9-ALKENYLCARBAZOLES.

6.* SYNTHESIS AND STRUCTURE OF cis-9-PROPENYLCARBAZOLES

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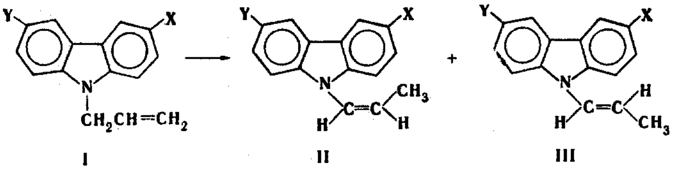
UDC 547.759.32:547.07:541.634

A number of cis-9-propenylcarbazoles were synthesized in good yields by isomerization of 9-allylcarbazoles by the action of tert-BuOK in dimethyl sulfoxide. It was established that cis-9-propenylcarbazole is less thermodynamically stable than its trans isomer. It was shown by ^{13}C NMR, UV, and IR spectroscopy that the effect of p–π conjugation in cis-9-propenylcarbazole decreases as compared with the trans isomer as a result of the noncoplanarity of the C=C bond and the carbazole ring.

The trans isomers of 9-alkenylcarbazoles are presently relatively easy to obtain [1, 2], whereas the cis isomers have not been obtained in pure form. Thus, the isomerization of 9-allylcarbazole (Ia) with potassium amide leads to a mixture of cis- and trans-9-propenylcarbazoles (IIa and IIIa) in a ratio of 67:33 [3], whereas isomerization with butyllithium gives a mixture of isomers with an 85:15 composition [4]. A mixture with approximately equal percentages of isomers IIa and IIIa is formed in the dehydrochlorination of 9-(2-chloropropyl)carbazole [5].

We studied the isomerization of 9-allylcarbazoles (Ia-d) under the influence of tert-BuOK in dimethyl sulfoxide (DMSO). As a result of the isomerization, carbazole I is converted completely to II and III, and other products were not detected. The reaction rate reaches a maximum at 0.2 mole % tert-BuOK with respect to carbazole Ia; a further increase in the catalyst concentration has virtually no effect on the rate of the process, and the reaction is complete in 30 min. According to the data from PMR spectroscopy, an increase in the reaction time and temperature leads to a decrease in the molar ratio of propenylcarbazoles IIa and IIIa (Table 1). An increase in the tert-BuOK concentration in tert-BuOH (from 0.54 to 1.1 N vis-à-vis a constant molar ratio of 0.2 of the catalyst to Ia) also leads to a certain decrease in the stereoselectivity of the reaction.



I, II, III a X=Y=H; b X=Cl, Y=H; c X=Y=Cl; d X=NO_2, Y=H

Thus, the results provide evidence that in the kinetically controllable reaction allylcarbazole Ia forms IIa, which undergoes isomerization to the thermodynamically more stable trans isomer IIIa; this is displayed particularly clearly when the reaction time or temperature is increased. This is in agreement with the data on the isomerization of some N-allylamines by the action of tert-BuOK [6].

Taking the results set forth above into account, we synthesized cis-propenylcarbazoles IIa-d in quantitative yields with an isomeric purity of 88-90% from the corresponding allylcarbazoles Ia-d (Table 2).

We estimated the relative thermodynamic stabilities of the cis- and trans-propenylcarbazoles by determining the isomerization equilibrium constants (K_{eq}), which were observed

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*See [1] for communication 5.

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0009-3122/80/1603-0252$07.50

TABLE 1. Dependence of the Composition of the Isomeric Mixture of Propenylcarbazoles IIa and IIIa on the Time and Temperature of Isomerization of Ia ([Ia] = 0.83 mole/liter, [tert-BuOK]* = 0.166 mole/liter)

Temp., °C	Time,† min	IIa/IIIa isomer ratio
20	30	88/12
	60	81/19
	180	73/27
	300	63/34
30	20	74/26
50	5	67/33
120	1	38/62
180	1	23/77

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*Here and subsequently, a 0.54 N solution in tert-BuOH.

†This is the reaction time corresponding to complete conversion of Ia.

TABLE 2. cis-9-Propenylcarbazoles IIa-d

Compound	Stereoselectivity (II/III)	Isomeric purity*	mp, °C (n_D^{19})	bp, °C (pressure mm)	PMR spectrum,† δ, ppm			Found, %			Empirical formula	Calc., %		
					H_α	H_β	CH_3	C	H	N		C	H	N
IIa	88/12	100	40—41	160—170 (5)	6.65	5.83	1.44	87.1	6.3	6.7	$C_{15}H_{13}N$	87.0	6.3	6.8
IIb	87/13	100	(1.6674)	180—190 (5)	6.45	5.84	1.45	74.4	5.0	6.0	$C_{15}H_{12}ClN$	74.5	5.0	5.8
IIc	88/12	95	62—63		6.48	5.85	1.46	65.4	4.1	5.1	$C_{15}H_{11}Cl_2N$	65.2	4.0	5.1
IId	90/10	95	93—95		6.65	6.0	1.55	71.7	4.7	11.9	$C_{15}H_{12}N_2O_2$	71.4	4.8	11.1

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*After crystallization from ethanol.

†For all of the compounds $J_{\alpha,\beta}$ = 8.0, J_{β,CH_3} = 7.0 and J_{α,CH_3} = 1.5 Hz.

by measuring the integral intensities of the signals of the CH_3 groups of both isomers in the PMR spectra; virtually identical results were obtained when allylcarbazole Ia, trans isomer IIIa, and its mixtures with cis isomer IIa were used (Table 3). Equilibrium is reached 3-4 h after the start of isomerization, and, within the limits of the error inherent in the method of analysis, the temperature has virtually no effect on the isomerization K_{eq} constant and, consequently, on the free energy. From the van't Hoff equation $\ln K_{eq} = -\Delta H/RT + \Delta S/R$ with allowance for the lack of a dependence of K_{eq} on the temperature we found that in the IIa $\rightleftarrows$ IIIa isomerization, $\Delta H \approx 0$, while $\Delta S = -6.7 \pm 0.6$ J·deg K^{-1}·mole^{-1} (for 298.15°K). Consequently, the high thermodynamic stability of propenylcarbazole IIIa with respect to cis isomer IIa is due mainly to the entropy factor. The gain in entropy on passing from cis isomer IIa to trans isomer IIIa is explained by the fact that isomer IIa, because of steric interaction of the substituents in the cis position, can exist only in the nonplanar conformation, while isomer IIIa can exist in both the nonplanar and planar conformations, in which the carbazole ring and the plane of the C=C bond are close to coplanar, which ensures the effect of p–π conjugation of the p electrons of the nitrogen atom with the π electrons of the double bond and increases the electron density on the vinyl C_β atom [2]. In the second nonplanar conformation that is peculiar to both isomers the effect of p–π conjugation is either weakened markedly or cannot be manifested at all. Certain spectral

TABLE 3. cis-trans Isomerization of Propenylcarbazoles IIa ⇌ IIIa (Starting Concentration of Ia or IIIa = 0.83 mole/liter, [tert-BuOK]* = 0.166 mole/liter, DMSO as the Solvent)

Temp., °C	K_{eq}	$-\Delta G$, kJ/mole
60	2.4±0.2	2.4±0.2
80	2.2±0.2	2.3±0.2
100	2.1±0.2	2.3±0.2

data constitute evidence for the substantial population of the planar conjugated conformation of trans isomer IIIa as compared with cis isomer IIa. Thus, the chemical shifts [relative to tetramethylsilane (TMS)] of the vinyl C_α and C_β atoms of trans isomer IIIa in the ^{13}C NMR spectra are 124.11 and 117.04 ppm [2], whereas in the case of cis-isomer IIa they are, respectively, 125.2 and 122.6 ppm. Using the approach proposed in [8], in which expressions that interrelate the overall electron density and the chemical shift of the corresponding ethylene carbon atom are presented, one can find the difference in the overall electron densities of the C_β atoms of cis- and trans-isomers IIa and IIIa. This value is 0.018 of an electron charge unit.

The UV spectrum of cis-isomer IIa [λ_{max} 328, 342 nm (log ε 3.54, 3.59)] shows a hypsochromic shift and a decrease in the intensities of both long-wave maxima as compared with the spectra of isomer IIIa [λ_{max} 334, 347 nm (log ε 3.64, 3.69)]. Using these data, we employed the Wepster formula [9] $\cos^2\theta = \varepsilon/\varepsilon_0$, where θ is the angle of deviation from coplanarity, and ε and ε_0 are the coefficients of extinction of the sterically hindered and unhindered isomers, to calculate the angle of rotation about the C_{sp^2}—N bond of the cis isomer in the nonplanar conformation as compared with the planar conformation of isomer IIIa. The calculation for both indicated absorption maxima gave virtually the same angle of rotation of 27°. The propenylcarbazole molecule IIIa is isosteric (with respect to the relative orientation of the plane of the carbazolyl ring and the C=C bond) with respect to 9-vinylcarbazole, whereas for the latter we used x-ray diffraction analysis to establish the existence in the crystalline state of two forms with angles of deviation of the planes of the fragments under consideration of 2.6 and 14° [10]. It follows from these data and from the θ value of 27° presented above that the deviation from coplanarity of cis isomer IIa ranges from 30 to 41°, which is quite close to the deviation from coplanarity of trans-propenylbenzene (35-40°C) [11].

It is interesting to note that the absorption band of the out-of-plane deformation vibrations of =CH shows up in the IR spectra of carbazole IIIa as a doublet with components of approximately equal intensity at 940 and 965 cm^{-1}, whereas the corresponding band of cis-isomer IIa is a singlet at 935 cm^{-1}. In [12] it was shown that the doublet character of the bands of the out-of-plane =CH vibrations, which probably corresponds to the planar and nonplanar conformations, is observed in the IR spectra of N-vinylpyrroles. With allowance for this, one may conclude that the above-mentioned doublet in the IR spectra of trans-isomer IIIa constitutes evidence for a certain population of the nonplanar unconjugated conformation. cis-Isomer IIa can exist only in the nonplanar conformation, and its conformational homogeneity corresponds to the singlet band at 935 cm^{-1}. However, a substantial difference from the data in [12] is the fact that conformational heterogeneity of IIIa is not displayed in the region of the stretching vibrations of the C=C bond: singlets at 1669 and 1685 cm^{-1} for isomers IIa and IIIa, respectively, are observed.

When one compares the results obtained for the isomerization of propenylcarbazoles IIa and IIIa with the data on the thermodynamics of the cis-trans isomerization of alkenyl ethers [13,14], it becomes apparent that the two isomers have virtually identical thermochemical stabilities. A possible explanation for this is the fact that the effect of p–π conjugation is smaller in the 9-alkenylcarbazole series than in the case of alkenyl ethers because of competitive delocalization of the p electrons of the nitrogen atom over the aromatic system of the carbazole ring [2, 7]. The increase in the thermochemical stability of the planar conjugated conformation of trans isomer IIIa as compared with the nonplanar conformation that is peculiar to cis isomer IIa may therefore be insignificant. However, one must also take into account the fact that the difference in the specific solvation of their strongly polar systems in which the isomerization was studied may also affect the stabilities of the isomers.

The inertness of isomer IIa as compared with isomer IIIa in acid hydrolysis, which proceeds via a mechanism involving electrophilic addition to the C=C bond, has also been demonstrated [15], as well as in cationic polymerization [16]. It follows from the results obtained in the present study that this difference in the reactivities of the two isomers cannot be explained by the relatively small difference in their thermodynamic stabilities.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra of solutions of the compounds in CCl_4 were recorded with the BS-487C and XL-100/12 spectrometers, respectively. The IR spectra of mineral oil suspensions were recorded with a UR-20 spectrometer. The UV spectra of solutions of the compounds in $CHCl_3$ were recorded with an SF-16 spectrophotometer.

cis-9-Propenylcarbazole (IIa). A 9-ml sample of a 0.54 N solution of tert-BuOK in tert-BuOH was added to a solution of 5 g (0.024 mole) of 9-allylcarbazole Ia in 20 ml of dry DMSO, and the mixture was allowed to stand at room temperature for 30 min. The course of the reaction was followed by means of thin-layer chromatography on Silufol plates [hexane—benzene (5:3)]. After complete conversion of Ia, the solution was poured onto ice, and the resulting oily substance was extracted with benzene. The benzene layer was washed with water and dried with potassium carbonate. According to the PMR data, the solution contained a mixture of isomers IIa and IIIa in a ratio of 88:12. Vacuum distillation and crystallization from methanol gave 3 g (60%) of propenylcarbazole IIa in the form of white acicular crystals.

Propenylcarbazoles IIb-d were obtained similarly and in the same yields; however, vacuum distillation was not carried out in the case of IIc,d (Table 2).

In conclusion, we sincerely thank G. A. Kalabin for recording the ^{13}C NMR spectrum of IIa.

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