The Reverse Mannich Reaction of Some 5-Hydroxyindoles[1]

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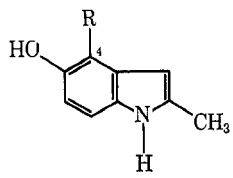
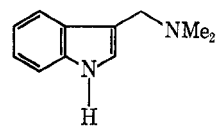
The C_4-dimethylaminomethyl Mannich adducts of 3-substituted 5-hydroxyindoles undergo a facile, amine catalyzed carbon–carbon bond cleavage to yield the corresponding C_4-hydrogen indole derivatives. Reverse Mannich condensation occurs most readily in C_3-carbethoxy substrates, then in C_3-ethyl derivatives; no reverse reaction was observed for C_3-hydrogen derivatives. An indole N–H group is not required for reverse reaction. This transformation is catalyzed by primary (most efficient), secondary, and tertiary amines. The role of the C_3 substituent is discussed in terms of both steric and electronic effects. It is concluded that a steric C_3–C_4 peri interaction is responsible for the observed difference in behavior between the C_3-carbethoxy and C_3-hydrogen derivatives.

Formation of a new carbon–carbon bond resulting in addition of a one carbon substituent to an existing skeleton by means of the Mannich reaction is a well-documented synthetic tool.[3] Recently it has been established[4] that Mannich condensation of 5-hydroxyindoles (*e.g.*, **1**) results in selective introduction of an



1, R = H
1a, R = CH_2NMe_2



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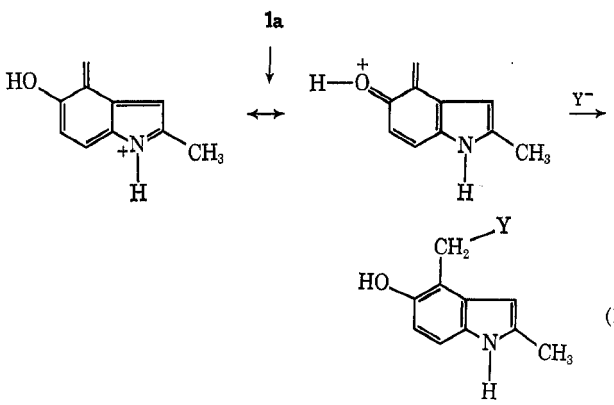
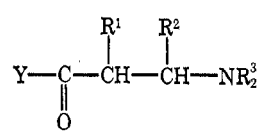


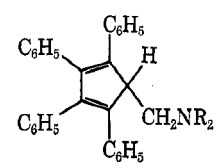
(1)

aminomethyl substituent at the C_4 position (*e.g.*, **1a**). It was anticipated that these C_4 indole adducts (*e.g.*, **1a**) would undergo net substitution *via* an elimination–addition mechanism (eq 1) analogous to that proposed[3,5] for gramine (**2**), the Mannich adduct of indole. In support of this hypothesis Mannich adducts of this general type have been used as synthetic intermediates in the construction of more complex hydroxyindole derivatives.[6]

An alternative, although less common, reaction course of Mannich adducts is a *reverse* Mannich condensation resulting in rupture of the previously formed carbon–carbon bond to regenerate the starting substrates.[7,8] The most common examples of reverse condensation involve cleavage of an sp^3–sp^3 carbon–carbon bond to yield a resonance stabilized anion. For example, acid- and/or base-catalyzed reverse Mannich condensations have been reported for aryl[7,8] and vinyl[9] ketone adducts (**3**), for aminomethyl fulvene derivatives[10] (**4**), and for the diphenylacetonitrile adduct **5**.[11,12]



3, Y = aryl or vinyl



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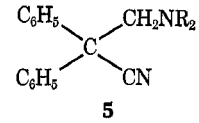

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By way of comparison, examples of reverse Mannich condensation involving formal cleavage of an sp^2–sp^3 carbon–carbon bond are much less common. Treatment of the β-naphthol adduct **6** with piperidine (sealed tube, 180°) or with refluxing morpholine resulted in 30–35% reverse reaction.[9] Formation of the diarylmethane derivative **8** from the primary amine adduct **7** was postulated to involve a reverse Mannich condensation of **7**, followed by addition of β-naphthol to a second molecule of **7** *via* the normal elimination–addition sequence.[13] The same product (**8**), however, could arise

(1) Financial support of this research by the National Institutes of Mental Health (MH15544) is gratefully acknowledged.

(2) A training stipend from the Food and Drug Administration, Public Health Service, DHEW, is gratefully acknowledged.

(3) (a) B. Reichert, "Die Mannich-Reaktion," Springer Verlag, Berlin, 1959; (b) H. Hellmann and G. Opitz, "α-Aminoalkylierung," Verlag Chemie, GMBH, Weinheim, 1960.

(4) (a) S. A. Monti, W. O. Johnson, and D. H. White, *Tetrahedron Lett.*, 4459 (1966), and references therein; (b) S. A. Monti and W. O. Johnson, *Tetrahedron*, in press.

(5) J. H. Brewster and E. L. Eliel, *Org. React.*, **7**, 99 (1953).

(6) (a) F. Troxler, *Helv. Chim. Acta*, **51**, 1214 (1968); (b) M. Julia and J. Y. Lallemand, *C. R. Acad. Sci., Ser. C*, **267**, 1506 (1968); (c) G. D. Castillo, unpublished results, this laboratory.

(7) H. Rivière, *Ann. Chim. (Paris)*, **5**, 1273 (1960).

(8) H. Larramona and B. Tchoubar, *Bull. Soc. Chim. Fr., C*, 53 (1953).

(9) B. V. Unkovskii, F. I. Psal'ti, and E. P. Badosov, *Zh. Org. Khim.*, **4**, 1546 (1968); *J. Org. Chem. (USSR)*, **4**, 1485 (1968).

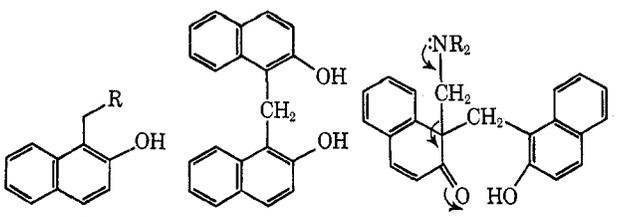
(10) D. Taber, E. I. Becker, and P. E. Spoerri, *J. Amer. Chem. Soc.*, **76**, 776 (1954); K. A. Kun and P. E. Spoerri, *ibid.*, **77**, 4676 (1955).

(11) H. E. Zaugg, B. W. Harrom, and M. R. Vernsten, *ibid.*, **75**, 288 (1953).

(12) For other examples of reverse Mannich reactions, see (a) H. R. Snyder and J. H. Brewster, *ibid.*, **71**, 1061 (1949); (b) M. Zief and J. P. Mason, *J. Org. Chem.*, **8**, 1 (1943); (c) H. R. Snyder, C. Y. Meyers, and D. B. Kellom, *J. Amer. Chem. Soc.*, **75**, 4672 (1953); (d) W. Kutscher and O. Klamerth, *Chem. Ber.*, **86**, 352 (1952); (e) R. Jacquier, M. Mousseron, and S. Boyer, *Bull. Soc. Chim. Fr.*, 1653 (1956); (f) D. R. Howton and D. R. V. Golding, *J. Org. Chem.*, **15**, 1 (1950); (g) W. E. Bachmann and L. B. Wick, *J. Amer. Chem. Soc.*, **72**, 3388 (1950); (h) W. Reid and G. Keil, *Justus Liebigs Ann. Chem.*, **616**, 96 (1958).

(13) W. J. Burke, W. A. Nasutavicus, and C. Weatherbee, *J. Org. Chem.*, **29**, 407 (1964).

via intermediate **9**, thus negating the requirement for a reverse Mannich reaction.[14]



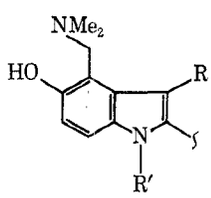
6, R = piperidino
7, R = NHR′

8 **9**

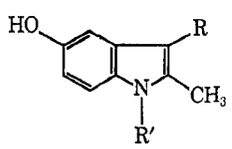
We now wish to report that this second reaction is available to the C_4 Mannich adducts of 5-hydroxyindoles. As discussed in detail below, Mannich adducts of general structure **10** readily undergo reverse Mannich condensation to yield the parent hydroxyindole precursor.

Results and Discussion

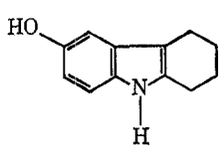
The C_4-dimethylaminomethyl Mannich adducts of the following 5-hydroxyindoles were used as substrates in this study: 2-methyl-5-hydroxyindole (**1**), 2-methyl-3-carbethoxy-5-hydroxyindole (**11**), 1,2-dimethyl-3-carbethoxy-5-hydroxyindole (**12**), 2-methyl-3-ethyl-5-hydroxyindole (**13**), and 6-hydroxytetrahydrocarbazole (**14**). In each case the Mannich adduct (part structure **15**) was heated under reflux with excess amine in ethanol.



10, R ≠ H
R′ = H or alkyl



11, R = CO_2Et; R′ = H
12, R = CO_2Et; R′ = CH_3
13, R = CH_2CH_3; R′ = H



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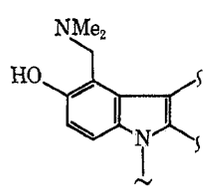

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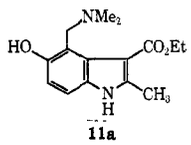
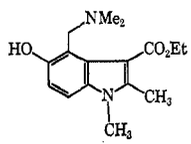
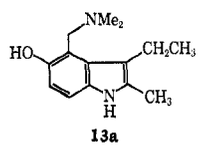
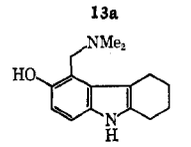
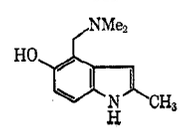
Reaction progress was monitored by tlc, and final product compositions were established by isolation and comparison to authentic samples, nmr spectroscopy, and tlc analysis. These results are summarized in Table I.

Consideration of the data in Table I delineates two structural features of the indole substrates that undergo reverse Mannich condensation. Most significantly, a C_3 substituent is a requirement; reverse reaction occurs most readily in C_3-carbethoxy substrates (**11a**), then in those with a C_3-ethyl group (**13a**). Under the conditions employed, the C_3-hydrogen substituted adduct (**1a**) did *not* undergo detectable reverse condensation. Secondly, the presence of an indole N–H group is not necessary for reverse reaction as seen by the behavior of the *N*-methyl derivative **12a**. In order to compare our results with those previously reported for formal

(14) A. Merijan and P. D. Gardner, *J. Org. Chem.*, **30**, 3965 (1965).

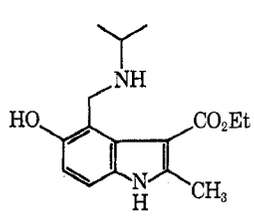
TABLE I
REVERSE MANNICH CONDENSATION OF SOME 4-DIMETHYLAMINOMETHYL-5-HYDROXYINDOLES

Substrate	Amine	Time, hr	Results
 **11a**	Cyclohexylamine	5	*ca.* 50% reverse
	Isopropylamine	6	*ca.* 50% reverse
	Isopropylamine	32	100% reverse
	Dimethylamine	50	84% reverse
	Triethylamine	50	*ca.* 40% reverse
	Ethanol	50	Trace reverse
 **12a**	Isopropylamine	6	35% reverse, 55% exchange
 **13a**	Isopropylamine	6	10% reverse, 65% exchange
	Isopropylamine	52	100% reverse
 **14a**	Isopropylamine	6	75% exchange, trace reverse
	Isopropylamine	52	*ca.* 100% exchange, trace reverse
 **1a**	Isopropylamine	28	100% exchange, no reverse
	Piperidine	6	*ca.* 90% exchange, no reverse

cleavage of sp^2–sp^3 carbon–carbon bonds,[9] the dimethylaminomethyl adduct of β-naphthol (**6**, R = NMe_2) was treated with isopropylamine in ethanol. The major product isolated was the diarylmethane **8**; no evidence for the formation of β-naphthol was found. As discussed above, the formation of **8** does not necessarily involve reverse Mannich condensation.[14]

With respect to the amine component, reverse reaction takes place most readily in the presence of primary amines but it does occur with secondary and tertiary amines.

In the reactions involving primary amines, amine exchange most probably precedes reverse condensation to yield the primary amine adducts (*e.g.*, **16**) which rapidly



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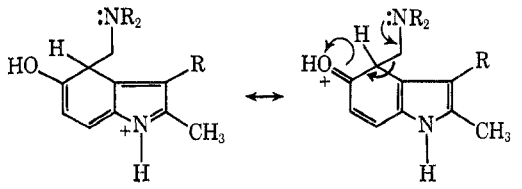
undergo reverse reaction. In support of this hypothesis, the unstable but spectrally characterized isopropylamine adduct **16** readily reversed to **11** during attempted recrystallization from acetonitrile or when heated to its melting point. The corresponding dimethylamine adduct **11a** is stable to these conditions. The piperidine adducts of these hydroxyindoles were stable to both amine exchange and reverse condensation reactions.

In general mechanistic terms, reverse Mannich condensation of these hydroxyindole adducts **10** involves (1) protonation at C_4 to yield the resonance stabilized intermediate **17**, followed by (2) carbon–carbon bond

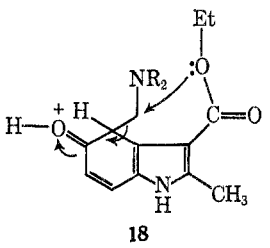


17

fragmentation to give the products. Theoretically three factors could account for the pronounced difference in behavior between the C_3-carbethoxy derivative **11a** and the C_3-hydrogen substrate **1a**: an electronic effect, a neighboring group effect, or a steric effect attributable to the C_3-ester function. If one assumes that protonation at C_4 (step 1 above) is the rate-determining step, then preferential protonation of **11a**, due to any of the three factors enumerated above, offers an attractive explanation for the observed difference. To test this postulate, both the C_3-hydrogen (**1**) and the C_3-carbethoxy (**11**) 5-hydroxyindoles were treated with isopropylamine in the presence of methanol-*O*-*d*. After 6 hr *complete* exchange[15] of the C_4 hydrogen by deuterium (nmr analysis) had occurred for *both* indoles, **1** and **11**.[16] Thus it seems reasonable to assume that both Mannich adducts, **1a** and **11a**, undergo facile C_4 protonation under the conditions of reverse condensation, thereby excluding step 1 as the rate-determining one.

The observed difference in behavior, therefore, must be explicable in terms of the carbon–carbon fragmentation step. In terms of electron logistics, rupture of the carbon–carbon bond in **17** results in reverse reaction while cleavage of the carbon–hydrogen bond simply reverses the protonation step to give back **10**. Clearly there is no conceivable mechanism by which a C_3-ester group could electronically distinguish between the electron pair in the C–H bond and that in the C–C bond. Thus an electronic effect can be excluded from further consideration.

Neighboring group participation of one of the ester oxygen atom lone electron pairs to assist carbon–carbon bond fragmentation *via* a six-centered process (see arrows in **18** for one possible mode) could explain the



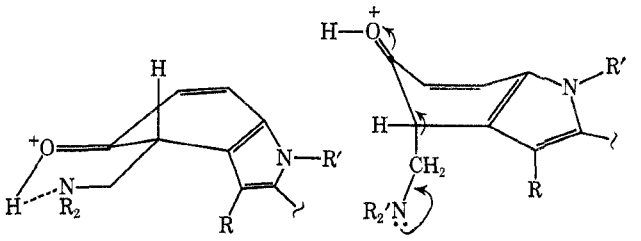
18

observed difference. The behavior of the C_3-ethyl adduct **13a**, however, clearly indicates that neighboring group participation of a heteroatom is not necessary for reverse condensation. Thus one is left with a steric effect.

(15) J. W. Daly and B. Witkop, *J. Amer. Chem. Soc.*, **89**, 1032 (1967).

(16) Under these conditions, no exchange of the other aromatic protons of **1** or **11** or of the C_3-H of **1** was observed.

The stereoelectronic requirements for maximum overlap during bond formation[17] require that initial protonation of **10** occur along an axis perpendicular to the plane of the ring carbons. This yields intermediate **19** with the C_4-hydrogen atom in a pseudoaxial position and the C_4-aminomethyl group in a pseudoequatorial orientation. For analogous reasons, rupture of the C–H bond (deprotonation) is the most favored process in this conformation. For reverse Mannich condensation to occur, a conformational "flip" to **20** is necessary.



19 **20**

Now continuous overlap with the existing π system can be maintained during cleavage of the pseudoaxial carbon–carbon bond. The observation that adduct **16** is stable in acid solution suggests that participation of the nitrogen atom lone electron pair (as shown in **20**) is necessary for bond cleavage.[18]

When the C_3 substituent R is small, conformer **19** with the large aminomethyl group in a pseudoequatorial position should be most stable. Intramolecular hydrogen bonding (see **19**) further stabilizes this conformer with respect to **20**. As the effective size of the C_3-R group increases, the resulting peri interaction between the C_4 pseudoequatorial substituent and the C_3-R function will destabilize **19** with respect to **20**.[19] In a qualitative sense, the observed behavior of the Mannich adducts summarized in Table I is consistent with such a steric effect. The infrared carbonyl absorption of the C_3-ester adduct **11a** (1650 cm^{-1}, vinylogous carbamate) indicates extensive delocalization between the indole nucleus and the carbonyl function. This restricted rotation maximizes the peri interaction in conformer **19**. Similarly, the freely rotating C_3-ethyl group of **13a** destabilizes **19** with respect to **20**, although the effective size of the ethyl group is less than that of the carbethoxy subtituent.

An examination of molecular models of the tetrahydrocarbazole adduct **14a** indicates that the C_3–C_4 peri interaction is diminished considerably due to the rigid nature of the cyclohexene ring. In the C_3-H adduct **1a** this peri effect is minimal.

The facile reverse reaction of the isopropylamine adduct **16** compared to the dimethylamine adduct **11a**, is consistent with the observation that the neutral imine leaving group **21** can be lost from **16** while the charged species **22** must be lost from **11a**.

21 **22**

(17) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 56–57.

(18) The practical consequence of this observation is that acid catalyzed Mannich condensations of C_3-ester derivatives **11** give optimum yields.[4]

(19) V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966); F. Johnson, *ibid.*, **68**, 375 (1968).

Experimental Section

Melting points are uncorrected and were obtained on a Mel-Temp apparatus. Nmr spectra were obtained on a Varian Associates Model A-60 spectrometer; ir spectra were run on a Perkin-Elmer Model 237B grating spectrophotometer. Microanalyses were performed by Chemalytics, Inc., Tempe, Ariz.

General Procedure for Reverse Mannich Reactions.—A solution of the Mannich adduct (*ca.* 100 mg) and the appropriate amine (3 ml) in ethanol (5 ml) was heated at reflux under a nitrogen atmosphere for the time indicated in Table I. Reaction progress was monitored conveniently by tlc (silica gel, 20% ethanol-benzene). The crude product(s) were isolated by evaporation of solvent *in vacuo*. In those cases where appreciable reverse reaction occurred (>30%) the relatively insoluble parent hydroxyindole (**11**, **12**, and **13**) was purified by crystallization and was characterized by melting point and mixture melting point and/or nmr and ir. The extent of amine exchange in all systems and the amount of reverse reaction in those cases involving <10% reverse reaction were estimated by nmr of the product mixture using characteristic peaks for each component. For adduct **1a** the amine exchange products were identified by nmr and/or comparison to authentic[4] samples; no evidence for the presence of the reverse reaction product **1** was observed by tlc and nmr analysis of the crude reaction mixtures. Nmr data for the isopropylamine exchange product from **1a** are (acetone-d_6) δ 1.10 [d, 6, J = 6.0 Hz, $CH(CH_3)_2$], 2.35 (s, 3, C_2-CH_3), 2.86 (heptet, 1, J = 6.0 Hz, $CHMe_2$), 4.12 (broad s, 1, $CH_2N<$), 6.03 (broad s, 1, C_3-H), 6.53 (d, 1, J = 8.0 Hz, C_6-H), and 7.03 (d, 1, J = 8.0 Hz, C_7-H).

The Mannich adducts **1a**,[4] **11a**,[4] **12a**,[20] and **14a**[4] were prepared as previously described.

2-Methyl-3-ethyl-5-hydroxyindole (13).[21]—A tetrahydrofuran solution of diborane (25 ml, 1.05 *M*, 26 mmol) was added slowly to a stirred suspension of 2-methyl-3-acetyl-5-hydroxyindole[22] (1.0 g, 5.3 mmol) in tetrahydrofuran (10 ml) under a nitrogen atmosphere. After hydrogen evolution was complete, the mixture was heated under reflux for 1 hr, cooled, and then added to acetone (75 ml). The resulting mixture was heated to boiling and then evaporated *in vacuo*. The residue was heated with methanol (50 ml) for 20 min, the solution was concentrated, and then hydrochloric acid (3 *N*, 40 ml) was added. This mixture was extracted with ether; the combined ether extracts were dried ($MgSO_4$) and evaporated to yield a yellow oil. Sublimation (90°, 0.05 mm) or recrystallization ($CHCl_3$–hexane) yielded pure product **13**: mp 108–108.5°; yield 0.76 g (82%), nmr (acetone-d_6) δ 1.14 (t, 3, J = 7.5 Hz, CH_2CH_3), 2.28 (s, 3, C_2-CH_3), 2.6 (q, 2, J = 7.5 Hz, $-CH_2CH_3$), 6.64 (dd, 1, J = 9 and 2.5 Hz, C_6-H), 6.91 (d, 1, J = 2.5 Hz, C_4-H), and 7.05 (d, 1, J = 9 Hz, C_7-H).

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.38; H, 7.48; N, 8.00. Found: C, 74.99; H, 7.69; N, 8.38.

2-Methyl-3-ethyl-4-(dimethylamino)methyl-5-hydroxyindole (13a).—A mixture of paraformaldehyde (0.13 g, 4.32 mmol) and dimethylamine (0.5 ml, 40% aqueous solution, 4.44 mmol) in ethanol (30 ml) was warmed to dissolve the paraformaldehyde. This solution was cooled and indole **13** (0.75 g, 4.29 mmol) and glacial acetic acid (3 ml) were added. The resulting mixture was stirred under nitrogen at room temperature for 12 hr. After evaporation of the ethanol, the residue was made basic (pH *ca.* 9) with Na_2CO_3 solution and extracted with ether. The combined ether extracts were dried ($MgSO_4$) and evaporated to yield a dark oil. Filtration through a silica gel column (10 g, benzene eluent) yielded a yellow oil which still contained a small amount of **13** (tlc). Purification of **13a** was accomplished by conversion to the water soluble oxalic acid salt, removal of starting indole **13** by ether extraction and liberation of **13a** by sodium carbonate neutralization to give pure **13a** as a homogeneous oil (tlc): yield 0.51 g (52%); nmr ($CDCl_3$) δ 1.11 (t, 3, J = 7.0 Hz, CH_2CH_3), 2.18 (s, 3, C_2-CH_3), 2.30 [s, 6, $N(CH_3)_2$], 2.67 (q, 3, J = 7.0 Hz, CH_2CH_3), 3.92 (s, 2, CH_2NR_2), 6.43 (d, 1, J = 8.5 Hz, C_6-H), and 6.77 (d, 1, J = 8.5 Hz, C_7-H).

2-Methyl-3-carbethoxy-4-(isopropylamino)methyl-5-hydroxyindole (16).—A mixture of paraformaldehyde (0.08 g, 2.8 mmol) and isopropylamine (0.16 g, 2.7 mmol) in ethanol (15 ml) was warmed to dissolve the paraformaldehyde. The solution was cooled and indole **11** (0.58 g, 2.65 mmol) and glacial acetic acid (3 ml) were added. The mixture was stirred under nitrogen at 65° for 4.5 hr. Tlc indicated appreciable conversion to product at this point. After evaporation of the ethanol the residue was made basic (pH *ca.* 9) with Na_2CO_3 solution and extracted with chloroform. The combined chloroform extracts were dried ($MgSO_4$) and evaporated to yield the crude product. Attempted purification by crystallization resulted in reverse condensation to give indole **11** (tlc, nmr). Chromatography on alumina(III) furnished a fairly homogeneous sample (tlc) of **16**, mp 130–132°, in low yield. Tlc analysis of the sample after melting indicated only **11** was present. The nmr ($CDCl_3$) of **16** showed δ 1.15 [d, 6, J = 6.5 Hz, $CH(CH_3)_2$], 1.38 (t, 3, J = 7.0 Hz, CH_2CH_3), 2.50 (s, 3, C_2-CH_3), 2.96 [m, 1, J = *ca.* 6 Hz, $CH(CH_3)_2$], 4.33 (q, 2, J = 7 Hz, CH_2CH_3), 6.69 (d, 1, J = 8.5 Hz, C_6-H), 7.01 (d, 1, J = 8.5 Hz, C_7-H), and 7.8 (broad, 2, OH, NH).

1-(Dimethylamino)methyl-2-naphthol (6, R = NMe_2).—A solution of 2-naphthol (1.44 g, 10.0 mmol), paraformaldehyde (0.30 g, 10.0 mmol), and dimethylamine (1.2 ml, 40% aqueous solution, 10.6 mmol) in ethanol (40 ml) was stirred under nitrogen at room temperature for 12 hr. The solvent was evaporated *in vacuo* to yield a mixture (tlc) which was purified by conversion *via* the hydrochloride salt to yield pure **6** (R = NMe_2): yield 1.3 g (65%); mp (hexane) 73–74° (lit.[24] 74–75°); nmr (CCl_4) δ 2.30 [s, 6, $N(CH_3)_2$], 3.95 (s, 2, CH_2NR_2), 6.9–7.8 (m, 6, aromatic H's), and 11.52 (s, 1, OH).

Treatment of 1-(Dimethylamino)methyl-2-naphthol with Isopropylamine.—Dimethylaminomethyl Mannich adduct **6**[23] (R = NMe_2) (0.82 g, 4.06 mmol) was refluxed in a mixture of isopropylamine (15 ml) and ethanol (20 ml) under nitrogen for 10 hr. Evaporation of the solvent yielded a solid which on repeated recrystallization from cyclohexane yielded pure product **8**: mp 191–193° (lit.[14] 193–196°); yield 0.47 g (39%); nmr (acetone-d_6) δ 4.92 (s, 2, $-CH_2-$), 7.1–7.4 (m, 8, aromatic H's), 7.5–7.8 (m, 4, aromatic H's), and 6.25–6.48 (m, 2, –OH). Nmr of the residue indicated *ca.* 30% amine exchange and *ca.* 30% unreacted **6**.

Deuterium Exchange Reactions.—The 3-carbethoxyindole **11** (0.105 g, 4.83 mmol) and the 3-H indole **1** (0.102 g, 6.98 mmol) were separately refluxed in a mixture of isopropylamine (6 drops), methanol-*O*-*d* (1 ml), and deuterium oxide (0.2 ml) under nitrogen for 6 hr. Nmr spectra obtained on the residues after evaporation of the solvent showed complete disappearance of the C_4-H doublet in both cases; the C_6-H now appeared as a doublet. The C_3-H of **1** was not exchanged for deuterium under these conditions.

Registry No.—**1a**, 25913-93-3; **11a**, 13098-13-0; **12a**, 25913-94-4; **13**, 25913-95-5; **13a**, 25913-96-6; **14a**, 25913-97-7; **16**, 25913-98-8.

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(21) Experiment performed by R. Schmidt of these laboratories.

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