1.0 g. (38% yield) of XI, m.p. 154–156°; $\lambda_{max}$ 215, 225 (sho.), 264, 316, 323 (sho.), 330, 338, 346 m$\mu$ ($\epsilon \times 10^{-3}$ 37.0, 28.3, 41.4, 10.0, 11.0, 16.0, 12.7, 20.0).

(b) *In excess morpholine.* A solution of 0.74 g. (0.0025 mole) of X in 15 ml. of morpholine was heated at reflux for 23 hr., and poured into 300 ml. of water. A recrystallization of the crude product from benzene-petroleum ether, with charcoal treatment, gave 0.48 g. (64% yield) of XI as colorless needles, m.p. 155–156°.

*Anal.* Calcd. for $C_{20}H_{18}N_2O$: C, 79.47; H, 5.96; N, 9.27. Found: C, 79.25; H, 6.09; N, 9.13.

*11-Piperidino-11H-indeno[1,2-b]quinoline* (XII). Fifteen milliliters of redistilled piperidine and 0.74 g. (0.0025 mole) of the bromide X were refluxed for 23 hr., after which the mixture was poured into 500 ml. of water to give 0.56 g. (80.0% yield) of a colorless solid, m.p. 139–140° (colorless needles from petroleum ether); $\lambda_{max}$ 215, 225 (sho.), 264, 316, 323 (sho.), 330, 338, 346 m$\mu$ ($\epsilon \times 10^{-3}$ 37.0, 28.3, 41.4, 10.0, 11.0, 16.0, 12.7, 20.0).

*Anal.* Calcd. for $C_{21}H_{20}N_2$: C, 83.96; H, 6.71; N, 9.33. Found: C, 83.89; H, 6.67; N, 9.66.

*11H-Indeno[1,2-b]quinolin 1-oxide* (XIII). A solution of 1.09 g. (0.005 mole) of the indenoquinoline II and 0.7 ml. of 30% hydrogen peroxide in 15 ml. of glacial acetic acid was heated at 69–70° for 3 hr., after which an additional 0.3 ml. of 30% hydrogen peroxide was added. After 17 hr. at 69°, a gold colored solid, XIII, wt. 0.99 g. (85.0% yield), was obtained by evaporation of the reaction medium under vacuum. A 0.200-g. sample of XIII was triturated with 10% sodium hydroxide, extracted with chloroform, dried and evaporated. Recrystallization of the residue from benzene gave 160 mg. of XIII as yellow plates, m.p. 216–219° dec.; $\lambda_{max}$ 226, 270, 278, 306, 322, 339, 355 m$\mu$ ($\epsilon \times 10^{-3}$ 29.7, 15.0, 15.2, 4.2, 3.7, 4.4, 4.0); infrared bands (saturated chloroform solution, 1.0 mm. cell), $\gamma_{C=N}$ 1625/32, $\gamma_{ArC=C}$ 1610/29, $\gamma_{N-O}$ 1337/55.

*Anal.* Calcd. for $C_{16}H_{11}NO$: C, 82.38; H, 4.75; N, 6.01. Found: C, 82.36; H, 4.68; N, 6.04.

Compound XIII gives a deep blue coloration,[8] as a positive *N*-oxide test, upon boiling a sample with dimethylaniline and hydrochloric acid, followed by ethanol addition to the cooled solution.

*10-Chloro-11H-indeno[1,2-b]quinoline* (XIV). 11*H*-Indeno-[1,2-*b*]quinolin 1-oxide (XIII) was chlorinated, presumably in the *para* position, *via* the procedure of Bachman and Cooper.[10] To 3 ml. of phosphorus oxychloride, chilled in ice, was added in portions, 0.5 g. (0.00215 mole) of the *N*-oxide XIII. After the addition was complete, the mixture was warmed gently under a condenser until refluxing began and continued for 45 min., at the end of which time solution was complete. The dark colored mixture, after cooling, was poured, with stirring, onto 15 g. of crushed ice. The oil which appeared initially, slowly solidified with stirring and scratching. The hydrochloride salt was collected and dried. Dissolving this product in a minimum amount of methanol and neutralizing to *p*H 8 with dilute ammonium hydroxide afforded pale tan colored needles of XIV. Recrystallization from aqueous acetone at room temperature gave 0.24 g. (44.5% yield) of an almost colorless solid, m.p. 152–153.5°; $\lambda_{max}$ 215, 265, 314, 321, 329, 336, 344 m$\mu$ ($\epsilon \times 10^{-3}$ 37.6, 49.2, 11.5, 10.6, 17.1, 11.5, 23.6).

*Anal.* Calcd. for $C_{16}H_{10}NCl$: C, 76.34; H, 4.00; N, 5.57. Found: C, 76.07; H, 3.98; N, 5.69.

*6-Chloro-11H-indeno[1,2-b]quinoline-10-carboxylic acid.* (XV). The Pfitzinger-Borsche reaction was employed, using 0.66 g. (0.005 mole) of 1-indanone and 1.09 g. (0.006 mole) of 7-chloroisatin in a solution of 1.5 g. of sodium hydroxide in 20 ml. of water. A treatment of the sodium salt with hot 25% acetic acid gave 0.85 g. (57.6% yield) of XV, as a tan powder; m.p. 284–287° dec. (recrystallized from acetone); $\lambda_{max}$ (methanol and potassium hydroxide) 215, 260 (sho.), 269, 318 (sho.), 330, 345 m$\mu$ ($\epsilon \times 10^{-3}$ 36.4, 34.7, 51.5, 11.9, 16.5, 18.8); infrared bands (potassium bromide pellet) $\gamma_{OH}$ 3400/39, $\gamma_{COOH}$ 1722/73, $\gamma_{C=N}$ 1622/57.

*Anal.* Calcd. for $C_{17}H_{10}NO_2Cl$: C, 6 .0 ; H, 3.41; Cl, 11.99. Found: C, 69.10; H, 3.47; Cl, 12.21.

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LINCOLN, NEB.

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[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

# Indenoquinolines. II.[1a] Derivatives of 6*H*-Indeno(2,1-*b*)quinoline

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6*H*-Indeno(2,1-*b*)quinolin-6-one (II) adds Grignard reagents and is catalytically reduced in a 1,2-fashion to produce carbinols. 6*H*-Indeno(2,1-*b*)quinoline (I) reacted with *N*-bromosuccinimide to produce the 6,6-dibromo derivative which was hydrolyzed to II. Attempts to prepare the *N*-oxide of I also produced II. The indenoquinoline I reacts with dimethyl sulfate to give a 5-methosulfate derivative which in turn reacts with aqueous base to produce the pseudo-azulene or anhydronium base, 5-methyl-5*H*-indeno(2,1-*b*)quinoline.

As a part of a program to develop the chemistry of the indenoquinolines[1a] in a search for new types of polycyclic heterocyclic compounds of biological interest,[2] reactions of the little studied 6*H*-indeno-(2,1-*b*)quinoline analogous to those studied for 11*H*-indeno(1,2-*b*)quinoline[1a] (A) have been investigated.

6*H*-Indeno(2,1-*b*)quinoline (I) was obtained in adequate amounts by the condensation of *o*-aminobenzaldehyde and 2-indanone following the procedure reported by Clemo and Felton.[3] Several

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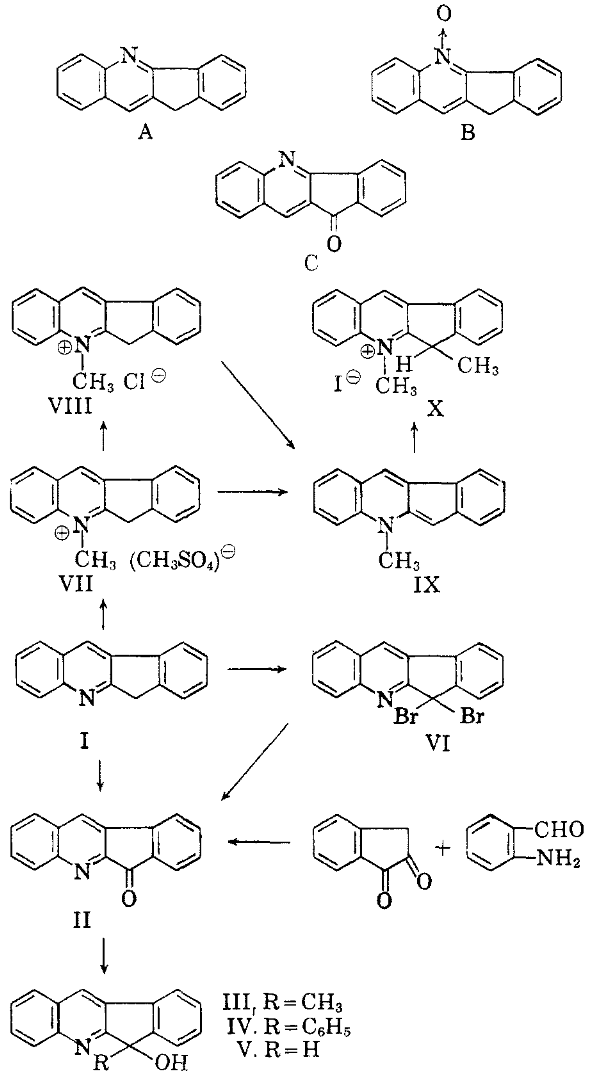
(1)(a) For paper I in this series see N. H. Cromwell and R. A. Mitsch, *J. Org. Chem.*, **26**, 3812 (1961). (b) U. S. Public Health Fellow, 1958–1960, National Institute of Allergy and Infectious Diseases.

(2) For new derivatives in the benz(c)acridine series, see (a) V. L. Bell and N. H. Cromwell, *J. Org. Chem.*, **23**, 789 (1958) and (b) N. H. Cromwell and V. L. Bell, *J. Org. Chem.*, **24**, 1077 (1959); for benz(b)acridines, see (c) N. H. Cromwell and J. C. David, *J. Am. Chem. Soc.*, **82**, 1138 (1960) and (d) *J. Am. Chem. Soc.*, **82**, 2046 (1960).

(3) G. R. Clemo and D. G. Felton, *J. Chem. Soc.*, 1658 (1952).



different methods for the preparation of 6*H*-indeno(2,1-*b*)quinolin-6-one (II) required in further syntheses were investigated. The base catalyzed condensation of *o*-aminobenzaldehyde with 1,2-indandione gave only a 27% yield of II while a chromic acid oxidation of I produced the ketone II in at least 50% amounts. Somewhat less successful was a modification of the novel oxidation technique using air/pyridine-Triton B, which has been applied by others to fluorene.[4] The ketone II was also obtained as the only isolable product in an attempted preparation of the *N*-oxide of I employing the conditions previously[1a] found to be useful in the synthesis of 11*H*-indeno(1,2-*b*)quinolin 1-oxide (B).

Both the methyl and phenyl Grignard reagents were found to add to the carbonyl group in ketone II to produce tertiary carbinols, III and IV, respectively, analogous to the behavior of the isomeric ketone C. Catalytic hydrogenation produced the secondary carbinol V in contrast to the complex behavior of the isomeric ketone C under these conditions.

A comparison of the ultraviolet absorption spectra of the carbinols III, IV, and V showed them to be quite similar to each other. When compared with the spectrum of the parent indenoquinoline I, there is seen to be a general reduction of extinction coefficients, bathochromic shifts of up to 5 m$\mu$ for each major peak, as well as a general diminishing of fine structure for each of the carbinols. The over-all effect of acidic media on I was to simplify greatly the fine structure in the 340–365 m$\mu$ area as well as to reduce the intensity of absorption. This suggests that hydrogen bonding in the carbinols may be important in reduction of fine structure. The solution infrared spectra of the carbinols III and IV both showed a nonbonded OH stretching vibration band at 3560 cm.$^{-1}$ and a broad complex H-bonded OH band between 3400 and 3100 cm.$^{-1}$

Previous investigations have shown that the active methylene groups in the dihydrobenz(*c*)acridines,[2a,b] dihydrobenz(*b*)acridines[2c] and the indenoquinoline A[1a] are readily monosubstituted by bromine using *N*-bromosuccinimide. In the present investigation indenoquinoline I has been found to give the dibromo derivative VI under the conditions previously employed with A. The course of the reaction in this case seems to be analogous to that which has been reported for quinaldine.[5] Hydrolysis of VI with sodium acetate in aqueous acetic acid produced the ketone II, thereby establishing the location of the two bromine atoms in the compound.

The methosulfate salt VII of the indenoquinoline I was obtained in good yield by refluxing I in benzene in the presence of excess dimethyl sulfate. This salt exhibited strong violet fluorescence in various hydroxylic solvents, as did the methochloride salt VIII, which was obtained by recrystallizing VII from hot dilute hydrochloric acid. A molecule of water was eliminated very readily to form the pseudo-azulene, or anhydronium base IX, as an intensely purple solid when an aqueous solution of the salts VII and VIII were treated with base. The ease of formation of the pseudo-azulene IX from the salts is further indicated by the fact that their ultraviolet spectra in methanol are essentially the same as that of IX.[6]

A comparison of the ultraviolet spectra of the anhydronium base IX (Fig. 2) with that of the indenoquinoline I (Fig. 1) and with the known

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[4] Y. Sprinzak, *J. Am. Chem. Soc.*, **80**, 5449 (1958).

[5] M. Hasegawa, *J. Pharm. Soc. Japan*, **71**, 256 (1951).

[6] For leading references on anhydronium bases see (a) W. H. Perkin and R. Robinson, *J. Chem. Soc.*, **115**, 933 (1919); (b) J. W. Armit and R. Robinson, *J. Chem. Soc.*, **121**, 827 (1922); **127**, 1604 (1925); (*c*) G. V. Boyd, *J. Chem. Soc.*, **55** (1959); (d) W. Treibs and W. Schroth, *Angew. Chem.*, **72**, 636 (1960), report they have obtained the pseudo-azulene IX by the methylation of the indenoquinoline I or from the condensation of 2-indanone with *N*-methylisatin, followed by decarboxylation.

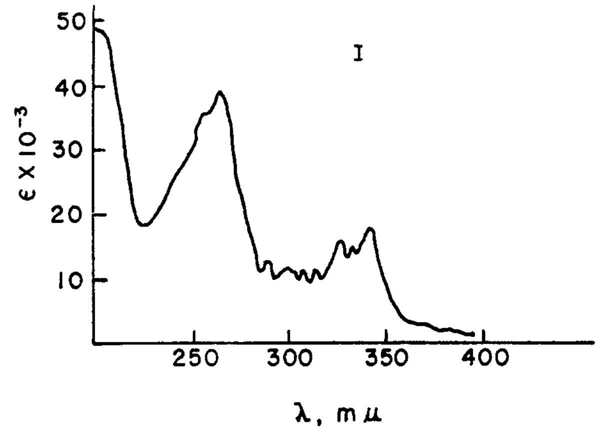

Figure 1

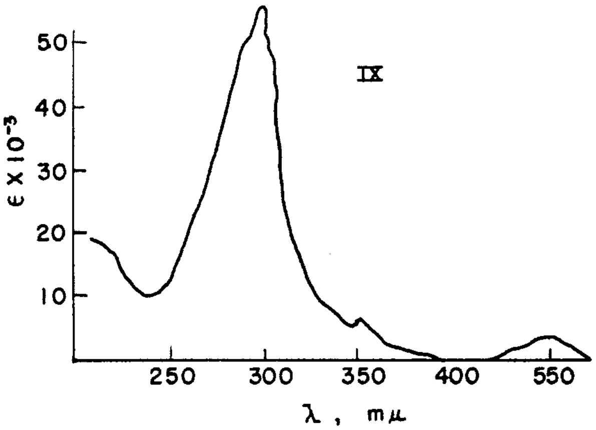

Figure 2

azulene, 1,2-benzazulene[6c] (Fig. 3) gives a clear indication of the relationship of these structures. There is a considerable shift in the wave length of the main absorption band of I from 264 mμ to 297 mμ with a development of absorption in the visible range for IX at 500–600 mμ, as is found for 1,2-benzazulene. The infrared spectrum of IX in carbon tetrachloride exhibits strong absorption at 1650 cm.$^{-1}$, which can be assigned with some confidence to the C=C stretching of an α,β-unsaturated tertiary amine.[7]

Armit and Robinson[6b] have shown that methyl iodide adds to the nitrogen ethylene system in pseudo-azulenes to give a methiodide salt. When IX was refluxed with excess methyl iodide a yellow salt precipitated from the purple reaction mixture which undoubtedly was the salt of structure X but which has not been studied further because of its unstable nature.

6*H* - Indeno(2,1 - *b*)quinoline - 11 - carboxylic acid (XI) and the 4-chloro derivative (XII) were synthesized from 2-indanone and the corresponding isatins by the Pfitzinger-Borsche reaction as employed by Noelting and Herzbaum[8] and Buu-Hoi and Cogniant.[9] These acids were desired for biological studies for comparison with the corresponding acids which have been prepared in the isomeric indenoquinoline series.[1a]

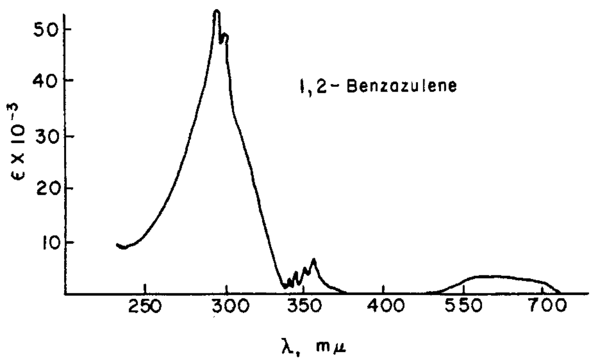

Figure 3

## EXPERIMENTAL[10]

*6H-Indeno(2,1-b)quinoline* (I). Compound I was prepared in 43% yield from *o*-aminobenzaldehyde and 2-indanone *via* the procedure employed by Clemo and Felton.[3] A colorless solid, m.p. 142.5–143.5°, was obtained after two sublimations at 141°/0.65 mm.; $\lambda_{max}$ 215, 264, 287, 300, 313, 320, 328, 335, 343 mμ ($\epsilon \times 10^{-3}$ 43.4, 39.7, 11.3, 10.0, 11.0, 10.3, 16.3, 13.0, 19.0); $\lambda_{max}$ (in 0.1*N* hydrochloric acid-methanol) 215, 260, 276, 354 (sho.), 365 mμ ($\epsilon \times 10^{-3}$ 31.0, 35.0, 21.6, 12.7, 13.7).

*6H-Indeno(2,1-b)quinolin-6-one* (II). (a) *Base catalyzed condensation.* A mixture of 8.0 g. (0.05 mole) of wet *o*-aminobenzaldehyde,[11] 7.3 g. (0.05 mole) of 1,2-indandione,[12] and 150 ml. of 95% ethanol was warmed after addition of 20 ml. of 33% aqueous potassium hydroxide. Cooling the dark green solution gave a pale green solid, m.p. 192–193.5°[13]; wt. 3.1 g. (27% yield); $\lambda_{max}$ 227, 287 mμ ($\epsilon \times 10^{-3}$ 28.6, 60.0); infrared bands (potassium bromide pellet) $\gamma_{C=O}$ 1720/89, $\gamma_{Ar}$ 1603/76; ($CCl_4$ sol.) $\gamma_{C=O}$ 1738/58.

(b) *Potassium dichromate oxidation of* I. A warm mixture of 24.0 g. of potassium dichromate, 32 ml. of glacial acetic acid, and 8 ml. of water was added dropwise to a stirred, gently refluxing solution of 10.85 g. (0.05 mole) of I in 80 ml. of glacial acetic acid. After 45 min. for the addition, the mixture was heated at reflux an additional 2.75 hr., then poured, with stirring, into 300 ml. of ice water. Filtration and drying gave 9.6 g. (83.1% yield) of a light rust colored solid, m.p. 167–175°. Further purification was effected by extraction of the crude ketone with methanol in a Soxhlet extractor, giving back 5.28 g. of a light yellow solid, m.p. 188–191°; sublima-

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[7] N. J. Leonard and V. W. Gash, *J. Am. Chem. Soc.*, **76**, 2781 (1954), have shown that a band characteristic of C=C in unsaturated tertiary amines usually may be found in the region, 1639–1665 cm.$^{-1}$ See also N. J. Leonard and D. M. Locke, *J. Am. Chem. Soc.*, **77**, 437 (1955).

[8] E. Noelting and A. Herzbaum, *Ber.*, **44**, 2585 (1911).

[9] N. G. Buu-Hoi and P. Cogniant, *Bull. Soc. Chim.*, **11**, 433 (1944).

[10] Melting points were read with a calibrated thermometer. Ultraviolet absorption spectra were determined with a Cary Model 11-MS recording spectrophotometer using reagent grade methanol solutions. Infrared spectra were measured with a Perkin-Elmer Model 21 double beam recording instrument employing sodium chloride optics and matched sodium chloride cells with indicated solvents unless otherwise stated.

[11] L. I. Smith and J. W. Opie, *Org. Syntheses*, 11 (1948).

[12] M. P. Cava, R. L. Litle, and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2257 (1958).

[13] W. Borsche, *Ann.*, **532**, 127 (1937).

tion at 190°/1.0 mm. gave a lemon-yellow solid II, m.p. 189–191°. Excellent purification was also realized by dissolving the crude product in benzene and slurrying with basic alumina, followed by filtration through an alumina packed filter.

(c) *Oxidation of* I *with air and Triton B.* A mixture of 1.0 g. (0.0046 mole) of I, 2 ml. of benzyltrimethylammonium hydroxide (40% solution), and 50 ml. of pyridine was stirred for 90 min. under a rapid stream of air. Additional pyridine had to be added occasionally to avoid dryness. The reaction mixture was acidified to litmus with acetic acid and poured into 400 ml. of water. After filtering a tar precipitate, a tan solid separated in the filtrate. Drying gave 0.15 g. (16.1% yield) of the ketone II as a yellow solid after recrystallization from methanol, m.p. 187–190°.

*6-Hydroxy-6-methyl-6H-indeno(2,1-b)quinoline* (III). To a slurry of 1.0 g. (0.0043 mole) of 6*H*-indeno(2,1-*b*)quinolin-6-one (II), in 150 ml. of anhydrous ether was slowly added 3 ml. (0.0085 mole) of commercial 3*M* methylmagnesium bromide in ether. The pale green mixture was stirred an additional 30 min. poured into a saturated ammonium chloride solution and worked up in the usual manner. Three crops, weighing 0.42 g. (39.6% yield), m.p. 145–175°, were obtained. A recrystallization from benzene–petroleum ether, with charcoal treatment gave a pale yellow solid, III, m.p. 173.5–175.5°; $\lambda_{max}$ 220, 228 (sho.), 250, 262 (sho.), 269, 290 (sho.), 305 (sho.), 332, 348 m$\mu$ ($\epsilon \times 10^{-3}$ 31.6, 22.6, 23.6, 26.3, 27.4, 12.7, 11.0, 10.0, 12.0); infrared bands (potassium bromide pellet) $\gamma_{\text{bonded OH}}$ 3260–3100/85, $\gamma_{C=N}$ 1625/54; (methylene chloride soln). $\gamma_{OH}$ 3560/35, $\gamma_{\text{bonded OH}}$ 3400–3100/14, $\gamma_{C=N}$ 1625/13.

*Anal.* Calcd. for $C_{17}H_{13}NO$: C, 77.39; H, 4.87; N, 11.29. Found: C, 77.63; H, 5.00; N, 11.32.

*6-Hydroxy-6-phenyl-6H-indeno(2,1-b)quinoline* (IV). To a refluxing solution of the Grignard reagent prepared from 1.88 g. (0.012 mole) of bromobenzene and 0.29 g. (0.012 g.-atom) of magnesium turnings in 15 ml. of ether, was slowly added 1.16 g. (0.005 mole) of ketone II, dissolved in 120 ml. of hot benzene. The green complex was decomposed with saturated ammonium chloride and worked up in the usual fashion. A recrystallization of the crude product from benzene–petroleum ether, treated with charcoal, gave 0.48 g. (31.2% yield) of carbinol IV as pale cream crystals, m.p. 180–181.5°; $\lambda_{max}$ 223, 254, 263 (sho.), 272, 300, 322, 336, 351 m$\mu$ ($\epsilon \times 10^{-3}$ 37.7, 29.0, 27.0, 26.3, 12.7, 5.7, 11.0, 13.3); infrared bands (potassium bromide pellet) $\gamma_{\text{bonded OH}}$ 3200/80, $\gamma_{C=N}$ 1620/28; ($CH_2Cl_2$ sol.) $\gamma_{OH}$ 3560/37, $\gamma_{\text{bonded OH}}$ 3400–3100/12 $\gamma_{\text{unassigned}}$ 1605/21.

*Anal.* Calcd. for $C_{22}H_{15}NO$: C, 85.44; H, 4.88; N, 4.53. Found: C, 85.55; H, 4.97; N, 4.61.

*6H-Indeno(2,1-b)quinolin-6-ol* (V). A suspension of 1.0 g. of 10% palladium-on-charcoal in a solution of 1.0 g. (0.00433 mole) of ketone II in 90 ml. of benzene was shaken under 45 lb./in.$^2$ of hydrogen for 12 hr. After catalyst filtration, the filtrate gave three crops of crude V; wt. 0.57 g. (55.6% yield). A sublimation at 130°/0.1 mm., which removed the unchanged ketone, followed by recrystallization of the residue from benzene–petroleum ether gave a colorless solid, m.p. 168–170° dec.; $\lambda_{max}$ 220, 251, 269, 286 (sho.), 319, 333, 348 m$\mu$ ($\epsilon \times 10^{-3}$ 34.8, 27.2, 31.7, 16.2, 6.0, 10.2, 11.8).

*Anal.* Calcd. for $C_{16}H_{11}NO$: C, 82.38; H, 4.75; N, 6.01. Found: C, 82.30; H, 4.81; N, 6.06.

*Bromination of 6H-indeno(2,1-b) quinoline* (I). Two grams (0.0092 mole) of I, 1.65 g. (0.0092 mole) of *N*-bromosuccinimide, and 100 mg. of benzoyl peroxide in 75 ml. of carbon tetrachloride were stirred with a high speed stirrer at room temperature, after slight warming to induce the reaction. After 26 hr., all of the heavy *N*-bromosuccinimide had been converted to light succinimide, which was removed by filtration. The filtrate was reduced in volume by evaporation and cooled. Filtration gave 2.20 g. of a light pink solid, instantaneous m.p. 157–160°. With gradual heating, compound VI slowly turned red in color from 65–90° and melted at 287–300°. A small sample was dissolved in acetone at room temperature and chilled on Dry Ice. Filtration gave a colorless solid (VI), instantaneous m.p. 158–160°; $\lambda_{max}$ 220, 270, 303 (sho.), 334, 348 m$\mu$ ($\epsilon \times 10^{-3}$ 30.3, 34.0, 13.3, 4.7, 5.0).

*Anal.* Calcd. for $C_{16}H_{10}NBr$: C, 64.88; H, 3.40; Br, 26.99; for $C_{16}H_9NBr_2$: C, 51.23; H, 2.49; Br, 42.62. Found: C, 51.41; H, 2.62; Br, 43.48.

Compound VI cannot be stored for long periods of time, since it gradually turns pink in a vacuum desiccator or if exposed to the atmosphere. In an attempt to locate the two bromine atoms in the system, a preliminary hydrolysis, assuming compound VI to be a *gem*-dibromide, using lead monoxide and water resulted in a very complex mixture of products, the infrared absorption spectrum of which had a carbonyl band at 1725 cm.$^{-1}$ in chloroform. Because of the limited amount of VI available, a heterogeneous hydrolysis employing calcium carbonate and water[14] was passed in favor of a system of better solubility potential. Hydrolysis of the dibromide was accomplished *via* the procedure of Wittig and Vidal.[15] A 1.0-g. sample of VI was heated at reflux for 18 hr. in a solution of 3 g. of sodium acetate in 10 ml. of 60% acetic acid. After cooling, the insoluble red-brown material was removed by filtration and a yellow solid precipitated from the acetic acid filtrate by dilution with water. A recrystallization of the crude yellow solid from aqueous acetone, with charcoal treatment, gave a small amount of lemon yellow needles, m.p. 187–190°. A mixture melting point experiment with authentic ketone II which showed no depression, and identical infrared spectra indicated the yellow solid to be 6*H*-indeno(2,1-*b*)quinolin-6-one (II).

*6H-Indeno(2,1-b)quinoline 5-methosulfate* (VII). The salt VII precipitated as yellow needles, when a solution of 4.9 g. (0.0225 mole) of I and 5.67 g. (0.045 mole) of dimethyl sulfate in 200 ml. of benzene was refluxed for 1 hr. After cooling, filtration gave VII; wt. 5.3 g. (69.0% yield). Alcoholic solutions of the salt were found to exhibit strong violet fluorescence. A recrystallization from absolute ethanol gave pale yellow needles, darkening at 225° and melting with decomposition at 235°; $\lambda_{max}$ 220 (sho.), 291 (sho.), 298, 320 (sho.), 355, 550 m$\mu$ ($\epsilon \times 10^{-3}$ 20.0, 49.5, 55.4, 19.0, 5.4, 3.0).

*Anal.* Calcd. for $C_{18}H_{17}NSO$: C, 62.95; H, 4.99; N, 4.08. Found: C, 62.84; H, 5.06; N, 3.71.

*6H-Indeno(2,1-b)quinoline 5-methochloride* (VIII). This salt was formed in a quantitative yield when 0.5 g. (0.00146 mole) of the methosulfate VII was dissolved in hot 2*N* hydrochloric acid and allowed to cool. Filtration gave pale yellow needles, which darkened at 217° and melted with decomposition at 229°, after a recrystallization from absolute ethanol; $\lambda_{max}$ 220 (sho.), 291 (sho.), 298, 320 (sho.), 355, 550 m$\mu$ ($\epsilon \times 10^{-3}$ 20.1, 49.5, 55.4, 19.1, 5.3, 3.0).

*5-Methyl-5H-indeno(2,1-b)quinoline* (IX). A molecule of water was eliminated when either quaternary salt VII or VIII was dissolved in water and treated with base. Two grams (0.00584 mole) of the methosulfate VII dissolved in water produced a deep purple coloration which gradually faded with the addition of 5 g. of potassium hydroxide pellets. The resulting purple solid was collected by filtration; wt. 1.26 g. (93.2% yield), m.p. 126–130°. Recrystallization from cyclohexane gave deep purple crystals, m.p. 130°; $\lambda_{max}$ 220 (sho.), 290 (sho.), 297, 320 (sho.), 354, 550 m$\mu$ ($\epsilon \times 10^{-3}$ 20.6, 52.4, 59.0, 20.6, 6.0, 4.0); infrared bands carbon tetrachloride soln.) $\gamma_{C=C}$ 1650/65, $\gamma_{Ar}$ 1605/59.

*Anal.* Calcd. for $C_{17}H_{13}N$: C, 88.28; H, 5.66; N, 6.06. Found: C, 88.00; H, 5.68; N, 6.30.

When a 0.5-g. sample of IX in 50 g. of methyl iodide was refluxed for 27 hr. and cooled, filtration produced 0.75 g. (93% yield) of the salt X [6-methyl-6*H*-indeno(2,1-*b*) quinoline 5-methiodide] as yellow needles, which darkened at 210° and melted with decomposition at 218–220°. This compound rapidly decomposed to a green solid on standing at room temperature and thus was not analyzed.

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(14) G. H. Coleman and G. E. Honeywell, *Org. Syntheses*, **Coll. Vol. II**, 89 (1943).

(15) G. Wittig and F. Vidal, *Ber.*, 81, 368 (1948).

*Attempted preparation of 6H-indeno(2,1-b)quinolin 1-oxide.* To 1.09 g. (0.005 mole) of I in 15 ml. of glacial acetic acid, was added 0.7 ml. of 20% hydrogen peroxide. The solution was heated at 65–69° for 3 hr., after which an additional 0.3 ml. of 30% hydrogen peroxide (0.0085 mole total) was added, followed by 19 hr. of supplementary heating at 69°. The brown-black mixture was evaporated to dryness under vacuum, triturated with hot saturated sodium carbonate solution until basic and extracted with chloroform. A red-brown solid, weighing 0.74 g. (63.8% yield), was obtained by ethanol treatment of the residue from chloroform evaporation. All attempts at purification by recrystallization techniques were fruitless; however, sublimation of 100 mg. at 150°/0.1 mm. resulted in 50 mg. of a yellow solid, m.p. 185–189°. A mixture melting point experiment and the infrared spectrum indicated the product to be ketone II.

*6H-Indeno(2,1-b)quinoline-11-carboxylic acid* (XI). A mixture of 4.0 g. (0.0302 mole) of 2-indanone and 7.0 g. (0.0476 mole) of isatin was heated on a steam bath for 30 min. in a basic media of 6 g. of sodium hydroxide in 70 ml. of water and allowed to cool overnight. The sodium salt of XI was collected by vacuum filtration, washed with cold water and heated in the presence of 25% acetic acid. A pale tan solid, weighing 4.85 g. (61.6% yield), was collected after trituration with methanol. Compound XI was quite insoluble in most organic solvents; however, recrystallization of the sodium salt from water, subsequent acidification with dilute acetic acid and washing with a variety of solvents gave a pale tan powder, which melted above 350°, after darkening at 275°; $\lambda_{max}$ (methanol and potassium hydroxide) 216, 259 (sho.), 265, 289, 314, 328, 343 mμ ($\epsilon \times 10^{-3}$ 35.4, 34.4, 36.3, 9.65, 12.9, 13.2, 15.1).

*Anal.* Calcd. for $C_{17}H_{11}NO_2$: C, 78.15; H, 4.24; N, 5.36. Found: C, 77.98; H, 4.55; N, 5.50.

*4-Chloro-6H-indeno(2,1-b)quinoline-11-carboxylic acid* (XII). A mixture of 0.66 g. (0.005 mole) of 2-indanone and 1.09 g. (0.006 mole) of 7-chloroisatin was heated in a basic solution of 1.5 g. of sodium hydroxide in 20 ml. of water. Heating was continued for 30 min., after which the mixture was cooled to precipitate needles of the sodium salt. Filtration, washing with cold water, and drying was followed by heating the salt in 25% aqueous acetic acid. The acid was collected which, after trituration with hot acetone, weighed 0.91 g. (61.5% yield). Three recrystallizations from pyridine-acetone gave XII as a pale tan powder, decomposing at 308–310° after darkening at 275°; $\lambda_{max}$ (methanol and potassium hydroxide) 216, 258 (sho.), 272, 317, 329, 344 mμ ($\epsilon \times 10^{-3}$ 33.7, 27.4, 30.1, 13.2, 13.2, 11.7); infrared bands (potassium bromide pellet) $\gamma_{OH}$ 3440/40, $\gamma_{COOH}$ 1715/80, 1681/51.

*Anal.* Calcd. for $C_{17}H_{10}NO_2Cl$: C, 69.04; H, 3.41; Cl, 11.99. Found: C, 68.51; H, 3.64; Cl, 11.52.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, COMMERCIAL SOLVENTS CORP.]

# Periodate Oxidations of Oxazolines

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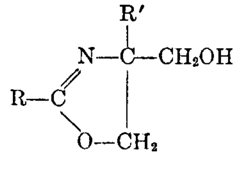
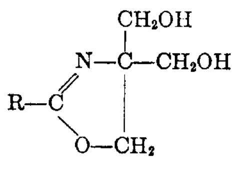
The reaction of 2-oxazolines with periodic acid has been studied. Those 2-oxazolines containing an hydroxymethyl group in position 4 are quantitatively oxidized in aqueous solution at room temperature. The effect of varying the ring substituents and the effect of the addition of alkali and acid to the reaction media have been determined. Oxidation products have been isolated in certain instances. A reaction scheme involving preliminary hydrolysis of the oxazoline is presented to account for the results obtained.

During the course of a study of methods for the analysis of mixtures of amino alcohols and oxazolines, it was discovered that 2-oxazolines containing one or more hydroxymethyl groups in position 4 are quantitatively oxidized by aqueous periodic acid according to Equations 1 and 2.



$$+ HIO_4 + H_2O \longrightarrow RCOOCH_2COR' + HCHO + HIO_3 + NH_3 \quad (1)$$



$$+ 2HIO_4 + H_2O \longrightarrow RCOOCH_2COOH + 2HCHO + 2HIO_3 + NH_3 \quad (2)$$

These results were unexpected in view of the information previously published regarding periodate oxidations.

Application of the glycol-splitting agent, periodic acid, to the cleavage of amino alcohols was first reported by Nicolet and Shinn.[1] As in the case of glycols, only those amino alcohols with the functional groups attached to adjacent carbon atoms are oxidized.

As *N*-acylated amino alcohols and tertiary amino alcohols are not oxidized or are only very slowly oxidized by periodic acid at room temperature, it was not expected that 4-hydroxymethyl-2-oxazolines would be readily oxidized. That 4-hydroxymethyl-2-oxazolines are readily oxidized by periodic acid is established by the results given in the Experimental Section of this report.

The quantitative nature of the reaction is indicated by the results shown in Table II. Products

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[1] B. H. Nicolet and L. A. Shinn, *J. Am. Chem. Soc.*, 61, 1615 (1939).