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The Sodium Borohydride Reductions of Indolylethylpyridinium Bromides. Hexahydroindoloquinolizines

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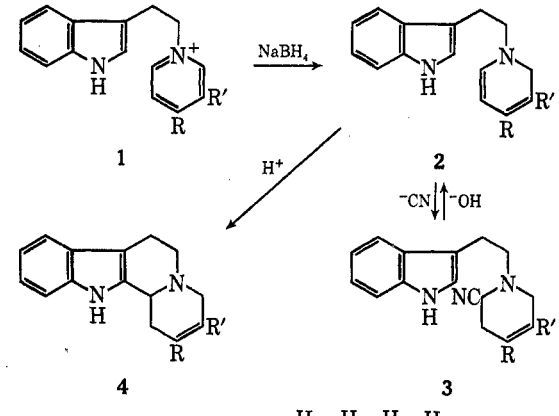
Sodium borohydride under ordinary conditions has not proved useful for the reduction of 1-(2-indol-3-ylethyl)pyridinium and the corresponding isoquinolinium salts to the dihydro bases **2**, intermediates for the synthesis of the quinolizines **4**.[1-4] The reduction to the tetrahydro bases which characterized this reagent was observed to a lesser extent with lithium aluminum hydride[1-5] and with lithium tri-*t*-butoxyaluminum hydride.[3] The results presented in this note show that control over the sodium borohydride reduction can be easily gained by using the alklai method of Panouse[6] together with the rapid removal of products from the reaction site. In addition, conversion of the dihydropyridines into nitriles in the reaction medium proved to be convenient and was usually desirable.[7a]

The advantages of using a nitrile in a sequence involving a 1,2-dihydropyridine lie in its stability relative to the parent diene and in the ease with which the nitrile reverts to the diene under basic and acidic conditions. Its availability, however, may be limited by the alkalinity of the parent sodium cyanide reduction system which may in itself be high enough to make the **2** ⇄ **3** equilibrium favor the diene. Lowering the alkalinity of the cyanide solution shifts the equilibrium toward the nitrile, but whether there is an accompanying increase in liability to further reduction is not presently known. Previous investigations have shown that annelations of the dienes require acid conditions, and in the present work the nitriles readily lost hydrogen cyanide in hot acid with closure to the quinolizine salts. Much milder conditions effect this ring closure when the dihydropyridine system is involved, so that the yield of quinolizine from a reduction mixture containing both **2** and **3** can in itself give no information on the relative amounts of the precursors.

A constant factor in all reductions and one of great importance is the two-phase liquid mixture of water, methanol, and ether which provided for a rapid separation of the initial reduction products from the foaming reaction mixture. By this means alone and without additional alkali a 66% yield of **2a** was obtained; in the presence of sodium hydroxide the recovery of this base rose to 89%. The dihydro base **2a** was also the main product from reductions in the more concentrated sodium cyanide solutions, and only in a moderately basic cyanide solution (partial neutralization with acid) did the nitrile form in appreciable amount in the reaction mixture. Not unexpectedly, **2a** was readily converted into **3a** (94%) in a similar cyanide solution. In contrast with the results obtained with the isoquinolinium salt, the water–methanol–ether mixture did not prevent reduction of the pyridinium bromide **1b** into its tetrahydro base in 78% yield; no quinolizine was obtained. The reduction of **1b** in sodium hydroxide followed by acid ring closure gave the hydrochloride of **4b** in 40% yield, and this was increased to 50% by the cyanide technique. Here noncrystalline products precluded assessment of the **2** ⇄ **3** interchange, but the ir absorption spectra indicated that this mixture was present in the crude oil.



a, R, R′(Benzo) = –C=C–C=C–
b, R = R′ = H
c, R = H; R′ = Me
d, R = H; R′ = Et
e, R = R′ = Me
f, R = Me; R′ = H

Among the variables to which little attention was given, but which made necessary a standardization of the synthetic procedure, are two which deserve special mention. The first of these is the alcohol used to dilute the aqueous solutions. Whether its contribution to the product yield stems from its role as a solvent or whether it also functions as a moderating nucleophile is a matter of conjecture. The second is the manner in which the acid annelation is conducted. Minor variations in solvent and acid sometimes had a marked effect on the yield of quinolizine salt. No attempt was made to identify a cause, but care was taken to duplicate conditions where comparisons were made.

Acid-induced elimination of hydrogen cyanide from related cyanotetrahydropyridines has been observed to be followed by a shift of the double bond into conjugation with the azomethine linkage. This isomerization has proved useful in controlling steric requirements of

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(6) (a) J. J. Panouse, *Bull. Soc. Chim. Fr., D*, 60 (1953); (b) J. J. Panouse, Thèse de Doctorate ès Sciences, Paris, 1952.
(7) (a) E. M. Fry, *J. Org. Chem.*, **29**, 1647 (1964); (b) E. M. Fry, *ibid.*, **28**, 1869 (1963).

substituted methanobenzazocines (benzomorphans)[7b,8] and might reasonably by expected here, but nmr examination of the suitably substituted examples **4c–e** showed the double bond to be in its original position. Additional evidence for the position of the double bond was provided in all cases by a strong band in the mass spectrum for the dihydro-β-carboline ion, *m/e* 170, resulting from a reverse Diels–Alder reaction.

Experimental Section

Analyses and mass and nmr spectra were performed by the Analytical Services Section of this laboratory, William C. Alford, Chief. Uv spectra were obtained by a Beckman DB-G grating spectrophotometer; ir spectra by a Perkin-Elmer Infracord Model 137B; nmr spectra by a Varian 60-Mc spectrometer with tetramethylsilane internal standard, and mass spectra by a Hitachi Perkin-Elmer RMU-7 mass spectrometer. Melting points are uncorrected; when reported as "vac mp," melting points were taken in evacuated capillary tubes made from Kimble disposable p'pets.

Pyridinium and isoquinolinium bromides (1) were made by heating a small excess of base with tryptophyl bromide at 50° for about 5 hr or by letting the mixture stand at room temperature for several days. The finely divided crystalline state used in the reductions was obtained by continuously scratching the test tube sides during the cooling of a hot concentrated solution. Yields are based on tryptophyl bromide.

2-(2-Indol-3-ylethyl)isoquinolinium bromide (1a) was obtained in 80% yield, mp 207–215°. After recrystallization from alcohol it melted at 215–217° (lit.[4] mp 211–212°).

1-(2-Indol-3-ylethyl)pyridinium bromide (1b) was obtained in a yield of 83% after recrystallization from aqueous alcohol, mp 230–232° (lit.[3] mp 231–233°).

3-Methyl-1-(2-indol-3-ylethyl)pyridinium bromide (1c) was recovered in 78% yield after recrystallization from alcohol. It melted at 204–206°.

Anal. Calcd for $C_{16}H_{17}BrN_2$: C, 60.57; H, 5.40; N, 8.83. Found: C, 60.66; H, 5.29; N, 8.96.

3-Ethyl-1-(2-indol-3-ylethyl)pyridinium bromide (1d) was obtained in 70% yield after recrystallization from methanol–acetone. It melted at 154–156° (lit.[3] mp 137–140°).

Anal. Calcd for $C_{17}H_{19}BrN_2$: C, 61.64; H, 5.79; Br, 24.12. Found: C, 61.35; H, 5.91; Br, 23.94.

3,4-Dimethyl-1-(2-indol-3-ylethyl)pyridinium bromide (1e) was obtained in 92% yield before purification. Recrystallized from water it sintered at 175°, resolidified, and melted at 220°. Recrystallized from alcohol it melted at 215–222°.

Anal. Calcd for $C_{17}H_{19}BrN_2$: C, 61.64; H, 5.78; N, 8.46. Found: C, 61.44; H, 5.98; N, 8.23.

4-Methyl-2(2-indol-3-ylethyl)pyridinium bromide (1f) was recovered in 88% yield, mp 197–200°. Recrystallized from alcohol it melted 199–201°.

Anal. Calcd for $C_{16}H_{17}BrN_2$: C, 60.57; H, 5.40; N, 8.83. Found: C, 60.58; H, 5.47; N, 8.65.

Reductions of 1b. A. In Methanol–Water. 1-(2-Indol-3-ylethyl)-1,2,5,6-tetrahydropyridine.—To a solution of 0.10 g of sodium borohydride in 1 ml of water was added 1 ml of methanol and 4 ml of ether. The addition of 0.40 g of **1b** gave a vigorously effervescing mixture which was stirred and intermittently cooled. The solid was consumed in about 10 min. The ether solution was separated and the crystalline product was recovered and converted to the picrate, 0.47 g (78%), mp 165–171°. After recrystallization from alcohol it melted at 173–175° (lit.[3] mp 173–174.5°).

Anal. Calcd for $C_{21}H_{21}N_5O_7$: C, 55.38; H, 4.65; N, 15.38. Found: C, 55.46; H, 4.90; N, 15.53.

Recovery of the base from the picrate with lithium hydroxide–ether gave material melting at 117–122°. The same base, mp 117–122°, was obtained in 35% yield by following the published procedure.[2a] After recrystallization from alcohol–petroleum ether, it melted at 119–123° (lit.[2a] mp 152–153°, similar melting points were reported in subsequent papers);[3,5b] mass spectrum M^+ 226; nmr ($CDCl_3$) ind-NH 8.4 (1 H), ind-α-H 7.0 (1 H), olefinic CH 5.8 ppm (2 H); uv spectrum in ethanol λ_{max} (log ε) 290.5 (3.69), 282 (3.74), 276 s (3.72), 229 (3.86); λ_{min} (log ε) 288 (3.66), 245 (3.14) [lit.[2a] λ_{max} (log ε) 291 (3.68), 283 (3.74), 275 s (3.71); λ_{min} (log ε) 288 (3.65), 244 (2.95)].

Anal. Calcd for $C_{15}H_{18}N_2$: C, 79.60; H, 8.02; N, 12.18. Found: C, 79.19; H, 8.16; N, 12.60.

In a duplicate experiment, a solution of the crude product in acid gave no **4b**.

B. In Methanol–Water–Sodium Hydroxide. 1,4,6,7,12,12b-Hexahydroindolo[2,3-*a*]quinolizine (4b).—To a solution of 30 mg of sodium borohydride in 0.5 ml of 2.1 *N* sodium hydroxide was added 0.5 ml of methanol and 2 ml of ether. The addition of 200 mg of **1b** resulted in a vigorous gas evolution and consumption of the solid was complete in 5 min. The product obtained from a sample of the ether solution showed a broad, strong band in the 6.1 μ region (diene) of the infrared. The ether solution was separated and extracted with 1 ml of 3 *N* hydrochloric acid. The yellow gum which formed began to yield crystalline material in 15 min, and after 1.5 hr the waxy solid was removed and triturated with alcohol to yield 68 mg (39.6%) of salt. Recrystallization from alcohol containing a drop of 1 *N* hydrochloric acid gave a product melting at 275–292°. In a duplicate run the ether solution was shaken with 1 ml of 3 *N* 95% ethanolic hydrochloric acid and the salt was obtained in only 23% yield.

Anal. Calcd for $C_{15}H_{17}ClN_2$: Cl, 13.60. Found: Cl, 13.40.

The salt was decomposed in sodium hydroxide containing a little alcohol and the base was recovered from ether. Recrystallized from ethanol it melted at 142–144° (lit.[3] mp 145–146°); picrate mp 187–190° (lit.[3] mp 184–187°).

Anal. Calcd for $C_{15}H_{16}N_2$: C, 80.32; N, 7.19. Found: C, 80.17; H, 7.39.

C. In Methanol–Water–Sodium Cyanide. 1,4,6,7,12,12b-Hexahydroindolo[2,3-*a*]quinolizine Hydrochloride (4b).—Sodium borohydride, 30 mg, was dissolved in a solution of 0.20 g of sodium cyanide in 0.6 ml of water. To this was added 0.5 ml of methanol and 2 ml of ether. **1b**, 200 mg, was added and the foaming mixture was stirred until the salt disappeared in about 10 min. The ether solution was then separated and distilled to a small volume and the residual methanol was removed under reduced pressure. The crude product showed a nitrile band at 4.5 μ and the 6.1-μ absorption was less intense than that observed in the B experiment above. The oil was redissolved in a small volume of ether and triturated with 1 ml of 3 *N* hydrochloric acid. In an 80° bath the mixture lost ether and hydrogen cyanide (sodium picrate vapor test). Crystal formation began in about 10 min, and after 35 min the material was filtered and then triturated with alcohol for a recovery of 90 mg (52%). Identification with the above described salt **4b** hydrochloride was made by comparison of infrared spectra and by conversion to the base.

In another experiment, an attempted ring closure in a dilute alcohol solution of lower acidity gave a very poor result.

3-Methyl-1,4,6,7,12,12b-hexahydroindolo[2,3-*a*]quinolizine (4c).—The hydrochloride was obtained from **1c** in 53% yield using the amounts and procedure described for **1b** under procedure C above. Recrystallized from alcohol containing 1 *N* hydrochloric acid, it melted at 290–295°.

Anal. Calcd for $C_{16}H_{19}ClN_2$: Cl, 12.90. Found: Cl 12.6.

The salt was decomposed by aqueous sodium carbonate–alcohol and the base was recovered from ether. It was recrystallized from alcohol: vac mp 174–176°; mass spectrum *m/e* 238 (M^+) 170; nmr ($CDCl_3$) Me 1.7 (3 H), olefinic CH 5.5 ppm (1 H).

Anal. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.76. Found: C, 80.21; H, 7.42; N, 12.11.

3-Ethyl-1,4,6,7,12,12b-hexahydroindolo[2,3-*a*]quinolizine (4d).—The hydrochloride was obtained in 49% yield by the cyanide method. The base melted at 147–148° (lit.[5b] mp 146–148°); mass spectrum *m/e* 252 (M^+) 170; nmr ethyl CH_3, triplet, 1.05 (3 H), olefinic CH 5.5 ppm (1 H).

6-Cyano-3,4-dimethyl-1-(2-indol-3-ylethyl)-1,2,5,6-tetrahydropyridine (3e) **Hydrochloride.**—**1e**, 200 mg, was reduced in the manner described for **1b** under the cyanide procedure C above. Approximately 1 hr was required for consumption of the solid. After separation, the ether solution was triturated with 0.2 ml of 3 *N* hydrochloric acid. The oil which formed crystallized in a few minutes. After decanting the ether, the product was washed with water to remove a little gum. It weighed 0.11 g (67.6%), mp 160° (gas).

Anal. Calcd for $C_{18}H_{22}ClN_3$: C, 68.45; H, 7.03; N, 13.30. Found: C, 68.55; H, 7.25; N, 12.91.

(8) R. L. Perry and N. F. Albertson, *J. Med. Chem.*, **10**, 1184 (1967).

The salt was decomposed in alcoholic sodium bicarbonate solution and the base was recovered as an oil from ether. Nmr spectrum ($CDCl_3$) showed ind-NH 8.2, *ind*-α-H 6.95 ppm.

2,3-Dimethyl-1,4,6,7,12,12b-hexahydroindolo[2,3-*a*]quinolizine (4e).—**3e** hydrochloride, 0.43 g, suspended in 4.3 ml of 1 *N* hydrochloric acid was held on steam for 1 hr during which time hydrogen cyanide was evolved and cottony crystals replaced the original salt. The suspension was chilled and 0.35 g (89%) of salt was recovered. It was recrystallized from water, mp 295°.

Anal. Calcd for $C_{17}H_{21}ClN_2$: Cl, 12.28. Found: Cl, 12.25.

The salt was decomposed in sodium bicarbonate solution containing alcohol and the base was recovered from ether. Recrystallized from alcohol it had vac mp 192–193°, with a slight sinter at 93°; mass spectrum *m/e* 252 (M^+) 170; nmr ($CDCl_3$) Me 1.68 ppm (6 H).

Anal. Calcd for $C_{17}H_{20}N_2$: C, 80.91; H, 7.99. Found: C, 81.10; H, 7.73; loss on drying, 3.34.

6-Cyano-4-methyl-1-(2-indol-3-ylethyl)-1,2,5,6-tetrahydropyridine (3f).—**1f**, 200 mg, was reduced as described for **1b** under procedure C above. After a reaction time of 30 min, the ether was separated and distilled to a small volume, and the remaining solvent was removed under reduced pressure to yield crystalline material which was triturated with petroleum ether and filtered, 0.15 g, mp 93–120°. After several recrystallizations from alcohol, it melted at 128–130°.

Anal. Calcd for $C_{17}H_{19}N_3 \cdot {}^1/_2H_2O$: C, 74.42; H, 7.34; N, 15.32. Found: C, 74.19; H, 6.84; N, 15.62.

2-Methyl-1,4,6,7,12,12b-hexahydroindolo[2,3-*a*]quinolizine (4f).—The hydrochloride was obtained from a like preparation after the crude crystalline cyano product was converted in the usual manner. The salt weighed 0.112 g (65%) and darkened without melting at 310° (hot stage).

Anal. Calcd for $C_{16}H_{19}ClN_2$: Cl, 12.90. Found: Cl, 12.64.

The salt was decomposed in aqueous sodium hydroxide–alcohol and the base was recovered with ether. Recrystallized from *n*-hexane–ether it melted at 121–123° (gas). After heating at 80° under reduced pressure for 45 min to remove solvent, it melted at 149–151°; mass spectrum *m/e* 238 (M^+) 170.

Anal. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.76. Found: C, 80.69; H, 7.73; N, 12.02.

Reductions of 1a. A. In Methanol–Water. 2-(2-Indol-3-ylethyl)-1,2-dihydroisoquinoline (2a).—A solution of 30 mg of sodium borohydride in 0.5 ml of water was mixed with 0.5 ml of methanol and 2.0 ml of ether. To this was added 200 mg of **1a** and the vigorously foaming mixture was stirred until the reaction ended in 3 min with exhaustion of the hydride. The ether layer was separated and 11 mg of **1a** was recovered. After concentration of the ether solution crystallization took place and 98 mg (66%) was recovered from a cold alcohol suspension, vac mp 136–144°. After recrystallization from alcohol it showed vac mp 148–151°; ir spectrum (Nujol) 6.18 (strong), 6.40 μ (medium); nmr spectrum ($CDCl_3$) ind-NH 7.8 (1 H), ind-α-H 6.9, olefinic CH, AB doublets (J = 7.8 Hz) 6.1 (1 H), 5.2 ppm (1 H); and uv spectrum (ethanol) λ_{max} (log ε) 334 (3.96), 291 (3.84), 283 (3.83), 276 sh (3.79), 229 (4.15); λ_{min} (log ε) 301 (3.70), 287 (3.81), 255 (3.63) [lit.[4] mp 100° for unpurified product; λ_{max} (log ε) 336 (3.83), 293 (3.85), 284 (3.88), 278 sh (3.87), 221 (4.69)].

Anal. Calcd for $C_{19}H_{18}N_2$: C, 83.18; H, 6.61. Found: C, 83.34; H, 6.37.

2-(2-Indol-3-ylethyl)-1,2,3,4-tetrahydroisoquinoline.—The noncrystalline product from the alcohol wash was converted to a picrate, 40 mg (15%), mp 161–169°. Purified from alcohol it melted at 170–173° (lit.[4] mp 170–171°). It was converted to the base with lithium hydroxide and recovered from ether. After recrystallization from alcohol, it melted at 118–120° (lit.[4] mp 121–122°).

B. In Methanol–Water–Sodium Hydroxide. 2-(2-Indol-3-ylethyl)-1,2-dihydroisoquinoline (2a).—By the procedure detailed for **1b**, 200 mg of **1a** was subjected to reduction in methanolic sodium hydroxide. It was consumed in 2 min. The ether was distilled to a small volume and the residual solvent was removed under reduced pressure. The crystalline residue was filtered from cold alcohol, 129 mg (83%), vac mp 152–154°. A second crop of 10 mg brought the total recovery of **2a** to 89%.

C. In Methanol–Water–Sodium Cyanide. 3-Cyano-2-(2-indol-3-ylethyl)-1,2,3,4-tetrahydroisoquinoline (3a).—A. Sodium borohydride, 30 mg, was dissolved in a solution of 0.2 g of sodium cyanide in 0.3 ml of water. Methanol, 0.5 ml, was added and the solution was layered with 2 ml of ether. **1a**, 200 mg, was added and the effervescing mixture was stirred. Consumption of the salt was complete in 5 min. The product, 98 mg (63%) mp 137–146°, was recovered from the ether solution in the usual manner. Its identity as **2a** was established by means of an infrared spectrum. The alcoholic filtrate yielded 11 mg (6%) of the crystalline nitrile. B. When the reduction was run in a solution less concentrated in sodium cyanide (0.2 g of sodium cyanide, 0.5 ml of water, 0.5 ml of methanol) the same products were isolated in 50% and 24% yields, respectively. C. To an ice-cold partial solution of 0.2 g of sodium cyanide in 0.3 ml of water was carefully added 0.3 ml of 6 *N* hydrochloric acid. Sodium borohydride, 30 mg, was then dissolved in the still alkaline solution and this was followed by the addition of 0.5 ml of methanol and 2 ml of ether. Reduction of 200 mg of **1a** gave 110 mg (65%) of the nitrile, mp 94–106°. The noncrystalline residue yielded 42 mg (15%) of the picrate of 2-(2-indol-3-ylethyl)-1,2,3,4-tetrahydroisoquinoline. No **2a** could be isolated. D. **2a**, 77 mg, was stirred with a sodium cyanide–hydrogen cyanide solution made as above. The solid became gummy in 30 min and then resolidified on continued trituration. Recovery gave 80 mg (94%), mp 95–105°. Identity with the other nitrile samples was established by its ir (Nujol) spectrum. Recrystallization from alcohol gave a product melting at 108–110°.

Anal. Calcd for $C_{20}H_{19}N_3$: C, 79.70; H, 6.35; N, 13.94. Found: C, 79.49; H, 6.33; N, 13.70.

The hydrochloride separated as finely divided crystals when the base was added to 3 *N* alcoholic (95%) hydrochloric acid.

Anal. Calcd for $C_{20}H_{20}ClN_3$: Cl, 10.48. Found: Cl, 10.83.

5,7,8,13,13b,14-Hexahydrobenzo[*g*]indolo[2,3-*a*]quinolizine (4a).—A. The hydrochloride from 60 mg of nitrile **3a** was obtained crystalline in 0.5 ml of 3 *N* alcoholic (95%) hydrochloric acid. The suspension was diluted with an equal volume of water and held on the steam bath for 5 min. The solid became less dense and the vapor was positive to the picrate test for hydrogen cyanide. After washing with alcohol 55 mg (89%) of salt was obtained. B. **2a**, 111 mg, was added portionwise with stirring to 2 ml of 2.4 *N* ethanolic (95%) hydrochloric acid to give a solution which began to deposit crystals in 5 min. Recovery after 1 hr gave 90 mg (71%) of the salt. Identity of material from the two sources was established by ir spectra (Nujol). The salt melted at 290° (lit.[1] mp 287–288°). C. Ether solutions containing mixtures of **2a** and **3a** (from sodium borohydride reductions in cyanide solutions) were extracted with 3 *N* aqueous hydrochloric acid to yield oils which crystallized to give the salt in 60–65% yields.

The base was recovered crystalline from ether–alcohol after decomposing the salt in sodium carbonate solution containing alcohol. It had vac mp 197–200°, air mp 192–195° (lit.[1] mp 188–189°); mass spectrum *m/e* 274 (M^+) 170.

Registry No.—Sodium borohydride, 16940-66-2; **1c**, 24716-23-2; **1d**, 24716-24-3; **1e**, 24716-25-4; **1f**, 24716-26-5; 1-(2-indol-3-ylethyl)-1,2,5,6-tetrahydropyridine, 24716-27-6; **2a**, 24716-28-7; **3a**, 24716-29-8; **3e**-HCl, 24716-30-1; **3f**, 24716-31-2; **4b** HCl, 24716-32-3; **4c**, 24716-33-4; **4c** HCl, 24716-34-5; **4e**, 24716-35-6; **4e** HCl, 24716-36-7; **4f**, 24716-37-8; **4f** HCl, 24716-38-9.

Biphenylene Insertion Products. Dibenzoselenophene and Diphenyldibenzostannole

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A conventional approach to the chemistry of biphenylene, involving synthesis and characterization of ring-substituted derivatives, has revealed a wealth of