were analyzed by determination of the long wave length ultraviolet absorption maxima (as above in the case of the aluminum isopropoxide reductions) and comparison with those of the pure chalcones, and in the case of the *trans*-chalcone consisted of 68–71.5% of reduction product and largely unchanged material in the case of the *cis* isomer.

Attempted sodium bisulfite addition was unsuccessful under the conditions employed successfully with dimesitoylethylene.[19] The method of Morisse[18] succeeded on both isomers but long refluxing time was required (10 hr.); yield 99%. (Reaction in neither case was complete after 8 hr. of refluxing time.) Upon addition to hot sodium hydroxide solution the addition compound gave *trans*-chalcone.

(19) R. E. Lutz and W. G. Reveley, THIS JOURNAL, **61**, 1859 (1939).

CHARLOTTESVILLE, VIRGINIA

[CONTRIBUTION FROM AVERY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

Some Methylphenanthrolines and Corresponding Aldehydes

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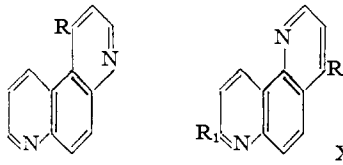
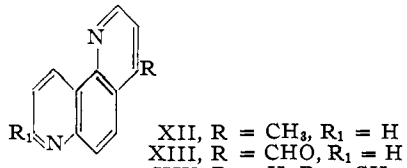
The synthesis of three new phenanthroline aldehydes by selenium dioxide oxidation of the appropriate methylphenanthroline is described. Two previously unknown methylphenanthrolines have been synthesized by a new route. An improved synthesis of 4-methyl-1,10-phenanthroline is presented.

Only a few mono-methylphenanthrolines have been described in the literature. For the most part these substances have been prepared from an aminoquinaldine[2] or an aminolepidine[3] by means of a Skraup reaction and have been obtained in very poor yields.

In the present investigation, an adaptation of a method studied by Campbell and Schaffner[4] for the preparation of some 4-methylquinolines was applied successfully to the synthesis of 1-methyl-4,7-phenanthroline (X) and 4-methyl-1,7-phenanthroline (XII).



X, R = CH_3
XI, R = CHO



XII, R = CH_3, R_1 = H
XIII, R = CHO, R_1 = H
XIV, R = H, R_1 = CH_3
XV, R = H, R_1 = CHO

The reaction was carried out by the dropwise addition of methyl vinyl ketone to an alcoholic solution of an aminoquinoline or its hydrochloride and ferric chloride. The two previously unknown methylphenanthrolines were obtained as white needles from benzene–petroleum ether and were soluble in ether, ethanol and hot water.

Although this method was successful for the preparation of X and XII, it failed in the case of 4-methyl-1,10-phenanthroline (XVI). This failure was due to the formation of the extremely stable ferrous complex salt of XVI from which only a small amount of XVI could be isolated. This difficulty was circumvented by applying a modification of the Skraup reaction described by Yale and Bernstein.[5] The formation of XVI proceeded in 26–30% yield when methyl vinyl ketone was added to a solution of 8-aminoquinoline (VI) and arsenic pentoxide in 85% phosphoric acid. This yield was somewhat better than the 14.9% obtained by Case[3] from 8-aminolepidine by means of the Skraup reaction.

The reaction of 5-aminoquinaldine (IX) with glycerol under the conditions of the Skraup reaction gave a 25% yield of 8-methyl-1,7-phenanthroline (XIV). This compound was first described by Gerdeissen[2] and was erroneously named 2-methyl-1,7-phenanthroline. It should be noted that only one substance was isolated in this investigation although Gerdeissen reported the formation of a second substance having the same empirical formula as XIV.

Many quinoline aldehydes have been prepared by the oxidizing action of selenium dioxide on methylquinolines,[6] but the extension of this useful reaction to the analogous methylphenanthrolines is not recorded in the literature.

Oxidation of X, XII and XIV with freshly prepared selenium dioxide proceeded readily in boiling xylene. The aldehydes crystallized from benzene as white needles after being isolated from the xylene solution as their bisulfite addition products. All of the aldehydes reduced Tollens reagent and formed high melting thiosemicarbazones which were insoluble in most solvents. The infrared absorption spectra of the aldehydes revealed a carbonyl stretching frequency of 1680 cm.$^{-1}$ for 4,7-phenanthroline-1-carboxaldehyde (XI) and 1690 cm.$^{-1}$ for 1,7-phenanthroline-8-carboxaldehyde (XV).

The oxidation of XVI proceeded with the precipitation of selenium, but no aldehyde could be isolated from the reaction mixture.

Experimental

6-Nitroquinoline (I).—This compound was prepared from *p*-nitroaniline in 48% yield as described by Capps and Hamilton.[7]

5-Nitro- (II) and 8-Nitroquinoline (III).—Nitration of quinoline by the method of Fieser and Hershberg[8] gave II (35%) and III (43%).

Aminoquinolines.—5-Nitro-, 6-nitro- and 8-nitroquinoline were reduced with iron and acetic acid as described by Linsker and Evans[9] for the synthesis of 6-aminoquinoline. The yields were: 5-amino- (IV) (71%), 6-amino- (V) (88%), 8-amino- (VI) (40.7%).

5-Nitro- (VII) and 8-Nitroquinaldine (VIII).—Quinaldine

(1) Parke, Davis and Company Fellow 1952–1953; E. I. du Pont Fellow 1953–1954.

(2) Gerdeissen, *Ber.*, **22**, 244 (1889).

(3) F. H. Case, THIS JOURNAL, **70**, 3994 (1948).

(4) K. N. Campbell and I. J. Schaffner, *ibid.*, **67**, 86 (1945).

(5) H. L. Yale and J. Bernstein, *ibid.*, **70**, 254 (1948).

(6) R. Adams, "Organic Reactions," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1949, Chap. 8.

(7) J. Capps and C. S. Hamilton, THIS JOURNAL, **60**, 2104 (1938).

(8) L. F. Fieser and E. B. Hershberg, *ibid.*, **62**, 1640 (1940).

(9) F. Linsker and R. L. Evans, *ibid.*, **68**, 874 (1946).

was nitrated as described by Doebner and v. Miller[10] to give VII (52%) and VIII (31%).

5-Aminoquinaldine (IX).—5-Nitroquinaldine was reduced with tin and hydrochloric acid according to the procedure of Doebner and v. Miller.[10] The yield of IX was 56%.

1-Methyl-4,7-phenanthroline (X).—To a mixture of 197 g. (0.728 mole) of ferric chloride hexahydrate, 62.7 g. (0.347 mole) of 6-aminoquinoline hydrochloride, 5 g. of anhydrous zinc chloride and 450 ml. of 95% ethanol, heated to 60°, was added dropwise 31.4 g. (0.382 mole) of methyl vinyl ketone (85% azeotrope) at such a rate that the temperature remained at 60–65°. After the addition was complete the mixture was heated under reflux for 2 hours and then allowed to stand overnight. The majority of the alcohol was removed by distillation, the residue dissolved in water, and made basic with 30% sodium hydroxide solution. After cooling, the solid was collected by suction filtration, and dried as much as possible on the filter. The product was extracted from the iron oxide residue with three 1-l. portions of boiling benzene. The benzene extracts were combined, dried over anhydrous sodium sulfate, and the benzene removed by distillation. The residue was distilled under reduced pressure and the fraction boiling at 194° (1.7 mm.) was collected. The yellow oil solidified and was recrystallized from benzene–petroleum ether to give 36.5 g. (54.2%) of white needles, m.p. 105–106°.

Anal. Calcd. for $C_{13}H_{10}N_2$: C, 80.38; H, 5.19; N, 14.43. Found: C, 80.42, 80.45; H, 5.40, 5.50; N, 14.28, 14.29.

4,7-Phenanthroline-1-carboxaldehyde (XI).—A solution of 8 g. (0.0412 mole) of 1-methyl-4,7-phenanthroline in 120 ml. of xylene was heated to 135° and 5.25 g. (0.0475 mole) of freshly prepared selenium dioxide was added over a period of 30 minutes. After the addition was complete, the mixture was heated under reflux for an additional 20 minutes, cooled and filtered from the precipitated selenium. The clear, red solution was then stirred for 3.5 hours with 60 ml. of a saturated solution of sodium bisulfite. The bisulfite addition product which formed was collected by filtration, washed with alcohol followed by ether, and dried. The white solid was dissolved in warm water, filtered from a small amount of selenium, and decomposed with solid sodium carbonate. The aldehyde which precipitated was dried and recrystallized from benzene to give 2.7 g. (31.5%) of white needles, m.p. 151–152°.

The above material was sublimed at 120° (0.1 mm.) to give an analytical sample, m.p. 151.75–152.25°.

Anal. Calcd. for $C_{13}H_8N_2O$: C, 74.99; H, 3.87; N, 13.46. Found: C, 75.20; H, 3.93; N, 13.24.

The thiosemicarbazone of the above aldehyde was prepared by heating an alcoholic solution of the aldehyde with the equivalent quantity of thiosemicarbazide dissolved in the minimum quantity of hot water. The thiosemicarbazone was insoluble in most organic solvents, but did dissolve in hot methylcellosolve and in dimethylformamide. For purposes of analysis the solid obtained from the reaction mixture was extracted three times with hot 50% ethanol and then dried 4 hours in a drying pistol at 76°. An analytical sample melted with decomposition at 230°.

Anal. Calcd. for $C_{14}H_{11}N_5S \cdot H_2O$: N, 23.40. Found: N, 23.43, 23.26.

4-Methyl-1,7-phenanthroline (XII).—This substance was prepared from 5-aminoquinoline and methyl vinyl ketone using the procedure described above for the preparation of X. The crude material was distilled under reduced pressure and the fraction boiling at 178–181° (3 mm.) was collected and recrystallized from benzene–petroleum ether. The substance crystallized as white needles and amounted to 45% of the theoretical amount of XII, m.p. 104–104.5°.

Anal. Calcd. for $C_{13}H_{10}N_2$: C, 80.38; H, 5.19; N, 14.43. Found: C, 80.57; H, 5.27; N, 14.47, 14.31.

1,7-Phenanthroline-4-carboxaldehyde (XIII).—The oxidation of XII was carried out in a manner identical with that used for the preparation of XI. After two recrystallizations from benzene the aldehyde, XIII, was obtained in 23.4% yield as white needles, m.p. 190–191°.

Anal. Calcd. for $C_{13}H_8N_2O$: C, 74.99; H, 3.87; N, 13.46. Found: C, 75.07; H, 4.03; N, 13.39.

The aldehyde formed a thiosemicarbazone which was insoluble in ether, ethanol, methylcellosolve and *n*-propyl alcohol; and was soluble in dimethylformamide. For purposes of analysis the solid from the original reaction mixture was washed three times with hot 50% ethanol and dried for 4 hours in a drying pistol at 76°. The melting point of an analytical sample was 252° dec.

Anal. Calcd. for $C_{14}H_{11}N_5S$: N, 24.90. Found: N, 24.85, 24.88.

8-Methyl-1,7-phenanthroline (XIV).—To a mixture of 65 g. (0.41 mole) of 5-aminoquinaldine, 152 g. (1.65 moles) of dry glycerol and 71 g. (0.308 mole) of arsenic pentoxide was added, with stirring, 68 ml. of concentrated sulfuric acid at such a rate that the temperature did not exceed 130°. The mixture was then cautiously heated to 130° and maintained at this temperature for 1 hour. The temperature was then gradually raised to 150° and the solution maintained at vigorous reflux for 6 hours, during which time the temperature gradually dropped to 135°. The dark brown solution was cooled and poured into 1 l. of water. The thoroughly stirred solution was made basic with 30% sodium hydroxide solution and allowed to stand until the oil which formed had congealed. The solution was then decanted from the oil and extracted with two 200-ml. portions of boiling benzene. These extracts were used to extract the oil residue along with another 200-ml. portion of boiling benzene. The benzene extracts were concentrated, and the residue fractionated under reduced pressure. The fraction boiling at 192–194° (13 mm.) was collected and redistilled through a short Vigreux column. Nearly all of the product distilled at 172–173° (4 mm.) and amounted to 20 g. (25%). The distillate gradually crystallized to a light yellow solid which could be recrystallized from petroleum ether (b.p. 30–60°) with some difficulty. Two recrystallizations gave long white needles which melted at 68–68.5°; lit.[2] m.p. 64–65°.

1,7-Phenanthroline-8-carboxaldehyde (XV).—This aldehyde was obtained by the oxidation of XIV in a manner identical with that used for the preparation of XI. The long, white needles obtained on recrystallization from benzene melted at 188–189° and represented a 22.9% yield of XV.

Anal. Calcd. for $C_{13}H_8N_2O$: C, 74.99; H, 3.87; N, 13.46. Found: C, 75.23; H, 3.59; N, 13.30, 13.48.

The aldehyde formed a white thiosemicarbazone which was soluble in dimethylformamide and in hot isopropyl alcohol. For purposes of analysis the solid from the original reaction mixture was washed three times with hot 50% ethanol and dried for 4 hours in a drying pistol at 76°. The melting point of an analytical sample was 240° dec.

Anal. Calcd. for $C_{14}H_{11}N_5S$: N, 24.90. Found: N, 24.61, 24.62.

4-Methyl-1,10-phenanthroline (XVI).—A mixture of 4 g. (0.0278 mole) of 8-aminoquinoline, 12.8 g. (0.055 mole) of arsenic pentoxide and 40 ml. of 85% phosphoric acid was stirred and the temperature raised to 100°. Methyl vinyl ketone, 3.44 g. (0.0416 mole, 85% azeotrope) was then added dropwise through the condenser at such a rate that the temperature remained at 99–101°. After the addition was complete the mixture was heated at 100° for 35 minutes, cooled and made alkaline with concentrated ammonia. The dark, tarry mixture was extracted with four 50-ml. portions of boiling benzene. The extracts were combined, dried over anhydrous sodium sulfate, treated with charcoal, and the solvent evaporated under reduced pressure to give a light brown oil which soon solidified. The solid was recrystallized twice from benzene to give 1.4 g. (26%) of 4-methyl-1,10-phenanthroline, m.p. 144–145°; lit. m.p.[3] 144–145°.

(10) O. Doebner and W. v. Miller, *Ber.*, **17**, 1701 (1884).

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