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NMR ANALYSIS OF ADAMANTANE DERIVATIVES

I. Eu $(DPM)_3$ AS SHIFT REAGENT FOR 2-ALKYL-2-ADAMANTANOLS

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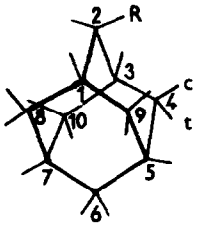
The NMR spectra of simple adamantyl derivatives have usually a complex character /6,7/. The adamantane protons can be identified by using chemical shift reagents. The spherical shape and the rigidity of the adamantane molecule make it possible to use adamantane derivatives as model substances for studying the properties of various NMR shift reagents. Eu $/DPM/_3$ and Pr $/DPM/_3$ were used recently (1,2,3,4) for the measurements of PMR spectra of adamantane derivatives.

In this paper we report NMR spectra of homologous 2-alkyl-2-adamantanols /RAdOH/using Eu $/DPM/_3$ as a NMR shift reagent. The NMR spectra of the corresponding 2-alkyladamantanes /RAd/ were measured for comparison.

In Table I, the values of chemical shifts of RAd protons are given. The methyl group protons $/H^m/$ give a triplet in all cases except for the case of the first member of this homologous series.

T A B L E I. 25 mg RAd/0,5 ml $CDCl_3$; TMS ; t = 37°C



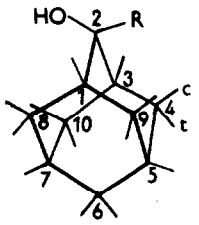
R

1. $-CH_3^m$
2. $-CH_2^e$ $-CH_3^m$
3. $-CH_2^p$ $-CH_2^e$ $-CH_3^m$
4. $-CH_2^b$ $-CH_2^p$ $-CH_2^e$ $-CH_3^m$

Compounds	Chemical shift δ (ppm)			
	H_1H_3	m	e,p,b	other
1.	1.56	1.04	-	1.80
2.	1.52	0.88	1.60 - 1.30	1.77
3.	1.55	0.90	1.45 - 1.20	1.80
4.	1.54	0.90	1.48 - 1.10	1.75

A detailed interpretation of individual protons was not possible. The δ values tabulated represent those of the maxima of the multiplets. The values of chemical shifts of RAdOH are listed in Table II, together with those of 2-adamantanol.

TABLE II. $1.30 \times 10^{-4} \pm 0.05 \times 10^{-4}$ MOL RAdOH/0,5 ml $CDCl_3$ TMS, t = 37°C,



1. $-CH_2^m$
2. $-CH_2^e$ $-CH_3^m$
3. $-CH_2^p$ $-CH_2^e$ $-CH_3^m$
4. $-CH_2^b$ $-CH_2^p$ $-CH_2^e$ $-CH_3^m$
5. $-H$

Compounds	Chemical shift δ (ppm)						
	$H_8H_{10}^c$	H_2	m	e	p	b	other
1.	2.18	-	1.32	-	-	-	1.70
2.	2.18	-	0.88	1.74	-	-	1.74
3.	2.20	-	0.92	1.50	1.76	-	1.76
4.	2.18	-	0.94	1.36	1.36	1.76	1.76
5.	2.06	3.84	-	-	-	-	1.76

The chemical shifts of the adamantane skeleton protons in RAdOH have the same value as in the case of AdOH./6/. The sharp singlet near δ = 1,4 ppm/37°C/ corresponds to the OH - proton for all members of the RAdOH series measured.

The relation between δ and R_p ($R_p = \frac{\text{mol.Eu/DPM}}{\text{mol.RAdOH}}/3$) was linear in the range $R_p = 0$ to $R_p = 0,6$. In the case of 2-methyl-2-adamantanol the linearity of the chemical shifts was confirmed up to $R_p = 1$.

Table III shows the values of chemical shifts for $R_p = 0,5$. The chemical shifts of AdOH found by using Eu/DPM/3 were published previously /3,5/ ; the results of our measurements were identical. Some differences appeared on comparing the chemical shift values for the adamantane skeleton protons in RAdOH and AdOH. The H_5 proton in RAdOH is shifted to higher fields than the H_6 protons. The H_7 proton is overlapped by the H_4H_7 multiplet. These phenomena may be explained by the fact that the alkyl group in RAdOH can change the geometrical arrangement of the complex with Eu/DPM/3. The identification of the chain protons in RAdOH was carried out utilizing the similarity of members of the homologous series /Table III./. It was simple to distinguish between the $-CH_3$ group protons and the $-CH_2$-protons regarding the typical signals of these groups. Chemical shifts of various chain protons groups /$-CH_2-$,$-CH_3$,/having the same distance from the adamantane skeleton are nearly the same for all members of the RAdOH series /the standard deviation lay in the range of 0-5.5 %/.

T A B L E III. R_p = 0.5 ; concentration of RAdOH $1.30 \times 10^{-4} \pm 0.05 \times 10^{-4}$ MOL 0.5ml $CDCl_3$, TMS, t = 37°C, concentr.of AdOH 1.125 MOL / 0.5 ml $CDCl_3$

Protons	Chemical shift δ (ppm)				
Compounds	1	2	3	4	5
H_8H_{10} /c/	9.75	10.6	9.9	9.8	10.3
H_1H_3	9.1	9.5	8.8	8.8	10.0
H_8H_{10} /t/	5.4	5.4	6.0	5.9	5.4
H_4H_9 /c/	4.7	4.8	4.6	4.4	4.8
H_4H_9 /t/	4.3	4.3	4.3	4.1	4.2
H_7	4.2	4.3	4.3	4.1	5.0
H_5	3.9	3.9	3.95	3.7	3.8
H_6H_6	3.65	3.7	3.75	3.5	4.0
m	8.2	5.2	1.45	0.55	-
e	-	8.0	5.3	1.70	-
p	-	-	7.5	5.1	-
b	-	-	-	7.5	-
H_2	-	-	-	-	18.4

Only in the case of 2-butyl-2-adamantanol /see Fig.1/ the $-CH_3$ protons were shifted towards higher fields.This indicates that the value /the angle O-Eu-H in the equation for the pseudocontact shift / lies in the range of 54–125° /8/.Plotting Rp versus δ the chemical shift for RAdOH without a chemical shift reagent can be obtained from the δ value corresponding to Rp = 0

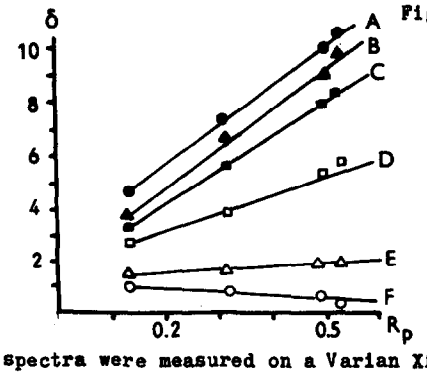


Fig.1.

A - $H_8H_{10}^{(c)}$
B - H_1H_3
C - CH_2^b -
D - CH_2^p -
E - CH_2^e -
F - CH_3^m -

The spectra were measured on a Varian XL - 100 - 15 spectrometer.All compounds measured were prepared from adamantanone /9/.

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