9-ALKENYLCARBAZOLES.

7.* REGIOSPECIFIC AND STEREOSPECIFIC ADDITION OF CARBAZOLE AND INDOLE TO PHENYLACETYLENE. STRUCTURE AND SOME PROPERTIES OF cis-9-(2-PHENYLVINYL)CARBAZOLE

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Under the influence of strong bases in dimethyl sulfoxide (DMSO) under mild conditions, carbazole and indole add smoothly to phenylacetylene to give cis isomers of 9-(2-phenylvinyl)carbazole and 1-(2-phenylvinyl)indole. A cis-phenyl group markedly reduces the activity of the double bond of phenylvinylcarbazole in acid hydrolysis, but, as in the case of other alkenylcarbazoles, protonation takes place at the vinyl C_β atom. It was established by ^{13}C NMR and UV spectroscopy that the carbazolyl group displays π-donor properties with respect to the styryl group.

The reaction of carbazole with acetylene, which leads to 9-vinylcarbazole (I), has been studied thoroughly [2] owing to its use in the preparation of photosensitive polymers and copolymers. However, no data on the reaction of carbazole with acetylene homologs are available, whereas it is completely apparent that it is a simple synthetic route to diverse 9-alkenylcarbazoles. We found that carbazole and indole add regiospecifically and stereospecifically in superbase media, viz., KOH or NaOH in dimethyl sulfoxide (DMSO), to phenylacetylene to give under mild conditions (as compared with acetylene) cis isomers of 9-(2-phenylvinyl)carbazole (IIa) and 1-(2-phenylvinyl)indole (IIb).

$$HNAr + C_6H_5C\equiv CH \xrightarrow[\text{DMSO}]{\text{KOH}} \overset{ArN}{\underset{H}{}}\!>\!\underset{A}{C}=\underset{B}{C}\!<\!\overset{C_6H_5}{\underset{H}{}}$$

IIa,b

a ArN= 9-carbazolyl; b ArN=1-indolyl

TABLE 1. cis-9-(2-Phenylvinyl)carbazole (IIa) and cis-1-(2-Phenyl)indole (IIb)

Compound	mp, °C	bp (2 mm), °C	IR spectrum,* cm^{-1}		PMR spectrum,† δ, ppm			Found, %			Empirical formula	Calculated, %		
			$\nu_{C=C}$	$\delta_{=C-H}$	H_A	H_B	J_{A-B}, Hz	C	H	N		C	H	N
IIa	99—100	233—238	1660	790	6,80	6,43	8,6	89,8	5,3	5,6	$C_{20}H_{15}N$	89,2	5,6	5,2
IIb	67—68	220—225	1670	790	6,90	6,17	9,75	73,1	4,8	5,5	$C_{16}H_{13}N$	72,4	4,9	5,3

*The out-of-plane δ_{C-H} vibrations and those of the 1-substituted phenyl ring for IIa and IIb lie at 700 and 756 and 700 and 749 cm^{-1}, respectively.

†The chemical shifts of the H_2 and H_3 protons of the pyrrole ring of IIb are found at 6.93 and 6.40, respectively, with J_{2-3} = 3.5 Hz.

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*See [1] for Communication 6.

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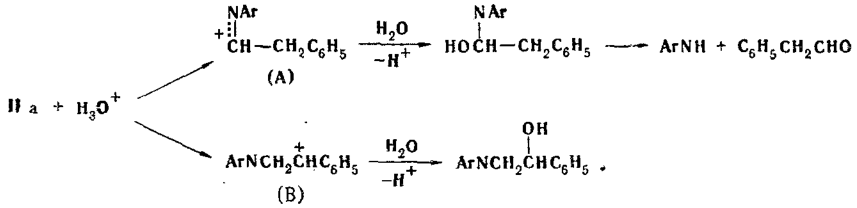
TABLE 2. UV Spectra of 9-Vinylcarbazole (I) and cis-9-(2-Phenylvinyl)carbazole (IIa) in Ethanol

Compound	λ_{max}, nm	log ε
I	338,5	3,59
	325,5	3,55
IIa	340	3,99
	326	4,00
	308,5	4,05

The structure of IIa, b was established by means of the IR and PMR spectra (Table 1), and their structure as cis isomers was confirmed unambiguously by the vicinal spin–spin coupling constants of 8.6 Hz for IIa and 9.75 Hz for IIb. The H_A and H_B chemical shifts of IIa are in good agreement with the values calculated by the additive scheme in [3], viz., 6.99 and 6.32 ppm, respectively.

It has been previously shown that an effect of p–π conjugation of the p electrons of the nitrogen atom with the π electrons of the C=C bond, which increases the electron density on the vinyl C_B atom, is manifested in the 9-alkenylcarbazole series [4, 5]. As a result of this, attack of the electrophile exclusively at the C_B atom is observed in reactions involving electrophilic addition to the C=C bond of these compounds and particularly in acid hydrolysis [6]. On the other hand, π–π conjugation in styrene also leads to a certain increase in the electron density on the terminal vinyl atom; this is recorded, in particular, by ^{13}C NMR spectroscopy [7]. In conformity with this effect, protonation of the terminal vinyl atom also occurs in the hydration of styrenes [8]. Compound IIa, which is a unique "hybrid" of vinylcarbazole I and styrene, makes it possible to determine the preponderance of one or another effect both in the ground state and in reactions involving electrophilic addition to the C=C bond.

From what we have stated above, it might have been proposed that acid-catalyzed hydration of IIa may proceed via two pathways with the intermediate formation of either carbenium-immonium ion A (as in the hydrolysis of the previously investigated alkenylcarbazoles [6]) or ion B, as in the case of styrenes:



We found that the hydrolysis of IIa in dioxane–water (80:20% by volume) under the influence of sulfuric acid (0.79 mole/liter) at 135°C is many orders of magnitude slower than in the case of I and leads to the formation of exclusively carbazole and phenylacetaldehyde. The latter was identified through its 2,4-dinitrophenylhydrazone. Thin-layer chromatography (TLC) of the reaction mixture after hydrolysis does not reveal any products other than carbazole. This result leads to the conclusion that the electron density is higher on the C_B atom of IIa as a result of predominance of the effect of p–π conjugation over the resonance effect of the phenyl group. At the same time, the sharp decrease in the reactivity of alkene IIa as compared with I constitutes evidence for the appreciable counteraction of p–π conjugation on the part of the phenyl ring. The data from the ^{13}C NMR spectrum of IIa are in agreement with these conclusions: C_1 109.24, C_2 124.04, C_3 118.28, C_4 118.43, C_{10} 137.37, C_{11} 122.19, C_A 124.43, C_B 120.13, C_i 132.95, C_o 126.44, C_m 126.89, and C_p 125.95 ppm. One's attention is first of all directed to the large shift of 16.83 ppm to the strong field of the C_B atom relative to the =CH atom of styrene (with a chemical shift of 136.96 ppm [7]); the magnitude of shielding of both vinyl atoms in IIa is the same as for 9-alkenylcarbazoles [4, 5] but is opposed to that of styrene [7]. In addition, one observes appreciable shifts to the strong field of the C_i, C_m, and C_p atoms of the phenyl ring of 4.45, 1.26, and 1.21 ppm, respectively, relative to the analogous positions of styrene [7]. All of this indicates that the carbazolyl ring displays a π-donor effect with respect to the styryl group in IIa. However, this effect should be reduced because of steric inhibition of p—π conjugation as a result of deviation of the carbazolyl ring and the phenyl group from the plane of the C=C bond, as previously demonstrated by means of UV and NMR spectroscopy and chemical methods for cis-9-alkenylcarbazoles [1, 5, 6]. In the case of IIa this is reflected in the certain shielding of all of the positions of the carbazolyl ring in the NMR spectrum relative to I [5],* since a decrease in the p—π conjugation is equivalent to a decrease in the π-acceptor properties of the C=C bond with respect to the carbazolyl ring. The $\Delta\delta$ values for C_1, C_2, C_3, C_4, C_{10}, and C_{11} are −0.94, −1.79, −1.56, −1.90, −2.44, and −1.75 ppm, respectively. Nevertheless, conjugation of the carbazolyl ring with the styryl fragment is not completely excluded, which follows from a comparison of the UV spectra of I and IIa. It is apparent from Table 2 that both long-wave absorption maxima of IIa have considerably greater intensities; this indicates extension of the conjugation system, which occupies all three structural fragments of the molecule.

EXPERIMENTAL

The ^1H NMR spectra of solutions of the compounds in CCl_4 were recorded with a BS-487C spectrometer; the ^{13}C NMR spectra of solutions of the compounds in $CDCl_3$ were recorded with a Brucker HX-90 spectrometer (22.63 MHz) under conditions of selective and complete suppression of the spin—spin coupling of ^{13}C with the proteins relative to tetramethylsilane with an accuracy of ±0.05 ppm. The IR spectra of Vaseline oil suspensions of the compounds were recorded with a UR-20 spectrophotometer. The UV spectra of $2 \cdot 10^{-4}$ and 10^{-4} mole/liter solutions of I and IIa, respectively, in ethanol were recorded with a Specord UV-vis spectrophotometer.

cis-9-(2-Phenylvinyl)carbazole (IIa). An 8-g (0.048 mole) sample of carbazole, 2 g of powdered KOH, and 10.5 ml (0.095 mole) of phenylacetylene were added to 100 ml of DMSO, and the mixture was heated to 110°C and stirred at this temperature for 7.5 h. It was then cooled to 20°C, and the dark reaction solution was treated with 100 ml of benzene. The mixture was poured into 500 ml of water, and the aqueous layer was separated and extracted with 50 ml of benzene. The benzene solutions were combined and washed with water, and then the benzene was removed by distillation, and the residue was distilled at 233-238°C (2 mm) to give 12.5 g (97%) of a yellowish substance that crystallized upon standing. Recrystallization from ethanol gave white acicular crystals with mp 99-100°C.

cis-1-(2-Phenylvinyl)indole (IIb). A mixture of 5 g (0.043 mole) of indole, 80 ml of DMSO, 1.25 g of powdered KOH, and 9.4 ml (0.085 mole) of phenylacetylene was stirred at 100°C for 2.5 h, after which the product was isolated as indicated above to give 7.5 g (80%) of a light-yellow substance that crystallized rapidly. Recrystallization from ethanol gave white lamellar crystals with mp 67-68°C.

Acid Hydrolysis of cis-9-(2-Phenylvinyl)carbazole (IIa). A 0.5-g (0.002 mole) sample of IIa was dissolved in 35 ml of a mixture of dioxane with water (80:20% by volume), 2.7 ml of concentrated H_2SO_4 (0.79 mole/liter) was added, and the mixture was heated at 135°C for 4 h. Thin-layer chromatography (TLC) of the reaction mixture on Silufol plates in a benzene—CCl_4—acetone system (85:14:1) demonstrated the absence of starting IIa (R_f 0.82) and the presence of carbazole (R_f 0.51). The solution was poured into 200 ml of water, and 0.25 g of precipitated carbazole was removed by filtration. A solution of 0.4 g of 2,4-dinitrophenylhydrazine in 65 ml of water acidified with 10 ml of H_2SO_4 was added to the filtrate, and the mixture was allowed to stand overnight. It was then filtered to give 0.4 g (70%) of phenylacetaldehyde 2,4-dinitrophenylhydrazone with mp 106-107°C (mp 110°C [9]).

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*In [5] the positions of the chemical shifts of the C_3 and C_4 atoms of 9-alkenylcarbazoles were erroneously interchanged.

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INDOLOBENZOTHIOPHENES.

2.* SOME ELECTROPHILIC SUBSTITUTION REACTIONS OF INDOLO[6,5-d]BENZO[b]THIOPHENE

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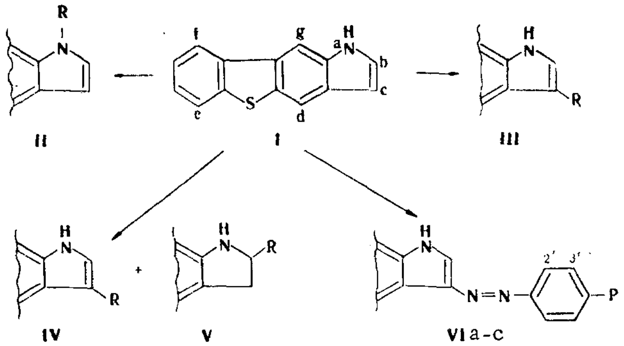
The behavior of indolo[6,5-d]benzo[b]thiophene in acylation, Mannich, Vilsmeier, and diazo coupling reactions was investigated. Acylation with acetic anhydride proceeds unambiguously at the pyrrole nitrogen atom to give 1-acetylindolo[6,5-d]benzo[b]thiophene. The products of formylation are 2- and 3-formylindolo[6,5-d]benzo[b]thiophenes. In the case of the Mannich reaction and diazo coupling substitution takes place in the 3 position of the indolobenzo[b]thiophene ring. The structures of the products obtained were proved by spectroscopic methods.

The present research was devoted to a study of the electrophilic substitution reactions of the previously synthesized indolo[6,5-d]benzo[b]thiophene (I) [1]. 1-Acetylindolo[6,5-d]benzo[b]thiophene (II) was obtained by the reaction of acetic anhydride with I. Data from PMR, IR, UV, and mass spectrometry show that the acetyl group is located in the 1 position.



II R=COCH$_3$; III R=CH$_2$N(CH$_3$)$_2$; IV,V R=CHO; VI a R=H; b R=Cl; c R=NO$_2$

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*See [1] for Communication 1.

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