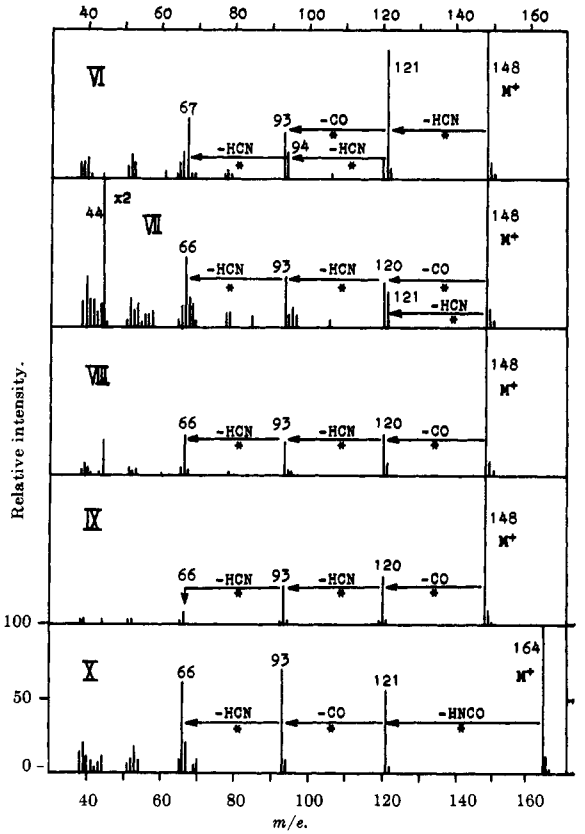


Figure 2.—Mass spectra of 2-hydroxypteridine (VI), 4-hydroxypteridine (VII), 6-hydroxypteridine (VIII), 7-hydroxypteridine (IX), and 2,4-dihydroxypteridine (X).

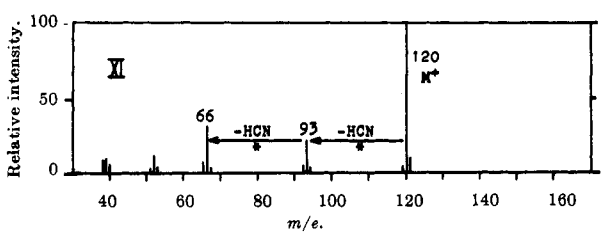
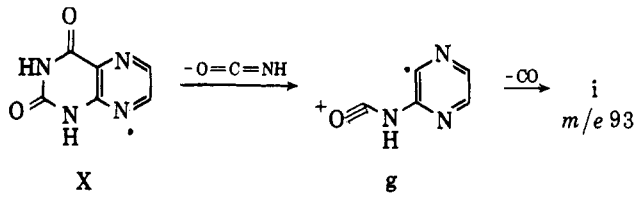


Figure 3.—Mass spectrum of purine (XI).

The rearrangement of the ion g to the ion h would be improbable since the structure of h can not account for the loss of carbon monoxide in the subsequent step.

Fragmentation patterns of 2,4-dihydroxypteridine (X) may be interpreted by analogy to the behavior of the 2-hydroxy derivative VI. Elimination of the fragment HNCO is followed by the loss of carbon monoxide to give the peak at *m/e* 93.



Most of the steps discussed above have been supported by the appropriate metastable peaks (indicated by asterisks in Figures 1 and 2).

Experimental

Materials.—Pteridine,[5] 2-methyl-, 4-methyl-, and 7-methylpteridine,[6] 6,7-dimethylpteridine,[6] 2- and 4-deuteriopteridine,[7] 2- and 4-hydroxypteridine,[5] 6- and 7-hydroxypteridine,[8] and 2,4-dihydroxypteridine[5] have been prepared by known methods. 4-Deuterio-7-methylpteridine was prepared from 4,5-diamino-6-deuteriopyrimidine[7] by the same method employed for the synthesis of 7-methylpteridine.[6] Deuterium content of the deuterio derivatives is about 35%.

Spectra.—The spectra were recorded using a Hitachi RMU-6C mass spectrometer equipped with an all-glass inlet system heated to 200°. The ionization energy was 80 e.v. and the ionizing current 80 μa.

Acknowledgment.—We are grateful for a grant from Toyo Rayon Company, Ltd., for the purchase of the spectrometer.

(5) A. Albert, D. J. Brown, and G. Cheeseman, *J. Chem. Soc.*, 474 (1951).
(6) A. Albert, D. J. Brown, and H. C. S. Wood, *ibid.*, 3832 (1954).
(7) S. Matsuura and T. Goto, *ibid.*, 623 (1965).
(8) A. Albert, D. J. Brown, and G. Cheeseman, *ibid.*, 1620 (1952).

Synthesis of Benzo[*a*]- and Naphtho[2,1-*a*]phenanthridizinium Salts*,[1]

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The synthesis of benzo[*a*]phenanthridizinium salts can be effected by cyclodehydration of quaternary salts derived from 1-phenylisoquinoline, even if no activating alkoxyl group is present. Similarly, 1-(2-naphthyl)isoquinoline is believed to yield naptho[2,1-*a*]phenanthridizinium salts.

In earlier work in this laboratory[2] it was shown that 1-phenyl-2-acetonylisoquinolinium salts (I, $R_2 = CH_3$; Z = O)[3] will not cyclize under conditions rather more drastic than used to effect the cyclization of 1-acetonyl-2-phenylpyridinium salts.[4] Subsequently,[5] it was found that introduction of a methoxyl group *para* to the position of expected cyclization, as in 1-(3-methoxyphenyl)-2-acetonyl-6,7-methylenedioxyisoquinolinium bromide made possible the preparation of a benzo[*a*]phenanthridizinium derivative.

It has now been found that the cyclization of unactivated systems, such as 1-phenyl-2-acetonylisoquinolinium bromide (I, $R_2 = CH_3$; Z = O), may be accomplished by heating them in polyphosphoric acid at 210–220°. Despite these vigorous conditions, little decomposition occurred and benzo[*a*]phenanthridizinium salts (II) were obtained, usually in good yields.

* To Professor Louis F. Fieser

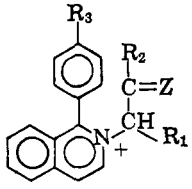
(1) This research was supported by a grant (CA-05509) from the National Cancer Institute of the National Institutes of Health.

(2) C. K. Bradsher and L. E. Beavers, *J. Am. Chem. Soc.*, **78**, 2459 (1956).

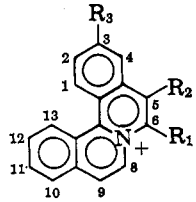
(3) Throughout this paper all R groups not otherwise specified represent hydrogen.

(4) C. K. Bradsher and L. E. Beavers, *J. Am. Chem. Soc.*, **77**, 453 (1955).

(5) C. K. Bradsher and K. B. Moser, *J. Org. Chem.*, **24**, 592 (1959).



I



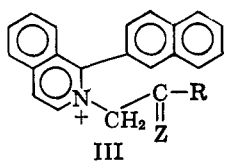
II

The salts (I) obtained by quaternization of 1-phenylisoquinoline with phenacyl bromide or with 3-bromo-2-butanone yielded the expected 5-phenyl (II, R_2 = C_6H_5) and 5,6-dimethyl (II, R_1 = R_2 = CH_3) salts. Desyl chloride failed to yield a quaternary salt with 1-phenylisoquinoline.

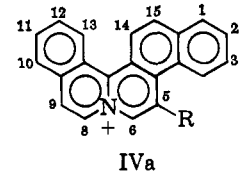
The unsubstituted benzo[*a*]phenanthridizinium nucleus (II) was synthesized by the general method recently developed[6] for the preparation of phenanthridizinium salts without substituents in ring B. The crude salt I (Z = NOH) obtained by quaternization of 1-phenylisoquinoline with chloro- or better with bromoacetaldoxime could be cyclized in 74% yield to the expected salt II by heating it for 24 hr. at 200° in a sealed tube with hydrobromic acid. As might be predicted from the properties of oximes only a small yield was obtained using polyphosphoric acid. Similarly, from 1-(*p*-tolyl)isoquinoline *via* the quaternary salt I (R_3 = CH_3; Z = NOH) the 3-methylbenzo[*a*]phenanthridizinium ion (II, R_3 = CH_3) was prepared.

Although our earlier attempts to employ 2-haloacetals as quaternizing agents have been unsuccessful it was found that 2-bromopropionaldehyde diethyl acetal with 1-phenylisoquinoline gave a low yield of an impure quaternary salt which on cyclization afforded what is presumably the 6-methyl derivative (II, R_1 = CH_3). Under the same conditions bromoacetal does not appear to form a quaternary salt with 1-phenylisoquinoline.

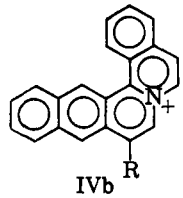
1-(2-Naphthyl)isoquinoline was prepared and two of its quaternary salts (III, Z = NOH, and III, Z = O; R = CH_3) cyclized. It is believed that the products are the naphtho[2,1-*a*]phenanthridizinium ion (IVa)



III



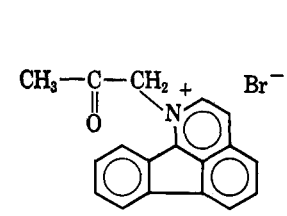
IVa



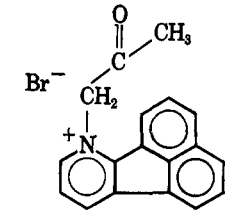
IVb

and its 5-methyl derivative (IVa, R = CH_3), the first fully aromatic derivatives of this series.[7] The choice of structure IVa rather than IVb is based upon the recognized[8] tendency for cyclization to occur in the α position rather than β, as well as upon a comparison of the ultraviolet absorption spectra with that reported[9] for the analogous hydrocarbons. Neither line of evidence is unambiguous, and the structure can not be regarded as proved.

It is of interest that the 1-acetonyl-1-azafluoranthene ion (V), which might be regarded as a 1-phenylisoquinolinium salt with an additional bridge between the rings, could not be cyclized, probably because of steric considerations. A similar failure was observed with the quaternary salt VI derived from 7-azafluoranthene.



V



VI

Experimental

All analyses were carried out by Ilse Beetz, Kronach, Germany. The melting points were determined in capillary tubes in a Mel-Temp apparatus and are corrected. The abbreviation S.T. is used to indicate that the melting point was taken in an evacuated sealed capillary. Ultraviolet absorption spectra were measured in 95% ethanol using 1-cm. quartz cells with a Cary Model 14 spectrophotometer.

5-Methylbenzo[*a*]phenanthridizinium (II, R_2 = CH_3) Perchlorate.—A mixture of 1.5 g. of 1-phenyl-2-acetonylisoquinolinium bromide[2] and 20 g. of polyphosphoric acid was stirred at 210–220° for 3 hr. The color of the mixture darkened rapidly. To the cooled mixture ice–water was added with stirring and the resulting solution was filtered to remove a small amount of gummy material. Addition of perchloric acid to the filtrate produced a flocculent buff-colored precipitate which showed no absorption in the carbonyl region of the infrared spectrum, and could be recrystallized from methanol, yield 1.2 g. (83%), m.p. 197.5–199.5°. Recrystallization from methanol afforded a pale yellow microcrystalline powder: m.p. 198–198.5°; λ_{max} mμ (log ϵ) 210 sh (4.37), 217 (4.48), 241 (4.28), 248 sh (4.24), 275 sh (4.41), 282 (4.58), 340 sh (3.71), 355 (3.92), and 391 (4.21).

Anal. Calcd. for $C_{18}H_{14}ClNO_4$: C, 62.91; H, 4.10; N, 4.08. Found: C, 63.16; H, 4.30; N, 4.43.

The **picrate** was crystallized from methanol as yellow prisms, m.p. 249–250°.

Anal. Calcd. for $C_{24}H_{16}N_4O_7$: C, 61.02; H, 3.41; N, 11.86. Found: C, 61.06; H, 3.43; N, 11.83.

2-(1-Acetylethyl)-1-phenylisoquinolinium (I, R_1 = R_2 = CH_3; Z = O) Bromide.—A solution of 2 g. of 1-phenylisoquinoline in 2.2 g. of freshly distilled 3-bromo-2-butanone in 8 ml. of dry acetone was refluxed for 12 hr. The precipitated solid was collected and washed with a small quantity of cold acetone. Crystallization from methanol–ethyl acetate gave 1.5 g. (43%) of material showing a strong absorption at 5.78 μ, m.p. 186–188°. The analytical sample consisted of colorless prisms: m.p. 191.5–192°; λ_{max} mμ (log ϵ) 236 (4.69), 272 (3.26), 280 (3.26), and 344 (3.38).

Anal. Calcd. for $C_{19}H_{18}BrNO$: C, 64.05; H, 5.09; N, 3.93. Found: C, 63.94; H, 5.03; N, 4.03.

The **perchlorate** crystallized from methanol–ethyl acetate as colorless prisms, m.p. 194.5–195.5°.

Anal. Calcd. for $C_{19}H_{18}ClNO_5$: C, 60.72; H, 4.83; N, 3.73. Found: C, 60.88; H, 4.74; N, 3.74.

5,6-Dimethylbenzo[*a*]phenanthridizinium (II, R_1 = R_2 = CH_3) Perchlorate.—Cyclodehydration of 1 g. of the bromide II (R_1 = R_2 = CH_3; Z = O) with polyphosphoric acid at 210–220° was carried out as described for the 5-methyl analog. The crude yellow perchlorate was crystallized from methanol, yield 0.8 g. (84%), m.p. 177–179°. The analytical sample consisted of fine yellow needles: m.p. 181.5–182.5°; λ_{max} mμ (log ϵ) 215 sh (4.43),

(6) R. W. L. Kimber and J. C. Parham, *J. Org. Chem.*, **28**, 3205 (1963).

(7) A 5,6,7,8-tetrahydroquinolizine analog has been reported by T. R. Govindachari and B. S. Thyagarayan [*Proc. Indian Acad. Sci.*, **39A**, 237 (1954); *Chem. Abstr.*, **49**, 9654*d* (1955)].

(8) W. S. Johnson, *Org. Reactions*, **2**, 123 (1944).

(9) E. Clar, "Aromatische Kohlenwasserstoffe, Polycyclische Systeme," 2 Auf., Springer-Verlag, Berlin, 1952, pp. 168, 207.

219 (4.52), 242 (4.30), 250 sh (4.22), 288 (4.63), 350 (3.75), 366 (3.94), 382 (4.08), and 402 (4.22).

Anal. Calcd. for $C_{19}H_{16}ClNO_4$: C, 63.78; H, 4.51; N, 3.92. Found: C, 63.81; H, 4.59; N, 3.77.

The **picrate** crystallized from methanol as light tan prisms, m.p. 209–211° (previous softening).

Anal. Calcd. for $C_{25}H_{18}N_4O_7$: C, 61.73; H, 3.73; N, 11.52. Found: C, 61.71; H, 3.62; N, 11.25.

1-Phenyl-2-phenacylisoquinolinium (I, R_2 = C_6H_5; Z = O) Bromide.—The quaternization of 2 g. of 1-phenylisoquinoline with 2.4 g. of phenacyl bromide was carried out in refluxing acetone in the usual way (3 hr.), yield 3.9 g. (98%), m.p. 208–210°, infrared absorption band at 5.87 μ. The analytical sample formed pale yellow prisms from methanol–ethyl acetate: m.p. 210–211.5°; λ_{max} mμ (log ε) 235 (4.76), 258 sh (3.86), 274 sh (3.81), 280 sh (3.79), and 342 (3.78).

Anal. Calcd. for $C_{23}H_{18}BrNO \cdot 0.5H_2O$: C, 66.83; H, 4.63; N, 3.39. Found: C, 66.47; H, 4.57; N, 3.46.

The **perchlorate** was obtained from methanol–ethyl acetate as colorless prisms, m.p. 190.5–191.5°.

Anal. Calcd. for $C_{23}H_{18}ClNO_5$: C, 65.19; H, 4.04; N, 3.30. Found: C, 65.14; H, 4.24; N, 3.42.

5-Phenylbenzo[*a*]phenanthridizinium (II, R_2 = C_6H_5) Perchlorate.—One gram of the quaternary salt I (R_2 = C_6H_5; Z = O) was cyclized at 220–225° except that 12 hr. was required[10] to effect cyclization. Recrystallization from methanol gave pale yellow needles: m.p. 246.5–248°; yield 0.5 g. (55%); λ_{max} mμ (log ε) 202 (4.52), 216 sh (4.50), 242 (4.32), 286 (4.62), 360 (4.02), 375 (4.19), and 394 (4.27).

Anal. Calcd. for $C_{23}H_{16}ClNO_4$: C, 68.06; H, 3.97; N, 3.45. Found: C, 68.12; H, 3.97; N, 3.56.

The **picrate** crystallized from methanol as yellow prisms, m.p. 178–179°.

Anal. Calcd. for $C_{29}H_{18}N_4O_7$: C, 65.17; H, 3.39; N, 10.48. Found: C, 65.48; H, 3.42; N, 10.35.

2-(2-Oximidoethyl)-1-phenylisoquinolinium (I, Z = NOH) Perchlorate.—A solution of 2 g. of 1-phenylisoquinoline and 1.5 g. of bromoacetaldoxime (b.p. 69–71° at 21 mm., prepared essentially as described for the chloro analog[6]) in 3 ml. of dry acetone was refluxed for 1 hr. and allowed to stand overnight. Addition of ethyl acetate gave a gum which solidified on trituration. Crystallization from methanol–ethyl acetate afforded the bromide, 1.8 g. (53%), m.p. 191.5–193.5°. This material was used in the cyclization, but was not obtained pure for analysis.

A sample converted to the perchlorate crystallized from methanol–ethyl acetate as colorless prisms: m.p. 185.5–186.5°; λ_{max} mμ (log ε) 222 (4.53), 236 (4.48), 280 (3.72), 333 (3.70), and 345 (3.70).

Anal. Calcd. for $C_{17}H_{15}ClN_2O_5$: C, 56.28; H, 4.17; N, 7.72. Found: C, 56.45; H, 4.08; N, 7.94.

Benzo[*a*]phenanthridizinium (II) Bromide.—A solution of 0.8 g. of the crude bromide I (Z = NOH) in 20 ml. of 48% hydrobromic acid was heated for 24 hr. in a sealed tube at 200°. The acid was removed under vacuum (aspirator) and the dark crystalline residue crystallized from methanol (charcoal), yield 0.5 g. (70%), m.p. 331–334°. Recrystallization yielded yellow plates: m.p. 340–342°; λ_{max} mμ (log ε) 211 sh (4.48), 216 (4.54), 240 (4.30), 274 sh (4.44), 283 (4.60), 340 sh (3.68), 355 (3.92), 377 (4.12), and 399 (4.23).

Anal. Calcd. for $C_{17}H_{12}BrN$: C, 65.82; H, 3.90; N, 4.52. Found: C, 65.77; H, 4.24; N, 4.64.

The **perchlorate** crystallized from methanol as yellow prisms, m.p. 282–283°.

Anal. Calcd. for $C_{17}H_{12}ClNO_4$: C, 61.92; H, 3.67; N, 4.25. Found: C, 61.87; H, 3.50; N, 4.34.

The **picrate** crystallized from methanol as yellow needles, m.p. 224.5–226.5°.

Anal. Calcd. for $C_{23}H_{14}N_4O_7$: C, 60.26; H, 3.08; N, 12.20. Found: C, 60.31; H, 3.15; N, 12.22.

6-Methylbenzo[*a*]phenanthridizinium (II, R_1 = CH_3) Perchlorate.—A solution of 1.5 g. of 1-phenylisoquinoline and 1.7 g. of 2-bromopropionaldehyde diethyl acetal in 6 ml. of dry acetone was refluxed for 15 hr. and the crude oily quaternary salt which resulted was precipitated by addition of ethyl acetate. The oil could not be crystallized and was washed with ethyl acetate, dissolved in polyphosphoric acid and heated at 210–220° for 3 hr. The reaction mixture was worked up in the usual way and the perchlorate, 200 mg. (9%), was obtained from methanol solution as yellow needles: dec. >250°; λ_{max} mμ (log ε) 214 sh (4.40), 218 (4.54), 242 (4.43), 277 sh (4.45), 286 (4.62), 350 sh (3.68), 365 (3.90), 381 (4.06), and 400 (4.20). The salt exhibited an intense blue fluorescence in dilute solution.

Anal. Calcd. for $C_{18}H_{14}ClNO_4$: C, 62.89; H, 4.11; N, 4.08. Found: C, 62.65; H, 3.95; N, 4.20.

The **picrate** crystallized from ethanol as yellow needles, m.p. 197.5–199.5°.

Anal. Calcd. for $C_{24}H_{16}N_4O_7$: C, 61.02; H, 3.41; N, 11.86. Found: C, 61.15; H, 3.63; N, 11.57.

2-(2-Oximidoethyl)-1-(*p*-tolyl)isoquinolinium (I, R_3 = CH_3; Z = NOH) Chloride.—From 2 g. of 1-(*p*-tolyl)isoquinoline and 1.4 g. of chloroacetaldoxime and using a procedure analogous to that used in the preparation of I (Z = NOH), 1.9 g. (63%) of product was obtained, m.p. 196.5–198.5°. Essentially the same results (70% yield) were obtained when quaternization was carried out in tetramethylene sulfone solution for 1 week at room temperature.

The salt crystallized from methanol–ethyl acetate as colorless prisms: m.p. 198.5–199.5°; λ_{max} mμ (log ε) 221 (4.59), 280 (3.79), 318 sh (3.66), 325 (3.71), and 350 sh (3.20).

Anal. Calcd. for $C_{18}H_{17}ClN_2O$: C, 69.11; H, 5.48; N, 8.96. Found: C, 68.79; H, 5.46; N, 9.13.

3-Methylbenzo[*a*]phenanthridizinium (II, R_3 = CH_3) Perchlorate.—The hydrobromic acid cyclization of 1 g. of the chloride I (R_3 = CH_3; Z = NOH) was carried out as in the preparation of II, affording 1.05 g. (95%) of product as the perchlorate. Crystallization from methanol afforded yellow needles: m.p. 272–273° with previous decomposition; λ_{max} mμ (log ε) 213 sh (4.47), 217 (4.52), 243 (4.26), 286 (4.61), 340 sh (3.62), 355 (3.94), 372 (4.16), and 390 (4.27).

Anal. Calcd. for $C_{18}H_{14}ClNO_4$: C, 62.89; H, 4.10; N, 4.08. Found: C, 62.55; H, 4.04; N, 4.26.

The **picrate** was crystallized from methanol as fine bright yellow needles, m.p. 221.5–222.5°.

Anal. Calcd. for $C_{24}H_{16}N_4O_7$: C, 61.02; H, 3.41; N, 11.86. Found: C, 60.70; H, 3.46; N, 11.72.

1-(2-Naphthyl)isoquinoline.—To a cooled solution of 2-naphthyllithium prepared from 7.5 g. of 2-bromonaphthalene, 4.5 g. of isoquinoline in 15 ml. of ether was added dropwise with stirring. After the addition (10 min.) the mixture was refluxed for 2 hr. Water was added to the deep green solution, and the ethereal layer was separated. To the ether solution 10 ml. of nitrobenzene was added; the mixture was distilled until the temperature of the vapor reached 170°. The residue was refluxed for 1 hr. and cooled, and ether was added. The ether solution was filtered to remove a small amount of solid and then extracted repeatedly with 10% hydrochloric acid. The combined acid extracts were washed with ether and then neutralized with ammonia solution. The dark oil which separated solidified on cooling. The resulting solid was crushed and sucked dry on the filter and then recrystallized from toluene–hexane, yield 3.0 g. (32%), m.p. 155–158°. The pure product gave colorless prisms: m.p. 161.5–162.5°; λ_{max} mμ (log ε) 217 (4.97), 238 sh (4.48), 245 sh (4.38), 266 sh (4.11), 275 (4.14), 285 sh (4.09), and 324 (3.98).

Anal. Calcd. for $C_{19}H_{13}N$: C, 89.38; H, 5.13; N, 5.49. Found: C, 89.16; H, 5.17; N, 5.50.

1-(2-Naphthyl)-2-acetonylisoquinolinium (III, R = CH_3; Z = NOH) Bromide.—The quaternization of 1 g. of 1-(2-naphthyl)isoquinoline with 0.82 g. of bromoacetone was carried out in refluxing acetone, yield 1 g. (67%). Recrystallization from methanol–ethyl acetate afforded pale yellow prisms, m.p. 209–211°, that showed an infrared absorption band at 5.81 mμ; λ_{max} (log ε) 221 (4.90), 239 (4.79), 270 (4.00), 280 sh (3.98), 320 sh (3.64), and 345 (3.86).

Anal. Calcd. for $C_{22}H_{18}BrNO$: C, 67.35; H, 4.62; N, 3.57. Found: C, 67.16; H, 4.70; N, 3.80.

The **perchlorate** crystallized from methanol–ethyl acetate as pale yellow prisms, m.p. 230–231°.

Anal. Calcd. for $C_{22}H_{18}ClNO_5$: C, 64.16; H, 4.40; N, 3.40. Found: C, 64.14; H, 4.43; N, 3.68.

5-Methylnaphtho[2,1-*a*]phenanthridizinium (IVa, R = CH_3) Perchlorate.—Cyclodehydration of 0.5 g. of the quaternary salt III (R = CH_3; Z = O) was carried out by refluxing for 20 hr. in 20 ml. of 48% hydrobromic acid. The acid was removed *in*

(10) The course of the cyclization was followed by withdrawing samples (3 drops) at intervals of 3 hr., dilution of the samples, and precipitation as the perchlorate. Cyclization was continued until the carbonyl band in the infrared had disappeared.

vacuo; the residue was crystallized from methanol as the bromide, yield 0.3 g. (67%). Recrystallization afforded pale orange needles, m.p. 323–324° (S.T.), which on analysis appeared to be associated with over 2 moles of water which could not be completely removed by drying *in vacuo* at 140°.

The **perchlorate** crystallized from methanol–acetonitrile as orange needles: m.p. 295–296° (S.T.) dec.; λ_{max} mμ (log ε) 206 (4.47), 228 (4.56), 248 sh (4.30), 278 (4.43), 298 (4.52), 308 (4.54), 317 (4.38), 345 sh (3.91), 366 (3.76), 388 sh (3.92), 406 (4.07), 415 (4.02), and 454 sh (3.32).

Anal. Calcd. for $C_{25}H_{16}ClNO_4$: C, 67.09; H, 4.10; N, 3.69. Found: C, 67.00; H, 4.19; N, 3.64.

Naphtho[2,1-*a*]phenanthridizinium (IVa) Perchlorate.—The quaternization of 0.8 g. of 1-(2-naphthyl)isoquinoline with 0.46 g. of chloroacetaldoxime was carried out in 8 ml. of tetramethylene sulfone in 14 days at room temperature. The oil which precipitated on addition of ethyl acetate could not be obtained solid. The iodide and perchlorate salts likewise appeared to be oils.

The crude chloride was refluxed for 22 hr. in 20 ml. of concentrated hydrochloric acid. Worked up in the usual way, 0.5 g. (51%) of crystalline material was obtained. The yellow prisms, m.p. 322–323° (S.T.), appeared to be hydrated and could not be made anhydrous by heating at 140°.

The **perchlorate** prepared from the chloride in the usual way, crystallized from methanol–acetonitrile as orange needles: m.p. 266–269° (S.T.) with previous darkening and softening; λ_{max} mμ (log ε) 206 sh (4.46), 227 (4.64), 258 sh (4.33), 278 (4.43), 294 sh (4.47), 305 (4.53), 310 sh (4.52), 325 (4.40), 370 (3.80), 391 (4.03), 409 (4.16), and 455 sh (3.34).

Anal. Calcd. for $C_{21}H_{14}ClNO_4$: C, 66.40; H, 3.72; N, 3.69. Found: C, 66.75; H, 3.68; N, 3.91.

1-Acetonyl-1-azafluoranthene Bromide (V).—The quaternization of 1 g. of 1-azafluoranthene with 1 g. of bromoacetone was carried out in boiling acetone (3 hr.). The product, 1.6 g. (80%), on recrystallization from methanol–ethyl acetate gave orange prisms, m.p. 241° dec.

Anal. Calcd. for $C_{18}H_{14}BrNO \cdot 0.5H_2O$: C, 61.90; H, 4.33; N, 4.01. Found: C, 61.51; H, 4.22; N, 4.09.

The **perchlorate** crystallized from methanol as orange needles, m.p. 213.5–214.5°.

Anal. Calcd. for $C_{18}H_{14}ClNO_5$: C, 60.00; H, 3.92; N, 3.89. Found: C, 60.24; H, 3.96; N, 4.05.

7-Acetonyl-7-azafluoranthene Bromide (VI).—The quaternization of 7-azafluoranthene was carried out as in the case of the 1 isomer, affording 1.4 g. (79%) of product. It crystallized from methanol–ethyl acetate as pale yellow prisms, dec. pt. >250°.

Anal. Calcd. for $C_{18}H_{14}BrNO$: C, 63.53; H, 4.15; N, 4.12. Found: C, 63.72; H, 4.21; N, 4.30.

The **perchlorate** was obtained from methanol as pale yellow prisms, m.p. 255–255.5°.

Anal. Calcd. for $C_{18}H_{14}ClNO_5$: C, 60.00; H, 3.92; N, 3.89. Found: C, 59.90; H, 3.63; N, 4.05.

Attempted Cyclization of V and VI.—The conditions tried for cyclization varied from heating on the steam bath with 48% hydrobromic acid to heating with polyphosphoric acid at 240° for 20 hr. Even under the most drastic conditions, where severe decomposition was observed, samples showed the carbonyl absorption in the infrared characteristic of the starting material.

Photosensitized Cycloaddition of Haloethylenes and 1,3-Dienes*

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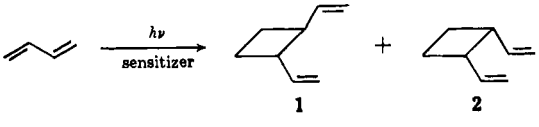
The photosensitized cycloaddition reactions of a number of 1,3-dienes and haloethylenes has been investigated. The formation of four-membered rings is invariably the predominant path of reaction in all the cases studied, although six-membered ring formation (Diels–Alder reaction) is competitive on occasion. The results are consistent with the attack of the triplet diene on haloethylene to form a biradical which rapidly cyclizes to products.

Photosensitized cycloaddition reactions to form cyclobutanes have long been known.[2] Although direct irradiation of suitably activated ethylenes often results in cyclobutane formation, the factors which direct the course of these reactions are not clear in most cases.[2,3] On the other hand, photosensitized dimerization of conjugated dienes is believed (a) to proceed *via* attack of a triplet diene on an unactivated diene and (b) to follow the rule that the products are determined by formation of the most stable biradical intermediate. This means that the predominant (often the exclusive) products formed may be predicted with remarkable accuracy merely by inspecting all of the possible biradical intermediates and then noting how resonance and inductive effects contribute to the stabilities of these intermediates. If one biradical is expected to be appreciably more stabilized than the others, we may expect the product of cyclization of this intermediate to predominate.

For example, the photosensitized dimerization of butadiene[4] results in a 98% yield of the dimers **1** and **2**, in a relative yield of 3 to 1. No 1,3-divinylcyclobutane (**3**) can be detected.



1 **2** (1)

The thermal cycloaddition reactions of a number of 1,3-dienes and fluoro olefins also yield products which closely follow the biradical postulate.[5,6] Thus, 1,1-dichloro-2,2-difluoroethylene (1122) yields only the adduct **4** when a solution of 1122 and butadiene is heated at 80°. The adduct **5** cannot be detected. In view of the formal similarities of the factors which

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(2) (a) For reviews, see A. Schönberg, "Präparative Organische Photochemie," Springer-Verlag, Berlin, 1958; (b) A. Mustafa, *Chem. Rev.*, **51**, 1 (1952); (c) P. deMayo, *Advan. Org. Chem.*, **2**, 367 (1960); (d) P. deMayo and S. T. Reid, *Quart. Rev.* (London), **15**, 393 (1961); (e) C. R. Masson, V. Boekelheide, and W. A. Noyes in "Technique of Organic Chemistry," Vol. II, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 257; (f) G. O. Schenck and R. Steinmetz, *Bull. soc. chim. Belges*, **71**, 781 (1962); (g) G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963); (h) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin Co., New York, N. Y., 1965.

(3) For recent investigations of the mechanism of photochemical cycloadditions, see (a) G. W. Griffin, A. F. Villturo, and K. Furukawa, *J. Am. Chem. Soc.*, **83**, 2725 (1961); (b) J. Bregman, K. Osaki, G. M. J. Schmidt, and F. I. Sonntag, *J. Chem. Soc.*, 2021 (1964); (c) P. Eaton and T. W. Cole, Jr., *J. Am. Chem. Soc.*, **86**, 963 (1964); (d) E. J. Corey, R. B. Mitra, and H. Uda, *ibid.*, **86**, 485, 5570 (1964).

(4) G. S. Hammond, N. J. Turro, and H. Fischer, *ibid.*, **83**, 4674 (1961); N. J. Turro, Ph.D. Thesis, California Institute of Technology, 1963.

(5) J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, (1962).

(6) P. D. Bartlett, L. K. Montgomery, B. Seidel, and K. Schueller, *J. Am. Chem. Soc.*, **86**, 616, 622, 628 (1964).