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Studies on Organic Fluorine Compounds. XIII.[1] Studies on Equilibrium of (Trifluoro- and/or Chlorodifluoromethyl)-dihydro-*s*-triazine Derivatives by ^{19}F-Nuclear Magnetic Resonance Spectra

Yoshiro Kobayashi, Akio Ohsawa, and Masamitsu Honda

Tokyo College of Pharmacy[2]

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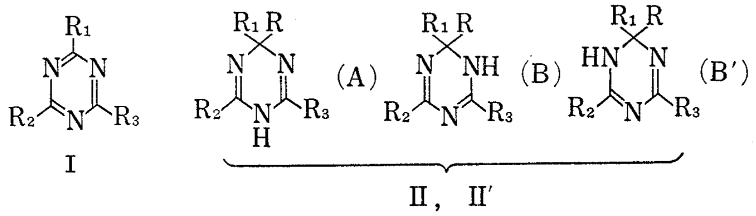
Behavior of the chemical shifts in ^{19}F-nuclear magnetic resonance spectra of [polyfluoro-(chloro)methyl]-dihydro-*s*-triazine derivatives in deuterochloroform and in methanol was examined and it was concluded that these compounds exist in the form of 1,4-dihydro type (A) and 1,2-dihydro type (B and B') and that they are in equilibrium in methanol solution.

We have already obtained some (trifluoro- and chlorodifluoromethyl)dihydro-*s*-triazine derivatives (II and II') by photoirradiation of [polyfluoro(chloro)methyl]-*s*-triazines[1] (I) (Chart 1).



I

II, II'

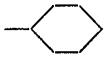
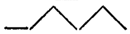
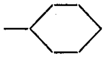
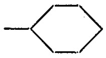
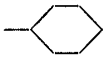
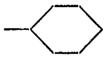
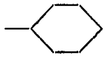
II	R_1	R_2	R_3	R
II—1a	CF_3	CF_3	CF_3	
II—1b	CF_3	CF_3	CF_3	
II—2a	CF_3	CF_3	CF_2Cl	
II—2b	CF_3	CF_3	CF_2Cl	
II'—2b	CF_2Cl	CF_3	CF_3	
II—3b	CF_3	CF_2Cl	CF_2Cl	
II'—3b	CF_2Cl	CF_3	CF_2Cl	
II—4a	CF_2Cl	CF_2Cl	CF_2Cl	
II—4b	CF_2Cl	CF_2Cl	CF_2Cl	

Chart 1

We found that the signals of these compounds in ^{19}F-nuclear magnetic resonance (^{19}F-NMR) spectra showed a marked difference in deuterochloroform and in methanol. 2,4,6-Tris-(trifluoromethyl)-2-pentyl-dihydro-*s*-triazine (II-1a) showed absorption signals at 12.3 and 22.8 ppm in methanol, in intensity ratio of 2: 1 (benzotrifluoride = 0 ppm as internal standard for all measurements, unless otherwise noted), while its absorption in deuterochloroform shows five signals at 12.0, 13.0, 13.5, 20.8, and 24.0 ppm in intensity ratio of 4: 1: 1: 2: 1. They are all in the higher field than the signal of the corresponding *s*-triazine (I-1) (9.25 ppm in $CDCl_3$). The signal at 12.3 ppm in methanol is approximately in the center of gravity of signals at 12.0, 13.0, and 13.5ppm in deuterochloroform, and the position of the signal at 22.8 ppm is approximately in the center of the signals at 20.8 and 24.0 ppm in deuterochloroform. In general, the signal of fluorine in CF_3 group on the sp^2 carbon appears in a lower field than that of fluorine in CF_3 group on the sp^3 carbon, so that the signals at 12.3 ppm in methanol and those at 12.0, 13.0, and 13.5 ppm in deuterochloroform are those of fluorine in (sp^2)C-CF_3, and the signals at 22.8 ppm in methanol and at 20.8 and 24.0 ppm in deutero-

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[1] Part XII: Y. Kobayashi, A. Ohsawa, and M. Honda, *Chem. Pharm. Bull.* (Tokyo), **21**, 1575(1973).

[2] Location: *Kitashinjuku 3-chome, Shinjuku-ku, Tokyo.*

chloroform are those of fluorine in (sp^3)C-CF$_3$. It follows, therefore, that there are three kinds of nonequivalent (sp^2)C-CF$_3$ and two kinds of nonequivalent (sp^3)C-CF$_3$ in deuterochloroform, and they appear as two signals in methanol. Similarly, in the ^{19}F-NMR spectrum of 2,4,6-tris(trifluoromethyl)-2-cyclohexyl-dihydro-*s*-triazine (II—1b), the signals of the same intensity ratio as that in II-1a appear at 12.1 and 16.4 ppm in methanol, while the signals appear at 12.0, 12.8, 13.1, 15.2, and 18.1 ppm in the same intensity ratio as that in II-1a in deuterochloroform. This phenomenon indicates that II-1 are present in 1,4-dihydro type (A) and 1,2-dihydro type (B) in 2: 1 ratio in deuterochloroform, and that a rapid equilibrium is established between A and B in methanol. And the collapse of signals was observed when a trace of methanol ($<1\%$) was added to the solution of II-1b in deuterochloroform, and the signals were almost identical with those in methanol when methanol added was increased up to 10%. There is a slight deviation in the signals in methanol from those in deuterochloroform, which is a solvent effect, probably caused by either a change in the chemical shift or a slight deviation in the equilibrium constant.

The spectra of ^{19}F-NMR of these compounds are shown in Figure 1.

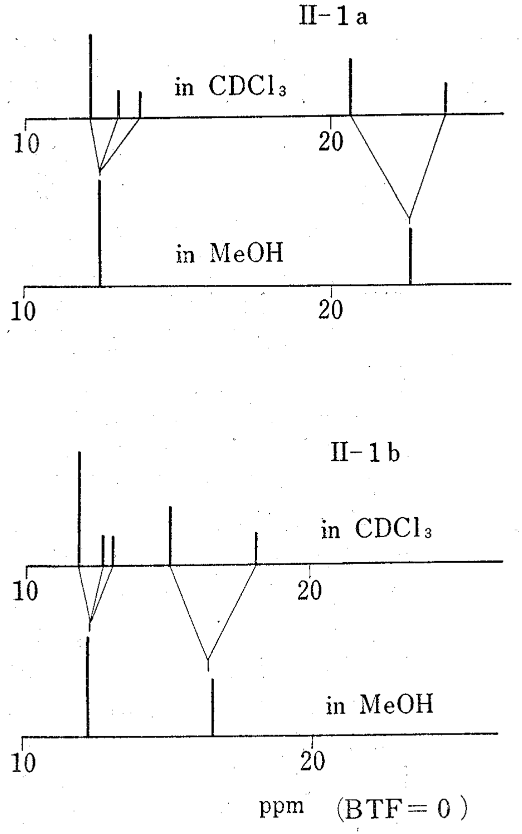

Fig. 1.

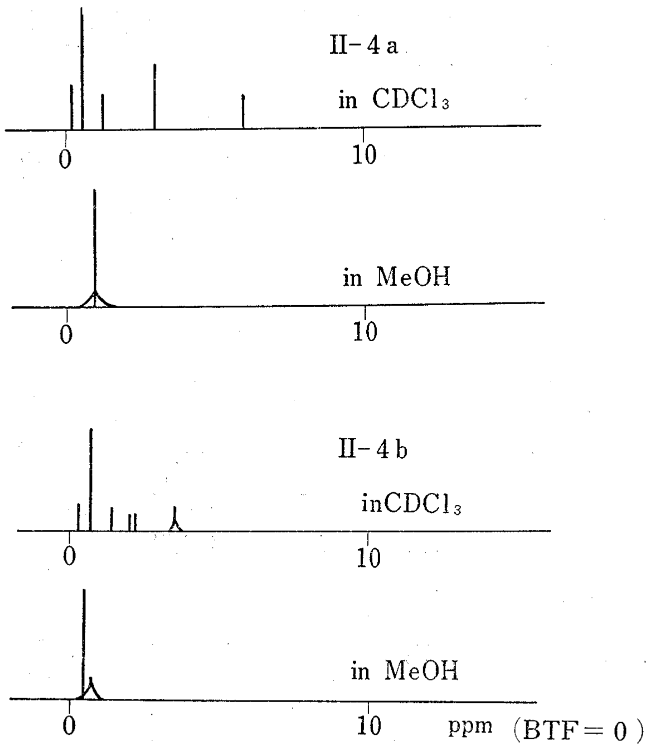

Fig. 2.

In the spectra of 2,4,6-tris(chlorodifluoromethyl)-2-pentyl-dihydro-*s*-triazine (II-4a) in methanol,[3] a sharp signal and a broad one appear at 1.0 ppm in intensity ratio of 1: 2 approximately, while the signals in deuterochloroform appear at 0.2, 0.6, 1.2, 3.0, and 6.0 ppm in intensity ratio of 1: 4: 1: 1: 2. These signals are all in a higher field than that where the signals of the corresponding *s*-triazine (I-4) (—1.0 ppm in CDCl$_3$) are.

^{19}F-NMR spectrum of 2,4,6-tris(chlorodifluoromethyl)-2-cyclohexyl-dihydro-*s*-triazine (II-4b) shows a pattern similar to that of II-4a. In practice, however, the signals are close

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[3] ^{19}F-NMR of 2,4,6-tris(chlorodifluoromethyl)-aryl-dihydro-*s*-triazines in trichlorofluoromethane is reported in *J. Org. Chem.*, 31, 3910 (1966) by L.O. Moore.

to each other, and correct integral ratio cannot be obtained; solvent effects mentioned above are significantly large in comparison with differences between the signals. Consequently, it is impossible to make an exact assignment. ^{19}F-NMR spectra of these compounds are shown in Figure 2.

Similar to the foregoing compounds, symmetric compounds show signals of comparatively simple pattern; 2,4-bis(trifluoromethyl)-6-(chlorodifluoromethyl)-6-cyclohexyl-dihydro-*s*-triazine(II′-2b), 2,4-bis(chlorodifluoromethyl)-6-(trifluoromethyl)-6-cyclohexyl-dihydro-*s*-triazine (II-3b), *etc.* In contrast, asymmetric compounds (II-2a, II-2b, II′-3b, *etc.*) show complex patterns, especially in deuterochloroform in which these exist as unequal 1,2-dihydro types (B and B′) and a precise assignment has not been made on chlorodifluoromethyl groups of some of the compounds.

In some cases, for chlorodifluoromethyl groups, the signals undergo splitting or broadening, but the reason for these phenomena is not fully analyzed. Chemical shifts and assignment of their signals in ^{19}F-NMR spectra are given in Table I.

From the results indicated in Table I, it is seen that II exists as the 1,4-dihydro type (A) and 1,2-dihydro types (B and B′) in deuterochloroform, in ratio of 4: 1: 1 approximately,

TABLE I. ^{19}F-NMR of Adduct II

Adducts	Solvents	Signals ppm$^{a)}$			Ratios of intensity, assignment					
II-1a	$CDCl_3$	12.0(4)	13.0(1)	13.5(1)	20.8(2)	24.0(1)				
		R_2,R_3(A)	R_2,R_3(B)		R_1(A)	R_1(B)				
	MeOH	12.3(2)	22.8(1)							
		R_2,R_3	R_1							
II-1b	$CDCl_3$	12.0(4)	12.8(1)	13.1(1)	15.2(2)	18.1(1)				
		R_2,R_3(A)	R_2,R_3(B)		R_1(A)	R_1(B)				
	MeOH	12.1(2)	16.4(1)							
		R_2,R_3	R_1							
II-2a	$CDCl_3$	0.6(8)	1.6(2)	2.0(2)$^{b)}$	11.8(12)	12.5(3)	13.0(3)	20.5(12)	23.8(3)	23.9(3)
		R_3(A)	R_3(B,B′)		R_2(A)	R_2(B,B′)		R_1(A)	R_1(B,B′)	
	MeOH	0.8(2)	12.3(3)	22.8(3)						
		R_3	R_2	R_1						
II-2b	$CDCl_3$	0.6(8)	1.6(2)	2.3(2)$^{b)}$	12.0(12)	13.0(3)	13.3(3)	15.4(12)	18.2(3)	18.4(3)
		R_3(A)	R_3(B,B′)		R_2(A)	R_2(B,B′)		R_1(A)	R_1(B,B′)	
	MeOH	0.75(2)	12.2(3)	16.4(3)						
		R_3	R_2	R_1						
II′-2b	$CDCl_3$	0.5(4)$^{c)}$	3.7(2)$^{c)}$	12.0(12)	12.5(3)	13.3(3)				
		R_1(A)	R_1(B)	R_2,R_3(A)	R_2,R_3(B)					
	MeOH	0.5(1)$^{c)}$	12.0(3)$^{c)}$							
		R_1	$R_2.R_3$							
II-3b	$CDCl_3$	0.6(8)	1.5(2)	2.3(2)$^{b)}$	15.2(6)	18.1(3)				
		R_2,R_3(A)	R_2,R_3(B)		R_1(A)	R_1(B)				
	MeOH	0.6(4)	16.5(3)							
		R_2,R_3	R_1							
II′-3b	$CDCl_3$	0.3(8)	0.8(8)	1.5(2)	2.3(2)$^{b)}$	3.7(4)$^{c)}$	11.8(12)	12.8(3)	13.3(3)	
		R_3(A)	R_1(A)	R_1,R_3(B,B′)			R_2(A)	R_2(B,B′)		
	MeOH	0.7(2)	1.3(2)$^{c)}$	12.1(3)						
		R_3	R_1	R_2						
II-4a	$CDCl_3$	0.2(1)	0.6(4)	1.2(1)	3.0(1)	6.0(2)				
	MeOH	1.0$^{d)}$	1.0$^{c,d)}$							
II-4b	$CDCl_3$	0.2(1)	0.5(4)	1.3(1)	2.0(2)$^{b)}$	3.5(1)$^{c)}$				
	MeOH	0.2—0.8$^{c,d)}$	0.6$^{d)}$							

a) in δ ppm, with benzotrifluoride= O ppm as internal standard
b) a signal accompanying a small split
c) broadened signals
d) Intensity measurement could not be made due to broadening or close approach of the signals.

while B and B′ will be the same in symmetric compound and the A: B ratio becomes 2: 1. This phenomenon agrees with the fact that ^{1}H-NMR spectra of II in deuterochloroform show two broad signals corresponding to NH around δ: 8 and 6 in ratio of 2: 1, approximately. And it is seen that in methanol, a rapid equilibrium is established among A, B, and B′.

Experimental

^{19}F-NMR spectra were all measured in *ca.* 5% solution, using a JNM-4H-100 spectrometer.

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