Notes

A Novel Cycloaddition Reaction for Obtaining 1*H*-Indoles from 3-(α,β-Unsaturated alkenyl)phenols

Masato Satomura*

Fujinomiya Research Laboratories, Fuji Photo Film Co., Ltd., Fujinomiya, Shizuoka, 418 Japan

Received September 14, 1992 (Revised Manuscript Received March 8, 1993)

Fused heteroaromatic systems, such as indoles and tetrahydrocarbazoles, are among the most sought after targets of organic synthesis.[1,2] Fused-ring heteroaromatics with functional groups at specific positions are considered especially desirable.

The Fischer indole and Borsche processes are very useful for obtaining 5-methoxy-1*H*-indole derivatives and 6-methoxy-3-substituted-2,3,4,9-tetrahydro-1*H*-carbazoles starting from (*p*-methoxyphenyl)hydrazine and the corresponding ketones.[3] However, these methods are not adequate for preparing 1*H*-indol-5-ols or 2,3,4,9-tetrahydro-1*H*-carbazol-6-ols directly.

On the other hand, using the Nenitzescu process, a 1*H*-indol-5-ol ring can be conveniently generated from a quinone and a β-alkoxycarbonyl enamine. The substituent at the 3-position of the 1*H*-indol-5-ols thus formed is restricted to an electron attractive group, such as the acyl or methoxycarbonyl group.[4]

In the process described herein, 1*H*-indol-5-ols are prepared directly by a diazo coupling reaction of selected 3-(α,β-unsaturated alkenyl)phenols, as shown in Scheme I.[1] The process described herein is especially suited to the preparation of 3-alkyl(or aryl)-substituted-1*H*-indol-5-ols and 2,3,4,9-tetrahydro-1*H*-carbazol-6-ols, especially 2-alkyl(or aryl)-substituted-2,3,4,9-tetrahydro-1*H*-carbazol-6-ols.

In this study, five types of phenols were investigated. Depending upon their substituents, the phenols were grouped as follows: type A, α,β-unsaturated group with two hydrogen atoms at the β-position (α-substituted ethenyl group); type B, α,β-unsaturated group with one hydrogen atom at the β-position (1-cycloalken-1-yl group); type C, α,β-unsaturated group with no hydrogen atoms at the β-position (2-substituted-1-cycloalken-1-yl group); type D, aryl group with one hydrogen atom at the ortho position (phenyl group); and type E, cycloalkyl group.

In the general procedure, an arenediazonium salt **1** was added to a solution of 1 equiv of 3-substituted-phenol **2** (type A) or **3** (type B) at −5 °C under alkaline conditions. The reaction mixture, containing a plausible intermediate **7**, was acidified with dilute acid at room temperature to obtain ring-closed derivatives **8** or **9** directly.[5] The phenylamino group is quantitatively removed by reduction with Raney nickel.

Upon diazo coupling, phenols **4** (type C), **5** (type D), and **6** (type E) gave conventional azo compounds.[6a]

Phenols grouped as type A include 3-(1-methylethenyl)-phenol (**2a**) and 3-(1-phenylethenyl)phenol (**2b**). Phenols grouped as type B include 3-(1-cyclohexen-1-yl)phenol (**3a**), 3-(4-methyl-1-cyclohexen-1-yl)phenol (**3c**), 3-(4-*tert*-butyl-1-cyclohexen-1-yl)phenol (**3d**), and 3-(4-phenyl-1-cyclohexen-1-yl)phenol (**3e**). Phenols grouped as type C, type D, and type E include 3-(2,6-dimethyl-1-cyclohexen-1-yl)phenol (**4**), 3-biphenylol (**5**), and 3-cyclohexylphenol (**6**), respectively.

Thus, 3-methyl-1*H*-indol-5-ol (**10**), 3-phenyl-1*H*-indol-5-ol (**11**), and 2,3,4,9-tetrahydro-1*H*-carbazol-6-ol (**12**) were readily prepared.[7,8] The yields of 3-substituted-1*H*-indol-5-ols (**8a–f**) obtained from various arenediazonium salts by using this method were good to excellent. In principle, a wide variety of substituents can be introduced at the 3-position of the 1*H*-indol-5-ol nucleus or the 2-position of the 2,3,4,9-tetrahydro-1*H*-carbazol-6-ol nucleus by changing the methyl group of **2a** or **3c** to another group.

Reaction Intermediate

Though a probable intermediate, 3-(1-alken-1-yl)-4-(phenylazo)phenol (**7**), was not isolated, this intermediate was nevertheless suggested by ^{1}H NMR and direct inlet MS spectra of alkaline reaction mixtures of arenediazonium salt with 3-(1-alken-1-yl)phenol.

^{1}H NMR and direct inlet MS spectra of the reaction mixture of the benzene-d_5-diazonium salt with 3-(1-cyclohexen-1-yl)phenol in alkaline media were inspected for signs of the intermediate, 3-substituted-4-(phenyl-d_5-azo)phenol. The ^{1}H NMR spectra did not exhibit a proton signal resulting from the 4-position, suggesting that the

(1) Compounds **8a** and **10** are disclosed in our patent. Satomura, M. U.S. Patent 4914213, 1990.

(2) For recent reports on indole synthesis, see: Krolski, M. E.; Renald, A. F.; Rudisill, D. E.; Stille, J. K. *J. Org. Chem.* **1988**, *53*, 1170. Benincori, T.; Sannicolo, F. *J. Org. Chem.* **1988**, *53*, 1309. Jones, W. D.; Kosar, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 5640. Fujiwara, F.; Fukutani, Y.; Sano, H.; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1983**, *105*, 7177. Hegedus, L. S. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1113. For reviews, see: (a) Houlihan, W. J. *Indoles, Part Two*; Wiley-Interscience: New York, 1972. (b) Houlihan, W. J. 4Indoles, *Part Three*; Wiley-Interscience: New York, 1979. (c) Bird, C. W.; Cheeseman, G. W. H. *Comprehensive Heterocyclic Chemistry*; Katritzky, A., Rees, C. W., Eds.; Pergamon Press: Oxford, 1984; *Vol. 4, Chapter 3.* (d) Livingstone, R. *Rodd' Chemistry of Carbon Compounds*; Elsevier: New York, 1984, Vol. 4, Chapter 5.

(3) Robinson, B. *The Fischer Indole Synthesis*; Wiley-Interscience: New York, 1982.

(4) Allen, G. R. *Org. React.* **1973**, *20* (Chapter 3).

(5) For detailed discussions of the chemistry of diazonium salts and diazo groups see: (a) Patai, S. *The Chemistry of Diazonium and Diazo Groups*; J. Wiley & Sons: New York, 1978. (b) Saunders, K. H. *Aromatic Diazocompounds*, 3rd ed.; Edward Arnold: London, 1985. (Widman–Stoermer cinnoline formation reaction is reviewed at 8.12. A diazotized (*o*-aminoaryl)ethylene cyclizes upon standing to give cinnoline by a spontaneous coupling reaction of an alkenyl group with a diazonium group.)

(6) UV spectra of 4-(phenylazo)phenols: (a) The UV spectra of some 3-alkyl-4-(phenylazo)phenol is summarized in: Gulati, A. S.; Subba Rao, B. C. *Ind. J. Chem.* **1967**, *5*, 55. (b) The influence of change from alcoholic to aqueous alkaline solution on the spectra of 4-(phenylazo)phenol is discussed by W. R. Brode. Brode, W. R. *The Rodger Adams Symposium*; John-Wiley & Sons: New York, 1955.

(7) For the preparation of 3-methyl-1*H*-indol-5-ol, see (a) Teuber, H. J.; Steiger, G. *Ber.* **1956**, *27*, 489. (b) Acheson, R. M.; Hands, A. R. *J. Chem. Soc.* **1961**, 746.

(8) For the preparation of tetrahydro-1*H*-carbazol-6-ol, see: (a) Berrier, C.; Jacquesy, J. C.; Jouanetaud, M. P.; Renoux, A. *Tetrahedron. Lett.* **1986**, *27*, 4565. (b) Milne, A. H.; Tomlinson, M. L. *J. Chem. Soc.* **1952**, 2789.

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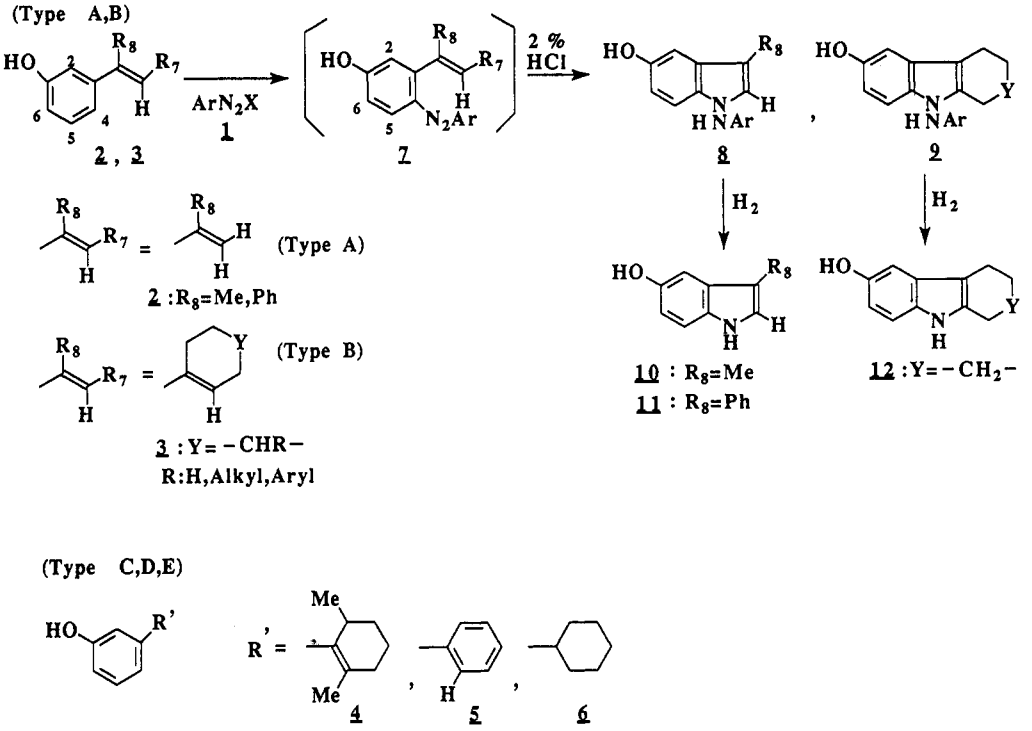
Scheme I. Diazo Coupling Reaction of 3-Alkenylphenol



diazo coupling occurs at the 4-position, rather than at the cyclohexene moiety. The MS spectra by direct inlet method suggested the presence of species corresponding to 3-(1-cyclohexen-1-yl)-4-(phenyl-d_5-azo)phenol, (m/e = 283). Finally, the HPLC spectrum showed the yield of the product or azo compound to be very high. These results strongly suggest that the reaction intermediate, the precursor of 9-(phenyl-d_5-amino)-2,3,4,9-tetrahydro-1*H*-carbazol-6-ol (**9b**), is 3-(1-cyclohexen-1-yl)-4-(phenyl-d_5-azo)phenol.

Conclusions

As shown above, *the reaction of a phenol which has at least one hydrogen atom at the β-position of the α,β-unsaturated double bond at the meta-position with an arenediazonium salt* provides a useful route for obtaining various kinds of 1*H*-indol-5-ols.

The 1*H*-indole products bearing the hydroxyl moiety at the 5-position seem to hold promise as building blocks for the elaboration of aromatics and fused heterocycles. The unusually mild reaction conditions should permit the construction of this ring system even in the presence of substituent groups sensitive to elevated temperature, strong acids, strong bases, or oxidation. Because of the ease of this procedure and the good yields, this method has some advantages over currently available procedures for the synthesis of 1*H*-indol-5-ols.

Research is currently in progress to clarify the scope and limitations of this new intramolecular cycloaddition reaction.

Experimental Section

Melting points and boiling points are uncorrected. ^{1}H NMR spectra were recorded on a Varian Gemini-3000 300-MHz spectrometer. The ^{1}H NMR spectra were determined, unless otherwise indicated, as solutions in $CDCl_3$. The internal standard was TMS. UV spectra were recorded on a Shimadzu MPS-2000 UV/vis spectrophotometer, as solutions in EtOH. HRMS spectra were recorded on a Hitachi M-80B double focusing gas chromatograph mass spectrometer. MS spectra by direct inlet method were recorded on a Shimadzu GCMS-QP1000EX. HPLC spectra were recorded on a Shimadzu LC-6A liquid chromatograph with an ODSH column.

3-(1-Methylethenyl)phenol (**3a**) was obtained from Mitsui Petrochemical Ind., Ltd. Other 3-substituted phenols were prepared starting from (1) cyclohexanones, (2) 1-(3-hydroxyphenyl)ethanone, or (3) 1-bromo-3-methoxybenzene.[11,12] Arylamine, 1-bromo-3-methoxybenzene, cyclohexanones, 1-(3-hydroxyphenyl)ethanone, and 3-biphenylol (**5**) were obtained from commercial suppliers and used without further purification.

General Procedures. Diazo Coupling Reaction. A 1*H*-Indol-5-ol Synthesis. To a flask containing 10 mmol of 3-substituted-phenol, 30 mL of CH_3OH, 50 mL of acetone, and 5 mL of Et_3N was added an arenediazonium salt over a period of about 10 min with stirring at −5 °C. The diazonium salt was prepared from 10 mmol of substituted aniline, 2.1 mL of HCl, 6 mL of H_2O, and 10 mmol of $NaNO_2$ in 6 mL of water by conventional methods.[5,6] The reaction mixture was stirred for 10 min after the addition was complete. After the cooling bath was removed, the reaction mixture was stirred for 30 min and the mixture was poured into a stirred solution of 300 mL of 2% aqueous HCl at rt. The organic products were separated and extracted with EtOAc or methyl ethyl ketone (150 mL × 2) from the mixture. The combined organic fractions were washed successively with a saturated aqueous NH_4Cl and H_2O and then dried over Na_2SO_4. After the solvent was evaporated, the 1*H*-indol-5-ol or 3-substituted-4-(phenylazo)phenol was purified by column chromatography on silica gel (Merck, silica gel 60). An EtOAc/hexane mixture (2:8) or acetonitrile/chloroform mixture (1:9) was used as the eluent. Then, it was recrystallized from benzene, hexane, or a benzene–hexane mixture (1:1) with small portions of EtOAc.

Reduction with Raney Nickel. An autoclave containing 0.5 g of **8g** (or **8a** or **9a**), 0.2 g of Raney nickel, and 80 mL of EtOH was charged with H_2 gas to 22 kg/cm^2 and was stirred for 3 h at 70 °C. In the case of **9a**, H_2 gas was charged to 60 kg/cm^2. Then,

(9) HMBC spectra pulse sequence: Himmelsbach, D. S.; van Halbeek, H.; Arrendale, R. F.; Severson, R. F. *Magnetic Resonance in Chemistry* **1990**, *28*, 682.

(10) For the preparation of 3-(1-phenylethenyl)phenol, see: Bruce, J. M.; Chaudry, A.; Dewes, K. *J. Chem. Soc. Perkin Trans. 1* **1974**, 288.

11, 10, and 12 were separated from aniline by column chromatography, respectively.

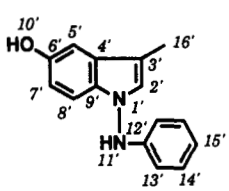
3-(1-Cyclohexen-1-yl)-4-(phenyl-d_5-azo)phenol. Preparation of reaction mixture; A diazonium salt was preapred from benzene-d_5-amine (0.49 g), D_2O (9 mL), aqueous DCl (37%) (1 mL), and $NaNO_2$ (0.35 g). The diazonium salt was slowly added to a solution of 3-(1-cyclohexen-1-yl)phenol (0.88 g), deuterated solvent (20 mL, acetone–methanol = 3:1), and NEt_3 (3 mL) at −20 °C under vigorous stirring.

Spectral data of the reaction mixture were as follows: (a) ^{1}H NMR δ (ppm) 5.69 (1H, olefinic proton at the cyclohexene part), 6.06–6.03 (2H, at the 2- and 6-position), and 7.66 (1H, d, at the 5-position) and a 1:2:1 area ratio of these peaks were observed. (b) Main MS peaks were 283, 186 (M^+−97), and 98. (c) The UV spectral change of the reaction mixture upon addition of strong base was observed; at first, the λ_{max} (nm) (absorbance; relative value) were 463 (0.56), 358 (1.30), 268 (0.76), and 229 (1.02). After addition of a few drops of sodium methoxide, the λ_{max} changed to 420 (0.97) and 280 (0.53). Meanwhile, the UV spectra of isolated **13** was observed in the presence of a few drops of sodium methoxide in EtOH: UV, λ_{max} 415 (1.07) and 280 (0.39).[6b] (d) HPLC spectrum, at 350 nm detection, showed the purity of the product or azo compound to be 97%.

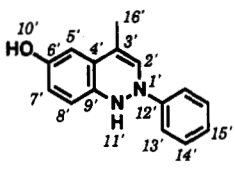
3-Methyl-1-(phenylamino)-1*H*-indol-5-ol (8a). ^{1}H-Detected heteronuclear multiple-bond correlation[9] (HMBC) was performed with a Varian UNITY-400 FT-NMR, to determine the ring structure of **8a**, i.e., whether it has an indole ring or cinnoline ring.[5b] A 20-mg sample in 1 mL of acetone-d_6 was used. Chemical shifts were measured in ppm relative to internal TMS.

The observed long-range couplings (^{1}H and ^{13}C) of (2′-^{1}H and 9′-^{13}C), (11′-^{1}H and 12′-^{13}C), and (11′-^{1}H and 13′-^{13}C) indicate the presence of C–N–C bonds in the ring, namely an indole ring and anilino group. The absence of (11′-^{1}H and 4′-^{13}C) and (11′-^{1}H and 8′-^{13}C) couplings indicate the absence of a cinnoline ring. The good correspondence of the UV absorption spectra of **8a** with that of **10** supports the above.

Numbering of (8a); 1*H*-indol-5-ol



Cinnolin-6-ol



Assignment of the compound (8a). HMBC spectra (acetone-d_6): ^{1}H NMR δ 8.23 (11′), 7.74 (10′), 7.12 (14′), 7.01 (8′), 6.98 (2′), 6.97 (5′), 6.78 (15′), 6.72 (7′), 6.48 (13′), 2.23 (16′); ^{13}C NMR 152.4 (6′), 150.1 (12′), 132.2 (9′), 130.1 (14′), 129.0 (4′), 128.1 (2′), 121.2 (15′), 113.6 (13′), 113.1 (7′), 111.0 (8′), 109.2 (3′), 104.3 (5′), 30.3 (16′). The numbering is as follows: 2′ to 9′, indole part; 12′ to 15′, anilino part; 10′, hydroxyl group; 11′, amino group; 16′, methyl group.

3-Methyl-1-(phenylamino)-1*H*-indol-5-ol (8a): yield 80%; mp 148–9 °C (recryst from benzene); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (dd, 2H, J = 7.4, J = 8.5 Hz), 7.08 (d, 1H, J = 8.6 Hz), 6.99 (d, 1H, J = 2.5 Hz), 6.93 (s, 1H), 6.88 (t, 1H, J = 7.4 Hz), 6.73 (dd, 1H, J = 8.6, J = 2.5 Hz), 6.51 (1H, s), 6.48 (dd, 2H, J = 8.5, J = 1 Hz), 4.66 (bs, 1H), 2.27 (s, 3H); UV (λ_{max}, nm, ε) in EtOH 226 (34400), 279 (11700), 306 (6000); HRMS calcd for $C_{15}H_{14}N_2O$ 238.1105, found 238.1062. Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.59; H, 5.88; N, 11.76. Found: C, 75.51; H, 5.96; N, 11.70.

3-Methyl-1-[(4-chlorophenyl)amino]-1*H*-indol-5-ol (8b): yield 63%; mp 141–2 °C (from hexane); ^{1}H NMR δ 7.13 (d, 2H, J = 8.7 Hz), 7.05 (d, 1H, J = 8.8 Hz), 6.99 (d, 1H, J = 2.4 Hz), 6.91 (s, 1H), 6.74 (dd, 1H, J = 8.7, J = 2.4 Hz), 6.54 (bs, 1H), 6.43 (d, 2H, J = 8.9 Hz), 2.26 (s, 3H); UV 226 (24300), 277 (8000), 303 (5500); HRMS calcd for $C_{15}H_{13}N_2OCl$ 272.0716, found 272.0725. Anal. Calcd for $C_{15}H_{13}N_2OCl$: C, 66.05; H, 4.81; N, 10.27. Found: C, 66.20; H, 4.83; N, 10.27.

3-Methyl-1-[(5-chloro-2-methoxyphenyl)amino]-1*H*-indol-5-ol (8c): yield 87%; mp 158.5–160 °C (from benzene); ^{1}H NMR δ 7.06 (d, 1H, J = 8.5 Hz), 7.00 (m, 2H), 6.91 (s, 1H), 6.79 (m, 2H), 6.75 (dd, 1H, J = 8.5, J = 2.5 Hz), 6.12 (s, 1H), 4.57 (bs, 1H), 3.94 (s, 3H), 2.29 (s, 3H); UV 225sh (45000), 278 (29000), 295 (6900); HRMS calcd for $C_{16}H_{15}N_2O_2Cl$ 302.0821, found 302.0814. Anal. Calcd for $C_{16}H_{15}N_2O_2Cl$: C, 63.47; H, 4.99; N, 9.25. Found: C, 63.73; H, 5.13; N, 9.02.

3-Methyl-1-[(2,6-dimethylphenyl)amino]-1*H*-indol-5-ol (8d): yield 60%; mp 180–181.5 °C (from hexane–benzene); ^{1}H NMR δ 7.22 (d, 1H, J = 8.5 Hz), 7.01 (d, 2H, J = 7.4 Hz), 6.95–6.93 (m, 2H), 6.89 (t, 1H), 6.82 (d, 1H), 6.76 (dd, 1H, J = 8.5, J = 2.3 Hz), 4.6 (bs, 1H), 2.20 (s, 3H), 2.10 (s, 6H); UV 214 (27400), 275 (8400), 310 (4400); HRMS calcd for $C_{17}H_{18}N_2O$ 266.1417, found: 266.1355. Anal. Calcd for $C_{17}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.52. Found: C, 76.26; H, 7.00; N, 10.17.

3-Methyl-1-[(2-chlorophenyl)amino]-1*H*-indol-5-ol (8e): yield 76%; mp 161–2 °C (from hexane–benzene); ^{1}H NMR δ 7.32 (dd, 1H, J = 8.0, J = 1.4 Hz), 7.06–7.03 (m, 2H), 7.02–6.96 (m, 2H), 6.93 (d, 1H), 6.81 (dd, 1H, J = 8.0 Hz), 6.74 (dd, 1H, J = 8.6, J = 2.4 Hz), 6.10 (dd, 1H, J = 8.0, J = 1.4 Hz), 4.62 (s, 1H), 2.28 (s, 3H); UV 225 (29800), 277 (10700), 305 (5350); HRMS calcd for $C_{15}H_{13}N_2OCl$ 272.0716, found 272.0687. Anal. Calcd for $C_{15}H_{13}N_2OCl \cdot {}^1/_2H_2O$: C, 63.94; H, 5.00; N, 9.94. Found: C, 64.22; H, 4.97; N, 9.81.

3-Methyl-1-[(4-nitrophenyl)amino]-1*H*-indol-5-ol (8f): yield 70%; mp 179–183.5 °C (from hexane–benzene–EtOAc); ^{1}H NMR ($CDCl_3$, a few drops of DMSO-d_6) δ 8.87 (s, 1H), 8.03 (d, 2H, J = 9.1 Hz), 7.34 (s, 1H), 7.00 (s, 1H), 6.99 (d, 1H, J = 8.6 Hz), 6.86 (d, 1H, J = 2.2 Hz), 6.79 (dd, 1H, J = 8.8, J = 2.2 Hz), 6.48 (d, 2H, J = 9.1 Hz), 2.27 (s, 3H); UV 226 (28700), 276 (9500), 321sh (12200), 349 (14400); HRMS calcd for $C_{15}H_{13}N_3O_3$ 283.0956, found 283.0955. Anal. Calcd for $C_{15}H_{13}N_3O_3$: C, 63.59; H, 4.62; N, 14.83. Found: C, 63.58; H, 4.74; N, 14.55.

3-Phenyl-1-(phenylamino)-1*H*-indol-5-ol (8g): yield 70%; mp 139–140 °C (from hexane–benzene); ^{1}H NMR (acetone-d_6) δ 8.55 (s, 1H), 7.89 (s, 1H), 7.72 (dd, 2H, J = 8.4, J = 1 Hz), 7.58 (s, 1H), 7.45 (dd, 2H, J = 7.4, J = 8.4 Hz), 7.41 (d, 1H, J = 2.3 Hz), 7.26 (t, 1H, J = 7.4 Hz), 7.20 (dd, 2H, J = 7.4, 8.4 Hz), 7.15 (d, 1H, J = 8.6 Hz), 6.85 (dd, 1H, J = 7.4, J = 1 Hz), 6.80 (dd, 1H, J = 8.6, J = 2.3 Hz), 6.59 (dd, 2H, J = 8.5, J = 1.0 Hz); UV 224 (29300), 273 (16000), 315 (8100); HRMS calcd for $C_{20}H_{16}N_2O$ 300.1261, found 300.1235. Anal. Calcd for $C_{20}H_{16}N_2O$: C, 79.97; H, 5.37; N, 9.32. Found: C, 80.11; H, 5.61; N, 9.12.

3-Methyl-1*H*-indol-5-ol (10): ^{1}H NMR δ 7.76 (bs, 1H), 7.19 (dd, 1H, J = 8.5, J = 0.6 Hz), 6.97 (d, 1H, J = 2.4 Hz), 6.94 (bs, 1H), 6.76 (dd, 1H, J = 8.5, J = 2.4 Hz), 2.26 (d, 3H, J = 1 Hz); mp 109–110 °C (from benzene) [lit. mp 108–9 °C,[7a] 116 °C[7b]]; UV 226 (16600), 278 (5000), 301sh (3600); HRMS calcd for C_9H_9NO 147.0683, found 147.0648.

3-Phenyl-1*H*-indol-5-ol (11): mp 139–141 °C (from benzene); ^{1}H NMR (acetone-d_6) δ 10.25 (bs, 1H), 7.72 (d, 1H, J = 1.7 Hz), 7.68 (dd, 2H, J = 8.4, J = 1.4 Hz), 7.55 (s, 1H), 7.42 (dd, 2H, J = 7.3, J = 8.4 Hz), 7.36 (s, 1H), 7.31 (dd, 1H, J = 8.7, J = 1.7 Hz), 7.22 (dd, 1H, J = 7.3, J = 1.4 Hz), 6.80 (d, 1H, J = 8.7 Hz), UV 223 (19100), 274 (12900), 305sh (6100); HRMS calcd for $C_{14}H_{11}NO$ 209.0840, found 209.0837. Anal. Calcd for $C_{14}H_{11}NO$: C, 80.36; H, 5.29; N, 6.69. Found: C, 80.55; H, 5.49; N, 6.58.

9-(Phenylamino)-2,3,4,9-tetrahydro-1*H*-carbazol-6-ol (9a): yield 79%; mp 170–1 °C (from hexane–benzene); ^{1}H NMR δ 7.17 (t, 2H, J = 7.4 Hz), 7.03 (d, 1H, J = 8.6 Hz), 6.90 (d, 1H, J = 2.4 Hz), 6.85 (t, 1H, J = 7.4 Hz), 6.63 (dd, 1H, J = 2.4, J = 8.6 Hz), 6.45 (d, 2H, J = 8.4 Hz), 6.34 (s, 1H), 4.58 (s, 1H), 2.66 (s, 2H), 2.56 (s, 2H), 1.85 (m, 4H); UV 229 (26700), 282 (9500); HRMS calcd for $C_{18}H_{18}N_2O$ 278.1418, found 278.1435. Anal. Calcd for $C_{18}H_{18}N_2O$: C, 77.67; H, 6.52; N, 10.06. Found: C, 77.96; H, 6.69; N, 9.88.

9-(Phenyl-d_5-amino)-2,3,4,9-tetrahydro-1*H*-carbazol-6-ol (9b): yield 66%; mp 177–8 °C (from hexane–benzene); ^{1}H NMR δ 7.37 (s, 1H), 7.04 (d, 1H, J = 8.5 Hz), 6.91 (d, 1H, J = 2.4 Hz), 6.64 (dd, 1H, J = 2.4, J = 8.5 Hz), 6.37 (s, 1H), 4.52 (bs, 1H), 2.66 (bs, 2H), 2.57 (bs, 2H), 1.85 (m, 4H); UV 228 (28900), 282 (10200); HRMS calcd for $C_{18}H_{13}D_5N_2O$ 283.1809, found 283.1746. Anal. Calcd for $C_{18}H_{13}D_5N_2O$: C, 76.29; H, 4.62; N, 9.86. Found: C, 76.45; H, 4.73; N, 9.62.

2-Methyl-9-(phenylamino)-2,3,4,9-tetrahydro-1*H*-carbazol-6-ol (9c): yield 71%; mp 139.5–141 °C (from hexane–benzene); ^{1}H NMR δ 7.17 (dd, 2H, J = 7.4, J = 8.5 Hz), 7.02 (d, 1H, J = 8.5 Hz), 6.90 (d, 1H, J = 2.4 Hz), 6.86 (dd, 1H, J = 7.4,

J = 1.0 Hz), 6.63 (dd, 1H, J = 2.4, J = 8.5 Hz), 6.45 (dd, 2H, J = 8.5, J = 1.0 Hz), 6.35 (s, 1H), 4.56 (bs, 1H), 2.69 (m, 3H), 2.17 (m, 1H), 1.95 (m, 2H), 1.49 (m, 1H), 1.07 (d, 3H, J = 6.4 Hz); UV 229 (33800), 282 (11700); HRMS calcd for $C_{19}H_{20}N_2O$ 292.1574, found 292.1544. Anal. Calcd for $C_{19}H_{20}N_2O$: C, 78.05; H, 6.89; N, 9.58. Found: C, 78.04; H, 6.89; N, 9.49.

2-*tert*-Butyl-9-(phenylamino)-2,3,4,9-tetrahydro-1*H*-carbazol-6-ol (9d): yield 71%; mp 212–3 °C (from hexane); ^{1}H NMR ($CDCl_3$ a few drops of DMSO-d_6) δ 7.87 (s, 1H), 7.14 (dd, 2H, J = 7.3, J = 8.5 Hz), 7.07 (s, 1H), 6.92 (d, 1H, J = 8.6 Hz), 6.81 (dd, 1H, J = 7.3, J = 1.0 Hz), 6.63 (dd, 1H, J = 2.2, J = 8.6 Hz), 6.46 (dd, 2H, J = 8.5, J = 1.0 Hz), 2.77–1.37 (m, 7H), 0.92 (s, 9H); UV 229 (32700), 282 (11400). Anal. Calcd for $C_{22}H_{26}N_2O$: C, 79.00; H, 7.84; N, 8.38. Found: C, 78.81; H, 7.96; N, 8.27.

2-Phenyl-9-(phenylamino)-2,3,4,9-tetrahydro-1*H*-carbazol-6-ol (9e): yield 66%; mp 199–200 °C (from hexane); ^{1}H NMR ($CDCl_3$ a few drops of DMSO-d_6) δ 8.37 (s, 1H), 8.18 (s, 1H), 7.28–7.18 (m, 5H), 7.12 (t, 2H, J = 7.4 Hz), 7.02 (d, 1H, J = 8.5 Hz), 6.92 (d, 1H, J = 2.3 Hz), 6.78 (t, 1H, J = 7.4 Hz), 6.68 (dd, 1H, J = 2.3, J = 8.5 Hz), 6.45 (d, 2H, J = 7.7 Hz), 3.05 (m, 1H), 2.81 (m, 4H), 2.19 (m, 1H), 2.0 (m, 1H); UV 229 (36600), 282 (12600). Anal. Calcd for $C_{24}H_{22}N_2O$: C, 81.33; H, 6.26; N, 7.90. Found: C, 81.16; H, 6.38; N, 7.80.

2,3,4,9-Terahydro-1*H*-carbazol-6-ol (12): yield 70%; mp 171–3 °C (from hexane–benzene–EtOAc) [lit.[8] mp 172 °C]; ^{1}H NMR (acetone-d_6) δ 9.4 (bs, 1H), 7.48 (s, 1H), 7.07 (d, 1H, J = 8.5 Hz), 6.78 (d, 1H, J = 2.4 Hz), 6.59 (dd, 1H, J = 2.4, J = 8.5 Hz), 2.71 (t, 2H), 2.60 (t, 2H), 1.85 (m, 4H); UV 228 (18400), 283 (6950).

3-(2,6-Dimethyl-1-cyclohexen-1-yl)-4-(phenylazo)phenol (13): yield 78% of a liquid; ^{1}H NMR δ 7.92–7.87 (m, 2H), 7.70–7.48 (m, 1H), 7.53–7.43 (m, 3H), 6.84–6.72 (m, 2H), 5.69 (bs, 1H), 2.20–2.13 (m, 2H), 1.8–1.6 (m, 2H), 1.58 (m, 1H), 1.50 (s, 3H), 1.36 (m, 1H), 0.93 (d, 3H, J = 6.8 Hz), 0.58 (m, 1H); UV 256 (8300), 356 (19100); HRMS calcd for $C_{20}H_{22}N_2O$ 306.1730, found 306.1723.

6-(Phenylazo)-3-biphenylol (14): yield 89% of a liquid; ^{1}H NMR δ 7.80 (d, 1H, J = 8.8 Hz), 7.75–7.72 (m, 2H), 7.49–7.40 (m, 9H), 7.00 (d, 1H, J = 2.7 Hz), 6.90 (dd, 1H, J = 2.7, J = 8.8 Hz), 5.61 (s, 1H); UV 229 (17800), 273 (9820), 357 (19600); HRMS calcd for $C_{18}H_{14}N_2O$ 274.1104, found 274.1048.

3-Cyclohexyl-4-(phenylazo)phenol (15): yield 71%; mp 89.3–90 °C (from hexane); ^{1}H NMR δ 7.89 (d, 2H, J = 7.1 Hz), 7.74 (d, 1H, J = 8.5 Hz), 7.51 (t, 2H, J = 7.1 Hz), 7.45 (t, 1H, J = 7.1 Hz), 7.26 (m, 1H), 6.86 (d, 1H, J = 2.2 Hz), 6.74 (dd, 1H, J = 2.2, J = 8.5 Hz), 3.74 (bs, 1H), 1.92–1.8 (m, 6H), 1.53–1.46 (m, 4H), 1.3 (m, 1H); UV 254 (9400), 357 (22200); HRMS calcd for $C_{18}H_{20}N_2O$ 280.1538, found 280.1532. Anal. Calcd for $C_{18}H_{20}N_2O$: C, 77.11; H, 7.19; N, 9.99. Found: C, 77.16; H, 7.33; N, 10.0.

3-(1-Phenylethenyl)phenol (2b): yield 76% of a liquid; bp 180–190 °C/13 mmHg [lit.[10] bp 140 °C/0.01 mmHg].

3-(1-Cyclohexen-1-yl)phenol (3a): yield 63%; mp 39–40 °C (bp 114–6 °C/2 mmHg) [lit.[11] bp 142 °C/0.2 mmHg].

3-(4-Methyl-1-cyclohexen-1-yl)phenol (3c): yield 61% of a liquid; HRMS calcd for $C_{13}H_{16}O$ 188.1199, found 188.1227.

3-(4-*tert*-Butyl-1-cyclohexen-1-yl)phenol (3d): yield 86%; mp 108–9 °C. Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.62. Found: C, 83.58; H, 9.86.

3-(4-Phenyl-1-cyclohexen-1-yl)phenol (3e): yield 61%; mp 106.5–109 °C (bp 196–203 °C/1.5 mmHg). Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.29; H, 7.39.

3-(2,6-Dimethyl-1-cyclohexen-1-yl)phenol (4): yield 52%; bp 98–110 °C/1.5 mmHg; HRMS calcd for $C_{14}H_{18}O$ 202.1356, found 202.1388.

3-Cyclohexylphenol (6): yield 69%; mp 49–49.5 °C [lit.[12] mp 52 °C].

Registry Numbers. 2a, 51985-06-9; **2b**, 51985-11-6; **3a**, 32960-79-5; **5**, 580-51-8; **6**, 1943-95-9; **8a**, 99777-70-5; **10**, 1125-40-2; **12**, 13314-76-6; 4-methylcyclohexanone (589-92-4); 4-*tert*-butylcyclohexanone (98-53-3); 4-phenylcyclohexanone (4894-75-1); 1-(3-hydroxyphenyl)ethanone (121-71-1); 1-bromo-3-methoxybenzene (2398-37-0).

Acknowledgment. The author is indebted to Mr. H. Kato and Mr. N. Yanagihara for their support in analysis of NMR and HMBC spectra. The author is also indebted to Dr. A. Umehara, Mr. S. Hanai, and Mr. H. Tateisi for technical suggestions to this manuscript.

(11) For the preparation of 3-(1-cyclohexen-1-yl)phenol, see (a) OLS 2060573 to Ciba-Geigy (Rossi, A.; Christian, E.). (b) Carissimi, M.; Gentili, G.; Milla, E.; Picciola, G.; Ravenna, F. *Arzeim*-Forsh. **1976**, *26*, 506.

(12) For the preparation of 3-cyclohexylphenol, see: Gardner, J. H.; Stevens, J. R. *J. Am. Chem. Soc.* **1947**, *69*, 3057.