TRIFLUOROACETYLATION OF 9-METHYLCARBAZOLE.

2.* PECULIARITIES OF THE REACTION DUE TO THE PRESENCE OF TRIFLUOROACETIC ACID

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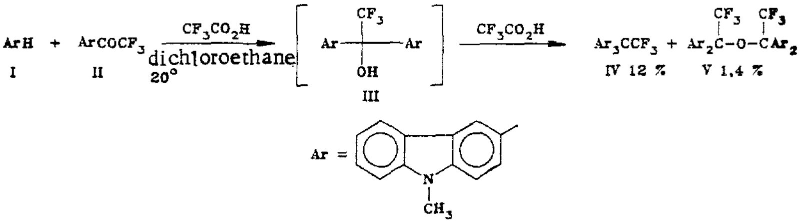
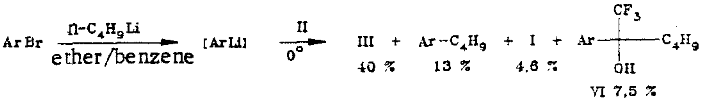
A satisfactory model of the intermediate in the formation of polyaryltrifluoromethylmethanes in the trifluoroacetylation of 9-methylcarbazole is 1,1,1-trifluoro-2,2-bis(9-methyl-3-carbazolyl)-2-hydroxyethane. The kinetic isotope effect of the reaction was evaluated. It is shown that the rate of the reaction is determined by the formation of a σ complex. The trifluoromethylation of 9-methyl-carbazole at 110°C is accompanied by demethylation of the substrate under the influence of trifluoroacetic acid.

We have previously shown [1] that the formation of polyaryltrifluoromethylmethanes in the trifluoroacetylation of 9-methylcarbazole (I) with trifluoroacetic anhydride involves acid-catalyzed condensation of the resulting 9-methyl-3-trifluoroacetylcarbazole (II) with the starting I:

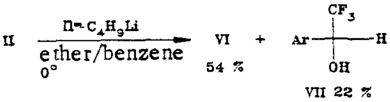


Resinous products are responsible for the intense color of the reaction mixture at 600 nm. It was assumed that the condensation of I and II is realized through a carbinol intermediate, viz., 1,1,1-trifluoro-2,2-bis(9-methyl-3-carbazolyl)-2-hydroxyethane (III).

To confirm the proposed scheme of the trifluoroacetylation of I we investigated the CF_3CO_2H-catalyzed transformations of carbinol III, which was synthesized via the scheme



From the reaction mixture we also isolated 3-n-butyl-9-methylcarbazole, I, and 1,1,1-trifluoro-2-(9-methyl-3-carbazolyl)-2-hexanol (VI). The latter is formed along with VII in the reaction of ketone II with n-butyllithium:



Carbinol III condenses readily with carbazole I in the presence of a small amount of CF_3CO_2H to give the expected IV and V:

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*See [1] for communication 1.

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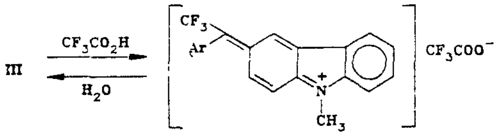
TABLE 1. Results of the Competitive Trifluoroacetylation of 9-Methylcarbazole and Mixtures of Its Deutero Analogs at 100°C

Deuterium content (No. of D atoms)	Substrate (I) (control expt.)		Reaction product (II)			
	m/z (M⁺)	intensities of the M⁺ peaks (I)	m/z (M⁺)	intensities of the M⁺ peaks (I)		
				1	2	3
0	181	150,0	277	11,00	3,5	8,50
1	182	26,5	278	2,70	0,3	1,50
2	183	5,5	279	1,15	0,45	0,70
3	184	9,2	280	1,50	0,55	0,70
4	185	27,0	281	3,60	0,10	1.60
5	186	43,5	282	5,10	1,10	1,90
6	187	61,3	283	3,60	2,20	1,50
7	188	63,5	284	3,30	0,70	1,50
8	189	27,2	—	—	—	—
$I_H/\Sigma I_D$	0,57			0,53	0,57	0,76
Av. $I_H/\Sigma I_D$	0,57				0,62	

$$\text{I} + \text{III} \xrightarrow[\text{CF}_3\text{CO}_2\text{H}]{20°,\ \text{dichloroethane}} \underset{65\ \%}{\text{IV}} + \underset{6{,}7\ \%}{\text{V}}$$

As in the trifluoroacetylation of I, the reaction mixture has a characteristic color due to absorption at 600 nm. The development of the color may be associated with the formation of structures of the quinoid type in the course of transformations of III under the influence of CF_3CO_2H:



IIIa

It is known that diaryltrifluoromethylcarbinols are extremely resistant with respect to dehydration [2, 3]. Compound III, on the other hand, is readily converted by the action of CF_3CO_2H to an unstable colored product (probably IIIa), the long-wave absorption maximum of which is shifted from 630 nm to 608 nm after storage for 3 days. In a paper devoted to ascertaining the reasons for the development of the blue coloration that accompanies many electrophilic reactions in carbazoles Bruck and co-workers [4] also observed a hypsochromic shift of the long-wave absorption band of the cation of bis(9-ethyl-3-carbazolyl)methyl tetrafluoroborate and associated this effect with aggregation of the substance during storage.

The noncoincidence of the positions of the long-wave absorption maxima of IIIa and the reaction mixture in the trifluoroacetylation of I may indicate the necessity for participation of the latter directly in the step involving the formation of the dye, since in the condensation of I and II or I and III the reaction mixtures have a color with λ_{max} 600 nm. A mixture of carbinol III with CF_3CO_2H — substance IIIa — does not give even a weak EPR signal, and we therefore excluded a radical nature of this substance from consideration.

All of the transformations presented above and the trifluoroacetylation of I by the action of $(CF_3CO)_2O$ are possible only owing to the presence of CF_3CO_2H. Thus the trifluoroacetylation of I does not take place in the presence of pyridine at 20°C. Trifluoroacetic anhydride that was specially purified to remove the acid does not react with I for at least a month. The reaction then slowly proceeds in the expected direction.

These results confirm the reaction scheme [1] and are in agreement with the results in [5, 6], in which it was shown that the trifluoroacetylation of five-membered heterocycles is realized via a mechanism that includes the formation of ion pairs of the $[(CF_3CO)_2O^+H]$-$CF_3CO_2^-$ type and obeys a third-order kinetic equation: $V = K[\text{substrate}][(CF_3CO)_2O][CF_3CO_2H]$.

It has been assumed [6] that the participation of trifluoroacetyl cations in acylation with trifluoroacetic anhydride is virtually excluded. Nevertheless, the concept of a tri-

TABLE 2. Relative Intensities of the M^+ Peaks from the Mass Spectra of the Reaction Mixtures in the Trifluoroacetylation of 9-Methylcarbazole (110°C)

I: $(CF_3CO)_2O : CF_3CO_2H$ molar ratio	Intensities of the M^+ ion peaks					
	167 (IX)	181 (I)	263 (X)	277 (II, VIII)	442 (XI)	621 (IV)
3 : 10 : 1	1,0	3,5	1,1	100	1,0	3,0
3 : 1 : —	6,4	100	1,1	1,6	0,7	2,5
1 : — : 10	33.3	100	0.2	20.0	4.0	—

fluoroacetyl cation is sometimes invoked in discussing the results of acylation under such conditions. For example, in [7] it is stated that the acylation of pyrimidines with unfluorinated carboxylic acids and their derivatives proceeds only in the presence of strong protic acids, while the trifluoroacetylation of pyrimidines is realized without catalysts owing to the "increased electrophilicity of the trifluoracetyl ion." The existing concepts regarding the mechanism of trifluoroacetylation make it possible to give another explanation for these facts. It is well known that carboxylic acid anhydrides in the absence of catalysts display weak activity in the acylation of aromatic substrates. Thus even pyrrole reacts with acetic anhydride only at an increased temperature (130°C) [8]. Acylation is therefore usually carried out in the presence of strong protic acids or Lewis acids, which are responsible for the formation of more active acylating particles. In contrast to unfluorinated aliphatic anhydrides, preparative $(CF_3CO)_2O$, as a consequence of its extreme tendency to undergo hydrolysis, may contain 5-10% CF_3CO_2H (according to PMR data) and thus is an effective "acylating mixture." For example, pyrrole is acylated by this reagent at 0°C [9]. In addition, considering the high electrophilic reactivity of the carbonyl carbon atom in $(CF_3CO)_2O$, one cannot exclude the possibility of acylation by even the neutral anhydride molecule [6], at least for highly nucleophilic substrates. At the same time, trifluoroacetylation is one of the most selective electrophilic reactions [10]; this is a direct consequence of the relatively "mild" nature of the acylating agent and does not correspond to the concepts regarding a mechanism that is realized through acyl cations.

As regards the trifluoroacetyl cation proper, it has been reported that it is formed from trifluoroacetyl bromide and silver hexafluoroantimonate (SO_2, −25°C) [11], whereas the trifluoroacetyl cation was not detected under conditions of treatment of $(CF_3CO)_2O$ with super acids (SO_2, −78°C) [12].

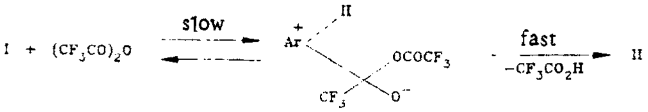
The elucidation of the rate-determining step of the reaction could serve as a confirmation of the proposed mechanism of trifluoroacetylation. An attempt to measure the kinetic isotope effect of the trifluoroacetylation of 2-methylfuran [6] was unsuccessful because of the fact that hydrogen exchange between CF_3CO_2H, which is present in its anhydride, and the aromatic substrate is apparently a significantly faster process than substitution.

We have developed a special method that makes it possible to obtain acid-free $(CF_3CO)_2O$ (according to PMR data). Using this anhydride and a sample of highly deuterated I, which was prepared by the method in [13], we evaluated the kinetic isotope effect of the trifluoroacetylation of I by a competitive method with the use of mass spectrometry. Since the reaction does not take place at 20°C, it was carried out at 100°C. The mass spectra of a control mixture and three reaction mixtures were then recorded. The m/z values and the intensities of the M^+ peaks for each mixture are presented in Table 1. The kinetic isotope effect of the reaction was calculated on the basis of the tabulated data:

$$\frac{K_H}{K_D} = \frac{\overline{(I_H/\Sigma I_D)}}{(I_H/\Sigma I_D)_0} = \frac{0.62}{0.57} = 1.09 \pm 0.1,$$

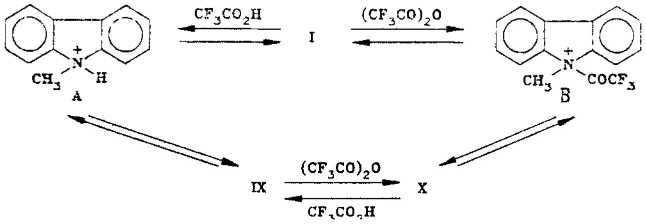
where the numerator is the average (from three measurements) ratio of the intensity of the M^+ peak of the nonisotopic product to the sum of the intensities of the M^+ peaks of the isotopic products, and the denominator is the ratio of the intensity of the M^+ peak of the nonisotopic substrate to the sum of the intensities of the M^+ peaks of the isotopic substrates.

Thus the kinetic isotope effect of the reaction under the selected conditions is approximately equal to unity, while the theoretical maximum calculated on the basis of IR spectral data from the approximate equation [14] $K_H/K_D = \exp[(hC/2KT)\Delta\nu]$ (where $\Delta\nu$ is the difference in the frequencies of the stretching vibrations of the C—H and C—D bonds in the substrate, h is the Planck constant, C is the speed of light in a vacuum, K is the Boltzmann constant, and T is the absolute temperature in degrees Kelvin) is ~4.6. It follows from this that the transition state in the trifluoroacetylation of I evidently has "late" character, the Ar—H bond is markedly weakened, and the rate-determining step is the formation of a σ complex:



This conclusion is in agreement with the absence of base catalysis in trifluoroacetylation [6] and with the relatively low reactivity of the $(CF_3CO)_2O$ electrophilic agent and suggests high sensitivity of the reaction to the electronic effects of substituents in the substrate. It is known, for example, that the Friedel—Crafts acylation of carbazoles always leads to mixtures of mono- and diacyl derivatives [15], while the reaction of I with $(CF_3CO)_2O$ proceeds regiospecifically in the $C_{(3)}$ position, thereby reflecting the high positional and substrate selectivity of the reaction.

Assuming that the introduction of two CF_3CO groups into the carbazole ring would become possible under more severe conditions, we carried out the reaction of I with $(CF_3CO)_2O$ in the presence of strong Lewis acids. We observed intensive resinification of the reaction mass, and absorption bands of a carbonyl group were absent in the IR spectrum of the resin. We therefore used the $(CF_3CO)_2O$—CF_3CO_2H (10:1) acylating mixture at 110°C. From the reaction mixture we isolated 45% ketone II, 2.4% 9-methyl-1-trifluoroacetylcarbazole (VIII), 1% carbazole (IX), 0.5% 9-trifluoroacetylcarbazole (X), and 36% resin. In addition, mass-spectral analysis of the reaction mixture (Table 2) made it possible to detect I, IV, and 1,1-bis(9-methyl-3-carbazolyl)-2,2,2-trifluoroethylidene (XI) (M^+ with m/z 442), which was previously identified in [13]. The presence of ketone VIII in the reaction mixture indicates a decrease in the positional selectivity of the process with an increase in the temperature. The presence of IX and X attests to demethylation of the starting I, which may be realized both through transition state A and through transition state B:



In connection with the lower steric requirements for transition state A, this demethylation pathway seems more likely to us. To verify this assumption we carried out the reaction of I with acid-free $(CF_3CO)_2O$ (according to PMR data) under conditions of insufficient acylating agent (reagent ratio 3:1, respectively).

If demethylation were realized to a significant degree through state B, the reaction mixture would contain more X than IX, since the equilibrium X ⇌ IX is shifted markedly to the left under these conditions. Judging from the composition of the reaction mixture (Table 2), the mixture contains six times more carbazole (IX) than X, which constitutes evidence in favor of protodemethylation under the influence of CF_3CO_2H, which is present in the anhydride and is liberated as a result of the C acylation of I. In the reaction of I with pure CF_3CO_2H (1:10, respectively) protodemethylation becomes the principal reaction pathway, and the ratio of components IX and X is 166:1 (Table 2); carbazole (IX) was isolated preparatively in 16% yield in this case.

Since the demethylation and trifluoroacetylation of I proceed under competitive conditions, the relative amounts of two groups of compounds, viz., IX and X and II, IV, VIII, and XI, reflect, to a certain extent, the relative rates of the corresponding processes, which, in turn, makes it possible to form a judgement regarding the effectiveness of an acylating agent. Thus it follows from Table 2 that when a mixture of the acid and its anhydride is used, trifluoroacetylation of the ring of I predominates over demethylation by a factor of

~50, which attests to the relatively high acylating qualities of this agent, whereas the use of pure $(CF_3CO)_2O$ is ineffective because of the low trifluoroacetylation/demethylation ratio, which is 0.6. Even when pure CF_3CO_2H is used this ratio is 0.7, which reflects the ability of CF_3CO_2H to acylate the carbazole ring, just as in the acylation of the indole ring [16].

One's attention is directed to the fact that the M^+ peak with m/z 621 of IV is absent in the mass spectrum of the mixture obtained in the reaction of I with CF_3CO_2H. It is likely that under the conditions of increased acidity of the medium "side" resinification processes occur at a higher rate than the sterically hindered condensation of carbinol III with starting I, which leads to IV.

Thus the following peculiarities of the trifluoroacetylation of I were ascertained. The presence of CF_3CO_2H is necessary for realization of the reaction at 20°C. Substitution proceeds regiospecifically at the $C_{(3)}$ position of the ring of I. An increase in the temperature to 110°C gives rise to a decrease in the positional selectivity of the reaction and initiates competitive protodemethylation of the substrate but does not lead to the formation of bis(trifluoroacetyl) derivatives.

The results obtained, in combination with the literature data, make it possible to exclude the possibility of the participation of trifluoroacetyl cations in acylation with trifluoroacetic anhydride.

EXPERIMENTAL

The course of the reactions was monitored by TLC [Silufol plates, hexane–benzene–dichloroethane (3:6:1), development in vapors of nitrogen oxides]. The electronic spectra were recorded with an SF-16 spectrophotometer. The IR spectra were recorded with a UR-20 spectrometer. The PMR spectra were obtained with a Tesla BS-487c spectrometer (80 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. The ^{19}F NMR spectra were measured relative to C_6F_6 with a Tesla BS-567A spectrometer (94.04 MHz). The EPR spectra were recorded with an EPR-20 spectrometer with $\lambda = 3.2$. The mass spectra were obtained with an MKh-1310 mass spectrometer with a system for direct introduction of the samples at an ionizing-electron energy of 20 eV. Separation of the mixtures was accomplished by column chromatography with activity II Al_2O_3 as the adsorbent. The kinetic isotope effect was determined by a competitive method with the use of mass spectrometry [17].

Trifluoroacetic Anhydride That Does Not Contain the Acid. Approximately equal amounts of $(CF_3CO)_2O$ and P_2O_5 were mixed in a flask with an efficient reflux condenser through which dry nitrogen was fed; the mixture was maintained at 20°C for 24 h, after which it was distilled (39-45°C) in a stream of nitrogen. Several small pieces of sodium metal were then added successively while striving to observe that gas bubbles were not liberated during the addition of fresh portions of sodium. The $(CF_3CO)_2O$ was then maintained over sodium for 24 h at 20°C, after which it was distilled over sodium in a stream of dry nitrogen at 39°C and stored in sealed ampuls that had been dried at 200°C and purged with nitrogen.

Method for the Measurement of the Kinetic Isotope Effect. A solution of 0.561 g (~3 mmole) of deuterated I (the average number of D atoms was 6.3 [13]) and 0.543 g (3 mmole) of I in 10 ml of dry dichloroethane (DCE) and a solution of 0.4 ml (3 mmole) of pure $(CF_3CO)_2O$ in 5 ml of DCE were prepared, after which 1 ml of the first solution (the substrate) was placed in four 10-ml glass ampuls that had been previously dried and purged with nitrogen, and 1 ml of the second solution (the acylating agent) was placed in three of the ampuls. The solution in the remaining ampul was used as a control. All of the ampuls were sealed and heated at 100°C for 10 min, after which they were cooled to 20°C, and the contents of each ampul were poured into 5 ml of ethanol. The solvent was removed in a vacuum desiccator over KOH, and the mass spectra of the samples were recorded at a sweep rate of 30 sec per mass decade.

1,1,1-Trifluoro-2,2-bis(9-methyl-3-carbazolyl)-2-hydroxyethane (III). A 20-ml sample of a solution of n-butyllithium in ether (from 8.6 g of lithium and 52.7 ml of n-butyl bromide) was added at 16°C to a solution of 5 g (19 mmole) of 3-bromo-9-methylcarbazole in 20 ml of dry benzene, and the mixture was refluxed in a nitrogen-purged flask for 1.5 h [18]. A solution of 11 g (40 mmole) of ketone II in 20 ml of dry benzene was added at 0°C to the resulting solution of the lithium derivative of I, and the mixture was maintained at 20°C for 18 h. The solution was washed with water (two 100-ml portions), dried with $CaCl_2$, concentrated under reduced pressure to a volume of 20 ml, and separated with a column packed with Al_2O_3 by elution with hexane—benzene (1:1) (760 ml) with selection of 10 ml portions to give 0.61 g (13%) of 3-n-butyl-9-methylcarbazole in the form of a colorless oil with R_f 0.56. IR spectrum (thin layer): 3050 (C—H, arom.), 2870-2980 (C—H, aliph.), 810, 750, 725 cm^{-1} (C—H, arom.). PMR spectrum (CCl_4): 1.22 (7H, m, $n-C_4H_9$), 2.65 (2H, t, J = 7.5 Hz, benzyl CH_2), 3.46 (3H, s, N—CH_3), 6.80-7.30 (5H, m, arom. H), 7.60-7.90 ppm (2H, m, 4-H, 5-H). Found, %: C 86.1, H 8.0, N 5.9, M^+ 237. $C_{17}H_{19}N$. Calculated, %: C 86.0, H 8.0, N 5.9.

Further elution gave 0.16 g (4.6%) of I. The IR spectrum and melting point coincided with those for a genuine sample of 9-methylcarbazole [19].

Subsequent elution with benzene—dichloroethane (1:1) (480 ml) gave a mixture of two substances with R_f 0.16 and 0.08, which, in turn, was separated with a column (3 by 40 cm, Al_2O_3) with successive elution with hexane (300 ml) and hexane—benzene (1:1) (250 ml) to give 1.0 g (7.5%) of carbanol VI with mp 74-75°C (CCl_4) and R_f 0.16. IR spectrum (CCl_4): 3620 (O—H), 3080 (C—H, arom.), 2885-2970 (C—H, aliph.), 1195, 1165 cm^{-1} (C—F); (thin layer): 2180-3630 (O—H...O—H), 3070 (C—H, arom., 2885-2970 (C—H, aliph.), 1136-1165 (C—F), 805, 750, 720 cm^{-1} (C—H, arom.). PMR spectrum (CCl_4): 1.10 (9H, m, $n-C_4H_9$), 2.60 (1H, s, OH), 3.44 (3H, s, N—CH_3), 6.80-7.25 (4H, m, arom. H), 7.20 (1H, d, J = 7 Hz, 5-H), 8.14 ppm (1H, s, 4-H). Found, %: C 68.2, H 6.1, N 4.2. $C_{19}H_{20}F_3NO$. Calculated, %: C 68.0, H 6.0, N 4.2.

Elution was then carried out with dichloroethane (250 ml). Removal of the solvent and recrystallization of the solid residue gave 3.5 g (40%) of carbinol III in the form of colorless cyrstals with mp 111-112°C (CCl_4) and R_f 0.08, 0.23, hexane—ether (1:1). IR spectrum (CCl_4): 3605 (O—H), 3080 (C—H, arom.), 2945 (C—H, CH_3), 1170-1260 (C—F), 1140 cm^{-1} (C—O). UV spectrum (ethanol), λ ($\varepsilon \cdot 10^{-3}$): 240 (13), 265 (900), 295 (5.8), 340 nm (1.9). PMR spectrum ($CDCl_3$): 3.06 (1H, s, O—H), 3.94 (6H, s, N—CH_3), 7.0-7.60 (10H, m, arom. H), 8.0 (2H, d, J = 8 Hz, 5-H, 5'-H), 8.28 ppm (2H, s, 4-H, 4'-H). ^{19}F NMR spectrum (benzene): −91.51 ppm (CF_3). Found, %: C 73.3, H 4.6, F 12.1, N 6.0, M^+ 458. $C_{28}H_{21}F_3N_2O$. Calculated, %: C 73.4, H 4.6, F 12.4, N 6.1.

<u>1,1,1,Trifluoro-2,2,2-tris(9-methyl-3-carbazolyl)ethane (IV).</u> Six drops (~1.2 mmole) of CF_3CO_2H were added with stirring to a solution of 0.458 g (1 mmole) of carbinol III and 0.543 g (3 mmole) of I in 5 ml of dichloroethane, and the mixture was allowed to stand at 20°C for 18 h. The crystalline precipitate that developed on the bottom of the reaction flask was removed by filtration, dried at 80°C, and recrystallized from benzene to give 403 mg (65%) of IV. With respect to its spectral and physical characteristics, the substance was identical to 1,1,1-trifluoro-2,2,2-tris(9-methyl-3-carbazolyl)ethane [1].

The filtrate was washed with 20 ml of water and separated with a column (1 by 25 cm, Al_2O_3) by successive elution with hexane—benzene (1:1) and hexane—ether (1:1) (100 ml of each mixture) to give 0.06 g (6.7%) of ether V. With respect to its spectral and physical characteristics, the substance was identical to 1,1,1,1',1',1'-hexafluoro-2,2,2',2'-tetrakis(9-methyl-3-carbazolyl)diethyl ether [1].

<u>Trifluoroacetylation of 9-Methylcarbazole at 110°C.</u> A 5.43 g (30 mmole) sample of I was dissolved in 15 ml of dichloroethane, 13 ml (93 mmole) of $(CF_3CO)_2O$ containing ~6% CF_3CO_2H (molar ratio 10:1) was added, and the mixture was heated in a sealed ampul for 6 h at 110°C. The mixture was then evaporated to half the original volume, and this concentrate was cooled to 0°C. The crystalline precipitate was removed by filtration and dried in vacuo to give 54 mg (1%) of carbazole (IX). With respect to its physical and spectral parameters, the substance was identical to carbazole.

The filtrate was poured with stirring into 50 ml of boiling hexane, and the flocculent precipitate was removed by filtration to give 1.97 g (36%) of a resin. IR spectrum (mineral oil): 1700 (C=O), 1160-1240 (C—F), 810, 765, 730 cm^{-1} (C—H, arom.). UV spectrum (dichloroethane), λ_{max}: 600 nm.

The filtrate obtained after separation of the resinous precipitate was evaporated to a volume of 5 ml and separated with a column (2 by 70 cm, Al_2O_3) by elution with hexane—benzene (1:1) (750 ml). The following substances were isolated successively. Ketone II [2.41 g (45%)] with mp 71-71.5°C (hexane). With respect to its physical and spectral characteristics, ketone II was identical to 9-methyl-3-trifluoroacetylcarbazole [1]. Compound X [27 mg (0.5%)] with mp 58-59°C (mp 61°C [5]). The IR spectrum of X was identical to that for a genuine sample of 9-trifluoroacetylcarbazole [5]. Ketone VIII [0.13 g (2.4%)] with mp

107.5-108.5°C (hexane) (mp 108-111°C [20]). With respect to its spectral parameters, ketone VIII was identical to 9-methyl-1-trifluoroacetylcarbazole [20].

Demethylation of 9-Methylcarbazole by the Action of CF_3CO_2H at 110°C. A 7.6-ml (100 mmole) sample of CF_3CO_2H was added to a solution of 1.81 g (10 mmole) of I in 10 ml of dichloroethane, and the mixture was heated in a sealed ampul at 110°C for 6 h. It was then evaporated to half its original volume, and this concentrate was cooled with ice and filtered to give 0.27 g (16%) of carbazole (IX), which, with respect to its physical and spectral characteristics, was identical to a genuine sample of carbazole.

Workup of the filtrate yielded 0.71 g (38%) of a resin, just as in the experiment on the trifluoroacetylation of 9-methylcarbazole at 110°C.

1,1,1-Trifluoro-2-(9-methyl-3-carbazolyl)-2-hexanol (VI). A 20-ml sample of an ether solution of n-butyllithium (from 8.6 g of lithium and 52.7 ml of n-butyl bromide) was added with stirring at 0°C to a solution of 5.54 g (20 mmole) of ketone II in 20 ml of dry benzene, and the resulting solution was washed with cold water (two 100-ml portions). The solvent was removed in vacuo up to a volume of ~10 ml, and this concentrate was separated with a column (3.5 by 40 cm, Al_2O_3) by elution with hexane—benzene (1:1) to give 3.6 g (54%) of carbinol VI. With respect to its characteristics, the substance was identical to the 1,1,1-trifluoro-2-(9-methyl-3-carbazolyl)-2-hexanol that was isolated in the preparation of carbinol III. Subsequent elution with hexane—ether (1:1) yielded 1.2 g (22%) of carbinol VII with mp 114.5-115°C (CCl_4) and R_f 0.19 [hexane—ether (1:1)]. IR spectrum (mineral oil): 3565, 3200-3430 (OH...OH), 1635, 1610 (C=C, arom.), 1235, 1120-1190 (C—F), 1090 (C—O), 815, 775, 750, 725, 700 cm^{-1} (C—H, arom.). IR spectrum (CCl_4): 3630 cm^{-1} (OH). PMR spectrum ($CDCl_3$): 2.60 (1H, s, OH), 3.90 (3H, s, CH_3), 5.0 (1H, q, J_{HF} = 8 Hz, CF_3—CH), 7.0-7.50 (5H, arom.), 7.90 (1H, d, 5-H), 8.0 ppm (1H, s, 4-H). Found, %: C 6.43, H 4.2, F 20.2, N 5.0. $C_{15}H_{12}F_3NO$. Calculated, %: C 6.45, H 4.3, F 20.4, N 5.0.

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