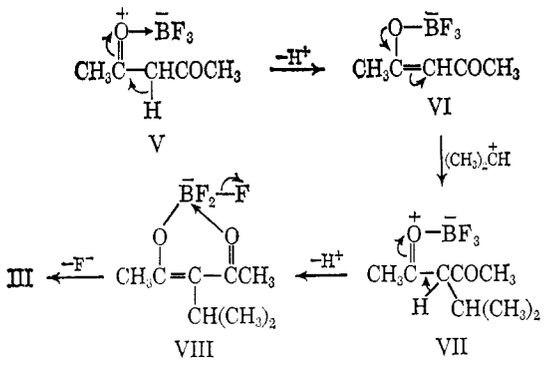
SCHEME I



fluoride ion in the presence of acetic anhydride to form difluoride complex IV, since IV was prepared in this manner in connection with the blank experiment mentioned above (see Experimental Section).

The present method of preparation of 3-isopropylacetylacetone (I) is superior to that involving acetylation of methyl isobutyl ketone by boron fluoride (which afforded mixtures)[5] and to the reaction of the sodium salt of acetylacetone with isopropyl iodide at 180° under pressure.[6] Although *t*-butylation of ethyl acetoacetate has been realized in low yield by this boron fluoride method,[2] that of acetylacetone afforded unsatisfactory results. Thus, the *t*-butyl derivative of this β-diketone was apparently obtained in about 15% yield in two experiments, but none was isolated in two other runs. Possibly the loss of fluoride ion from enol-type intermediate VI to form difluoride complex IV competed favorably with the condensation of VI with the *t*-butyl carbonium ion, which might be expected to be less reactive than the isopropyl carbonium ion.

Experimental Section[7]

3-Isopropylacetylacetone (I).—In a 500-ml flask equipped with a thermometer, gas inlet and outlet tubes, a drying tube, and a stirrer were placed 30.0 g (0.50 mole) of acetylacetone and 30.0 g (0.50 mole) of isopropyl alcohol. The flask was kept in an ice–alcohol bath while boron fluoride was passed into the flask. The rate of addition of boron fluoride was so regulated that the temperature of the reaction mixture was generally 0–10° and did not exceed 25°. After the mixture was saturated with boron fluoride, as evidenced by the presence of copious white fumes at the exit tube, the flask was stored overnight in a refrigerator. The resulting mixture was refluxed with 200 ml of 4 *M* sodium acetate solution for 1 hr. After cooling in an ice bath, the organic and aqueous layers were separated. The aqueous layer was extracted three times with ether and the extracts were combined with the organic layer. The ethereal solution was dried over Drierite. After filtering, the solution was condensed on a rotary evaporator. The residue was distilled to give 40.5 g (58%) of 2-isopropylacetylacetone (I), bp 79° (19 mm) [lit.[8] bp 80–84° (20 mm)], n^{29}D 1.4250.

In another experiment on the same scale, the reaction mixture was stored overnight in a refrigerator and then suction filtered (without treating it with sodium acetate). The solid residue was washed with water, dried in a desiccator over Drierite, and finally recrystallized from chloroform–hexane to give 40 g (42%) of the boron difluoride complex III. The nmr spectrum of complex III showed a doublet at 1.25 ppm (assigned to the methyl groups of the isopropyl moiety), a singlet at 2.38 ppm (assigned to the methyl groups on the acetylacetone moiety), and a multiplet centered at 2.92 ppm (assigned to the tertiary hydrogen of the isopropyl group). The integrated peak areas agreed with the theoretical values. **Decomposition** of complex III by means of hot aqueous sodium acetate gave 3-isopropylacetylacetone (I) in 79% yield, bp 81° (20 mm). **Cleavage** of a 7.1-g (0.05 mole) sample of the free β-diketone I with 2.2 g (0.055 mole) of sodium hydroxide in 40 ml of water (refluxed 1.5 hr) afforded 2.7 g (54%) of methyl isobutyl ketone, bp 115–118° (lit.[9] bp 119°). The vpc retention time of the methyl isobutyl ketone was identical with that of an authentic sample.

Blank Experiment with Boron Difluoride Complex IV.—This complex was prepared by saturating a solution of 20 g (0.20 mole) of acetylacetone in 61.2 g (0.6 mole) of acetic anhydride with boron fluoride at 0–10° and refluxing the reaction mixture on the steam bath for 3 hr. After the mixture was stored overnight in a refrigerator, the precipitate was collected on a funnel and recrystallized from aqueous methanol to give 6 g (20%) of complex IV, mp 43–44° (lit.[4] mp 43°). A suspension of 7.1 g (0.048 mole) of complex IV in 50 ml of isopropyl alcohol was saturated with boron fluoride and the reaction mixture refluxed with aqueous sodium acetate essentially as described above for the preparation of isopropylacetylacetone (I). Vpc analysis of the crude product showed that it consisted largely of recovered acetylacetone and only a trace of the isopropyl derivative I.

3,5-Dimethyl-4-isopropylpyrazole (II).—Into a flask equipped with a dropping funnel and condenser was placed 14.2 g (0.1 mole) of 3-isopropylacetylacetone (I) in 40 ml of absolute ethanol. The flask was cooled in an ice bath while 5.5 g of 64% hydrazine (0.11 mole) in 10 ml of ethanol was added; the solution was stirred with a magnetic stirring bar during the addition. The ice bath was removed and the solution was refluxed for 18 hr. Solvent was then removed on a rotary evaporator and the resulting oil was distilled *in vacuo* to give 7.8 g (57%) of 3,5-dimethyl-4-isopropylpyrazole (II), bp, 142–143° (15 mm).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.50; H, 10.23; N, 20.27. Found: C, 69.11; H, 10.14; N, 20.39.

Registry No.—I, 1540-38-1; II, 13084-76-9; acetylacetone, 123-54-6; isopropyl alcohol, 67-63-0; boron fluoride, 7637-07-2.

(5) C. R. Hauser and J. T. Adams, *J. Am. Chem. Soc.*, **66**, 345 (1944).

(6) G. T. Morgan and R. W. Thomason, *J. Chem. Soc.*, **125**, 754 (1924).

(7) Gas chromatograms were obtained on F & M Model 500 and 700 gas chromatographs equipped with 6 ft × 1/8 in. Se-30 columns. The nmr spectra were obtained on a Varian A-60 high-resolution spectrometer. Microanalyses were performed by Jansses Pharmaceutica, Beerse, Belgium. Reagents were obtained from commercial sources and used without purification. Boron fluoride was passed through concentrated sulfuric acid before use.

(8) C. R. Hauser, F. C. Frostick, and E. H. Man, *J. Am. Chem. Soc.*, **74**, 3231 (1952).

(9) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., p 316.

Naphthyridine Chemistry. VII. Syntheses and Spectral Data on Some Benzo[*f*][1,7]naphthyridines

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Several publications[1-4] describe the cyclization of 3-aminoquinoline under the conditions of the Skraup, Conrad–Limpach, and ethoxymethylenemalonic ester (EMME) condensations. These reactions could potentially afford derivatives of either the linear benzo-1,5-naphthyridines (pyrido[3,2-*b*]quinolines) **1** or the angular benzo-1,7-naphthyridines (pyrido[2,3-*c*]quino-

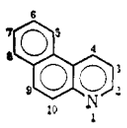
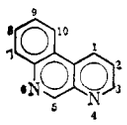
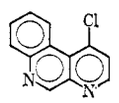
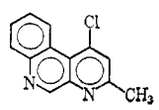
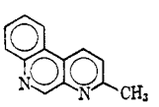
(1) M. Shimizu, *J. Pharm. Soc.* (Japan), **64**, 489 (1944).

(2) C. Hauser and G. Reynolds, *J. Org. Chem.*, **15**, 1224 (1950).

(3) N. Buu-Hoi, R. Royer, and M. Hubert-Hubart, *J. Chem. Soc.*, 2048 (1956).

(4) C. F. H. Allen, "The Chemistry of Heterocyclic Compounds," Vol. 12, Interscience Publishers, Inc., New York, N. Y., 1958, pp 98–100.

TABLE I
NMR SPECTRAL DATA OF SOME AZAPHENANTHRENES

Compound (CDCl₃ solution)	Chemical shifts (τ) H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9	H-10	CH₃
	...	1.10	2.63	1.30	1.58	2.37[a]	2.37[a]	2.37[a]	2.00	2.18	...
	1.37	2.45	1.08	...	0.55	...	1.78	1.75[a]	1.75[a]	1.78	...
	...	2.48	1.42	...	0.80	...	1.97	2.45[a]	2.45[a]	0.73	...
	...	2.60	...	...	0.73	...	1.87	2.33[a]	2.33[a]	0.65	7.38[b]
	1.52	2.62	...	...	0.63	...	1.80	2.43[a]	2.43[a]	1.80	7.47[b]

[a] Center of a nonanalyzed complex multiplet. [b] Singlet.

lines) **2**, depending upon the direction of cyclization. Based on the observation that 3-aminopyridines condense to yield 1,5-naphthyridines, Hauser and Reynolds[2] described the products obtained from the Conrad–Limpach and the EMME condensations as the linear compounds **3** and **9**. Buu-Hoi and coworkers,[3] on the other hand, describe the Skraup condensation product of 3-aminoquinoline as possessing the angular structure **2**. This structure assignment is based entirely upon the similarity of the ultraviolet spectrum of this material with that of some azaphenanthrenes, and is contrary to the structural assignment made earlier by Shimizu,[1] who describes the substance as the linear benzo-1,5-naphthyridine **1**.

In view of our interest in naphthyridine chemistry,[5] and the search for more suitable syntheses of 1,7-naphthyridines, it became necessary to reinvestigate these condensations in an effort to establish the structures of the different cyclization products.

The Skraup condensation product from glycerol and 3-aminoquinoline is described[3] as a pale yellow solid which melts at 114°. Our compound, prepared with Sulfo-mix,[5] is a white crystalline solid which melts at 113.5–114.5°. The elemental analysis and ultraviolet spectrum of our material agrees with the corresponding data reported for the pale yellow crystalline material. The nmr spectrum of the Skraup reaction product shows a one-proton singlet (τ 0.55) as the most deshielded proton of the compound. If this material were the linear compound **1**, the most deshielded proton would be part of an ABX system and would be due to H-2. Thus, the nmr spectrum strongly suggests that we are dealing with the angular benzo-1,7-naphthyridine **2**. Since the nmr spectrum of benzo[*f*]-quinoline is reported,[6] a comparison of this spectrum with that of the benzo-1,7-naphthyridine lends additional structural support, as is clearly shown by the data presented in Table I.

The mass spectrum of the benzonaphthyridine establishes its structure beyond doubt. The linear compound **1** would be expected to lose one molecule of HCN only, while the angular compound **2** should lose two molecules of HCN upon electron impact.[7] The formation of a *m/e* 153 ion from the parent ion and the loss of 27 mass units from the former fragment to afford the *m/e* 126 species are substantiated by the presence of the appropriate metastable peaks (*m** 130.4 and *m** 103.5, respectively).

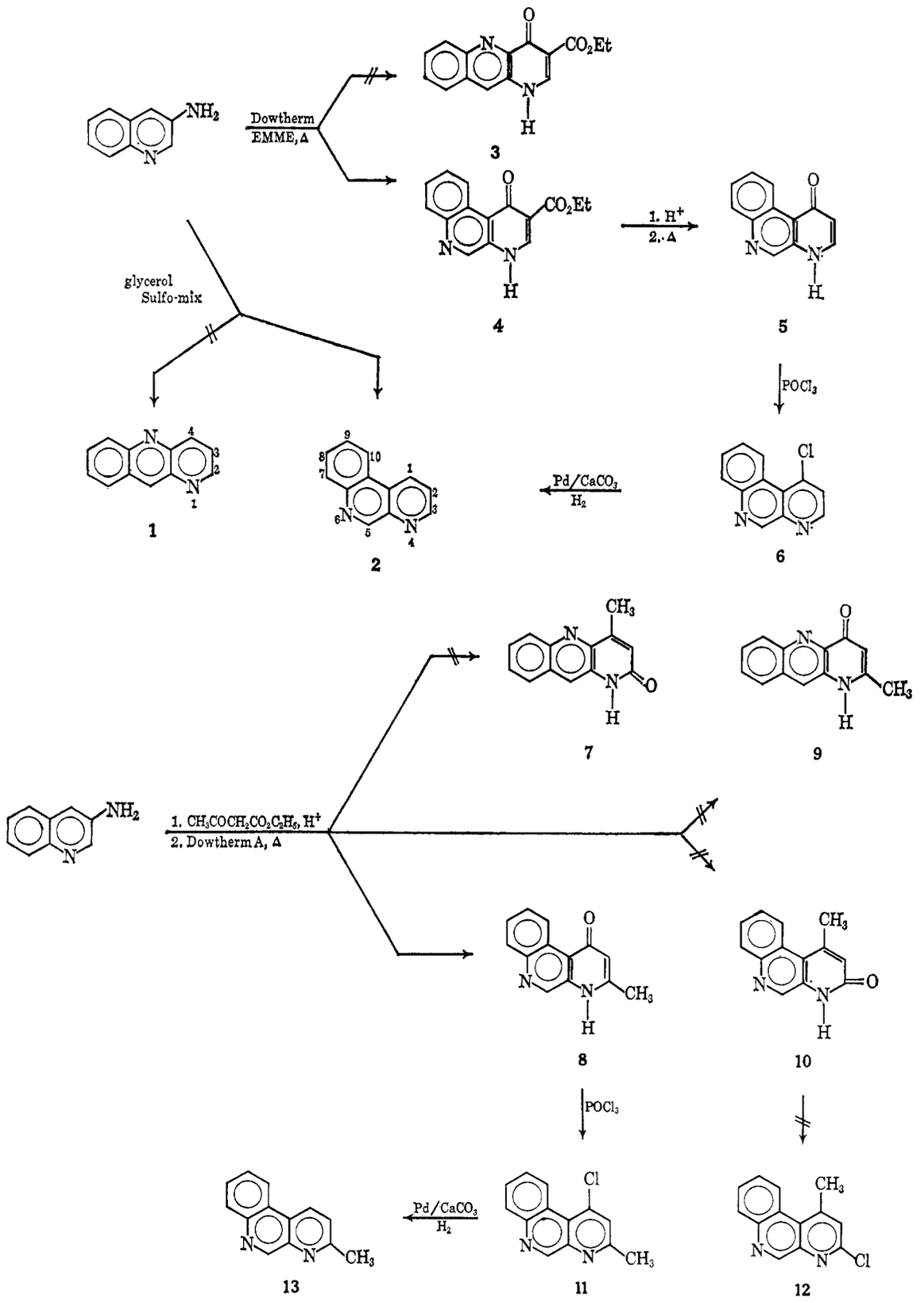
The condensation of 3-aminoquinoline with EMME is reported to yield the benzo-1,5-naphthyridine **3**.[2] We have now repeated this condensation and have converted the keto ester (later shown to have structure **4**) into the 1-keto compound **5** by hydrolysis followed by thermal decarboxylation of the keto acid. The keto compound is readily converted into the 1-chloro product **6** by treatment with phosphorus oxychloride. The nmr spectrum of the chloro compound shows the highly deshielded proton singlet (*cf.* Table I) observed in benzo[*f*][1,7]naphthyridine (**2**). In addition to this deshielded proton, there is a one-proton multiplet at an even more deshielded position. This is only consistent with the angular structure **6** for the chloro compound and is in agreement with the deshielding effect observed in similar "angular" proton interactions.[6] That the Skraup product possesses the same ring skeleton as the EMME product was finally established by removal of the chloro group from compound **6**, to afford the same benzonaphthyridine as is obtained from the Skraup reaction. These reactions are outlined in Scheme I.

(5) W. W. Paudler and T. J. Kress, *J. Heterocyclic Chem.*, in press; *J. Org. Chem.*, **32**, 832 (1967).

(6) E. V. Donckt, R. H. Martin, and F. Geerts-Evrard, *Tetrahedron*, **20**, 1495 (1964).

(7) The loss of HCN from certain heteroaromatic compounds is a well-known process (H. Budzikiewicz, C. Djerassi, D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, pp 225–262).

SCHEME I



The Conrad–Limpach condensation is reported to afford the 2-methyl-4-hydroxybenzo[*b*][1,5]naphthyridine (**9**) rather than the alternate 4-methyl-2-hydroxybenzo[*b*][1,5]naphthyridine (**7**). The condensation of 3-aminoquinoline with ethyl acetoacetate, followed by thermal cyclization in Dowtherm, yields a compound which affords a chlorobenzonaphthyridine upon treatment with phosphorus oxychloride. The nmr spectrum of this substance again shows the one-proton, strongly deshielded multiplet due to H-10 (τ 0.73) observed in the 1-chlorobenzo[*f*][1,7]naphthyridine (τ 0.65). This strongly suggests that the Conrad–Limpach condensation affords the 1-hydroxy-3-methylbenzo[*f*][1,7]naphthyridine.

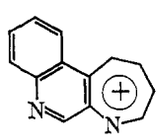
Further proof of this structure is obtained by the observation that removal of the chloro group from com-

pound **11** affords a methyl compound (**13**) which no longer exhibits this highly deshielded proton at position 10. This proton resonates at τ 1.80 in the methyl compound **13** and is similar to the chemical shift (τ 1.78) of this proton in the parent compound (**2**).

The remainder of the nmr spectrum (*cf.* Table I) further substantiates the structure assignment of compound **13** and consequently also proves the structures of compounds **8** and **11**.

The virtual identity of the ultraviolet spectra of the parent compound **2** and of the 3-methyl derivative constitute final proof of the structures (*cf.* Figure 1).

The mass spectrum of the 3-methylbenzo[*f*][1,7]-naphthyridine (**13**) shows the loss of HCN (*m/e* 167 fragment) and the loss of H (*m/e* 193 ion), followed by elimination of HCN from the presumed ring-expanded *m/e* 193 ion (**14**).[7] The loss of acetonitrile (substantiated by a metastable at 121.2) from the parent ion is also of some interest.



14

The mass spectra of the compounds described in this paper are of some interest since they reflect the similarity in the fragmentation patterns of the benzo-[*f*]quinoline and the benzo[*f*][1,7]naphthyridines, as well as the considerable stability of these compounds to electron bombardment, as is evidenced by the scarcity of fragment ions. Mass spectral data is presented in Table II.

TABLE II

MASS SPECTRAL DATA

Compound	*m/e* (relative abundance, %)
Benzo[*f*]quinoline	180 (14), 179 (100), 178 (39), 177 (5), 152 (15), 151 (20), 150 (9), 76 (17), 75 (9), 74 (5), 63 (10)
Benzo[*f*][1,7]-naphthyridine	181 (14), 180 (100), 179 (39), 153 (13), 152 (13), 127 (13), 126 (12), 125 (8), 100 (6), 99 (5), 90 (5), 77 (5), 76 (11), 75 (10), 74 (9), 63 (12), 52 (5), 51 (8), 50 (11), 39 (8)
3-Methylbenzo-[*f*][1,7]naph-thyridine	195 (16), 194 (100), 193 (18), 179 (6), 167 (7), 166 (11), 152 (7), 140 (8), 139 (7), 127 (5), 76 (5), 75 (6), 74 (5), 63 (6), 51 (5), 50 (5), 39 (7)

Experimental Section[8]

1-Hydroxybenzo[*f*][1,7]naphthyridine-2-carboxylic Acid.—1-Hydroxy-2-carbethoxybenzo[*f*][1,7]naphthyridine[2] (**4**, 11.8 g, 0.041 mole) was refluxed in a 50% aqueous solution of sulfuric acid for 6 hr, cooled, and filtered. The filtrate was washed with water, acetone, and ether until dry. The acid (10.6 g, 99%, mp 277–278°) was obtained as a pale yellow-green powder.

1-Hydroxybenzo[*f*][1,7]naphthyridine (**5**).—The above acid (2.5 g, 0.014 mole) was heated at its melting point (277–278) until effervescence ceased. The cooled solid was collected and sublimed at 300° (0.5 mm) to afford golden clusters of **5** (mp 304–306°, 1.7 g, 68%).

(8) The nmr spectra were obtained with a Varian A-60 spectrometer. The purity of the compounds was ascertained by thin layer chromatography (silica gel G, ether). The mass spectra were determined with a Hitachi Perkin-Elmer RMU-6E mass spectrometer with the liquid sample injection unit at 200° and the ionization voltage at 80 ev.

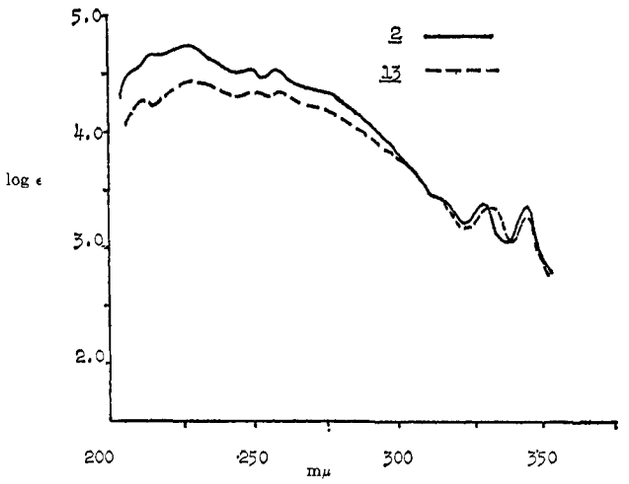


Figure 1.—Ultraviolet spectra of benzo [*f*][1,7]naphthyridine and of 3-methylbenzo [*f*][1,7]-naphthyridine.

Anal. Calcd for $C_{12}H_8N_2O$: C, 73.46; H, 4.11; N, 14.28. Found: C, 73.40; H, 4.06; N, 14.32.

1-Chlorobenzo[*f*][1,7]naphthyridine (**6**).—Phosphorus oxychloride (5 ml) and 0.37 g (1.9 mmoles) of **5** were heated on a steam bath for 1 hr. The reaction mixture was cooled and poured onto ice. To this solution was added 200 ml of chloroform and the aqueous layer was adjusted to pH 5 with sodium acetate. The layers were separated, and the water layer was again extracted with two 100-ml portions of chloroform. The combined chloroform extracts were washed with an aqueous solution of sodium carbonate, followed by water. The organic extract was then dried over anhydrous magnesium sulfate and filtered. Removal of the solvent *in vacuo* yielded white crystals (0.35 g). Sublimation at 100° (0.1 mm) afforded white needles (0.30 g, 75%, mp 116–117°).

Anal. Calcd for $C_{12}H_7N_2Cl$: C, 67.15; H, 3.29; N, 13.05. Found: C, 67.00; H, 3.20; N, 13.15.

Benzo[*f*][1,7]naphthyridine (**2**). **A.**—The chloro compound **6** (89 mg, 0.42 mmole) was dissolved in 10 ml of a methanol solution containing 2.5% of potassium hydroxide. This solution was added to a suspension of 100 mg of reduced palladium hydroxide (0.5%) on calcium carbonate in 50 ml of 2.5% of methanolic potassium hydroxide. This mixture was then treated with hydrogen gas, and, after the uptake of gas had ceased (10 min), the solution was filtered and the filtrate was evaporated to dryness. The residue was then extracted several times with ether and the combined ether extracts were evaporated to dryness to afford 73 mg (97%) of a white crystalline solid (mp 114°).

B (the Skraup Reaction).—The details of the Skraup reaction as applied to the synthesis of naphthyridines has been previously described by us.[1] The same procedure was employed for the condensation of 3-aminoquinoline with glycerol. The crude reaction product was isolated by steam distillation and was chromatographed. Chromatography on neutral (Brockman grade 3) alumina and elution with ether afforded a white crystalline solid which was sublimed at 100° (0.5 mm) to yield 1.4 g (10%), of the benzo[*f*][1,7]naphthyridine, mp 113.5–114.5° (lit.[3] mp 114°). A mixture melting point with the product obtained by procedure A was not depressed. The ultraviolet and nmr spectra of the two products are identical.

3-Methyl-1-chlorobenzo[*f*][1,7]naphthyridine (**11**).—3-Methyl-1-hydroxybenzo[*f*][1,7]naphthyridine[2] (**8**), (1.4 g, 6.7 mmoles) dissolved in 13 ml of phosphorus oxychloride was heated on a steam bath for 1 hr. The remainder of the procedure was the same as that described for the preparation of compound **6**. The product was chromatographed on neutral (Brockman grade 3) alumina and eluted with ether. Removal of the eluent yielded 0.8 g (53%) of **11** as white needles (mp 141–142°).

Anal. Calcd for $C_{13}H_9Cl$: C, 68.28; H, 3.97; N, 12.25. Found: C, 68.35; H, 4.01; N, 12.15.

3-Methylbenzo[*f*][1,7]naphthyridine (**13**).—The chloro compound (**11**) was dehalogenated by the same procedure as that described for the preparation of compound **2**. Sublimation of the reduction product at 80° (0.1 mm) gave 180 mg (78%) of **13** (mp 101–102°, white clusters): $\lambda_{max}^{CH_3OH}$ 208 (sh) mμ (log ε 4.60), 216 (sh) (4.70), 224 (sh) (4.75), 229 (4.78), 250 (4.53),

258 (4.53), 276 (sh) (4.34), 303 (sh) (3.70), 315 (sh) (3.42), 331 (3.36), 346 (3.32).

Anal. Calcd for $C_{13}H_{10}N_2$: C, 80.39; H, 5.19; N, 14.42. Found: C, 80.60; H, 5.28; N, 14.41.

Registry No.—2, 230-10-4; 5, 13100-44-2; 6, 13084-79-2; 11, 13084-80-5; 13, 13084-81-6; benzo[*f*]-guinoline, 85-02-9; 1-hydroxybenzo[*f*][1,7]naphthyridine-2-carboxylic acid, 13095-02-8.

The Halogenation of Acenaphthene Derivatives

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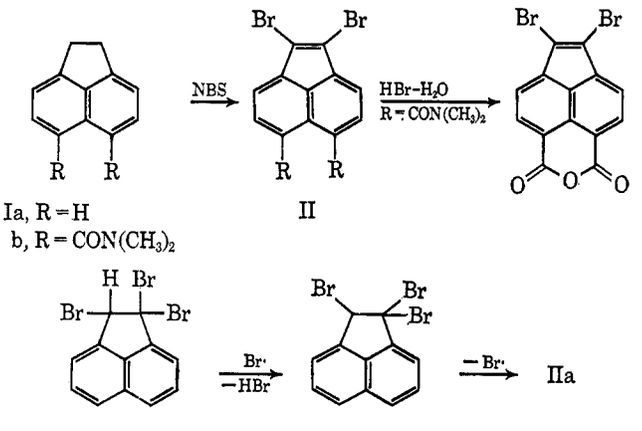
Received February 6, 1967

A common route for the preparation of acenaphthylenes from acenaphthenes involves bromination followed by elimination.[1,2] In conjunction with other synthetic studies, we required 1,2-dihaloacenaphthylenes which we believed would be available by similar methods. When this work began, the only report of such compounds involved a long, tedious procedure.[3] In light of a recent communication,[4] we wish now to report our work toward a simple preparation of 1,2-dibromo- and 1,2-dichloroacenaphthylenes.

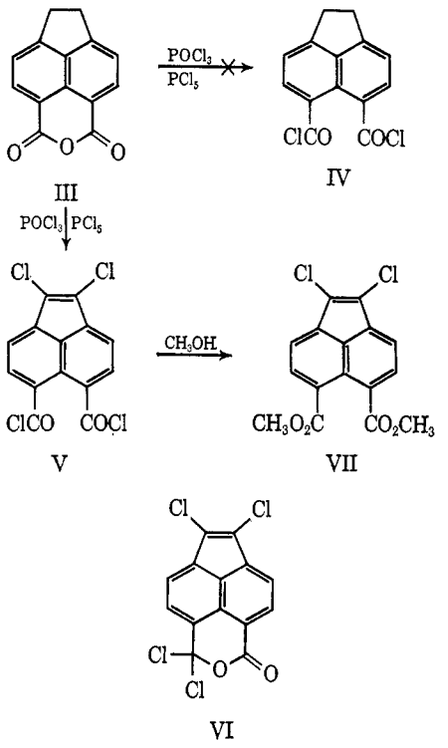
Treatment of acenaphthene with 4 equiv of N-bromosuccinimide yields approximately 80% of a single compound whose spectral properties identify it as 1,2-dibromoacenaphthylene. This procedure was extended to a 5,6-disubstituted acenaphthene with equal success as illustrated in Scheme I. In this latter case, the product was also characterized by hydrolysis to the corresponding acid anhydride. A reasonable rationalization for these reactions involves the tribromide which loses HBr probably by a free-radical pathway as depicted in Scheme I.

SCHEME I



Attempted extension of this free-radical bromination reaction to chlorination has produced equivocal results. Treatment of Ia or b with *t*-butyl hypochlorite has produced only complex mixtures. However, an attempt to convert the acid anhydride III to its acid chloride IV led surprisingly only to the dichloroacenaphthylene diacid chloride V. The nmr spectrum (see the Experimental Section) confirms the acid chloride structure and eliminates the pseudo-acid chloride structure VI. Although we were unable to obtain a good elemental analysis on V owing to sensitivity to hydrolysis, all the spectral data support its structure. It was further characterized by conversion to the dimethyl ester VII (upon treatment with hot methanol) and to the acid anhydride (Scheme II).

SCHEME II



The pathway for formation of V is not clear. This reaction failed with either Ia or Ib. If the reaction proceeded by simple free-radical chlorination by chlorine generated from either PCl_5 or $POCl_3$, both Ia and Ib should react. It is conceivable the formation of V involves a vinylogous Hell–Volhard–Zelinsky reaction.

Experimental Section[5]

1,2-Dibromoacenaphthylene (IIa).—To 1.54 g (10 mmoles) of acenaphthene dissolved in 50 ml of hot carbon tetrachloride was added 7.12 g (40 mmoles) of N-bromosuccinimide and a few crystals of dibenzoyl peroxide. After refluxing for 1 hr, the deep orange mixture was cooled and the succinimide was removed by filtration. The solution was washed with aqueous sodium thiosulfate and then dried over anhydrous magnesium sulfate.

(1) (a) S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *J. Am. Chem. Soc.*, **78**, 4939 (1956); (b) A. G. Anderson, Jr., and R. G. Anderson, *ibid.*, **77**, 6610 (1955).

(2) For other studies involving the halogenation of acenaphthenes, see (a) S. D. Ross, M. Finkelstein, and R. C. Petersen, *ibid.*, **80**, 4327 (1958); (b) F. D. Greene, W. A. Remers, and J. W. Wilson, Jr., *ibid.*, **79**, 1416 (1957).

(3) A. I. Tochilkin, *Zh. Vses. Khim. Obshchestva im. D. I. Mindeleeva*, **6**, 591 (1961); *Chem. Abstr.*, **56**, 7232b (1962).

(4) K. Rasheed, *Tetrahedron*, **22**, 2957 (1966).

(5) Melting points were taken on a Thomas–Hoover melting point apparatus and are corrected. Infrared spectra were determined on a Beckman IR-8 spectrophotometer, and ultraviolet spectra were recorded on Cary Models 11 and 15 spectrophotometers. Nmr spectra were determined on a Varian Associates Model A-60 spectrometer fitted with a variable-temperature probe. Chemical shifts are given in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. Mass spectra were taken on a CEC 103 C mass spectrometer at an ionizing current of 40 ma and ionizing voltage of 70 v. Analyses were performed by Spang Microanalytical Laboratory and Micro-Tech Laboratories, Inc. Unless otherwise indicated, extractions were performed with chloroform and magnesium sulfate was employed as a drying agent.