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Stereochemical Dependence of ^{13}C-Shift and ^{31}P-^{13}C-Coupling in 3-Substituted Bicyclo[2.2.1]hept-5-en-2-yl- and Bicyclo[2.2.2]oct-5-en-2-yl-phosphonates

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Steric influences operating on ^{13}C-shifts and ^{31}P-^{13}C-coupling constants have been investigated on phosphonates with a rigid framework.

(Keywords: Bicyclo[2.2.1]hept-5-en-2-ylphosphonates; Bicyclo[2.2.2.]oct-5-en-2-ylphosphonates; ^{13}*C-Shifts;* ^{31}P-^{13}*C-Coupling constants)*

Stereochemische Abhängigkeit von ^{13}*C-Verschiebungen und* ^{31}P-^{13}*C-Kopplungskonstanten in 3-substituierten Bicyclo[2.2.1]hept-5-en-2-yl- und Bicyclo[2.2.2]oct-5-en-2-yl-phosphonaten*

Der sterische Einfluß auf ^{13}C-Verschiebungen und ^{31}P-^{13}C Kopplungskonstanten wurde an Phosphonaten mit starrer Struktur untersucht.

Introduction

The study of spin coupling between ^{31}P and ^{13}C gives valuable information about hybridisation of the phosphorus, the carbon and the stereochemistry of two- or more-bond fragments[1]. In recent years several authors have investigated J(PC)-couplings over one to seven bonds in saturated phosphonates[2,5]. The existence of an angular dependence of the ^3J(PC) has been demonstrated for the fragments P—O—C—C and P—C—C—C in various compounds and an attempt has been made to derive a generalized *Karplus* equation for each of these fragments[3,4].

In this paper we report the determination of ^{13}C chemical shifts and ^nJ(PC) ($n = 1—4$) in a series of diisopropyl(bicyclo[2.2.1]hept-5-en-2-yl)phosphonates **1**-**4** with different carbonylsubstituents in position 3 and with defined stereochemistry, diisopropyl(bicyclo[2.2.2]-oct-5-en-2-yl)phosphonates **5** and **6** have also been included in this study.

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Experimental

Compounds

Compounds **1**-**6** have been synthesized by *Diels-Alder*-reaction of the corresponding β-substituted vinylphosphonates with cyclopentadiene resp. cyclohexadiene. Preparation, separation and purification of the isomers have been described elsewhere[6].

Spectra

The NMR-spectra have been measured with a Bruker WM 250 NMR-spectrometer. The solutions of the compounds were approx. 0.5 *M* in $CDCl_3$ and the deuterium resonance of the solvent provided the field-frequency lock. All measurements have been made in sample tubes with 5 mm diameter. The assignment of the ^{13}C signals has been made by selective $\{^1H\}$-^{13}C-double resonance experiments and is based mainly on the full assignment of the ^1H spectra, which has been achieved using chemical arguments and homo- and heteronuclear double resonance experiments; (see Ref.[6]).

We assume the accuracy of the chemical shifts to ± 0.01 ppm and that of the coupling constants to ± 0.3 Hz.

Typical spectral parameters are: ^{13}C: SW = 12 000 Hz; number of scans: 1 000-2 000; puls width: 8 μs (≃ 45°); aquisition time: 4 s; ^1H noise decoupling power ≃ 2 W; temperature 300 K; line broadening function: 0.3 Hz.

Results and Discussion

Chemical Shifts

The ^{13}C-chemical shifts of compounds **1** to **6** are given in Table **1**, together with the shifts of bicyclo[2.2.1]hept-2-ene (**7**)[7], *exo*-dimethyl-(bicyclo[2.2.1]hept-2-yl)phosphonate (**9**)[3] and bicyclo[2.2.1]heptane (**8**)[12].

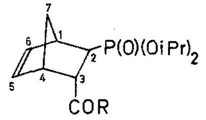
It has been shown that replacement of an *exo*-hydrogen in **8** by a dimethylphosphinyl residue deshields C-2 by 7.4 ppm[3]. We observe a similar deshielding at C-2 for both (*exo* and *endo*) positions of the phosphorus atom. Comparing the chemical shifts of compounds **1 c**, **2 c**, **3 c** and **4 c** one can see the different shielding influence of the substituents in *exo*- or *endo*-position. Table 2 gives the shift differences ($\Delta\delta$ values) derived from compounds **1 c**-**4 c**.

When the methoxycarbonyl substituent is in *exo*-position and the diisopropylphosphinyl fragment is in *endo*-(**4**) or *exo*-(**2 c**) position significant shielding resp. deshielding effects occur: C-2 is more shielded ($\Delta\delta = 0.9$ ppm) in the epimer with *endo*-P.

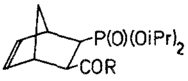
Increased shielding has also been observed for the carbons bearing an axial P-function in conformationally homogenous cyclohexanes[4,8,9,12,13] and the shift difference between both epimers is in the range from 1.6 to 0.8 ppm for P(IV) and P(III) substituents. If the

P-atom is bearing a positive charge, this shielding behaviour is reversed[4].

In our compounds C-1 and C-3 are more shielded in the P-*exo* substituted epimer. This can be explained by *gauche* interactions between the P—O bonds and these carbon atoms which has been found in similar molecules[4], and substantial shielding effects have been noted for carbons *gauche* to S—O functions[10,11]. In compounds with P(III) substituents without P—O bonds this influence on the β-shielding effect is absent[4].



1



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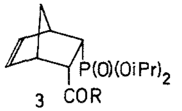

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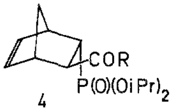

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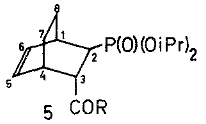

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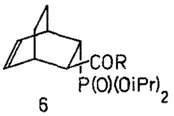

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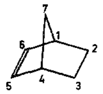
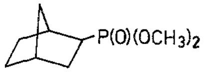


7*

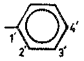
8



9

a) R = $-CH_3$

b) R =



c) R = $-OCH_3$

C-4, C-6 and C-7 are more shielded in the P-*exo* isomer **2c** and the usual γ-shielding effect is very likely the explanation for this. The same is true for the shielding of C-6 in **4c** (P-*endo*).

C-5 appears at slightly lower field in the *exo*-isomer **2c**, which is also observed in bicyclo[2.2.1]heptanes[4].

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* For the sake of clarity, corresponding carbon atoms have been numbered in the same way as in compounds **1**-**5**.

Table 1. ^{13}C-*shifts of compounds* **1 a**-**1 c**, **2 c**, **3 c**, **4 a**-**4 c**, **5 a**, **6 a**, **7**, **8**, *and* **9** *in ppm*

	1 a	**1 b**	**1 c**	**2 c**	**3 c**	**4 a**	**4 b**	**4 c**	**5 a**	**6 a**	**7**[7]	**8**[12]	**9**[3]
C													
1	46.67	45.54	*45.72	44.60	46.94	44.98	45.13	45.11	30.42	30.20	42.0	36.8	37.9
2	37.37	38.11	39.66	42.13	43.13	39.43	39.46	41.23	35.62	36.81	24.8	30.1	37.5
3	54.28	49.43	*46.88	45.10	47.68	54.49	49.77	46.58	52.55	53.24	24.8	30.1	31.7
4	45.19	48.83	45.13	46.92	46.50	47.55	49.61	48.78	33.55	32.46	42.0	36.8	36.0
5	133.01	132.34	133.76	137.26	136.39	135.81		135.84	130.17	132.65	135.8	30.1	28.4
6	138.69	138.92	139.00	139.05	134.56	136.77		136.45	136.99	134.56	135.8	30.1	31.6
7	48.09	48.60	47.85	46.12	49.34	47.43	47.32	47.89	25.40	19.51	48.8	38.7	36.9
8									21.31	26.99			
CO	204.31	197.14	172.90	174.01	172.30	206.39	198.65	174.55	204.76	205.90			
CH_3	28.58					29.44			27.93	28.73			
OCH_3			51.54	51.57	51.03			51.62					
1′		137.45											
2′		128.50											
3′		128.83											
4′		132.73											

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* Assignment may be reversed.

Similar shielding influences of the P-function in *endo*-resp. *exo*-position exist in the isomers with an *endo*-carbonyl substituent, except for C-2 and C-5. This is likely due to increased steric strain in **3c** where both substituents are in *endo*-position.

In the same way one can investigate the shielding influence of the carbonyl substituents in either *exo*- or *endo*-position. The results are also shown in Table 2 and are qualitatively in agreement with earlier results obtained on bicyclo[2.2.1]heptanes[12]. Exceptions are caused probably by increased steric interactions in the *endo*-*endo*-compound **3c**.

Table 2. ^{13}C-*shift differences showing the shielding influence of the phosphonate function (a, b) and of the carbomethoxy-group (c, d) in endo- resp. exo-position in ppm*

C	a *exo*-acyl $\Delta\delta$ (δ**4c**–δ**2c**)	b *endo*-acyl $\Delta\delta$ (δ**3c**–δ**1c**)	c *exo*-P $\Delta\delta$ (δ**1c**–δ**2c**)	d *endo*-P $\Delta\delta$ (δ**3c**–δ**4c**)
1	0.51			1.83
2	—0.90	3.47	—2,47	1.90
3	1.48			1.10
4	1.86	1.37	—1.79	—2.28
5	—1.42	2.63	—3.50	0.55
6	—2.60	—4.44	—0.05	—1.89
7	1.77	1.49	1.73	1.45
CO	0.54	—0.60	—1.11	—2.25
OCH_3	0.05	—0.51	—0.03	—0.59

Coupling Constants

Table 3 gives the absolute values of all ^{n}J (PC) which could be resolved.

^{1}J (PC)

The sign of this coupling constant is assumed to be positive from earlier work[14]. Couplings in the P-*endo*-compounds are considerably larger than in the *exo*-phosphonates and are only slightly influenced by size and position of the C-3 substituent. Comparing ^{1}J (CP) in **5a** and **6a** shows that the ring size has only a minor influence. Generally ^{1}J (PC) has a similar stereochemical dependence as ^{1}J (CH) in such bicyclic systems.

Theoretical calculation of the latter in bicyclo[2.2.1]heptane demands that ^{1}J (CH) for the *endo* proton should be 7 Hz larger than the corresponding coupling to the *exo*-H[15]. Different ^{1}J (PC) coupling constants have also been found in conformationally pure cyclohexanes for equatorial (144 Hz) and axial (139 Hz) phosphinylsubstituents[8,19]. Thus ^{1}J (PC) can be used to assign the configuration of C-2 in bicyclo[2.2.1]hept-5-en-2-ylphosphonates and bicyclo[2-2-2]oct-5-en-2-yl-phosphonates.

Table 3. *Absolute values of the* ^{31}P-^{13}C-*coupling constants from compounds* **1 a**-**1 c**, **2 c**, **3 c**, **4 a**-**4 c**, **5 a** *and* **6 a** *in Hz*

	1 a	**1 b**	**1 c**	**2 c**	**3 c**	**4 a**	**4 b**	**4 c**	**5 a**	**6 a**
C										
1	3.2	0.0	*2.3	1.9	2.3	1.9	0.9	1.4	1.4	3.2
2	143.8	143.3	144.3	142.4	156.8	156.3	156.8	156.3	142.0	148.9
3	2.3	3.7	*3.2	0.0	1.4	1.4	2.3	1.4	1.9	2.3
4	0.0	3.7	0.0	1.4	4.2	7.4	7.9	7.4	4.6	6.0
5	0.0	0.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6	15.3	14.8	14.8	13.4	4.6	3.7	0.0	4.2	18.0	1.4
7	0.0	0.0	0.0	0.0	14.8	16.7	16.7	16.6	0.0	0.9
8									1.9	17.1
CO	4.2	4.2	5.6	9.7	8.3	4.2	3.7	5.1	4.6	3.7

* Assignment may be reversed.

^{2}J (PC)

The geminal coupling between ^{31}P and ^{13}C is in the range of 0-3.7 Hz (Table 3). No specific trends can be elucidated and the need for more systematic work is apparent.

^{3}J (PC)

The vicinal coupling is taken as positive[14] and shows a significant dependence on the dihedral angle, which may be analysed in terms of a generalized *Karplus* relation[16,17]. Previous workers have derived a *Karplus* curve for phosphonates showing maxima for ^{3}J (PC) at $\Phi = 0^\circ$ and 180° with a minimum near 80°[4,18]. Our study provides an abundance of coupling constants at different dihedral angles and to carbons of different hybridisation type. However due to steric influences of the carbonyl substituents it is difficult to get the exact dihedral angles. Attempts to evaluate these angles by force field calculations[21,22] are under progress.

Conclusion

The data of the present work are obtained on molecules with a rigid framework and give insight into steric influences operating on ^{13}C shifts and ^{31}P-^{13}C coupling constants. Contributions to the ^{13}C shifts due to orientation of the substituents in *exo*- or *endo*-positions could be observed. It has been shown, that the ^1J (PC) can be used to determine whether the position of the phosphonyl residue is *exo* or *endo*.

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