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#### SHORT COMMUNICATION

# Trifluoromethyl-aryl(alkyl)carbodiimides

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The previously reported methods of preparation of fluorine containing carbodiimides are not very common and have rather small accessibility [1-3]. Recently, it has been shown [4] that perfluoro-2-azapropene and primary arylamines produce derivatives of di-aza-cyclobutane and tri-aza-cyclohexane. However, properties and physical constants of these compounds and experimental details have not been published. The authors propose that this reaction proceeds through the intermediate formation of trifluoromethylcarbodiimides, but these substances have not been isolated.

We found, that products of the reaction between perfluoro-2-azapropene (I) and primary amines are determined by the reaction conditions and the correlation: between starting materials. For example, an excess of (I) with aniline in the presence of triethylamine leads, according to the NMR <sup>19</sup>F spectrum to the formation of nearly equal quantities of N-phenyl-tetrafluoro-2-azapropenylamine (II) and N-phenyl-N-trifluoromethylcarbodiimides (III).

This reaction in the presence of anhydrous KF leads to the formatio of only N-aryl-N-trifluoromethylcarbodiimides (III,a,b) in good yield

$$(I) + Ar - \overline{M}H_2 \xrightarrow{2KF, ether} CF_3 - N = C = N - Ar \qquad (III, a, b)$$
  
a: Ar = C<sub>6</sub>H<sub>5</sub>; b: Ar = p - CH<sub>3</sub>O - C<sub>6</sub>H<sub>4</sub>

The interaction of I with aliphatic amines can be interrupted at the stage of N-alkyl-tetrafluoro-2-azapropenylamine (IV) formation. It is probably a result of different influence of alkyl- and arylgroups upon the proton abstraction reaction for IV and II. Neverthe less, the corresponding aliphatic carbodiimides (V) may be easily obtained by distillation of IV over anhydrous KF.

$$I + R-NH_{2} \xrightarrow{KF, ether} CF_{3}-N=CF-NH-R$$
(IV, a-d)  
-KF+HF  
CF\_{3}-N=C=N-R (V, a-d)  
CF\_{3}-N=C=N-R (V, a-d)

a:  $\mathbf{R} = C_2H_5$ ; b:  $\mathbf{R} = C(CH_3)_3$ ; c:  $\mathbf{R} = C_6H_{11}$ ; d:  $\mathbf{R} = CH_2CH=CH_2$ Thus, the reaction of perfluoro-2-azapropene with primary amine seems to be a universal method for the production of trifluoromethyl carbodiimides.

#### EXPERIMENTAL

## Trifluoromethyl-aryl(alkyl)carbodiimides.

A solution of amine (0.1 mole in 20 ml anhydrous diethyl ether) was slowly added to stirred mixture of perfluoro-2-azapropene (15g, 0. mole), 50 ml anhydrous diethyl ether, 0.1g triethylamine and 20g anhydrous KF cooled to -35°. After stirring for 5 h at room tempera ture, two phases separated and the ether layer was distilled. Com

### Table 1. Characteristics of trifluoromethyl-aryl(alkyl)carbodiimides

Compo- und	R	yield (%)	b.p. (°C/torr)	Formula	Analysis exp. (calc.)		
					С	H	N
III,a	<sup>C</sup> 6 <sup>H</sup> 5	80	45-47/4	<sup>C</sup> 8 <sup>H</sup> 5 <sup>N</sup> 2 <sup>F</sup> 3	51.54	2.73	14.78
	N.				(51.60)	(2.70)	(15.05)
III,b	<sup>CH</sup> 3 <sup>OC</sup> 6 <sup>H</sup> 5	69	81/2	<sup>C</sup> 9 <sup>H</sup> 7 <sup>N</sup> 2 <sup>F</sup> 3 <sup>O</sup>	49.69	3.33	12.42
					(50.00)	(3.24)	(12.96)
V,a	с <sub>2</sub> н <sub>5</sub>	46	75/90	$C_4H_5N_2F_3$	34.92	3.58	20.64
					(34.78)	(3.62)	(20.28)
V,b	C(CH <sub>3</sub> ) <sub>3</sub>	58	46/70	<sup>C</sup> 6 <sup>H</sup> 9 <sup>N</sup> 2 <sup>F</sup> 3	43.11	5.09	16.28
					(43.37)	(5.42)	(16.87)
V,c	C6H11	69	61/9	<sup>C</sup> 8 <sup>H</sup> 11 <sup>N</sup> 2 <sup>F</sup> 3	50.89	5.47	13.72
					(50.00)	(5.73)	(14.58)
V,d	CH2CH=CH2	72	111	<sup>C5<sup>H</sup>5<sup>N</sup>2<sup>F</sup>3</sup>	40.16	2.86	19.23
					(39.70)	(3.20)	(18.57)

 $CF_3 - N = C = N - R^{\frac{3}{2}}$ 

 \*) Carbodiimides (III and V) have characteristic adsorbtion bands in IR-spectra at 2150-2200 cm<sup>-1</sup>; NMR <sup>19</sup>F spectra of the compounds: CF<sub>3</sub> (s) -28.9 : -29.0 ppm relatively CF<sub>3</sub>COOH (ext)

pounds IIIa, b were obtained by direct distillation, compounds V a, b, c, d were obtained by redistillation over lOg anhydrous KF. The properties of compounds are summarised in Table 1.

## N-Alkyl-tetrafluoro-2-azapropenylamines.

Compounds IV a,b,c,d were obtained analogously to compounds III by direct distillation (without addition of anhydrous KF). The properties of the compounds are summarised in Table 2.

Compo- und	R	yield (%)	b.p. (°C/torr)	Formula	Analysis exp. (calc)		
					С	Н	N
IV,a	с <sub>2</sub> н <sub>5</sub>	52	58/12	C4 <sup>H6N2F4</sup>	29.54	3.48	17.43
					(30.38)	(3.80)	(17.72)
IV,b	C(CH <sub>3</sub> ) <sub>3</sub>	61	60/12	$C_6^{H_{10}N_2F_4}$	38.10	4.73	15.19
					(38.70)	(5.37)	(15.05)
IV,c	C6 <sub>H</sub> 11	73	83/4	<sup>C</sup> 8 <sup>H</sup> 12 <sup>N</sup> 2 <sup>F</sup> 4	45.40	5.67	13.20
					(45.28)	(5.66)	(13.21)
IV,d	CH <sub>2</sub> CH=CH <sub>2</sub>	76	58/8	°5 <sup>H</sup> 6 <sup>№</sup> 2 <sup>₽</sup> 4	34.87	3.01	16.50
					(35.29)	(3.53)	(16.47)

CF<sub>3</sub>N≈CF-NH-R<sup>#</sup>

 \*) NMR <sup>19</sup>F spectra of IV, a-d: CF<sub>3</sub> (s) -28.1 : -28.8 ppm; CF (q) -32.6 : -35.4 ppm

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