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STUDIES ON QUINOLIZINIUM SALTS—VIII[1]
THE REDUCTION OF BENZO[*b*]QUINOLIZINIUM BROMIDE WITH SODIUM BOROHYDRIDE WITH EQUILIBRATING PROTONATION OF 6*H*-BENZO[*b*]QUINOLIZINE INTERMEDIATE[2]

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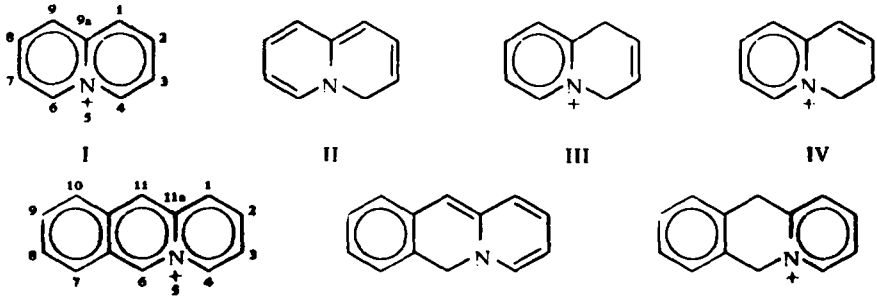
Abstract—Benzo[*b*]quinolizinium bromide (VIII) undergoes reduction with sodium borohydride in ethanol with the formation of 1,6,11,11a-tetrahydro-4*H*-benzo[*b*]quinolizine (XI), accompanied by small amounts of benzol[*b*]quinolizidine and 3,6,11,11a-tetrahydro-4*H*-benzo[*b*]quinolizine (IX and X). Experiments using ethanol-d as solvent indicate that this reduction proceeds via 6*H*-benzo[*b*]quinolizine (VI) which significantly equilibrates with its C-11 protonated form (VII) prior to further reduction. This was confirmed by the sodium borohydride reduction of 6,11-dihydrobenzo[*b*]quinolizinium bromide (XIX) in ethanol-d. The reduction mechanism is compatible with that previously proposed for the hydride reduction of 4*H*-quinolizine (II) arising from quinoliznium ion (I). The sodium borohydride reduction of 8,9-dimethoxybenzo[*b*]quinolizinium bromide (XII) was also carried out.

IN EARLIER papers[3] it was shown that quinolizinium ion (I) reacts with nucleophiles such as Grignard reagents, metal hydrides ($NaBH_4$ and LAH) and aniline giving butadienylpyridines, quinolizines and quinoline derivatives. In continuing our mechanistic studies on the $NaBH_4$ reduction of I, our interest was directed towards 6*H*-benzo[*b*]quinolizine (VI) resulting from benzo[*b*]quinolizinium bromide (VIII). The benzoquinolizine (VI) is structurally related to 4*H*-quinolizine (II) which is an interesting intermediate in the $NaBH_4$ and LAH reductions of I.[3c] Although II has not been isolated, probably II undergoes isomerization to 2-(1,3-butadienyl)pyridine in aprotic solvents, whereas it is protonated preferentially at C-1 in protic solvents to give 1,4-dihydroquinolizinium ion (III). This protonation proceeds with rapid equilibration between II and III prior to the hydride reduction of III. In addition, it was noted that some C-3 protonation of II concurrently occurs with the formation of the thermodynamically more stable 3,4-dihydroquinolizinium ion (IV).[3c]



I II III IV

V VI VII

CHART 1

On the other hand, a similar protonation should be impossible in VI, since C-6a protonation would destroy the aromaticity of the benzene ring. This, in addition to the availability of the protonated bromide (XIX) will clarify the reduction mechanism of VIII. The purpose of the present investigation is to provide further evidences for the reduction mechanism of I by examining the sodium borohydride reduction of VIII.

Benzo[*b*]quinolizinium ion (V) is known to be most reactive towards nucleophiles at C-6[4] and undergoes reaction with a Grignard reagent giving rise to a 6-substituted 6-*H*-benzo[*b*]quinolizine.[4a] In basic solution the ion sustains ring opening via 6-hydroxy-6*H*-benzo[*b*]quinolizine.[4b] Bradsher and Yarrington carried out the $NaBH_4$ reduction of VIII in boiling water, and isolated only 1,3,4,6,11,11a-hexahydro-2*H*-benzo[*b*]quinolizine (benzo[*b*]quinolizidine, IX).[5] We investigated the $NaBH_4$ reduction of VIII in ethanol under the same mild conditions as for the quinolizinium ion (I).[3d] Column and preparative gas chromatography of the reduction mixture afforded 1,6,11,11a-tetrahydro-4*H*-benzo[*b*]quinolizine (XI) as the major product, along with small amounts of IX and 3,6,11,11a-tetrahydro-4*H*-benzo[*b*]quinolizine (X). These products (IX–XI) were more effectively separated by a combination of column and preparative gas chromatography. The minor ene product (X) was first eluated with facile separation from the other two, although it was obtained as the intermediate fraction by gas chromatography. The product ratio differed slightly in the two following procedures: (i) a solution of VIII is added to the solution of $NaBH_4$; (ii) the order of addition is reversed. Gas chromatographic analysis showed the resulting products formed in ratios of 3·1:1·0:95·9 and 7·2:3·3:89·5, respectively. The octahydro product was characterized as IX and identified by comparison with an authentic sample.[6] The proposed structure for the major product is based on the

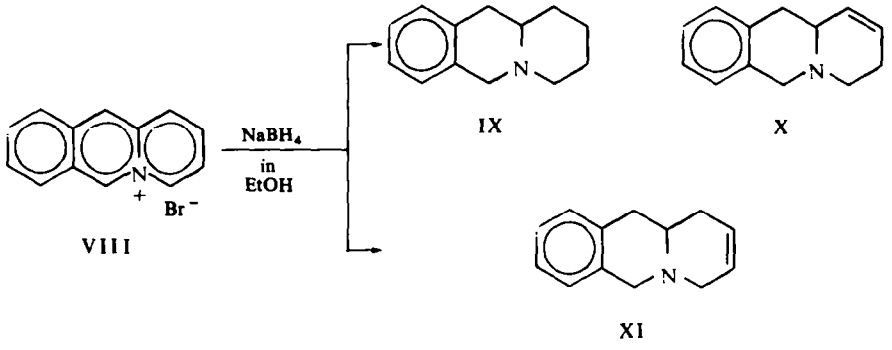


CHART 2

NMR, IR and mass spectral data, and catalytic hydrogenation with the consumption of one mole-equivalent of hydrogen leading to IX. The ene compound (XI) has no enamine structure, as is evident from the IR comparison of the base with its hydriodide.[7] The mass spectrum shows the parent peak at *m/e* 185, a fragment peak at 130 (M—C_4H_6—H) and the base peak at *m/e* 104 corresponding to a loss of dihydropyridine or butadiene and hydrogen cyanide. The NMR spectrum (Fig. 1) contains a symmetrical signal due to four aromatic protons centered at 2·94 τ and signals centered at 4·30 τ due to two olefinic protons which resemble those of 1,2,5,6-tetra-

hydropyridine,[8] 1,6,9,9a-tetrahydro- and 1,6,7,8,9,9a-hexahydro-4*H*-quinolizine.[3c] The C-11 methylene protons should be deshielded under the influence of the adjacent nitrogen and phenyl group, and thus were associated with two doublets of an AB

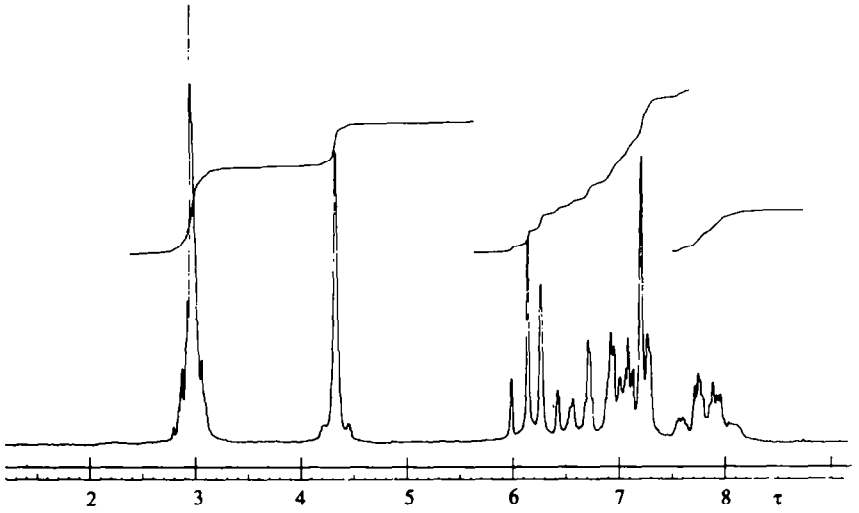


FIG. 1 NMR spectrum of XI in $CDCl_3$

system (J_{gem} = 16 c/s) centered at 6·03 and 6·30 τ. The more shielded proton should be the one oriented *trans* to the nitrogen lone pair. Shielding is greater when the nitrogen lone pair and the adjacent C—H bond have a *trans*-diaxial relationship.[9] The C-4 methylene protons appear as a broad AB quartet (doublets centered at 6·60 and 6·96 τ, J_{gem} = 17 c/s) apparently with further coupling. The signals partly overlapped those of the C-11a protons near 7·0 τ. The C-1 methylene protons appear as a broadened AB quartet (two doublets centered at 7·62 and 7·96 τ, J_{gem} = 17 c/s) exhibiting further coupling. The remaining C-11 methylene protons should be assigned to the two broad peaks centered at 7·2 τ.

The minor ene product was formulated as another possible tetrahydroquinolizine (X), although a more precise characterization as described for XI was precluded by the difficulty in the isolation of sufficient quantities. Support was provided by its NMR and mass spectra. The latter shows the molecular ion peak at *m/e* 185, the base peak at *m/e* 184 and a prominent fragment ion peak at *m/e* 104 from a loss of dihydropyridine. In the NMR spectrum, X shows four aromatic proton peaks centered at 2·92 τ, two olefinic proton signals (a broadened doublet ($J_{1,2}$ = 10c/s) centered at 4·42τ due to C-1 H; two multiplets centered at 4·17 τ due to C-2 H) and two doublets of an AB system (J_{gem} = 15 c/s) centered at 6·05 and 6·44 τ arising from the C-6 methylene protons. The remaining protons appear as an overlapping multiplet in the region 6·9–8·2 τ. The olefinic proton signals resemble closely the pattern exhibited by quinolizine derivatives containing a double bond at the corresponding position.[3c]

Similarly, 8,9-dimethyoxybenzo[*b*]quinolizinium bromide (XII) was reduced with sodium borohydride in ethanol. Gas chromatographic analysis showed the crude product to contain approximately 96% of the major product which was isolated in a good yield by recrystallization and characterized as 1,6,11,11a-tetrahydro-8,9-dimethoxy-4*H*-benzo[*b*]quinolizine (XV). Apparently the hexahydro derivative

(XIII) was not produced, although it was uncertain whether XIV was formed as the minor product. The structure of XV was confirmed by spectral data and catalytic

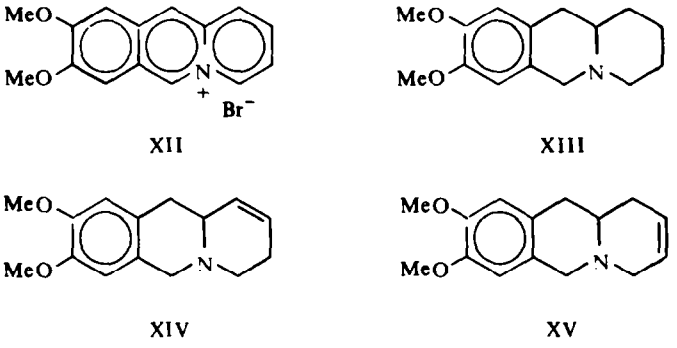


CHART 3

hydrogenation to 8,9-dimethyoxybenzo[*b*]quinolizidine (XIII). Signals in the NMR spectrum of XV can be allocated as follows: singlets at 3·46 and 3·48 τ (two aromatic protons), signals centered at 4·30 τ closely resembling those of XI (two olefinic protons), two doublets of an AB system centered at 6·12 and 6·24 τ (J_{gem} = 16 c/s, C-6 methylene protons), singlet at 6·18 τ (two O—Me groups), two broad doublets of an AB system centered at 6·61 and 6·98 τ (J_{gem} = 17 c/s, C-4 methylene protons), multiplet at ca. 6·80–7·15 τ (C-11a H) overlapped with the upfield signals of the C-4 methylene protons, a broad doublet at 7·30 τ (C-11 methylene protons), and two broad doublets of an AB system centered at 7·62 and 7·98 τ (J_{gem} = 17 c/s, C-1 methylene protons).

The $NaBH_4$ reduction of VIII may proceed by C-6 hydride ion attack with the formation of VI as would be expected from the preceding discussion. The benzoquinolizine VI is obtained as an unstable product on treatment of the dihydrobenzo[*b*]quinolizinium bromide (XIX) with sodium hydroxide solution.[10] From a protic solvent VI should be protonated at C-11 and the resulting iminium ion (VII) can undergo further reduction at C-2, C-11a or C-4 leading to benzo dienamine intermediates XVI, XVII and XVIII, respectively. These dienamines are thought to afford IX, X and XI, respectively by kinetically controlled protonation and immediate

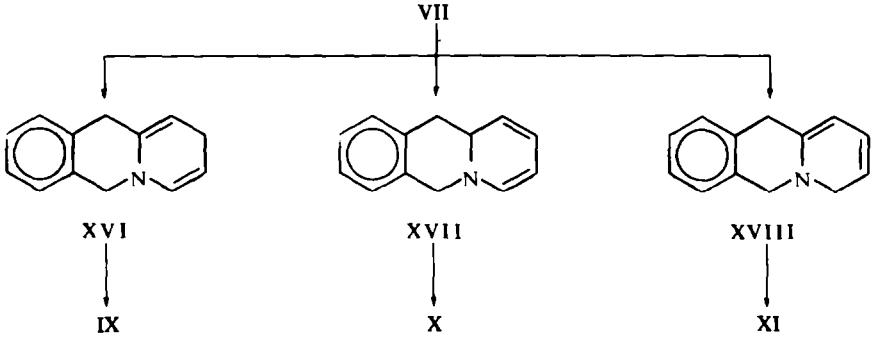


CHART 4

reduction as in dihydro pyridine or dienamine systems.[11, 12] To elucidate the mechanism, the sodium borohydride reduction of VIII was carried out in ethanol-d. Evidently D atoms were incorporated into the reduction products by deuteration from the deuterated solvent. The IR spectrum of the major product shows C-D stretching bands[13] in the region 2100–2200 cm^{-1}, but the absorption bands due to olefinic deuterium[13] and deuterium on carbons adjacent to nitrogen were not observed.[12, 14] The NMR spectrum revealed the disappearance of 1·6–1·7 atoms of H of the C–11 methylene protons and approximately one atom of H of the C–1 methylene protons. The C-1 methylene protons appear as two broad signals equivalent to a half proton in area at 7·68 and 7·97 τ with disappearance of large geminal coupling. The spectrum is almost identical, excepting the C-11 methylene proton region, with that of the deuterated product (Fig. 2) obtained from another reduction as will be

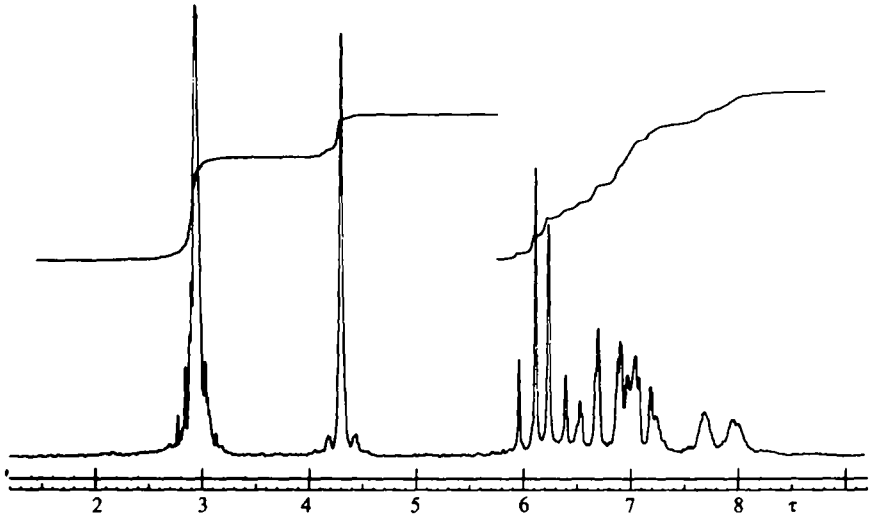


FIG. 2 NMR spectrum of the deuterated analogue of XI (main, XXVIII) obtained from the $NaBH_4$ reduction of XIX in C_2H_5OD.

described later. The spectral data indicate incorporation of 2·6–2·7 atoms of D per molecule into the reduction product during the hydride reduction of VIII. Further evidence was obtained from the mass spectrum in which the molecular ion and the prominent fragment peaks shifted mostly from *m/e* 185 and 104 in XI to *m/e* 188 and 106 in the deuterated product. As is apparent from the comparison of the molecular ion peak region with that of the undeuterated base (XI; Fig. 3), the product contained trideuterated 2-ene (XXVIII) as the main component, some dideuterated analogue and small amounts of a tetradeuterated analogue. However, the ratio of the deuterated analogues could not be determined precisely because of the uncertainty of M—H/M—D ratio. The incorporated D atoms probably resulted from deuteration of enamine intermediates, since XI underwent no H-D exchange in the ethanol-d solution containing $NaBH_4$. In this treatment, XI was quantitatively recovered without isomerization to the other isomer (X) and further reduction to IX.

Although the other two deuterated products were not obtained in sufficient quantities to take the NMR spectra, the mass spectra show that the benzoquinolizidine and 1-ene product contained tetradeuterated (XXVI) and trideuterated

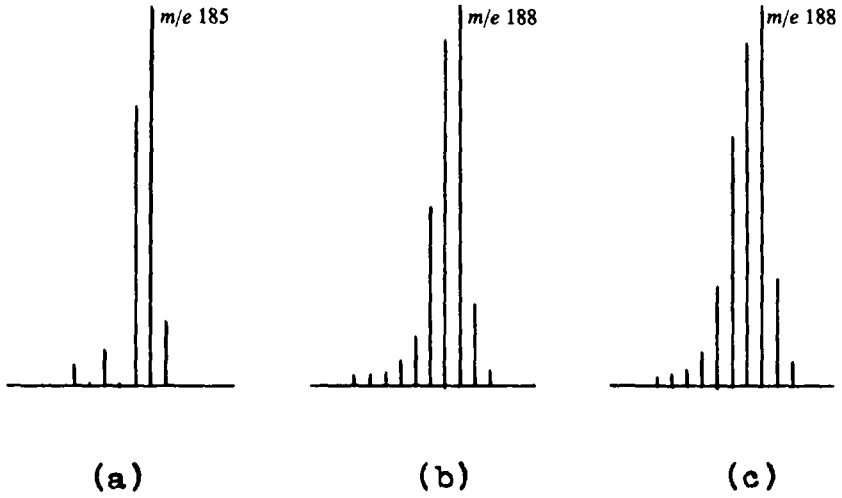


FIG. 3 Molecular ion peak regions in the mass spectra of: (a) XI; (b) the deuterated analogue (main, XXVIII) of XI obtained from the $NaBH_4$ reduction of VIII in C_2H_5OD; (c) the deuterated analogue (main, XXVIII) of XI obtained from the $NaBH_4$ reduction of XIX in C_2H_5OD.

analogues (XXVII), respectively as the main deuterated component. Both spectra show the prominent fragment peak at *m/e* 106 suggesting two deuterium incorporation at C-11.

These facts imply that the hydride reduction of VIII proceeded by a pathway involving an equilibrating and an almost non-equilibrating deuteration in two deuteration steps. Such significant equilibration has not been observed in the sodium borohydride reductions of quaternary pyridinium ions,[11] 1,2,3,4-tetrahydro- and 3,4-dihydroquinolizinium ions.[12] The former two are preferentially reduced at the carbons adjacent to the quaternary nitrogen and the resulting dienamines undergo non-equilibrating deuteration and immediate reduction to the tetrahydro derivatives. If the reduction of VIII proceeds in the same manner as described above, one deuter-

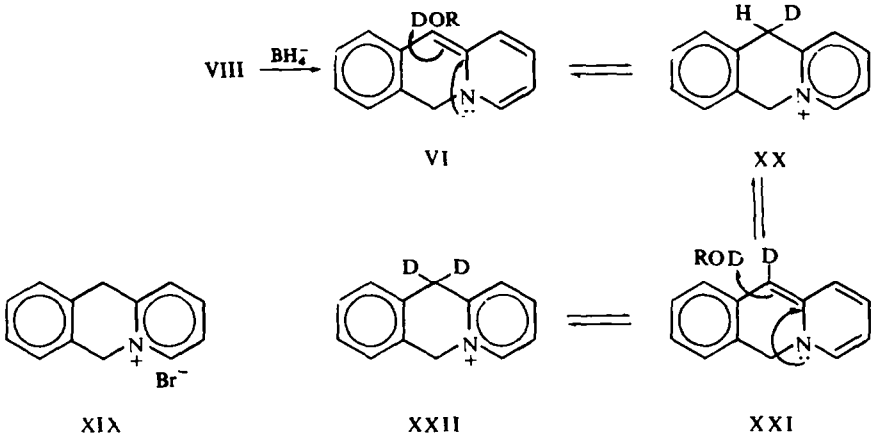


CHART 5

ium each should be distributed at C-1 and C-11 of the ene products. Thus, the one remaining deuterium should have resulted from equilibration between the dihydrobenzoquinolizinium ion (VII) and the deprotonated form VI. The D atoms can be introduced at C-11 with excess deuterated solvent by a pathway (VI → XX → XXI → XXII) shown in Chart 5. The equilibration is facilitated by the Ph group, since the base-catalysed deprotonation of VII leads to an extended conjugation system. The dihydrobenzoquinolizinium ion (VII) is known to undergo extremely slow H—D exchange at C-11 in deuterium oxide.[10] However, the exchange was shown to take place rapidly under basic conditions, i.e., even on addition of small amounts of NaOD solution.

In connection with the above mechanistic assumption, 6,11-dihydrobenzo[*b*]-quinolizinium bromide (XIX) was similarly reduced with sodium borohydride in ethanol-d. On dropwise addition of XIX to a stirred solution of sodium borohydride in ethanol-d, the resulting mixture turned a reddish colour, but immediately the colour faded possibly because of rapid reduction. The colouration is ascribable to the appearance of the benzoquinolizine (VI) by deprotonation from XIX in the alkaline medium. The benzoquinolizine (VI) seems to be rapidly formed prior to the hydride reduction of XIX which seemingly occurs within a few seconds. The NMR spectrum (Fig. 2) of the deuterated 2-ene product shows signals similar to those of the corresponding deuterated product described above. In this case, however, H—D exchange at C-11 seems to have occurred to a lesser extent. On the basis of the signals near 7·2 τ, it was proved that 1·4–1·5 atoms of H at C-11 were replaced with deuterium by the H—D exchange at C-11 of the ion VII. The incorporation of the D atoms at C-11 should not occur appreciably in the 1-deuterated iminium ion resulting from the C-1 deuteration of the dienamine intermediate XVIII. Apparently about one D atom was incorporated at C-1 resulting in the appearance of two broad peaks, equal in area, at 7·68 and 7·97 τ due to the non-equivalent C-1 protons. Integration showed the combined area of these two peaks corresponded to one proton. Mass spectral comparison of the molecular ion peak region of the both deuterated compounds (Fig. 3) shows that the hydride reduction of XIX in ethanol-d proceeded partially with that of the undeuterated iminium ion (VII) yielding the monodeuterated 2-ene product (possibly C-1 deuterated analogue). The mass spectra of the other two minor products were also compared with those of the undeuterated bases (IX and X) indicating significant H—D exchange at C-11 of VII. The results imply that the H—D exchange is not fast enough to occur completely prior to its hydride reduction, although the C-11 methylene protons are exchanged with more than one deuteron. This equilibration is comparable to that between 4*H*-quinolizine (II) and the protonated form (III) during the hydride reduction[3c] in which the H—D exchange at C-1 has taken place predominantly, but not completely. In this case, the equilibration is facilitated by the presence of the 2,3-double bond in the iminium ion (III). Interestingly the 6,7-dihydro derivative of II does not undergo significant equilibrating deuteriation at C-9 prior to the hydride reduction.[12]

The dideuterated iminium ion (XXII) thus formed may be reduced at C-2, C-4 or C-11a leading to the dienamines XXIII, XXV and XXIV, respectively. Further hydride reductions follow kinetically controlled deuteration of the dienamines XXIV and XXV to afford trideuterated products (XXVII and XXVIII). The other dienamine (XXIII) also may be reduced to a tetradeuterated benzo[*b*]quinolizidine (XXVI) by

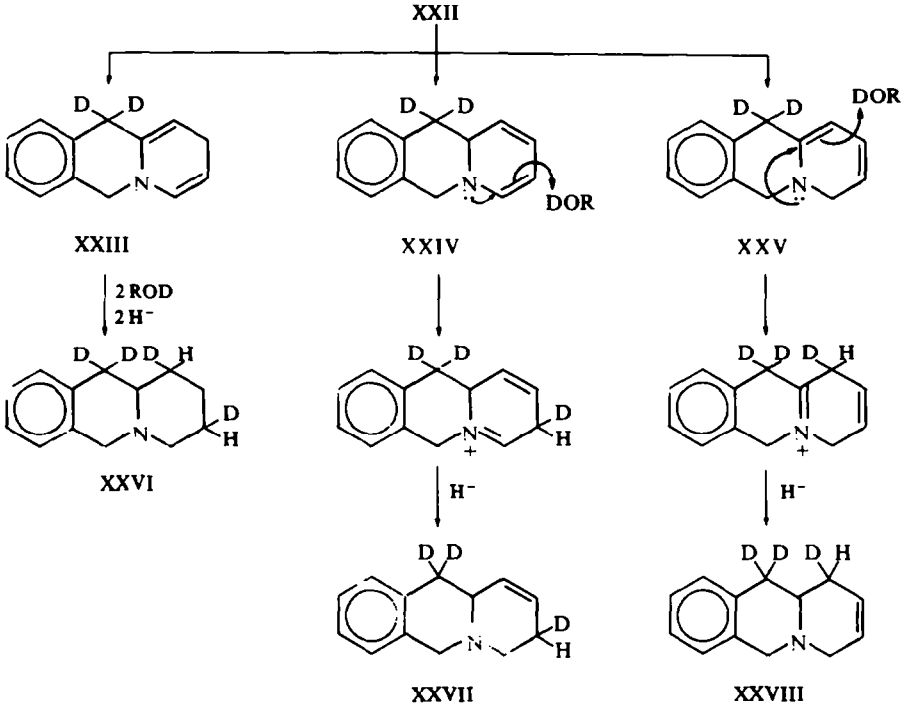


CHART 6

repeated almost non-equilibrating deuteration and immediate reduction. Similarly, the monodeuterated dihydrobenzo[*b*]quinolizine (XX) seems to be reduced partially prior to the H—D exchange to afford the tri- and dideuterated analogues of the hexahydro-(IX) and tetrahydroquinolizines (X and XI), respectively.

The hydride ion attack at the γ-position of the pyridinium ring did not take place in the reduction of 1,2,3,4-tetrahydroquinolizinium bromide with ethanol as solvent in which 1- and 2-ene compounds were produced with a higher proportion of the 1-ene.[12] In contrast, the dihydrobenzo[*b*]quinolizinium ion (VII) were reduced preferentially at C-4 to afford the 2-ene (XI), accompanied by the minor C-11a and C-2 hydride reductions.* It seems probable that the phenyl π-electron prevents the hydride ion from attacking at C-11a. However, it is uncertain whether the much less hydride ion attack at C-11a should be mostly ascribed to the phenyl participation or a change in stereochemistry.

In conclusion, the sodium borohydride reduction of VIII in ethanol should proceed with significant equilibration in the protonation step of 6*H*-benzo[*b*]quinolizine (VI) resulting from the initial reduction.

* Rubtsov *et al.*[15] have reported that 6,7,8,9,10,11-hexahydro- and 6,6a,7,8,9,10,10a,11-octahydrobenzo-[*b*]quinolizinium salts are reduced with sodium borohydride in methanol to afford 1,6,7,8,9,10,11,11a-octahydro- and 1,6,6a,7,8,9,10,10a,11,11a-decahydro-4H-benzo[*b*]quinolizine, respectively. However, the structural determination of the products and separation of the other expected products have not been attempted.

EXPERIMENTAL

All m.ps were uncorrected. The NMR spectra were measured with a Varian HA-100 spectrometer in $CDCl_3$. Chemical shifts were given in τ values with TMS as the internal standard. The IR spectra were obtained on a Perkin–Elmer Model 221 double-beam spectrophotometer. All mass spectra were determined using JEDL-JMS-OIS mass spectrometer with ionizing voltage of 75 eV. Samples were introduced through an inlet system at 25–30°. Preparative gas chromatography was performed isothermally at 195° with He gas on a Yanagimoto GCG-3 Chromatograph equipped with a thermal conductivity detector. Column used was 30% polydiethyleneglycol succinate on 60–80 mesh Chromosorb-W (2 m × 5 mm i.d.). Column chromatography was carried out on silica gel (> 100 mesh, Kanto Chemical Co. Inc.).

Reduction of benzo[b]*quinolizinium bromide* (VIII) *with sodium borohydride in ethanol.* VIII[6a] was obtained as the anhydrous bromide when the powdered monohydrate was dried at 120° *in vacuo*. A soln of $NaBH_4$ (454 mg) in EtOH (50 ml) was added to a stirred and ice-cooled soln of VIII (2·60 g) in EtOH (100 ml) during 20 min. Stirring was continued with cooling for 3 hr and then at room temp for 3 hr. The soln was acidified with AcOH, the solvent evaporated *in vacuo*, Na_2CO_3aq added to the residue and the mixture extracted with ether. The residue from the dried (Na_2SO_4) ether extracts was distilled to afford a 7·2:3·3:89·5 mixture of IX, X and XI (810 mg), b.p. 120–140° (bath temp)/1 mm. Although the three components were readily analyzed by gas chromatography, it was difficult to separate preparatively X from the other two. IX was effectively isolated from the first eluent when column chromatography was carried out with benzene-AcOEt (1:1) as eluent. The three products thus separated were characterized as follows: (i) compound IX was obtained as the first component by preparative gas chromatography and subsequent distillation *in vacuo*. Its identification was made by IR spectral comparison and mixed m.p. with an authentic sample which was prepared from the catalytic hydrogenation of VIII.[6]; (ii) The structure of X, an almost colourless oil, was provided by the mass and NMR spectra. Mass spectrum *m/e*: 185 (M^+), 184 (base peak), 104. The NMR spectral data are described in the Discussion section. The hydriodide, m.p. 213–214° from EtOH. (Found: C, 49·64; H, 5·27; N, 4·41. $C_{13}H_{16}NI$ requires: C, 49·85; H, 5·15; N, 4·47%); (iii) Compound XI was obtained as colourless crystals, m.p. 26·5–27·5°, b.p. 120–125° (bath temp)/1 mm. (Found: C, 83·91; H, 8·16; N, 7·60. $C_{13}H_{15}N$ requires: C, 84·28; H, 8·16; N, 7·56%); ν_{max}^{liq} cm^{-1}: 1668 (C=C). Mass spectrum *m/e*: 185(M^+), 184, 130, 104 (base peak), 78, 77. The NMR spectral data are described in the Discussion section. The hydriodide, m.p. 188–189° from EtOH. (Found: C, 49·61; H, 5·09; N, 4·49. $C_{13}H_{16}NI$ requires: C, 49·85; H, 5·15; N, 4·47%); ν_{max}^{Nujol} cm^{-1}: 1668 (weak, C=C). The picrate, m.p. 147–148° from EtOH. (Found: C, 54·94; H, 4·54; N, 13·67. $C_{19}H_{18}N_4O_7$ requires C, 55·07; H, 4·38; N, 13·52%).

The $NaBH_4$ reduction was also carried out as follows. A soln of VIII (2·60 g) in EtOH (100 ml) was added to a stirred and ice-cooled soln of $NaBH_4$ (0·454 g) in EtOH (50 ml) during 20 min. The resulting mixture was treated as described above to give a 3·1:1·0:95·9 mixture of IX, X and XI, yield 1·34 g.

Catalytic hydrogenation of XI. A soln of XI (300 mg) in glacial AcOH (20 ml) was hydrogenated at room temp over 5% Pd-C(50 mg). The soln was filtered and evaporated to dryness. The residue was dissolved in water, made alkaline with Na_2CO_3 and extracted with ether. Preparative gas chromatography of the residue obtained from the dried (Na_2SO_4) ether extract and subsequent distillation afforded IX as colourless crystals, m.p. 47–48°, identical with an authentic sample.

Reduction of VIII *with sodium borohydride in ethanol-d.* Ethanol-d was prepared by the method of Shiner and Smith.[16] A soln of VIII (1·3 g) in EtOD (50 ml) was added to a stirred and ice-cooled soln of $NaBH_4$ (0·345 g) in EtOD (50 ml) during 20 min. The soln was stirred with cooling for 3 hr and then at room temp for 3 hr. The resulting mixture was worked up as described above and the residue obtained from the ether extract was distilled. The distillate was shown to be a 5·1:1·8:93·1 mixture of the deuterated analogues of IX, X and XI which were separated by gas chromatography. The mass and NMR spectra showed that XXVI, XXVII and XXVIII were formed as the main deuterated product. The spectral data are described in the Discussion section. The deuterated analogues of IX and XI showed no depression in mixed m.p. with the undeuterated bases (IX and XI).

Reduction of 6,11-*dihydrobenzo*[b]*quinolizinium bromide* (XIX) *with sodium borohydride in ethanol-d.* The bromide (XIX) was prepared by the method of Braun and Bradsher.[10] A soln of XIX (650 mg) in EtOD (25 ml) was added to a soln of $NaBH_4$ (173 mg) during 20 min. The usual work-up gave a 5·8:1·7:92·5 mixture of the deuterated analogues of IX, X and XI which were separated by preparative gas chromatography. The NMR and mass spectra showed that XXVI, XXVII and XXVIII were formed as the main deuterated product. The spectral data are described in the Discussion section.

Reduction of 8,9-*dimethyoxybenzo*[b]*quinolizinium bromide* (XII) *with sodium borohydride in ethanol.* The bromide (XII) was prepared as the hydrate by the modified method of Kupchan *et al.*[6b] A soln of XII

hydrate (3·38 g) in EtOH (300 ml) was added to a stirred and ice-cooled soln of $NaBH_4$ (0·454 g) in EtOH (50 ml) during 20 min. After the resulting mixture was stirred with cooling for 3 hr and then at room temp for 3 hr, the soln was worked up as described. The crude product was shown to comprise XV (ca. 96%) and an unknown material by gas chromatography (an F & M 402 Chromatograph equipped with 5% XE-60 on 60–80 mesh Chromosorb W (1 m × 3 mm i.d.), col. temp, 185°). The residue from the ether extract was recrystallized from benzene to give the major product (XV), m.p. 114–115°, yield, 1·65 g, 67·3%. (Found: C, 73·31, H, 7·81; N, 5·93. $C_{15}H_{19}NO_2$ requires: C, 73·44; H, 7·81; N, 5·71%); ν_{max}^{Nujol} cm^{-1}: 1668 (C=C); mass spectrum *m/e*: 245 (M^+), 244, 191, 165, 164 (base peak), 149, 121.

Catalytic hydrogenation of XV. A soln of XV (500 mg) in glacial AcOH (50 ml) was hydrogenated over 5% Pd-C (50 mg). The resulting soln was worked up as described above to give XIII as colourless crystals, m.p. 108–109° (from EtOH). This was identical with an authentic sample which was prepared from the catalytic hydrogenation of the 8,9-dimethoxybenzo[*b*]quinolizinium salt.[17]

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