## REACTION OF CARBOXYLIC ACID

## AMIDINES WITH KETIMINES

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Diphenyl- and trifluoromethylphenylketimines undergo the Diels - Alder reaction with amidines of benzoic and trichloro- and trifluoroacetic acids to give dihydro-sym-triazines through intermediate azadienes. The structures of the synthesized compounds were proved by means of their IR, PMR, and mass spectra.

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In [1, 2] we established that dihydro-sym-triazines are obtained in the reaction of amidines with Schiff bases. It might be assumed that, by analogy, ketimines should react with amidines to give dihydro-sym-triazines through intermediate azadienes, which undergo cyclization via a [4 + 2] cycloaddition scheme.

In the present research we studied the reaction of benzoic and trichloro- and trifluoroacetic acid amidines (IIa-d) with diphenyl- and trifluoromethylphenylketimines (Ia, b). Benzoic and trichloroacetic acid amidines (IIa-c) react with ketimines Ia, b to give dihydro-sym-triazines (IIIa-e).



Trifluoroacetic acid amidine reacts with ketimine Ia to give azadiene IV, which does not undergo cyclization to dihydro-sym-triazine III. The presence of two phenyl groups attached to the terminal C atom and of a  $CF_3$  group attached to the  $C_2$  atom of azadiene IV determines its conformation, which hinders cycloaddition.

Amidine IId reacts somewhat differently with ketimine Ib – a stable product of addition to the C = N bond is formed. The reaction in this case stops at this stage because of stabilization under the influence of electronegative substituents. Ammonia is split out in the case of heating under severe conditions, and cyclization with the production of salt VI takes place through an azadiene intermediate. The formation of ammonium salt VI is explained by the fact that under the influence of three acceptor trifluoromethyl groups dihydro-sym-triazine IIIf is a rather strong NH acid. Compound IIIf is liberated by acidification of a solution of ammonium salt VI.

The structure of III is confirmed in the case of dihydro-sym-triazine IIIa, which is identical to the compound obtained by the method in [3]. Multiplets of protons of aromatic rings at 6.6-8.6 ppm, singlets of methyl groups for dihydro-sym-triazines IIIb, d (2.3-2.4 ppm), and broad singlets with an intensity of 1H at 9.2-11.4

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ppm, which vanish when trifluoroacetic acid is added (which makes it possible to assign them to signals of the NH group), are observed in the PMR spectra of IIIa-f.

Absorption bands of NH groups  $(3380-3450 \text{ cm}^{-1})$  and of triazine ring C = N bonds, which are found at  $1640-1740 \text{ cm}^{-1}$ , depending on the substituents in the ring, are observed in the IR spectra of IIIa-f. The <sup>19</sup>F NMR spectra contain signals of a  $CF_3$  group in the 2 position (3-5 ppm) and in the 4 and 6 positions (-2.5 ppm).

A molecular-ion peak (M<sup>+</sup>) with m/z 276 is observed in the mass spectrum of azadiene IV, and two absorption bands of C = N bonds (1660 and 1550 cm<sup>-1</sup>) and a band of  $CF_3$  group (1150-1250 cm<sup>-1</sup>) are identified in the IR spectrum. A singlet of an NH group with an intensity of 1H at 9.3 ppm and a multiplet of protons of benzene rings with an intensity of 10H centered at 7.5 ppm are present in the PMR spectrum. The <sup>19</sup>F NMR spectrum contains a singlet of a  $CF_3$  group (-5.3 ppm).

A multiplet of protons of a benzene ring with an intensity of 5H at 7.7 ppm and two broad singlets with an intensity of 2H at 6.1 and 2.7 ppm are observed in the PMR spectrum of V. The signal at 2.7 ppm was assigned to the NH<sub>2</sub> group attached to C<sub>4</sub> in analogy with the signal at 2.3 ppm of the NH<sub>2</sub> group of diaminobis (trifluoromethyl)methane [4]. The singlet at 6.1 ppm can be assigned to the NH<sub>2</sub> group of the  $-N=C(CF_3)NH_2$ fragment, since it is shifted to weak field as a consequence of the deshielding effect of the C = N bond.

The signal at 3.1 ppm in the <sup>19</sup>F NMR spectrum was assigned to a  $CF_3$  group attached to a C = N bond, while the singlet at 4.4 ppm was assigned to a  $CF_3$  group attached to a quaternary carbon atom. A complex absorption band of  $NH_2$  groups at 3300-3420 cm<sup>-1</sup> and an intense band of a C = N bond at 1690 cm<sup>-1</sup> are observed in the IR spectrum of V.

The data from IR spectra confirm the structure of salt VI. The intense band at 1630-1640 cm<sup>-1</sup> corresponds to the vibrations of an anion that has aromatic character as a consequence of delocalization of the negative charge. This sort of band is absent in the spectrum of IIIf, but the spectrum does contain an intense absorption band of a C = N - C = N fragment (1740 cm<sup>-1</sup>). The spectra of IIIf and VI contain NH (3400 cm<sup>-1</sup>) and NH<sub>4</sub><sup>+</sup> (broad 3400 cm<sup>-1</sup>) absorption bands, respectively.

The IR spectra of all of the compounds that contain a  $CF_3$  group contain an intense absorption band at 1200 cm<sup>-1</sup>.

## EXPERIMENTAL

The PMR spectra of the compounds were recorded with a Tesla BS-467C spectrometer (60 MHz) at 25°C with hexamethyldisiloxane as the external standard. The <sup>19</sup>F NMR spectra were recorded with a Tesla BS-487C spectrometer (80 MHz) at 25°C with  $CF_3CO_2H$  as the external standard. The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The mass spectrum was obtained with DS-50 and MS-1302 spectrometers at ionizing-electron energies of 70 and 50 eV. The individuality of the compounds obtained was monitored by means of thin-layer chromatography (TLC) on  $Al_2O_3$  (activity II) in a benzene -methanol system (5:1) with development by iodine vapors or in UV light.

2,2-Diphenyl-4,6-diaryl-1,2-dihydro-sym-triazines (IIIa,b). A mixture of 18 mmole of amidines IIa, b and 18 mmole of ketimine Ia was heated at 120°C for 50 h, after which the excess ketimine Ia was removed by vacuum distillation. The residue was treated with ether, and IIIa, b were removed by filtration and crystallized from ethanol.

2-Trifluoromethyl-2-phenyl-4,6-diaryl-1,2-dihydro-sym-triazines (IIIc, d). A mixture of 10 mmole of amidines IIa, b and 10 mmole of ketimine Ib was heated at 120°C until ammonia evolution ceased (5-6 h). The solidified mass was filtered, and the crystalline reaction product was washed with ether. Compounds IIIc, d were crystallized from ethanol or benzene.

2-Trifluoromethyl-2-phenyl-4,6-bis(trichloromethyl)-1,2-dihydro-sym-triazine (IIIe). A solution of 7 mmole of amine IIc and 7 mmole of ketimine Ib in 4 ml of dry chloroform was refluxed for 5 h, after which the solvent and excess ketimine Ib were removed by vacuum distillation. The residue began to crystallize when it was triturated with ether.

The results of elementary analysis, the melting points, and the yields are presented in Table 1.

<u>1,3-Diaza-2-trifluoromethyl-4,4-diphenyl-1,3-butadiene (IV).</u> A mixture of 1.75 g (15 mmole) of amidine IId and 2.7 g (15 mmole) of ketimine Ia was heated at 110°C for 30 h, after which it was cooled, and crystalline IV was washed with heptane and removed by filtration to give 3 g (70%) of a product with mp 94-95°C (from heptane). Found: C 65.0; H 3.9; F 20.2; N 9.9%.  $C_{15}H_{11}F_{3}N_{2}$ . Calculated: C 65.2; H 4.0; F 20.6; N 10.1%.

TABLE 1. Dihydro-sym-triazines IIIa-e

Com~ pound	mp <b>, °</b> C	Found, %				Empirical	Calculated, %				Yield,
		с	н	F	N	formula	с	н	F	N	%
IIIa[3] IIIb IIIc IIId IIIe	191—192 212—213 207—208 221—222 114—115	83,5 83,7 69,6 71,7 31,6	5,2 5,9 4,2 4,8 1,4		11,1 10,0 11,2 10,5 9,2	C <sub>27</sub> H <sub>21</sub> N <sub>3</sub> C <sub>29</sub> H <sub>25</sub> N <sub>3</sub> C <sub>22</sub> H <sub>16</sub> F <sub>3</sub> N <sub>3</sub> C <sub>24</sub> H <sub>20</sub> F <sub>3</sub> N <sub>3</sub> C <sub>12</sub> H <sub>6</sub> Cl <sub>6</sub> F <sub>3</sub> N <sub>3</sub>	83,7 83,8 69,6 70,7 31,2	5,5 6,0 4,2 4,9 1,3		10,8 10,1 11,0 10,3 9,0	30 34 89 90 35

TABLE 2. Spectral Characteristics of Dihydro-sym-triazines IIIa-e

Com - pou <b>nd</b>	IR	spectrum	, cm <sup>-1</sup>	Рλ	1R spectrum,*	19F NMR spec-	
	NH	C=N	CF3	NH	Ar	CH3	trum,* ppm, 2-CF <sub>3</sub>
III a III b III c III d III e	3400 3445 3445 3450 3380	1640 1650 1640 1640 1680		9,2 9,5 11,4 9,7 10,5	$\left \begin{array}{c} 6,6-8,3\\7,3-8,6\\7,75-8,25\\7,1-8,1\\7,5\end{array}\right $	2,4 2,3	3,0 4,6 3,14

 $\overline{* \text{In } (\text{CD}_3)_2 \text{CO}}$  (in d<sub>6</sub>-DMSO in the case of IIIb, c).

<u>3-Aza-2,4-diamino-1,1,1,5,5,5-hexafluoro-4-phenyl-2-pentene (V).</u> A) A 2.1-g (20 mmole) sample of amidine IId was added to 3.2 g (20 mmole) of ketimine Ib, and the solution was heated at 75°C for 4 h. The crystalline V was removed by filtration and washed on the filter with heptane go give 4 g (77%) of a product with mp 67-68.5°C (from heptane). Found: C 42.2; H 3.1; F 39.8; N 14.7%.  $C_{10}H_9F_6N_3$ . Calculated: C 42.1; H 3.2; F 39.9; N 14.7%.

B) Equimolar amounts of ketimine Ib and amidine IId were mixed, and the solution was allowed to stand at 20°C. After several days, the reaction mass began to crystallize. Workup gave the product in 75% yield.

2,4,6-Tris (trifluoromethyl)-2-phenyl-1,2-dihydro-sym-triazine (IIIf). A solution of 0.6 g (16 mmole) of salt VI was acidified to pH 6 with 2 N HCl, and dihydro-sym-triazine IIIf was extracted with ether (three 10-ml portion). The ether extracts were dried with calcined magnesium sulfate, and the ether was removed by distillation to give 0.5 g (83%) of an oily product with mp 122-124°C and  $n_D^{25}$  1.4262. IR spectrum: 3390 (NH), 1740 (C=N), and 1150-1250 cm<sup>-1</sup> (CF<sub>3</sub>). PMR spectrum in (CD<sub>3</sub>)<sub>2</sub>CO: 7.4 (5H, m) and 5.0 (1H, s). <sup>19</sup>F NMR spectrum: 5.4 (2-CF<sub>3</sub>, s) and -2.5 (4,6-CF<sub>3</sub>, s). Mass spectrum:  $M^+$  363 m/z. Found: C 40.1; H 1.9; F 46.7; N 11.5%. C<sub>12</sub>H<sub>6</sub>F<sub>9</sub>N<sub>3</sub>. Calculated: C 39.7; H 1.7; F 47.0; N 11.6%.

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