Indenoquinolines. III. Derivatives of 11*H*-Indeno[1,2-*b*]quinoxaline and Related Indenoquinolines

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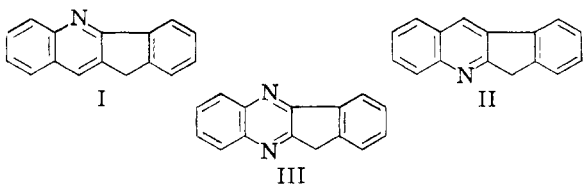
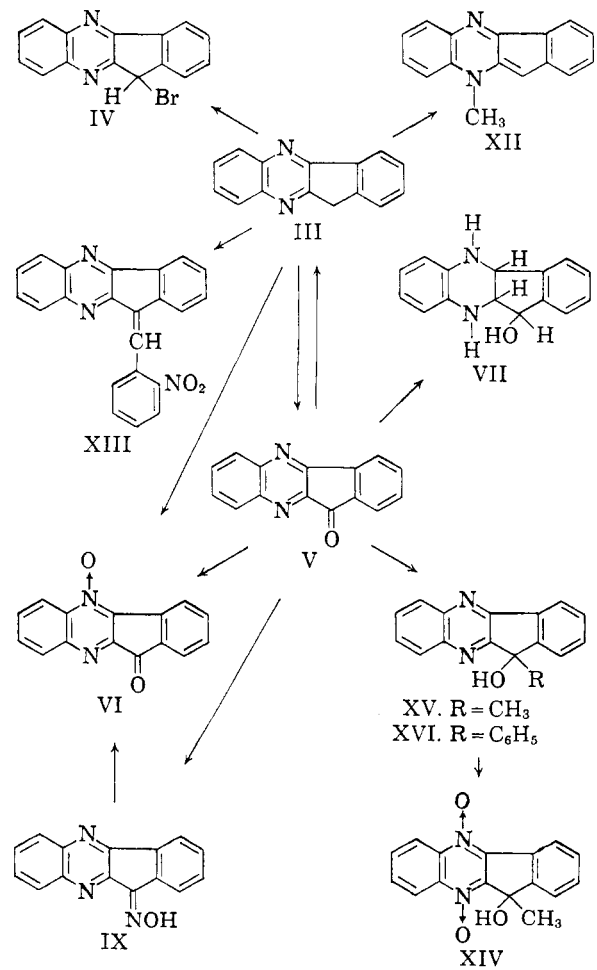
Oxidation of 11*H*-indeno[1,2-*b*]quinoxaline (III) with chromic acid gave 11*H*-indeno[1,2-*b*]quinoxalin-11-one (V) in high yield. Reaction of III with *N*-bromosuccinimide produced 11-bromo-11*H*-indeno[1,2-*b*]quinoxaline and dimethyl sulfate gave 10′-methyl-10*H*-indeno[1,2-*b*]quinoxaline. Meerwein-Ponndorf reduction of V yielded III, whereas catalytic hydrogenation gave 4a,5,10,10a-tetrahydro-11*H*-indeno[1,2-*b*]quinoxalin-11-ol. With methylmagnesium bromide the ketone V yielded the methylcarbinol XV which was oxidized with peracetic acid to the di-*N*-oxide XIV. Peracetic acid oxidation of III or V yielded an *N*-oxide of V. The ultraviolet and infrared spectra and the chemical reactivity of some indenoquinolines and indenoquinoxalines have been compared.

Previous papers in this series have developed the chemistry of the 11*H*-indeno[1,2-*b*]quinolines (I)[2] and the 6*H*-indeno[2,1-*b*]quinolines (II).[3] We have now extended our studies to include derivatives of 11*H*-indeno[1,2-*b*]quinoxaline (III) as these compounds are closely related to the indenoquinolines and are also of biological interest.

An interesting feature of the chemistry of the indenoquinolines and indenoquinoxalines is the different reactivity of the methylene group in the systems I, II, and III. The methylene group in the indenoquinoline (I) is bonded to a phenyl group and to a carbon atom *meta* to the conjugated nitrogen atom. In 6*H*-indeno[2,1-*b*]quinoline the methylene group is bonded to a phenyl group and to a carbon atom *ortho* to the nitrogen atom. The reactivity of the methylene groups in these two cases has been compared with that of the methyl group in 3- and 2-methylquinoline, respectively.[3] The 11*H*-indeno[1,2-*b*]quinoxaline molecule is in effect a mixture of both the indenoquinoline molecules I and II. Some differences and similarities between the reactivities of the three systems are summarized in Tables I and II.



Thus, upon bromination with *N*-bromosuccinimide, 6*H*-indeno[2,1-*b*]quinoline adds two bromine atoms to the methylene group, whereas the indenoquinoline II and the indenoquinoxaline III add only one bromine atom. However, of the three bromo compounds, only 11-bromo-11*H*-indeno[1,2-*b*]quinoline reacts normally with amines such as morpholine or piperidine. All attempts to treat 11-bromo-11*H*-indeno[1,2-*b*]quinoxaline (IV) with amines were unsuccessful as only a red compound VIII, m.p. 350–360°, could be isolated from the reaction mixture. The compound VIII may be formed by a free radical mechanism as it was also obtained when the bromo compound IV was heated slowly, filtered through basic alumina (*p*H 10–11) in benzene, refluxed with methanol, exposed to ultraviolet light, or treated with benzoyl peroxide in benzene, sodium in benzene, or sodium



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(2) N. H. Cromwell and R. A. Mitsch, *J. Org. Chem.*, **26**, 3812 (1961).

(3) N. H. Cromwell and R. A. Mitsch, *ibid.*, **26**, 3817 (1961).

TABLE I

REACTIONS OF THE INDENOQUINOLINES AND INDENOQUINOXALINES

	6H-Indeno[2,1-b]quinoline	11H-Indeno[1,2-b]quinoline	11H-Indeno[1,2-b]quinoxaline (III)
N-Bromosuccinimide	6,6′-Dibromo-6H-indeno[2,1-b]-quinolin-6-one	11-Bromo-11H-indeno[1,2-b]quinoline	11-Bromo-11H-indeno[1,2-b]-quinoxaline (IV)
Chromic acid	6H-Indeno[2,1-b]quinolin-6-one	11H-Indeno[1,2-b]quinolin-11-one and a chromium complex of 11H-indeno-[1,2-b]quinoline	11H-Indeno[1,2-b]quinoxalin-11-one (V)
Peracetic acid	6H-Indeno[2,1-b]quinolin-6-one	11H-Indeno[1,2-b]quinoline 1-oxide	N-Oxide of 11H-indeno[1,2-b]-quinoxalin-11-one (VI)

TABLE II

REDUCTION PRODUCTS OF INDENOQUINOLINE AND INDENOQUINOXALINE KETONES

	6H-Indeno[2,1-b]quinolin-6-one	11H-Indeno[1,2-b]quinolin-11-one	11H-Indeno[1,2-b]quinoxalin-11-one (V)
Meerwein-Ponndorf reduction	No reaction	11H-Indeno[1,2-b]quinolin-11-ol	11H-Indeno[1,2-b]quinoxaline (III)
Palladium-on-charcoal hydrogenation[a]	6H-Indeno[2,1-b]quinolin-6-ol	4a,5,10,10a-Tetrahydro-11H-indeno[1,2-b]quinolin-11-one[b]	4a,5,10,10a-Tetrahydro-11H-indeno-[1,2-b]quinoxalin-11-ol (VII)

[a] One g. of 10% palladium-on-charcoal to 1.16 g. of the ketone. [b] Using a lower catalyst/compound ratio (0.4 g. of catalyst/1.16 g. of ketone) 11H-indeno[1,2-b]quinolin-11-ol can be isolated.

methoxide in acetone. No molecular weight value was obtained for compound VIII as it was very insoluble in all organic solvents, but elemental analysis suggested that it might be a polymer of basic unit $C_{15}N_2H_9$. A similar high-melting (m.p. 287–300°), very insoluble red compound was also obtained when 6,6′-dibromo-6H-indeno[2,1-b]quinoline was heated slowly.

Unusual behavior toward peracetic acid oxidation was observed with compounds II and III, whereas 11H-indeno[1,2-b]quinoline (I) reacted normally to form an N-oxide. 6H-Indeno[2,1-b]-quinoline (II) was oxidized to 6H-indeno[2,1-b]quinolin-6-one and 11H-indeno[1,2-b]quinoxaline (III) to an N-oxide of 11H-indeno[1,2-b]quinoxalin-11-one (VI). The same N-oxide ketone VI was also formed when either the ketone V or the oxime IX was oxidized with peracetic acid. An absolute orientation of the N-oxide ketone VI has not been undertaken but we suggest, by analogy with the oxidation reactions of the indenoquinolines, that it is 11H-indeno[1,2-b]quinoxalin-11-one 5-oxide. The N-oxide ketone VI did not react with organometallic reagents to give carbinols.

The reaction of either 6H-indeno[2,1-b]quinolin-6-one or 11H-indeno[1,2-b]quinolin-11-one to form the corresponding N-oxide ketones was unsuccessful and the ketones were recovered unchanged. However, it was found that oxidation of 11H-indeno[1,2-b]quinoline 5-oxide with chromic acid gave 11H-indeno[1,2-b]quinolin-11-one 5-oxide in low yield.

Chromic acid oxidation of compounds I, II, and III gave the corresponding ketones in good yield. This method represents an improved synthesis of 11H-indeno[1,2-b]quinoxalin-11-one (V) which had previously been synthesized by the condensation of 1,2,3-indantrione hydrate with o-phenylenediamine.[4] A chromium complex of the indenoquinoline (I) was isolated in 55% yield as well as 11H-indeno[1,2-b]quinolin-11-one in 41% yield. The complex can be decomposed by heating with dilute mineral acids and the indenoquinoline (I) recovered.

11H-Indeno[1,2-b]quinoxaline (III) reacted with dimethyl sulfate to form the pseudo azulene 10′-methyl-10H-indeno[1,2-b]quinoxaline (XII). A similar pseudo azulene was obtained from 6H-indeno[2,1-b]quinoline but not from 11H-indeno-[1,2-b]quinoline. The black-colored solid XII was purified with difficulty, by recrystallization from n-hexane. Chromatography of the pseudo azulene (XII) on alumina (pH 10–11) yielded another black-colored compound, m.p. 94°, which has resisted purification but is probably a keto-enol mixture derived from 11-hydroxy-10′-methyl-10H-indeno[1,2-b]quinoxaline, since infrared spectra indicated the presence of a carbonyl group ($\nu_{C=O}$ 1730 cm.$^{-1}$). An attempt to prepare the pseudo azulene XII by the condensation of N-methyl-o-phenylenediamine with 1,2-indandione was unsuccessful.

The reactivity of the methylene group in the indenoquinolines and indenoquinoxalines has been further illustrated by their ability to react with o- and p-nitrobenzaldehydes. Thus 11H-indeno-[1,2-b]quinoxaline (III) yielded 11-(o-nitrostyryl)-11H-indeno[1,2-b]quinoxaline (XIII), 11H-Indeno-[1,2-b]quinoline gave 11-(p-nitrostyryl)-11H-indeno-[1,2-b]quinoline, and 6H-indeno[2,1-b]quinoline gave 6-(o-nitrostyryl)- and 6-(p-nitrostyryl)-6H-indeno[2,1-b]quinoline.

The ketones derived from compounds I, II, and III react normally with organometallic reagents to yield tertiary carbinols but show marked differences in their reactions with reducing agents. Thus, under Meerwein-Ponndorf conditions, ketone V was reduced to the hydrocarbon III, whereas 11H-indeno[1,2-b]quinolin-11-one was reduced to the

(4) S. Ruheman, *J. Chem. Soc.*, 1449 (1910).

corresponding carbinol and 6*H*-indeno[2,1-*b*]quinolin-6-one was recovered unchanged. A previous case of the reduction of a ketone to a hydrocarbon under Meerwein-Ponndorf conditions has been observed but is unusual.[5]

Using catalytic reduction, 6*H*-indeno[2,1-*b*]quinolin-6-one added one mole of hydrogen; 11*H*-indeno[1,2-*b*]quinolin-11-one added two moles of hydrogen (or only one mole if less catalyst was used), and the indenoquinoxaline III added three moles of hydrogen to yield the carbinol VII. Infrared spectra showed that compound VII possessed OH and NH groupings.

A di-*N*-oxide XIV was obtained from the peracetic acid oxidation of 11-hydroxy-11-methyl-11*H*-indeno[1,2-*b*]quinoxaline (XV).

The infrared spectra of the ketones derived from compounds I, II, and III exhibit normal carbonyl vibrations for five-membered ring ketones.[6] However 11*H*-indeno[1,2-*b*]quinolin-11-one absorbs at 1723 cm.$^{-1}$, whereas 6*H*-indeno[2,1-*b*]quinolin-6-one and 11*H*-indeno[1,2-*b*]quinoxalin-11-one absorb at 1737 and 1735 cm.$^{-1}$ (carbon tetrachloride solutions), respectively. The slightly higher frequencies for the latter two compounds may result from a dipolar effect between the lone pair of electrons on the nitrogen atom and the π-electrons of the carbonyl group. The effect may be likened to that in the α-halo ketones[6] but is smaller in the indenoquinolines, possibly because of a lessened dipolar effect caused by the increased angle between the interacting bonds.

Katritzky[7,8] has reported that the *N*-oxide stretching frequency for a large number of substituted pyridine 1-oxides forms a band of variable intensity between 1200 and 1300 cm.$^{-1}$. In accord with these values, 11*H*-indeno[1,2-*b*]quinolin-11-one 5-oxide and the *N*-oxide ketone VI possess bands of weak intensity at 1265 and 1255 cm.$^{-1}$, respectively, the frequencies of the carbonyl groups being little changed from those of the parent ketones. 11*H*-Indeno[1,2-*b*]quinolin 5-oxide[2] exhibits a medium intensity band at 1272 cm.$^{-1}$ and the di-*N*-oxide XIV has a weak band at 1240 cm.$^{-1}$ and a medium intensity band at 1290 cm.$^{-1}$. The spectrum of this latter compound XIV in a potassium bromide pellet showed an unusually weak bonded OH band at 3180 cm.$^{-1}$ in comparison to a strong bonded OH band observed at 3300 cm.$^{-1}$ for the parent carbinol XV. Thus, the two bands observed in the infrared spectrum of the di-*N*-oxide XIV at 1240 and 1290 cm.$^{-1}$ may result from the stretching frequencies of the *N*-oxide groupings at the 5- and 10-positions, respectively. The weak band at 3180 cm.$^{-1}$ may represent the tertiary carbinol OH band shifted to a lower frequency by hydrogen bonding (probably intermolecular).

The ultraviolet spectra of the indenoquinolines I and II consist of an intense absorption band near 265 mμ and a weaker, broad doublet with maxima near 330 and 345 mμ. The indenoquinoxaline III also exhibits a band near 265 mμ but the maxima of the doublet are moved to 345 and 360 mμ The spectra of compounds I, II, and III thus resemble those of the corresponding quinoline derivatives.[9] The band near 265 mμ is probably a β-band while the doublet may be a merged *p*- and α-band.

In the indenoquinoline and indenoquinoxaline ketones the predominant chromophore now involves a carbonyl group. Thus, only a two-band absorption system is observed. The maxima are near 230 and 290 mμ, the latter being particularly intense. In acid solutions the intensity of the 290 mμ band decreases and a weak long wave-length band appears near 360 mμ.

Experimental[10]

11*H*-Indeno[1,2-b]quinoxaline (III).—The procedure of Perkin, Roberts, and Robinson[11] was employed with a slight solvent modification. 1,2-Indandione (1.46 g., 0.01 mole) and *o*-phenylenediamine (1.08 g., 0.01 mole) were dissolved separately in the minimum amount of hot methanol. Mixing the two solutions followed by cooling and dilution with water gave the quinoxaline (1.70 g. 78%). Purification by filtration through alumina in benzene and recrystallization from the same solvent gave colorless needles, m.p. 159–160° (lit.,[11] 164–165°); λ_{max} 268, 345, and 360 mμ ($\epsilon \times 10^{-3}$ 28.6, 19.0, and 20.6); (CH_3OH/0.1 *M* HCl) 269, 347 (sho.), 363, and 383 mμ ($\epsilon \times 10^{-3}$ 20.5, 12.0, 15.7, and 13.3). Infrared bands (KBr pellet) 3050 w, 2920 w, 1615 w, 1475 m, 1410 s, 1380 m, 1340 s, 1125 m, 1015 m, 780 s, 765 s, and 740 s cm.$^{-1}$.

11-Bromo-11*H*-indeno[1,2-b]quinoxaline (IV).—*N*-Bromosuccinimide (3.56 g., 0.02 mole) and benzoyl peroxide (0.25 g.) were added to a solution of 11*H*-indeno[1,2-*b*]-quinoxaline (4.36 g., 0.02 mole) in carbon tetrachloride (175 ml.). The solution was refluxed 3 hr., the succinimide collected, and the filtrate washed with 5% aqueous sodium bicarbonate and water. Removal of the solvent gave a tar which was stirred with acetone (25 ml.) yielding 11-bromo-11*H*-indeno[1,2-*b*]quinoxaline (4.57 g., 77%). Recrystallization from acetone gave colorless needles, m.p. 201–203°. If the bromo compound is heated slowly it turns to a red solid VIII at 160° and the red solid melts between 350 and 360°; λ_{max} 272, 292 (sho.), 346, and 364 (sho.) mμ ($\epsilon \times 10^{-3}$ 21.4, 10.7, 12.3, and 12.0).

Anal. Calcd. for $C_{15}H_9N_2Br$: C, 60.62; H, 3.05; Br, 26.89. Found: C, 60.92; H, 3.29; Br, 26.56.

10′-Methyl-10*H*-indeno[1,2-b]quinoxaline (XII).—11*H*-Indeno[1,2-*b*]quinoxaline (1.0 g.) was suspended in 4 *N*

(5) A. L. Wilds, *Org. Reactions*, **II**, 191 (1944).

(6) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley, New York, 1958, p. 132.

(7) A. R. Katritzky and J. N. Gardener, *J. Chem. Soc.*, 2192 (1958).

(8) A. R. Katritzky, J. A. T. Beard, and N. A. Coats, *ibid.*, 3680 (1959).

(9) N. H. Cromwell and G. D. Mercer, *J. Am. Chem. Soc.*, **79**, 6201 (1957).

(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 unless otherwise stated. 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) W. H. Perkin, W. M. Roberts, and R. Robinson, *J. Chem. Soc.*, 232 (1912).

sodium hydroxide solution (5 ml.), and dimethyl sulfate (0.5 g.) was added. The solution was boiled gently for 1 hr. and kept alkaline by the addition of 10 *N* sodium hydroxide solution. A further amount of dimethyl sulfate (0.5 g.) was added and the solution boiled for another hour. Next day a black solid (1.05 g.) was collected and dried. Four recrystallizations of this black solid from *n*-hexane at Dry Ice temperatures gave 10′-methyl-10*H*-indeno[1,2-*b*]quinoxaline (0.2 g.; 19%) as a black amorphous solid, m.p. 148–149°; λ_{max} 268, 344, 360, and 575 mμ ($\epsilon \times 10^{-3}$ 26.8, 18.3, 11.6, and 1.40). Infrared bands (CCl_4): 3065 w, 1475 m, 1455 m, 1430 w, 1410 m, 1395 m, 1340 s, 1320 w, 1310 w, 1185 w, 1145 m, 1140 m, 1125 m, cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.77; H, 4.89; N, 12.19.

11-(*o*-Nitrostyryl)-11*H*-indeno[1,2-*b*]quinoxaline (XIII).—11*H*-Indeno[1,2-*b*]quinoxaline (1.0 g., 0.0046 mole) was refluxed with *o*-nitrobenzaldehyde (0.71 g., 0.0046 mole) in acetic anhydride (2.5 g., 0.025 moles) for 6 hr. After cooling, a brown solid (1.47 g., 90%) was collected. Recrystallization from acetic acid gave 11-(*o*-nitrostyryl)-11*H*-indeno-[1,2-*b*]quinoxaline as yellow needles, m.p. 259–260°; λ_{max} 228, 286, 360 (sho.) mμ ($\epsilon \times 10^{-3}$ 37.9, 30.3, and 12.5). Infrared bands (KBr pellet) ν_{NO_2} 1520 vs, 1340 vs, $\nu_{C=C}$ 1610 m; other strong bands at 1325, 1120, 775, 760, and 725 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{13}NO_2$: C, 75.20; H, 3.73; N, 11.96. Found: C, 75.03; H, 3.70; N, 11.96.

11*H*-Indeno[1,2-*b*]quinoxalin-11-one (V). (A).—1,2,3-Indantrione hydrate (3.56 g., 0.02 mole) and *o*-phenylenediamine (2.16 g., 0.02 mole) were dissolved separately in the minimum amount of warm aqueous acetic acid (4:1 v./v.) and the solutions mixed. Cooling and stirring precipitated the ketone (4.10 g., 88%) which was purified by filtration through alumina in benzene–ethyl acetate followed by crystallization from the same solvent to give yellow needles, m.p. 222° (lit.,[4] 218–219°); λ_{max} 223 and 291 mμ ($\epsilon \times 10^{-3}$ 23.4 and 39.4); (CH_3OH/0.1 *M* HCl) 218, 277, 286 (sho.), 344, and 363 mμ ($\epsilon \times 10^{-3}$ 24.6, 24.2, 23.8, 8.9, and 8.0). Infrared bands (CCl_4 solution) $\nu_{C=O}$ 1735 s (KBr pellet) $\nu_{C=O}$ 1727 s, other strong bands at 1575, 1515, 1337, 1200, and 770 cm.$^{-1}$.

B.—A slurry of potassium dichromate (2.4 g.), acetic acid (4 ml.), and water (0.8 ml.) was slowly added to a stirred solution of 11*H*-indeno[1,2-*b*]quinoxaline (1.00 g.) in acetic acid (8 ml.). The mixture was slowly raised to the reflux and then refluxed for 2.5 hr. The hot solution was poured into water (200 ml.) and the yellow 11*H*-indeno[1,2-*b*]-quinoxalin-11-one (0.90 g., 85%) collected.

11-Oximino-11*H*-indeno[1,2-*b*]quinoxaline (IX).—11*H*-Indeno[1,2-*b*]quinoxalin-11-one (1.0 g.) was warmed on a water bath with sodium hydroxide solution (10% aq., 25 ml.), water (15 ml.), hydroxylamine hydrochloride (2.5 g.), and ethanol (12 ml.) for 30 min. Cooling precipitated the sodium salt of the oxime (0.48 g., 45%) which upon recrystallization from ethanol gave yellow needles, m.p. 345° dec.

Anal. Calcd. for $C_{15}H_8N_3ONa$: C, 66.80; H, 2.97. Found: C, 66.08; H, 3.48.

Stirring the yellow sodium salt with 0.1 *N* hydrochloric acid liberated the free oxime in quantitative yield, as a white solid. Recrystallization from ethanol–water (2:1 v./v.) gave white needles, m.p. 257°; λ_{max} 227, 262 (sho), 285, 365 mμ, ($\epsilon \times 10^{-3}$ 32.8, 27.0, 36.0, and 6.7); $\nu_{C=N}$ 1640 m, other bands: 1340 m, 1000 s, 945 s, and 760 cm.$^{-1}$ (KBr pellet).

Anal. Calcd. for $C_{15}H_9N_3O$: C, 72.86; H, 3.67; N, 17.00. Found: C, 72.66; H, 3.94; N, 16.59.

11-Hydroxy-11-methyl-11*H*-indeno[1,2-*b*]quinoxaline (XV).—Commercial 3 *M* methylmagnesium bromide (6.5 ml., 0.02 mole) was slowly added to a stirred suspension of 11*H*-indeno[1,2-*b*]quinoxalin-11-one (2.32 g., 0.01 mole) in ether (125 ml.), and the mixture was stirred for 30 min. The deep red-colored complex was decomposed with a saturated solution of aqueous ammonium chloride. The residue from an ether extraction was dissolved in benzene (charcoal). Addition of petroleum ether precipitated 11-hydroxy-11-methyl-11*H*-indeno[1,2-*b*]quinoxaline (1.08 g., 43%) as pale yellow needles, m.p. 207–208°; λ_{max} 270, 348, and 364 mμ ($\epsilon \times 10^{-3}$ 24.6, 16.7, and 17.7). Infrared bands (CH_2Cl_2 solution) ν_{-OH} 3580, $\nu_{-OH\ bonded}$ 3300, other bands at 1622, 1580, and 1520 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{12}N_2O$: C, 77.39; H, 4.87; N, 11.29. Found: C, 77.63; H, 5.00; N, 11.32.

11-Hydroxy-11-phenyl-11*H*-indeno[1,2-*b*]quinoxaline (XVI).—11*H*-Indeno[1,2-*b*]quinoxalin-11-one (1.16 g., 0.005 mole) reacted with the Grignard reagent prepared from bromobenzene (1.88 g., 0.012 mole) and magnesium (0.29 g., 0.012 g.-atom) in refluxing ether–benzene (1:1 v./v., 150 ml.). After refluxing for 1 hr. the green-brown complex was decomposed with a saturated aqueous ammonium chloride solution. Extraction with benzene and evaporation, followed by crystallization of the 11-hydroxy-11-phenyl-11*H*-indeno[1,2-*b*]quinoxaline (1.08 g., 70%) from aqueous dioxane (charcoal) gave colorless needles, m.p. 248°; λ_{max} 258 (sho.), 270, 351, and 368 mμ ($\epsilon \times 10^{-3}$ 20.3, 22.0, 15.3, and 17.0); infrared bands (CH_2Cl_2 solution) ν_{-OH} 3560, $\nu_{-OH\ bonded}$ 3250; other bands at 1625, 1575, and 1510 cm.$^{-1}$.

Anal. Calcd. for $C_{21}H_{14}N_2O$: C, 81.27; H, 4.55; N, 9.03. Found: C, 81.21; H, 4.82; N, 9.01.

Meerwein-Ponndorf Reduction of 11*H*-Indeno[1,2-*b*]-quinoxalin - 11 - one.—11*H* - Indeno[1,2 - *b*]quinoxalin-11-one (1.0 g.) was refluxed, in isopropyl alcohol (75 ml.), with aluminum isopropoxide (4.7 g.) for 16 hr. Then 60 ml. of the solvent was slowly removed by distillation, and the remaining reaction mixture was hydrolyzed by the addition of hydrochloric acid (*d* 1.2, 35 ml.) and water (175 ml.). The solution was kept overnight and the buff precipitate was then collected, triturated with 5% aqueous sodium bicarbonate solution, washed with water, and dried (0.66 g., m.p. 135–142°).

The product was dissolved in benzene and chromatographed on an aluminum oxide column (2.5 × 20 cm.), prepared in the same solvent. Elution with benzene–ethyl acetate (10:1 v./v.) gave first a pale yellow band (a) and then a deep yellow band (b). Removal of the solvents gave:

(a) 11*H*-indeno[1,2-*b*]quinoxaline; 0.42 g., 45%, m.p. 159° (benzene–hexane), lit.,[11] 158–160°.

(b) 11*H*-indeno[1,2-*b*]quinoxalin-11-one; 0.09 g., 9%, m.p. 220° (benzene–hexane), lit.,[4] 218–219°.

4a,5,10,10a-Tetrahydro-11*H*-indeno[1,2-*b*]quinoxalin-11-ol (VII).—11*H*-Indeno[1,2-*b*]quinoxalin-11-one (1.16 g., 0.005 mole) was hydrogenated in benzene (125 ml.) using a 10% palladium-charcoal catalyst (1.0 g.) and hydrogen at 45 p.s.i. for 5 hr. Removal of the catalyst and evaporation of the solvent gave 4a,5,10,10a-tetrahydro-11*H*-indeno-[1,2-*b*]quinoxalin-11-ol (0.49 g., 47%) as a yellow solid which was recrystallized from benzene to give colorless needles, m.p. 167–168°; λ_{max} 310 mμ ($\epsilon \times 10^{-3}$ 5.7); Infrared bands (CH_2Cl_2 solution) ν_{-OH} 3580, $\nu_{-OH\ bonded}$ 3400, ν_{NH} 3300 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{14}N_2O$: C, 75.61; H, 5.92; N, 11.76. Found: C, 75.44; H, 5.93; N, 11.75.

11*H*-Indeno[1,2-*b*]quinoxalin-11-one 5-Oxide (VI). A.—11*H*-Indeno[1,2-*b*]quinoxaline (1.0 g.) was dissolved in acetic acid (20 ml.). Hydrogen peroxide (30%, 5.0 ml.) was added dropwise and the solution was heated at 60° for 18 hr. Upon cooling the solution, orange needles were deposited (0.90 g., 79%, m.p. 271° dec.). Recrystallization from benzene gave 11*H*-indeno[1,2-*b*]quinoxalin-11-one 5-oxide as short orange needles, m.p. 275° dec.; λ_{max} 244, 311, 341 (sho.) mμ ($\epsilon \times 10^{-3}$ 22.8, 29.8, and 12.2); infrared bands (KBr pellet) $\nu_{C=O}$ 1727 vs; $\nu_{C=N}$ 1596 m; $\nu_{N^+-O^-}$ 1255 w cm.$^{-1}$ (CCl_4 solution) $\nu_{C=O}$ 1739 vs cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_8N_2O_2$: C, 72.57; H, 3.25; N, 11.29. Found: C, 72.54; H, 3.22; N, 11.29.

B.—11*H*-Indeno[1,2-*b*]quinoxalin-11-one (1.0 g.) was dissolved in acetic acid (12 ml.). Hydrogen peroxide (30%, 5.0 ml.) was added dropwise and the solution was heated at 60° for 18 hr. Upon cooling the solution, orange needles of VI were deposited (0.90 g., 84%), collected and recrystallized from benzene, m.p. 275° dec.

C.—11-Oximino-11*H*-indeno[1,2-*b*]quinoxaline (0.30 g.) was warmed with acetic acid (6 ml.) and hydrogen peroxide (30%, 1.7 ml.) at 65° for 18 hr. At the end of this time the solution was diluted with water (30 ml.) and extracted with benzene (3 × 50 ml.). The benzene solution was washed with 5% aqueous sodium bicarbonate, water, dried, and reduced in volume. Addition of hexane then precipitated orange needles (0.21 g., 70%) of VI, m.p. 275° dec.

11-Methyl-11*H*-indeno[1,2-*b*]quinoxalin-11-ol 5,10 di-*N*-oxide (XIV).—11-Methyl-11*H*-indeno[1,2-*b*]quinoxalin-11-ol (1.0 g.) was warmed with acetic acid (18 ml.) and hydrogen peroxide (30%, 5.0 ml.) at 65° for 18 hr. The volume of the solution was then reduced to about 10 ml. by flash evaporation and hexane (10 ml.) was added. After stirring the solution for a few minutes a yellow precipitate of 11-methyl-11*H*-indeno[1,2-*b*]quinoxalin-11-ol 5,10-di-*N*-oxide (0.54 g., 48%, m.p. 229–231° dec.) formed and was collected. Recrystallization from benzene, in which the compound is not very soluble, gave yellow crystals, m.p. 237–238° dec. λ_{max} 208, 226 (sho.), 287, 355 (sho.) mμ ($\epsilon \times 10^{-3}$ 40.0, 24.7, 9.2, and 2.63); infrared bands (KBr pellet) $\nu_{-OH\ (bonded)}$ 3180 w, $\nu_{C=N}$ 1560 m, ν_{N-O} 1240 w, and 1290 m, other strong bands at 1150, 1120, 1085, 920, 890, 785, 765, 745, and 690 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{12}N_2O_3$: C, 68.56; H, 4.32; N, 10.00. Found: C, 68.26; H, 4.41; N, 9.77.

Chromic Acid Oxidation of 11*H*-Indeno[1,2-*b*]quinoline.—A solution of potassium dichromate (2.4 g.), acetic acid (4 ml.), and water (1 ml.) was slowly added to a stirred solution of 11*H*-indeno[1,2-*b*]quinoline (1.0 g.) in acetic acid (8 ml.). The solution was slowly raised to the reflux temperature and then refluxed for 2.5 hr. The hot solution was poured into water (200 ml.) and the buff solid (1.32 g.) collected and dried.

The buff solid was extracted with benzene (2 × 25 ml.) and the solution filtered giving a brown solid, m.p. 360°, and a yellow filtrate.

The filtrate was reduced in volume to 10 ml. and chromatographed on alumina giving 11*H*-indeno[1,2-*b*]quinolin-11-one as a yellow solid; 0.43 g., 41%, m.p. 175°, lit.,[12] 175°.

The brown solid (0.85 g., 55%) was assumed to be a chromium π-complex of 11*H*-indeno[1,2-*b*]quinoline owing to its high melting point and low solubility in organic solvents.

Anal. Calcd. for $C_{16}H_{12}N \cdot CrO_4$: C, 57.50; H, 3.62; N, 4.18. Found: C, 57.42; H, 3.94; N, 4.04.

Infrared spectrum (in potassium bromide) of the chromium complex showed strong band at 2500 (broad), 1900 (broad), 1655 (—C=N—), 1350, 950, 930, 875, 765, and 735 cm.$^{-1}$.

When the brown solid was dissolved in hydrochloric acid and acetone, warmed, and the solution then basified with ammonia, 11*H*-indeno[1,2-*b*]quinoline was precipitated.

11*H*-Indeno[1,2-*b*]quinolin-11-one 5-Oxide.—A mixture of potassium dichromate (2.4 g.), acetic acid (4.0 ml.), and water (1.0 ml.) was slowly added to a stirred solution of 11*H*-indeno[1,2-*b*]quinoline 5-oxide[2] (1.0 g.) in acetic acid (8.0 ml.). The resultant solution was refluxed for 2.5 hr. and then poured onto water (200 ml.). The orange solid was collected, dried, and extracted with benzene (3 × 20 ml.) leaving an insoluble residue (0.35 g.) which was probably a chromium complex, m.p. 350°.

Evaporation of the benzene filtrate gave 11*H*-indeno-[1,2-*b*]quinolin-11-one 5-oxide (0.25 g., 21%) as an orange solid which was recrystallized from benzene–ethyl acetate to give orange-brown needles, m.p. 241–242°; λ_{max} 253, 258, 304, and 334 mμ ($\epsilon \times 10^{-3}$ 23.5, 24.2, and 8.0); infrared bands (KBr pellet): $\nu_{C=O}$ 1710 vs, ν_{N-O} 1265 w; other strong bands at 1620, 1600, 1195, 1170, 785, and 770 cm.$^{-1}$ (CCl_4 solution) $\nu_{C=O}$ 1724 vs cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_9O_2N$: C, 77.72; H, 3.67; N, 5.67. Found: C, 77.53; H, 3.68; N, 5.78.

6-(*o*-Nitrostyryl)-6*H*-indeno[2,1-*b*]quinoline.—6*H*-Indeno[2,1-*b*]quinoline (1.0 g., 0.0046 mole) was refluxed with *o*-nitrobenzaldehyde (0.71 g., 0.0046 mole) in acetic anhydride (2.5 g., 0.025 moles) for 6 hr. After cooling, a buff solid (1.04 g., 64%) was collected. Chromatography in benzene on alumina gave a tan solid which was recrystallized from benzene–hexane to give 6-(*o*-nitrostyryl)-6*H*-indeno-[2,1-*b*]quinoline as tan needles m.p. 199–201°; λ_{max} 230, 243 (sho.), 285, 320 (sho.) mμ ($\epsilon \times 10^{-3}$ 43.5, 40.8, 40.4, and 20.2); infrared bands (KBr pellet) ν_{NO_2} 1523 s, 1343 s, $\nu_{C=C}$ 1608 m; other strong bands at 1398, 858, 795, 750,, and 725 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{13}NO_2$: C, 78.84; H, 4.03; N, 8.00 Found: C, 78.95; H, 4.32; N, 8.32.

6-(*p*-Nitrostyryl)-6*H*-indeno[2,1-*b*]quinoline.—6*H*-Indeno[2,1-*b*]quinoline (1.0 g.; 0.046 mole) was refluxed with *p*-nitrobenzaldehyde (0.71 g.; 0.046 mole) in acetic anhydride (2.5 g.; 5 moles) for 6 hr. After cooling, a yellow solid (1.06 g.; 65%) was collected. Chromatography in benzene–ethyl acetate (5:1 v./v.) and subsequent recrystallization from the same solvent gave 6-(*p*-nitrostyryl)-6*H*-indeno[2,1-*b*]quinoline as orange flakes, m.p. 214–215°; λ_{max} 250, 284, and 370 mμ ($\epsilon \times 10^{-3}$ 48.5, 45.0, and 24.2); infrared bands (KBr pellet) ν_{NO_2} 1522 s, 1345 s; $\nu_{C=C}$ 1595 m; other strong bands at 893, 865, 805, and 758 cm.$^{-1}$.

Anal. Calcd. for $C_{23}H_{14}N_2O_2$: C, 78.84; H, 4.03; N, 8.00. Found: C, 78.63; H, 4.23; N, 7.60.

11-(*p*-Nitrostyryl)-11*H*-indeno[1,2-*b*]quinoline.—11*H*-Indeno[1,2-*b*]quinoline (1.0 g., 0.0046 mole) and *p*-nitrobenzaldehyde (0.71 g., 0.0046 mole) were refluxed in acetic anhydride (2.5 g., 0.025 moles) for 6 hr. After cooling, a yellow solid (0.80 g.; 49%) was collected, and recrystallization from benzene–ethyl acetate gave 11-(*p*-nitrostyryl)-11*H*-indeno[1,2-*b*]quinoline as yellow fluffy needles, m.p. 222–224°; λ_{max} 231 (sho.), 248, 283, 330 mμ ($\epsilon \times 10^{-3}$ 32.4, 38.2, 36.6, and 19.0); infrared bands (KBr pellet) ν_{NO_2} 1520 s, 1345 vs; $\nu_{C=C}$ 1600 m; other strong bands at 1115, 865, 770, 760, and 730 cm.$^{-1}$.

Anal. Calcd. for $C_{23}H_{14}N_2O_2$: C, 78.84; H, 4.03; N, 8.00. Found: C, 78.83; H, 4.39; N, 8.57.

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(12) E. Noelting and A. Herzbaum, *Ber.*, **44**, 2585 (1911).