workers[1] the synthesis of 25-oxo-27-norcholesteryl acetate, a key intermediate for the synthesis of 25-hydroxy vitamin D_3,[2-4] was undertaken. We wish to report an efficient preparation of this intermediate (4) starting from pregnenolone (1). The main steps are the Wittig reaction of pregnenolone with the ketal phosphorane shown below, and subsequent hydrogenation of the $\Delta^{20(22)}$ double bond of the product. A slightly higher overall yield can be obtained if the 3-hydroxyl is protected as the tetrahydropyranyl ether during the Wittig reaction.

The stereochemistry of the Wittig product (2) was found to be exclusively *E* as expected.[1] The NMR spectrum showed the 21-methyl as a singlet at δ 1.64 which is characteristic of the *E* isomer (lit. δ 1.65)[2] whereas the chemical shift in the *Z* isomer falls in the range δ 1.67–1.70. Deketalization and acetylation of 2 gave the keto acetate 3 which was identical with an authentic sample.[5] It was selectively hydrogenated in dioxane in the presence of acetic acid with platinum oxide as catalyst. A 90% yield of the 20*R* epimer (4) was obtained.[6] The 20*S* epimer was detected by NMR spectroscopy in the mother liquor from recrystallization of the hydrogenation product. The signal for the 21-methyl in this epimer appeared as a doublet centered at δ0.84 while that for the 20*R* epimer appeared at δ 0.94. The epimers could be separated by GLC. Their identity was confirmed by comparison with authentic samples.[5] The overall yield of 4 from pregnenolone was 62%.

Experimental Section

Melting points (uncorrected) were determined on a Köfler apparatus and NMR and ir spectra on Varian (220 MHz) and Beckman IR 18 A-X spectrometers, respectively. A Varian 2100 Aerograph was used for GLC analysis.

$\Delta^{5,20(22)}$-27-norcholestadien-3β-ol-25-one 25-Ketal (2). [3-(2-Methyl-1,3-dioxalan-2-yl)propyl]triphenylphosphonium bromide[7] (5.2 g, 11 mmol) in 5.7 ml of a benzene solution of potassium *tert*-amylate[8] (2.1M) was refluxed under argon for 45 min, then 500 mg of pregnenolone dissolved in 8 ml of hot benzene was added to the dark red solution. The combined solution was refluxed for 3 h, cooled, and poured into water and the resulting mixture extracted with ether. The ether extract was washed successively with 5% hydrochloric acid, 10% sodium bicarbonate solution, and water and dried over $MgSO_4$. Removal of the solvent and chromatography of the residue (silica gel, ethyl acetate–petroleum ether, 4:1) gave 470 mg (69%) of product: mp 139–140 °C; NMR ($CDCl_3$) δ 0.54 (s, 18-Me), 1.00 (s, 19-Me), 1.32 (s, 26-Me), 1.64 (s, 21-Me), 3.52 (m, 1 H, 3α-H), 3.97 (d, J = 1 Hz, 4 H, OCH_2CH_2O), 5.16 (t, J = 6.7 Hz, 1 H, 22-H), 5.33 (m, 1 H, 6-H). Cleavage of the ketal, by keeping a solution of the product in ethanol–water with toluenesulfonic acid for 12 h, followed by acetylation with acetic anhydride–pyridine overnight afforded $\Delta^{5,20(22)}$-27-norcholestadien-3β-ol-25-one acetate (3) in 98% yield: mp 115–118 °C (lit. 120–121 °C[2]); ir (KBr) 1740, 1720 cm^{-1}; NMR ($CDCl_3$) δ 0.53 (s, 18-Me), 1.02 (s, 19-Me), 1.64 (s, 21-Me), 2.03 (s, acetate), 2.14 (s, 26-Me), 4.59 (m, 1 H, 3α-H), 5.10 (t, J = 6.7 Hz, 22-H), 5.35 (m, 1 H, 6-H). The ir and NMR spectra were identical with those of an authentic sample.[5]

25-Oxo-27-norcholesteryl Acetate (4). The acetate 3 (300 mg) dissolved in 15 ml of dioxane–acetic acid (50:1) was hydrogenated in the presence of 30 mg of prereduced platinum oxide at room temperature and atmospheric pressure. After 4 h more platinum oxide (30 mg) was added. The reaction was complete after 7 h. The catalyst was separated by filtration and the solvent removed from the filtrate to give the crystalline product which was recrystallized from ethanol (yield 276 mg, 90%): mp 140–142 °C (lit. 139–140 °C);[2] ir (KBr) 1738, 1720 cm^{-1}; NMR ($CDCl_3$) δ 0.68 (s, 18-Me), 0.95 (d, J = 6 Hz, 21-Me), 1.02 (s, 19-Me), 2.02 (s, acetate), 2.13 (s, 26-Me), 4.61 (m, 3α-H), 5.39 (m. 6-H). The ir and NMR spectra were identical with those of an authentic sample.[5] The retention times on GLC (3% OV-17 on Gaschrom Q at 300 °C) were the same but differed from that of the 20*S* epimer.

Acknowledgment. This work was supported by Grant GM21350 from the National Institutes of Health.

Registry No.—1, 145-13-1; 2, 60065-10-3; 3, 53139-44-9; 20*R*-4, 7548-94-9; 20*S*-4, 55122-55-9; 3-(2-methyl-1,3-dioxolan-2-yl)propylidenetriphenylphosphorane, 3054-93-1.

References and Notes

(1) J. P. Schmit, M. Piraux, and J. F. Pilette, *J. Org. Chem.*, **40**, 1586 (1975).
(2) T. A. Narwid, K. E. Cooney, and M. R. Uskoković, *Helv. Chim. Acta*, **57**, 771 (1974).
(3) A. Rofman and Y. Mazur, *J. Chem. Soc., Chem. Commun.*, 15 (1974).
(4) J. Wicha and K. Bal, *J. Chem. Soc., Chem. Commun.*, 968 (1975).
(5) Kindly supplied by Dr. Milan R. Uskoković, Hoffmann-La Roche, Inc., Nutley, N.J.
(6) The high stereoselectivity in the hydrogenation was similar to that found by Piraux and co-workers.[1] However, Uskoković and co-workers obtained poor stereoselectivity in similar hydrogenations.[2] See also (a) E. D. Bergmann, M. Rabinovitz, and Z. H. Levinson, *J. Am. Chem. Soc.*, **81**, 1239 (1959); (b) R. Ikan, A. Markus, and E. D. Bergmann, *J. Org. Chem.*, **36**, 3945 (1971); (c) A. M. Porto and E. G. Gros, *J. Labelled Compd.*, **6**, 369 (1970).
(7) L. Crombie, P. Hemesley, and G. Pattenden, *J. Chem. Soc. C*, 1016 (1969).
(8) C. A. Brown, *J. Org. Chem.*, **39**, 3913 (1974).

Approaches to the Synthesis of 1,2-Cyclooctatrienedione

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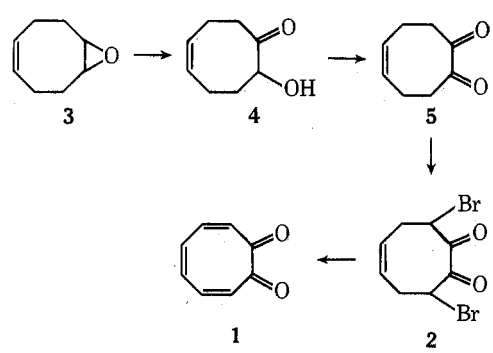
The recent interest[1-6] in the synthesis of the elusive 1,2-cyclooctatrienedione (1) and its isomers prompts this report of our successful synthesis of the quinoxaline derivative of 1 together with the chemistry of precursors to this potentially aromatic compound.

As a likely precursor to 1 a four-step synthesis of 3,8-dibromo-5-cyclooctene-1,2-dione (2) was undertaken. Epoxidation of 1,5-cyclooctadiene afforded the known[7] epoxy olefin 3 which was converted to keto alcohol 4 upon treatment with boron trifluoride in dimethyl sulfoxide. Cupric acetate oxidation of 4 gave 5-cyclooctene-1,2-dione (5) which has been prepared previously by another route.[1]

Cupric bromide dibromination of 5 resulted in the formation of 2 as a white, crystalline material. The infrared carbonyl absorptions of 2 at 1740 and 1727 cm^{-1} established[8] that the molecule exists in the trans diequatorial configuration. Confirmation of this assignment was obtained from the ^1H NMR spectrum ($CDCl_3$) which exhibits a single methine hydrogen absorption at δ 5.15 as an ABX doublet of doublets.[9]

Scheme I

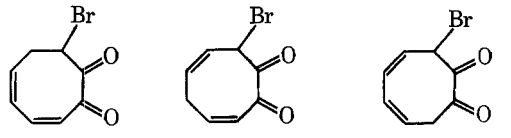


3 4 5 1 2

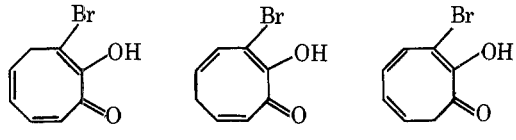
To date all efforts to convert 2 to 1 by direct dehydrobromination have proven unsuccessful. Numerous procedures have been attempted which result in either recovered starting material or a multitude of intractable products.

Treatment of 2 with warm hexamethylphosphoric triamide,[10] however, resulted in the formation of the monodehydrobrominated product 3-bromo-5,7-cyclooctadiene-

1,2-dione (6). Compound 6 exists predominantly as the enol 7 as evidenced by the infrared intramolecular hydrogen bonded hydroxy absorption at 3365 cm^{-1}. Corroboration of the structure 7 was derived from its ^1H NMR spectrum (Me_2SO-d_6) which showed, in addition to four olefin hydrogen absorptions, a doublet (J = 8.0 Hz) at δ 3.16 indicative of a pair of doubly allylic hydrogens coupled to a single olefinic hydrogen. The isomeric bromocyclooctadienediones 8 and 9 have been recently reported[11] and have been shown to exist as their enol tautomers 10 and 11, respectively. Attempts to convert 6 to 1 have failed to produce an isolable product.



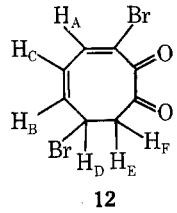
6 8 9



7 10 11

The reaction of 7 with *N*-bromosuccinimide efficiently produced 3,7-dibromo-3,5-cyclooctadiene-1,2-dione (12). The composition of 12 was established by elemental analysis and mass spectral data. The infrared carbonyl absorptions at 1677 and 1724 cm^{-1} suggested the presence of α,β-unsaturated ketone and saturated ketone moieties.

The ^1H NMR spectrum ($CDCl_3$) of 12 exhibits a doublet at δ 7.68 (H_A, $J_{H_A-H_C}$ = 6.0 Hz), a doublet of doublets at δ 6.55 (H_B, $J_{H_B-H_D}$ = 8.5 Hz), a doublet of doublets at δ 5.95 (H_C, $J_{H_C-H_B}$ = 12.0 Hz), a heptet at δ 5.23 (H_D, $J_{H_D-H_E}$ = 5.5 Hz), a doublet of doublets at δ 3.84 (H_E, $J_{H_E-H_F}$ = 13.5 Hz), and a doublet of doublets converged to a triplet at δ 3.22 (H_F, $J_{H_F-H_D}$ = 13.5 Hz).



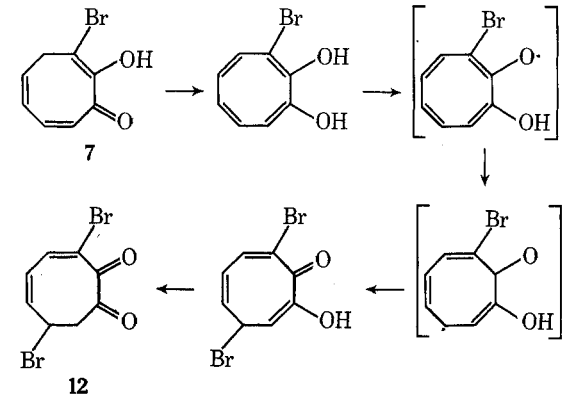
12

The coupling between H_A and H_C is lower than the expected 9–13 Hz.[12] The observed value of 6 Hz, however, is consistent with a conformation of 12 in which the angle between H_A and H_C is approximately 45 °. A molecular model of such a conformation shows that the angles between H_D and the methylene hydrogens H_E and H_F are approximately 80 and 170°, respectively. The H_D–H_E and H_D–H_F coupling constants of 5.5 and 13.5 Hz, respectively, are consistent with this conformation in accordance with the Karplus relationship.[13]

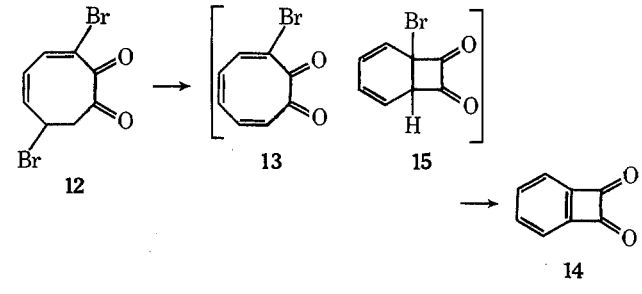
The formation of 12 from 7 may be envisioned as proceeding by a one-electron oxidation of the bis enol of 7 followed by rearrangement of the resultant radical and bromination as depicted in Scheme II.

Dehydrobromination of 12 was expected to lead to the formation of 3-bromocyclooctatriene-1,2-dione (13). Treatment of 12 with an excess of triethylamine in chloroform produced an immediate reaction. The infrared spectrum of the reaction mixture showed carbonyl absorption identical with that of benzocyclobutadienequinone (14) and lacked the carbonyl absorption of 12. Use of a deficient quantity of base resulted in a mixture of 12 and 14. Infrared and ^1H NMR spectra of this mixture failed to demonstrate the presence of additional identifiable components. The conversion of 12 to

Scheme II



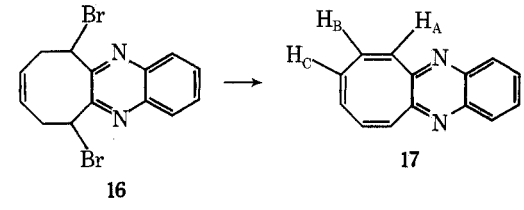
Scheme III



14, however, clearly implicates the intermediacy of 13 and its bicyclic tautomer 15.

The failure to isolate a 1,2-cyclooctatrienedione by dehydrobromination of an appropriate precursor indicated that this system may be quite labile and suggested the selection of a carbonyl substituted derivative of 1 as a synthetic target. Toward this end quinoxaline 16 was prepared by the action of *o*-phenylenediamine on 2. Dehydrobromination of 16 with 1,5-diazabicyclo[4.3.0]nonene-5 afforded 17, the quinoxaline derivative of 1.

Scheme IV



16 17

The ^1H NMR spectrum ($CDCl_3$) of 17 shows an aromatic AA'BB' pattern centered at δ 7.92 which corresponds to the benzenoid hydrogens. The α-imino hydrogen, H_A, appears at δ 6.88 as a doublet of an AB quartet (J = 11.5 Hz). The other half of the AB quartet at δ 6.43 arises from H_B and appears as a doublet of doublets (J = 1.5 Hz) due to coupling to H_C, the latter appearing as a doublet at δ 6.15. The small coupling constant between H_B and H_C indicates a nonplanar structure[12] for the eight-membered ring of 17.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 237B spectrophotometer. The NMR spectra were obtained using a Varian T-60 spectrometer with chemical shifts reported as δ values measured from an internal standard of tetramethylsilane. The uv spectra were recorded on a Unicam Model SP-800 spectrophotometer using 1-cm quartz cells. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6 mass spectrometer. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich., or Galbraith Laboratories, Inc., Knoxville, Tenn. Molecular models were constructed from Framework Molecular Models by Prentice-Hall, Englewood Cliffs, N.J.

5-Cyclooctene-1,2-dione (5). A three-neck, 1-l., round-bottom

flask equipped with a mechanical stirrer and a reflux condenser was charged with 52.7 g (0.375 mol) of 2-hydroxy-5-cyclooctenone, 168 g (0.84 mol) of cupric acetate monohydrate, 35 ml of methanol, and 420 ml of 50% aqueous acetic acid. The mixture was heated to reflux with stirring for 2 h. After cooling the solid material was filtered and washed with water and ether. The combined filtrate and washes were poured into 500 ml of saturated sodium chloride solution. The aqueous solution was then extracted with six 100-ml portions of ether. The combined extracts were washed with saturated sodium bicarbonate solution until neutral and then with saturated sodium chloride solution. After drying over anhydrous magnesium sulfate the ether was removed. The resulting yellow oil was distilled under reduced pressure yielding 26.4 g (51%) of 5-cyclooctene-1,2-dione: bp 56–57 °C (0.5 mm); mp 35–36.5 °C; ir ($CHCl_3$) 3050 (C–H), 1723, 1708, and 1692 cm^{-1} (C=O); NMR ($CDCl_3$) δ 5.88 (m, 2, olefinic) and 2.53 (m, 8, allylic and α-carbonyl); uv max (cyclohexane) 230 nm (ϵ 99), 281 (35.6), 288 (33.3), and 345 (17.2); mass spectrum (70 eV) *m/e* 138 (parent), 110 (− CO), and 82 (− 2CO).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.62; H, 7.30. Found: C, 69.40; H, 7.16.

***trans*-3,8-Dibromo-5-cyclooctene-1,2-dione (2).** A three-neck, 500-ml, round-bottom flask equipped with a magnetic stirrer, a gas inlet tube, and a reflux condenser was charged with 6.9 g (0.05 mol) of 5-cyclooctene-1,2-dione, 44.6 g (0.2 mol) of cupric bromide, and 200 ml of a 1:1 ethyl acetate–chloroform solution. The mixture was stirred under nitrogen for 15 min at room temperature and then at 75 °C for 12 h. Upon cooling the cuprous bromide was filtered and washed with chloroform. The combined organic phases were washed with water until neutral followed by a wash with saturated sodium chloride solution. After drying over anhydrous magnesium sulfate, the solvents were removed giving a brown solid material. Trituration with cyclohexane removed the brown material affording white crystals. Recrystallization of the crude product from methylene chloride–cyclohexane provided 5.0 g (34%) of dibromide **2**, mp 136–139 °C. An analytical sample was obtained by sublimation: mp 138–141 °C; ir ($CHCl_3$) 3000, 2925 (C–H), and 1740, 1727 cm^{-1} (C=O); NMR ($CDCl_3$) δ 6.07 (m, 2, olefinic), 5.15 (ABX quartet, 2, CHBr), and 2.90 (m, 4, allylic); uv max (cyclohexane) 288 nm (ϵ 244), 280 (302), and 224 (742); mass spectrum (70 eV) *m/e* 298, 296, 294 (parent).

Anal. Calcd for $C_8H_8Br_2O_2$: C, 32.46; H, 2.73. Found: C, 32.71; H, 2.82.

3-Bromo-2-hydroxy-2,5,7-cyclooctatrienone (7). A solution of 3.0 g (0.01 mol) of 3,8-dibromo-5-cyclooctene-1,2-dione in 70 ml of dry hexamethylphosphoric triamide was maintained at 80 °C with stirring for 18 h. The yellow-red solution was poured into 500 ml of saturated sodium chloride solution and extracted with four 100-ml portions of cyclohexane. The extracts were washed with two 150-ml portions of water and then saturated sodium chloride solution and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure provided 0.8 g of a red-brown semisolid which was chromatographed on silica acid eluting with carbon tetrachloride–benzene (10:2). Fractions 6–18 (20 ml) afforded 0.325 g (15%) of ketone **7**. Sublimation of the crude product afforded **7** as white crystals: mp 101–103 °C; ir ($CHCl_3$) 3365 (O–H), 1662 (C=O), 1622 and 1600 cm^{-1} (C=C); NMR ($CDCl_3$) δ 7.86 (s, 1, hydroxyl), 6.64 (m, 3, H_6, H_8), 6.73 (q, J = 8 Hz, 1, H_5), and 3.16 (br m, 2, allylic); uv max (cyclohexane) 297 nm (ϵ 5 × 10^3), 254 (1.27 × 10^4), 246 (1.23 × 10^4), 239 (1.04 × 10^4), and 198 (6.55 × 10^3); mass spectrum (70 eV) *m/e* 216, 214 (parent).

Anal. Calcd for $C_8H_7BrO_2$: C, 44.69; H, 3.28. Found: C, 44.65; H, 3.27.

3,7-Dibromo-3,5-cyclooctadiene-1,2-dione (12). A solution of 108.7 mg (0.5 mmol) of 3-bromo-2-hydroxy-2,5,7-cyclooctatrienone and a catalytic amount of benzoyl peroxide in 15 ml of carbon tetrachloride and 89.0 mg (0.5 mmol) of *N*-bromosuccinimide was heated to reflux with simultaneous irradiation with a sun lamp for 30 min. The succinimide was filtered upon cooling and the solvent removed under reduced pressure. The residue was purified by preparative thin layer chromatography on silicic acid eluting with benzene–methylene chloride (10:12). There was obtained 125 mg (85%) of dione **12** as a yellow, crystalline material. An analytical sample was obtained by sublimation: mp 106–109 °C; ir ($CHCl_3$) 1724, 1677 (C=O), and 1575 cm^{-1} (C=C); NMR ($CDCl_3$) δ 7.68 (d, 1, olefinic, H_A), 6.55 (d of d, 1, olefinic, H_B), 5.95 (d of d, 1, olefinic, H_C), 5.23 (heptet, 1, bromomethine, H_D), 3.84 (d of d, 1, α-carbonyl, H_E), and 3.22 (t, 1, α-carbonyl, H_F); uv max (cyclohexane) 299 nm (ϵ 7.5 × 10^3), 235 (3.83 × 10^3), and 212 (6.47 × 10^3); mass spectrum (70 eV) *m/e* 296, 294, 292 (parent).

Anal. Calcd for $C_8H_6Br_2O_2$: C, 32.65; H, 2.04. Found: C, 32.68; H, 2.11.

Reaction of 3,7-Dibromo-3,5-cyclooctadiene-1,2-dione (12) and Triethylamine (14). To a solution of 100 mg (0.47 mmol) of 3,7-dibromo-3,5-cyclooctadiene-1,2-dione in 0.4 ml of deuterated chloroform was added one drop of triethylamine. The solution immediately turned light brown. The NMR spectrum of the reaction mixture showed absorptions corresponding to the starting material and benzocyclobutadienedione. The ir spectrum of the reaction mixture exhibited the carbonyl absorptions characteristic of **14**. Thin layer chromatographic analysis of the reaction mixture on silicic acid eluting with chloroform demonstrated the presence of **14** as the only identifiable product.

2,7-Dibromo-10,11-benzo-9,12-diazabicyclo[6.4.0]-4,8,10,12-dodecatetraene (16). To a solution of 3.4 g (1.5 mmol) of 3,8-dibromo-5-cyclooctene-1,2-dione in 140 ml of glacial acetic acid was added a solution of 1.24 g (1.5 mmol) of freshly distilled *o*-phenylenediamine in 40 ml of glacial acetic acid. The resulting solution was stirred at room temperature for 24 h. The solution was poured into 500 ml of water and extracted with four 100-ml portions of ether. The extracts were washed with water, saturated sodium bicarbonate solution, water, and saturated sodium chloride solution and then dried over anhydrous sodium sulfate. Removal of the solvent gave 3.9 g (72%) of quinoxaline **16** as a white powder, mp 177–182 °C. An analytical sample was prepared by sublimation: mp 180–182 °C; ir ($CHCl_3$) 2975 cm^{-1} (C–H); NMR ($CDCl_3$) δ 8.00 (AA'BB' pattern, 4, aromatic), 5.93 (t, J = 9 Hz, 2, CHBr), 5.54 (t, J = 4 Hz, 2, olefinic), and 3.30 (m, 4, allylic); mass spectrum (70 eV) *m/e* 370, 368, 366 (parent).

Anal. Calcd for $C_{14}H_{12}Br_2N_2$: C, 45.69; H, 3.29. Found: C, 45.72; H, 3.28.

10,11-Benzo-9,12-diazabicyclo[6.4.0]-2,4,6,8,10,12-dodecahexene (17). To a solution of 3.68 g (10 mmol) of quinoxaline **16** in 85 ml of dimethyl sulfoxide was added a solution of 2.5 g (20 mmol) of 1,5-diazabicyclo[4.3.0]nona-5-ene in 25 ml of dimethyl sulfoxide and the resulting solution was stirred at room temperature for 18 h. The reaction mixture was poured into 500 ml of water and extracted with five 100-ml portions of methylene chloride. The extracts were washed well with water and saturated sodium chloride solution and then dried over anhydrous sodium sulfate. Removal of the solvent gave 1.6 g of a red powder which was chromatographed on neutral alumina eluting with benzene. The first three 20-ml fractions which were collected consisted of a mixture of starting material and product. Subsequent fractions upon removal of the solvent provided 1.0 g (48.5%) of quinoxaline **17** as a very light yellow powder. An analytical sample was prepared by recrystallization from pentane: mp 143–145 °C; NMR ($CDCl_3$) δ 7.94 (AA'BB' pattern, 4, aromatic), 6.88 (d of AB quartet, J = 11.5 Hz, 2, H_A), 6.43 (coupled d of AB quartet, J = 1.5 Hz, 2, H_B), and 6.15 (d, 2, H_C); uv max (cyclohexane) 354 nm (ϵ 3.09 × 10^4), 334 (5.15 × 10^3), 284 (4.12 × 10^3), 245 (227 × 10^4), and 205 (2.78 × 10^4); mass spectrum (70 eV) *m/e* 206 (parent).

Anal. Calcd for $C_{14}H_{10}N_2$: C, 81.62; H, 4.89. Found: C, 81.54; H, 4.84.

Acknowledgment. We gratefully acknowledge support of this investigation by the National Science Foundation (Grant GP-17015).

Registry No.—**1**, 20665-78-5; **2**, 60183-99-5; **4**, 57858-30-7; **5**, 35353-89-0; **7**, 60184-00-1; **12**, 60184-01-2; **14**, 6383-11-5; **16**, 60184-02-3; **17**, 262-86-2; *o*-phenylenediamine, 95-54-5.

References and Notes

(1) P. Yates, E. G. Lewars, and P. H. McCabe, *Can. J. Chem.*, **50**, 1548 (1972).
(2) L. A. Carpino and P. H. Gund, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, No. 023.
(3) P. A. Chaloner, A. B. Holmes, M. A. McKervey, and R. A. Raphael, *Tetrahedron Lett.*, 265 (1975).
(4) M. Oda, Y. Kayama, H. Miyazaki, and Y. Kitahara, *Angew. Chem.*, **87**, 414 (1975).
(5) M. Oda, H. Miyazaki, Y. Kayama, and Y. Kitahara, *Chem. Lett.*, 627 (1975).
(6) J. Tsunetsugu, M. Sato, and S. Ebine, *J. Chem. Soc., Chem. Commun.*, 363 (1973).
(7) J. K. Crandall, D. B. Banks, R. A. Colyer, R. J. Watkins, and J. P. Arrington, *J. Org. Chem.*, **33**, 423 (1968).
(8) N. J. Leonard and G. C. Robinson, *J. Am. Chem. Soc.*, **75**, 2143 (1953).
(9) A. Nickon, M. A. Castle, C. E. Berkoff, and R. O. Williams, *J. Am. Chem. Soc.*, **85**, 2185 (1963).
(10) R. Hanna, *Tetrahedron Lett.*, 2105 (1968).
(11) (a) Y. Kitahara, M. Oda, and S. Miyakoshi, *Tetrahedron Lett.*, 4141 (1975); (b) Y. Kitahara, M. Oda, S. Miyakoshi, and S. Nakanishi, *ibid.*, 4145 (1975).
(12) R. M. Silverstein and G. C. Bassler, "Spectroscopic Identification of Organic Compounds", Wiley, New York, N.Y., 1968.
(13) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).