phenylhydrazine containing 100 mg of HCl and the mixture was refluxed overnight. Filtration gave 65 mg (55%) of acetone 2,4-dinitrophenylhydrazone, mp 122–124°

Compound **10** melted at 130–138°: molecular ion *m/e* 194; nmr (DMSO-d_6) δ 2.32 (s, 3, NCH_3), 3.23 (s, 2, CH_2), 4.88 (d, 1, -NCHN-), 6.27 (t, 1, NH), 7.00 (d, 1-CH=C-), 7.66 (d, 2, aromatic), 8.17 (d, 2, aromatic). Deuteration caused the peak at δ 6.27 to disappear and the peaks at 4.88 and 7.00 to become singlets.

Acid Hydrolysis of 10.—Compound **10** (125 mg) was suspended in a vigorously stirred solution of 10 ml of 10% HCl. The orange color of **10** gradually turned to a pale yellow or sometimes tan color. The reaction mixture was filtered to give 50 mg (78%) of *p*-nitrobenzaldehyde.

Conversion of 1a to 11.—To a solution of 540 mg (1.75 mmol) of **1a** in 50 ml of C_6H_6 was added 1 g of 85% *m*-chloroperbenzoic acid. The mixture was kept at room temperature for 2 days and then it was washed several times with a saturated solution of Na_2CO_3. The benzene layer was dried and filtered. Evaporation of the C_6H_6 gave 260 mg (45%) of **11**. Several recrystallizations from methanol gave **11**, mp 161–163°.

Anal. Calcd for $C_{18}H_{17}N_3O_3$: C, 66.88; H, 5.30; N, 12.99. Found: C, 67.10; H, 5.30; N, 12.69.

Reduction of 11 to 12.—To 646 mg (1.99 mmol) of **11** in 40 ml of a 1:1 mixture of absolute ethanol and 2-propanol was added 1 g of $NaBH_4$. The reaction mixture was stirred at 40° overnight. The solvents were evaporated and water and $CHCl_3$ were added to the residue. The chloroform layer was separated and dried over $MgSO_4$. Evaporation of the $CHCl_3$ and recrystallization of the residue from CCl_4 gave 412 mg (60%) of **12**, mp 165–166°.

Anal. Calcd for $C_{18}H_{19}N_3O_3$: C, 66.45; H, 5.89; N, 12.91. Found: C, 66.03; H, 5.68; N, 12.71.

Conversion of 12 to 11.—To a mixture of 108 mg of **12** in 30 ml of C_6H_6 was added 36 mg of *tert*-butyl hypochlorite. The reaction mixture was stirred for 15 min. The solvent was evaporated to give a 97% yield of **11**.

Reaction of 11 with *N*-Phenylmaleimide.—A mixture of 270 mg (0.832 mmol) of **11** and 144 mg (0.831 mmol) of *N*-phenylmaleimide in 12 ml of dry toluene was refluxed for 2.5 hr. Evaporation of the solvent and recrystallization of the residue from 2-propanol gave 267 mg (65%) of **13**, mp 257–259°.

Anal. Calcd for $C_{28}H_{24}N_4O_5$: C, 67.07; H, 4.97; N, 11.51. Found: C, 67.28; H, 5.01; N, 11.55.

Reaction of 11 with Diethyl Azodicarboxylate (Method A).—A mixture of 356 mg (1.10 mmol) of **11** and 187 mg (1.07 mmol) of diethyl azodicarboxylate in 12 ml of toluene was refluxed for 2 hr. Evaporation of the solvent and recrystallization from 1-propanol gave 422 mg (79%) of **14**, mp 155–157°.

Anal. Calcd for $C_{24}H_{27}N_5O_7$: C, 57.93; H, 5.46; N, 14.06. Found: C, 57.98; H, 5.58; N, 14.08.

Conversion of 11 to 14 (Method B).—A mixture of 452 mg of **11** and 244 mg of diethyl azodicarboxylate in 150 ml of C_6H_6 was irradiated for 2 hr. Evaporation of the solvent and slurrying the residue in a small quantity of C_2H_5OH gave 447 mg of **14**. The melting points and infrared spectra of **14** obtained by methods A and B were identical. A control run of 220 mg of **11** and 140 mg of diethyl azodicarboxylate was allowed to stand for 20 hr at room temperature. Evaporation of the solvent and slurrying the residue in EtOH resulted in the recovery of 183 mg of **11**.

Oxidation of 15 to 14.—A mixture of 350 mg of **15** and 743 mg of 85% *m*-chloroperbenzoic acid in 15 ml of C_6H_6 was allowed to stand at room temperature for 15 hr. The benzene layer was washed twice with Na_2CO_3 solution and twice with H_2O and dried over $MgSO_4$. The C_6H_6 was evaporated and the glassy residue was slurried with a small quantity of EtOH. The EtOH was evaporated and a small quantity of EtOH was again added. Constant scratching of the walls of the container with a glass rod gave 62 mg of **14**, mp 152–154°, having the same ir spectrum as **14** obtained from methods A and B above.

Registry No.—**1a**, 13591-65-6; **3**, 37500-32-6; **5**, 37488-69-0; **6**, 37488-70-3; **8**, 37488-71-4; **10**, 37488-72-5; **11**, 37528-70-4; **12**, 37488-73-6; **13**, 37488-74-7; **14**, 37500-33-7; diazomethane, 334-88-3.

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Polycyclic Aziridines. 1-Alkyl-6-keto-1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-*b*]azirines

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A previously reported investigation[2b] of the reaction of 2,3-dibromo-3-phenylindanone with cyclohexyl and methyl amines, respectively, to form 1-alkyl-6-(alkylimino)-1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-*b*]-azirines (**3**) has been extended to include similar reactions with other primary amines. Schiff base formation in this series is catalyzed by the presence of the amine hydrobromide salt. Hydrolysis of the Schiff bases to the previously unknown tricyclic aziridinyl ketones (**8**) can be accomplished on a silica gel column. The aziridinyl ketones undergo thermal valence tautomerism and yield 1,3-dipolar cycloaddition products similar to those observed with the analogous Schiff bases.

The reactions of the bromine derivatives of cyclic α,β-unsaturated ketones with primary and secondary amines have been the subjects of previous investigations in this laboratory.[1] Aziridinyl ketones are the usual products when primary amines are employed. It has been shown that 2,3-dibromo-3-phenylindanone (**1**) and 2-bromo-3-phenylindenone (**2**) react with cyclohexyl or methyl amine to give the Schiff base derivative (**3a,b**) of the expected aziridinyl ketone.[2] Previous attempts to obtain the aziridinyl ketone from its Schiff base by partial hydrolysis have resulted in ring opening and formation of either the diketone **4** or the α-aminoindenone **5**.[2b]

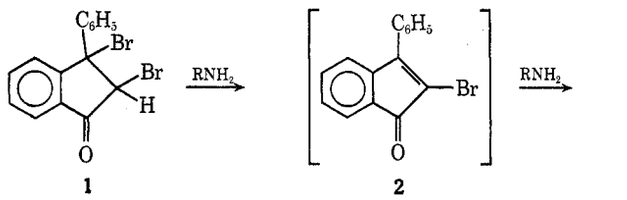
This paper reports the characterization of additional aziridinyl Schiff bases in the 3-phenylindenone-1 system and an unexpectedly simple method of obtaining the corresponding aziridinyl ketones.

(1) (a) N. H. Cromwell and R. D. Campbell, *J. Org. Chem.*, **22**, 520 (1957), and previous papers in the series; (b) A. Hassner and N. H. Cromwell, *J. Amer. Chem. Soc.*, **80**, 901 (1958); (c) E. M. Wu, Ph.D. Thesis, University of Nebraska, 1966; (d) B. D. Pearson, R. P. Ayer, and N. H. Cromwell, *J. Org. Chem.*, **27**, 3038 (1962).

(2) (a) A. E. Pohland, M. C. McMaster, R. C. Badger, and N. H. Cromwell, *J. Amer. Chem. Soc.*, **87**, 2510 (1965); (b) N. H. Cromwell and M. C. McMaster, *J. Org. Chem.*, **32**, 2145 (1967).

Results and Discussion

Schiff Base Formation.—2,3-Dibromo-3-phenylindanone (**1**) reacts readily at room temperature with benzyl, cyclohexyl,[2b] ethyl, isopropyl, and methyl[2b] amines to yield the appropriate 1-alkyl-6-(alkylimino)1,1a,-6,6a-tetrahydro-1a-phenylindeno[1,2-*b*]azirines (**3a–e**). All except the ethyl derivative have been obtained as white or nearly white crystalline solids by direct or fractional crystallization from benzene–petroleum ether (bp 60–70°) solutions. The ethyl derivative has been obtained only as a yellow-orange colored oil, identified through ample spectral and chemical evidence. Reaction of **1** with *tert*-butylamine resulted only in dehydrohalogenation to 2-bromo-3-phenylindenone (**2**). No trace of the anticipated Schiff base or of any aziridine was detected in the *tert*-butylamine reaction mixture, even when elevated temperatures, excessive amounts of the amine, or sealed tube techniques were employed. This must be attributed to the steric bulk of the *tert*-butyl group, particularly in light of the fact that benzylamine, a weaker base, did react readily to produce an aziridinyl Schiff base.



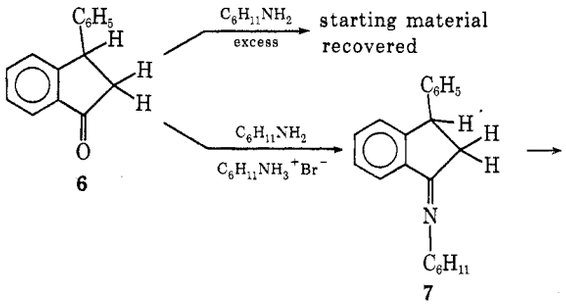
1 **2**

a, R = C_6H_{11}
b, R = CH_3
c, R = CH_2CH_3
d, R = $CH(CH_3)_2$
e, R = $CH_2C_6H_5$

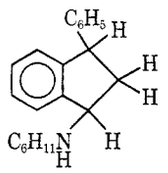
3

Identification of these aziridine systems is simplified by the characteristic medium to intense C=N absorption in the infrared spectrum near 1660 cm^{-1}. Integration of the pmr spectrum clearly indicates the presence of two alkyl groups. The presence of the aziridine ring is revealed by a characteristic singlet due to the bridgehead proton at τ 6.8. Mass spectral and ultraviolet data are in all cases consistent with the reported structures. Further evidence for the established structural assignments is provided by the hydrolysis of **3** to the diketone **4** using concentrated sulfuric acid.

The above reaction proceeds *via* dehydrohalogenation of the dibromide to the α-bromo-α,β-unsaturated ketone, which then undergoes addition of the amine to form the α-bromo-β-amino ketone.[2b] In the case of primary amines, ring closure to form the aziridine ring with loss of HBr can occur. The sequential step of Schiff base formation remains uncertain, but experiments indicate that it occurs after the initial dehydrohalogenation of the dibromide. Formation of the Schiff base is catalyzed by the presence of the amine hydrobromide salt in the reaction mixture. The reaction of 3-phenylindanone-1 (**6**) with cyclohexylamine resulted in 90% recovery of unreacted starting material, whereas the same reaction run in the presence of cyclohexylamine hydrobromide gave a 71% yield of the Schiff base, 1-cyclohexylimino-3-phenylindan (**7**). Thus the hydrobromide salt appears necessary for Schiff base formation to proceed. This is further supported by the fact that nearly quantitative yields of the 2-bromo-3-phenylindenone can be recovered immediately following addition of the amine to the dibromide solution, with no evidence for the existence of either the Schiff base or the aziridine in the reaction mixture.

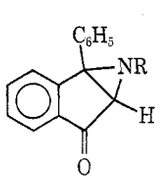


6 **7**

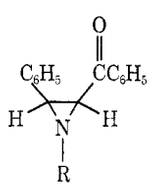


11

Hydrolysis.—During the course of study of this new aziridinyl Schiff base system, it was desired to obtain the corresponding ketones **8** for comparison with their acyclic analogs **9**, to see whether they might be involved in the reported rearrangement of *cis*-1-cyclohexyl-2-phenyl-3-benzoylethylenimine to 2-cyclohexylamino-3-phenylindenone (**5a**).[2a]



8

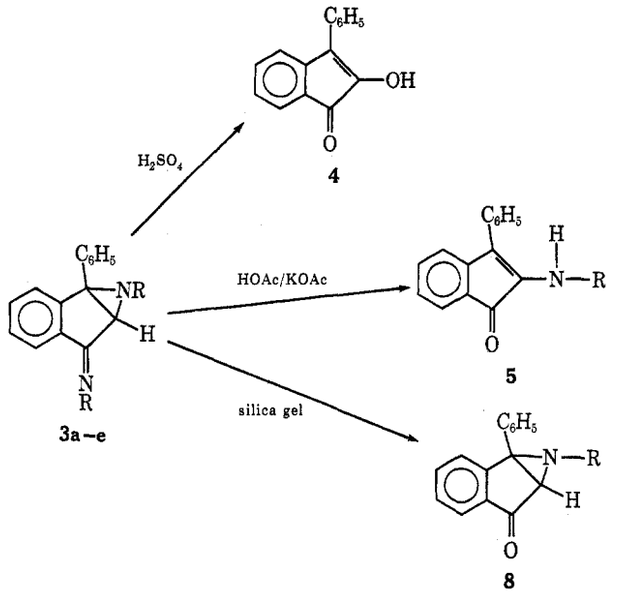


9

Methods which may be used for the hydrolysis of the imino group are severely limited by the reactivity and facile opening of the aziridine ring and the ability of the system to undergo a valence tautomerism to an isoquinolinium imine[3] at elevated temperatures. In addition, the Schiff base seems to exhibit a marked degree of stability not always associated with imines, owing to conjugation with the phenyl ring of the indanone system.[4]

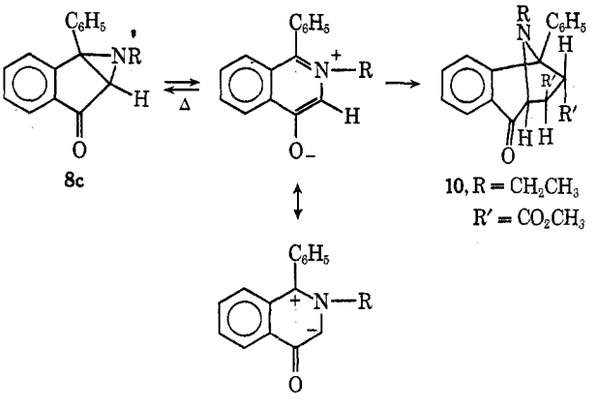
The equilibrium involving Schiff base formation for the indanone system lies almost completely to the side of the imine, and attempts to force the reaction in the reverse direction were initially unsuccessful. Schiff base **3a** would not react with water either with or without the presence of the amine hydrobromide salt to yield any trace of the ketone. Acid hydrolysis had already been shown to lead to other products.[2b]

(3) (a) J. W. Lown and K. Matsumoto, *Chem. Commun.*, 692 (1970); (b) *J. Org. Chem.*, **36**, 1405 (1971).
(4) J. Lown and K. Matsumoto, *Can. J. Chem.*, **49**, 3443 (1971).



When attempts to crystallize the ethyl derivative **3c** from its reaction mixture were unsuccessful, column chromatography on silica gel produced a nearly quantitative conversion of the aziridinyl Schiff base to the corresponding aziridinyl ketone (**8c**, R = Et). The cyclohexyl, methyl, and ethyl aziridinyl ketones (**8a–c**), crystallized from methanol–water, have been obtained as solids to date from the hydrolysis of the corresponding Schiff bases on silica gel columns. This class of ketones is characterized by great instability to air and light, turning from colorless to pale yellow during attempts at recrystallization, or upon standing at room temperature. The structural assignments are supported by ir, pmr, mass, and uv spectroscopy. Hydrolysis on silica gel columns may provide a new method for the hydrolysis of Schiff bases in the presence of other reactive functional groups. The pmr spectra are nearly identical with those of the Schiff bases, except for the absence of one alkyl group and slight shifts in the positions of the bridgehead proton. Nitrogen inversion was observed at room temperature for the methyl aziridinyl ketone **8b**. Nitrogen inversion was not observed in the corresponding Schiff base **3b**, suggesting that the presence of the imino alkyl group may, through steric hindrance, lock the *N*-alkyl group of the aziridine into a preferred conformation. Further evidence for the assigned structures is provided by hydrolysis to the diketone **4** with concentrated sulfuric acid. Column chromatography on alumina gave similar results, although with lesser efficiency.

Valence Tautomerism.—Lown and Matsumoto have reported the thermally disallowed valence tautomerization of the iminoaziridines to isoquinolinium imines[3] and an analogous tautomerism for the isoelectronic epoxyindanone system.[4] We wish to report that our new ethyl aziridinyl ketone **8c** also undergoes a thermally disallowed valence tautomerization, as shown by trapping of the carbonyl ylide in a 1,3-dipolar cycloaddition with dimethylfumarate. A mixture of isomers is obtained in which the endo product **10** appears to predominate. Further studies are underway to establish the course of similar cycloadditions to the valence tautomer. The intermediate qualifies as an *azomethine ylide* 1,3 dipole without a double bond but with internal octet stabilization.[5]



The reduction of the C=N bond in 1-cyclohexylimino-3-phenylindan (**7**) to 1-cyclohexylamino-3-phenylindan (**11**) with sodium borohydride was readily accomplished, but a similar reaction attempt with the aziridinyl Schiff base **3a** gave an impure product.

Experimental Section[6]

3,3-Diphenylpropionic Acid.[7]—3,3-Diphenylpropionic acid was prepared in 98% yield according to the method of Pfeiffer and de Waal.

3-Phenyl-1-indanone.[8]—3-Phenyl-1-indanone was prepared by the method of Kohler in 92% yield.

2,3-Dibromo-3-phenylindanone[9] (**1**).—2,3-Dibromo-3-phenylindanone was prepared in 92% yield according to the method of Weisz and Luft.

1-Cyclohexyl-6-(cyclohexylimino)-1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-*b*]azirine (3a).[2b]—This compound was prepared as described by Cromwell and McMaster.

1-Methyl-6-(methylimino)-1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-*b*]azirine (3b).[2b]—This compound was prepared as described by Cromwell and McMaster.

1-Ethyl-6-(ethylimino)-1,1a,6,6a-tetrahydro-1a-phenylindeno-[1,2-*b*]azirine (3c).—A 5-g (0.0137 mol) sample of the dibromo ketone **1** was dissolved in 75 ml of dry ether, to which was added 4.5 ml (0.0685 mol) of $EtNH_2$. After 3 days of stirring in a foil-wrapped flask at room temperature, 3.30 g (96.3%) of ethylamine hydrobromide was filtered from the solution. The filtrate was washed with water and dried over $CaSO_4$, and solvent was evaporated to leave a brown-orange colored oil which could be neither decolorized with charcoal nor crystallized: $\nu_{C=N}^{CCl_4}$ 1660 cm^{-1}; pmr τ 2.23–2.93 (9 H, aromatic multiplet), 6.12–6.76 (2 H, $=NCH_2$ multiplet), 6.81 (1 H, bridgehead singlet), 7.43–8.18 (2 H, aziridine NCH_2 multiplet), and 8.54–9.09 (6 H, two CH_3 groups, overlapping triplets).

1-Isopropyl-6-(isopropylimino)-1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-*b*]azirine (3d).—A 5-g (0.0137 mol) sample of the dibromo ketone **1** was dissolved in 50 ml of dry benzene, to which was added 6 ml (0.704 mol) of isopropylamine. After 3 days of stirring in a foil-wrapped flask at room temperature, 125 ml of dry ether was added to precipitate 3.5 g (91.2%) of the isopropylamine hydrobromide, mp 162–164°. Filtration gave a brown-colored solution, which was washed with water and dried over $CaCl_2$, and the solvent was evaporated to leave a brown, sticky oil which crystallized after standing in the freezer for 2 days with occasional stirring. Recrystallization from petroleum ether (bp 60–70°) gave 3.0 g of **3d** (72.0%) as a white, crystalline solid:

(5) (a) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565 (1963); (b) P. B. Woller and N. H. Cromwell, *J. Org. Chem.*, **35**, 888 (1970).

(6) Infrared spectra were obtained in carbon tetrachloride solutions using a Perkin-Elmer 237 instrument, unless otherwise noted. Pmr spectra were obtained using a Varian A-60 instrument. Ultraviolet spectra were obtained in isooctane using a Cary 14 spectrophotometer. Melting points were determined using the Mel-Temp apparatus.

(7) P. Pfeiffer and H. L. de Waal, *Justus Liebigs Ann. Chem.*, **520**, 185 (1935).

(8) E. P. Kohler, *Amer. Chem. J.*, **31**, 649 (1904).

(9) R. Weisz and S. Luft, *Monatsh. Chem.*, **48**, 338 (1927).

mp 91–92°; molecular ion *m/e* 304; ir $\nu_{C=N}^{CCl_4}$ 1646 cm^{-1}; uv λ_{max} 252 mμ (ε 19,500); pmr τ 2.14–2.86 (9 H, aromatic multiplet), 5.71–6.29 (1 H, C=NCH), 6.80 (1 H, singlet, bridgehead), 7.68–8.38 (1 H, aziridinyl methine multiplet), and 8.62–9.22 (12 H, multiplet of overlapping doublets from 4 CH_3).

Anal. Calcd for $C_{21}H_{24}N_2$: C, 82.89; H, 7.96; N, 9.21. Found: C, 82.87; H, 7.60; N, 9.51.

1-Benzyl-6-(benzylimino)-1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-*b*]azirine (3e).—A 5-g (0.0137 mol) sample of the dibromoindanone **1** was dissolved in 30 ml of dry benzene, to which was added 8 ml (0.0720 mol) of benzylamine. After stirring for 3 days in the dark at room temperature, 100 ml of dry ether was added and 4.8 g (93.3%) of benzylamine hydrobromide was filtered off, mp 204–210°. After washing with water, drying over $CaCl_2$, and solvent removal, a brown oil remained which was crystallized from benzene–petroleum ether to yield 2.32 g (42.4%) of **3e**: mp 88–89°; ir $\nu_{C=N}^{CCl_4}$ 1659 cm^{-1}; uv λ_{max} 254 mμ (ε 14,400); pmr τ 1.84–2.86 (19 H, aromatic multiplet), 5.10–5.25 (2 H, C=NCH_2–), 6.37–6.66 (2 H, aziridinyl methylene), and 6.60 (1 H, bridgehead).

Anal. Calcd for $C_{29}H_{24}N_2$: C, 86.97; H, 6.04; N, 7.00. Found: C, 87.14; H, 6.06; N, 7.08.

Reaction of 1 with *tert*-Butylamine.—A 3-g (0.00820 mol) sample of the dibromoindanone **1** was dissolved in 11.7 ml of dry benzene to which 4.25 ml (0.0406 mol) of *tert*-butylamine was added. After stirring in the dark at room temperature for 23 days, addition of 50 ml of anhydrous ether precipitated 1.26 g of *tert*-butylamine hydrobromide (99.8% yield for removal of only one bromine atom). The filtrate was washed with water and dried over $CaSO_4$, and solvent was removed to yield 1.80 g (77%) of 2-bromo-3-phenylindenone (**2**), mp 113–114° after recrystallization from MeOH.

This same reaction, attempted with larger excesses of amine, at elevated temperatures, and in a sealed tube resulted in similarly high yields of the same product.

Reaction of 1 with Ammonia.—A 5-g (0.0137 mol) sample of the dibromo-3-phenylindanone **1** was dissolved in 300 ml of anhydrous ether and saturated with NH_3 gas. After stirring for 5 days in the dark at room temperature, 1.2 g of ammonium bromide was filtered from the reaction mixture (89% yield for removal of only one Br atom). Solvent removal left 3.20 g (81.8%) of 2-bromo-3-phenylindenone (**2**), mp 113–114° after recrystallization from MeOH.

1-Cyclohexylimino-3-phenylindan (7).—A 16-g (0.0769 mol) sample of 3-phenylindanone-1 (**6**), 17.6 ml (0.1538 mol) of cyclohexylamine, and 13.8 g (0.0769 mol) of cyclohexylamine hydrobromide were placed in 160 ml of dry benzene and allowed to stir at room temperature in the dark for 4 days. Addition of 480 ml of dry ether precipitated 98.9% of the hydrobromide salt. After filtration and solvent removal, the Schiff base **7** was crystallized from *n*-hexane to yield 15.8 g (71.1%): mp 97–98°; $\nu_{C=N}^{CDCl_3}$ 1648 cm^{-1}; pmr τ 2.17–3.19 (9 H, aromatic multiplet), 5.49–5.75 (1 H, methylene quartet), 6.50–7.55 (2 H, methylene multiplet), and 8.00–9.17 (11 H, cyclohexyl multiplet); uv λ_{max} 248 mμ (ε 17,510), 279.5 (34,800), 287 (46,800), and 297 (43,900).

Anal. Calcd for $C_{21}H_{23}N$: C, 87.15; H, 8.01; N, 4.84. Found: C, 87.00; H, 8.06; N, 4.79.

An identical control experiment in which the cyclohexylamine hydrobromide was not included in the reaction mixture resulted in 90% recovery of unreacted starting materials.

Attempted Reaction of 3a with Water.—A 0.1-g (0.00261 mol) sample of **3a** and 0.096 g (0.00051 mol) of cyclohexylamine hydrobromide were dissolved in a mixture of 20 ml of benzene, 10 ml of ether, and 1 ml of water and stirred in the dark at room temperature for 2 days. The reaction was diluted with 50 ml of ether, washed three times with 25-ml portions of water, and dried over $CaCl_2$. Solvent removal left a yellow oil, recrystallized from petroleum ether to yield 95% of unreacted starting material **3a**. The infrared spectrum of the yellow oil was superimposable on that of the starting material, with only an extremely weak C=O absorption. An identical experiment, conducted without the cyclohexylamine hydrobromide, gave the same results.

1-Ethyl-6-keto-1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-*b*]azirine (8c).—A 3.78-g (0.0137 mol) sample of **3c** was placed on a silica gel column and eluted with successively increasing portions of ether in petroleum ether. A 3.31-g (0.0133 mol) sample of **8c** was obtained (97% yield) as a colorless oil which rapidly turned yellow on exposure to air and light. Recrystallization from MeOH–H_2O gave a pale yellow solid: mp 57–58°; ir $\nu_{C=O}^{CCl_4}$ 1721 cm^{-1}; mass spectrum molecular ion *m/e* 249; pmr τ 2.33–3.00 (9 H, aromatic multiplet), 7.02 (1 H, singlet, bridgehead), 7.17–7.83 (2 H, methylene multiplet), and 8.72–9.13 (3 H, methyl triplet); uv λ_{max} 229 mμ (ε 18,800), 240 (14,400), and 270–280 (3200–2240).

Anal. Calcd for $C_{17}H_{15}NO$: C, 81.89; H, 6.06; N, 5.62. Found: C, 81.87; H, 6.10; N, 5.59.

Hydrolysis of 8c.—A 1.0-g (0.00402 mol) sample of **8c** was dissolved in 50 ml of concentrated H_2SO_4 to give a dark red-brown solution, which was poured into 400 ml of water at 70° and allowed to stir overnight. Filtration yielded 0.73 g (0.00330 mol) of 2-hydroxy-3-phenylindenone (**4**) as a red-brown solid, mp 140–144° (82%). The infrared spectrum was superimposable on that for an authentic sample of the diketone.[10]

1-Cyclohexyl-6-keto-1,1a-6,6a-tetrahydro-1a-phenylindeno-[1,2-*b*]azirine (8a).—A 0.118-g (0.00307 mol) sample of **3a** was placed on a silica gel column and eluted with successively increasing portions of ether in petroleum ether. The product **8a** was obtained as 0.088 g (95%) of a colorless oil which rapidly turned yellow on exposure to air or light. Crystallization from MeOH–H_2O gave a pale yellow solid: mp 103–105°; ir $\nu_{C=O}^{CCl_4}$ 1710 cm^{-1}; mass spectrum molecular ion *m/e* 303; pmr τ 2.27–2.90 (9 H, aromatic multiplet), 7.05 (1 H, bridgehead singlet), and 7.88–9.35 (11 H, cyclohexyl multiplet).

Anal. Calcd for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62. Found: C, 83.00; H, 7.44; N, 4.26.

1-Methyl-6-keto-1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-*b*]-azirine (8b).—A 0.512-g (0.00207 mol) sample of **3b** was placed on a silica gel column and eluted with successively increasing portions of ether in petroleum ether. The product **8b** was obtained as 0.292 g (60%) of a colorless oil which rapidly turned yellow on exposure to air or light. Crystallization from MeOH–H_2O gave a white solid: mp 109–110°; ir $\nu_{C=O}^{CCl_4}$ 1718 cm^{-1}; mass spectrum molecular ion *m/e* 235; pmr τ 2.17–2.76 (9 H, aromatic multiplet), 6.95 (1 H, bridgehead singlet), and 7.70 (3 H, methyl protons, doublet at room temperature due to nitrogen inversion, singlet upon heating).

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 82.00; H, 5.51; N, 5.78.

Hydrolysis of 8a and 8b.—Compounds **8a** and **8b** were hydrolyzed to **4** in the same manner as **8c** above.

Thermal Valence Tautomerism and Dipolar Cycloaddition to 8c.—A 3-g (0.00121 mol) sample of **8c**, 0.174 g (0.00121 mol) of dimethyl fumarate, and 10 ml of dry toluene were placed in a sealed tube under a nitrogen atmosphere and heated to 135° (oil bath) for 12 hr. Solvent removal, followed by trituration with petroleum ether, gave a purple colorled solution and a brown colored gum, separated by decantation. Solvent removal gave a purple colored gum which was crystallized from MeOH–H_2O to yield 0.1035 g (21.8%) of the dipolar cycloaddition product **10**: mp 110–111°; $\nu_{C=O}^{CDCl_3}$ 1740–1680 cm^{-1} (unresolved); mass spectrum molecular ion *m/e* 393; pmr τ 2.17–3.48 (9 H, aromatic), 5.33–5.57 (2 H), 6.19 (3 H), 6.56 (3 H), 6.19–6.56 (1 H), 7.72–7.95 (2 H), and 9.0–9.21 (3 H).

Anal. Calcd for $C_{23}H_{23}NO_5$: C, 70.20; H, 5.75; N, 3.57. Found: C, 70.40; H, 5.85; N, 3.73.

1-Cyclohexylamino-3-phenylindan (11).—A 1.5-g (0.00519 mol) sample of **7** was dissolved in 50 ml of dry EtOH and allowed to stir in the dark at room temperature with 0.2 g (0.00529 mol) of $NaBH_4$. After stirring for 3.75 hr, a large amount of a white flocculent precipitate had formed and effervescence had ceased. The mixture was poured into 50 ml of ice water, extracted with 250 ml of ether (in three portions), and washed with two 50-ml portions of water, and the ether layer was dried over $CaSO_4$. Solvent removal left 0.879 g (59%) of a white solid, recrystallized from benzene–petroleum ether: mp 116–117.5°; ir 3450 cm^{-1} (weak, NH, very broad), no C=O or C=N bands present; mass spectrum, parent ion *m/e* 291; pmr τ 2.50–3.16 (9 H, aromatic multiplet), 5.49–6.04 (2 H, multiplet), 6.76–7.50 (2 H, multiplet), and 7.83–9.17 (12 H, multiplet).

Anal. Calcd for $C_{21}H_{25}N$: C, 86.59; H, 8.59; N, 4.81. Found: C, 86.58; H, 8.93; N, 4.74.

Registry No.—**1**, 37528-66-8; **2**, 19772-61-3; **3a**, 1981-53-9; **3b**, 13118-16-6; **3c**, 37528-67-9; **3d**, 37666-

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06-1; **3e**, 37528-68-0; **4**, 1713-37-7; **6**, 16618-72-7; **7**, 37488-35-0; **8a**, 37488-36-1; **8b**, 37488-37-2; **8c**, 37488-38-3; **10**, 37500-24-6; **11**, 37488-39-4; isopropylamine hydrobromide, 29552-58-7; benzylamine hydrobromide, 37488-40-7.

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Ionization in Liquid Ammonia of Methyl and Amino Groups Bonded to Pyridine and Pyrazine. A Method of Determining Their pK_a Values[1]

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Proton magnetic resonance spectra of ionized 2-methyl and 2-amino derivatives of pyridine and pyrazine along with spectra of 2-pyridone and 2-pyrazinone in liquid ammonia are reported. Changes in chemical shifts produced by ionization of the pyridines are linearly related to those for the pyrazines. Competition experiments show that 2-methyl- is less acidic than 4-methylpyridine; estimates of the pK_a values for these two acids are given. It is suggested that the results provide a basis for determining the equilibrium acidities of weak heterocyclic acids.

The acidities of heterocyclic molecules containing carbon or nitrogen side chains having pK_a values >20 are largely undetermined.[3,4] Liquid ammonia is an attractive solvent for the determination of pK_a values of these weak acids. Ammonia has long been used to study the kinetic acidities of weak acids, both carbocyclic and heterocyclic.[3,7] Its very low self-ionization constant (pK = 32.5 at −33°)[8] allows high concentrations of the conjugate bases of the weak acids to be formed. The recent determination of pK_a values for a few carbocyclic nitrogen and carbon acids in ammonia by means of potentiometry, nmr, and ultraviolet spectroscopy[9] encouraged us to study weak heterocyclic acids.

We have found nmr to be a useful way to study the ionization of pyridines and pyrazines in ammonia and report results dealing with the ionization of methyl and amino groups bonded to these heterocyclic rings. That simple ionization takes place in the presence of amide ion was established by consideration of nmr spectra and by a correlation involving changes in chemical shifts resulting from the deprotonation of these weak acids and the more readily ionizable compounds 2-pyridone and 2-pyrazinone.[10] Our results pave the way for the determination of pK_a values for these and many more weakly acidic heterocyclic molecules in ammonia. They also provide the first reliable estimates of the pK_a values for 2- and 4-methylpyridines.

Results and Discussion

Pyridines.—Addition of 2-methylpyridine to an excess of KNH_2 in ammonia gives a highly colored solution. Its nmr spectrum shows at −40° no evidence of unreacted starting material or any other component in addition to ionized substrate. Chemical shifts and coupling constants are given in Table I. The ring protons of the anion are shielded by 1.6, 1.7, 2.3, and 1.3 ppm for the 3, 4, 5, and 6 positions, respectively, relative to the starting carbon acid in ammonia. The methylene group shows a clear AB pair of doublets at −40°, τ 7.4 and 7.55 (J = 3.2 Hz). These shifts are very similar to that of the methyl group, τ 7.5. No change in the spectrum could be detected after the sample stood for 1 week at room temperature, indicating a surprising stability. The large shielding values and the nonequivalent methylene protons indicate that a largely ionic compound is formed;[13] charge delocalization into the ring leads to double-bond character and restricted rotation about the methylene–ring bond. When the carbon acid is incompletely neutralized, signals for both the acid and its conjugate base are present. There is no evidence of signal averaging. This is to be expected.[16]

The nmr spectrum of this 2-pyridylmethylpotassium in ammonia is very similar to that of 2-pyridylmethyllithium in tetrahydrofuran.[17] The shielding of ring and methylene protons of the sample in ammonia is no greater than 12 Hz; coupling constants for ring protons

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