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The Stereochemistry of Some New Flexible 2,2,5,5-Tetrasubstituted 1,3-Dioxanes

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Summary. The stereochemistry of some new 2,2,5,5-tetrasubstituted 1,3-dioxane derivatives was investigated. Peculiar cases of prostereoisomerism and the NMR spectroscopic identification of pro-*R*, pro-*S*, pro-*cis*, and pro-*trans* groups are reported for these achiral flipping compounds.

Keywords. Flipping 1,3-dioxanes; Prostereogenic carbon atoms; NMR discrimination of pro-*R*, pro-*S*, pro-*cis*, and pro-*trans* groups; NMR spectra with chiral shift reagents.

Zur Stereochemie einger neuer flexibler 2,2,5,5-tetrasubstituierter 1,3-Dioxane

Zusammenfassung. Die Stereochemie einiger neuer 2,2,5,5-tetrasubstituierter 1,3-Dioxanderivate wurde untersucht. Spezielle Fälle von Prostereoisomerie sowie die NMR-spektroskopische Unterscheidung der pro-*R*-, pro-S-, pro-*cis*- und pro-*trans*-Substituenten werden diskutiert.

Introduction

Investigations of 2,2,5,5-tetrasubstituted 1,3-dioxanes bearing homomorphic groups in one and different groups in the other substituted position of the heterocycle have revealed flipping or anancomeric structures in correlation with the differences of conformational free enthalpy between the different geminal substituents [1–6]. If this difference is high, the compound shows an anancomeric structure, and the conformational equilibrium due to the flipping of the heterocycle (Scheme 1) is shifted towards the conformer with the bulky group in equatorial orientation. If the two substituents exhibit very close conformational free enthalpies, the two conformers involved in the equilibrium exist in almost equal ratio. Due to the fast equilibrium, the ^{1}H NMR spectra exhibit averaged signals for the axial and equatorial orientations of the homomorphic groups at room temperature.

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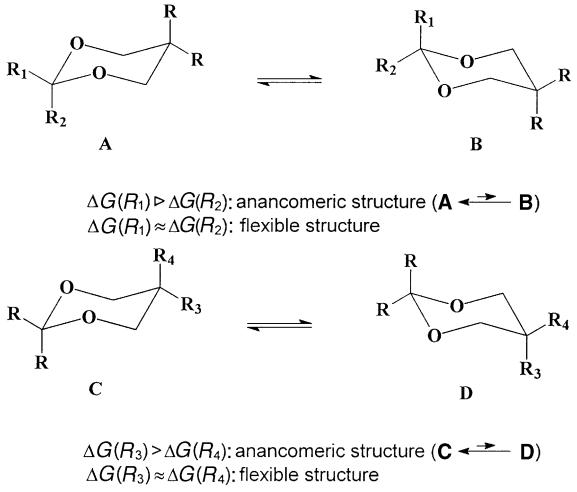


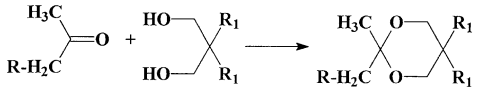
Scheme 1

The problem of differentiation of homomorphic ligands located close to a prostereogenic (prochiral) center or axis by the molecular environment is of high actuality [7]. The main methods used to perform these differentiations are correlated with stereoselective reactions or NMR spectroscopic investigations [8]. Thus it was of interest to investigate the stereochemistry of some flexible 2,2,5,5-tetrasubstituted-1,3 dioxanes bearing identical substituents in one and different substituents in the other of these positions and to determine the steric relations between the homomorphic atoms and groups belonging to these structures, by NMR methods. The flexibility of the ring (resulting in the elimination of the differences between axial and equatorial orientations) has been considered essential for the proposed study, because in anancomeric structures the homomorphic protons of positions 4 and 6 and the homomorphic groups located in positions 2 or 5 are in different molecular environments, some of them showing axial and the other ones equatorial orientations.

Results and Discussion

Suitable 1,3-dioxane derivatives have been obtained by acetalization reactions (Schemes 2 and 3). Compounds **1–10** exhibit flipping structures (Scheme 4) despite of the unsymmetrical substitution in positions 2 or 5 of the heterocycle. The conformational free enthalpies of the methyl ($\Delta G^0_{Me} = 0.80$–0.89 kcal/mol) [9] and ethyl $\Delta G^0_{Et} = 0.75$–0.81 kcal/mol [9] groups at position 5 of the 1,3-dioxane ring as well as the conformational free enthalpies of the methyl and substituted methyl groups ($R = COOCH_3$, $COOC_2H_5$, C_6H_5) located in the ketal part of the heterocycle (position 2) are very close [9] and cannot induce the anancomericity of the ring. The flexible structure of some other related 1,3-dioxane derivatives has already been reported [1, 4–6, 10, 11].

The stereochemisty and NMR spectra of flexible and anancomeric 2,2,5,5-substituted-1,3 dioxane derivatives are different. The NMR spectra of anancomeric



$R = COOCH_3$, $R_1 = CH_3$ **1**

$R = COOC_2H_5$, $R_1 = CH_3$ **2**

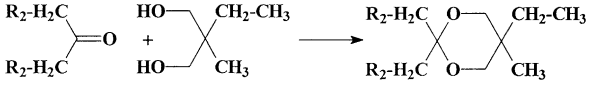
$R = COOCH_3$, $R_1 = COOC_2H_5$ **3**

$R = R_1 = COOC_2H_5$ **4**

$R = C_6H_5$, $R_1 = CH_3$ **5**

$R = C_6H_5$, $R_1 = COOC_2H_5$ **6**

Scheme 2



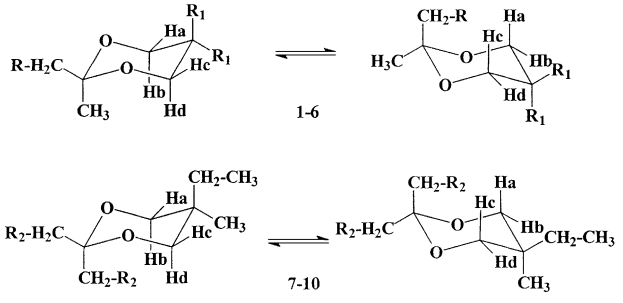
$R_2 = H$ **7**

$R_2 = CH_3$ **8**

$R_2 = C_2H_5$ **9**

$R_2 = C_6H_5$ **10**

Scheme 3



Scheme 4

2,2,5,5-tetrasubstituted-1,3 dioxanes exhibit different signals for the equatorial and axial protons of the heterocycle and for the protons and carbon atoms of the similar axial and equatorial groups, whereas the spectra of flexible compounds show unique signals at mean chemical shifts values for these protons and carbon atoms.

The differences of chemical shifts between the equatorial and axial protons of the positions 4 (6) of the 1,3-dioxane ring (anancomeric compounds) are usually in the range of $\Delta\delta = 0.2$–0.6 ppm [2–5, 12], whereas the differences between the chemical shifts of the axial and equatorial methyl groups of position 5 are considerably higher ($\Delta\delta = 0.5$–1.0 ppm; [3–5, 12]). The differences between the chemical shifts of the protons of the axial and equatorial ethyloxycarbonyl groups

[2–5] are smaller ($\Delta\delta(CH_2)_{ax-eq} = 0.10$–$0.30$ and $\Delta\delta(CH_3)_{ax-eq} = 0.05$–$0.20$ ppm). The smaller differences of the chemical shifts between the axial and equatorial protons of positions 4 and 6 recorded for some anancomeric compounds bearing two substituents in position 2 of the heterocycle are due to the deshielding through space (steric compression) of the axial protons of the heterocycle by the axial substituent in position 2.

Despite the flipping of the 1,3-dioxane ring, the NMR spectra of compounds **1**–**10** exhibit different signals for the homomorphic protons of positions 4 and 6 and for the homomorphic groups of positions 2 or 5 (they are different from a steric point of view). The differences of the chemical shifts are considerably smaller than those recorded for anancomeric compounds, out of the range of values reported for differences of chemical shifts of axial and equatorial groups, and prove the flexible structure of the rings. In order to get more information, low temperature NMR spectra of some representative compounds of the series have been recorded. The barrier of the ring inversion in 2,2-substituted-1,3 dioxanes is smaller than in unsubstituted 1,3-dioxane [9] or in other derivatives; coalescence of the signals of the heterocycle could not be observed even at $-90°C$ (toluene-d_8). However, during the variable temperature experiments significant modifications of the shape of the signals pertaining to the ring substituents were observed. As an example, in the case of compound **1** the ^1H NMR spectrum recorded at room temperature exhibits two close singlets ($\delta = 0.82$ and $\delta' = 0.76$ ppm) for the two methyl groups at position 5, whereas the low temperature spectrum ($-80°C$) shows two shifted unresolved signals, centered at $\delta_{ax} = 1.25$ and $\delta_{eq} = 0.30$ ppm, assigned to the axial and equatorial methyl groups at position 5 of the two diastereoisomers with frozen conformation. Important modifications have also been observed in the variable temperature experiment of compound **7**. The ^1H NMR spectrum (toluene-d_8) of this compound recorded at room temperature (Fig. 1a) exhibits two close singlets ($\delta = 1.67$ and $\delta' = 1.68$ ppm) for the protons of the methyl groups located in position 2 and a quartet ($\delta = 1.53$ ppm), a triplet ($\delta = 0.86$ ppm), and a singlet ($\delta = 0.89$ ppm) pertaining to the protons of the ethyl and methyl groups located in

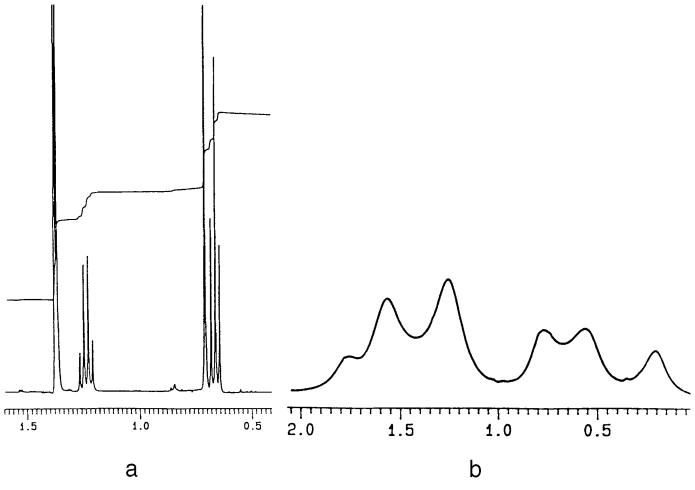


Fig. 1. Partial ^1H NMR spectra of compound **7** at 293 K (a) and 213 K (b)

position 5. Instead of these signals, the low temperature spectrum (−80°C; Fig. 1b) shows six shifted groups of unresolved signals ($\delta = 0.2$–1.8 ppm) assignable to the equatorial and axial methyl and ethyl groups of the two possible diastereoisomers (the ethyl group in equatorial or in axial orientation).

In order to explain the complex NMR spectra of compounds **1**–**10**, the steric relations between the homomorphic groups were investigated. Positions 4 and 6 are prostereogenic centers. The protons at positions 4 and 6 exhibit different prochiralities: the protons H_a, H_d are pro-*S* and the protons H_b, H_c are pro-*R*. The substitution test (Scheme 5) shows that if protons H_a and H_b (structures, **I** and **II**) are replaced by a group *X* (considered to be of highest priority), the new structures are diastereoisomers; thus, protons H_a and H_b are diastereotopic. If proton H_a is replaced by a group *X*, the carbon atoms at positions 6 and 2 (structures **Ia** (**Ib**)) or at positions 6 and 5 (structures **IIa** (**IIb**)) become chiral. The resulting structures (**Ia** and **Ib** or **IIa** and **IIb**) show one chiral carbon atom with the same configuration, whereas the second chiral carbon atom is of opposite configuration. Hence, the two considered structures represent diastereoisomers, and the protons involved in the substitution test are diastereotopic.

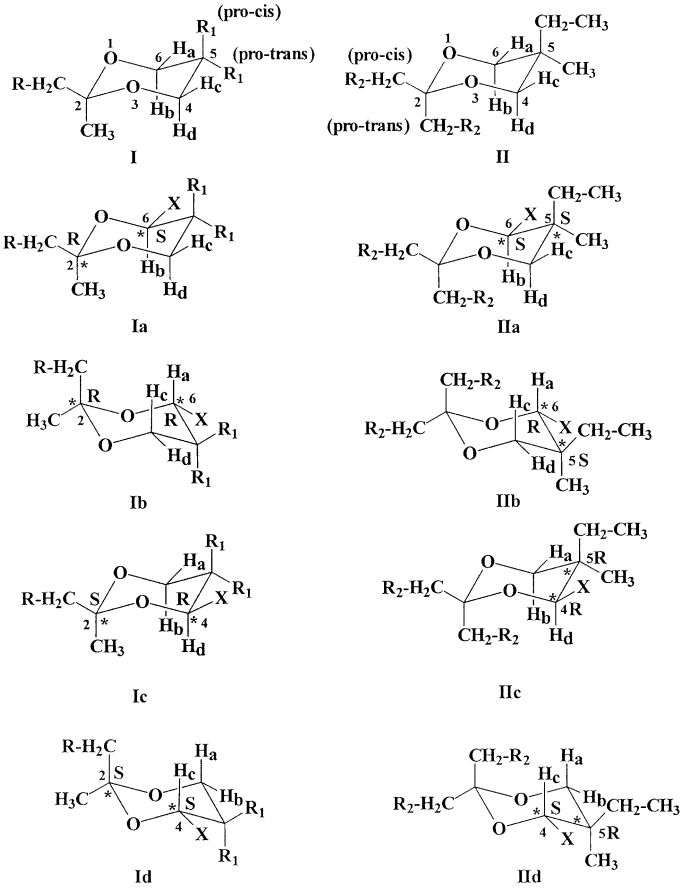
Protons H_a and H_b are diastereotopic, despite the missing of chiral elements in the considered structures **I** or **II**. A similar situation has been recently reported in the case of citric acid [13]. The diastereotopicity of protons H_a and H_b or H_c and H_d in the case of compounds **1**–**10** can also be explained using the pro-*cis* and pro-*trans* concept in the agreement with the disposition of the considered protons on the same side with the group (*r*-group) displaying the higher priority located at C^2 (structures **I**) or C^5 (structures **II**). These dispositions are conserved during the flipping of the 1,3-dioxane ring, and the two types of protons (pro-*cis* and pro-*trans*) exist in different average molecular environments.

The protons H_a and H_c (as well as H_b and H_d) are enantiotopic. The substitution test (Scheme 5) shows that structures **Ia** and **Ic** (**IIa** and **IIc**) are enantiomers (in the compared isomers, all chiral carbon atoms exhibit opposite configurations). The enantiotopicity of protons H_b and H_d can be observed analyzing the configurations of chiral carbon atoms in structures **Ib** and **Id** (**IIb** and **IId**). The steric relations between the protons at positions 4 and 6 are summarized in Table 1.

Positions 2 (structure **I**, compounds **1**–**6**) and 5 (structure **II**, compounds **7**–**10**) are also prostereogenic centers. Despite of the flipping of the 1,3-dioxane rings, the similar groups located in these positions are not equivalent from the steric point of view (heterotopic ligands). One of these groups is pro-*cis*, and the other one is pro-*trans*, the reference (*r*-groups: 2-CH_2R for compounds **1**–**6** and 5-C_2H_5 for compounds **7**–**10**) being the substituent with higher priority from the differently substituted position of the heterocycle (Scheme 5).

The pattern of the ^1H NMR spectra (recorded at room temperature) of compounds **1**–**10** shows an AB system for the protons of the heterocycle (different signals belonging to the above mentioned diastereotopic protons, Fig. 1, Table 2) and exhibits different signals for the diastereotopic groups at positions 2 or 5.

The diastereotopicities are in the range of values measured for chiral 1,3-dioxane derivatives, but are considerably smaller than the differences of chemical shifts recorded for axial and equatorial protons in anancomeric 1,3-dioxane derivatives.



Scheme 5

Table 1. Steric relations between the hydrogen atoms at positions 4 and 6 (*d*: diastereotopic; *e*: enantiotopic) of the 1,3-dioxane rings in flipping compounds **1–10**

Hydrogen atom	Configurations of chiral carbon atoms in structures **Ia–d** and **IIa–d**	H_a	H_b	H_c	H_d
H_a	**Ia**: 2*R*,6*S*; **IIa**: 5*S*,6*S*	–	*d*	*e*	*d*
H_b	**Ib**: 2*R*,6*R*; **IIb**: 5*S*,6*R*	*d*	–	*d*	*e*
H_c	**Ic**: 2*S*,4*R*; **IIc**: 5*R*,4*R*	*e*	*d*	–	*d*
H_d	**Id**: 2*S*,4*S*; **IId**: 5*R*,4*S*	*d*	*e*	*d*	–

As an example, the ^{1}H NMR spectrum of compound **1** (recorded in C_6D_6, Fig. 2a), exhibits close doublets for the protons of the heterocycle (AB system; $\delta_{4(6)} = 3.27$, $\delta'_{4(6)} = 3.34$ ppm). The signal corresponding to the protons of the ester group is overlapped with the more deshielded doublet of the AB system. Instead of the AB system, only a singlet ($\delta = 3.53$ ppm) can be observed in $CDCl_3$ (Fig. 2b), the diastereotopicity of the protons of the heterocycle in this solvent being too small to be observed.

Table 2. ^{1}H NMR data (C_6D_6; δ (ppm)) for H_a, H_c and H_b, H_d of the heterocycles and of the similar groups in positions 2 or 5

	C_4, C_6		2-C(α)			5-CH_3			5-$COOCH_2$-		
	$\delta_{a,c}$, $\delta_{b,d}$	$\Delta\delta$	δ	δ'	$\Delta\delta$	δ	δ'	$\Delta\delta$	δ	δ'	$\Delta\delta$
1	3.270, 3.343	0.073	–	–	–	0.678	0.715	0.037	–	–	–
2	3.335, 3.435	0.100	–	–	–	0.718	0.811	0.093	–	–	–
3	4.497, 4.497	0.000	–	–	–	–	–	–	3.887	3.887	0.000
4	4.520, 4.520	0.000	–	–	–	–	–	–	3.876	3.900	0.026
5	3.308, 3.342	0.033	–	–	–	0.560	0.837	0.277	–	–	–
6	4.379, 4.651	0.271	–	–	–	–	–	–	3.842	3.950	0.108
7	3.393, 3.460	0.067	1.445	1.450	0.005	–	–	–	–	–	
8	3.316, 3.384	0.068	1.719	1.762	0.043	–	–	–	–	–	–
9	3.354, 3416	0.062	1.730	1.762	0.032	–	–	–	–	–	–
10	3.361, 3.425	0.066	2.932	2.963	0.031	–	–	–	–	–	–

Important modifications of the positions of the signals in the NMR spectra recorded in different solvent (ASIS effect) have also been observed for compounds **5** and **6**. The diastereotopicities measured in $CDCl_3$ are significantly smaller (*e.g.* **6**: $\Delta\delta(H_{a,c}-H_{b,d}) = 0.15$ ppm; **5**: $\Delta\delta(5\text{-}CH_3) = 0.06$ ppm) than in C_6D_6 (larger than 0.27 ppm; Table 2).

The NMR spectra of compounds **1**–**10** also exhibit different signals (Tables 2 and 3) for the diastereotopic groups (pro-*cis* and pro-*trans*) at positions 5 (**1**–**6**) or 2 (**7**–**10**). In these cases, the differences of chemical shifts are very small, too (*e.g.* $\Delta\delta(5\text{-}CH_3) = 0.03$–$0.06$ (**1**, **2**) and $\Delta\delta(2\text{-}CH_3) = 0.005$–$0.043$ ppm (**7**–**10**)) and well out of the range of values recorded for similar axial and equatorial groups in anancomeric compounds.

In order to differentiate the enantiotopic protons and carbon atoms (C^4 and C^6) the spectra in the presence of a chiral salt of praseodymium[a] have been recorded. Spectacular results have been obtained for compounds **1** and **2**. The initial signals ($CDCl_3$) for the protons of the 1,3-dioxane ring (**1**: singlet; **2**: AB system) and for the protons of the methylene group (singlets) of the -CH_2-COO*R* substituents were transformed into three shielded AB systems upon addition of the chiral shift reagent, two of them belonging to the protons H_a, H_b and H_c, H_d and the third one corresponding to the enantiotopic protons of the prochiral carbon atom of the ester group. In the spectrum of compound **1** obtained in the presence of Pr-optishift-I (Fig. 2c), the doublets of doublets corresponding to the protons of the 1,3-dioxane ring overlap to triplets. The differences of chemical shifts measured between the enantiotopic protons (*i.e.* diastereotopic in the chiral complex obtained with the chiral salt of Pr) are about 0.04–0.05 ppm. The differences between the chemical shifts of the diastereotopic protons increased to $\Delta\delta \approx 0.2$ ppm (Table 4), and a better

[a] Pr-optishift-I, NMR reagent, Willow Brook Labs., Wankesha, Wisconsin 53186, WBL # 143, USA

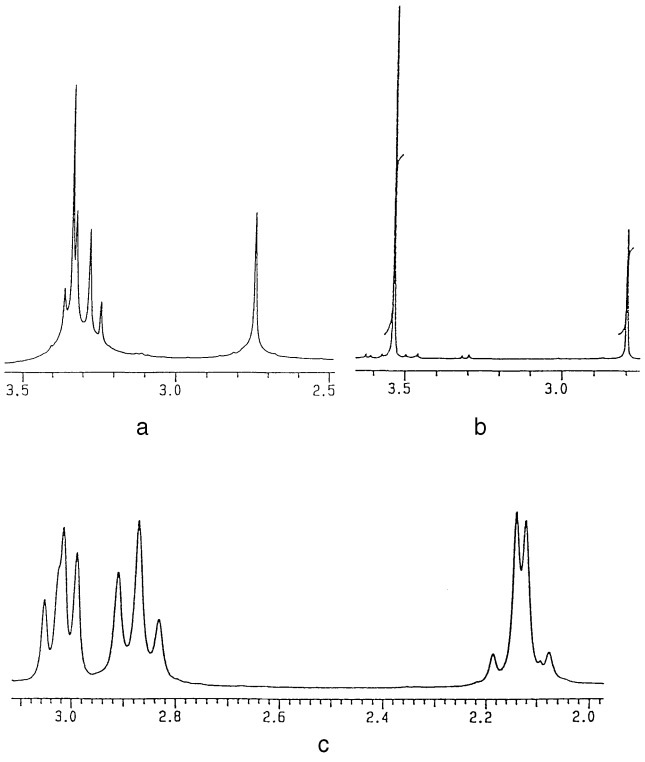


Fig. 2. Partial ^{1}H NMR spectra of compound **1** in C_6D_6 (a), $CDCl_3$ (b), and upon addition of chiral shift reagent (c)

Table 3. ^{13}C NMR data (δ in ppm) for the heterotopic substituents at positions 2 or 5 of **1–10**

	Position 2 C(α)	Position 5			
		$-CH_3$	$-CO-$	$-COOCH_2-$	$-COOCH_2CH_3$
1	–	22.42, 22.53	–	–	–
2	–	22.39, 22.60	–	–	–
3	–	–	167.80	61.80	13.87
4	–	–	167.76, 167.85	61.39, 61.80	14.12
5	–	22.42, 22.80	–	–	–
6	–	–	167.94, 168.94	61.75	13.88, 13.99
7	23.88, 24.31	–	–	–	–
8	26.04, 26.43	–	–	–	
9	36.35, 36.79	–	–	–	–
10	40.41, 40.97	–	–	–	–

differentiation was obtained for the enantiotopic protons belonging to the prochiral carbon atom of the ester group ($\Delta\delta = 0.09$ ppm).

The ^{13}C NMR spectrum of compound **1** recorded in the presence of the chiral praseodymium salt shows two shielded signals ($\delta = 58.93$ and $\delta' = 58.89$ ppm) for

Table 4. ^{1}H NMR data ($CDCl_3$; δ (ppm)) of compounds **1** and **2** upon addition of chiral shift reagent

	Conditions	$C^{4,6}$: H_a, H_b and H_c, H_d	$-CH_2$-COO*R*
1	usual	3.53	2.79
1	with CSR[a]	2.62, 2.67; 2.82, 2.86	1.82, 1.91
2	usual	3.51; 3.56	2.79
2	with CSR[a]	2.44, 2.52; 2.68, 2.72	1.69, 1.78

[a] CSR: chiral shift reagent

the carbon atoms at positions 4 and 6 instead of the unique signal obtained in the usual spectrum ($\delta = 70.55$ ppm).

Conclusions

The NMR investigations of the 1,3-dioxanes **1–10** revealed a flexible structure of these compounds. The peculiar substitution of the heterocycle determines the heterotopicity (different average molecular environments) of the protons and groups located in the three prostereogenic centers of the 1,3-dioxane ring (positions 4, 6; 2; 5). The diastereotopic groups were observed in the usual NMR spectra, whereas the enantiotopic groups could be differentiated upon addition of a chiral shift reagent.

Experimental

General

NMR spectra were recorded on Bruker AM 400 and Varian Gemini 300 spectrometers operating at 400 and 300 MHz for protons and 100 and 75 MHz for carbon atoms respectively. No Me_4Si was added; the chemical shifts were referenced to the solvent line.

Compounds **1–10**, *general procedure*

Equimolar amounts of 1,3-diol and carbonyl compound (0.1 mol) together with a catalytic amount of *p*-toluenesulfonic acid (0.1 g) were dissolved in 200 ml benzene. The mixture was refluxed, and the water was removed using a *Dean-Stark* trap. When 80% of the theoretical amount of water had separated, the mixture was cooled to room temperature, and the catalyst was neutralized under stirring with an excess of CH_3COONa (0.2 g). After washing twice with 100 ml water and drying over Na_2SO_4, the benzene was removed and the 1,3-dioxane derivatives were purified by crystallization from ethanol or by vacuum distillation. Compounds **6–10** are new, whereas the synthesis of compounds **1** [14], **2** [15], **3**, **4** [1], and **5** [16] has been already reported. The elemental analysis data of the new compounds agreed satisfactorily with the calculated ones.

2-Benzyl-5,5-bis(ethyloxycarbonyl)-2-methyl-1,3-dioxane (**6**; $C_{18}H_{24}O_6$)

Yield: 52%; liquid; b.p.: 94–96°C (0.05 mm Hg); ^{1}H NMR (C_6D_6): $\delta = 0.80$ (3H, t, $J = 7.1$ Hz, 5-$COOCH_2CH_3$), 0.89 (3H, t, $J = 7.1$ Hz, 5-$COOCH_2CH_3$), 1.17 (3H, s, 2-CH_3), 2.96 (2H, s, 2-CH_2-C_6H_5), 3.84 (2H, q, $J = 7.1$ Hz, 5-$COOCH_2CH_3$), 3.95 (2H, q, $J = 7.1$ Hz, 5-$COOCH_2CH_3$), 4.37

(2H, d, $J = 11.7$ Hz, 4,6-H), 4.65 (2H, d, $J = 11.7$ Hz, 4.6-H), 7.20–7.30 (5H, overlapped peaks, aromatic protons) ppm; ^{13}C NMR (C_6D_6): $\delta = 13.88$ (5-COOCH$_2$*C*H$_3$), 13.99 (5-COOCH$_2$*C*H$_3$), 19.54 (2-CH$_3$), 44.95 (2-*C*H$_2$-C$_6$H$_5$), 54.37 (C^5), 61.75 (5-COO*C*H$_2$CH$_3$), 62.76 (C^{4,6}), 100.11 (C^2), 126.65, 128.07, 131.13 (tertiary aromatic carbon atoms), 136.35 (quaternary aromatic carbon atom), 167.94 (5-*C*OOCH$_2$CH$_3$), 168.94 (5-*C*OOCH$_2$CH$_3$) ppm.

5-Ethyl-2,2,5-trimethyl-1,3-dioxane (**7**; $C_9H_{18}O_2$)

Yield: 70%; liquid; b.p.: 80–81°C (1.5 mm Hg); ^{1}H NMR (C_6D_6): $\delta = 0.72$ (3H, t, $J = 7.6$ Hz, 5-CH$_2$C*H*$_3$), 0.77 (3H, s, 5-CH$_3$), 1.30 (2H, q, $J = 7.6$ Hz, 5-C*H*$_2$CH$_3$), 1.445 (3H, s, 2-CH$_3$), 1.450 (3H, s, 2-CH$_3$), 3.39 (2H, d, $J = 11.1$ Hz, 4,6-H), 3.46 (2H, d, $J = 11.1$ Hz, 4,6-H) ppm; ^{13}C NMR (C_6D_6): $\delta = 7.58$ (5-CH$_2$*C*H$_3$), 19.06 (5-CH$_3$), 23.88 (2-CH$_3$), 24.31 (2-CH$_3$), 28.01 (5-*C*H$_2$CH$_3$), 32.57 (C^5), 69.13 (C^{4,6}), 97.81 (C^2) ppm.

2,2,5-Triethyl-5-methyl-1,3-dioxane (**8**; $C_{11}H_{22}O_2$)

Yield: 60%; liquid; b.p.: 85–86°C (1 mm Hg); ^{1}H NMR(C_6D_6): $\delta = 0.66$ (3H, t, $J = 7.5$ Hz, 5-CH$_2$C*H*$_3$), 0.71 (3H, s, 5-CH$_3$), 0.968 (3H, t, $J = 7.4$ Hz, 2-CH$_2$C*H*$_3$), 0.973 (3H, t, $J = 7.4$ Hz, 2-CH$_2$C*H*$_3$), 1.24 (2H, q, $J = 7.5$ Hz, 5-C*H*$_2$CH$_3$), 1.719 (2H, q, $J = 7.4$ Hz, 2-C*H*$_2$CH$_3$), 1.737 (2H, q, $J = 7.4$ Hz, 2-C*H*$_2$CH$_3$), 3.316 (2H, d, $J = 11.2$ Hz, 4,6-H), 3.384 (2H, d, $J = 11.2$ Hz, 4.6-H) ppm; ^{13}C NMR (C_6D_6): $\delta = 7.54$ (5-CH$_2$*C*H$_3$), 7.93 (2-CH$_2$*C*H$_3$), 19.18 (5-CH$_3$), 26.08 (2-*C*H$_2$CH$_3$), 26.42 (2-*C*H$_2$CH$_3$), 28.11 (5-*C*H$_2$CH$_3$), 32.33 (C^5), 68.55 (C^{4,6}), 100.87 (C^2) ppm.

5-Ethyl-5-methyl-2,2-dipropyl-1,3-dioxane (**9**; $C_{13}H_{26}O_2$)

Yield: 62%; liquid; b.p.: 120–122°C (2 mm Hg); ^{1}H NMR (C_6D_6): $\delta = 0.67$ (3H, t, $J = 7.5$ Hz, 5-CH$_2$C*H*$_3$), 0.72 (3H, s, 5-CH$_3$), 0.926 (3H, t, $J = 7.1$ Hz, 2-CH$_2$CH$_2$C*H*$_3$), 0.933 (3H, t, $J = 7.1$ Hz, 2-CH$_2$CH$_2$C*H*$_3$), 1.25 (2H, q, $J = 7.5$ Hz, 5-C*H*$_2$CH$_3$), 1.54 (4H, overlapped peaks, 2-CH$_2$C*H*$_2$CH$_3$), 1.730 (2H, t, $J = 6.5$ Hz, 2-C*H*$_2$CH$_2$CH$_3$), 1.762 (2H, t, $J = 6.5$ Hz, 2-C*H*$_2$CH$_2$CH$_3$), 3.354 (2H, d, $J = 11.2$ Hz, 4,6-H), 3.416 (2H, d, $J = 11.2$ Hz, 4,6-H) ppm; ^{13}C NMR (C_6D_6): $\delta = 7.59$ (5-CH$_2$*C*H$_3$), 14.77 (2-CH$_2$CH$_2$*C*H$_3$), 17.07 (2-CH$_2$*C*H$_2$CH$_3$), 17.12 (2-CH$_2$*C*H$_2$CH$_3$), 19.21 (5-CH$_3$), 28.13 (5-*C*H$_2$CH$_3$), 32.37 (C^5), 36.35 (2-*C*H$_2$CH$_2$CH$_3$), 36.79 (2-*C*H$_2$CH$_2$CH$_3$), 68.63 (C^{4,6}), 100.49 (C^2) ppm.

5-Ethyl 2,2-dibenzyl-5-methyl-1,3-dioxane (**10**; $C_{21}H_{26}O_2$)

Yield: 80%; liquid; b.p.: 92–93°C (0.5 mm Hg); ^{1}H NMR (C_6D_6): $\delta = 0.47$ (3H, s, 5-CH$_3$), 0.55 (3H, t, $J = 7.5$ Hz, 5-CH$_2$C*H*$_3$), 0.93 (2H, q, $J = 7.5$ Hz, 5-C*H*$_2$CH$_3$), 2.932 (2H, s, 2-C*H*$_2$C$_6$H$_5$), 2.963 (2H, s, 2-C*H*$_2$C$_6$H$_5$), 3.361 (2H, d, $J = 11.2$ Hz, 4,6-H), 3.425 (2H, d, $J = 11.2$ Hz, 4,6-H), 7.05–7.25 (10H, overlapped peaks, aromatic protons) ppm; ^{13}C NMR (C_6D_6): $\delta = 7.51$ (5-CH$_2$*C*H$_3$), 18.79 (5-CH$_3$), 27.62 (5-*C*H$_2$CH$_3$), 32.25 (C^5), 40.41 (2-CH$_2$C$_6$H$_5$), 40.97 (2-CH$_2$C$_6$H$_5$), 69.04 (C^{4,6}), 100.24 (C^2), 126.49, 127.95, 128.06, 131.33, 131.39 (tertiary aromatic carbon atoms) and 137.41, 137.49 (quaternary aromatic carbon atoms) ppm.

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