The water layer was extracted with 3 × 100 ml of pentane. The combined pentane extracts were dried ($MgSO_4$) and evaporated to give a foul-smelling, viscous, colorless oil. Bulb-to-bulb distillation at 1 mm gave 0.486 g (16% yield) of a colorless liquid which was identified as tricyclo[2.2.1.$0^{2,6}$]-3-heptylthiol: nmr τ 7.25 (d, J = 7 Hz, 1 H), 8.17 (d, J = 7 Hz, 1 H), overlapping with 8.25 (b s, 1 H), 8.70 (b s, 3 H), 8.87 (m, 4 H); ir 3.25, 3.88 μ; mass spectrum m/e (rel intensity) 128 (5), 127 (5), 126 (60), 97 (19), 83 (95), 81 (100), 79 (25), 78 (15), 77 (65).

Anal. Calcd for $C_7H_{10}S$: C, 66.73; H, 8.06; S, 25.30. Found: C, 66.66; H, 7.94; S, 25.39.

Reaction of *exo,exo*-2,8-Dibromo-4-thiatricyclo[3.2.1.$0^{3,6}$]octane (3) with Tri-*n*-butyltin Hydride.—A dry 25-ml one-neck flask was equipped with a short path distillation head and receiver flask immersed in a −78° bath. In the flask was placed 1.42 g (5.0 mmol) of *exo,exo*-2,8-dibromo-4-thiatricyclo[3.2.1.$0^{3,6}$]octane and 8.73 g (0.03 mol) of freshly distilled tri-*n*-butyltin hydride. A trace of AIBN was added and the reaction was heated to 100° at a pressure of 15 mm. The reaction was kept at 100° for 2 hr. A distillate was collected and was identified by vpc, ir, and nmr as pure tricyclo[2.2.1.$0^{2,6}$]heptylthiol. The yield was 100 mg (31%).

Reaction of Tricyclo[2.2.1.$0^{2,6}$]heptyl-3-thiol (8) with Acetic Anhydride.—Tricyclo[2.2.1.$0^{2,6}$]heptylthiol (0.10 g, 0.79 mmol) and 0.0829 g (0.80 mmol) of acetic anhydride were dissolved in 2 ml of dry pyridine. The mixture was heated at 90° for 1 hr and then poured into 20 ml of water. The water was extracted with 2 × 5 ml of ether. The combined ether layers were dried ($MgSO_4$) and the ether was removed by evaporation. A clear liquid (0.140 g, 100% yield) was recovered and identified as 3-thiolacetoxytricyclo[2.2.1.$0^{2,6}$]heptane[10] by mixed injection with authentic material on vpc (8 ft × 0.25 in. column of 20% Dow 710 on Chromosorb P at 138°, retention time, 64 min) and by nmr analysis: nmr (CCl_4) τ 6.62 (s, 1 H), 7.78 (s, 3 H), 8.00 (bs, 1 H), 8.32–9.00 (m, 7 H); ir 3.22, 5.90 μ; mass spectrum m/e (rel intensity) 170 (1), 169 (2), 168 (34), 140 (8), 127 (4), 126 (15), 125 (50), 110 (18), 93 (100), 92 (32), 91 (80), 79 (17), 77 (50), 66 (44), 65 (20).

(10) T. van Auken and E. A. Rick, *Tetrahedron Lett.*, 2709 (1968).

Reaction of 2,8-Dibromo-4-thiatricyclo[3.2.1.$0^{3,6}$]octane (8) with Lithium Dimethylcuprate. A.—Tetrakis[iodo(tri-*n*-butylphosphene)copper(I)], 7.84 g (0.20 mol), was dissolved in 100 ml of dry ether. The mixture was stirred and cooled to −78°. Methyllithium (1.42 *M*, 0.05 mol, 28 ml) in ether was added by syringe to the cold solution over a 2-min period to generate the lithium dimethylcuprate. The colorless solution was then stirred for 10 min.

2,8-Dibromo-4-thiatricyclo[3.2.1.$0^{3,6}$]octane (2.84 g, 0.01 mol) was dissolved in 50 ml of dry ether and this solution was added all at once *via* syringe to the −78° lithium dimethylcurprate solution. The solution remained colorless. After the solution was stirred at −78° for 1 hr, 1.23 g (0.01 mol) of dry nitrobenzene was added all at once by syringe and the solution turned to a deep green color. The Dry Ice bath was removed and the solution was allowed to warm to 0°. The solution was then added to 250 ml of water and the water–ether mixture was filtered through Celite to remove insoluble copper salts. The ether layer was separated and washed with 3 × 100 ml of water, dried ($MgSO_4$), and evaporated. The resultant orange liquid was distilled to give 1.75 g (80% yield) of an orange liquid, bp 52° (0.1 mm). The product was identified as a new compound, *endo*-2-methylthio-*exo*-3-bromo-5-norbornene: nmr (CCl_4) τ 3.85 (m, 2 H), 6.48 (t, J = 2 Hz, 1 H), 6.68 (t, J = 2 Hz, 1 H), 6.94 (bs, 2 H), 7.81 (s, 3 H), 8.10 (m, 2 H); ir (CCl_4) 6.10, 14.50 μ; mass spectrum m/e (rel intensity) 220 (3), 218 (3), 154 (79), 152 (79), 141 (5), 140 (10), 139 (100), 124 (5), 123 (7), 92 (22), 91 (99), 73 (14).

Anal. Calcd for $C_8H_{11}BrS$: mol wt, 219.9745. Found: mol wt, 219.9710.

Registry No.—**1**, 6557-78-4; **3**, 37406-72-7; **5**, 37406-73-8; **6**, 22061-73-0; **8**, 37163-84-1; **10**, 37163-85-2; 3-thiolacetoxytricyclo[2.2.1.$0^{2,6}$]heptane, 37163-86-3.

Acknowledgment.—We wish to thank the National Science Foundation and the National Institutes of Health for their generous support of our program.

Aziridines. XXVI. Reactions of 1,3-Diazabicyclo[3.1.0]hex-3-enes

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The selective methylation and oxidation of 4-phenyl-6-*p*-nitrophenyl-3-diazabicyclo[3.1.0]hex-3-ene (**1a**) by trimethyloxonium tetrafluoroborate and *m*-chloroperbenzoic acid to form 2,2,3-trimethyl-4-phenyl-6-*p*-nitrophenyl-1-aza-3-azoniabicyclo[3.1.0]hex-3-ene tetrafluoroborate (**3**) and 2,2-dimethyl-4-phenyl-6-*p*-nitrophenyl-1,3-diazabicyclo[3.1.0]hex-3-ene 3-oxide (**11**), respectively, have been achieved. The addition of nucleophiles such as potassium cyanide and sodium borohydride to **3** as well as the reaction of **3** with diazomethane were studied. The cycloadditions of **11** to *N*-phenylmaleimide and diethyl azodicarboxylate were also investigated.

Three earlier papers in this series described the synthesis of the fused aziridines 1,3-diazabicyclo[3.1.0]hex-3-enes (**1**) and 1,4-diazabicyclo[4.1.0]hept-4-enes (**2**) and their thermal cycloadditions to alkenes, alkynes, and diethyl azodicarboxylate.[1–4] These thermal reactions of **1** and **2** were readily accounted for by carbon–carbon fission of the aziridine rings of **1** and **2** to form 1,3-dipolar intermediates (azomethine ylides) which subsequently added to the unsaturated substrates (Scheme I).

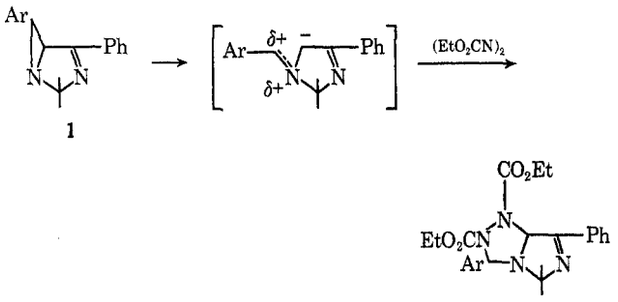
Recently the photolysis of **1** has been reported in detail[5–7] and the colored species produced have been identified also as 1,3 dipoles[7] which can be trapped with suitable 1,3 dipolarphiles.

The present paper describes the methylation and oxidation of **1** by trimethyloxonium tetrafluoroborate and *m*-chloroperbenzoic acid, respectively, and the chemical reactions of the resulting methylated and oxidized derivatives of **1**.

Treatment of a methylene chloride solution of 2,2-dimethyl-4-phenyl-6-*p*-nitrophenyl-1,3-diazabicyclo-

(1) H. W. Heine, R. W. Weese, R. A. Cooper, and A. J. Durbetaki, *J. Org. Chem.*, **32**, 2708 (1967).
(2) H. W. Heine, A. B. Smith III, and J. D. Bower, *ibid.*, **33**, 1097 (1968).
(3) H. W. Heine and R. P. Henzel, *ibid.*, **34**, 171 (1969).
(4) See also H. W. Heine, R. H. Weese, and R. A. Cooper, U. S. Patent 3,609,165 (Sept 28, 1971).
(5) A. Padwa, S. Clough, and E. Glazer, *J. Amer. Chem. Soc.*, **92**, 1778 (1970).
(6) T. DoMinh and A. M. Trozzolo, *ibid.*, **92**, 6997 (1970).
(7) T. DoMinh and A. M. Trozzolo, *ibid.*, **94**, 4046 (1972).

SCHEME I



[3.1.0]hex-3-ene (**1a**) with trimethyloxonium tetrafluoroborate formed compound **3** (Scheme II). That methylation had occurred at the N-3 position of **1a** was evident from the acid hydrolysis of **3** to the known *trans*-2-benzoyl-3-*p*-nitrophenylaziridine (**4**) and from the infrared spectrum of **3**, which exhibited a strong absorption band at 1631 cm^{-1} characteristic of ternary iminium salts.[8,9] Other evidence confirming the structure of **3** was the reactions of **3** with potassium cyanide to form **5** and with sodium borohydride to form **6**. These reactions are typical of ternary iminium salts.[10,11] Compound **6** was also obtained by treatment of **5** with sodium borohydride. The conversion of **5** to **6** is analogous to the reaction of 10-cyanoquinolizidine with lithium aluminum hydride to give quinolizidine.[11]

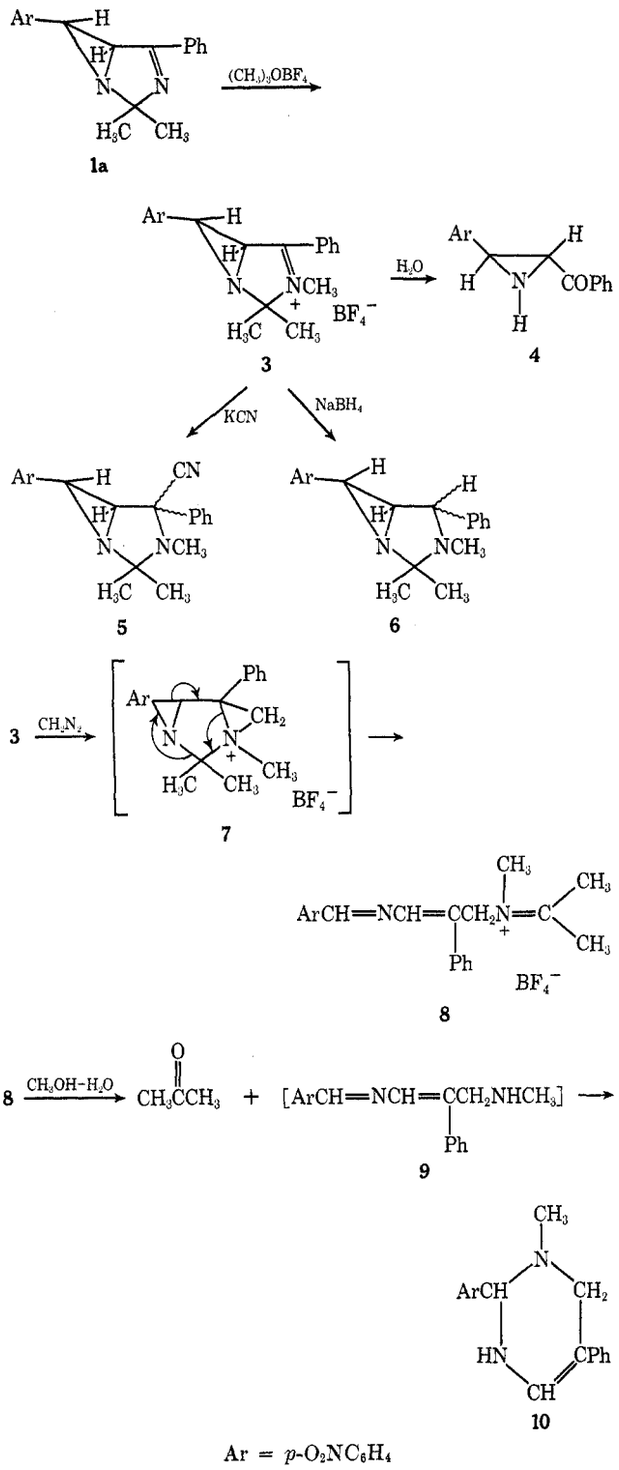
A most novel transformation occurred when **3** was treated with diazomethane. Compound **8** was formed, presumably through the intermediacy of the aziridinium ion **7** (Scheme II). An infrared spectrum of **8** exhibited a very broad absorption peak at approximately 1050 cm^{-1} which is characteristic of tetrafluoroborate salts and two absorption peaks at 1670 and 1598 cm^{-1} that were assigned to the iminium and imino groups, respectively. The nmr spectrum of **8** in CD_3CN at $-10°$ showed the typical splitting pattern of the *p*-nitrophenyl group at δ 8.20 (2 H) and 8.44 (2 H), the benzal proton as a singlet at 8.72, the vinylic proton and the phenyl protons coincidently absorbing as a single peak at 7.63 (6 H), the methylene group as a singlet at 5.58, the *N*-methyl moiety at 3.38, and the two remaining methyl groups as singlets at 2.67 and 2.43.

Compound **8** was further characterized by its hydrolysis in aqueous methanol to acetone (identified as a 2,4-dinitrophenylhydrazone) and **10**. The structure of **10** was confirmed by nmr and mass spectroscopy and by acid hydrolysis to *p*-nitrobenzaldehyde. The nmr spectrum of **10** established the presence of the XCH-NHCHY moiety and the absence of a benzal proton, signifying that the anticipated hydrolysis product of **8**, namely, **9**, spontaneously cyclized to **10** (Scheme II).

The suggested intermediacy of **7** in the reaction of **3** with diazomethane seems quite reasonable, since it is well known that addition of diazomethane to ternary iminium salts is a general method for the preparation of aziridinium salts.[12,13]

A benzene solution of **1a**, when treated with *m*-chloroperbenzoic acid at room temperature, gave the *N*-oxide **11** (Scheme III). The infrared spectrum of **11** exhibited strong absorption bands at 1250 cm^{-1}, the region that has been assigned to the N–O stretch of nitrones,[14] and at 1540 cm^{-1}, which is characteristic of nitrones such as Δ^1-pyrroline *N*-oxides.[14,15a,b] It was easy to reduce **11** with sodium borohydride to the *N*-

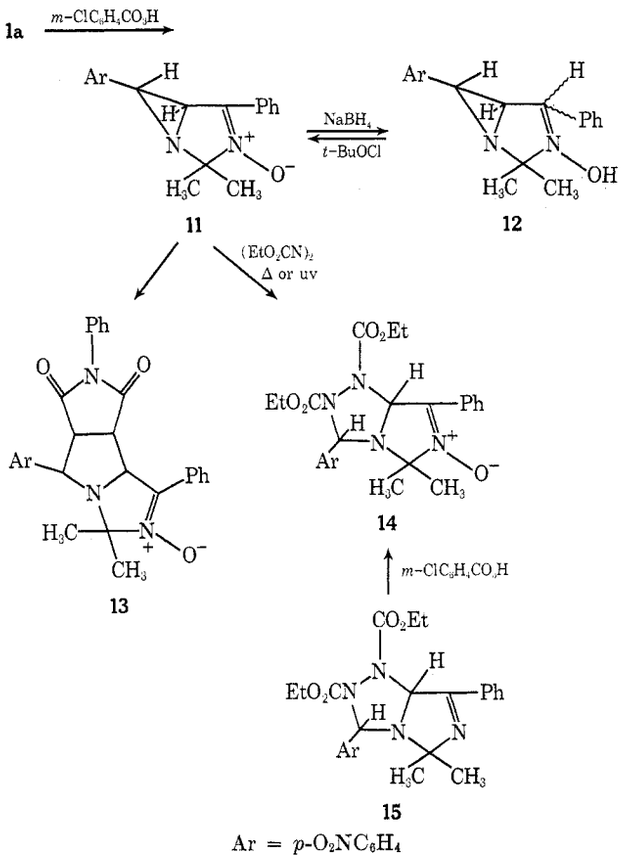
SCHEME II



Ar = *p*-$O_2NC_6H_4$

(8) N. J. Leonard and V. W. Gash, *J. Amer. Chem. Soc.*, **76**, 2781 (1954).
(9) N. J. Leonard and J. V. Paukstelis, *J. Org. Chem.*, **28**, 3021 (1963).
(10) N. J. Leonard, P. D. Thomas, and V. W. Gash, *J. Amer. Chem. Soc.*, **77**, 1552 (1955).
(11) N. J. Leonard and A. S. Hay, *ibid.*, **78**, 1984 (1956).
(12) N. J. Leonard and K. Jann, *ibid.*, **82**, 6418 (1960); **84**, 4806 (1962).
(13) N. J. Leonard, *Rec. Chem. Progr.*, **26**, 211 (1965).
(14) P. A. Smith and J. E. Robertson, *J. Amer. Chem. Soc.*, **84**, 1197 (1962).
(15) (a) R. Bonnett, R. F. C. Brown, V. M. Clark, I. O. Sutherland, and A. J. Todd, *J. Chem. Soc.*, 2094 (1959); (b) M. C. Kloetzel, F. L. Chubb, R. Gobran, and J. L. Pinkus, *J. Amer. Chem. Soc.*, **83**, 1128 (1961).

SCHEME III



hydroxy compound **12** and to oxidize **12** to **11** with *tert*-butyl hypochlorite.

Compound **11**, like **1**, formed an azomethine ylide when heated. In refluxing toluene with *N*-phenylmaleimide and diethyl azodicarboxylate **11** gave the cycloadducts **13** and **14**, respectively. Interestingly, irradiation of a benzene solution of **11** and diethyl azodicarboxylate also gave **14** identical in all respects with **14** obtained from the thermolysis reaction. The structure of **14** was determined by elemental analyses and nmr spectroscopy and by an independent synthesis involving the oxidation of the known bicyclic compound **15**[2] with *m*-chloroperbenzoic acid. The nmr spectrum of **14** showed the two methine protons as singlets at δ 6.65 and 6.83, as would be expected if cleavage of the carbon–carbon bond of the aziridine ring of **11** had occurred in the reaction.

We have assigned a cis configuration to **14**. The starting aziridine **1a** had been shown earlier to have a trans configuration[1] and the same stereochemistry is present in **11**, since oxidation of the imino nitrogen should not alter the spatial relationship of the ring hydrogens. On the basis of orbital symmetry rules trans **11** would undergo conrotatory opening to a syn 1,3-dipolar intermediate. Capture of the syn 1,3 dipole by diethyl azodicarboxylate should yield *cis*-**14**. Huisgen and coworkers have verified conrotatory ring openings for other ground-state aziridine systems[16] and DoMinh and Trozzolo reported similar conclusions[7] for aziridine **1a**. It has also been observed that the thermal and photolytic cycloaddition of **1a** to TCNE or dimethyl acetylenedicarboxylate gave cycloadducts having identical stereochemistry. It was suggested that the photoinduced reaction involved electronically excited states which internally convert to vibrationally excited states.[7] Presumably a similar situation arises in the photolytic cycloaddition of **11** to diethyl azodicarboxylate, since both the thermal and photolytical processes yield identical **14**.

(16) R. Huisgen, W. Scheer, and H. Huber, *J. Amer. Chem. Soc.*, **89**, 1753 (1967).

Experimental Section

Compound 3.—To a stirred solution of 500 mg (1.62 mmol) of **1a** in 35 ml of anhydrous CH_2Cl_2 under nitrogen was added 250 mg of freshly prepared trimethyloxonium tetrafluoroborate. After 6 hr the reaction mixture was filtered to give 620 mg (93%) of crude **3**. Five recrystallizations from absolute ethanol gave **3**, mp 190–191°.

Anal. Calcd for $C_{19}H_{20}N_3O_2BF_4$: C, 55.77; H, 4.93; N, 10.27. Found: C, 55.50; H, 4.73; N, 10.16.

Conversion of 3 to 4.—A suspension of 300 mg (0.733 mmol) of **3** in 200 ml of Et_2O and 150 ml of H_2O was stirred for 8 hr. The ether layer was removed and dried over $MgSO_4$. The solvent was evaporated to give 105 mg (53%) of **4**.[1]

Reaction of 3 with KCN.—A suspension of 425 mg (1.03 mmol) of **3** in 10 ml of Et_2O was shaken vigorously with 500 mg of KCN in 20 ml of H_2O. The ether layer was washed with three 50-ml portions of H_2O and dried over $MgSO_4$. Evaporation of the ether layer gave 300 mg (84%) of **5**, which melted at 151–153° after three recrystallizations from hexane.

Anal. Calcd for $C_{20}H_{20}N_4O_2$: C, 68.97; H, 5.97; N, 16.08. Found: C, 69.17; H, 5.92; N, 15.94.

Reaction of 3 with $NaBH_4$.—A mixture of 920 mg (2.24 mmol) of **3** and 320 mg of $NaBH_4$ in 45 ml of absolute ethanol was stirred vigorously for several hours. The EtOH was evaporated and 50 ml of H_2O was added to the residue. The solution was neutralized with glacial acetic acid and then extracted with Et_2O. The ether layer was separated and dried over $MgSO_4$. The ether was evaporated and the yellow, oily residue was slurried with petroleum ether (bp 30–60°). The solvent was evaporated and fresh petroleum ether was added and evaporated. After this procedure was repeated several times 629 mg (87%) of **6** precipitated and was filtered. Recrystallization from petroleum ether gave **6** melting at 105–107°.

Anal. Calcd for $C_{19}H_{21}N_3O_2$: C, 70.57; H, 6.55; N, 12.99. Found: C, 70.86; H, 6.63; N, 13.23.

Conversion of 5 to 6.—To a solution of 820 mg (2.35 mmol) of **5** in 45 ml of absolute EtOH was added 320 mg of $NaBH_4$. The reaction mixture was stirred overnight and the solvent was evaporated. The residue was slurried with 50 ml of H_2O and the solution was neutralized with glacial acetic acid. The solution was extracted with Et_2O and the ether extract was dried. The Et_2O was evaporated and the 500 mg (66%) of **6** that was obtained was purified as described above.

Conversion of 3 to 8.—Employing the usual precautions involved in the preparation of diazomethane, a solution of 500 mg of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in 20 ml of Et_2O was added to a 125-ml distilling flask that was connected to a condenser delivering into two receiving flasks in series and both cooled in ice. The first receiver contained a magnetic stirring rod and 10 ml of Et_2O and the second receiver contained 20 ml of ether and the inlet tube dips below the surface of the solvent. To the cooled solution was added 10 ml of 95% EtOH in which two pellets of KOH had previously been dissolved. The diazomethane was distilled and to the distillate was added 8 ml of CH_3CN containing 409 mg of **3**. Evolution of nitrogen occurred immediately. The reaction mixture was stirred for 1 hr. If no solid had precipitated, small portions (3–5 ml) of dry Et_2O were added to the mixture over a period of 0.5 hr. The crystalline **8** was filtered and purified by dissolving it in a minimum of acetone and reprecipitating it by the addition of dry Et_2O. Compound **8** was obtained in 48–73% yields and melted at 121–122°. It was placed in a desiccator and stored in a refrigerator.

Anal. Calcd for $C_{20}H_{22}BF_4N_3O_2$: C, 56.75; H, 5.25; N, 9.93. Found: C, 56.48; H, 5.39; N, 10.01.

Hydrolysis of 8.—To a well-stirred solution of 20 mg of NaOH in 8 ml of H_2O was suspended 200 mg of **8**. Methanol (6 ml) was immediately added, and the suspension was stirred overnight and then filtered to give 125 mg (90%) of **10**. The filtrate was added to 10 ml of a 1% ethanolic solution of 2,4-dinitro-

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.

Acknowledgment.—We thank Drs. William Vanden-Heuvel and Byron A. Arison for discussions on the mass spectrum and nmr spectrum of compound **11** and Dr. Anthony Trozzolo for some stimulating conversations. Acknowledgment is made to the National Institutes of Health for Grant CA-10015.

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).