A NEW METHOD OF SYNTHESIS OF CONJUGATED SYSTEMS WITH TRIS(FLUOROMETHINE) CHAIN

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Summary: The interaction of compounds having the active methylene group with perfluoroallyliodide leads to the formation of conjugated systems with the tris(fluoromethine) chain.

Polyfluoromethine compounds are a new type of conjugated systems¹. Their uniqueness consists in the fact that in nature there are no other atoms besides fluorine ones which during the hydrogen substitution in the polymethine systems would induce strong space difficulties preventing the transfer of the effect of conjugation.

We have found the one-step method for the synthesis of the conjugated systems with the tris(fluoromethine) chain. The method lies in the interaction of the compounds having the active methylene group with perfluoroallyliodide.

We have shown previously that the interaction of the methylene bases of nitrogen heterocycles with perfluoroalkyliodide leads to the formation of β -perfluoroalkylcarbocyanines².



 $\mathbf{Z} = \mathbf{C}(\mathbf{CH}_3)_2, \mathbf{D}, \mathbf{S}, \mathbf{S}_{\Theta}, \mathbf{CH} = \mathbf{CH}, \mathbf{NC}_2\mathbf{H}_5$

The reaction proceeds with the participation of ICF_2 -group whose carbon atom gives the central atom of the polymethine chain. However, the interaction of methylene bases with perfluoroallyliodide results in the production of β , χ , δ -trifluorodicarbocyanines rather than of β -perfluorovinylcarbocyanines. In contrast to perfluoroalkyliodides which react with methylene bases under the UV-radiation, the interaction with perfluoroallyliodide in acetonitrile proceeds smoothly when mixing reagents. Presumably, the first step of the reaction is the nucleophilic attack on the double bond of the methylene group with the subsequent cleavage of fluorohydrogen, iodine and fluorine atoms in the CF₂I group:



 $Z = C(CH_3)_2$, R = H(1); $Z = N-C_2H_5$, $R = CF_3SO_2$ (2); Z = CH=CH, R = H(3); Z = quino-4, R = H(4).

The reaction is of general character and proceeds not only with the methylene bases but also with other nucleophiles which are able to delocalize the negative charge. The reaction of malonodinitrile with perfluoroallyliodide leads to the formation of the anion dye with the completely fluorine substituted chain:

Previously we have synthesized the cation dye with the completely fluorine substituted polymethine chromophore³.

To confirm the possibility for addition of methylene bases of nitrogen-containing heterocycles by the double bond of perfluoroolefines we have studied the reaction of 1-methyl-2-methylene-2H-quinoline with perfluoropropylene. It has been found that quinocarbocyanine with the CF_3CFH group in meso-position readily forms in this case. Evidently, the addition product along the double bond also forms in the first step. This product after fluorohydrogen evolution cannot be stabilized by the elimination of the fluorine atom of the stable CF_3 group contrary to the iodine atom of the labile CF_2I group. The splitting out and the addition of HF occurs with the subsequent reaction along the carbon atom of salt C with the methylene base B.



The ¹⁹F NMR spectra of carbocyanines show two types of signals corresponding to two types of fluorine atoms being in β , χ and δ -positions of the polymethine chain. The signal of χ -fluorine has the appearance of triplet-triplets with constants 80 and 3Hz, the signal of fluorine β , δ -atoms is more complex. It represents a broadened singlet for compound I. At -50-80°C it is possible to reveal a fine structure evidencing for the existence of the dye in several conformations. Similar picture is observed in spectra of other compounds.

Studies on the NMR spectra of the synthesized compounds will be continued.

The ¹⁹F NMR spectra are recorded in CD₃CN on a "Bruker" WP 200 spectrometer, operating at 188 MHz relative to the internal standard CFCI₃.

General Procedure.

Dicarbocyanines (1-4). Perfluoroallyliodide (0.01 mol) and the corresponding methylene base (0.04 mol) are mixed in 15 ml of anhydrous CH_3CN . The mixture is stirred for 20 min, then the dye is precipitated by the addition of ether, transformed to perchlorate and recrystallized from CH_3CN . The compound (5) is obtained from malonodinitrile in the presence of $N(C_2H_5)_4OH^-$.

Carbocyanine (6). Perfluoropropylene (0.01 mol) is passed into the solution of the methylene base (0.01 mol) obtained from 1,2-dimethylquinoline quaternary salt (0.01 mol) in 15 ml of CH_3CN . The dye is precipitated by ether, transformed into perchlorate, purified by SiO₂ chromatography.

N com- pound	Yield in %	Mel- ting point T ^o C	λ_{\max} (E. 10 ⁻⁴)	19 _{F NMR} chemical shift	J, Hz
I*	41	204	648	-104.77 b.s. (2F)	³ (F H) 42.1
			(9.27)	-168.25 t.t (1F)	³ (FH) 82.7 ⁴ (FH) 3.3
2**	-	-	580	-78.4 (6F)	³ (F F) 73.2
				-114.8 d (2F)	
				-176.9 t.t (1P)	_
3	54	248	694	-120.4 d.m (2F)	³ (FF) 73.2
				-173.0 t.t (1F)	³ (HF) 33.7
4	58	250	769	-120 d.m (2F)	³ (FF) 67
			(12.49)	-172.2 t.t (1F)	
					³ (FH) 36.4
					⁴ (FH) 3.5
5	49	130	439	-111.6 d(2F)	³ (FF) 88.5
				-183.2 t (1F)	<u> </u>
6	55	195	649	-76.3 d.d (3F)	² (FH) 43.5
				-190.3 d.q (1F)	³ (FF) 11.7
* 19 ₁	' NMR si	ectrum (of CD ₂ Cl ₂ at -70) ⁰ C-105.6 d.m (2F); -170.13 (t.t) 1F	
** The	dye is	unstab.	le, fixed spectr	ally	
The dated st	ita of u ructure	ltimate ∺s.	analysis and PM	IR spectra correspond t	o the sugges-
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(Received in UK 17 June 1991)