Indole Rearrangements: the Action of Acid on the Dimer of 3-Hydroxy-2,3-dimethyl-3*H*-indole

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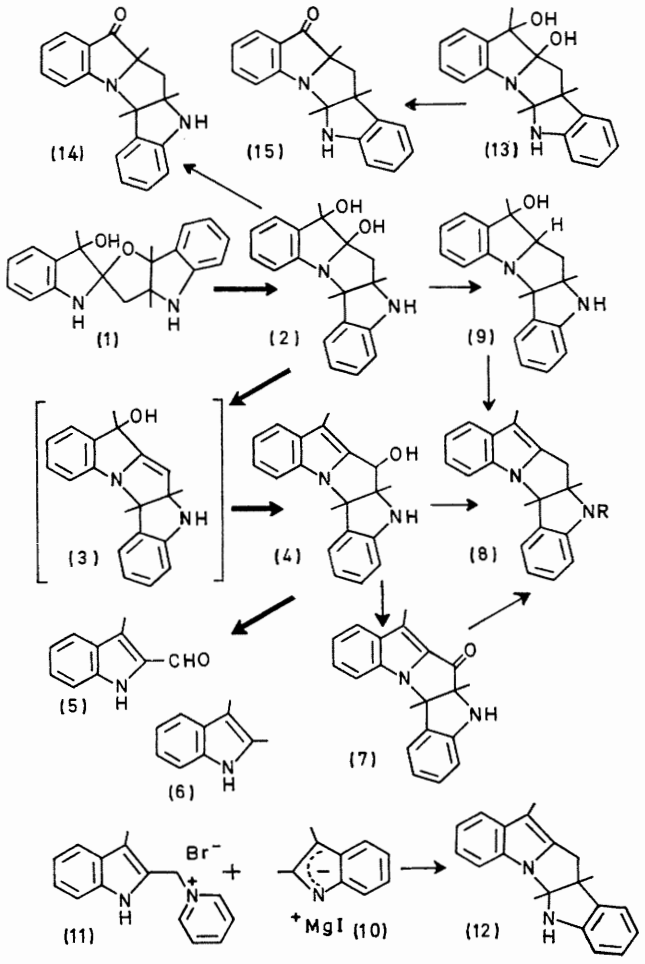
Summary Dilute hydrochloric acid converts the title compound (**1**) into (**2**), then into (**4**), and finally into (**5**) and (**6**): this fact requires revision to (**2**) and (**14**) of the structures (**13**) and (**15**) suggested by others.

IN a recent paper[1] suggesting a revised structure (**1**)† for the dimer of 3-hydroxy-2,3-dimethyl-3*H*-indole[2] (the dimeric autoxidation product of 2,3-dimethylindole), some acid-catalysed reactions were reported. These transformations

† Independent and unequivocal proof for this same structure was presented by us at the 52nd Conference of the Chemical Institute of Canada in Montreal, May 25—28, 1969.

are, in fact, much more complex than described,[1] and some of the structures put forward are incorrect. The actual contortions undergone by this molecule are reported here.



When the dimer (**1**) is heated in a nitrogen atmosphere with dilute hydrochloric acid, it is converted into equimolar amounts of 2-formyl-3-methylindole (**5**) and 2,3-dimethylindole (**6**) as reported,[1] but there are at least two isolable intermediates probably on the reaction path. At room temperature after 15 min with 0·1 N-HCl–acetone, a compound, m.p. 115° (decomp.)‡ more polar than (**1**) is the only product detectable by t.l.c. This compound, (**2**) is identical by direct comparison with the BF_3 isomerisation product of (**1**) reported by the Italian workers[1] whose suggested structure (**13**) should be revised to accord with our evidence.

Further reaction of (**2**) for *ca.* 3 h at room temperature with the dilute hydrochloric acid reagent gives [presumably *via* (**3**)] the secondary alcohol (**4**), m.p. 169° (*O*-acetate, m.p. 175°) which is slowly cleaved to (**5**) and (**6**). The secondary alcohol (**4**) is oxidised by CrO_3–pyridine to a pale-yellow ketone (**7**), m.p. 194°, which on Wolff–Kishner reduction yields a deoxo-derivative, m.p. 126°, δ ($CDCl_3$) 1·34 (s, Me), 1·74 (s, Me), 2·20 (s, Me), 2·96, and 3·12 (*J* 16, CH_2), also obtained by Na–Bu^{t}OH reduction of the secondary alcohol (**4**). This deoxo-compound must be assigned structure (**8**; R = H) since it is not identical with the isomeric compound (**12**),§ m.p. 194°, δ ($CDCl_3$) 1·44 (s, Me), 1·79 (s, Me), 2·12 (s, Me), 3·06, and 3·42 (*J* 16, CH_2), prepared earlier by the Italian workers from reaction of the Grignard reagent (**10**) with the pyridinium salt (**11**).[3] Moreover, the ketone (**7**) is stable to sodium hydroxide in refluxing methanol; such inertness would not be expected for the ketone corresponding to (**12**). Additional support for these revised structural assignments comes from the $NaBH_4$ reduction product (**9**), m.p. 140°, of (**2**) which on acetylation by Ac_2O–NaOAc gives (**8**; R = Ac), m.p. 275°. Alteration of the formula of the acid-catalysed isomerisation product to (**2**) requires a corresponding change to (**14**) [instead of (**15**)[1]] in the structure of the ψ-indoxyl formed from (**2**).[1]

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‡ Satisfactory analyses and i.r., u.v., and n.m.r. spectra have been obtained for all compounds mentioned.
§ Compound (**12**) can exist as *cis*- and *trans*-racemates. However, formation of the fifth ring of the carbon skeleton by reversible ring closure (addition of nitrogen to an imine) would give only the lower energy *cis* 5/5 ring fusion.

[1] G. Berti, A. DaSettimo, G. DiColo, and E. Nannipieri, *J. Chem. Soc.* (*C*), 1969, 2703.
[2] J. W. Kershaw and A. Taylor, *J. Chem. Soc.*, 1964, 4320.
[3] G. Berti, A. DaSettimo, and E. Nannipieri, *J. Chem. Soc.* (*C*), 1968, 2145.