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TRIFLUOROACETYLATION OF 9-METHYLCARBAZOLE. EXAMPLE OF THE FORMATION OF A TRIARYLFLUOROETHANE IN THE HETEROCYCLIC SERIES

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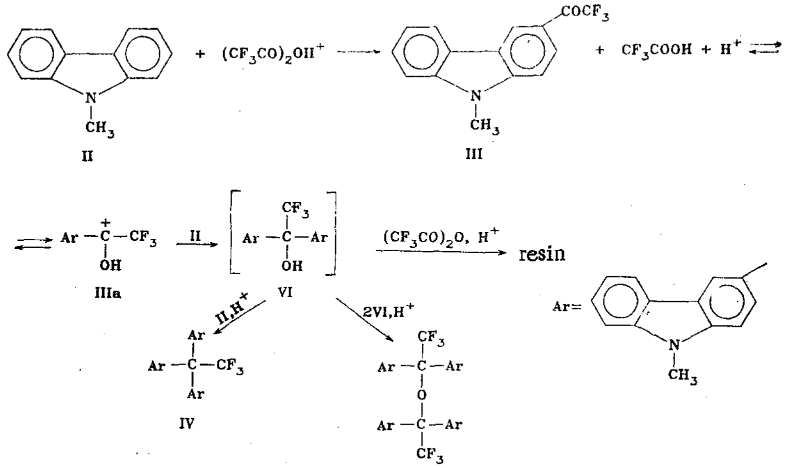
It is shown that the trifluoroacetylation of 9-methylcarbazole proceeds regiospecifically in the 3 position of the ring. 1,1,1-Tris(9-methyl-3-carbazolyl)-2,2,2-trifluoroethane and 1,1,1',1'-tetrakis(9-methyl-3-carbazolyl)-2,2,2,2',2',-2'-hexafluorodiethyl ether were also isolated from the reaction mixture. Bis(trifluoroacetyl) derivatives were not detected. Only a 3-trifluoroacetyl derivative is formed when the reaction is carried out by heating in the presence of pyridine.

It is known that carbazole (I) is trifluoroacetylated at the heteroatom [1]. 9-Methyl-1-trifluoroacetylcarbazole was obtained through the corresponding 1,2,3,4-tetrahydracarbazole derivative [2].

We have observed that 9-methylcarbazole (II) reacts with trifluoroacetic anhydride (TFAn) in the absence of a catalyst at room temperature to give 9-methyl-3-trifluoroacetylcarbazole (III) and a small amount of resinous products. Resin formation becomes predominant when the temperature is raised to 100-120°C. The addition of condensing agents such as boron trifluoride etherate, aluminum chloride, and tin tetrachloride leads to complete resinification of the reaction mass. The reaction does not take place in the presence of equimolar (with respect to product II) amounts of pyridine at room temperature, and only ketone III is formed when the mixture is heated to 100-120°C. We noted that a significant induction period, which was absent when a mixture of TFAn and trifluoroacetic acid (TFAc) was used, was observed in the course of the reaction when TFAn that had been thoroughly purified by repeated distillation over phosphorus pentoxide was used. This indicates that the process evidently takes place under conditions of self-catalysis by the liberated TFAc.

$$(CF_3CO)_2O + CF_3COOH \rightleftarrows (CF_3CO)_2OH^+ + CF_3COO^-$$



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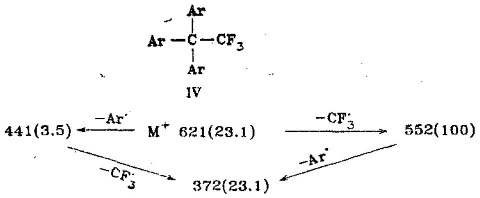
In addition to ketone III, we isolated small amounts of 1,1,1-tris(9-methyl-3-carbazolyl)2,2,2-trifluoroethane (IV) and 1,1,1',1'-tetrakis(9-methyl-3-carbazolyl)-2,2,2,2',2',-2'-hexafluorodiethyl ether (V), the structures of which were proved by IR, PMR, and mass spectrometry. An excess amount of 9-methylcarbazole and an increase in the reaction time promote an increase in the yields of IV and V. The formation of the isolated products may occur in conformity with the scheme. The presence of ether V in the products makes it possible to assume that the condensation of carbazoles II and III proceeds through a step involving the formation of carbinol VI. To confirm the proposed scheme of the trifluoroacetylation of 9-methylcarbazole we carried out the condensation of ketone III with excess II in the presence of TFAc. The reaction proceeds readily at room temperature to give products with melting points, R_f values, and IR and PMR spectra that are identical to the corresponding data for IV and V. The IR and PMR spectra were not very informative in establishing the structures of IV and V. The mass spectrum of IV contains an intense peak of an ion at 552 (100),* which is formed as a result of ejection of a trifluoromethyl group by the molecular ions (M^+). Judging from the intensities of the peaks of the ions at 552 (100) and 621 (24), the molecular ion is less stabilized, probably as a consequence of the effect of the electron-acceptor CF_3 group. Another pathway of fragmentation of M^+ involving the elimination of one of the carbazolyl substituents and the formation of an even less stabilized ion at 441 (4) is also realized. The one-step character of this fragmentation pathway is confirmed by the presence of a peak of a metastable ion at 313.2 (calculated 621 → 441 + 180, m* = 313.17). The scheme of the fragmentation of IV at an electron energy of 70 eV has the form



When the ionization energy is decreased to 12 eV, only an M^+ peak at 621 (100) and the peak of an ion at 552 (63), as well as the peak of a metastable ion with an apparent mass of 490.7 (calculated: $621^+ \rightarrow 552^+ + 69$, m* = 490.66), are observed in the spectrum. The following peaks were observed in the mass spectrum of V at an ionization energy of 12 eV: a molecular-ion peak at 898 (100), a fragment-ion peak at 829 (14), and a metastable-ion peak at 765.3 (calculated: $898^+ \rightarrow 829^+ + 69$, m* = 765.30).

Similar condensations leading to the formation of polyphenylmethanes are known [3-5]; it is assumed that fluorinated ketones are not as active in these reactions as their nonfluorinated analogs [6, 7]. In this connection, the fact that 3-acetyl-9-methylcarbazole does not react with 9-methylcarbazole under the same conditions is interesting. Protonation of the carbonyl oxygen atom in this case evidently leads to the formation of a more stable and, consequently, less active carbonium ion than in the case of ketone III. The formation of resins is probably associated with transformations of carbinol VI in acidic media. The participation of a protonated molecule of III in the reaction is confirmed by the bathochromic shift (10 cm^{-1}) of the absorption band of stretching vibrations of the carbonyl group of ketone III under the influence of TFAc in dichloroethane.

It should be noted that the trifluoroacetylation of carbazole II proceeds regiospecifically regardless of the temperature and the ratio and sequence of mixing of the reagents, in contrast to Friedel—Crafts acetylation, which always leads to mixtures of mono- and diacetyl derivatives [8].

EXPERIMENTAL

Monitoring of the course of the reactions and determination of the R_f values were realized by means of thin-layer chromatography (TLC) on Silufol UV-254 [elution with benzene—hexane (1:1)]. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The PMR spectra were recorded with a BS-487 spectrometer (80 MHz) with

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*Here and subsequently, the m/z values (and relative intensities in percent) are presented in the discussion of the mass spectra.

hexamethyldisiloxane as the internal standard. The ^{19}F NMR spectra[†] of solutions in chloroform were recorded with a Varian A56A/8A spectrometer (56.4 MHz) with hexafluorobenzene as the internal standard. The mass spectra were recorded with an MKh-1310 spectrometer with direct introduction of the samples; the ionizing-electron energies were 70 and 12 eV, and the temperature of the ionization chamber was 250°C.

9-Methyl-3-(trifluoroacetyl)carbazole (III). A 1.4-ml (20 mmole) sample of TFAn was added to a solution of 1.81 g (10 mmole) of 9-methyl-carbazole in 5 ml of dichloroethane, and the mixture was allowed to stand at room temperature for 24 h. The mixture was then poured with stirring into 50 ml of hexane, and the resulting mixture was allowed to stand. The resinous precipitate was removed by filtration, and the filtrate was allowed to stand for crystallization to give 1.12 g (40%)[†] of III with mp 71-71.5°C (hexane) and R_f 0.45. IR spectrum: 1700 (C=O); 1130, 1200 (C—F); 725, 760, 780, 825 cm^{-1} (C—H, aromatic). PMR spectrum (CCl_4): 3.75 (3H, s, N—CH_3), 7.30 (5H, m, aromatic), 8.0 (1H, m, 5-H), and 8.5 ppm (1H, d, 4-H). ^{19}F NMR spectrum: —92.4 ppm (3F, s, CF_3CO). Found: C 65.1; H 3.6; F 20.0; N 4.9%; M^+ 277. $C_{15}H_{10}F_3NO$. Calculated: C 65.0; H 3.6; F 20.6; N 5.0%.

1,1,1-Tris(9-methyl-3-carbazolyl)-2,2,2-trifluoroethane (IV). The mother liquor remaining after crystallization of III obtained in the preceding experiment was evaporated to dryness on a water bath, the residue was dissolved in 5 ml of benzene, and the solution was separated with a 70-cm long column (d = 1 cm) packed with activity II (Brockmann scale) Al_2O_3. The separation was monitored by TLC. This procedure gave 0.20 g of IV with mp 277-278°C (benzene) and R_f 0.30. IR spectrum: 1605 (C=C, aromatic); 1140, 1230, 1255 (C—F); 725, 750, 760, 810 cm^{-1} (C—H, aromatic). PMR spectrum (d_6-benzene): 3.0 (9H, s, N—CH_3) and 6.9-7.6 ppm (21H, m, aromatic H). Found: C 79.6; H 5.0; F 8.9; N 6.8%; M^+ 621. $C_{41}H_{30}F_3N_3$. Calculated: C 79.2; H 4.9; F 9.1; N 6.8%.

1,1,1',1'-Tetrakis(9-methyl-3-carbazolyl)-2,2,2,2',2',2'-hexafluorodiethyl Ether (V). After the IV obtained in the preceding experiment emerged from the column (monitoring by TLC), a solution of V began to be eluted. The V was isolated by crystallization to give 0.09 g of a product with mp 239-240°C (benzene) and R_f 0.11. IR spectrum: 1605 (C=C, aromatic); 1130 (C—O—C); 1140, 1230, 1255 (C—F); 725, 750, 780, 810 cm^{-1} (C—H, aromatic). PMR spectrum (d_6-benzene): 3.0 (12H, s, N—CH_3) and 6.9-7.8 ppm (28H, m, aromatic H). Found: C 77.7; H 4.3; F 12.4; N 6.3%; M^+ 898. $C_{56}H_{40}F_6N_4O$. Calculated: C 77.8; H 4.5; F 12.7; N 6.2%.

Synthesis of IV and V by Condensation of 9-Methylcarbazole with Ketone III in the Presence of TFAc. A 0.76-ml (10 mmole) sample of TFAc was added to a solution of 1.81 g (10 mmole) of 9-methylcarbazole and 1.40 g (5 mmole) of product III in 2 ml of dichloroethane, and the mixture was allowed to stand at room temperature for 2 h. The mixture was then poured into 20 ml of hexane, and the precipitate was removed by filtration and dissolved in 5 ml of benzene. The solution was separated with a 70-cm long column packed with activity II (Brockmann scale) Al_2O_3 just as described above to give 0.39 g of IV and 0.07 g of V, the physical and spectral characteristics of which were in agreement with the corresponding data for IV and V obtained in the trifluoroacetylation of 9-methylcarbazole.

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†Here and subsequently, the preparative yields are indicated.