# New Tetracyclic Systems Incorporating the Benzo[c]quinolizinium Cation[1]

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*Received June 24, 1966*

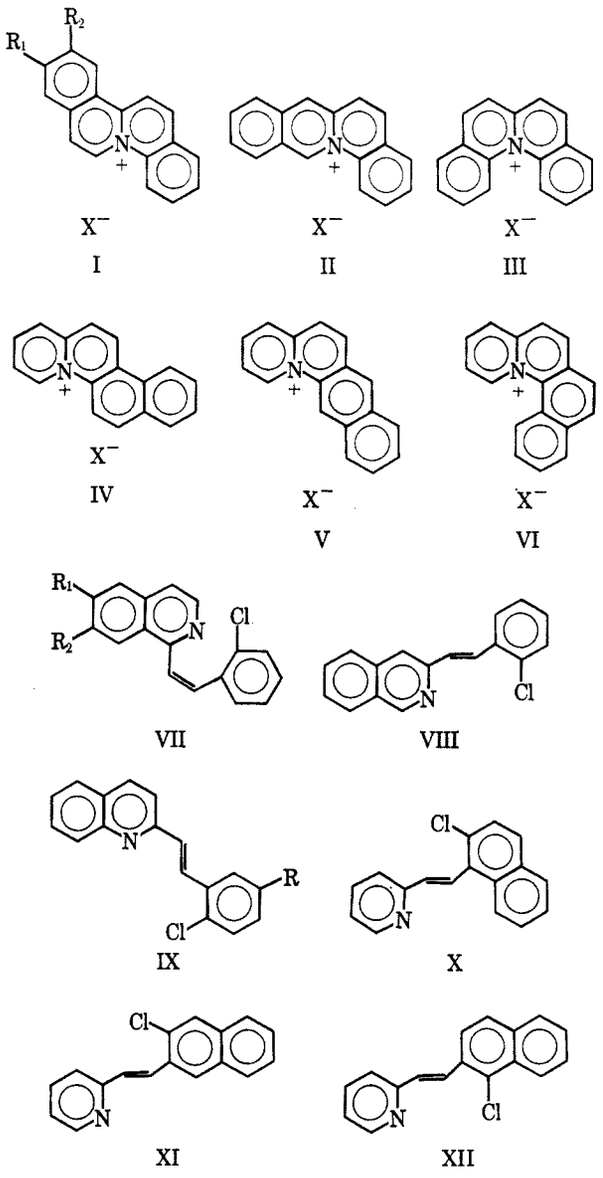
*cis*-Chlorostyrylisoquinolines and β-(chloronaphthyl)-2-vinylpyridines, obtained mainly by irradiation of the *trans* form, have been cyclized to afford four of the possible simple tetracyclic systems incorporating the benzo[c]quinolizinium cation. Unsuccessful attempts to prepare the other two systems are reported.

Recent publications[2,3] have described a general synthesis of benzo[c]quinolizinium derivatives from appropriate *trans*-2′-chloro-2-stilbazoles. This synthesis involves photochemical isomerization of the *trans* stilbazoles in benzene solution to give crude *cis–trans* mixtures. The *cis* isomers, on heating, undergo intramolecular quaternization during which quinolizinium salts are precipitated. It was of interest to determine whether this method could be extended to the preparation of new tetracyclic systems which might provide models for the synthesis of aza steroids or azonia helicenes.

Apart from the *peri*-fused and the dibenzo[a,c]-quinolizinium systems, there are six possible tetracyclic aromatic structures incorporating the benzo[c]quinolizinium cation. For the synthesis of structures I, II, and III, the appropriate styrylquinolines or isoquinolines are required as intermediates (*e.g.*, VII → I), while for structures IV, V, and VI, chloronaphthyl-2-vinylpyridines are needed.

2′-Chloro-1-styrylisoquinoline (VII, $R_1 = R_2 = H$) was readily prepared in good yield by a sealed-tube condensation of 1-methylisoquinoline with 2-chlorobenzaldehyde, using conditions analogous to those described by Mills and Smith[4] for condensation with benzaldehyde. Somewhat surprisingly, the styrylisoquinoline (VII, $R_1 = R_2 = H$) could be cyclized to the quinolizinium salt (I, $R_1 = R_2 = H$; X = Cl)[5] in 70% yield by heating at 200° with no previous irradiation. No change was observed in the ultraviolet spectrum of the isoquinoline (VII, $R_1 = R_2 = H$) when a benzene solution was irradiated with ultraviolet light, and this, combined with the facile cyclization to the quaternary salt (I) suggests that the styrylisoquinoline is in the *cis* form. However, 6,7-dimethoxy-2′-chloro-1-styrylisoquinoline (VII, $R_1 = R_2 = OCH_3$) was not cyclized simply by heating. On irradiation in benzene solution, this compound (VII, $R_1 = R_2 = OCH_3$) showed some shift to shorter wavelengths in its ultraviolet spectrum, though considerably less than that observed for the stilbazoles.[3,6] The crude *cis–trans* mixture obtained from irradiation was readily cyclized by heating at 165° to give the dimethoxy salt (I, $R_1 = R_2 = OCH_3$), isolated as the perchlorate (X = $ClO_4$).

Because of the well-known lack of activity of the 3-methyl substituent of isoquinolines, 3-styrylisoquinoline (VIII) had to be prepared indirectly *via* the methiodide. The base-catalyzed condensation of 3-methylisoquinoline methiodide with 2-chlorobenzaldehyde occurred readily under the conditions described[7] for the analogous condensation with benzaldehyde. The product (VIII as methiodide) was demethylated by heating to 300°, affording a 25% over-all yield of 2′-chloro-3-styryl-isoquinoline (VIII). As this isoquinoline derivative (VIII) was irradiated, a noticeable lowering of intensity of the longer wavelength absorptions in the ultraviolet spectrum occurred. However, on heating the crude *cis–trans* material isolated from the irradiation, only minute quantities of what may have been the cyclized product (II) were produced. The product showed a typical benzo[c]quinolizinium ultraviolet spectrum but




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

(2) A. Fozard and C. K. Bradsher, *Chem. Commun.*, 288 (1965).

(3) A. Fozard and C. K. Bradsher, *J. Org. Chem.*, **31**, 2346 (1966).

(4) W. B. Mills and J. L. B. Smith, *J. Chem. Soc.*, 2724 (1922).

(5) S. Sugasawa and K. Kakemi [*Ber.*, **71**, 1860 (1938)] have prepared the 2,3,9,10-tetramethoxy derivative of this system by dehydrogenation of the corresponding dibenzo[a,f]quinolizidine.

(6) L. Horwitz, *J. Org. Chem.*, **21**, 1039 (1956).

(7) L. G. S. Brooker and F. L. White, *J. Am. Chem. Soc.*, **73**, 1094 (1951).

was not obtained in sufficient quantities for positive identification. The failure of VIII to undergo cycloquaternization satisfactorily is of particular interest as an indication that the internal quaternization is not solely the consequence of favorable geometry, which must be very nearly the same for the *cis*-1- and 3-(2′-chlorostyryl)isoquinolines (VII and VIII), but must depend heavily upon the shift of electrons from the halogen-bearing carbon to the nitrogen atom *via* the conjugated system. It would be predicted that the low bond order of the C–N bond between positions 2 and 3 of the isoquinoline nucleus would make this route less effective for the transmission of electronic effects than that *via* the C–N bond of higher bond order between atoms 1 and 2.

*trans*-2′-Chloro-2-styrylquinoline (IX, R = H) also showed a shift in spectrum on irradiation, but heating the *cis–trans* mixture from irradiation gave only the pure *trans* isomer (IX, R = H). Since isomerization is always a competing reaction in these cycloquaternizations, it is obvious that in this case the weakly basic character of the quinoline nitrogen results in preferential isomerization. In an attempt to overcome this factor, the 5′-nitro derivative (IX, R = $NO_2$) was prepared, but this too showed no tendency to undergo cyclization.

The remaining three tetracyclic systems (IV, V, and VI) were all prepared by irradiating the appropriate chloronaphthyl-2-vinylpyridines and heating the crude *cis-trans* mixtures obtained on irradiation. It is probably significant that cycloquaternization of the crude β-(1′-chloro-2′-naphthyl)-2-vinylpyridine (XII), conjugated through the bond between carbon atoms 1 and 2 of the naphthalene nucleus, gives a better yield (50%) than that from the crude 3′-chloro isomer (XI, 27%) conjugated through the bond of lower order between carbon atoms 2 and 3.

While the great facility with which dibenzo[*a*,*f*]-quinolizinium cation can be prepared suggests the applicability of the new method to aza steroid synthesis, the failure of 2′-(2′-chlorostyryl)quinoline to undergo cycloquaternization seems to eliminate the possibility that an easy route to azoniahelicenes is at hand.

## Experimental Section

All analyses were carried out by Janssen Pharmaceutica, Beerse, Belgium. Melting points were determined using a Laboratory Devices Mel-Temp apparatus and are uncorrected. Irradiation experiments were carried out on stirred benzene solutions in Pyrex beakers with a 110-v, 250-w box-type lamp placed 6 in. away. Ultraviolet spectra were determined with a Cary Model 14 spectrophotometer.

**1-(2′-Chloro)styrylisoquinoline (VII, $R_1$ = $R_2$ = H).**—1-Methylisoquinoline (7.5 g), 2-chlorobenzaldehyde (7.5 g), and the zinc chloride complex of 1-methylisoquinoline (0.5 g) (obtained by addition of a solution of zinc chloride in ethanol to an ethanolic solution of the isoquinoline) were heated in a sealed tube at 140° for 20 hr. The cooled solid was triturated with ligroin (bp 60–90°) and collected giving 11.9 g (80%) of the styrylisoquinoline which was recrystallized from ligroin giving colorless needles: mp 100°; $\lambda_{max}^{95\%\ EtOH}$ 232, 276, 297, and 348 mμ (log ε 4.45, 4.06, 4.14, and 4.25).

*Anal.* Calcd for $C_{17}H_{12}ClN$: C, 76.81; H, 4.55; N, 6.09. Found: C, 77.14; H, 4.64; N, 5.97.

**Dibenzo[*a*,*f*]quinolizinium Chloride (I, $R_1$ = $R_2$ = H; X = Cl).**—The styrylisoquinoline (VII, $R_1$ = $R_2$ = H; 2.0 g) was heated in a 50-ml erlenmeyer flask at 200° (Woods metal bath) for 1.5 hr. The solid formed was cooled, suspended in ethyl acetate, and collected. The almost pure material obtained (1.4 g, 70%) was recrystallized from absolute ethanol–ethyl acetate as a yellow, microcrystalline solid: mp 340–342°; $\lambda_{max}^{H_2O}$ 220, 241, 278, 350, 368, and 387 mμ (log ε 4.45, 4.20, 4.32, 3.92, 4.16, and 4.29).

*Anal.* Calcd for $C_{17}H_{12}ClN \cdot H_2O$: C, 71.95; H, 4.97; N, 4.93. Found: C, 71.64; H, 4.91; N, 4.77.

**The perchlorate** (I, $R_1$ = $R_2$ = H; X = $ClO_4$) was prepared by addition of 25% aqueous perchloric acid to an aqueous solution of the chloride. It crystallized from acetonitrile as tan-colored needles, mp 327–329°.

*Anal.* Calcd for $C_{17}H_{12}ClNO_4$: C, 61.90; H, 3.67; N, 4.24. Found: C, 61.89; H, 3.55; N, 4.11.

**6,7-Dimethoxy-1-(2′-chloro)styrylisoquinoline (VII, $R_1$ = $R_2$ = $OCH_3$).**—6,7-Dimethoxy-1-methylisoquinoline (5.4 g), obtained from homoveratrylamine by the method previously reported,[8] 2-chlorobenzaldehyde (4.1 g), and the zinc chloride complex of the isoquinoline (0.3 g) were heated in a sealed tube at 140° for 20 hr. After cooling, the contents of the tube were suspended in benzene and filtered. The product was crystallized from benzene affording 6.6 g (68%) of small, colorless needles: mp 164–165.5°; $\lambda_{max}^{95\%\ EtOH}$ 209, 242, 250, 277 sh, and 355 mμ (log ε 4.54, 4.46, 4.46, 4.32, and 4.20).

*Anal.* Calcd for $C_{19}H_{16}ClNO_2$: C, 70.02; H, 4.94; N, 4.29. Found: C, 70.31; H, 4.89; N, 4.46.

**9,10-Dimethoxydibenzo[*a*,*f*]quinolizinium Perchlorate (I, $R_1$ = $R_2$ = $OCH_3$; X = $ClO_4$).**—6,7-Dimethoxy-1-(2′-chloro)-styrylisoquinoline (2.0 g) in dry, thiophen-free benzene (400 ml) was irradiated with ultraviolet light for 48 hr. At the end of this period there was a significant decrease in intensity of the absorption over 300 mμ in the ultraviolet spectrum of the isoquinoline. The benzene was evaporated and the oily solid remaining was heated at 165° (oil bath) for 1 hr. After cooling, the solid was triturated with hot ethyl acetate and collected, and 25% perchloric acid was added to an aqueous solution to precipitate 1.0 g (42%) of the perchlorate which was recrystallized from methanol as an orange, microcrystalline powder: mp 305° dec (chars above 270°); $\lambda_{max}^{95\%\ EtOH}$ 225, 268, 280 sh, 350 sh, 390, and 407 mμ ($\log_{10}$ ε 4.38, 4.66, 4.44, 3.82, 4.21, and 4.35).

*Anal.* Calcd for $C_{19}H_{16}ClNO_6 \cdot 0.5H_2O$: C, 57.32; H, 4.30; N, 3.52. Found: C, 57.37; H, 4.13; N, 3.91.

**3-(2′-Chloro)styrylisoquinoline Methiodide (Methiodide of VIII).**—3-Methylisoquinoline methiodide (25 g), 2-chlorobenzaldehyde (25 g), and piperidine (20 ml) were stirred and heated under reflux at 135–140° (oil bath) for 0.25 hr. During this period, a homogeneous mixture was first formed and just before the end of the reaction an oily solid separated. The solid was suspended in acetone and collected, then triturated with boiling methanol giving 14.0 g (35%) of a light orange solid sufficiently pure for demethylation. It recrystallized from ethanol to give tan-colored needles, mp 266–267°.

*Anal.* Calcd for $C_{18}H_{15}ClIN$: C, 53.15; H, 3.60; N, 3.34. Found: C, 52.95; H, 3.71; N, 3.22.

**3-(2′-Chloro)styrylisoquinoline (VIII).**—The methiodide prepared above (14.0 g) was heated (Woods metal bath) in a reduced-pressure distillation apparatus to 325° (5 mm) at which temperature refluxing commenced. After 2 min of further refluxing, the reaction mixture was allowed to cool and the product dissolved in benzene. The benzene solution was treated with Norit and evaporated to dryness. The solid obtained was recrystallized from ligroin (bp 60–90°), affording 6.3 g (70%) of pale yellow stellate clusters: mp 109–110°; $\lambda_{max}^{95\%\ EtOH}$ 220, 272, and 316 mμ (log ε 4.55, 4.26, and 4.46).

*Anal.* Calcd for $C_{17}H_{12}ClN$: C, 76.81; H, 4.55; N, 5.26. Found: C, 76.80; H, 4.63; N, 5.32.

**Attempted Cyclization of 3-(2′-Chloro)styrylisoquinoline (VIII).**—The isoquinoline (5.0 g) in benzene (400 ml) was irradiated at 25° for 60 hr. The ultraviolet spectrum of a sample at this point showed the virtual disappearance of the absorption peak at 316 mμ. The benzene was then evaporated and the residue was carefully heated to boiling point and refluxed for 5 min. After allowing the reaction mixture to cool, water (40 ml) was added and the mixture was heated on a water bath for 2 hr. The mixture was cooled and the insoluble solid material was filtered off. Aqueous 25% perchloric acid was added to the filtrate precipitating 0.07 g of a yellow perchlorate which could not be satisfactorily purified, $\lambda_{max}^{95\%\ EtOH}$ 222, 240 sh, 290, 358, 405, and 428 mμ.

**2-(2′-Chlorostyryl)quinoline (IX, R = H).**—This was prepared by essentially the same procedure described by Kaslow

(8) C. K. Bradsher and N. L. Dutta, *J. Org. Chem.*, **26**, 2232 (1961).

and Stayner[9] for 2-styrylquinoline. Quinaldine (5.75 g), 2-chlorobenzaldehyde (5.6 g), and acetic anhydride (7.5 ml) were boiled under reflux for 16 hr. The excess reagents were distilled off under reduced pressure and the remaining oil was poured into ice-cold water. The solid formed was filtered off, dried, dissolved in benzene, and passed through a column of neutral alumina. After evaporation of the eluent and recrystallization of the residue from ligroin (bp 60–90°), 8.6 g (81%) of product was obtained as colorless, prismatic clusters: mp 76–77° (lit.[10] 78–79°); $\lambda_{max}^{95\%\ EtOH}$ 222, 282, 327, and 339 mμ (log ε 4.38, 4.40, 4.36, and 4.34).

**Irradiation of 2-(2′-Chlorostyryl)quinoline.**—The quinoline (2.0 g) in benzene (400 ml) was irradiated for 48 hr. On evaporation, the benzene solution afforded an oily *cis–trans* mixture, the ultraviolet spectrum of which showed a considerable diminution of peaks over 300 mμ. When this crude *cis–trans* mixture was heated at 200° for 1 hr, only a quantitative yield of the *trans* isomer (mp 75°) was obtained.

**2-(2′-Chloro-5′-nitrostyryl)quinoline (IX, R = $NO_2$).**—This was prepared in the same way as 2-(2′-chlorostyryl)quinoline (IX, R = H) using 2-chloro-5-nitrobenzaldehyde as the condensing aldehyde. After recrystallization from ethanol, an 80% yield of the product was obtained as a microcrystalline, yellow solid: mp 195–197°, $\lambda_{max}^{95\%\ EtOH}$ 205, 220 sh, 275, and 330 mμ (log ε 4.46, 4.32, 4.52, and 4.33).

*Anal.* Calcd for $C_{17}H_{11}ClN_2O_2$: C, 65.50; H, 3.88; N, 8.98. Found: C, 65.65; H, 3.71; N, 8.86.

When the styrylquinoline (IX, R = $NO_2$) was irradiated in benzene solution, a *cis–trans* mixture melting at 145.5–147° could be isolated. Upon heating at 170° for 1 hr, the material isomerized to give a quantitative yield of the *trans* isomer, mp 193–195°.

**2-Chloro-1-naphthaldehyde.**—This was prepared from 2-hydroxy-1-naphthaldehyde by a modification of the method of Shoesmith and Mackie.[11] The modification consisted of carrying out the reaction between 2-hydroxy-1-naphthaldehyde (12 g) and phosphorus pentachloride (27.5 g) in a sealed tube for 16 hr at 160°. The reaction mixture was then worked up as described.[11] The yield after one recrystallization from ligroin (bp 60–90°) was 4 g (30%), mp 72–74° (lit.[11] mp 75°).

**β-(2′-Chloro-1′-naphthyl)-2-vinylpyridine (X).**—2-Chloro-1-naphthaldehyde (4.0 g), 2-picoline (2.0 g), and the zinc chloride complex of 2-picoline (0.25 g) were heated in a sealed tube at 180° for 16 hr. After cooling, the solid was triturated with ligroin (bp 60–90°) and filtered. The crude product was dissolved in benzene and passed through a neutral alumina column, and the benzene was evaporated. The solid was recrystallized from ligroin affording 1.7 g (33%) of pale yellow needles: mp 103–104.5°; $\lambda_{max}^{95\%\ EtOH}$ 205, 225, 253, 274, 287, and 325 mμ (log ε 4.24, 4.42, 4.25, 4.40, 4.36, and 4.50).

*Anal.* Calcd for $C_{17}H_{12}ClN$: C, 76.81; H, 4.55; N, 5.26. Found: C, 77.10; H, 4.64; N, 5.32.

**Naphtho[1,2-*c*]quinolizinium Chloride (IV, X = Cl).**—The vinylpyridine (X, 1.5 g) in benzene (400 ml) was irradiated at at 25° for 48 hr. During this period, the long wavelength maximum of the ultraviolet spectrum of the compound changed from 325 to 285 mμ. The solution was filtered from a small amount of insoluble material and the filtrate was evaporated leaving an oil. The oil was then heated at 180° (oil bath). Almost immediately an exothermic reaction occurred and the mixture solidified. After a further 15 min of heating, the reaction mixture was allowed to cool and the solid was triturated with acetone and collected giving 1.15 g (75%) of crystalline product, mp 335–337°. The compound crystallized from ethanol as small, pale yellow needles: $\lambda_{max}^{H_2O}$ 224, 242, 262, 278, 333, 370, and 388 mμ (log ε 4.54, 4.21, 4.37, 4.36, 3.62, 4.08, and 4.21).

*Anal.* Calcd for $C_{17}H_{12}ClN \cdot 0.25H_2O$: C, 75.57; H, 4.66; N, 5.18. Found: C, 75.68; H, 4.55; N, 5.22.

**The perchlorate** (IV, X = $ClO_4$) crystallized from acetonitrile as pale yellow needles, mp 320–322° dec.

*Anal.* Calcd for $C_{17}H_{12}ClNO_4$: C, 61.90; H, 3.67; N, 4.24. Found: C, 61.60; H, 3.69; N, 4.36.

**3-Chloro-2-naphthoyl chloride** was prepared from 3-hydroxy-2-naphthoic acid by heating with phosphorus pentachloride according to the method of Strohbach.[12] The product, bp 187–198° (9 mm), was obtained in 35% yield.

**3-Chloro-2-naphthaldehyde** was prepared by a Rosenmund reduction of 3-chloro-2-naphthoyl chloride[11] (17 g) in xylene (150 ml) using a 5% palladium on barium sulfate catalyst (3.0 g) and thiourea (0.1 g) as an added catalyst poison. The yield of product after one recrystallization from ligroin (bp 60–90°) was 5.4 g (38%), mp 118.5–119.5 (lit[11] mp 121°).

**β-(3′-Chloro-2′-naphthyl)-2-vinylpyridine (XI).**—3-Chloro-2-naphthaldehyde (9.00 g), 2-picoline (4.5 g), and the zinc chloride complex of 2-picoline (0.5 g) were heated in a sealed tube at 180° for 16 hr. The mixture was cooled and worked up as for the previously described case (compound X). The yield after one recrystallization was 9.2 g (73%) of pale yellow, crystalline clusters: mp 106–107.5°; $\lambda_{max}^{95\%\ EtEH}$ 222, 274, 285 sh, and 326 mμ (log ε 4.50, 4.43, 4.34, and 4.35).

*Anal.* Calcd for $C_{17}H_{12}ClN$: C, 76.81; H, 4.55; N, 5.26. Found: C, 76.44; H, 4.56; N, 5.44.

**Naphtho[2,3-*c*]quinolizinium Chloride (V, X = Cl).**—The 2-vinylpyridine (XI, 1.0 g) in benzene (400 ml) was irradiated at 25° for 48 hr and the solution was worked up and then heated as described for the tetracyclic system IV (X = Cl). The product (0.27 g, 27%) recrystallized from ethanol–ethyl acetate as bright yellow needles: mp 344° dec; $\lambda_{max}^{H_2O}$ 225, 239, 246, 285 sh, 299, 313, 365 sh, 384, and 400 mμ (log ε 4.42, 4.51, 4.57, 4.31, 4.38, 4.58, 3.69, 3.75, and 3.75).

*Anal.* Calcd for $C_{17}H_{12}ClN \cdot 0.75H_2O$: C, 72.99; H 4.89; N, 5.22. Found: C, 73.10; H, 4.87; N, 4.90.

**The perchlorate** (V, X = $ClO_4$) was recrystallized from acetonitrile as a yellow, microcrystalline solid, mp 273–275°.

*Anal.* Calcd for $C_{17}H_{12}ClNO_4$: C, 61.90; H, 3.67; N, 4.24. Found: C, 61.95; H, 3.64; N, 4.25.

**1-Chloro-2-methylnaphthalene.**[11]—2-Methylnaphthalene (20 g) and sulfuryl chloride (19 g) were mixed and left overnight. The mixture was then poured into water and extracted with ether, and the ether extracts were dried ($Na_2SO_4$) and distilled. The portion boiling at 111–116° (3 mm) was collected (17.8 g, 77%).

**1-Chloro-2-bromomethylnaphthalene.**—1-Chloro-2-methylnaphthalene (17.8 g), N-bromosuccinimide (17.8 g), and benzoyl peroxide (0.2 g) in dry carbon tetrachloride (150 ml) were boiled under reflux for 20 hr. The succinimide which formed was filtered off, the carbon tetrachloride was distilled, and the crystalline residue was recrystallized from ligroin (bp 60–90°). The yield was 17.9 g (72%), mp 79–81° (lit.[11] mp 81°).

**1-Chloro-2-naphthaldehyde.**—1-Chloro-2-bromomethylnaphthalene (15.0 g) in chloroform (75 ml) was treated with hexamethylenetetramine (9.0 g). The mixture was boiled under reflux for 0.5 hr, the solution was cooled, and the quaternary salt was filtered off. The salt was boiled with 50% aqueous acetic acid (110 ml) for 2 hr, concentrated hydrochloric acid (15 ml) was added, and the mixture was boiled for a further 10 min. The aldehyde crystallized on cooling. It was recrystallized from ligroin (bp 60–90°) affording 6 g (53%) of colorless needles, mp 104.5–106°.

*Anal.* Calcd for $C_{11}H_7ClO$: C, 69.31; H, 3.70. Found: C, 69.10; H, 3.72.

**β-(1′-Chloro-2′-naphthyl)-2-vinylpyridine (XII).**—1-Chloro-2-naphthaldehyde (12.0 g), 2-picoline (6.0 g), and the zinc chloride complex of 2-picoline (0.6 g) were heated in a sealed tube for 16 hr at 180°. The reaction was worked up as previously described for similar compounds to give 11.4 g (68%) of product, recrystallized from ligroin (bp 60–90°) as pale yellow needles: mp 104–105°; $\lambda_{max}^{95\%\ EtOH}$ 205, 224, 253, 274, 286, and 325 mμ (log ε 4.24, 4.41, 4.24, 4.40, 4.36, and 4.50).

*Anal.* Calcd for $C_{17}H_{12}ClN$: C, 76.81; H, 4.55; N, 5.26. Found: C, 76.35; H, 4.51; N, 5.28.

**Naphtho[2,1-*c*]quinolizinium Chloride (VI, X = Cl).**—The 2-vinylpyridine (XII, 3.0 g) in benzene (400 ml) was irradiated at 25° for 48 hr and the benzene was then evaporated. The residue was heated at 180° for 1 hr and then worked up as previously described for other naphtho[*c*]quinolizinium salts. The product (1.5 g, 50%) was recrystallized from ethanol–ethyl acetate as small pale yellow needles: mp 271.5–273°; $\lambda_{max}^{H_2O}$ 214, 249, 273, 308, 380, and 398 mμ (log ε 4.51, 4.44, 4.16, 4.26, 3.75, and 3.81).

*Anal.* Calcd for $C_{17}H_{12}ClN \cdot 0.25H_2O$: C, 75.57; H, 4.66; N, 5.18. Found: C, 75.45; H, 4.78; N, 4.89.

**The perchlorate** (VI, X = $ClO_4$) was recrystallized from acetonitrile as pale yellow needles, mp 215.5–216°.

*Anal.* Calcd for $C_{17}H_{12}ClNO_4$: C, 61.90; H, 3.67; N, 4.24. Found: C, 61.76; H, 3.72; N, 4.40.

(9) C. E. Kaslow and R. D. Stayner, *J. Am. Chem. Soc.*, **67**, 1716 (1945).
(10) J. C. E. Simpson, *J. Chem. Soc.*, 673 (1946).
(11) J. B. Shoesmith and A. Mackie, *ibid.*, 1584 (1930).
(12) E. Strohbach, *Ber.*, **34**, 4159 (1901).