9-ALKENYLCARBAZOLES.

13.* TRIFLUOROACETYLATION OF trans- AND cis-9-ALKENYLCARBAZOLES

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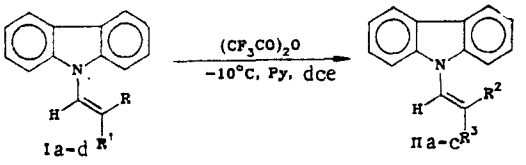
The trifluoroacetylation of 9-alkenylcarbazoles in pyridine takes place regio- and stereospecifically with the formation of the β-trifluoroacetyl derivatives. The cis isomers are inert to trifluoroacetic anhydride.

It is known that vinyl ethers, vinylamides [2], and vinyl sulfides [3] react with trifluoroacetic anhydride in pyridine, giving the corresponding β-trifluoroacetyl derivatives, whereas the reaction in the case of N-vinylpyrroles takes place at the $C_{(2)}$ position of the pyrrole ring [4]. There are hardly any data on the trifluoroacetylation of β-substituted activated alkenes and the stereochemistry of the reaction.

In 9-alkenylcarbazoles (Ia-e) there are two possibilities for electrophilic attack, i.e., one of the positions of the aromatic ring and the β-carbon atom of the alkenyl substituent. In order to assess the relative reactivity of the two nucleophilic centers and to synthesize new carbazole monomers containing a CF_3 group we realized the trifluoroacetylation of a series of 9-alkenylcarbazoles.

During the trifluoroacetylation of 9-vinyl-, trans-9-propenyl-, and trans-9-butenylcarbazoles (Ia, b, c), in contrast to the N-vinylpyrroles [4], the corresponding β-trifluoroacetyl-substituted compounds (IIa-c) are formed readily.



I a—c R=H, a R^1=H, b R^1=CH_3, c R^1=C_2H_5; d, e R^1=H, d R=CH_3, e R=C_6H_5;
II a R^2=H, R^3=$COCF_3$; b, c R^2=$COCF_3$, b R^3=CH_3, c R^3=C_2H_5

cis-9-Propenylcarbazole (Id) and cis-9-(1-vinyl-2-phenyl)carbazole (Ie) remain unchanged under the indicated conditions.

This result agrees with data to the effect that trans-9-alkenylcarbazoles undergo acid hydrolysis through the controlling stage of protonation of the C(β)-alkenyl atom at a substantially higher rate than the cis isomers [5]. It confirms the conclusion that the key stage in the trifluoroacetylation of activated alkenes is electrophilic attack by the cationoid trifluoroacetyl intermediate on the $C_{(\beta)}$-alkenyl atom [2].

The spin—spin coupling constants of the vicinal olefinic hydrogen atoms of (IIa) are equal to 14 Hz, which demonstrates unambiguously the trans configuration of the molecule. We note that the other familiar reaction involving direct substitution in the vinyl group of (Ia), i.e., phosphorylation, also takes place as a trans-stereoselective process [6].

A long-wave shift of the absorption band of the C=O group in the IR spectrum is observed in the transition to compounds (IIb) and (IIc). Such a shift may result from differences in the steric structure of the molecules. In addition, the significant upfield shift (~6 ppm) of the signals for the CF_3 groups in the ^{19}F NMR spectra of compounds (IIb)

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TABLE 1. Chemical Shifts in ^{13}C NMR Spectra of Compounds (IIa-c) (deutrochloroform)

Compound	δ, ppm								
	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(9a)}$	$C_{(4a)}$	$C_{(\alpha)}$	$C_{(\beta)}$	CO
IIa	112,06	127,00	123,94	120,05	137,98	125,80	140,37	98,09	179,58
IIb	110,94	126,25	121,84	120,13	138,28	123,04	138,65	110,49	184,32
IIc	110,49	126,30	121,83	120,33	138,53	124,51	137,64	110,46	182,68

and (IIc) compared with (IIa) agrees more with the cisoid arrangement of the carbazole ring and the CF_3CO substituent, the CF_3 group of which is evidently situated in the cone of the magnetic anisotropy of the aromatic ring. A similar situation is observed in the ^{13}C NMR spectra of cis- and trans-9-propenylcarbazoles; the methyl group of the latter is descreened by ~2 ppm compared with the cis isomer [7].

From examination of the chemical shifts in the ^{13}C NMR spectra of compounds (IIa-c) (Table 1) it follows that the $C_{(1)}$, $C_{(4a)}$, and $C_{(3)}$ positions of the last two compounds are screened substantially (~2 ppm) in comparison with (IIa). Such an effect is typical of the ^{13}C NMR spectra of cis-olefins [8], but it is not so significant in the case of known 9-alkenylcarbazoles [7, 9].

Thus, the substantial spectral differences between (IIa), which has the trans configuration, and the similar compounds (IIb, c) make it possible to assign the latter compounds the Z configuration conclusively. Without entering into a discussion on the reasons for the Z-stereospecificity in the trifluoroacetylation of compounds (Ib, c) we suppose only that intramolecular donor-acceptor interaction between the π system of the carbazole ring and the CF_3CO group in the transition state may play some role in the stereospecificity of the reaction. A similar proposal was recently made to explain the stabilization of the Z configuration in vinyl ethers containing a CF_3 group at the β position [10].

The simplest stereochemical calculations demonstrate the impossibility of the coplanar arrangement of the carbazole and alkenyl fragments in the cis-9-alkenylcarbazoles [11]. This leads to weakening of the conjugation between the p electrons of the nitrogen atom and the π system of the alkenyl fragment and to a decrease in the nucleophilic reactivity of the β-carbon atom. In view of this it could be expected that one of the positions of the aromatic ring would become the object of electrophilic attack in compounds (Id, e), as in 9-methylcarbazole [12]. However, the cis isomers (Id, e) do not change under the conditions for the trifluoroacetylation of the trans isomers, and 9-methylcarbazole even under more drastic conditions (125°C). The reaction of trifluoroacetic anhydride with (Id) in the absence of pyridine at room temperature also does not take place, but heating of the reagents in dichloroethane (DCE) is accompanied by resin formation, and carbazole (5%) and a significant amount of the unreacted (Id) (52%) were isolated from the reaction mixture. Compound (Ie) behaves in a similar way.

The inertness of compounds (Id, e) in reaction with trifluoroacetic anhydride evidently provides experimental evidence for the previous conclusion about the presence of residual p–π conjugation in cis-9-alkenylcarbazoles [5]; the degree of this conjugation is such that the carbazole ring becomes less reactive than in 9-methylcarbazole [9], but the nucleophilicity of the C(β) atom of the alkenyl group does not reach the value corresponding to the trans isomers.

EXPERIMENTAL

The reactions were monitored by TLC on Silufol plates with a 6:3:1 mixture of benzene, hexane, and DCE as eluant. The IR spectra were recorded in Vaseline oil on a UR-20 instrument. The UV spectra were obtained in hexane on a SF-16 spectrophotometer. The ^1H NMR spectra were obtained on a Tesla BS-487C spectrometer at 80 MHz with HMDS as internal standard. The ^{13}C NMR and ^{19}F NMR (with reference to hexafluorobenzene) spectra were obtained on a Tesla BS-567A spectrometer at 25.142 and 94.04 MHz respectively. The reaction mixtures were separated by column chromatography on aluminum oxide of II activity.

trans-9-(1-Vinyl-2-trifluoroacetyl)carbazole (IIa). To a solution of 2.26 g (12 mmole) of (Ia) in 3 ml of DCE and 2 ml (24 mmole) of pyridine at −30°C we added with stirring a solution of 4 ml (28 mmole) of trifluoroacetic anhydride in 5 ml of DCE and 4 ml (48 mmole) of pyridine. The mixture was left at −10°C for 1 h. The precipitate was filtered off and

washed with warm water (3 × 50 ml). After recrystallization from hexane we obtained 2.2 g (65%) of (IIa) in the form of yellow needles; mp 137-137.5°C; R_f 0.2. IR spectrum: 1705 (C=O), 1630, 1570 (C=C); 1210-1130 (C–F); 800, 760, 720 cm^{-1} (C–H). UV spectrum λ_{max} (ε): 235 ($4.2 \cdot 10^4$), 265 ($4.1 \cdot 10^4$), 285 ($4.2 \cdot 10^4$), 295 ($3.9 \cdot 10^4$), 345 nm ($4.6 \cdot 10^3$). ^1H NMR spectrum (deuterochloroform): 6.65 (1H, d, J = 14 Hz, β-H); 7.0-7.67 (6H, m, 1-, 2-, 3-, 6-, 7-, and 8-H); 7.85 (2H, d, J = 6 Hz, 4-, and 5-H); 8.56 ppm (1H, d, J = 14 Hz, α-H). ^{19}F NMR spectrum (DMSO); −88.21 ppm (s, CF_3CO). Found, %: C 66.4; H 3.5; N 1.2. $C_{16}H_{10}F_3NO$. Calculated, %: C 66.4; H 3.46; N 1.4.

Z-9-(1-Propenyl-2-trifluoroacetyl)carbazole (IIb). The compound was obtained under the conditions for the synthesis of (IIa) from 2.1 g (10 mmole) of (Ib) and 4 ml (28 mmole) of trifluoroacetic anhydride. At the end of the reaction the mixture was left at room temperature overnight and was then washed with hot water (3 × 50 ml). The organic layer was separated and dried with calcium chloride.

The solvent was distilled at reduced pressure, and the residue was crystallized from 20 ml of chloroform. The yield was 1.51 g (49%), and the product formed yellow prisms; mp 96-96.5°C, R_f 0.55. IR spectrum 1685 (C=O); 1635, 1590 (C=C); 1240-1140 (C–F); 880, 750, 725 cm^{-1} (C–H). UV spectrum, λ_{max} (ε): 235 ($2 \cdot 10^4$), 285 ($7.2 \cdot 10^3$), 355 nm ($5.7 \cdot 10^3$). ^1H NMR spectrum (carbon tetrachloride): 1.87 (3H, s, CH_3); 6.92-7.37 (6H, m, 1-, 2-, 3-, 6-, 7-, and 8-H), 7.85 (2H, d, J = 7 Hz, 4- and 5-H), 8.10 ppm (1H, s, α-H). ^{19}F NMR spectrum (DMSO): −82.46 ppm (s, CF_3CO). Found, %: C 67.0; H 4.1; N 4.6. $C_{17}H_{12}F_3NO$. Calculated, %: C 67.3; H 3.9; N 4.6%.

Z-9-(1-Butenyl-2-trifluoroacetyl)carbazole (IIc). The compound was obtained similarly to (IIb) from 2.2 g (10 mmole) of (Ic) and 4 ml (28 mmole) of trifluoroacetic anhydride. The yield was 1.36 g (42.5%), and the product formed yellow prisms; mp 95.5-96°C (from chloroform), R_f 0.60. IR spectrum: 1690 (C=O); 1630, 1580 (C=C); 1240-1140 (C–F); 865, 750, 725 cm^{-1} (C–H). UV spectrum, λ_{max}(ε): 235 ($1 \cdot 10^5$), 252 ($1.2 \cdot 10^5$), 285 ($2.5 \cdot 10^4$), 360 nm ($2 \cdot 10^4$). ^1H NMR spectrum (carbon tetrachloride): 0.80 (3H, t, CH_3); 2.43 (2H, q, CH_2); 7.0-743 (6H, m, 1-, 2-, 3-, 6-, 7-, and 8-H), 7.75-8.0 ppm (3H, m, 4-, 5-, and α-H). ^{19}F NMR spectrum (DMSO): −82.36 ppm (s, CF_3CO). Found, %: C 68.0; H 4.2; N 4.3. $C_{18}H_{14}F_3NO$. Calculated, %: C 68.1; H 4.4; N 4.4%.

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