a white solid, mp 86–87° (EtOH): nmr δ 7.16 (s, 5, aromatic), 6.93 (s, 4, aromatic), 3.63 (AB, J_{AB} = 13.4 Hz, ΔV_{AB} = 59.3 Hz, 2, N–CH_2Ph), 3.60–0.80 (m, 12, aliphatic).

Anal. Calcd for $C_{20}H_{23}N$: C, 86.59; H, 8.36; N, 5.05. Found: C, 86.47; H, 8.41; N, 4.83.

***trans*-1-Benzyl-7,8-dimethoxy-1,2,3,4,4a,5,10,10a-octahydrobenzo[*g*]quinoline (1f).** Using the above procedure, **1d** gave an 87% yield of **1f** as a clear oil: nmr δ 7.20 (s, 5, aromatic), 6.61 (s, 1, aromatic), 6.54 (s, 1, aromatic), 3.89 (s, 6, OCH_3), 3.71 (AB, J_{AB} = 13.4 Hz, ΔV_{AB} = 61.6 Hz, 2, N–CH_2Ph), 3.60–0.80 (m, 12, aliphatic). Conversion of the base to the hydrochloride, mp 159–161° (H_2O), and reconversion of the salt to the base gave an analytically pure sample of **1f**.

Anal. Calcd for $C_{22}H_{27}NO_2$: C, 78.30; H, 8.07; N, 4.15. Found: C, 78.63; H, 7.98; N, 4.11.

Acknowledgment. The authors gratefully acknowledge support of this project by the National Institutes of Health Grants NS 90399 and GM 49441.

Registry No.—**1a,** 53011-21-5; **1a** $HClO_4$, 53011-22-6; **1a** HCl, 53011-23-7; **1b,** 53011-24-8; **1b** $HClO_4$, 53011-25-9; **1b** HCl, 53011-26-0; **1c,** 53011-27-1; **1d,** 53011-28-2; **1e,** 53011-29-3; **1f,** 53011-30-6; **1f** HCl, 53011-31-7; *cis*-**3a,** 53011-32-8; *trans*-**3a,** 53060-09-6; *cis*-**3b,** 53011-33-9; *trans*-**3b,** 53011-34-0; *cis*-**6a,** 53011-35-1; *trans*-**6a,** 53011-36-2; *cis*-**6b,** 53011-37-3; *trans*-**6b,** 53011-38-4; *cis*-**7a,** 53011-39-5; *trans*-**7a,** 53011-40-8; *cis*-**7b,** 53011-41-9; *trans*-**7b,** 53011-42-0; **8b,** 53011-43-1; **8b** HCl, 41191-52-0; **8c,** 53011-44-2; **8c** HCl, 53011-45-3; **8d,** 53011-46-4; **8d** HCl, 53011-47-5; **13a,** 10343-99-4; **13b,** 767-92-0; **14a,** 5710-04-3; **14b,** 22218-33-3; **15a,** 53011-48-6; **15b,** 784-85-0; **15b** HCl, 784-85-0; benzoyl chloride, 98-88-4.

References and Notes

(1) E. E. Smissman and T. L. Pazdernik, *J. Med. Chem.*, **16,** 18 (1973).
(2) (a) W. F. Michne and N. F. Albertson, *J. Med. Chem.*, **12,** 402 (1969); (b) *ibid.*, **13,** 522 (1970).
(3) (a) E. E. Smissman, S. El-Antably, L. W. Hedrich, E. J. Walaszek, and L-F. Tseng, *J. Med. Chem.*, **16,** 109 (1973); (b) E. E. Smissman, S. El-Antably, and D. A. Walsh, to be published.
(4) (a) R. E. Lyle and J. J. Thomas, *Tetrahedron Lett.*, 897 (1969); (b) R. E. Lyle, J. J. Thomas and D. A. Walsh in "Conformational Analysis," G. Chiurdoglu, Ed., Academic Press, New York, N.Y., 1971, p 157; (c) R. E. Lyle and L. N. Pridgen, *J. Org. Chem.*, **38,** 1618 (1973); (d) R. E. Lyle, G. A. Heavner, L. N. Pridgen, and J. J. Kaminski, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 9–14, 1972.
(5) L. N. Pridgen, Ph.D. Thesis, University of New Hampshire, 1972; Dissertation Abstract 73-4365.
(6) R. A. Johnson, H. C. Murray, L. M. Reineke, and G. S. Fonken, *J. Org. Chem.*, **33,** 3207 (1968).
(7) R. A. Johnson, *J. Org. Chem.*, **33,** 3627 (1968).
(8) H. Paulsen and K. Todt, *Chem. Ber.*, **100,** 3385 (1967).
(9) W. Huckel and F. Stepf, *Justus Liebigs Ann. Chem.*, **453,** 193 (1927).

Sodium Borohydride Reduction of Sterically Hindered Pyridinium Salts[1]

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The sodium borohydride reduction of 1-triphenylmethylpyridinium salts gave a mixture of dihydropyridines, with the 1,2 isomer predominating. Thermal decomposition gave loss of triphenylmethane and the original pyridine, suggesting the use of this derivative for protection of the pyridine ring during hydride reductions. The 2-hydroxyimino-1,1-dimethylethylpyridinium salts gave largely the tetrahydropyridine with sodium borohydride. Thermal or basic decomposition of the product removed the nitrogen substituent to give the 1-unsubstituted-1,2,3,6-tetrahydropyridine. This constitutes the only satisfactory reductive procedure for the synthesis of such compounds.

The mechanism of the reduction of pyridinium ions by sodium borohydride has been well defined, and the effect of substituents on the heterocyclic ring has been explored and can be predicted to some extent.[3] A large nitrogen substituent, because of steric interference to approach of the hydride reagent, causes the reduction to occur to a greater extent at the 4 position and gives the saturated piperidine. A nitrogen substituent with a π bond which can overlap the occupied p orbital of nitrogen stabilizes the intermediate dihydropyridine by decreasing the nucleophilicity of the enamine system.

Synthetic methods were found for preparing two unusual salts of pyridine, the triphenylmethyl- and 2-hydroxyimino-1,1-dimethyl ethyl salts, and examples of these salts were studied with sodium borohydride. The products from these reductions provide interesting applications to organic syntheses.[4]

Pyridine was reported to undergo reaction with triphenylmethylcarbonium ion to form a pyridinium salt with the large triphenylmethyl group on the nitrogen. An improved method of synthesis was used to prepare 1-triphenylmethylpyridinium fluoroborate (**1**) in yields of about 85%. The reduction of 1-triphenylmethylpyridinium fluoroborate (**1**) with sodium borohydride gave a mixture of the 1,4- and 1,2-dihydropyridine (**2** and **3**) which did not undergo further reduction. Addition of water to the solution caused the precipitation of the dihydropyridines which then could be analyzed by the nuclear magnetic resonance spectrum. In this manner a very high yield of crude material was obtained which was shown to be 23% of the 1,4-dihydropyridine (**2**) and 77% of the 1,2-dihydropyridine (**3**). The compounds rapidly underwent decomposition on warming to give pyridine and triphenylmethane. The presence of 1,2-dihydropyridine (**3**) as the predominant product was further demonstrated by the successful Diels–Alder reaction using *N*-phenylmaleimide to give **4**. The stereochemistry and structure of **4** are based on the nmr spectrum. The endo stereochemistry would be expected, and the low-field signal for 2 hydrogens centered at 3.1 ppm suggest that these hydrogens are anti to the double bond.

The attempts to carry out similar reactions with substituted pyridines were less successful. The preparations of 1-triphenylmethyl-3-cyanopyridinium fluoroborate and 1-triphenylmethyl-3-methylpyridinium fluoroborate were accomplished; however, the products could not be obtained in analytical purity. The sodium borohydride reduction reactions on the crude compounds indicated the presence of large amounts of 1,2-dihydropyridine; however, the results were not conclusive.

A second series of pyridinium salts were formed by the reaction of 2-chloro-2-methylpropionaldehyde oxime, formed from isobutylene and nitrosyl chloride, with pyridines. The 1-(2-hydroxyimino-1,1-dimethylethyl)pyridinium chlorides prepared by this method are shown in Table I.

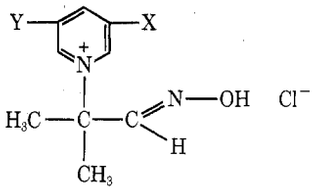
The sodium borohydride reduction of these pyridinium

Table I
1-(2-Hydroxyimino-1,1-dimethylethyl)pyridinium Chlorides

Salt[a] of	Procedure	Yield, %	Mp, °C (dec)	Formula	Anal. Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
Pyridine (5a)	A	95	164–165	$C_9H_{13}ClN_2O$	53.86	6.53	13.96	53.72	6.66	14.07
	B	100	172.5–174							
3-Picoline (5b)	A	98	151–153	$C_{10}H_{15}ClN_2O$	55.94	7.04	13.05	55.88	7.00	12.98
	B	97	153–154.5							
3,5-Lutidine (5c)	A	96	155–156	$C_{11}H_{17}ClN_2O$	57.76	7.44	12.49	57.77	7.69	12.38
	B	84	155–156							
3-Methoxypyridine (5d)	B	98	116–117	$C_{10}H_{15}ClN_2O_2$	52.06	6.55	12.14	48.36	6.87	11.15
3-Methanesulfonyloxypyridine (5e)	B	56	121–121.5	$C_{10}H_{15}ClN_2O_4S$	40.74	5.13	9.50	40.43	4.97	9.26

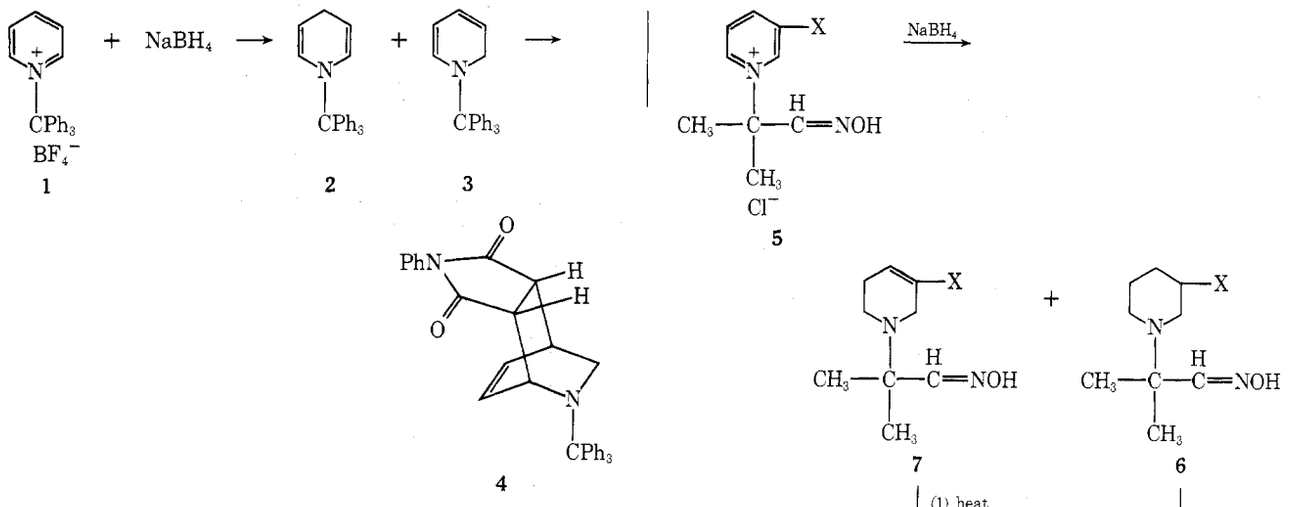
[a] The nmr spectra of these compounds are in complete agreement with the proposed structures.

Table II
Reduction of 1-(2-Hydroxyimino-1,1-dimethylethyl)pyridinium Chloride



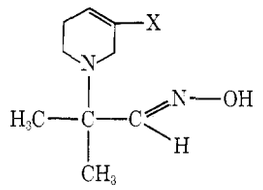
Number	X	Y	In EtOH (%) Yield	Piperidine 6	Tetrahydro 7	In water (%) Yield	Piperidine 6	Tetrahydro 7
5a	H	H	85	1	99	89	15	85
5b	CH_3	H	94	1	98	88	19	74
5c	CH_3	CH_3	83	5	95[a]	88	9	91
5d	CH_3O	H	78	*b*		77	*b*	99
5e	CH_3SO_3	H		*b*		81	*b*	

[a] The product was not purified and characterized except *via* spectral analysis. [b] Some dihydropyridine was present as seen in the nmr.



salts gave tetrahydropyridine and piperidine derivatives which underwent decomposition on heating. The corresponding piperidine (**6**) or tetrahydropyridine (**7**) was converted to the *N*-formyl derivative (**8** or **9**) quantitatively by treating them with methyl formate. The gas–liquid chromatographic analysis of these *N*-formyl derivatives is shown in Table II. The relative yields of the tetrahydropyridine and piperidines seem to be dependent upon the conditions under which the hydrogenations were conducted as

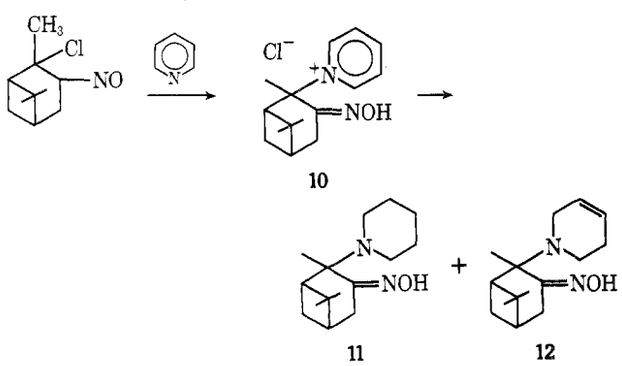
Table III
Properties of Tetrahydropyridines from Table II



Number	X	Mp, °C	Molecular Formula	Anal. Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
7a	H	115–116	$C_9H_{16}N_2O$	63.87	10.12	16.55	64.04	9.88	16.66
7b	CH_3	106–107	$C_{10}H_{18}N_2O$	65.89	9.96	15.37	65.96	10.19	15.56
7d	CH_3O	132–133	$C_{10}H_{18}N_2O_2$	60.58	9.16	14.14	60.71	9.44	14.26
7e	CH_3SO_3	142–143	$C_{10}H_{18}N_2O_4S$	45.78	6.92	10.68	45.93	7.04	10.88

well as upon the structure of the compound (Table III). The use of water or aqueous solutions promoted the formation of piperidines presumably from 1,4-dihydropyridine intermediates. The use of alcoholic solvents, on the other hand, decreased the amount of this product and promoted the formation of only tetrahydropyridines from the 1,2-dihydropyridine. These results suggest that either the nature of the hydride ion causing the reduction or the degree of solvent separation of ion pairs may have very significant bearing on the relative amounts of 1,4- and 1,2-dihydropyridines formed as intermediates.

The related salt (**10**) of pyridine was prepared from the nitrosyl chloride addition product[5] of α-pinene. The salt (**10**) was converted to the known piperidine derivative **11**[6] by catalytic hydrogenation; however, analysis of the mixture of **11** and the tetrahydropyridine (**12**) proved to be difficult by nuclear magnetic resonance. The isolated yield of **12** was 65% giving a lower limit for the partial reduction product.



10

11 **12**

The results of these experiments have synthetic significance in addition to the importance relative to the mode of reaction of borohydride with pyridinium ions. It will be noted that in the case of triphenylmethyl derivatives the reaction stops at the dihydropyridine stage and thermal decomposition of the dihydropyridine returns the compound to its original, aromatic oxidation state. It appears possible that the triphenylmethyl substituent on the pyridine nitrogen could provide a method of protecting this aromatic system during reactions in other parts of the molecule.

The use of the nitrosyl chloride adducts to alkenes to form salts with the pyridine ring provides a method of preparing 1-unsubstituted tetrahydropyridines. It is possible to convert a substituted pyridine to the corresponding 1-(2-hydroxyimino-1,1-dimethylethyl) derivative, which then on reduction with sodium borohydride would give the desired tetrahydropyridine (**7**). This compound on thermal decomposition or heating with base would produce the 1-unsubstituted tetrahydropyridine. Since reduction of pyridines and acid salts of pyridines to tetrahydropyridines is difficult to achieve, this route provides a convenient method of preparation of such compounds.

Experimental Section

Preparation of 1-Triphenylmethylpyridinium Fluoroborate (1). A solution of 17 g of triphenylmethyl fluoroborate in 200 ml of dry methylene chloride was added to 10 ml of pyridine in 50 ml of dry methylene chloride. The orange color of the triphenylmethylcarbonium ion disappeared immediately, and after a few minutes, solid began to precipitate. The solid was collected to give 17.9 g (85%) of 1-triphenylmethylpyridinium fluoroborate (**1**), mp 177–186° dec.

Anal. Calcd for $C_{24}H_{20}BF_4N$: C, 70.43; H, 4.92; N, 3.42. Found: C, 70.36; H, 4.83; N, 3.50.

Sodium Borohydride Reduction of 1-Triphenylmethylpyridinium Fluoroborate. To a suspension of 4 g of sodium borohydride in 50 ml of absolute ethanol was added 4 g of 1-triphenylmethylpyridinium fluoroborate (**1**). The suspension was stirred for 10 min and 100 ml of water was added. The solid which precipitated was removed by filtration and washed with methanol to give 3.05 g (96%) of a mixture of 1-triphenylmethyl-1,4- and 1,2-dihydropyridines. Analysis of the nmr spectrum showed the mixture to be 23% 1,4-dihydro- (**2**) and 77% 1,2-dihydropyridine (**3**). Recrystallization of the mixture from ether or methylene chloride–methanol gave an analytical sample of the mixture, mp 80–150°.

Anal. Calcd for $C_{24}H_{21}N$: C, 89.12; H, 6.55; N, 4.33. Found: C, 88.78; H, 6.42; N, 4.20.

A solution of 2.87 g of crude 1-triphenylmethyl-1,2-dihydropyridine (**3**) in 200 ml of ether was mixed with 2 g of *N*-phenylmaleimide in 25 ml of ether. The solution was concentrated to a total of 150 ml and allowed to stand for 12 hr. The volume was reduced to 30 ml and allowed to stand for 2 days in a refrigerator. The solid which separated was collected and washed with ether to give 1.2 g (27%) of the Diels–Alder adduct (**4**), mp 203–214°. Recrystallization of the solid from methanol–methylene chloride gave an analytical sample of **4**: mp 226–228.5°; nmr δ 7.0–7.7 ppm (m, 20 H, ArH), 5.61 (t, J = 6.5 Hz, 1 H, C=CH), 5.28 (dd, J = 8.0 and 6.5 Hz, 1 H, C=CH), 4.39 (m, 1 H, bridge C—H), 3.72 (dd, J = 8.0 and 4.0 Hz, 1 H, bridge C—*H*), 3.40 (broad d, J = 10 Hz, 1 H, $C(H_{en})H_{ex}$), 3.1 (m, 2 H, –*CH*C*H*–), 2.43 (broad d, J = 10 Hz, 1 H, $C(H_{en})H_{ex}$).

Anal. Calcd for $C_{34}H_{28}N_2O_2$: C, 82.33; H, 5.68; N, 5.64. Found: C, 82.11; H, 5.67; N, 5.57.

3-Hydroxypyridine Methanesulfonate. A solution of 108.5 g of 3-hydroxypyridine hydrobromide and 50 g of sodium hydroxide in 250 ml of water was cooled and treated with 21 g of methanesulfonyl chloride keeping the temperature below 15°. After the addition was complete, stirring was continued for 30 min and the mix-

ture was seeded. The solid which separated was collected by filtration and recrystallized from 750 ml of water with decolorization with charcoal. After seeding, 78.5 g (64%) of 3-hydroxypyridine methanesulfonate, mp 59–60°, was obtained.

Anal. Calcd for $C_6H_7NO_3S$: C, 41.61; H, 4.07; N, 8.09. Found: C, 41.60; H, 3.95; N, 8.02.

1-Nitroso-2-chloro-2-methylpropane. A solution of 76 g of isobutylene in 300 ml of methylene chloride was cooled and 84.0 g of nitrosyl chloride was added at temperatures below 10°. The mixture was cooled in a Dry Ice–acetone bath and the solid which separated was collected and washed with cold ether. The filtrates were concentrated and further solid was collected. The crude solid, 129 g, was dissolved in a minimum of methylene chloride and the solution was filtered and diluted with an equal volume of petroleum ether (bp 30–60°). The product was isolated as a series of crops; first, 77.7 g mp 105–106°, and second, 35.7 g, mp 81–102°.

Preparation of 1-(2-Hydroxyimino-1,1-dimethyl)pyridinium Chloride Derivatives (5). Procedure A. The 1-nitroso-2-chloro-2-methylpropane was mixed with a 6–8-fold excess of pyridine derivative and the temperature maintained near 60° by heating or cooling as necessary. After about 1–1.5 hr the reaction mixture was cooled and the solid which separated was washed with benzene and air dried. The properties for **5** are given in Table I.

Procedure B. A solution of 1-nitroso-2-chloro-2-methylpropane in acetonitrile was cooled and the pyridine was added. The mixture was allowed to stand, and the product was crystallized from solution. The solid was separated by filtration and washed with cold solvent and dried. See Table I for the properties of **5.**

General Method for Reduction of 1-(2-Hydroxyimino-1,1-dimethylethyl)pyridinium Salts (5). A suspension or solution of 0.05 mol of the 1-(2-hydroxyimino-1,1-dimethylethyl)pyridinium salt (**5**) in 150 ml of absolute ethanol was cooled on an ice bath to about 10°. To this suspension was added 3.8 g (0.1 mol) of sodium borohydride in small portions so that the temperature did not rise over 15°. When the addition was complete, the mixture was stirred at room temperature for 30 min, the solution was made acidic with concentrated hydrochloric acid, and any borate salts which separated were removed by filtration. The solution was evaporated under reduced pressure to about 20 ml and the residue was dissolved in 150 ml of water and made basic by the addition of ammonium hydroxide. In most cases, the oil which separated crystallized. If the product did not crystallize, the aqueous mixture was extracted with ether and the ether extracts were dried over magnesium sulfate, filtered, and reduced to dryness.

Crude yields were obtained from these residues. The crude product was sampled by removing 0.5–1 g of material and subjecting this sample to pyrolytic distillation at room temperature.

The distillate was collected in a container partly filled with methyl formate. After several hours standing at room temperature, the excess methyl formate was removed by evaporation on a steam bath. The residue was analyzed by glc on a 1-m column of Carbowax 20M on Chromosorb W. The temperatures ranged from 130° for pyridine to 160° for methoxypyridine. The results are shown in Table II.

Preparation of (*d*)-*N*-(3-Oximino-2-pinanyl)pyridinium Chloride (10). A solution of 20 g (0.16 mol) of *d*-α-pinene in 250 ml of methylene chloride was cooled to about −20° and treated with 10 g of gaseous nitrosyl chloride. The temperature was not allowed to rise over 0°. The reaction mixture was stirred for 15 min at 0° and then for 15 min at −20°. The precipitate which formed was racemic adduct and was removed by filtration, and the filtrate was cooled to −78° on a Dry Ice–acetone bath for 1 hr. The cold blue-green solution was filtered again. The filtrate was treated with 50 ml of pyridine and allowed to warm to room temperature. The methylene chloride was removed under reduced pressure at room temperature. The gummy precipitate which had formed was isolated by filtration and washed thoroughly with pyridine. Washing with pyridine converted the gummy material into a fine crystalline precipitate. The precipitate was dissolved in a minimum amount of water and acetone and the first crop of solid was 3.6 g of largely racemic **10,** mp about 100° dec, $[\alpha]^{22}D$ +61°.

The filtrates were diluted with an equal volume of acetone, and the mixture was cooled to −10°. The crystals were removed by filtration and washed with acetone to give 4.1 g of the dextrorotatory **10,** mp about 100° dec, $[\alpha]^{22}D$ +168°.

Anal. Calcd for $C_{15}H_{21}ClN_2O$: C, 64.16; H, 7.54; N, 9.98. Found: C, 64.14; H, 7.67; N, 10.01.

Catalytic Hydrogenation of *N*-(3-Oximino-2-pinanyl)pyridinium Chloride (10). A solution of 1.4 g of *N*-(3-oximino-2-pinanyl)pyridinium chloride (**10**) in 25 ml of glacial acetic acid was treated with 0.1 g of platinum oxide and hydrogenated for 6 hr under a positive pressure of hydrogen. During the course of the hydrogenation a precipitate appeared. The precipitate and platinum were removed by filtration and the organic precipitate was dissolved in methanol–water. The aqueous methanolic solution was made basic with sodium carbonate and extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate and filtered. Evaporation of the solvent gave a crude yield of 1.1 g (91%) of *N*-(3-oximino-2-pinanyl)piperidine (**11**). Recrystallization from ligroin gave pure **11,** mp 119–122° (lit.[6] 118–119°).

Sodium Borohydride of *N*-(3-Oximino-2-pinanyl)pyridinium Chloride (10). A solution of 1.4 g of **10** in 25 ml of methanol cooled in an ice bath was treated with 1.5 g of sodium borohydride in small portions. When the addition was complete, the solution was allowed to warm to room temperature overnight. The inorganic precipitate was removed by filtration and methanol was evaporated under reduced pressure. The residue was taken up in water and extracted with ether. The ether extracts were dried over magnesium sulfate, filtered, and evaporated to dryness. The residue was dissolved in 60–75° ligroin, and the solution was treated with Norite, filtered, and set aside to crystallize. Two crops were obtained which were combined and recrystallized from ligroin to yield 0.8 g (65%) of the tetrahydro derivative (**12**), mp 102–105°.

Anal. Calcd for $C_{15}H_{24}N_2O$: C, 72.54; H, 9.74; N, 11.28. Found: C, 72.57; H, 10.06; N, 11.35.

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Registry No.—**1,** 26156-84-3; **2,** 52843-62-6; **3,** 52843-63-7; **4,** 52843-64-8; **5a,** 52843-65-9; **5b,** 52920-66-8; **5c,** 52843-66-0; **5d,** 52920-67-9; **5e,** 52843-67-1; **7a,** 52843-68-2; **7b,** 52843-69-3; **7d,** 52843-70-6; **7e,** 52843-71-7; **10,** 52843-72-8; **11,** 52843-73-9; **12,** 52843-74-0; triphenylmethyl fluoroborate, 341-02-6; pyridine, 110-86-1; sodium borohydride, 16940-66-2; *N*-phenylmaleimide, 941-69-5; 3-methanesulfonyloxypyridine, 52843-75-1; 3-hydroxypyridine HBr, 52843-76-2; methanesulfonyl chloride, 124-63-0; 1-nitroso-2-chloro-2-methylpropane, 44580-06-5; isobutylene, 115-11-7; nitrosyl chloride, 2696-92-6; *d*-α-pinene, 7785-70-8; 3-picoline, 108-99-6; 3,5-lutidine, 591-22-0; 3-methoxypyridine, 7295-76-3.

References and Notes

(1) This research was presented in part at the 4th Heterocyclic Symposium Brno, Czechoslovakia, Sept 22–24, 1969.
(2) Author to whom correspondence should be addressed.
(3) R. E. Lyle and P. Anderson, *Advan. Heterocycl. Chem.*, **6,** 45 (1966).
(4) (a) R. E. Lyle, P. S. Anderson, and W. E. Krueger, *Tetrahedron Lett.*, 4011 (1965); (b) M. Ferles and O. Koccan, *Collect. Czech. Chem. Commun.*, **39,** 1210 (1974).
(5) J. L. Simonsen, "The Terpines," Vol. II, University Press, Cambridge, England, 1957, p 179.
(6) O. Wollack, *Justus Liebigs Ann. Chem.*, **245,** 253 (1888).
(7) Melting points were determined using a Thomas-Hoover capillary melting point apparatus or a Mel-Temp apparatus and were not corrected for thermometer stem exposure. Elemental analyses were determined using an F&M Model 185 C, H, and N analyzer. Infrared spectra were determined using Perkin-Elmer Model 137 or 337 spectrometers with samples prepared as mulls or KBr pellets. The ultraviolet absorption spectra were measured on a Cary 15 spectrometer in the solvent indicated, and the nuclear magnetic resonance spectra were determined using a Varian A-60 spectrometer.