dry HCl in benzene was added. The benzene was removed under vacuum to give 73 mg of **5b** (90%).

Reaction of 1b with Methanol. An 80-mg sample of **1b** in 0.3 ml of methanol was stirred at 25° for 6 hr. Solvent removal gave 81 mg (93%) of **7b**: ir 2.95, 3.34, 6.25, 6.70, 9.15, 13.3, 14.3 μ; nmr δ 0.57 (m, 1), 0.75 (m, 2), 1.02 (m, 1), 3.15 (s, 3), 3.97 (broad s, 1), 4.48 (s, 1), 6.60 (d, 3, J = 7 Hz), 7.03 (t, 2, J = 7 Hz), and 7.18 (m, 5) purified by column chromatography.

Anal. Calcd for $C_{17}H_{19}NO$: C, 80.60; H, 7.56; N, 5.53. Found: C, 80.3; H, 7.8; N, 5.4.

An 80-mg sample of **1b** was dissolved in 0.3 ml of CD_3OD and its disappearance was followed by nmr at 15° to determine its approximate half-life. For CD_3OD stirred over solid $NaHCO_3$, $\tau_{1/2}$ was ~58 min; for neutral CD_3OD, $\tau_{1/2}$ was ~42 min; and for 0.01% AcOD in CD_3OD, $\tau_{1/2}$ was ~4 min. The reaction was over in 1% AcOD in CD_3OD before a spectrum could be recorded.

Reaction of Diphenylmethylenecyclopropane[12] (2c) with Phenyl Azide. A 1.0-g sample of **2c** and 1.0 g (1.7 equiv) of phenyl azide were heated on a steam bath for 48 hr, after which time **2c** had completely reacted upon nmr examination. Addition of 100 ml of pentane gave 0.1 g of a dark brown solid whose nmr had only aromatic absorption. Removal of this solid by filtration, concentration of the pentane solution to 25 ml, and cooling to −20° gave 0.8 g (51%) of solid **3c** (mp 145–147°, gas evolution at 180°): ir 3.3, 6.25, 6.80, 6.90, 7.5, and 9.4 μ; nmr δ 0.55 (m, 2), 1.50 (m, 2), and 6.6–7.2 (m, 15); mass spectrum m/e (rel intensity) 325 (<1), 297 (19), 296 (38), 282 (11), 269 (46), 170 (100), and 165 (23).

Anal. Calcd for $C_{22}H_{19}N_3$: C, 81.20; H, 5.89; N, 12.91. Found: C, 81.0; H, 5.8; N, 12.6.

Photolysis of 3c. A 100-mg sample of **3c** in 1 ml of CH_2Cl_2 was irradiated with a medium-pressure Hanovia system through Pyrex. Observation by nmr indicated a reaction time of 60 min. Solvent removal gave a dark brown oil identified as **5c**: ir 5.90, 6.27, 6.82, 6.93, 7.91, 9.0, 9.8 μ; nmr δ 2.83 (m, 4), 6.8–7.8 (m, 15). Purification by column chromatography on basic alumina gave 80 mg (91%) of a light yellow oil.

Anal. Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 89.0; H, 6.3; N, 4.5.

Photolysis of **3c** in $CDCl_3$ under the same conditions as above at −78° gave 90% conversion of **3c** to **1c** as observed by low-temperature nmr: δ 1.11 (m, 2), 1.55 (m, 2), and 6.4–7.4 (m, 15). This sample of **1c** was stable up to −30° for periods up to 6 hr. Rapid warming to 20° gave quantitative conversion to **5c** in 10 min as monitored by nmr.

Photolysis of 3c in Methanol. A 100-mg sample of **3c** in 5 ml of MeOH was irradiated with 3100-Å bulbs in a Rayonet reactor for 3 hr. Removal of the MeOH under vacuum gave 82 mg (92%) of **5c**, pure by nmr.

Hydrolysis of 5c. A 100-mg sample of **5c** was stirred with 100 ml of a 5% HCl solution for 2 hr. The HCl solution was extracted with ether, the ether was dried, and the solvent was removed under vacuum to give 70 mg (93%) of 2,2-diphenylcyclobutanone: ir 5.61 μ; nmr δ 2.76 (t, 2, J = 8.5 Hz), 3.08 (t, 2, J = 8.5 Hz), 7–7.8 (m, 10).

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 5.92. Found: C, 86.4; H, 5.9.

The HCl aqueous layer was neutralized with $NaHCO_3$ and extracted with ether. Drying and solvent removal gave 25 mg (80%) of aniline.

Registry No. **1a**, 42540-58-9; **1b**, 40323-60-2; **1c**, 42540-60-3; **2a**, 6142-73-0; **2b**, 7555-67-1; **2c**, 7632-57-7; **3a**, 42540-63-6; **3b**, 40323-62-4; **3c**, 42540-65-8; **5a**, 42540-66-9; **5b**, 40323-63-5; **5c**, 42540-68-1; **6a**, 42540-69-2; **7a**, 42540-70-5; **7b**, 40323-64-6; **10**, 42540-72-7; phenyl azide, 622-37-7; 2-phenylcyclobutanone, 42436-86-2; 2,2-diphenylcyclobutanone, 24104-20-9.

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Octahydrophenanthreneaziridines. *syn*- and *anti*-9,10-Imino-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene

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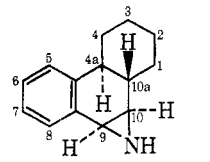
Preparation of *anti*-9,10-imino-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (2) is reported. A comparison of the results of ring opening reactions of these syn and anti aziridines (1 and 2) is made. Both isomers are converted to β-chloro amides when treated with benzoyl chloride and subsequently converted to the isomeric oxazolines. Acid-catalyzed ring opening produces amino alcohols in both cases with 1 affording a 57:43 ratio of cis and trans products, 22 and 23. Opening of 2 afforded a 10:90 mixture of cis and trans amino alcohols, 24 and 25.

Current studies required finding suitable methods for the preparation of the isomeric aziridines 1 and 2. Obtention of these aziridines provided a convenient system for study of the stereochemistry of the ring opening process. These compounds offer advantages similar to steroidal aziridines, with the additional quality of the regioselectivity of opening being somewhat predetermined because of the adjacent phenyl group; thus C–N bond breaking would occur primarily at the benzylic position. In previous studies, products of both carbonium ion opening and displacement mechanisms had been reported from styrylaziridines and aziridinium ions.[1-3]

In a previous study,[4] *syn*-9,10-imino-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (**1**)[5,6] was prepared. Reaction of **1** with benzoyl chloride afforded oxazoline **5**. More carefully controlled conditions (0°, ether, 1 equiv of pyridine) led to an intermediate 9(a)-chloro-10(e)-benzamido-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene[7] (**3**), which was readily converted to **5** (75°, $CHCl_3$, 30 min). We therefore sought to prepare the analogous anti aziridine, **2**, to look at this process, as well as to study the ring opening process under hydrolytic conditions.



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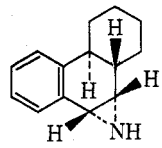

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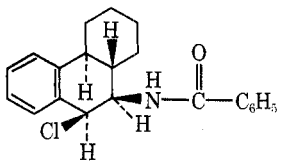

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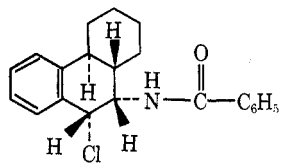

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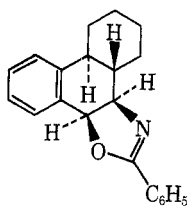

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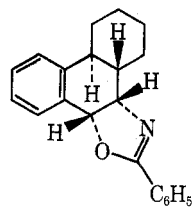

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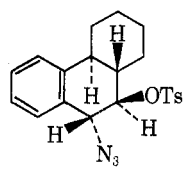
A successful route to **2** was found in the method of Ponsold,[8] which involved the reductive cyclization of 9(e)-azido-10(e)-tosyloxy-1,2,3,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (**7**) using hydrazine and a Raney



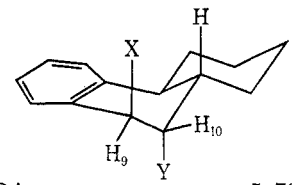
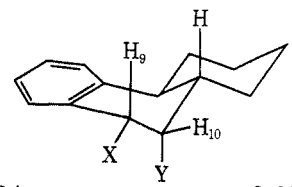
7

nickel catalyst. This method has previously been applied to 1,2-trans-diaxial azido mesylates in steroidal systems.[8-11] The process of preparation of an azido mesylate or tosylate from an epoxide, followed by reaction with hydrazine–Raney nickel, affords a convenient route to aziridines of opposite stereochemistry from the starting epoxide.

The azide function of **7** had been shown to undergo a facile 1,2 shift under acetolysis conditions.[12] The success of that process suggested possible utilization of **7** in the Ponsold reaction, although no precedent of a diequatorial[7] system has previously been reported. Under these conditions aziridine **2** was produced in 80% yield. The nmr spectrum was consistent with the structure, showing signals for H_9 and H_{10} at δ 2.97 and 2.48, respectively, $J_{9,10} = 6$, $J_{10,10a} \cong 0$ Hz.

Reaction of **2** with benzoyl chloride afforded a β-chloro benzamide, **4**, which cyclized to the oxazoline **6** only upon heating at 80° for several hours, more strenuous conditions than those necessary to convert **1** to **5**.[4] The structure of oxazoline **6** was confirmed by converting a sample of amino alcohol **10** to **6** by reaction with ethyl benzimidate.[12] The isolation of an intermediate β-halo amide is consistent with previous results and speculation concerning the conversion of *N*-acylaziridines to oxazolines.[4,13,14]

Table I
60-MHz Nmr Data on Selected 9(e),10(a)- and 9(a),10(a)-Disubstituted Octahydrophenanthrenes

Compd	δ, H_9	$J_{9,10(e)}$, Hz
		
8,[a] X = OAc; Y = NHAc	5.78	3.0
9,[a] X = OAc; Y = N_3	5.95	3.0
10,[a] X = OH; Y = Br	4.75	2.3
11,[a] X = $NHCO_2Me$; Y = I	5.59	2.0
12,[b] X = Y = OH	4.30	2.5
13,[b] X = Y = OCOPh	6.02	2.5
14,[b] X = Y = $OCNH_2$	5.55	2.0
15,[c] 6β,7α-Dichloroestrone	5.28	2.2
		
16,[a] X = OAc; Y = NHAc	6.06	5.0
17,[a] X = OAc; Y = N_3	6.18	4.5
18,[b] X = Y = OH	4.57	4.0
19,[b] X = Y = OCOPh	6.08	4.0
20,[b] X = Y = $OCNH_2$	5.83	4.0
21,[c] 6α,7α-Dichloroestrone	5.54	4.0

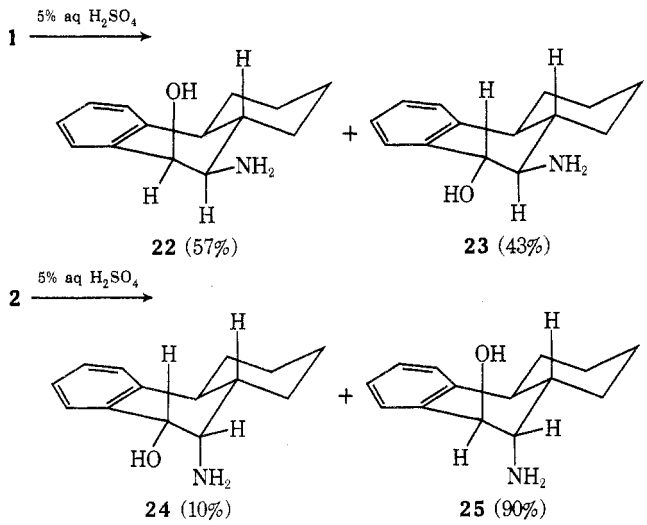
[a] Reference 12. [b] B. E. Sherwood, Ph.D. Thesis, University of Washington, 1973. [c] Y. Osawa and M. Newman, *J. Amer. Chem. Soc.*, **85**, 2856 (1963).

The stereochemistry of the chlorine atom in **4** is tentatively assigned the 9(e) position on the basis of the nmr spectrum, requiring **4** to be a *cis*-β-chlorobenzamide. The nmr spectrum showed $J_{9,10} = 4.5$ Hz, consistent with either a 9(e) or 9(a) proton. However, in related systems (Table I), consistently larger J values are observed for the 9(a),10(e) coupling than for the 9(e),10(e) disposition of protons. Dreiding models show that $\theta_{9(e),10(e)}$ is *ca.* 70–75°, consistent with an expected larger J value for the former distribution of protons.[15]

The similarity in stereochemistry of **3** and **4**, both cis, would suggest that similar processes are involved. However, the structures of these two compounds, and the subsequent oxazoline formation under the described conditions, are not consistent with the normal displacement mechanisms expected for opening of *N*-acylaziridines or their conversion to oxazolines. The difference in ease of conversion of the two intermediate β-halo amides to oxazolines may be a consequence of small differences in energy of the transition states of the processes involved. Additional work on these and other compounds would be needed to validate this interpretation.

The distribution of products of ring opening of **1** and **2** under aqueous acid (5% aqueous H_2SO_4) conditions were

determined. These products are the amine alcohols, **22**, **23**, **24**, and **25**. Ring opening of **1** afforded a 57:43 ratio of cis and trans amino alcohols **22** and **23**. Under similar conditions **2** is converted to a 10:90 ratio of cis and trans amino alcohols **24** and **25**. The products of opening of **1** are determined by acetylation of the amino alcohols followed by glpc determination of the diacetates (see Experimental Section). No difficulties were encountered in a direct glpc determination of alcohols **24** and **25**. Under these conditions all of the aziridine is consumed as determined by glpc.



These results suggest that, while the acid-catalyzed opening of **1** may occur through a benzylic carbonium ion which is nearly equally accessible from either side of the molecule, the opening of **2** may be more of a concerted process in which water molecules approach the β face of the molecule during bond-breaking process.

It would seem that, if both SN1 and SN2 processes are occurring in both openings, the SN2 process in the opening of **1** may require a greater activation energy because in the transition state a colinear disposition of functional groups would require a boat conformation, in contradistinction to a half-chair conformation for a similar transition state in the opening of **2**.

Small differences in the activation energies of the processes in each opening may be reflected in these product ratios. Additional experiments to consider some of these factors are in progress. The preparation of the aziridines and the relatively simple method for determination of product ratios will facilitate additional work.

Experimental Section

Peaks given in the mass spectral fragmentations are within 5.0 millimass units from calculated values. Unless otherwise stated, anhydrous sodium sulfate was used to dry solutions in organic solvents.

***syn*-9,10-Imino-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (1).** This compound was prepared by the method of Nelson and Miller,[4] mp 125–127° (lit.[4] mp 129–130°).

***anti*-9,10-Imino-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (2).** A mixture of 9(e)-azido-10(e)-*p*-toluenesulfonyloxy-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (**7**,[12] 795 mg, 2.0 mmol), hydrazine hydrate (99%, 25 g, 0.5 mol), and Raney nickel [activity W-4, 348 mg (6.0 mg-atoms)] in 80 ml of MeOH was stirred at room temperature for 20 hr, during which the time 5.0-g portions of hydrazine were added every 3 hr. The mixture was diluted with H_{20} and extracted with ether. The combined ether solutions were washed with H_{20}, dried, and evaporated. The residual oil crystallized on standing and was recrystallized from hexane, affording 320 mg (80%) of **2**: mp 109–110°; ir (KBr) 3300 (NH), 3050 (ArCH), 2970 and 2900 (aliphatic CH), 1490, 1450, 1410, 1260, 1240, 1050, 890, 880, 860, 845, 820, 805 and 785, 725 and 755 cm^{-1}; nmr ($CDCl_3$) δ 7.23 (s, 4, ArH), 2.97 (d, broadened, 1, $J_{9,10}$ = 6.0, $J_{9,NH} \cong$ 0–1 Hz, H_9), 2.50–1.10 (m, 12, NH, H_{10} and $CHCH_2$ envelope); nmr ($CDCl_3$ + D_{20}) δ 4.53 (s, 1, HDO), 2.48 (d, 1, $J_{10,10a} \cong$ 0 Hz, H_{10}); mass spectrum (70 eV) *m/e* (rel intensity, fragment) 201 (9, M + 2), 200 (55, M + H), 199 (100, M), 198 (61, M − 1), 182 (61, M − NH_3), 181 (17, M − NH_4), 170 (39, $C_{12}H_{12}N$), 156 (52, $C_{11}H_{10}N$), 141 (90, $C_{11}H_9$), 128 (74, $C_{10}H_8$), 91 (23, C_7H_7), 77 (23, C_6H_5); *m/e* 199.1362 (calcd for $C_{14}H_{17}N$, 199.1358).

Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.51; H, 8.45; N, 6.91.

9(e)-Chloro-10(a)-benzamido-1,2,3,4,4a,9,10,10a-(*trans*-4a,-10a)-octahydrophenanthrene (4). To a stirred solution of *anti*-9,10-imino-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (**2**, 80 mg, 0.42 mmol) and pyridine (33 mg, 0.42 mmol) in 40 ml of ether was added dropwise benzoyl chloride (141 mg, 1.0 mmol) in 10 ml of ether, maintaining the temperature below 5° with an ice bath. The mixture was stirred for 3.5 hr, filtered, and evaporated. The solid residue liquefied upon exposure to air; so it was redissolved in ether and the ether solution was washed with water, dried, concentrated to 2 ml, and placed in the refrigerator. The solute crystallized to give 9(e)-chloro-10(e)-benzamido-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (**4**): 74 mg (58%); mp 151–151.5°; ir (KBr) 3350 (NH), 3100 (aromatic CH), 2950 and 2880 (aliphatic CH), 1640 (amide I), 1580 (amide II), and 740, 715, and 690 cm^{-1} (aromatic CH); nmr ($CDCl_3$) δ 7.83–7.60 (m, 2, ArH), 7.55–7.27 (m, 7, ArH), 6.17 (d, br, 1, $J_{10,NH}$ = 11 Hz, NH), 5.60 (d, 1, $J_{10,9}$ = 4.5 Hz), 4.91 (dd, 1, $J_{10,NH}$ = 11, $J_{9,10}$ = 4.5, $J_{10,10a} \cong$ 0.1 Hz, H_{10}), 2.85–1.10 (m, 10, CH_2CH envelope); nmr (DMSO-d_6, D_2O) absorption at δ 6.17 is exchangeable with D_2O and the signal at δ 4.91 collapses to a slightly broadened doublet ($J_{10,9}$ = 4.5, $J_{10,10a}$ = 0–1 Hz, H_{10}); mass spectrum (70 eV) *m/e* (rel intensity, fragment) 304 (12, M − Cl), 303 (47, M − HCl), 302 (7, M − H_2Cl), 275 (5, M − C_2H_5Cl), 274 (22, M − C_2H_6Cl), 198 (16, $C_{14}H_{16}N$), 182 (100, $C_{14}H_{14}$), 154 (43, $C_{12}H_{10}$), 122 (100, C_7H_8NO), 105 (100, C_7H_5O), 91 (11, C_7H_7), 77 (100, C_6H_5); *m/e* 304.1644 (calcd for $C_{21}H_{22}NO$, 304.1680); *m/e* 303.1600 (calcd for $C_{21}H_{21}NO$, 303.1622).

Anal. Calcd for $C_{21}H_{22}NOCl$: C, 74.22; H, 6.53; N, 4.12. Found: C, 74.22; H, 6.50; N, 4.12

2-Phenyloxazoline of 9(e)-Hydroxy-10(a)-amino-1,2,3,4,4a,-9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (6). A solution of 9(e)-chloro-10(a)-benzamido-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (**4**, 20 mg, 0.06 mmol) in 0.5 ml of deuteriochloroform ($CDCl_3$) was heated at 80° for 67 hr while progress of the reaction was monitored by nmr, since during the conversion the H_9 signal at δ 5.60 ($J_{9,10}$ = 4.5 Hz) is replaced by a new H_9 signal at δ 6.60 (J = 9 Hz). The solution was treated with 10% aqueous sodium bicarbonate and ether, the phases were separated, and the ether phase was washed with water, dried, and evaporated. The crude product was chromatographed on 12 g of alumina (Merck, reagent aluminum oxide, neutral) using benzene as the eluent. Evaporation of the first 100 ml of eluent afforded 16 mg of white solid which was recrystallized from hexane to give the 2-phenyloxazoline of 9(e)-hydroxy-10(a)-amino-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (**6**): 14 mg (77%); mp 111–112° (lit.[12] mp 111°); nmr ($CDCl_3$) δ 8.07–7.83 (m, 2, ArH), 7.55–7.20 (m, 7, ArH), 5.80 (d, 1, $J_{9,10}$ = 10.0 Hz, H_9, appears at 6.60 in the HCl salt), 4.61 (dd, 1, $J_{10,10a}$ = 4.0 Hz, H_{10}), 2.73–0.80 (m, 10, CH_2CH envelope); mass spectrum (70 eV) *m/e* (rel intensity, fragment) 305 (1, M + 2), 304 (2, M + 1), 303 (12, M), 302 (2, M − 1), 275 (1, M − C_2H_4), 274 (7, M − C_2H_5), 200 (1, $C_{14}H_{16}O$), 198 (2, $C_{14}H_{16}N$), 182 (100, $C_{14}H_{14}$), 154 (15, $C_{12}H_{10}$), 122 (19, C_7H_8NO), 105 (46, C_7H_5O), 103 (2, C_7H_5N), 91 (12, C_7H_7), 77 (29, C_6H_5).

Hydrolysis of *syn*-9,10-Imino-1,2,3,4,4a,9,10,10a-(*trans*-4a,-10a)-octahydrophenanthrene (1). A solution of *syn*-9,10-imino-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (**1**, 10 mg, 0.05 mmol) in 10 ml of 5% aqueous sulfuric acid was refluxed for 1 hr, cooled, made alkaline (to pH 11) with 4 *N* aqueous sodium hydroxide, and extracted with ether. The ether solution was washed with water, dried, and treated with 0.5 ml of pyridine and 0.5 ml of acetic anhydride for 30 hr at room temperature. The ether solution was washed with water followed by 10% aqueous hydrochloric acid, 10% aqueous sodium hydroxide, and water, dried, and evaporated. The solid residue was dissolved in 0.5 ml of methanol and analyzed by glc using a 1.88 m × 0.32 cm 10% UC-W98 silicone rubber column, operating temperature 230°, helium flow rate 50 ml/min. The product composition was determined to be 57% 9(a)-acetoxy- and 43% 9(e)-acetoxy-10(e)-acet-

amido-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (26 and 27) by comparison of the glc retention times of the product components with those of authentic samples of these acetoxy acetamides prepared in this laboratory[12] and by adding authentic samples to the unknown. Retention times were 35.4 min for 26 and 11.2 min for 27.

Hydrolysis of *anti*-9,10-Imino-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (2). A solution of *anti*-9,10-imino-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (2, 10 mg, 0.05 mmol) in 10 ml of 5% aqueous sulfuric acid was refluxed for 1 hr, cooled, made alkaline (to pH 11) with 4 *N* aqueous sodium hydroxide, and extracted with ether. The ether solution was washed with water, dried, and evaporated. The solid remaining was dissolved in 0.5 ml of methanol and analyzed by glc using a 1.88 m × 0.32 cm 10% UC-W98 silicone rubber column (Hewlett-Packard, F & M Scientific Division), operating temperature 230°, helium carrier gas flow rate 50 ml/min. The product composition was determined to be 90% 9(a)-hydroxy- and 10% 9(e)-hydroxy-10(a)-amino-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (25 and 24) by comparison of the glc retention times of the product components with the retention times of authentic samples of these amino alcohols prepared in this laboratory[12] and adding authentic amino alcohols to the unknown samples. Retention times were 11.2 min for 25 and 12.2 min for 24.

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(6) All materials are racemic, although only a single isomer is drawn.
(7) The central ring is arbitrarily assigned the half-chair conformation where the axial (a) and equatorial (e) substituents are, in fact, pseudoaxial and pseudoequatorial, respectively.
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Some Reactions of Tetrahydrocarbazolechloroindolenine

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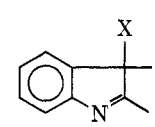
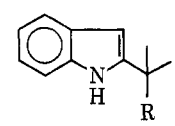
Tetrahydrocarbazolechloroindolenine (9), when allowed to react with NaOMe at −10°, gave 4a-methoxy-1,2,3,4-tetrahydrocarbazoleindolenine (10), while reaction with NaOH–MeOH under reflux gave 2-methoxyspiro[cyclopentane-1,3′-indolenine] (12). The relative proportion of 10 and 12 formed was dependent upon both base and temperature. When 10 was allowed to react with $LiAlH_4$, tetrahydrocarbazole was the product, while acid treatment gave bis[1,9-(1,2,3,4-tetrahydrocarbazole)] (11). $LiAlH_4$ reduction of 12 followed by Ac_2O–pyridine gave 1-acetoxyspiro[cyclopentane-1,3′-indoline] (14). Acid treatment of 12 gave spiro[cyclopentane-1,3′-indolin]-2′-one (13). 1-Methoxy-1,2,3,4-tetrahydrocarbazole (16) was prepared by NaOMe treatment of 1-pyridinium 1,2,3,4-tetrahydrocarbazole bromide (15).

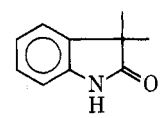
The reaction of indole derivatives with *tert*-butyl hypochlorite or sodium hypochlorite to yield chloroindolenines (1) is a well-known reaction.[1-3] Transformation of these highly reactive intermediates has yielded a variety of products depending on the conditions used. Buchi[4] found that the chloroindolenine of ibogaine, when treated with methanolic HCl, gave a methoxy derivative of structure 2, and reaction with potassium cyanide gave structure 3. The formation of oxindoles (4) has been reported by gentle acid treatment in aqueous media of the chloroindolenines of certain yohimbine alkaloids by Zinnes and Shavel.[5] Taylor and Finch[6] reported the formation of imido ethers of structure 5 by treating the chloroindolenines of various yohimbine alkaloids with methanolic base. Treatment of these imido ethers with aqueous acetic acid readily provided the corresponding oxindoles of structure 4. Recently, Gassman, *et al.*,[3] have reported a series of reactions on the chloroindolenine of 2,3-dimethylindole, where they found that treatment with silver ion and methanol gave direct substitution of the chlorine atom and formation of the 3-methoxyindolenine 6. They reported that



1, X = Cl
6, X = OCH_3



2, R = OCH_3
3, R = CN
7, R = OAc



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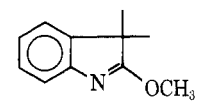

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brief warming of a solution of the chloroindolenine caused rearrangement, evidenced by alteration of the ultraviolet and nmr spectra. When treated with NaOMe or $Th(OAc)_2$, the rearranged product gave derivatives of structure 2 and 7, respectively.

Because of our interest in certain aspects of tetrahydrocarbazole (THC, 8) chemistry, we decided to study some