taining 5.5 g (30 mmol) of 2-chloro-6-nitrobenzonitrile in 60 ml of DMF. The mixture was stirred in the cold for 0.5 hr and then poured into ice water. The crude product was collected and crystallized from alcohol to yield 3.4 g of product, mp 115–116° (lit.[10] mp 114.5°).

2-Dimethylamino-α,α,α-trifluoro-6-nitro-p-tolunitrile (17). To a cold solution (ice bath) containing 10.4 g (40 mmol) of α,α,α-trifluoro-2,6-dinitro-p-tolunitrile and 5 g (62 mmol) of dimethylamine hydrochloride in 80 ml of DMF was added dropwise a solution containing 6 g of potassium hydroxide in 20 ml of water. The mixture was stirred in the cold for 1.5 hr and then poured into ice water. The solid was collected and crystallized from alcohol–water to yield 8.1 g of product, mp 67–69°. An analytical sample, mp 68–69°, was recrystallized from alcohol–water.

2-Ethoxy-α,α,α-trifluoro-6-methoxy-p-tolunitrile (19). To a cold solution (ice bath) containing 4.9 g (20 mmol) of 6-nitro-4-trifluoromethyl-o-anisonitrile (14) in 60 ml of absolute alcohol was added dropwise a solution containing 2 g of potassium hydroxide in 15 ml of water. The mixture was stirred in the cold for 0.5 hr and at room temperature for 2 hr and then poured into ice water. The solid was collected and crystallized from alcohol–water to yield 4.5 g of product, mp 61.5–63°.

2,6-Bis(dimethylamino)-α,α,α-trifluoro-p-tolunitrile (25). A solution containing 5.2 g (20 mmol) of 2-dimethylamino-α,α,α-trifluoro-6-nitro-p-tolunitrile (17), 4.5 g (55 mmol) of dimethylamine hydrochloride, and 7 g of anhydrous potassium carbonate in 50 ml of DMF was heated at steam-bath temperature for 68 hr and then poured into ice water. The crude product was collected and crystallized from alcohol to yield 3.4 g of product, mp 111.5–113°.

2-Chloro-α,α,α-trifluoro-6-nitro-p-tolunitrile (26). Hydrogen chloride gas was bubbled into a warm solution containing 15 g (58 mmol) of α,α,α-trifluoro-2,6-dinitro-p-tolunitrile in 60 ml of DMF. An exothermic reaction occurred at about 100°, and the solution was heated to reflux for 10 min and then poured into ice water. The solid was collected and crystallized from alcohol–water to yield 9.7 g of product, mp 52–53°.

6-Nitro-4-trifluoromethylsalicylonitrile (27). A solution containing 25 g (96 mmol) of α,α,α-trifluoro-2,6-dinitro-p-tolunitrile and 10 g of moist potassium fluoride in 100 ml of DMF was heated to reflux for 1 hr and then poured into ice water. The crude product was collected, but was not washed with water since it appeared to dissolve, and crystallized from water to yield 14.5 of product, mp 194–196°.

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Registry No.—**1**, 35213-00-4; **2**, 16932-49-3; **3**, 38469-85-1; **4**, 51271-32-0; **5**, 51271-33-1; **6**, 6575-07-1; **7**, 6575-10-6; **8**, 51271-34-2; **9**, 51271-35-3; **10**, 35213-02-6; **11**, 51271-36-4; **12**, 51271-37-5; **13**, 51364-43-3; **14**, 51271-38-6; **15**, 51271-39-7; **16**, 51271-40-0; **17**, 51271-41-1; **18**, 51271-42-2; **19**, 51271-43-3; **20**, 51271-44-4; **21**, 51271-45-5; **22**, 51271-46-6; **23**, 51271-47-7; **24**, 51271-48-8; **25**, 51271-49-9; **26**, 51271-50-2; **27**, 51271-51-3.

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Synthesis of Several Phenanthridines and a Quinazoline from Ortho-Substituted Arenediazonium Salts and Organic Nitriles[1]

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The thermal decomposition of 2-biphenyldiazonium tetrafluoroborates **3a** (R′ = H) and **3b** (R′ = NO_2) in the presence of representative aliphatic or aromatic nitriles is shown to afford the substituted phenanthridines **4a–g**. Little competition from the Baltz–Schiemann reaction was noted and in only one case was the competitive Meerwein quinazoline-forming reaction observed. The infrared spectrum of all phenanthridines studied exhibited two very strong absorption bands at 720–730 and 750–765 cm^{-1}, probably characteristic of this ring system.

The thermal decomposition of arenediazonium tetrafluoroborate salts (**1**) in the presence of organic nitriles results in the formation of *N*-arenenitrilium tetrafluoroborate salts (**2**). In several cases, it has been possible to isolate these salts and characterize them.[3,4] Infrared studies[5,6] on **2** have shown that *N*-alkyl- and *N*-arylnitrilium ion derivatives exhibit carbon–nitrogen triple bond stretching frequencies between 2300 and 2400 $cm,^{-1}$ while nmr investigations[6] of *N*-alkyl- and *N*-H nitrilium salts also indicate that only the linear nitrilium ions **2a** are present in detectable amounts. The imino carbocation form of the nitrilium ions **2b** can contribute very little to the reso-

$$\underset{\mathbf{1}}{ArN_2^+BF_4^-} \qquad \underset{\mathbf{2a}}{\left[ArN^+{\equiv}CR\right.} \longleftrightarrow \underset{\mathbf{2b}}{\left.ArN{=}\overset{+}{C}R\right]} BF_4^-$$

nance hybrid. However if the *N*-arylnitrilium ion could react with an adjacent substituent either as **2** or as a true carbocation, with which it might be in equilibrium (the angular form shown in **7**), then a new synthetic route to various N heterocycles would become available. We describe here the use of this approach as applied to the synthesis of phenanthridines.

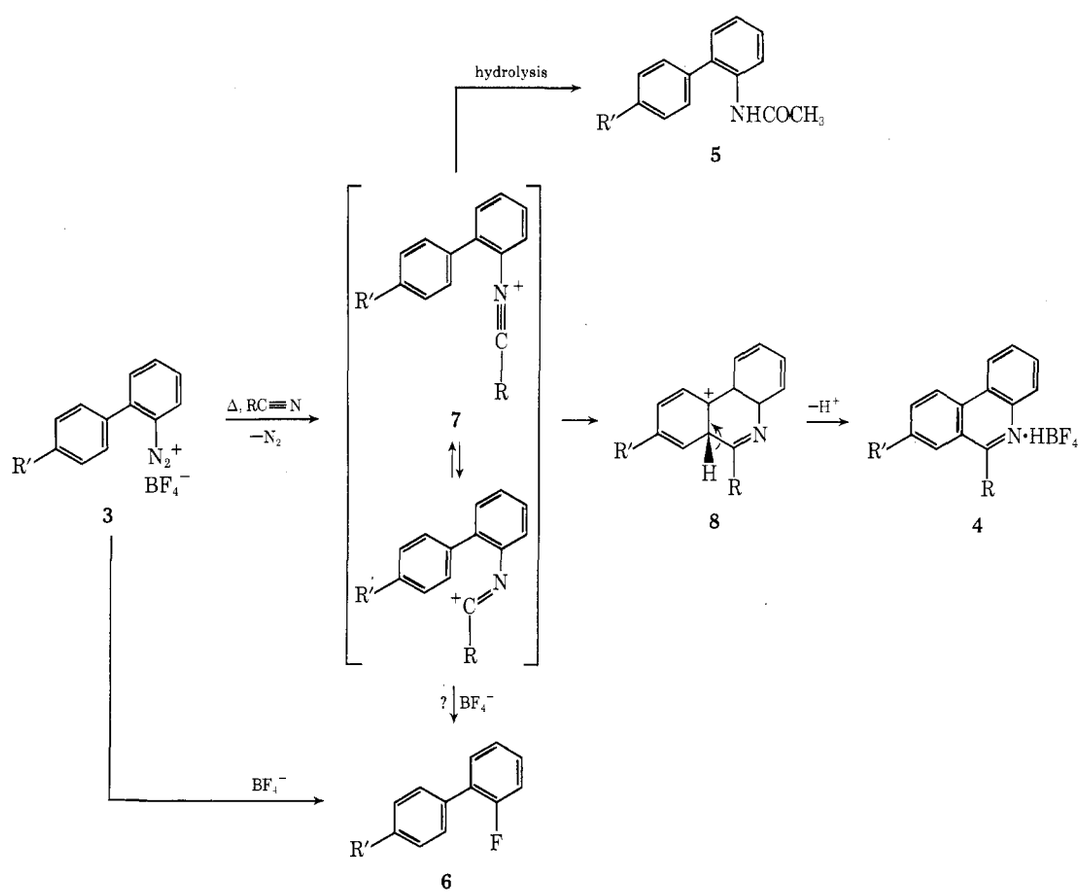
Phenanthridines. The thermal decomposition of the 2-biphenyldiazonium tetrafluoroborates **3a** (R′ = H) and **3b** (R′ = NO_2) in anhydrous aliphatic or aromatic nitriles leads to the formation of 6-substituted phenanthridines (**4a–g**). The yield of these phenanthridines was sensitive to both the time and temperature of the reaction. Thus, for example, the addition of **3a** to boiling acetonitrile over a 1-hr period, followed by hydrolysis, gave the 6-methyl derivative **4a** in 20% yield. The formation of **4a** was accompanied by a considerable amount of 2-acetamidobiphenyl (**5**) from hydrolysis of unreacted nitrilium ions. When the reaction time was increased to 12 hr, **4a** was obtained in 86% yield. In this case none of the amide **5** was

Table I
Synthesis of Phenanthridines

Registry no.	Phenanthridine obtained	R	R′	RC≡N/3, ml/g	Temp, °C	Time, hr	Work-up method	Yield, %[b] Picrate	Free base	2-Fluorobiphenyl
3955-65-5	**4a**	CH_3	H	23	82	12	A		86	4.5
13362-58-8	**4b**	C_2H_5	H	39	97	24	B	60[c]	43	
51381-75-0	**4c**	n-C_3H_7	H	26	117	96	B	71		
		n-C_3H_7	H	26	100	47	B	45		
2720-93-6	**4d**	C_6H_5	H	12	100	48	B	40[d]	36	7
		C_6H_5	H	12	100	24	B	32	22	
		C_6H_5	H	12	100	12	B	25	14	11[e]
46493-82-7	**4e**	CH_3S	H	25	100	48	B	53[f]	52	
		CH_3S	H	25	132	48	B	57	32	
51381-78-3	**4f**	CH_3	NO_2	25	82	96	B	35[g]	33	
51381-80-7	**4g**	C_2H_5	NO_2	25	97	72	A		9	

[a] Method of work-up: A, conventional acid extraction; B, picration. [b] Yields are based on the quantity of starting diazonium fluoroborate. [c] Registry no., 51381-74-9. [d] Registry no., 51381-76-1. [e] Registry no., 321-60-8. [f] Registry no., 51381-77-2. [g] Registry no., 51381-79-4.

Scheme I

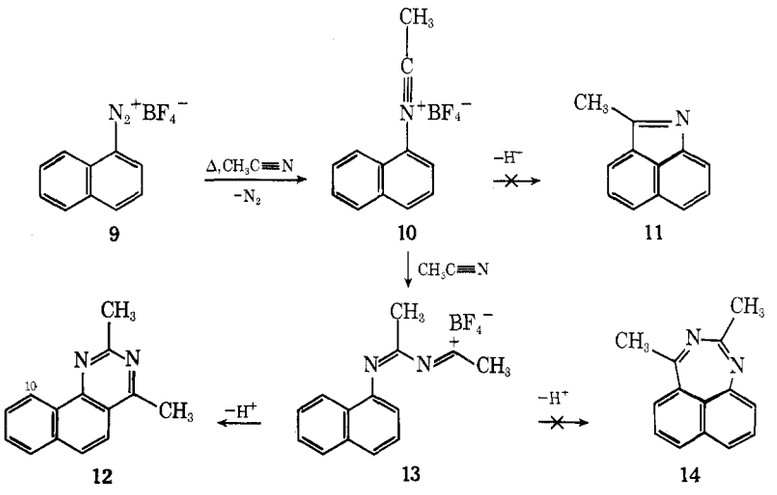


detected; a little (4.5%) 2-fluorobiphenyl (**6**) was the only low molecular weight by-product observed. The beneficial effect of increasing the reaction time is dramatically demonstrated in the synthesis of the 6-phenyl derivative **4d** from **3a** and benzonitrile. The effect of temperature is particularly notable in the synthesis of the methylthio derivative **4e**; an increase of 32° causes a decrease in yield of 20%. Table I summarizes the results which have been obtained for the decompositions of **3a** and **3b** while dissolved in various nitriles.

The isolation of the phenanthridines was accomplished using two isolation procedures: (A) acid extraction and (B) isolation *via* its picrate ("picration"). The latter method (B) proved to be the more useful one. Most of the phenanthridines described here are such weak bases that even several extractions with mineral acids does not assure complete removal of the heterocycle. However, all of the phenanthridines involved in this study formed picrates rapidly and quantitatively. The picrates were generally quite pure and the free bases could easily be recovered from them, usually in a high state of purity.

The formation of the phenanthridines, outlined in Scheme I, may be viewed as a two-step process. The first step is considered to involve replacement of the $-^+N{\equiv}N$ group of the diazonium salt **3** by RC≡N, which leads to the formation of the nitrilium salt **7**. This step is presumed to be fast, since evolution of the theoretical quantity of nitrogen is usually complete within a few minutes at the temperatures employed. The nitrilium salt **7** then cyclizes in a slower step to give the ion **8**, which after loss of a proton affords the phenanthridine **4** as an HBF_4 salt. That the cyclization reaction is the slow step in the for-

Scheme II



mation of the new ring is demonstrated by the fact that in two cases in which the effect of time was evaluated (**4a** and **4d**, Table I) the longer the reaction time, the better the yield of the phenanthridine. The isolation of amide **5**, which must result from hydrolysis of uncyclized nitrilium ion **7** (R = CH_3, R′ = H) in the decomposition of **3a** after 1 hr, provides additional support for this interpretation. Electronic stabilization of the nitrilium salt **7** and/or steric requirements imposed on the ring-closure reaction (**7** → **8**) may be factors retarding the rate of this second step. The formation of 2-fluorobiphenyl (**6**) is accounted for by competition of BF_4^- (Baltz-Schiemann reaction) with RC≡N for diazonium salt **3**, although the reaction of BF_4^- with nitrilium salt **7** has not been ruled out as a source of **6**.

Quinazolines. To further test the scope and limitations of this heterocyclization reaction, the thermal decomposition of 1-naphthalenediazonium tetrafluoroborate (**9**) in acetonitrile was investigated. A solution of **9** in refluxing acetonitrile gave as the major reaction product (56%) a new compound which was shown to be 2,4-dimethylbenzo[*h*]quinazoline (**12**). The structure assigned to **12** rests on its elemental analysis and an examination of its spectral properties. Its nmr spectrum showed a 1 H singlet at δ 9.30 and two 3 H singlets at δ 2.97 and 2.94, in addition to a 5 H multiplet centered at δ 7.80. The signal at δ 9.30 is assigned to the proton at C-10. This unusually low-field absorption must be caused by the anisotropic deshielding effect of the nitrogen at N-1. A very similar deshielding effect on the C-10 proton in the closely related compound benzo[*h*]quinoline by the spacially proximate nitrogen at N-1 has been noted.[7]

The formation of quinazoline **12** (Scheme II) is accounted for by reaction of the nitrilium salt **10** with a second molecule of acetonitrile to give the salt **13**, which then attacks the 2 position of the naphthalene ring to give the quinazoline **12**. It is interesting to note that compounds **11** and **14**, which might be formed by ring closure of **10** and **13**, respectively, at the 8 position (peri position), were not detected.

This synthesis of the dimethylquinazoline **12** has precedent in the literature.[4b] It is significant, however, that a reasonable yield of **12** is obtained. In the earlier studies[4b] of aryldiazonium tetrafluoroborate decompositions in acetonitrile solutions, only low and erratic yields of the desired 2,4-dimethylquinazolines were obtained. The apparent discrepancy between the earlier studies and the results described here is tentatively ascribed to the facts that in these previous studies only alkyl- and *p*-chlorobenzenediazonium salts were employed, and the decomposition of these salts in acetonitrile solution was further complicated by the fact that the methyl-substituted quinazolines formed underwent secondary condensation reactions at rates comparable with those of their formation. It appears that electron-donating groups on the aromatic ring tend to promote the reaction of *N*-arylnitrilium ions with a second molecule of nitrile. Electron-withdrawing substituents such as phenyl and *m*-nitrophenyl groups appear to slow the rate of attack of the nitrilium ion on another nitrile group to the point that the slow phenanthridine-forming reaction becomes dominant. Although considerable starting material is unaccounted for in some of our experiments, it is unlikely that more than minute amounts of it went to quinazolines; if so the phenanthridine picrates would have been contaminated with troublesome quantities of quinazoline picrates and this was not the case. The best single experimental fact[4b] supporting these speculations is the observation that benzenediazonium tetrafluoroborate in methyl thiocyanate was converted to 2,4-bis(methylthio)quinazoline (41%) in only 5 min at 110° but no quinazoline was formed in our synthesis of **4e** (48 hr, 100°).

The only other general method of phenanthridine synthesis is the classical Morgan–Walls reaction of *o*-amidobiphenyls with $POCl_3$;[8] a few modifications of it have been found useful.[9] It is perhaps surprising and certainly fortunate that, although both methods probably involve the same intermediate carbocation (as in **7**), the environment of the cation is so different that the yields of heterocycles do not change in a parallel manner as the R group of RCN is altered. Instead the methods tend to be complimentary. For example the original Morgan–Walls method[8] affords a much better yield (85%) of the 6-phenyl isomer than our procedure (36%). On the other hand, no more than a trace of the 6-methyl-8-nitro compound **4f** could be obtained by the standard Morgan–Walls method,[9] while our approach provides at least a 33% yield; the best yield reported in the literature[9] for **4f** is 25% and a special variation of the Morgan–Walls reaction had to be employed.

The synthetic method described here was discovered[1b] at almost the same time by Schmidt and his students,[10] who reported obtaining good yields of the HBF_4 salts of four 6-substituted phenanthridines by merely heating very concentrated solutions of diazonium salt **3a** in nitriles at 80° until all gas evolution ceased. We attempted to duplicate the synthesis of 6-phenylphenanthridine following their procedure as closely as possble but obtained the free

base **4d** only in low yield. It was accompanied by sizable amounts of 2-benzoylamidobiphenyl and 2-fluorobiphenyl.

The fact that we found reaction times much longer than those reported by Schmidt and his students to be necessary for good yields might be explained if considerable water were present in all our reaction mixtures, hydrolyzing nitrilium ions to amides. The amides might cyclize slowly in an HBF_4-catalyzed Morgan-Walls reaction. This possibility is excluded by the reproducibility of our yields as well as by the fact that no phenols could be found in the two cases where we sought them assiduously. It is probable that even a little water would compete with the nitriles for the diazonium ions and give detectable quantities of phenols. We are at a loss to explain the differences between our results and those of the German group. As noted previously in this work and in other related work,[11] it has been our experience that cyclization of nitrilium ions to phenanthridines is a slow process and that high concentrations of diazonium fluoroborates leads to significant competition from the Balz–Schiemann reaction.

Phenanthridine Ir Bands. It is noteworthy that without exception the ir spectrum of each of the seven substituted phenanthridines studied was dominated by two very strong absorption peaks, one at 720–730 and the other at 750–765 cm^{-1}, which may well be characteristic of this particular heterocyclic system.

Experimental Section[12]

Preparation of Phenanthridines (4a–g). 6-Methylphenanthridine (4a). Method A. A solution of 2-biphenyldiazonium tetrafluoroborate[13] (**3a** 1.07 g) in acetonitrile (25 ml) was heated to reflux for 12 hr. Care was taken to protect the refluxing solution from moisture. Nitrogen evolution was complete in a few minutes. After cooling, the unreacted acetonitrile was evaporated and the solid residue was treated with chloroform (15 ml) and 5% aqueous sodium hydroxide. The organic layer was extracted with 8% phosphoric acid (3 × 15 ml). The combined extracts were washed with chloroform, neutralized (NaOH solution), and then extracted with chloroform. Upon drying (anhydrous Na_2SO_4) and evaporation of the chloroform, there remained 0.66 g (86%) of **4a** (R = CH_3; R′ = H), mp 84° (lit.[14] mp 84°). Glpc analysis revealed that 2-fluorobiphenyl (**6**) was present in 4.5% yield.

6-Ethylphenanthridine (4b). Method B. A solution of **3a** (R′ = H, 0.649 g) in propionitrile (25 ml) was heated to reflux for 24 hr, cooled, and treated with saturated aqueous $NaHCO_3$. This mixture was then extracted with CH_2Cl_2 (6 × 35 ml) and the combined extracts were dried (anhydrous Na_2SO_4) and evaporated, which provided a brown oil. To an ethanol (5 ml) solution of the oil was added 15 ml of saturated alcoholic picric acid, which thus afforded 0.63 g (60%) of **4b** picrate, mp 211–212° (lit. mp 210–211°). A portion of the picrate (0.115 g) was decomposed by heating it for 5 min with 2 *N* NaOH (25 ml) on a steam bath. The aqueous solution was extracted with $CHCl_3$, washed with saturated aqueous Na_2SO_4, dried (anhydrous Na_2SO_4), and evaporated to give 87.7 mg (70%) of **4b** (R = C_2H_5; R′ = H) as an oil which crystallized when seeded, mp 51–53°. Recrystallization from ether gave pure **4b**, mp 53–54° (lit. mp 51–53°,[15] 54–55°[16]), ir (Nujol) 725 s, 750 cm^{-1} vs.

The following compounds were prepared according to methods A or B as indicated in Table I.

6-Propylphenanthridine (4c). From 1.0 g of diazonium salt **3a** was obtained 0.772 g of the picrate of **4c**, mp 194–201° dec (lit.[17] mp 196–197.5°). Decomposition of this picrate generated **4c** as an oil.

6-Phenylphenanthridine (4d). Method B was followed with the following modification. When 1.0 g of diazonium salt **3a** was decomposed in a benzonitrile (25 ml) solution, most of the unreacted benzonitrile was vacuum distilled prior to picration. The crude picrate, mp 246–251° dec (lit.[18] mp 251° dec), was decomposed to give the free base, mp 102–105°. Recrystallization from ligroin gave pure **4d**: mp 105–107° (lit.[18] mp 106°); ir (Nujol) 780 s, 765 vs, 755 vs, 695 cm^{-1} (C_6H_5 and phenanthridine ring bands). The by-product **6** in the mother liquor of the picrate was estimated by glpc.

6-(Methylthio)phenanthridine (4e). Decomposing 1.01 g of diazonium salt **3a** in a methyl thiocyanate solution gave, by method B, the picrate of **4e**, mp 190–192° dec, as analytically pure material.

Anal. Calcd for $C_{20}H_{14}N_4O_7S$: N, 12.33. Found: N, 12.36.

From the picrate, the free base **4e**, mp 58–62°, was obtained in 99% yield. Recrystallization from ethanol gave pale yellow needles of **4e**: mp 68–70° (lit.[19] mp 70–71°); ir (Nujol) 720 vs, 755 cm^{-1} vs; nmr ($CDCl_3$) δ 8.55–7.15 m (8 H, aromatic), 2.76 s (3 H, $-SCH_3$).

Preparation of 4′-Nitrobiphenyl-2-diazonium Tetrafluoroborate (3b). 4′-Nitro-2-biphenylamine (1.5 g), obtained from 2-biphenylamine by the method of Scarborough and Waters,[20] was dissolved in hot 48% HBF_4 and cooled to 20°, and to this stirred solution was added, dropwise, an aqueous solution of $NaNO_2$ (1.5 g) in 4 ml of water. Stirring was continued for 10 min. The colorless diazonium salt crystals were filtered, washed with cold 10% HBF_4 and then with 10 ml of ether, dried under vacuum, and recrystallized once from cold methanol–ether, affording 1.23 g (56%) of the diazonium salt **3b**, mp 89–91° dec.

Anal. Calcd for $C_{12}H_8BF_4N_3O_2$: C, 46.04; H, 2.58. Found: C, 46.23; H, 2.45.

6-Methyl-8-nitrophenanthridine (4f). Method B was followed with a 1.00-g sample of the diazonium salt **3b**. The crude product (0.87 g) was dissolved in boiling absolute ethanol (100 ml) and to this solution was added 50 ml of saturated alcoholic picric acid. Heating was continued for an additional 30 min. Cooling afforded 0.53 g (35%) of the picrate of **4f** as yellow needles, mp 220–226° dec. The pure picrate melted at 229–231° dec.

Anal. Calcd for $C_{16}H_{13}N_5O_9$: N, 12.15. Found: N,12.11.

The free base **4f** was isolated from the picrate in essentially quantitative yield (0.59 g): mp 243–246° (lit.[9] mp 242–243°); ir (Nujol) 730 vs, 765 vs, 785 m, 900, 1110 w, 1325 vs, 1590 cm^{-1} m; nmr ($CDCl_3$) δ 9.06 m (7 H, aromatic protons), 3.07 (3 H, CH_3).

6-Ethyl-8-nitrophenanthridine (4g). Method A was followed with the modification that extractions with both 10% HCl and 8% H_3PO_4 were used. From 1.0 g of the diazonium salt **3b** was obtained **4g**, mp 172°, in 9% yield: nmr ($CDCl_3$) δ 9.00–7.15 m (7 H, aromatic protons), 3.34 q (2 H, J = 7.5 Hz, $-CH_2-$), 1.54 t (3 H, J = 7.5 Hz, $-CH_3$).

Anal. Calcd for $C_{15}H_{12}N_2O_3$: C, 71.41; H, 4.79. Found: C, 71.24; H, 4.47.

The yellow picrate of **4g**, mp 214–217°, was prepared.

Anal. Calcd for $C_{21}H_{15}N_5O_9$: N, 14.54. Found: N, 14.28.

2,4-Dimethylbenzo[*h*]quinazoline (10). A solution of 1-naphthalenediazonium tetrafluoroborate (0.75 g) in acetonitrile (15 ml) was heated to reflux for 30 hr. After cooling, the mixture was neutralized with 20% aqueous NaOH and extracted with ether. The organic fraction was dried and evaporated, and the resulting solid was sublimed (120°, 0.1 Torr), affording 0.37 g (57%) of **10**, mp 110–114°. Recrystallization from ethanol gave colorless crystals of **10**: mp 119–121°; nmr ($CDCl_3$) δ 9.30 m (1 H), 7.80 m (3 H, aromatic protons), 2.97 s (3 H, $-CH_3$), 2.94 s (3 H, $-CH_3$).

Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 81.03; H, 5.90; N, 13.33.

Synthesis of 6-Phenylphenanthridine (4d) under the Conditions of Schmidt and Coworkers.[10] A mixture of diazonium fluoroborate **3a** (4.44 g) and dry benzonitrile (12 ml) in a flask equipped with a tube leading to an oil-filled inverted cylinder to follow gas evolution was swirled for 5 min and then lowered into an 80° bath. Gas evolution ceased completely after 15 sec, after which the heating bath was removed and 30 ml of cyclohexane was added. No crystallization of the HBF_4 salt of phenanthridine **4d** being observed upon cooling, the mixture was perforce worked up by our method B. After removal of the CH_2Cl_2 and distillation of unreacted benzonitrile *in vacuo*, a subliminate of 2-fluorobiphenyl, mp 70–72° (0.114 g, 4%), was collected (the yield of this by-product was probably higher, since a 12% yield of the fluoro compound was obtained in a similar experiment). The picrate of 6-phenylphenanthridine, mp 249–251°, obtained weighed 1.34 g (16%, lit.[10] 56%, as HBF_4 salt). The picrate mother liquor afforded 1.86 g (41%) of 2-benzoylamidobiphenyl, mp 87–91° (lit.[21] 95°), ir (Nujol) 3415 vw and 3250 m (NH), 1640 s and 1575 m (amide I and II).

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Registry No.—**3a**, 51381-71-6; **3b**, 51381-73-8; **4g** picrate, 51381-81-8; **9**, 28912-93-8; **12**, 51464-55-2.

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Mass Spectroscopy of Indolo[2,3-a]quinolizidines. I. Fragmentation Patterns of C-3, C-4, C-6, C-7, and C-12b Deuterated Derivatives

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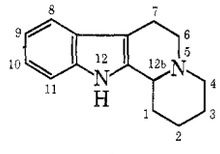
The mass spectra of the C-3, C-4, C-6, C-7, and C-12b deuterated derivatives of the indole alkaloid 1,2,3,4,6,7,12,12b-octahydroindolo[2,3-a]quinolizine (1). (*Dracontomelum mangiferum*) show that the P − 1 (base) peak at 70 eV is a mixture of four discrete ions, resulting from loss of C-4 H, C-6 H, C-7 H, and C-12b H. The labeling results show that the previously proposed structure for *m/e* 197 arising from a retro Diels–Alder reaction of *m/e* 225 only accounts for about 20% of *m/e* 197. The revised structure accounting for most of *m/e* 197 arises from a stepwise fragmentation from the parent ion (*m/e* 226). New fragmentation pathways and ion structures are also proposed and supported for the peaks at *m/e* 184, 156, 144, 97, 83, and 69.

Since its first application to indole alkaloids,[3] mass spectrometry has become a very important technique for the elucidation of the structure of alkaloids and other natural products.[4,5]

Although mass spectrometry has been applied to several members of the *Corynanthe-Yohimbe* family,[4-6] there is no consensus and little direct support for the various proposed fragmentation pathways for this class of indole alkaloids.[7] The indole alkaloid 1,2,3,4,6,7,12,12b-octahydroindolo[2,3-a]quinolizine (**1**)[8] is the simplest structure for



1

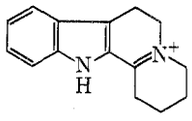
which a mass spectral fragmentation pattern representative of the *Corynanthe-Yohimbe* class of indole alkaloids may be expected.[6] The mass spectrum of **1** has been previously published,[6] but without direct support for the proposed fragments. We now report a mass spectral study of selected deuterated derivatives of **1**.

Results and Discussion

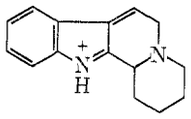
The 70-eV mass spectra of **1** is reproduced in Figure 1 and each of the main fragment clusters will be discussed in turn.

Parent Ion Cluster. It has been widely assumed[6,9-11] that the P − 1 (base) peak (*m/e* 225 for **1**) observed in the mass spectra of *Corynanthe-Yohimbe* indole alkaloids and other tetrahydro-β-carboline alkaloids is due to the loss of C-12b H leading to **2**. Only in systems where for steric reasons a C-12b iminium ion cannot form have alternate P − 1 ions been suggested.[12]

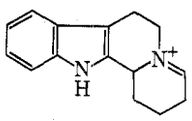
Our results (Table I) show that the P − 1 ion is a *mixture* of ions **2**–**5**, arising by hydrogen loss from C-12b, C-7,



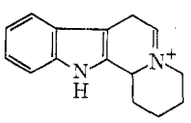
2 (*m/e* 225)



3 (*m/e* 225)



4 (*m/e* 225)



5 (*m/e* 225)

C-4, and C-6, respectively. For example, P − 2 (*m/e* 225, loss of D) is intense in the spectrum of 1-*7*-d_2 and P − 1 (*m/e* 226, loss of H) is intense in the spectrum of **1**-*12b*-d_1, both indicating the importance of other ions to P − 1. In contrast, **1**-*3*-d_2 (statistically adjusted for isotopic inhomogeneity) shows complete retention of deuterium in the