

^{17}O AND ^{13}C NMR SPECTRA OF SOME GEMINAL DIACETATESAntonín LYČKA^a, Josef JIRMAN^a and Jaroslav HOLEČEK^b^a *Research Institute of Organic Syntheses, 532 18 Pardubice-Rybitví and*^b *Department of General and Inorganic Chemistry
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Dedicated to Dr D. Šnobl on the occasion of his 65th birthday.

The ^{17}O and ^{13}C NMR spectra of eight geminal diacetates $\text{RCH}(\text{O}(\text{CO})\text{CH}_3)_2$ derived from simple aldehydes have been measured. In contrast to the dicarboxylates $\text{R}^1\text{R}^2\text{E}(\text{O}(\text{CO})\text{R}^3)_2$, where $\text{E} = \text{Si}, \text{Ge}$ or Sn , whose ^{17}O NMR spectra only contain a single signal, and, on the other hand, in accordance with organic carboxylic esters, the ^{17}O NMR spectra of the compound group studied always exhibit two well-resolved signals with the chemical shifts $\delta(^{17}\text{O})$ in the regions of 183–219 ppm and 369–381 ppm for the oxygen atoms in the groups $\text{C}-\text{O}$ and $\text{C}=\text{O}$, respectively.

Our previous communications¹⁻³ dealt with results of studies of the ^{17}O NMR spectra of organometallic carboxylates $\text{R}^1\text{R}^2\text{R}^3\text{EO}(\text{CO})\text{R}$ and dicarboxylates $\text{R}^1\text{R}^2\text{E}(\text{O}(\text{CO})\text{R})_2$, where $\text{E} = \text{Si}, \text{Ge}, \text{Sn}$ and $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}$ are organic substituents. In the ^{17}O NMR spectra of the dicarboxylates $\text{R}^1\text{R}^2\text{E}(\text{O}(\text{CO})\text{R})_2$ ($\text{E} = \text{Si}, \text{Ge}, \text{Sn}$) and carboxylates $\text{R}^1\text{R}^2\text{R}^3\text{EO}(\text{CO})\text{R}$ ($\text{E} = \text{Ge}, \text{Sn}$), the oxygen atoms of $\text{R}(\text{CO})\text{O}$ groups were observed as equivalent, which was explained by rapid exchange of the oxygen atoms on the NMR time scale¹⁻³, and/or by a formation of asymmetrical chelate complex between the metal atom of the IVB group of the periodic table and the bidentately bound carboxylic group, which particularly applies to the organotin(IV) compounds^{1,2}. On the other hand, the ^{17}O NMR spectra of triorganosilicon(IV) carboxylates³ showed two well-resolved signals of both oxygen atoms of the carboxylic group similar to those of the ^{17}O NMR spectra of organic carboxylate esters measured so far (see refs⁴⁻⁷ and the literature quoted therein).

The aim of the present work was to measure the ^{17}O NMR spectra of a group of geminal diacetates $\text{RCH}(\text{O}(\text{CO})\text{CH}_3)_2$, where $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, 1-\text{C}_6\text{H}_{13}, \text{CCl}_3, \text{C}_6\text{H}_5, \text{C}_6\text{H}_5\text{CH}=\text{CH}$, and $\text{C}_4\text{H}_3\text{O}$ (Table I), derived from simple aliphatic, aromatic, and heterocyclic aldehydes, and to decide whether or not there can exist the equivalence of the two oxygen atoms of carboxylic groups on the NMR time scale also with purely organic carboxylates. The ^{13}C NMR spectra served for characterization of the compounds measured and their purity check.

EXPERIMENTAL

The ^{17}O and ^{13}C NMR spectra were measured with a JNM-FX 100 apparatus (JEOL, Japan) equipped with a 10 mm tunable probe at 13.505 and 25.047 MHz, respectively. The compounds were measured as neat liquids or melts. The deuterium oxide used in the coaxial capillary served as a lock substance and as the standard ($\delta(^{17}\text{O}) = 0.0$). Pentadeuterionitrobenzene was used for the same purpose ($\delta(^{17}\text{O}) = 579.0$) in the measurements at 400 K. The temperatures of the measurements (Table II) were determined by means of a thermocouple. The following parameters were used in the measurements of ^{17}O NMR spectra: 10 000 Hz spectral width, 1 K (zero filling to 8 K), 90° pulse, 60 ms pulse repetition, proton-noise decoupling, 50–100 Hz exponential broadening factor to the FID prior to Fourier transformation. The chemical shifts $\delta(^{13}\text{C})$ were measured in a standard way at the digital resolution of 1.22 Hz/point (~ 0.06 ppm/point) using the same samples as in the ^{17}O NMR measurements. The $\delta(^{13}\text{C})$ chemical shifts are related to external neat tetramethylsilane or hexamethyldisiloxane (at higher temperatures). The $\delta(^{13}\text{C})$ values measured were transformed to the δ scale after a correction of +1.2 (tetramethylsilane) or +2.3 (hexamethyldisiloxane).

TABLE I
The $\delta(^{13}\text{C})$ chemical shifts of the geminal diacetates $\text{RCH}(\text{O}(\text{CO})\text{CH}_3)_2$

Compound ^a		T K	$\delta(^{13}\text{C})$			
No.	R		COO	CH ₃ COO	RCH	R
I	H	300	171.2	21.5	80.9	—
II	CH ₃	300	170.3	21.8	90.1	20.7
III	C ₂ H ₅	300	170.4	21.9	92.9	28.3 (CH ₂), 9.1 (CH ₃)
IV	1-C ₆ H ₁₃	300	170.2	21.9	92.2	35.1, 33.6, 30.7, 25.2, 24.4 (CH ₂), 15.3 (CH ₃)
V	CCl ₃	300	169.5	22.3	91.8	98.5
VI	C ₆ H ₅	350	169.4	21.0	91.2	137.1 (<i>i</i>), 127.6 (<i>o</i>), 129.6 (<i>m</i>), 130.5 (<i>p</i>)
VII	C ₆ H ₅ CH=CH	370	169.4	21.3	90.9	123.8 (CH=CH—), 136.3 (C ₆ H ₅ CH), 136.7 (<i>i</i>), 128.1 (<i>o</i>), 129.8 (<i>m</i>), 129.8 (<i>p</i>)
VIII	C ₄ H ₃ O ^b	370	169.3	20.8	85.0	149.8 (C-2), 144.8 (C-5), 111.6 and 111.1 (C-3 and C-4)

^a The standard was external neat tetramethylsilane (compounds I–V) and hexamethyldisiloxane (compounds VI–VIII); ^b 2-furyl.

The compounds *I–VIII* (Table I) were prepared by known procedures^{8,9} by the reaction of the respective aldehyde with a slight excess (c. 5%) of acetanhydride and with catalytic action of sulphuric acid or $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$. 2,4,6-Trinitrophenyl acetate (*IX*) was prepared by the reaction of 2,4,6-trinitrophenol with acetanhydride¹⁰. The compounds were purified by vacuum distillation or crystallization.

RESULTS AND DISCUSSION

In the ^{13}C NMR spectra of compounds *I–VIII* (Table I) the number of signals always corresponded to that of magnetically non-equivalent carbon atoms of the given compound, which, along with the expected multiplicity of signals in the proton-coupled spectra, fully confirms not only the identity of the compounds but also their sufficient degree of purity from the point of view of NMR.

TABLE II

The temperature dependence of the $\delta(^{17}\text{O})$ chemical shifts and half-widths of signals of compounds *I–VIII*

Compound	T K	$\delta(^{17}\text{O})$			
		$\delta(\text{C}=\text{O})^a$	$w_{1/2}^b$	$\delta(\text{C}-\text{O})^a$	$w_{1/2}^b$
<i>I</i>	300	369	340	185	360
	350	370	160	183	200
	400	371	80	183	85
<i>II</i>	300	372	400	197	420
	350	373	165	202	185
	400	375	95	202	100
<i>III</i>	300	377 ^c	600	203 ^c	660
	350	375	220	200	260
	400	372	145	197	200
<i>IV</i>	350	369	550	201	800
	400	375	220	202	260
<i>V</i>	350	379 ^c	540	188 ^c	680
	400	379	220	190	240
<i>VI</i>	350	373 ^c	820	195 ^c	1 100
	400	379	300	207	330
<i>VII</i>	400	381	320	219	350
<i>VIII</i>	400	377	430	201 ^d	580

^a ppm; ± 2 ppm; ^b Hz; $\pm 10\%$; ^c ± 4 ppm; ^d $\delta(\text{CH}-\text{O}-\text{C}) = 241$ ($w_{1/2} = 380$).

Table II gives the $\delta(^{17}\text{O})$ chemical shifts of compounds *I–VIII* at various temperatures. A characteristic feature of the ^{17}O NMR spectra of these geminal organic diacetates (in contrast to diorganosilicon(IV) and -tin(IV) dicarboxylates^{1–3}) consists in the presence of two well-resolved signals for the oxygen atoms in the C—O and C=O groups. A temperature increase causes not their coalescence but only diminishing of the half-widths of the signals as a consequence of lowered viscosity of the liquid samples measured.

The $\delta(^{17}\text{O})$ values of compounds *I, II,* and *VI* are always shifted downfield, viz. by 9–18 ppm ($\delta(\text{C}=\text{O})$) and by 24–37 ppm ($\delta(\text{C}-\text{O})$) as compared with analogous monoacetates (methyl-, ethyl-, and benzylacetates, respectively)^{5,11}.

From ref.³ it follows that the probability of equivalence of the oxygen atoms of carboxylate group in the carboxylates containing metals of the IVB group ($\text{R}^1\text{R}^2\text{E}(\text{O}(\text{CO})\text{R})_2$ and $\text{R}^1\text{R}^2\text{R}^3\text{EO}(\text{CO})\text{R}$) will increase (i) with increasing atomic number of the element E, (ii) with number of the carboxylic groups bound to E, (iii) with increasing electron-acceptor ability of the substituents R^1 , R^2 , and R^3 , (iv) with increasing temperature of the measurement.

The situation of the organic geminal diacetates *I–VIII* is, as compared with other (organometallic) dicarboxylates, the least favourable for the equivalence of oxygen atoms of carboxylate group on the NMR time scale. Out of all elements of the IVB group, the carbon atom has the highest electronegativity, the smallest atomic radius, and the shortest length bond to oxygen. An activation of carbon atom by the proton, substituent R, or by acetyl group is insufficient for the equivalence of COO oxygen atoms to make itself felt on the NMR time scale. The effect is insufficient even in the case of 2,4,6-trinitrophenyl acetate, where three nitro groups markedly lower the electron density at the carbon atom C(1) making thus the situation more favourable for observation of the equivalence of their oxygen atoms (of course, sterical requirements are less favourable in this case). With this compound, too, the ^{17}O NMR spectra show two well-resolved signals of acetoxy oxygen atoms beside those of the O atoms of NO_2 groups ($\delta(\text{C}-\text{O}) = 186$, $\delta(\text{C}=\text{O}) = 386$, $\delta(\text{NO}_2) = 613$ for c. 30% solution in acetone at 320 K, and $\delta(\text{C}-\text{O}) = 188$, $\delta(\text{C}=\text{O}) = 386$, $\delta(\text{NO}_2) = 613$ for c. 30% solution in toluene at 370 K).

From the results given it follows that the equivalence of oxygen atoms of carboxylic group in organic esters or diesters is highly unlikely at the conditions corresponding to NMR experiment.

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