INDOLE DERIVATIVES

XLVII*. THE PRODUCT OF THE TRANSFORMATION OF 4-(INDOL-3-YL)BUT-1-YL TOSYLATE ON A COLUMN OF SILICA

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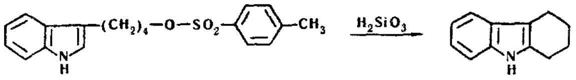
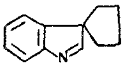
It has been established that when 4-(indol-3-yl)butan-1-ol is passed through a column containing hydrated silica, 3H-indole-3-spiro-1'-cyclopentane is formed and this then rearranges into tetrahydrocarbazole.

On being passed through a column of hydrated silica [2], 4-(indol-3-yl)but-1-yl tosylate alkylates itself in position 2 of the indole nucleus with the formation of tetrahydrocarbazole (II).

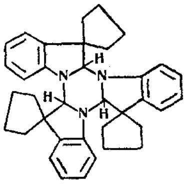


I II

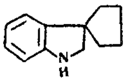
According to the new theory of electrophilic substitution in 3-substituted indoles [3], it may be considered that II is formed as the result of a Plancher rearrangement of the 3H-indole-3-spiro-1'-cyclopentane (III) first formed.



III



IV



V

To confirm this hypothesis, we obtained III by the method described for 3H-indole-3-spiro-1'-cyclopropane [4]. On contact with silica, III was converted almost completely into tetrahydrocarbazole. On storage for some days, compound III was converted into the trimer IV. The structures of III and IV were confirmed by comparing their spectroscopic characteristics with those of 3,3-disubstituted 3H-indoles and the products of their trimerization [5, 6], by a determination of the molecular weight of compound IV, and by converting the 3H-indole III by hydrogenation into the indoline V. We have obtained compound IV previously in the alkylation of potassium isopropylideneglycerate with 4-(indole-3-yl)but-1-yl tosylate [7], as is confirmed by a comparison of their IR spectra and the absence of a depression of the melting point of a mixture of them.

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*For Communication XLVI see [1].

Mendeleev Chemical and Technological Institute, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 6, pp. 759-760, June, 1970. Original article submitted February 23, 1968.

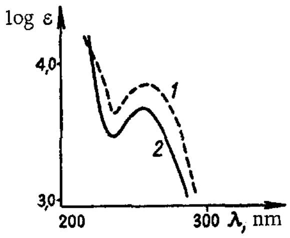

Fig. 1. UV spectra: 1) 3H-indole-3-spiro-1'-cyclopentane; 2) 2-ethyl-3H-indole-3-spiro-1'-cyclopentane. Solvent ethanol.

EXPERIMENTAL

The IR spectra were taken on a UR-10 instrument in the form of mills in paraffin oil (for crystalline compounds) or as a liquid film (for oily products). The PMR spectra* were recorded on a model N-6013 instrument with chloroform as the solvent and tetramethylsilane as internal standard. The UV spectra were taken on an SF-4 instrument in ethanol.

3H-Indole-3-spiro-1'-cyclopentane (III). A mixture of 20 ml of dry tert-butanol and 0.39 g (0.01 g-atom) of metallic potassium was boiled under reflux until all the potassium had reacted (2 h to 2 h 30 min). The excess of the alcohol was distilled off in vacuum, the potassium tert-butoxide obtained was suspended in 45 ml of absolute tetrahydrofuran, and, with stirring at 20°C, 3.43 g (0.01 mole) of 4-(indol-3-yl)but-1-yl tosylate (I) [6] in 25 ml of absolute tetrahydrofuran was added over 10 min. The mixture was stirred in a current of dry nitrogen for 4 h, the precipitate of potassium p-toluenesulfonate was filtered off and washed with tetrahydrofuran, and the filtrates were combined and evaporated in a current of nitrogen. This gave III in the form of a colorless oil, yield quantitative. UV spectrum (Fig. 1): λ_{max} 253 nm (log ε 3.479). PMR spectrum: singlet at about 7.98 ppm (δ scale) – proton at C_2; broad multiplets in the 7.7-6.3 and 2.8-1.4 ppm regions – aromatic protons and the protons of the cyclopentane ring, respectively; very small singlets in the 4.92, 4.35, and 4.18 ppm regions – three protons of the hexahydrotriazine ring of the trimer IV present in the monomer III. IR spectrum: 1550, 1600 cm^{-1} (C=N and C=C atom). Picrate of III: dark red crystals (from ethanol), mp 145°C. Found, %: C 53.7; H 4.2; N 14.1. $C_{18}H_{16}N_4O_7$. Calculated, %: C 54.0; H 4.0; N 14.0.

On standing for a day, III crystallized. This gave 1.5 g (88%) of IV, mp 136-137°C (from cyclohexane). PMR spectrum: singlets in the 4.94, 4.25, and 4.13 ppm regions – three protons of a hexahydrotriazine ring. UV spectrum: λ_{max}, nm (log ε): 256 (4.24); 298 (3.70). Found, %: C 84.6; H 7.8; N 8.2. Mol. wt. 487 (cryoscopically in benzene). $C_{36}H_{33}N_3$. Calculated, %: C 84.2; H 7.6; N 8.2; mol. wt. 513.

Tetrahydrocarbazole (II). A solution of 1 g (0.006 mole) of freshly prepared III in 10 ml of chloroform was deposited on a column containing hydrated silica, and after 12 h chloroform eluted 0.9 g (90%) of II, mp 113-114°C (from methanol) [7]. A mixture with an authentic sample of tetrahydrocarbazole showed no depression of the melting point.

The Indoline-3-spiro-1'-cyclopentane (V). A solution of 0.35 g (0.002 mole) of III in 15 ml of tetrahydrofuran was treated with 30 mg of Pd/C and 2 to 3 drops of conc. HCl, and hydrogenation was carried out at 30 cm of water. After 2 h, 45 ml (0.002 mole) of hydrogen had been absorbed. The catalyst was filtered off and washed with tetrahydrofuran, the filtrates were combined, the solvent was distilled off in vacuum, the residue was dissolved in ether, and the ethereal solution was washed with bicarbonate solution and with water and dried; the ether was distilled off in vacuum and the residue was subjected to molecular distillation (10^{-3} mm, 160°C). This gave 0.22 g (64%) of V, mp 49-50°C. IR spectrum: 3200 cm^{-1} (N–H), 1600 cm^{-1} (C=C of a benzene ring), 740 cm^{-1} (ortho-disubstituted benzene ring). UV spectrum, λ_{max}, nm (log ε): 242 (3.74); 293 (3.34). Found, %: C 83.2; H 8.5; N 7.9. $C_{12}H_{15}N$. Calculated, %: C 83.2; H 8.7; N 8.1. Picrate of V: light yellow crystals, mp 169°C (from ethanol). Found, %: C 54.0; H 4.5; N 13.9. $C_{18}H_{18}N_4O_7$. Calculated, %: C 53.7; H 4.5; N 13.9.

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