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HETEROCYCLIC DERIVATIVES OF FULLERENE C_{60}.

2*. CYCLOADDITION TO FULLERENE C_{60} OF THE PRODUCTS OF DEHYDROCHLORINATION OF N-BENZYLTRIFLUOROACETIMIDOYL CHLORIDES

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It has been shown that, depending on the structure, the products of dehydrochlorination of N-benzyltrifluoroacetimidoyl chlorides react with C_{60} under the action of triethylamine as a [3 + 2] cycloaddition (with the formation of fulleropyrrolines) or a [4 + 2] cycloaddition (with the formation of fulleropiperideines).

Keywords: N-benzyltrifluoroacetimidoyl chloride, N-(methylbenzyl)trifluoroacetimidoyl chloride, N-(*p*-methoxybenzyl)trifluoroacetimidoyl chloride, fulleropiperideines, fulleropyrrolines, [3 + 2] cycloaddition, [4 + 2] cycloaddition.

Cycloaddition reactions to fullerene C_{60} offer the most efficient possibility for functionalizing it and especially for constructing heterocyclic fragments on the fullerene sphere (see, for example, the review [2]). One of the main methods of synthesizing fulleropyrrolines is the 1,3-dipolar cycloaddition of nitrile ylides to C_{60} [4]. For the overwhelming majority of nitrile ylides, reaction with C_{60} leads exclusively to the closed [6,6]-cycloadduct (see for example [4]). An anomalous course for such a reaction was discovered for the first time for 1-(4-nitrophenyl)-3-phenylnitrile ylide, when together with the closed [6,6]-fulleropyrroline a mixture was formed of the diastereomeric open [5,6]-fulleroid adducts [5]. It subsequently turned out that this result was reproduced for other substituted 1,3-diarylnitrile ylides [6], especially those having a nitro group in the *para* and *meta* positions of the C-aryl substituent, however the reason for this phenomenon has not been finally clarified up to the present time. For a clear answer to the problem of the reasons for the generation of fulleroid cycloadducts it is necessary to investigate as many nitrile ylides of varied structure as possible. The present investigation has been carried out in just this key and is devoted to the study of [3 + 2] cycloaddition processes of nitrile ylides generated from N-benzyltrifluoroacetimidoyl chlorides **1a-c** by the action of triethylamine. The monoadducts **4a,b** and **5a,b** were isolated as a result of the interaction of nitrile ylides, generated from N-benzyltrifluoroacetimidoyl chlorides **1a,b** by the action of triethylamine, with fullerene in boiling chlorobenzene.

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* For Part 1 see [1].

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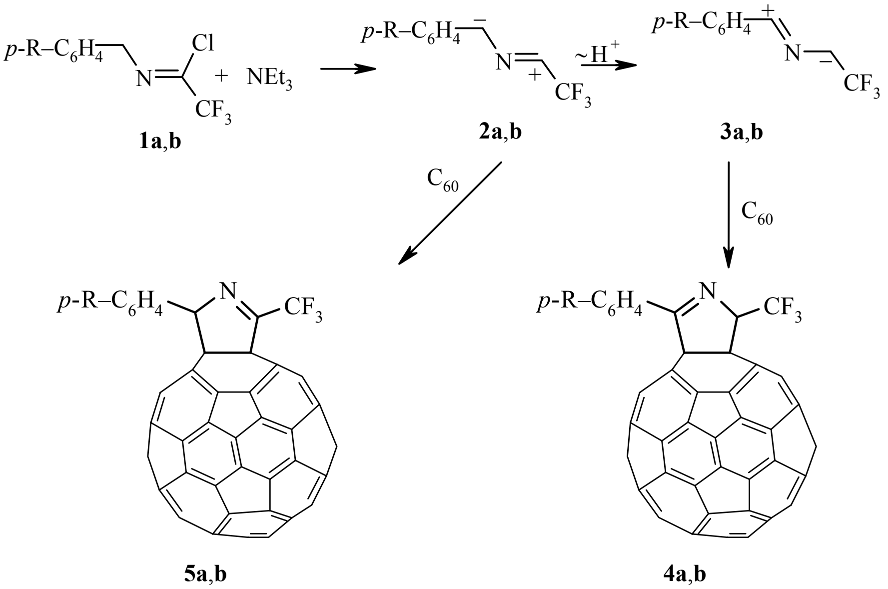


1–5 **a** R = H, **b** R = MeO

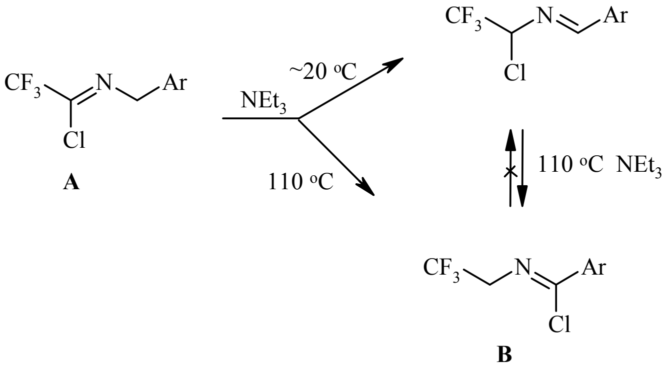
For the analysis of the compounds obtained we have used MALDI (Matrix Assisted Laser Desorption/Ionization), one of the mildest methods of ionization in mass spectrometry. This method has successfully recommended itself as one of the most reliable analytical means for characterizing organic fullerene derivatives [7], which are, as a rule, subject to complete or significant fragmentation or degradation on using traditional methods (EI mass spectrometry).

Adducts **4a,b**, 1,2-[5-phenyl-2-trifluoromethyl-3,4-dihydro-2H-pyrrolo]fullerene-60 and 1,2-[5-(4-methoxyphenyl)-2-trifluoromethyl-3,4-dihydro-2H-pyrrolo]fullerene-60, are the main reaction products. Results obtained by MALDI mass spectrometry prove that these compounds are monoadducts. In the negative ion mass spectra the most intense peaks, with *m/z* 906 and 936 were assigned to the molecular ions of monoadducts **4a** and **4b** respectively, the content of the fragmentary anion of C_{60} was insignificant in both cases.

The sole reliable method permitting determination of whether closed [6,6]-cycloadducts or open [5,6]-fulleroid structures are formed is ^{13}C NMR spectroscopy. The appearance in a spectrum of signals of sp^3-hydridized carbon atoms is characteristic of the formation of closed [6,6]-isomers. In the ^{13}C NMR spectrum of compound **4b**, apart from the signals of the carbon atoms of the fullerene, the aromatic nucleus and the CF_3 and C=N groups, there were signals at 54.6 (CH_3O) and at 73.4, 86.2, and 86.4 ppm for the sp^3-hybridized carbon atoms, which correspond to the $C_{(2)}$, $C_{(3)}$, and $C_{(4)}$ atoms of the pyrroline ring, indicating the formation of a closed [6,6]-cycloadduct. When forming fulleroid structures the signals of the nuclei of atoms $C_{(3)}$ and $C_{(4)}$ must be absent from the aliphatic region.

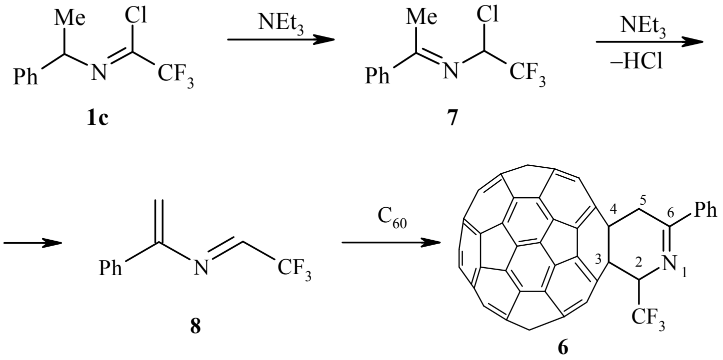
The ^1H NMR spectra of these compounds give exhaustive information on the fine special features of the structure of the annelated pyrroline fragment. In the ^1H NMR spectra of both adducts **4a** and **4b** quadruplet signals were observed at ~6.6 ppm corresponding to the methine protons located in the position α to the CF_3 group. The double C=N bond in the adducts proved to be displaced in comparison with the initial imidoyl halide.

According to the data of [8, 9], N-benzyltrifluoroacetimidoyl chloride **A** may undergo conversion in the presence of base into the isomeric imidoyl chlorides **B**. It is possible that the **A→B** rearrangement proceeds more rapidly than 1,3-dipolar addition to the fullerene, and nitrile ylides **3a,b**, interacting with the fullerene with the formation of the main products **4a,b**, are generated from imidoyl chlorides **B**.



Adducts **5a,b** are formed in insignificant amounts, insufficient to obtain their ^{1}H NMR spectra. However, according to the data of MALDI mass spectrometry, they are, like adducts **4a,b**, products of monoaddition. We propose that 1,2-[2-phenyl-5-trifluoromethyl-3,4-dihydro-5H-pyrrolo]fullerene-60 and 1,2-[2-(4-methoxyphenyl-5-trifluoromethyl-3,4-dihydro-5H-pyrrolo]fullerene-60 are the products of addition of nitrile ylides **2a,b**, generated from **A**.

Unexpected results were obtained on going to N-(methylbenzyl)trifluoro-acetimidoyl chloride (**1c**). In place of the expected fulleropyrroline, 6-phenyl-2-trifluoromethyl-2,3,4,5-tetrahydropyridino[3',4':1,2]fullerene-60 (**6**) was obtained.



According to the data of MALDI mass spectra the main signal in the high mass region was the molecular ion of *m/z* 920, which corresponds to the molecular mass of adduct **6**. In difference to the spectra of the pyrroline structures **4**, the ^{1}H NMR spectrum of compound **6** clearly indicates the formation of a six-membered ring. In fact the appearance in the spectrum of signals for an AB system of nonequivalent protons at position **5** of the annelated ring as two doublets at 4.70 and 5.06 ppm with J = 14.2 Hz serves as an argument in favor of this assertion. The remaining signals correspond to the proposed structure. The formation of compound **6** may be explained by a [4 + 2] cycloaddition of diene **8** to fullerene. Compound **8** may be formed from imidoyl chloride **1c** by the proposed scheme. Probably the isomer of imidoyl chloride **7** is formed initially, according to the isomerization scheme given previously for imidoyl chlorides, and is subject to dehydrochlorination under the action of triethylamine, being converted into azadiene **8**.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Varian XL-400 instrument (400 and 100 MHz respectively), internal standard was TMS.

Analysis by the MALDI method was carried out on a Vision 2000 time-of-flight mass spectrometer with a N_2 lazer of radiation wavelength 336 nm.

Orthorhombic sulfur was successfully used by us as matrix. The order of preparing samples of substances for analysis is as follows [10]. Several drops (less than 1 μl) of a saturated toluene solution of the matrix were applied to a metal target with a fine capillary to form, after evaporation of the solvent, a thin film. A fraction of the substance being analyzed, obtained by TLC, was also dissolved in toluene. The surface of the matrix film was then wetted with several drops of this solution with the aid of a fine capillary. A check on the progress of reactions and the purity of the compounds obtained was effected by TLC on Silufol UV-254 plates. Separation and purification of substances was carried out on a column of silica gel L 40/100, eluting with hexane–benzene, 1 : 10.

N-Benzyltrifluoroacetimidoyl Chlorides 1a-c and their precursor **N-trifluoroacetamides** were synthesized by the methods of [8, 9].

N-Benzyltrifluoroacetimidoyl Chloride (1a). Yield 35%; bp 110-112°C (10 mm Hg). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 4.83 (2H, s, CH_2); 7.35 (5H, m, Ph).

N-*p*-Methoxybenzyltrifluoroacetimidoyl Chloride (1b). Yield 40%; bp 96-100°C (15 mm Hg). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.81 (3H, s, CH_3O); 4.77 (2H, s, CH_2); 6.90 (2H, d, $J = 9.3$, 3-, 5-H_{Ph}); 7.27 (2H, d, $J = 9.3$, 2-, 6-H_{Ph}).

N-(Methylbenzyl)trifluoroacetimidoyl Chloride (1c). Yield 30%; bp 65-70°C (12 mm Hg). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.68 (3H, d, $J = 7$, CH_3); 5.12 (1H, q, $J = 7$, CH); 7.50 (5H, m, Ph).

Fulleropyrrolines 4a,b, 5a,b and Fulleropiperideine 6. A solution of imidoyl chloride (0.21 mmol) in dry chlorobenzene (10 ml) was added during 1 h to a solution of fullerene C_{60} (50 mg, 0.07 mmol) and triethylamine (100 μl, 0.73 mmol) in boiling dry chlorobenzene. After the addition the mixture was boiled for a further 2 h. After distilling off the solvent in vacuum, the residue was treated with methanol, the solid filtered off, washed several times with methanol, and separated by column chromatography, eluent was benzene–hexane, 1:3.

5-Phenyl-2-trifluoromethyl-3,4-dihydro-2H-pyrrolo[3',4':1,2]fullerene-60 (4a). Yield 25%. MALDI mass spectrum: *m/z* 906 $[M]^{-\cdot}$. ^1H NMR spectrum (CS_2–acetone-d_6, 5:1), δ, ppm (*J*, Hz): 6.68 (1H, q, $J = 7.9$, CF_3CH); 7.53 (3H, m, 3-, 4-, 5-H_{Ph}); 8.10 (2H, d, 2-, 6-H_{Ph}).

5-(4-Methoxyphenyl)-2-trifluoromethyl-3,4-dihydro-2H-pyrrolo[3',4':1,2]fullerene-60 (4b). Yield 30%. MALDI mass spectrum: *m/z* 935 $[M]^{-\cdot}$. ^1H NMR spectrum (CS_2–acetone-d_6, 5:1), δ, ppm (*J*, Hz): 3.87 (3H, s, CH_3O); 6.60 (1H, q, $J = 7.8$, CF_3CH); 7.00 (2H, d, $J = 9.3$, 3-, 5-H_{Ph}); 8.18 (2H, d, $J = 9.3$, 2-, 6-H_{Ph}). ^{13}C NMR spectrum (CS_2–acetone-d_6, 5:1), δ, ppm: 54.6 (CH_3O); 73.4 (Csp^3); 86.2 (Csp^3); 86.4 (Csp^3); 116 (CF_3), a group of signals for carbon nuclei at 120-161, 175 (C=N).

Adduct 5a. MALDI mass spectrum: *m/z* 906 $[M]^{-\cdot}$.

Adduct 5b. MALDI mass spectrum: *m/z* 935 $[M]^{-\cdot}$.

6-Phenyl-2-trifluoromethyl-2,3,4,5-tetrahydropyridino[3',4':1,2-]fullerene-60 (6). Yield 25%. MALDI mass spectrum: 920 $[M]^{-\cdot}$. ^1H NMR spectrum (CS_2–acetone-d_6, 5:1), δ, ppm (*J*, Hz): 4.70 (1H, d, $J = 14.2$, 5-H); 5.06 (1H, d, $J = 14.2$, 5'-H); 5.82 (1H, q, $J = 7.5$, CF_3–CH); 7.56 (3H, m, 2*m*-, *p*-H_{Ph}); 8.22 (2H, m, 2*o*-H_{Ph}).

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