DETERMINATION OF THE STRUCTURES OF ESTERS OF POLYBRANCHED MONOCARBOXYLIC ACIDS BY ^{13}C NMR SPECTROSCOPY

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The telomerization of unsaturated compounds by esters of carboxylic acids is accompanied by rearrangement of the radicals with migration of a hydrogen atom; as a result, a complex mixture of long-chain molecules that contain side-chain alkyl groups in various positions in the chain is formed. The establishment of the structures of compounds of this type is of both theoretical and practical interest, since the telomerization of olefins opens up a pathway to the synthesis of difficult-to-obtain and valuable branched monocarboxylic acids and their derivatives [1]. The most informative method for the study of the structures of these compounds is ^{13}C NMR spectroscopy.

In the present research we have ascertained some principles involved in the change in the chemical shifts of the ^{13}C signals in the most characteristic groups of atoms as a function of the structure of the carbon skeleton of the molecule. This has made it possible in a number of cases to identify individual telomer-isomers in the mixture (without separation of them). The ^{13}C NMR spectra of simpler standard compounds were examined in [2]. It was shown that the $C^{13}COO$ and $^{13}CH_3C$ signals are shifted to weak field as the number of substituents attached to the adjacent C atom increases; an increase in the number of substituents attached to the β-C atom leads to a shift of the $^{13}CH_3$ signals to strong field.

The parameters of the ^{13}C NMR spectra for a number of esters of branched monocarboxylic acids obtained by the reaction of esters of lower acids with propylene (I-III [3]), isobutylene (IV-VI [4]), and ethylene (VII-XIV) are presented in Tables 1 and 2. All of these compounds contain a number of key C atoms, the chemical shifts of which depend substantially on the change in the structure of the molecule.

First and foremost, C atoms of this sort are those of the functional group (C_1), viz., $CH_2{}^{13}COO$, $>CH^{13}COO$, $>C-{}^{13}COO$. The ^{13}COO chemical shifts are sensitive to substitution at both α-C_2 and other C atoms. Thus in the case of complex molecules substitution at C_2 shifts the ^{13}COO (C_1) signal to weak field (compare I and X) as compared with the unsubstituted compounds ($\delta CH_2CH_2{}^{13}COO$ ~ 173 ppm [2]). The accumulation of CH_3 groups in the γ position (C_4) (IV and V) also has a similar effect. The appearance of substituents in the β position (C_3) (VII and VIII) shifts the same signal to strong field. The chemical shifts for the ^{13}CH signals also differ substantially as a function of their orientation with respect to the COO group. In one case the chemical shift is 39-45 ppm (I-IV), while in the other it is 25-30 ppm (C_2 and C_4 in II-IV). The degree of substitution of the adjacent C atom also has a marked effect on the chemical shift of the $^{13}CH_3$ signal, which increases in the order $^{13}CH_3CH_2C$ [~9 ppm, for X, XII, and XIV], $^{13}CH_3CH_2CH$ [~12 ppm for IX], $^{13}CH_3CH_2CH_2$ [~14 ppm for I-III, VII, and VIII], $^{13}CH_3CHCOO$ [~17 ppm for IV], $^{13}CH_3CHCH_2$ [~20 ppm for II and III], $^{13}CH_3CCOO$ [~23 ppm for X, XII, and XIV], and $^{13}CH_3CCH_2$ [~27 ppm for V, VII, and VIII].

The use of data from the spectra of standard substances, the indicated principles, and the multiplicity of the signals in the spectra recorded without suppression of the coupling with the protons made it possible to assign the signals, to establish the structures of the compounds with the most complex structure (VI), and to identify the compounds with different structures in the mixture of isomers (see Table 2). Thus in the case of telomerization of ethylene with a mixture of methyl isovalerate and α-methylbutyrate one might have expected the simultaneous formation of three series of telomers, viz., $H(CH_2CH_2)_nC(CH_3)_2CH_2CO_2CH_3$ (T_n,

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TABLE 1. Parameters of the ^{13}C NMR Spectra of Esters of Branched Carboxylic Acids

Compound	Formula	δ, ppm from tetramethylsilane				
		COO	$\underline{CH_3O}$— $\underline{CH_3CH_2}$—	$CH_3C\lesssim$ $\underline{CH_3CH}\gtrless$	—CH— —C$\lesssim$	—CH_2—
(I)	$(CH_3CH_2CH_2)_2CHCO_2CH_3$	174,9	50,5(1,1) 13,9	–	44,7	34,6(3), 20,5(4)
(II)	$CH_3CH_2CH_2\underset{\underset{CH_3}{\vert}}{CH}CH_2\underset{\underset{CH_2CH_2CH_3}{\vert}}{CH}CO_2CH_3$	174,9	50,5(1,1) 14,0 14,2	19,7	38,6(2) 30,5(4)	35,4, 34,7(3) 42,7, 39,8(5,3′) 20,4, 19,7(6,4′)
(III)	$(CH_3CH_2CH_2\underset{\underset{CH_3}{\vert}}{CH}CH_2)_2CHCO_2CH_3$	175,3	50,5(1,1) 14,2	19,8	38,7(2) 30,5(4)	40,6, 39,9(3) 42,0(5), 19,8(6)
(IV)	$(CH_3)_2CHCH_2CH(CH_3)CO_2CH_3$	175,4	50,7	22,4(5) 17,4(3′)	43,0(2) 25,8(4)	37,1
(V)	$(CH_3)_2CHCH_2C(CH_3)_2CH_2\underset{\underset{CH_3}{\vert}}{CH}CO_2CH_3$	176,4	50,6	27,1, 27,2(5′) 25,4(7) 20,2(3′)	35,2(2) 33,7(4) 23,9(6)	51,3(5), 46,4(3)
(VI)	$\overset{7}{(CH_3)_2}\overset{6}{CH}\overset{5}{CH_2}\overset{4}{C}\overset{5'}{(CH_3)_2}\overset{3}{CH_2}\overset{2}{C}\overset{3'}{(CH_3)}\overset{1}{CO_2}\overset{1,1}{CH_3}$ $\underset{\underset{3''\ 4''\ 5''\ 6''}{\vert}}{CH_2C(CH_3)=CH_2}$	176,5	50,6	28,7, 27,0(5′) 25,7(7) 23,9(5″) 21,3(3′)	45,1(2) 35,0(4) 23,4(6) 131,3(4″)	115,0(6″), 54,8(3″) 53,0(3), 51,6(5)

TABLE 2. Parameters of the ^{13}C NMR Spectra and Results of Elementary Analysis of the Products of Telomerization of Ethylene by Methyl Isovalerate and α-Methylbutyrate

Compound	Formula	δ, ppm from tetramethylsilane					Found/calc., %	
		COO	CH_3O CH_3CH_2	CH_3—C CH_3CH	CH C	—CH_2—	C	H
(VII)	$CH_3CH_2CH_2CH_2CH_2CH_2C(CH_3)_2CH_2CO_2CH_3$	170,9	50,3(1,1) 13,9(9)	27,2(4′)	24,0(3)	45,2(2), 42,1(4) 30,0(5), 31,7(6) 32,9(7), 22,6(8)	72,01 72,0	12,03 12,00
(VIII)	$CH_3CH_2CH_2(CH_2)_3CH_2CH_2C(CH_3)_2CH_2CO_2CH_3$	170,8	50,3(1,1) 14,0(1,1)	27,3(4′)	23,9(3)	45,2(2), 42,2(4) 30,3(5), 31,8 32,9(9), 29,2 22,6(10)		
(IX)	$CH_3^{4}CH_2^{3}CH[CH(CH_3)_2]^{2}CH_2^{1}CH_3^{1,1}$	174,2	50,2(1,1) 11,9(4)	20,1(4′)	54,0(2) 22,5(3′)	30,2(3)	66,38 66,66	11,11 11,13
(X)	$(CH_3CH_2)_2C(CH_3)CO_2CH_3$	175,8	50,6(1,1) 8,7(4)	22,5(3′)	46,3	31,4(3)		
(XI)	$CH_3CH_2CH_2CH_2CH[CH(CH_3)_2]CH_2CH_3$	174,3	50,4(1,1) 13,9(6)	20,3, 20,7(4′)	52,2(2) 22,7(3′)	31,9(4), 26,7(3) 23,1(5)	69,79 69,76	11,41 11,62
(XII)	$CH_3CH_2CH_2CH_2C(CH_2CH_3)CO_2CH_3$ (CH₃ branch)	175,7	50,8(1,1) 13,9(6) 8,9(4′)	22,7(3′)	45,9(2)	38,7(3), 29,9, 30,5(3) 29,1(4), 23,1(5)		
(XIII)	$CH_3CH_2CH_2CH_2CH_2CH_2CH[CH(CH_3)_2]CO_2CH_3$	174,5	50,2(1,1) 13,9(8)	20,2, 20,6(4′)	52,2 22,5	30,4(4), 27,6 27,1(3), 31,7(4) 29,7	71,43 72,00	11,83 12,00
(XIV)	$CH_3CH_2CH_2CH_2CH_2CH_2C(CH_2CH_3)CO_2CH_3$ (CH₃ branch)	175,7	50,6(1,1) 13,9 8,7(4′)	22,5(3′)	45,8(2)	30,9(3), 31,7(4,5) 24,4(7), 29,7		

TABLE 3. Parameters of the ^{13}C NMR Spectra of Esters of Chloro-Substituted Carboxylic Acids*

Compound	Formula	δ, ppm from tetramethylsilane				
		COO	$\underline{CH_3O}$— $\underline{CH_3CH_2}$—	$\underline{CH_3C}\lessgtr$ $\underline{CH_3CH}<$	—C $\lessgtr$ —CH $<$	—CH_2—
(XV)	$CH_3CH_2CH_2CHClCO_2CH_3$	169,2	52,1(1,1) 13,1(5)	–	56,4(2)	36,7(3), 19,1(4)
(XVI)	$(CH_3CH_2CH_2)_2CClCO_2CH_3$	171,4	52,5(1,1) 13,7(5)	–	74,1(2)	42,9(3), 17,8(4)
(XVII)	$CH_3CH_2CH_2CCl_2CO_2CH_3$	165,7	53,6(1,1) 13,1(5)	–	84,3(2)	47,1(3), 18,4(4)
(XVIII)	$CH_3CHClCH_2CCl_2CO_2CH_3$	165,9	53,9(1,1)	26,2(5)	83,1(2) 55,1(4)	54,9
(XIX)	$(CH_3)_2CHCH_2CHClCO_2CH_3$	169,3	52,2(1,1)	22,3 21,2	55,3(2) 25,1(4)	43,4
(XX)	$(CH_3)_2CHCH_2C(CH_3)_2CH_2CHClCO_2CH_3$	169,8	52,2(1,1)	27,2(5′) 25,5(7)	53,1(2) 34,0(4) 24,0(6)	51,4(5), 47,2(3)
(XXI)	$(\overset{7}{CH_3})_2\overset{6}{C}H\overset{5}{C}H_2\overset{4}{C}(\overset{5'}{CH_3})_2\overset{3}{C}H_2\overset{2}{C}Cl\overset{1}{C}O_2\overset{1,1}{C}H_3$ $\underset{3''\ 4''\ 5''\ 6''}{CH_3C(CH_3)=CH_2}$	170,8	52,7(1,1)	28,4 27,0(5′) 25,6(7) 23,9(5″)	139,7(4″) 71,8(2) 35,0(4) 23,9(6)	116,2(6″) 53,6(5) 52,7, 52,1(3,3″)

*The order of numbering of the atoms in parentheses is shown in the case of XXI.

n = 3 and 4, VII and VIII), $H(CH_2CH_2)_mC(CH_2CH_3)CO_2CH_3$ (T_m, m = 1-3, X, XII, and XIV), and

CH_3

$H(CH_2CH_2)_pCHCO_2CH_3$ (T_p, p = 1-3, IX, XI, and XIII).

$CH(CH_3)_2$

We were able to isolate compounds in individual form and assign them to the T_n series with respect to the following characteristic signals (in parts per million): ~171 for ^{13}COO (at strongest field for signals of this type), 45.2 for $^{13}CH_2COO$, ~24 for ^{13}C, and 27.2 for $^{13}CH_3$ with doubled intensity. Two other series of telomers were isolated in the form of mixtures of isomers (IX + X, XI + XII, and XIII + XIV, see Table 2). The assignment of the isomers in the mixture to the T_m and T_p series was made with respect to the following signals (in parts per million): for the T_m series (X, XII, and XIV), ~9 for $^{13}CH_3CH_2C$, 175.8 for $C^{13}COO$ (the weakest field signal of the ^{13}COO signals, and 46 for $^{13}CCOO$; for the T_p series (IX, XI, and XIII), 11.9 for $^{13}CH_3CH_2CH$, 52-54 and 22-23 for the two ^{13}CH signals under markedly different shielding conditions, 20-21 for $(^{13}CH_3)_2CH$ (with doubled intensity), and 174.5 for $CH^{13}COO$ (at stronger field than $\rangle C-{}^{13}COO$ in T_m).

Additional possibilities for identification of the complex structures are created when Cl atoms are introduced in the α position relative to the COO group (Table 3). These compounds were obtained by reaction of methyl mono-, di-, or trichloroacetate with propylene [5-7] and isobutylene [8]. The introduction of Cl at C_2 shifts the ^{13}COO signal to strong field (compare I and XVI), while the $^{13}CCOO$ signal is shifted 10-20 ppm to weak field for each Cl atom (XV, XVI, and XVII). At the same time, the introduction of a Cl atom in the γ position (C_4) has virtually no effect on the position of the $^{13}C-{}^{13}COO$ signals (XVII and XVIII). Thus a characteristic signal that makes it possible to distinguish the $R^{13}CHClCOO$, $R_1R_2{}^{13}CClCOO$, and $R^{13}CCl_2COO$ groupings appears at 55-85 ppm.

These assignments made it possible to confirm the structure of XXI. The characteristic signals with allowance for their multiplicity in the $^{13}C-{}^{1}H$ spectrum demonstrated the presence in this compound of the $R_1R_2{}^{13}CClCOO$, $C{=}CH_2$, $CH(CH_3)_2$, and $\rangle C-$ groupings, which, taking into account the agreement of the remaining signals with the signals of the standard compounds (XVI, XIX, and XX), confirms the structure proposed for XXI.

EXPERIMENTAL

The ^{13}C NMR spectra were recorded with a Bruker Physik HX-90 spectrometer (22 and 635 MHz) with CCl_4 as the internal standard (the chemical shifts in the tables are the values relative to tetramethylsilane).

Preparative gas–liquid chromatography (GLC) was carried out with a PAKhV chromatograph with a 2.6 m by 10 mm column filled with 20% SKTFT-50 on Chromaton N-AW.

The telomerization of ethylene with a mixture of methyl isovalerate and α-methylbutyrate was carried out in a 0.5-liter rotating steel autoclave; 200 g of a mixture of methyl isovalerate (70%) and methyl α-methylbutyrate (30%), 5 g of tert-butyl peroxide, and ethylene (40-50 atm) were used in the experiment. The mixture was heated at 140°C for 3 h. The mixture of telomers (128 g) obtained after removal of the starting materials from six similar experiments was distilled to give narrow fractions, from which the telomers were isolated by means of preparative gas–liquid chromatography (GLC) (see Table 2). The yield of the mixture of T_1-T_3 telomers of all three series was 55% (based on the sum of the reaction products). The ratio of the yields of telomers with respect to the series (based on the T_1-T_3 sum) was $T_n:T_m:T_p$ = 20:35:45.

CONCLUSIONS

1. The ^{13}C NMR spectra of esters of polybranched acids contain characteristic signals of COO, CH_3, and CH groups that are sensitive to the β and γ effects of substituents, and this makes it possible to use the data from the ^{13}C NMR spectra to establish the structures of complex molecules.

2. The telomerization of ethylene by methyl isovalerate proceeds with cleavage of the C–H bond in both the α-CH_2 and β-CH groups.

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^{13}C NMR SPECTRA OF STEREOISOMERIC DERIVATIVES OF BICYCLO[2.2.1]-HEPT-5-ENE AND 3-OXATRICYCLO[3.2.1.0^{2,4}]OCTANE

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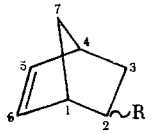
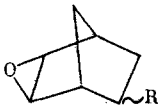
Considerable attention has been given in recent years to the synthesis of stereoisomeric bicyclo[2.2.1]hept-5-enes (norbornenes) and epoxides of these compounds related to the study of a broad range of chemical problems: double-bond strain [1], anchimeric acclerations in reactions related to substituent stereochemistry, ring current in epoxides [2], and some features of the reactivity of these compounds [3, 4]. In addition, bicyclo[2.2.1]hept-5-enes, in light of their ready availability and high double-bond reactivity in most reactions, are used for the preparation of physiologically active compounds, valuable polymer materials, and stabilizers.

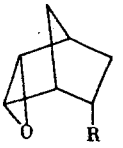
The stereochemical features of substituted norbornenes are almost not evident in IR spectra [5]. These features are seen in the PMR spectra in the nonequivalence of the protons at the double bond and the bridge protons and also in the chemical shift and multiplicity of the proton at the substituent [6-8]. Hence it was of interest to study the effect of the nature and stereochemistry of the substituent on the chemical shifts in the ^{13}C NMR spectra in derivatives of bicyclo[2.2.1]hept-5-en-2-carboxylic acids and their corresponding epoxides with exo and endo configuration of the epoxide ring.



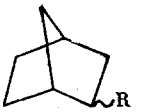
(Ia-f) (exo)
(IIa-f) (endo)



(IIIa-e) (exo)
(IVa,b,d) (endo)



(Va,b,d)



(VIa,b,c) (exo)
(VIIa,b,c) (endo)

R for a-f, respectively: H, CN, CO_2H, CO_2CH_3, $CON(CH_3)_2$, and CH_3.

In addition to our results, we used literature data on the ^{13}C NMR spectra of bicyclo-[2.2.1]heptanes (VI) and (VII) and endo- and exo-2-methylbicyclo[2.2.1]hept-5-enes [9].

Assignment of the signals for all the compounds was carried out by comparison of the spectra of the members of each series with the spectrum of that compound, for which assignment was made using selective ^{13}C–{H} resonance and also on the basis of literatrue data. In the epoxide derivative series, selective resonance was carried out for compounds (IIIb) and (IVb) and in the norbornene series, for compounds (Ib) and (IIb). The data of Zimmerman et al. and Davies et al. [10] were used.

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