

FORMATION OF DIINDOLYLMETHANE DERIVATIVES FROM
INDOLE DERIVATIVES AND SCHIFF BASES

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UDC 547.759.1

Indoles react with aromatic aldehydes to form diindolylmethane derivatives.

It is known [1] that Schiff bases readily form addition products with enamines. Indole, whose chemical behavior is somewhat reminiscent of enamines, also reacts with Schiff bases. It reacts with aliphatic aldimines to form 3-aminomethyl derivatives of indole, which are convenient starting compounds for the synthesis of various compounds of the indole series.

We have shown that aromatic aldimines react with indole to form diindolylmethane derivatives. The reaction proceeds on prolonged refluxing of the components in toluene or at 20°C in acetic acid. The expected aminomethylindoles are possibly formed in the first stage of the reaction but subsequently react with a second molecule of indole and are converted to diindolylmethane derivatives:

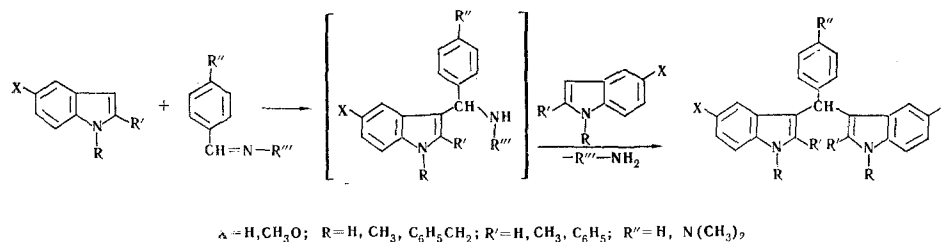


TABLE 1.

X	R	R'	mp, °C	Empirical formula	Found, %			Calc., %			IR spectrum,* ν , cm^{-1}	Yield, %
					C	H	N	C	H	N		
H	$\text{C}_6\text{H}_5\text{CH}_2$	H	137	$\text{C}_{37}\text{H}_{30}\text{N}_2$	88,8	6,0	5,5	88,4	6,0	5,6	1495, 1470	100
H	CH_3	H	192	$\text{C}_{25}\text{H}_{22}\text{N}_2$	85,8	6,2	8,0	85,7	6,3	8,0	1610, 1485	50
H	H	CH_3	248	$\text{C}_{25}\text{H}_{22}\text{N}_2$	86,9	6,5	8,1	85,7	6,3	8,0	3400, 1610, 1490	66
H	H	C_6H_5	265	$\text{C}_{35}\text{H}_{26}\text{N}_2$	88,8	5,7	5,6	88,6	5,5	5,9	3420, 1600	56
H	H	H	106	$\text{C}_{23}\text{H}_{18}\text{N}_2$	85,5	6,0	8,7	85,7	5,6	8,7	3410, 1610, 1490	63
CH_3O	CH_3	CH_3	226	$\text{C}_{29}\text{H}_{32}\text{N}_2\text{O}$	79,2	7,1	—	79,1	7,3	—	1620, 1580, 1490	82

*The IR spectra of KBr pellets were recorded with a UR-10 spectrophotometer.

Institute of Chemistry, Academy of Sciences of the Moldavian SSR, Kishinev. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp.1209-1210, September, 1971. Original article submitted September 11, 1970.

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Compounds of this type are formed in appreciable quantities on introduction of indole and its homologs into the Mannich reaction, and their yields increase as the temperature at which the reaction is carried out is raised [3]. The formation of diindolylmethane derivatives in the reaction of Schiff bases with indole and its homologs is independent of the temperature at which the reaction is carried out, since we obtained the same compounds when the reaction was run at 20° (in acetic acid) or at -50° (in ether-acetic acid), which indicates the particularly high instability of the intermediate aminomethyl derivatives.

The structures of the addition products were proved by the fact that the same diindolylmethane derivative is obtained on reaction of indole with various anils of the same aldehyde. The structures were confirmed by IR spectroscopy. The purities of the addition products were proved by chromatography in a thin layer of aluminum oxide in various solvent systems.

EXPERIMENTAL

Di(3-indolyl)(p-dimethylaminophenyl)methane. A solution of 1.12 g (0.005 mole) of p-dimethylaminobenzalaniline in 10 ml of acetic acid was added slowly with stirring to a solution of 1.17 g (0.01 mole) of indole in 5 ml of acetic acid, and the mixture was allowed to stand at 20° for 12 h. The crystalline precipitate was removed by filtration and recrystallized from alcohol or from benzene-petroleum ether to give 1.8 g (100%) of a product with mp 203°. Found %: C 82.2; H 6.5; N 11.2. $C_{25}H_{23}N_3$. Calculated %: C 82.2; H 6.3; N 11.5. IR spectrum (UR-10, KBr pellet): 3400 (NH), 1610 and 1480 cm^{-1} (indole ring C-C) [4].

The same compound was obtained in 67% yield under similar conditions from indole and N-(p-dimethylaminobenzal)-p-toluidine. Their melting points, IR spectra, and R_f values (thin-layer chromatography on aluminum oxide) were identical.

Bis(1-methyl-3-indolyl)(p-dimethylaminophenyl)methane. This was obtained as described in the preceding example by the reaction of 1-methylindole and p-dimethylaminobenzalaniline (61% yield) of N-(p-dimethylaminobenzal)-p-toluidine (20% yield) and had mp 217°. Found %: C 83.0; H 7.0; N 10.7. $C_{27}H_{27}N_3$. Calculated %: C 82.3; H 6.9; N 10.7. IR spectrum: 1615 and 1480 cm^{-1} (indole ring C-C).

The characteristics of the other compounds of this type, which were obtained as described above, are presented in Table 1.

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