NEW SYNTHESIS OF 5,6-BENZINDOLE

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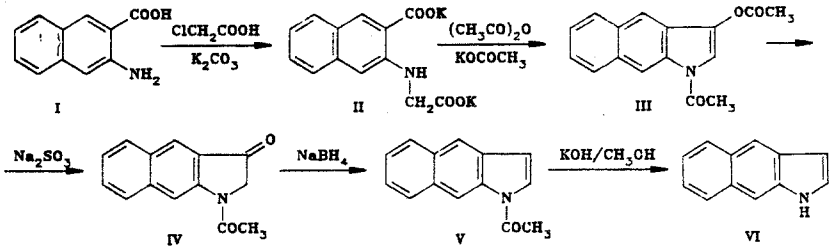
A method has been developed for the synthesis of linear 5,6-benzindole by reduction of N-acetyl-5,6-benzindoxyl with $NaBH_4$ and subsequent hydrolysis of the N-acetyl group.

Many biologically active materials have been found among compounds of the indole and benzindole series. In this respect, derivatives of linear 5,6-benzindole are of great interest. However, at the present time the biological and chemical properties of linear benzindole have been studied very little due to the difficulty in obtaining these compounds. Attempts to synthesize linear benzindole have been made repeatedly. However, the methods known in the literature [1-3] for the synthesis of unsubstituted 5,6-benzindole are laborious and proceed with low yields.

We propose a method of synthesis which consists of the reduction of N-acetyl-5,6-benzindoxyl (IV) and the subsequent hydrolysis of the acyl group in compound V; this makes it possible to obtain 5,6-benzindole by a less difficult route and in higher yield compared to those known previously. The yield of linear benzindole was 26% based on the initial 2,3-aminonaphthylcarboxylic acid (I).



The synthesis of compounds II-IV has been reported previously [4, 5]. At all stages except for the formation of acetylbenzindole V, the yield was close to quantitative.

By using the proposed method it is possible to obtain 5,6-benzindole and its derivatives in sufficient quantities for studying their chemical and biological properties and also for their practical application.

EXPERIMENTAL

The PMR spectra were obtained on a Varian H-100 spectrometer in solutions of acetone-d_6 and chloroform-d_3 with TMS as internal standard. IR spectra were recorded on a Perkin–Elmer 180 spectrometer in KBr disks or in chloroform solutions in standard cells. TLC was conducted on Silufol UV-254 plates, with chloroform as eluent.

N-Acetyl-5,6-benzindole (V). To 1 g (4.6 mmole) of compound IV in 35 ml of diglyme at 0-2°C was added dropwise a solution of 0.4 g (15.8 mmole) of $NaBH_4$ in 10 ml of diglyme and after that a solution of 0.96 g (8.9 mmole) of boron trifluoride etherate in 5 ml of diglyme. The reaction mass was kept at 20°C for 15 h then poured onto crushed ice and extracted with chloroform, dried with $MgSO_4$, and the solvent was evaporated. The blue-violet crystals were purified on 40/100 μm silica gel (Czechoslovakia), a mixture of petroleum ether–ether (1:1) being used as eluent. Yield 0.28 g (30%), R_f 0.70, mp 110-111°C. IR spectrum (KBr): 1697 cm^{-1} (N–CO). PMR spectrum [$(CD_3)_2CO$]: 2.70 (3H, s, CH_3); 7.91 (1H, d, J_{23} = 4.45 Hz, 2-H)

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6.84 (1H, q, J_{39} = 2.2 Hz, 3-H); 8.10 (1H, s, 4-H); 8.95 (1H, s, 9-H); 8.02 and 7.98 (2H, m, 5-H and 8-H); 7.46 ppm (2H, m, 6-H and 7-H). Found, %: C 80.5, H 5.4, N 6.4. $C_{14}H_{11}NO$. Calculated, %: C 80.4, H 5.3, N 6.7.

5,6-Benzindole (VI). 25 ml of a 5% methanol solution of KOH was added to 0.1 gram (0.478 mmole) of compound V. The mixture was kept at 40-50°C for 15 min, then at 20-22°C for 24 h. The methanol was evaporated and the residue extracted with ether. The ether layer was washed with water and dried over $MgSO_4$. After evaporation of ether, 5,6-benzindole was obtained in the form of white or light pinkish flakes, yield 0.07 g (88%), R_f 0.80, mp 180-181°C. IR spectrum in $CHCl_3$: 3490 (NH); in KBr: 3415 (NH), 1610 (w), 1580 (w), 1560 (w), 1518 (m), 1492 (m) (skeletal vibrations with primary participation of multiple bonds), 860 (s), 736, 703 cm^{-1} (s) (nonplanar vibrations of CH and NH). PMR spectrum ($CDCl_3$): 7.16 (1H, m, J_{23} = 3.17, $J_{2'}$ = 2.68 Hz, 2-H); 6.48 (1H, m, J_{31} = 1.95, J_{39} = 0.98 Hz, 3-H); 7.95 (1H, s, 4-H); 7.76 and 7.69 (2H, m, 5-H and 8-H); 7.22 and 7.12 (2H, q, 6-H and 7-H); 7.72 ppm (1H, s, NH).

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SYNTHESIS OF TETRAPHENYLPORPHINES WITH ACTIVE GROUPS IN THE PHENYL RINGS. 4.* FUNCTIONALLY SUBSTITUTED MONOHYDROXY DERIVATIVES OF TETRAPHENYLPORPHINE

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Monosubstituted porphyrins bonded to 8-hydroxyquinoline, α-naphthalene, anthraquinone, and naphthoquinone residues, as well as dimeric porphyrins, were obtained by alkylation of monohydroxyphenyltriphenylporphines.

In nature metalloporphyrins function in the composition of protein formations, the active groups of which have a pronounced effect on the properties of the metal complexes [2]. The synthesis and study of porphyrins having on the periphery of their molecules active functional groups that are capable of interacting with the central metal atom of the porphyrin ring are therefore of great value.

The synthesis of such compounds, which is based on modification of natural porphyrins, is quite complex and includes a large number of steps [3]. In addition, the bonds formed after "tying" of residues with active groups are not very strong (this is primarily the case for amide bonds [4]).

For the synthesis of such compounds it is interesting to use synthetic porphyrins with hydroxy groups that are capable of forming ether bonds. For this, we selected tetraphenylporphine derivatives that have high stabilities and are readily formed in the condensation of pyrrole with benzaldehydes [5].

*See [1] for communication 3.

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