The Plancher Rearrangement of 2,3-Disubstituted 3*H*-Indoles

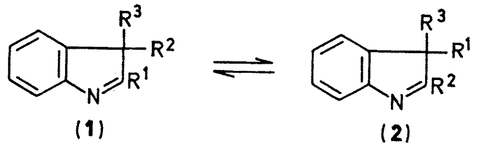
By Y. KANAOKA,* K. MIYASHITA, and O. YONEMITSU

(*Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo, Japan*)

Summary The Plancher rearrangement of 3*H*-indoles has been quantitatively examined in polyphosphoric acid at 150°.

ALTHOUGH the Plancher rearrangement is one of the well known "name reactions,"[1] information on its nature has been limited. In connection with studies on 3*H*-indoles,[2] we report some quantitative studies on the reaction.

Compound (**1a**) (polyphosphoric acid, 150°, 2 hr.) gave (gas chromatography) a mixture of (**1a**) and (**2a**) of constant ratio *K* = (**1a**) : (**2a**) = 3·5. Under the same conditions, (**2a**) gave the same mixture: the rearrangement is therefore an equilibrium (Scheme 1). The fact that the value of *K* for (**1b**) and (**2b**) is 0·83 indicates that the equilibrium is highly dependent on the substituents. The only quantitative study of the reaction[3] was re-examined with (**1c**) and (**2c**) (Table 1) as substrates: we confirm the results, but find the ratio to be 1·4, not 2·3.



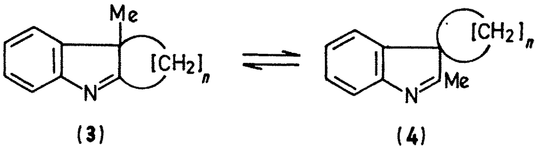
(**1**) (**2**)

a; R^1 = R^3 = Me, R^2 = Et
b; R^1 = Me, R^2 = R^3 = Et

SCHEME 1

TABLE 1.† *Equilibrium constants of aryl-*3H-*indoles* (I; R^1 = R^3 = Me, R^2 = *p*-X-C_6H_4-)

X	Cl	F	H	Me	MeO
K	2·2	1·5	1·4	0·50	0·32



(**3**) (**4**)

SCHEME 2

Systematic alteration of the *p*-substituent in 2-phenyl-3,3-dimethyl-3*H*-indoles demonstrates the polar effect on the reaction (Table1). Electron-donating substituents decrease the *K* values, apparently through mesomeric stabilization of the *N*-protonated species, and *vice versa*. Interesting ring-isomerism (Scheme 2) is generally observed under these conditions (Table 2). The equilibrium point is highly sensitive to relative ring size.

TABLE 2.† *Equilibrium constants of ring-isomerism*

n	4	5	6
(**3**) : (**4**)	0·09	28	0·80

† Satisfactory analytical and spectral data were obtained for all compounds.

(*Received, August 26th,* 1969; *Com.* 1313.)

---

[1] P. L. Julian, E. W. Meyer, and H. C. Prins, in "Heterocyclic Compounds," ed. R. C. Elderfield, Wiley, New York, 1952, vol. 3, p. 1; M. Nakazaki, *Bull. Chem. Soc. Japan*, 1960, **33**, 461; M. Nakazaki, K. Yamaoto and K. Yamagami, *ibid.*, p. 466; M. Nakazaki, *ibid.*, p. 472; A. H. Jackson and P. Smith, *Tetrahedron*, 1968, **24**, 2227.

[2] Y. Kanaoka, K. Miyashita, and O. Yonemitsu, *Tetrahedron*, 1969, **25**, 2752.

[3] F. J. Evans, G. G. Lyle, J. Watkins, and R. E. Lyle, *J. Org. Chem.*, 1962, **27**, 1553.