, which gave pure Ib (63 mg), m.p. 70–70·5°, on recrystallization from ether–pet. ether, and elution with Chf–benzene (1:9) gave oily XXV (81 mg). ν_{max}^{film} 1741 cm^{-1}.

$NaBH_4$ *reduction of* Ib. To a soln of Ib (49 mg) in abs MeOH (3 ml), $NaBH_4$ (54 mg) was added and the mixture was stirred at 24° for 1 hr. Working up left a crystalline residue (54 mg), m.p. 109–113°. Two recrystallization from ether–pet. ether gave needles of pure XIX, m.p. 119·5–120°.

$NaBH_4$ *reduction of* II. The reduction of II (23 mg) with $NaBH_4$ (24 mg) in abs MeOH (1·5 ml) afforded crude XXI (20 mg), m.p. 75–80°, which was twice recrystallized from ether–pet. ether giving needles of the pure sample, m.p. 81–81·5°; ν_{max}^{Nujol} 3290 cm^{-1}; $\lambda_{max}^{95\%\ EtOH}$ 259·0, 265·7, 273·0 mμ (ε 365, 491, 523). (Found: C, 82·55; H, 8·54. $C_{13}H_{16}O$ requires: C, 82·93; H, 8·57%).

$NaBH_4$ *reduction of* XXV. Working up with XXV (37 mg) in a manner similar to the case of Ib gave a crystalline residue (33 mg), which was twice recrystallized from ether–pet. ether affording plates of XXVI, m.p. 89·5–90°; ν_{max}^{Nujol} 3328 cm^{-1}. (Found: C, 82·82; H, 8·69. $C_{13}H_{16}O$ requires: C, 82·93; H, 8·57%).

exo-3,4-*Dibromo*-6,7-*benzobicyclo*[3.2.1]*octadiene* (XXVIIIa). A soln of freshly distilled $CHBr_3$ (202 g) in pentane (100 ml) was dropwise added with stirring at 0–−10° under a stream of argon to a mixture of t-BuOK (90 g) and XXVII (57 g) in pentane (150 ml) over a period of 4 hr. Stirring was continued for 30 min. The organic layer was washed with H_2O, dried and distilled to remove t-BuOH, $CHBr_3$ and excess benzonorbornadiene. Further distillation under reduced pressure gave XXVIIIa (46·2 g; 36·7%), b.p. 150–153° (0·4 mm), which was recrystallized from pentane affording rods of the pure sample, m.p. 83·5–84°; ν_{max}^{Nujol} 1615, 668 cm^{-1}; NMR in CCl_4: 2·6–3·0 τ (4-H, m, aromatic H), 3·44 τ (1-H, d, J = 7·0 Hz, C_2-H), 5·45 τ (1-H, d, J = 2·2 Hz, C_4-H_{endo}), ~6·23 τ (1-H, m, C_1-H), ~6·12 τ (1-H, m, C_5-H), 7·2–8·0 τ (2-H, m, C_8-H). (Found: C, 46·22; H, 3·18; Br, 50·89. $C_{12}H_{10}Br_2$ requires: C, 45·90; H, 3·21; Br, 50·89%).

Synthesis of 6,7-*benzobicyclo*[3.2.1]*octen*-3-*one* (III) *from* XXVIIIa. A soln of XXVIIIa (32 g) in abs ether (700 ml) was dropwise added to a stirred slurry of LAH (14·8 g) in abs ether (400 ml) below 15° over a period of 30 min and the mixture was refluxed for 24 hr. The excess hydride was destroyed with H_2O and the mixture was worked up in the usual manner. Distillation under reduced press gave XXVIIIb (19·4 g; 81·1%), b.p. 113° (3 mm), ν_{max}^{film} 1632, 688 cm^{-1}, which was used for the next step. The ice-cooled conc H_2SO_4 (15 ml) was dropwise added at 0° to XXVIIIb (2·4 g) under stirring and the mixture was kept at 0° for 30 min, hydrolyzed with ice and extracted with ether. The extract was washed with H_2O, saturated

Na_2CO_3 aq and with H_2O, dried, and evaporated to give a residue (1·712 g), which was chromatographed over neutral Al_2O_3 (100 g, Woelm act. I). Elution with ether and recrystallization of the residue from pentane gave pure III (348 mg; 19·8%), m.p. 67–68°; ν_{max}^{Nujol} 1710 cm^{-1}. (Found: C, 83·90; H, 6·97. $C_{12}H_{12}O$ requires: C, 83·68; H, 7·02%).

3-*Bromo*-4-exo-*hydroxy*-6,7-*benzobicyclo*[3.2.1]*octadiene* (XXVIIIc). A suspension of XXVIIIa (6·32 g) and $CaCO_3$ (6·2 g) in THF (20 ml) and H_2O (90 ml) was refluxed under a stream of N_2 for 25 hr. The mixture was extracted with ether. Evaporation of the ether gave quantitative yield of XXVIIIc. Two recrystallization from n-hexane gave the pure sample (3·52 g; 69·5%), m.p. 121·5–122·5°, as needles ν_{max}^{Nujol} 3285, 1630, 682 cm^{-1}, NMR: 2·5–3·0 τ (4-H, m, aromatic H), 3·31 τ (1-H, d, J = 7·0 Hz, C_2-H), 5·93 τ (1-H, d, J = 2·1 Hz, C_4-H) ~6·5 τ (2-H, m, C_1-H and C_2-H) ~7·7 τ (2-H, m, C_8-H). (Found: C, 57·50; H, 4·51; O, 6·55; Br, 32·09. $C_{12}H_{11}OBr$ requires: C, 57·39; H, 4·42; O, 6·37; Br, 31·82%).

GLC *Analyses of the products obtained by hydroboration, oxymercuration and epoxidation*-LAH *reduction of* XII. GLC was performed using a Hitachi Perkin–Elmer gas chromatograph Model F-6D and product ratios cited in Table 1 were obtained from the comparison of the heights of the peaks corresponding to the respective products.

Prodcedure:			
Apparatus	Model F-6D	Support	Chromosorb W (80–100 mesh)
Detector	FID	Coat	SE-30, 10%
Colum	45 m Golay CW-45	Carrier gas	N_2, 1·5 kg/cm^2
Reference Column	Stainless steel	Column temp	180°
	Diameter 3 mm	Inj and FID temp	250°
	Length 1 m		

Retention times (min) of the products: XIX (8·7), XX (9·5), XXI (6·5), XXII (9·1), XXIV (10·5) and XXVI (7·9).

Preparation of 3,4-*benzobicyclo*[3.2.1]*octen*-7-*one oxime* (XXIX) *and its separation into* XXIXa *and* XXIXb. A soln of Ia (954 mg) and hydroxylamine hydrochloride (500 mg) in EtOH (9 ml) and pyridine (18 ml) was left at room temp for 2 days. Evaporation of the solvent under reduced press left a residue, which was extracted with ether. The ether extract was washed with 10% HCl, 5% $NaHCO_3$, and then with H_2O, dried and evaporated to give a mixture of XXIX (1·013 g; 97·7%), which was recrystallized 6-times from ether–n-hexane to yield pure *syn*-oxime XXIXa, m.p. 112–112·5°; ν_{max}^{Nujol} 3280 cm^{-1}. (Found: C, 76·97; H, 6·97; N, 7·49. $C_{12}H_{13}ON$ requires: C, 76·98; H, 7·00; N, 7·48%). The mother liquor of the recrystallization was evaporated to dryness leaving a residue (862 mg) which was chromatographed over neutral SiO_2 (172 g, Woelm, act. II). Elution with n-hexane–ether (4:1) left a mixture (243 mg), which was separated into pure *syn*-oxime (77 mg) and pure *anti*-oxime XXIXb (36 mg; 3·5%) by preparative TLC using SiO_2 and n-hexane–ether (1:2). Further elution with the same solvent gave another crop of *syn*-oxime (273 mg). Total yield of *syn*-oxime was 533 mg (51·4%). An analytical sample of XXIXb, m.p. 115°, was obtained by recrystallization from n-hexane–ether; ν_{max}^{Nujol} 3266 cm^{-1}. (Found: C, 77·17; H, 6·91; N, 7·30. $C_{12}H_{13}ON$ requires: C, 76·98; H, 7·00; N, 7·48%).

8-endo-Me-3,4-*benzobicyclo*[3.2.1]*octen*-7-*one oxime* (XXX) and its separation into XXXa *and* XXXb. A soln of Ib (7·805 g) and hydroxylamine hydrochloride (3·80 g) in EtOH (70 ml) and pyridine (140 ml) was left at room temp for 23 hr. Working up left crude oxime (7·92 g), m.p. ~105°, which was twice recrystallized from n-hexane–ether to give pure *syn*-isomer XXXa (1·108 g), m.p. 115–116°; ν_{max}^{Nujol} 3470, 3160, 3030, 973, 951 cm^{-1}. (Found: C, 77·62; H, 7·54; N, 6·64. $C_{13}H_{15}ON$ requires: C, 77·58; H, 7·51; N, 6·96%). Evaporation of the mother liquor of the recrystallization gave a mixture of XXXa and XXXb (6·70 g), which was chromatographed over SiO_2 (670 g, Woelm, act. II) using n-hexane–ether (7:3) as the solvent. The first eluate (1 l.) gave *anti*-isomer XXXb (760 mg), which was recrystallized from ether to afford the pure sample, m.p. 149–151°; ν_{max}^{Nujol} 3241, 977, 923, 723 cm^{-1}. (Found: C, 77·86; H, 7·49; N, 7·26. $C_{13}H_{15}ON$ requires: C, 77·58; H, 7·51; N, 6·96%). The second eluate (2 l.) gave a mixture (4·4 g) of XXXa and XXXb, which was used for LAH reduction without further purification. The last eluate (1·5 l.) gave another crop (1·014 g) of *syn*-isomer XXXa.

Preparation of 8-endo-Me-3,4-*benzobicyclo*[3.2.1]*octen*-6-*one oxime* (XXXI) *and isolation of* XXXIa. A soln of II (796 mg) and hydroxylamine hydrochloride (433 mg) in EtOH (10 ml) and pyridine (20 ml) was stirred at room temp for 4 hr. Working up left crude oxime (860 mg) which was recrystallized 4-times from ether to give pure *syn*-oxime XXXIa (518 mg; 60·2%), m.p. 135·5–136·5°; ν_{max}^{Nujol} 3493, 3233, 954, 938, 918 cm^{-1}; NMR: ~6·63 τ (1-H, C_5-H). (Found: C, 77·51; H, 7·42; N, 6·83. $C_{13}H_{15}ON$ requires: C, 77·58; H, 7·51; N, 6·96%). Evaporation of the mother liquor and twice recrystallization from ether gave needles

(138 mg) of m.p. 115–120°, which was composed of *syn*-form and *anti*-isomer XXXIb in a ratio of 1·13:1·0 from its NMR data: ~6·63 τ (C_5-H in XXXIa), ~5·95 τ (C_5-H in XXXIb).

LAH *reduction of* XXIX. A. *Separation of* XXXIIa, XXXIIIa *and a mixture of* XXXIVa *and* XXXVa. A soln of a mixture (973 mg) of XXIXa and XXIXb in THF (40 ml) was dropwise added with stirring at 0–7° to a suspension of LAH (798 mg) in THF (40 ml) over a period of 10 min and the mixture was refluxed for 3·5 hr. Under cooling in ice, the excess LAH was decomposed with H_2O and the mixture was extracted with ether. Evaporation of the organic layer, which was dried over anhyd K_2CO_3, left a residue (894 mg), which was dissolved in ether and extracted with cold 5% HCl aq. The acidic layer was carefully basified under cooling in ice with 5% K_2CO_3 aq and extracted with ether. The ethereal layer, which was dried over K_2CO_3, was evaporated to give a basic mixture (806 mg), which was chromatographed over 1% H_2O-containing neutral Al_2O_3 (40 g, Woelm). Elution with pet. ether–ether (4:1) gave oily XXXIIa (285 mg), $\nu_{max}^{CCl_4\,(grating)}$ 3300 cm^{-1} and fractions eluted with pet. ether–ether (1:1) and MeOH–ether (1:4) afforded an oily residue (302 mg), which was a mixture of XXXIIa, XXXIIIa, XXXIVa and XXXVa. The residue was further chromatographed over neutral Al_2O_3 (11·5 g, Woelm, act. II). Fractions eluted with pet. ether–ether (4:1) were subjected to preparative TLC using SiO_2 and Chf:MeH (20:1). Together with another crop of XXXIIa (12 mg), oily XXXIIIa (13 mg), $\nu_{max}^{CCl_4\,(grating)}$ 3320 cm^{-1} and a mixture (48 mg) of XXXIVa and XXXVa were obtained. Further elution with pet. ether–ether (1:1) and MeOH–ether (1:9) gave another mixture (119 mg) of XXXIVa and XXXVa. Attempts to separate the mixture into the components on column-chromatography or preparative TLC failed.

Separation of XXXIVa *and* XXXVa *as their* N-*formates* (XXXIVb *and* XXXVb). A soln of a mixture (165 mg) of XXXIVa and XXXVa in ethyl formate (2 ml) was heated at 100° in a sealed tube for 4 hr. After cooling, the reaction mixture was extracted with ether. The extract was washed with 10% HCl aq, 5% $NaHCO_3$ aq and then with H_2O, dried and evaporated to dryness leaving a residue, which showed two spots [R_f-values; 0·63 (XXXIVb) and 0·55 (XXXVb)] on TLC using SiO_2 and benzene–AcOEt (1:2). Recrystallization from ether gave pure XXXIVb (70 mg). The mother liquor of the recrystallization was subjected to preparative TLC affording XXXVb (32 mg) and another crop of XXXIVb (86 mg). An analytical sample of XXXIVb, m.p. 141·5–142·5°, as prisms was obtained by recrystallization from ether; ν_{max}^{Nujol} 3210, 1649 cm^{-1}; NMR: 2·02 τ (1-H, s, CHO), ~4·43 τ (1-H, m, NH), ~5·40 τ (1-H, m, C_7-H), 7·46 τ (1-H, d-q, J = 13, 11, 6 Hz, C_6-H_{exo}), 8·63 τ (1-H, d-m, C_6-H_{endo}). (Found: C, 77·80; H, 7·52; N, 6·79. $C_{13}H_{15}ON$ requires: C, 77·58; H, 7·51; N, 6·96%). Recrystallization from ether gave pure XXXVb, m.p. 107–107·5°, as prisms; ν_{max}^{Nujol} 1646 cm^{-1}. (Found: C, 77·63; H, 7·51; N, 6·89. $C_{13}H_{15}ON$ requires: C, 77·58; H, 7·51; N, 6·96%).

Characterization of the aziridines, XXXIIa *and* XXXIIIa, *as their* p-*nitrobenzoates* (XXXIIb *and* XXXIIIb). To a cooled soln of *endo*-aziridine XXXIIa (17 mg) and $(C_2H_5)_3N$ (11 mg) in abs benzene (1 ml), a soln of *p*-nitrobenzoyl chloride (20 mg) in abs benzene (1 ml) was dropwise added with stirring. The mixture was left at room temp for 1 hr and the ppt was filtered off. Evaporation of the filtrate *in vacuo* left a crystalline residue (31 mg; 98·7%), which was recrystallized from ether to yield pure XXXIIb, m.p. 139–140° as rods; ν_{max}^{Nujol} 1664 cm^{-1}; NMR: ~6·18 τ (1-H, m, C_5-H), ~6·60 τ (2-H, m, C_6-H and C_7-H). (Found: C, 71·29; H, 5·08; N, 8·93. $C_{16}H_{19}O_3N$ requires: C, 71·24; H, 5·03; N, 8·75%).

Working up with XXXIIIa (7 mg) gave a crystalline residue (11 mg; 86·6%), which was recrystallized from acetone–ether affording plates of XXXIIIb, m.p. 159–160°; ν_{max}^{Nujol} 1678 cm^{-1}. (Found: C, 70·95; H, 5·00; N, 8·88. $C_{16}H_{19}O_3N$ requires: C, 71·24; H, 5·03; N, 8·75%).

LAH *reduction of* anti-*oxime* XXIXb. A soln of XXIXb (112 mg) in THF (5 ml) was dropwise added below 10° with stirring to a suspension of LAH (90 mg) in THF (5 ml) and the mixture was refluxed for 3·5 hr. Working up left an oily basic residue, which was chromatographed over 1% H_2O-containing neutral Al_2O_3 (5·5 g, Woelm). Elution with ether gave a mixture (5 mg) of the aziridines, and fractions eluted with ether and MeOH–Chf (1:9) afforded the amine XXXIVa (60·7 mg; 58·7%), which was characterized as its N-formate, undepressed on admixture with an authentic sample of XXXIVb.

LAH *reduction of* syn-*oxime* XXIXa. A soln of XXIXa (973 mg) in THF (40 ml) was dropwise added at 7° to a stirred suspension of LAH (798 mg) in THF (4 ml) over a period of 10 min and the mixture was refluxed for 3·5 hr. Working up left an oily basic residue (806 mg), which was twice chromatographed over neutral Al_2O_3 (Woelm, act. II). Elution with pet. ether–ether (4:1) gave a mixture (297 mg; 33·4%) of XXXIIa and XXXIIIa, and fractions eluted with pet. ether–ether (1:1) and ether afforded the primary amine XXXIVa (200 mg; 22%). The *p*-nitrobenzoate prepared from the above mixture of XXXIIa and XXXIIIa had a m.p. of 139–140°. This was identical with XXXIIb in all respects.

LAH *reduction of* XXX. A soln of a mixture (3·139 g) of XXXa and XXXb in THF (75 ml) was dropwise added below 10° with stirring to a suspension of LAH (2·36 g) in THF (150 ml) and the mixture was refluxed

for 4 hr. Working up left an oily basic residue (2·936 g), which was chromatographed over 1% H_2O-containing neutral Al_2O_3 (116 g, Woelm). Elution with ether–pet. ether (1:9) gave a crystalline residue (1·056 g), which was recrystallized 3-times from ether affording rods of pure *endo*-aziridine XXXVIa (674 mg; 23·3%), m.p. 92–93°; $\nu_{max}^{CCl_4(grating)}$ 3298 cm^{-1}; $\lambda_{max}^{n\text{-heptane}}$ 260·0 266·3, 273·7 mμ (ε 359, 547, 619). (Found: C, 84·13; H, 8·27; N, 7·38. $C_{13}H_{15}N$ requires: C, 84·28; H, 8·16; N, 7·56%). Elution with ether–pet. ether (1:9–1:1) afforded a mixture (508 mg) of XXXVIa, XXXVIIa, XXXVIIIa and XXXIXa, and fractions eluted with ether and MeOH–ether (1:49) gave crude XXXIXa (951 mg; 32·5%). Distillation of crude XXXIXa under reduced press and purification of the distillate (756 mg), b.p. 81–83° (0·12 mm) through its hydrochloride, m.p. 244° (dec) gave crystalline XXXIXa, m.p. 51–53°, which was transformed to its N-formate XXXIXb, m.p. 156–157°, as rods by twice recrystallization from ether; ν_{max}^{Nujol} 3200, 1689, 1647, 1380, 1251 cm^{-1}; NMR: 2·02 τ (1-H, s, CHO), ~5·45 τ (1-H, m, C_7-H), 9·03 τ (3-H, d, CH_3). (Found: C, 78·05; H, 7·89; N, 6·72. $C_{14}H_{17}ON$ requires: C, 78·10; H, 7·96; N, 6·51%). The secondary amine XXXVIIIa was isolated as follows: the mother liquor from the recrystallization of *endo*-aziridine XXXVIa was evaporated to dryness giving an oil (269 mg), which was heated with 4N H_2SO_4 (5 ml) at 100° for 4 hr, resulting in the ring-cleavage of the aziridine involved. After cooling, the acidic layer was made alkaline with K_2CO_3 and extracted with Chf. The extract was washed with H_2O, dried over anhyd K_2CO_3 and evaporated to give a yellow oil (218 mg), which, on distillation at 110–130° (oil-bath) under reduced press (0·02 mm), gave crude secondary amine XXXVIIIa (209 mg; 7·2%) as an oil, ν_{max}^{film} 3300, 1097, 947 cm^{-1}. The N-formate XXXVIIIb prepared by treatment of XXXVIIIa with ethyl formate had a m.p. of 105–106°, as prisms from ether; ν_{max}^{Nujol} 1674, 1658 cm^{-1}. (Found: C, 78·05; H, 7·96; N, 6·68. $C_{14}H_{17}ON$ requires: C, 78·10; H, 7·96; N, 6·51%).

To a soln of XXXVIa (56 mg) in pyridine (2 ml), Ac_2O (1 ml) was added and the mixture was allowed to stand at room temp for 19 hr. Evaporation of the solvent left oil XXXVIb, ν_{max}^{film} 1690, 1271, 1167 cm^{-1}, which was used for NMR measurement.

LAH *reduction of* XXXI. A soln of a mixture (1·508 g) of XXXIa and XXXIb in THF (30 ml) was dropwise added below 10° with stirring to a suspension of LAH (1·14 g) in THF (30 ml) over a period of 10 min and the mixture was refluxed for 4 hr. Working up left an oily basic residue (1·379 g), which was chromatographed over 1% H_2O-containing neutral Al_2O_3 (70 g, Woelm). Elution with ether–pet. ether (1:9–1:4) gave crude *endo*-aziridine XXXVIa (165 mg; 11·9%), which afforded, on recrystallization from ether, the pure sample (33 mg), m.p. 92–92·5° as rods, identical with that obtained from LAH reduction of XXX. Further elution with ether–pet. ether (1:4) gave crude *exo*-aziridine XXXVIIa (112 mg; 8·0%), which was twice recrystallized from ether–pet. ether yielding the pure sample (19 mg), m.p. 89–89·5° as rods; $\nu_{max}^{CCl_4(grating)}$ 3316 cm^{-1}; $\lambda_{max}^{n\text{-heptane}}$ 259·5, 266·0, 273·3 mμ (ε 329, 492, 553). (Found: C, 84·42; H, 8·19; N, 7·69. $C_{13}H_{15}N$ requires: C, 84·28; H, 8·16; N, 7·56%). Elution with ether–pet. ether (1:4) and ether gave a mixture (130 mg) of azitridines and primary amines, and fractions eluted with ether and MeOH–ether (1:4) afforded oily *endo*-amine XLa (693 mg; 49·4%), which was characterized as its N-formate XLb, m.p. 74–75° as needles by recrystallization 5-times from ether; ν_{max}^{Nujol} 3186, 1700, 1747, 1379, 748 cm^{-1}; NMR: 2·12 τ (1-H, s, CHO) ~5·38 τ (1-H, m, C_6-H), 9·07 τ (3-H, d, CH_3). (Found: C, 76·83; H, 8·01; N, 6·08. $C_{14}H_{17}ON \cdot \frac{1}{5}H_2O$ requires: C, 76·81; H, 8·01; N, 6·40%). Treatment of XXXVIIa with Ac_2O and pyridine afforded the acetate XXXVIIb as an oil, which was used for NMR-measurement. ν_{max}^{film}1689, 1264, 1176, 984, 751 cm^{-1}.

Reduction of XXX *with sodium and ethanol.* To a refluxing soln of XXX (200 mg) in abs EtOH (30 ml), Na (6 g) was added in portions with stirring in an atmosphere of N_2 over a period of 1 hr and the mixture was refluxed for further 2 hr. Under cooling in ice, EtOH (80 ml) was added to decompose excess Na. After addition of H_2O (100 ml), the mixture was extracted with ether. The extract was treated with 10% HCl aq and the acidic layer was basified with K_2CO_3 and extracted with ether. The ethereal layer was washed with H_2O, dried over anhyd K_2CO_3 and evaporated leaving an oil (172 mg), of which GLC showed the presence of *endo*-amine XXXIXa as main product.

Reduction of XXXI *with sodium and ethanol.* Working up with XXXI (24 mg) gave an oily basic residue (18 mg), which was identical with XLa obtained by LAH reduction of XXXI on examination by GLC.

Catalytic reduction of XXXVI *to* XXXIXa *and* XLa. A soln of XXXVIa (20 mg) in EtOH (3 ml) was shaken in the presence of H_2 over 13% Pd–C catalyst (46 mg) for 14 hr until 1 molar equiv of H_2 was absorbed. After removal of the catalyst, the solvent was evaporated *in vacuo* leaving an oily residue (19 mg), which was composed of almost equal amount of XXXIXa and XLa on examination by GLC.

Synthesis of XXXVIIIa *through Beckmann rearrangement of* XXXb. To a stirred soln of XXXb (100 mg) in pyridine (2·5 ml), *p*-toluenesulfonyl chloride (134 mg) was added under cooling in ice and the cooled mixture was stirred for 3 hr. After addition of benzene (13 ml), the mixture was submitted to chromatography over neutral Al_2O_3 (2 g, Woelm, act. III). Fractions eluted with benzene–Chf (4:1–1:1) gave a yellow oil,

which was further chromatographed over neutral Al_2O_3 (3 g, Woelm, act. III). Elution with benzene–Chf (4:1–1:1) gave a residue (85 mg; 85%), which, on recrystallization from Chf–benzene, afforded prisms of pure XLV (59 mg; 59%), m.p. 233–235°; ν_{max}^{Nujol} 3206, 1662 cm^{-1}. (Found: C, 77·93; H, 7·60; N, 7·18. $C_{13}H_{15}ON$ requires: C, 77·58; H, 7·51; N, 6·96%). A suspension of XLV (22 mg) in THF (5 ml) was dropwise added below 10° with stirring to a suspension of LAH (26 mg) in THF (2 ml) over a period of 10 min and the mixture was refluxed for 5 hr. Working up left a quantitative yield of oily XXXVIIIa (21 mg), which was converted to its N-formate, m.p. 104–105° (prisms from ether). This was identical with XXXVIIIb in all respects.

Synthesis of XLII *from* XXXa. *p*-Toluenesulfonyl chloride (132 mg) was added under cooling in ice to a stirred soln of XXXa (100 mg) in pyridine (2 ml) and the mixture was stirred at 8–20° for 6 hr. After addition of benzene (10 ml), the mixture was chromatographed over neutral Al_2O_3 (1 g, Woelm, act. II). Elution with benzene gave a yellow crystalline residue, which was chromatographed over the same Al_2O_3 (5·5 g). Elution with Chf–benzene (1:4–1:1) gave crude XLI (37 mg; 37%), m.p. 235° (dec), which was recrystallized from AcOEt to yield the anlytical sample, m.p. 248–249° (dec) as prisms; ν_{max}^{Nujol} 3243, 1670, 1641 cm^{-1}. (Found: C, 77·64; H, 7·48; N, 6·96. $C_{13}H_{15}ON$ requires: C, 77·58; H, 7·51; N, 6·96%). A soln of XLI (415 mg) in dioxane (40 ml) was dropwise added below 10° with stirring to a suspension of LAH (784 mg) in THF (20 ml) over a period of 10 min and the mixture was refluxed for 20 hr. Working up left oily XLII (264 mg; 68%).

Synthesis of XLIV *from* XXXIa. To a stirred soln of XXXIa (518 mg) in pyridine (6 ml), *p*-toluenesulfonyl chloride was added under cooling in ice and the mixture was stirred at 0–23° for 4 hr. After addition of benzene (30 ml), the mixture was chromatographed over neutral Al_2O_3 (10 g, Woelm, act. II). Fractions eluted with Chf–benzene (1:19–1:1) gave a yellow oil (374 mg), which on further column-chromatography over neutral Al_2O_3 (26 g, Woelm, act. III), afforded a crystalline residue (128 mg) from the fractions eluted with Chf–benzene (1:1) and Chf only. Recrystallization of the residue from Chf–benzene gave pure XLIII (98 mg; 17·9%), m.p. 200–201°; ν_{max}^{Nujol} 3246, 1658, 1628 cm^{-1}. (Found: C, 77·47; H, 7·45; N, 6·97. $C_{13}H_{15}ON$ requires: C, 77·58; H, 7·51; N, 6·96%). To a soln of XLII (8 mg) in dioxan (3 ml), LAH (23 mg) was added below 10° with stirring and the mixture was refluxed for 5 hr. Working up left oily XLIV (6 mg; 79%); $\nu_{max}^{CCl_4}$ 3250 cm^{-1}.

GLC *analyses of the reduction products from the oximes* (XXX *and* XXXI) *and the lactams* (XLI, XLIII *and* XLV). All GLC analyses were performed using a Hitachi gas chromatograph Model K-53 and biphenyl-ether as internal reference.

Apparatus	Hitachi K-53	Support	Gas-chrom Q (80–100 mesh)
Detector	FID	Coat.	Carbowax 20 M 5%
Column	Stainless steel:		KOH, 5%
	Diameter, 3 mm:	Carrier gas	N_2, 20 cc/min
	Length, 2 m	Column temp.	150°
		Inj. temp.	270°

Retention times (min): XXXVIa (16·0), XXXVIIa (18·6), XXXVIIIa (8·4), XXXIXa (9·4), XLa (7·9), XLII (9·1) and XLIV (8·4).

Preparation of the oxime XLVI. A mixture of III (310 mg) and hydroxylamine hydrochloride (190 mg) in EtOH (1·5 ml) and pyridine (3 ml) was left overnight at room temp. Working up gave a residue (299 mg), which was twice recrystallized from n-hexane–ether to afford pure oxime XLVI, m.p. 158–160° as needles; ν_{max}^{Nujol} 3245, 956, 945, 928 cm^{-1}. (Found: C, 76·94; H, 6·87; N, 7·57. $C_{12}H_{13}ON$ requires: C, 76·97; H, 7·00; N, 7·48%).

LAH *reduction of* XLVI. A soln of XLVI (840 mg) in THF (30 ml) was added at 0–5° to a suspension of LAH (1·0 g) in THF (20 ml) over a period of 30 min and the mixture was refluxed for 3 hr. Working up left an oily residue, which was chromatographed over neutral Al_2O_3 (42 g, Woelm, act. II). Elution with ether–pet. ether (1:24–1:19) gave crude XLVIIa (198 mg), and fractions with ether–pet. ether (1:9) afforded a mixture (158 mg) of aziridines, which was further chromatographed over neutral Al_2O_3 to separate the mixture into *exo*-aziridine (71 mg) and *endo*-isomer XLVIIIa (70 mg). Further elution with ether–pet. ether (1:4) and ether gave *endo*-aziridine (299 mg). The yields of *exo*- and *endo*-aziridines was 269 mg (35·0%) and 368 mg (47·9%), respectively. A pure sample of XLVIIa, m.p. 45·5–46° as needles, was obtained by twice recrystallization from pentane; $\nu_{max}^{CCl_4\,(grating)}$ 3318 cm^{-1}. (Found: C, 84·17; H, 7·60; N, 8·28. $C_{12}H_{13}N$ requires: C, 84·17; H, 7·65; N, 8·18%). Attempts to crystallize *endo*-aziridine were unsuccessful; $\nu_{max}^{CCl_4\,(grating)}$ 3286 cm^{-1}.

A soln of phenylisocyanate (37 mg) in abs benzene (1 ml) was added to a soln of *endo*-aziridine (54 mg) in

abs benzene (1 ml). Filtration of the resultant colourless crystals (58 mg) and recrystallization from CH_2Cl_2–ether gave its phenylcarbamoyl derivative XLVIIIc (26 mg), m.p. 197° as needles. ν_{max}^{Nujol} 1659, 1606 cm^{-1}. (Found: C, 78·52; H, 6·21; N, 9·73. $C_{19}H_{18}ON_2$ requires: C, 78·57; H, 6·25; N, 9·65%). A soln of dimethyl pyrocarbonate (90 mg) in abs ether (1 ml) was added to a soln of XLVIIa (66 mg) in abs ether (2 ml) and the mixture was left at room temp for 1·5 hr. The mixture was evaporated to dryness *in vacuo* leaving a crystalline residue, which was recrystallized from n-hexane to give pure sample of XLVIIb (51 mg), m.p. 112·5–114° as needles; ν_{max}^{Nujol} 1716 cm^{-1}; NMR: 6·32 τ (3-H, s, $COOCH_3$). (Found: C, 73·05; H, 6·49; N, 5·89. $C_{14}H_{15}O_2N$ requires: C, 73·34; H, 6·59; N, 6·11%). Working up with XLVIIIa (74 mg) in a similar manner described above gave almost quantitative yield of XLVIIIb, which was twice recrystallized from n-hexane–pentane affording the pure sample, m.p. 119–119·5 as needles; ν_{max}^{Nujol} 1718 cm^{-1}; NMR: 6·48 τ (3-H, s, $COOCH_3$). (Found: C, 73·38; H, 6·64; N, 6·04. $C_{14}H_{15}O_2N$ requires: C, 73·34; H, 6·59; N, 6·11%).

GLC *analysis of the products obtained by* LAH *reduction of* XLVI. Product yields cited in Table 4 were obtained using a Hitachi gas chromatograph model K-53, which was equipped with a 1 m × 3 mm stainless steel tubing column, packed with 5 wt% Polyphenyl Ether (6 rings) on 80–100 mesh Gas-chrom Q. The retention times of XLVIIa and XLVIIIa were 18·5 and 22·4 min, respectively, at 140° (column temp) with 0·7 kg/cm^2 of N_2 (carrier gas).

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