SYNTHESIS AND STEREOCHEMISTRY OF SOME NEW 1,3-DIOXANES OBTAINED FROM AROMATIC CARBONYL COMPOUNDS

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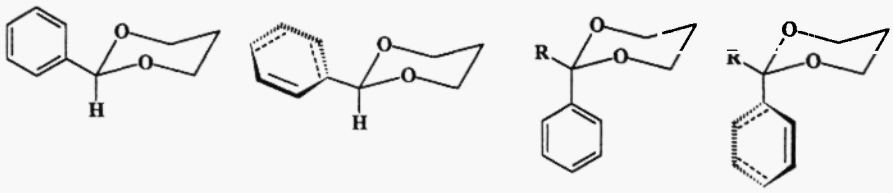
Abstract: The study on the stereochemistry of some new 2-aryl-1,3-dioxanes bearing identical geminal substituents in position 5 of the heterocycle was performed by means of NMR methods. The investigations pointed out the anancomeric structure of the compounds. The equatorial or axial preferences of the aryl groups were correlated with the structure of the other substituents located in the acetal part of the heterocycle. The influence of the chirality on some 1,3-dioxanes obtained by the acetalization of benzoin was investigated by means of the diastereotopicity of protons and carbon atoms.

INTRODUCTION

The studies concerning the conformational analysis of 1,3-dioxane compounds displaying aromatic substituents in the acetal part of the heterocycle revealed some interesting aspects (1-6). In the derivatives bearing the aryl group as unique substituent in position 2 of the 1,3-dioxane ring, the aromatic substituent prefers the equatorial orientation. The high value of the free conformational enthalpy of the phenyl group located in this position [ΔG°=3.12 kcal./mol; found by thermodynamically data (1)] suggests that an aryl substituent in the acetal part of the 1,3-dioxane ring is an efficient holding group. The compounds bearing two different substituents in position 2 (an aryl and an alkyl one) also exhibit anancomeric structures, but in this case the aromatic group prefers the axial orientation. The value of the free conformational enthalpy found for 2-methyl, 2-phenyl-1,3-dioxane shows the high preference of the phenyl group for the axial orientation [ΔG°=2.41 kcal./mol (1)] and it is about three times larger than the calculated value [$\Delta G^{\circ}_{calcd} = \Delta G_{Me}^{\circ} - \Delta G_{Ph}^{\circ}$=0.86 kcal./mol (1)] using the free conformational enthalpies of the methyl and phenyl groups measured for the corresponding monosubstituted compounds. The rotameric behaviors of the aromatic substituents in axial or equatorial positions are quite different. The phenyl group can adopt in each of these positions bisectional (IA, IIA) or (ortho)gonal (IB, IIB) orientations (Scheme 1). In solid state the equatorial aryl substituent shows fortuitously (the packing forces are involved) a bisectional or gonal orientation (2), whereas in solution a free rotation of the equatorial phenyl group was considered. In axial position the aromatic substituents prefer the gonal rotamer (displaying minimal hindrance with the axial protons of positions 4 and 6 of the heterocycle), as it was proved in solid state by X-ray structure determinations (2-4) and in solution by dipole moment measurements (5) and NMR investigations (6). This preference for the gonal rotamer is associated with a hindrance of the rotation of the aromatic group.

On the other hand the studies developed on the stereochemistry of some 1,3-dioxane compounds bearing chiral substituents in positions 2 or 5 of the heterocycle (7-11) showed the influence of the chiral elements on the NMR spectra



IA IB IIA IIB

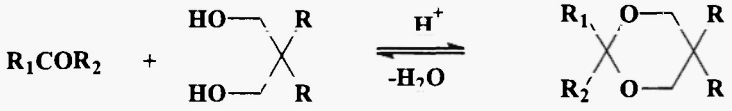
Scheme 1

of the compounds by means of the diastereotopicity of the similar protons and carbon atoms.

It was considered of interest to develop a study concerning the stereochemistry and NMR spectra of some 1,3-dioxane compounds bearing one or two different aromatic substituents in position 2 of the 1,3-dioxane ring, to investigate the axial or equatorial preferences of the aryl groups, the rotameric behavior of the aromatic substituents and the influences on the NMR spectra of the presence of chiral carbon atoms.

RESULTS AND DISCUSSION

New 1,3-dioxane derivatives (1-6) bearing aromatic substituents in position 2 of the heterocycle have been obtained by the acetalization of some aromatic aldehydes and ketones (Scheme 2).



R=CH_3; R_1=H; R_2=2'-C_4H_3S (thiophenyl) 1

R=CH_3; R_1=H; R_2=β-$C_{10}H_7$ 2

R=CH_3; R_1=H; R_2=p-$(CH_3)_2NC_6H_4$ 3

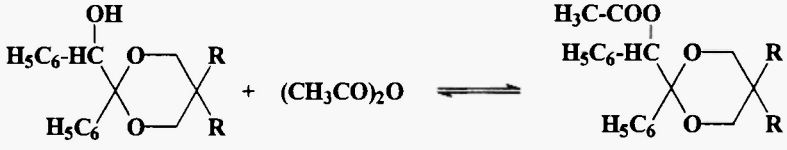
R=$COOC_2H_5$; R_1=H; R_2= p-$(CH_3)_2NC_6H_4$ 4

R=CH_3; R_1=C_6H_5; R_2=$C_6H_5CH(OH)$- 5

R=$COOC_2H_5$; R_1=C_6H_5; R_2=$C_6H_5CH(OH)$- 6

Scheme 2

Compounds 5 and 6 were subjected to esterification up to ester 7 and triester 8, respectively (Scheme 3).



5 R=C_2H_5 7

6 R=$COOC_2H_5$ 8

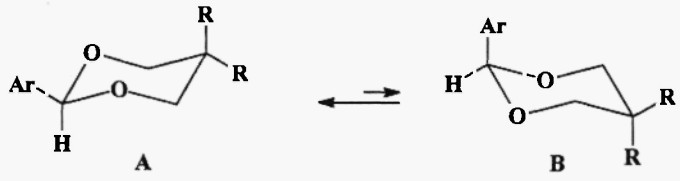
Scheme 3

The investigations on the stereochemistry of these compounds followed three main directions:

- the flexibility or anancomericity of the 1,3-dioxane ring and the preferences of the substituents for the equatorial position,

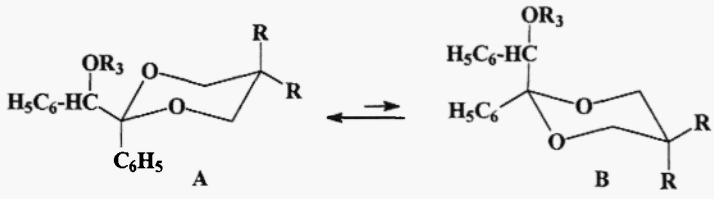
- the rotameric behavior of the aromatic groups,
- the influence of the chiral center (compounds **5-8**).

All the investigated compounds exhibit anancomeric structures. The conformational equilibria for compounds **1-4** are shifted towards the conformations showing the aromatic substituents in equatorial orientation (A, Scheme 4). The free conformational enthalpies of the phenyl and of the hydroxybenzyl groups are quite different, thus the conformational equilibria of compounds **5-8** are shifted towards the conformations that display the phenyl group in axial orientation and the phenyl-hydroxymethyl group [a substituted methyl group (with Cl, Br, COOR) can be considered similar to a methyl group, having close value of the free conformational enthalpies with the parent aikyl group (2)] in the equatorial one (Scheme 5).



1-4

Scheme 4



5-8

Scheme 5

The anancomeric structure of the compounds was deduced from their NMR spectra. The "rigidity" of the heterocycle determines the recording in the NMR spectra of different signals for the equatorial and axial positions of the protons of the ring and of the protons and carbon atoms belonging to the similar groups located on it (Tables I and II).

As example, the ^{1}H NMR spectrum of compound **2** (Figure 1) shows an AB splitting pattern for the axial (δ_{ax}=3.38

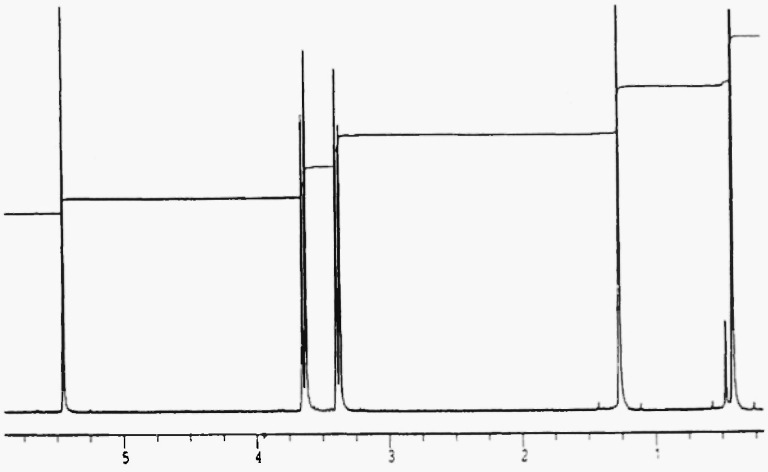


Figure 1. ^{1}H NMR spectrum of compound 2 (fragment).

ppm) and equatorial (δ_{eq}=3.63 ppm) protons belonging to positions 4 and 6, as well as two singlets (δ_{eq}=0.42 ppm) and(δ_{ax}=1.27 ppm) belonging to the protons of the equatorial and axial methyl groups of position 5 The equatorial aromatic groups (compounds 1-4) show a free rotation around their bonds with the heterocycle. No influences of the presence of any "rigid" rotamer (one set of signals was recorded) or of the anysotropic magnetic field associated with a rigid aromatic ring were observed. Differently, the axial phenyl group has a hindered rotation, the structures being frozen with the aromatic substituent in orthogonal conformation (Scheme 1, IIB). The protons of the equatorial groups located in position 5 of the heterocycle are significantly shielded by the magnetic field of the rigid gonal phenyl substituent. This phenomenon was observed for some 2-methyl, 2-aryl-1,3-dioxane (6) and was rendered evident by the analysis using the diagram of the anysotropy of the magnetic field of the benzene ring published by Haigh and Mallion (12). The data of Table I show higher differences between the chemical shifts of the axial and equatorial methylene protons of the ester groups of position 5 for compounds 6 and 8 ($\Delta\delta$=0.42-0.51 ppm; due to the shielding of the equatorial protons) then for compound 4 ($\Delta\delta$=0.27 ppm) and very low chemical shifts for the protons of the equatorial methyl groups of compounds 5 and 7 (δ=0.10 ppm) compared with the values recorded for compounds 1-3 (δ=0.32-042 ppm).

Table I. ^{1}H NMR data (C_6D_6, δ ppm) of compounds 1-8

Compound	C (4.6)		-$COOCH_2$-		-CH_3	
	ax.	eq.	ax.	eq.	ax.	eq.
1	3.23	3.50	-	-	1.18	0.32
2	3.38	3.63	-	-	1.27	0.42
3	3.39	3.63	-	-	1.29	0.41
4	4.10	5.15	4.09	3.82	0.98	0.84
5	3.22	3.32; 3.33	-	-	1.15	0.10
6	4.06; 4.13	4.80; 4.83	4.14	3.63	1.06	0.67
7	3.26	3.34; 3.35	-	-	1.03	0.10
8	4.11; 4.17	4.85; 4.88	4.009; 4.018	3.59	1.02	0.63

Table II. ^{13}C NMR data (C_6D_6, δ ppm) of compounds 1-8

Compound	C (4.6)	-COO-		-CH_2- (5)		-CH_3 (5)	
		ax.	eq.	ax.	eq.	ax.	eq.
1	76.89	-	-	-	-	22.67	21.18
2	77.21	-	-	-	-	22 83	21.33
3	77.18	-	-	-	-	22.94	21.43
4	69.55	167.67	166.91	61.43	61.27	13.68	13.48
5	71.19; 71.28	-	-	-	-	22.67	21.09
6	63.72; 63.95	167.85	166.26	61.76	61.29	13.76	13.71
7	71.18	-	-	-	-	22.30	21.07
8	63.61; 63.71	167.13	166.38	61.50	61.29	13.71	13.24

The presence of a chiral carbon atom in compounds **5-8** determines the diastereotopicity of the protons and carbon atoms of the positions 4 and 6 of the heterocycle. The pattern of the ^{1}H NMR spectra shows (for the above protons) two AB (or AX) systems with different signals for the equatorial and axial protons of each diastereotopic position 4 and 6. Thus, the spectrum of compound **8** (Figure 2) displays two doublets for the axial protons δ_{4ax}=4.11 and δ_{6ax}=4.17 ppm and two overlapped doublets of doublets for the equatorial protons δ_{4eq}=4.85 and δ_{6eq}=4.88 ppm. The signals of the equatorial protons show a further splitting due to a long range coupling (J=2.4 Hz) between the diastereotopic equatorial protons, made possible by the W (M) disposal of the bonds H_{eq}-C^4-C^5-C^6-H_{eq}.

The values of the diastereotopicities (Table I) for both axial ($\Delta\delta_{6ax-4ax}$) and equatorial ($\Delta\delta_{6eq-4eq}$) protons are somewhat smaller than those recorded for other 1,3-dioxane bearing chiral groups in positions 2 or 5 of the heterocycle (7-11, 13-15). The diastereotopicities for the carbon atoms ($\Delta\delta_{6-4}$) also show smaller values (Table II) as those reported in the literature for other chiral 1,3-dioxanes (7-11, 13-15).

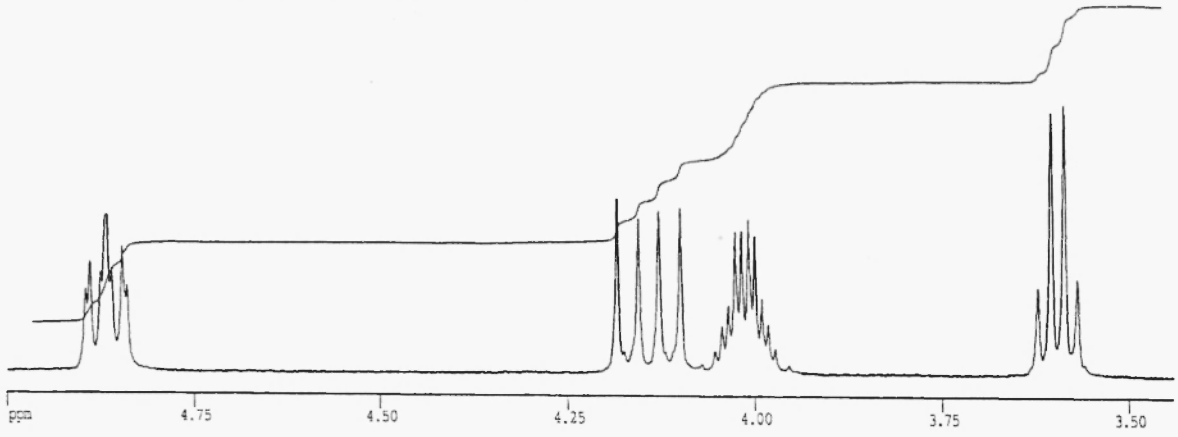
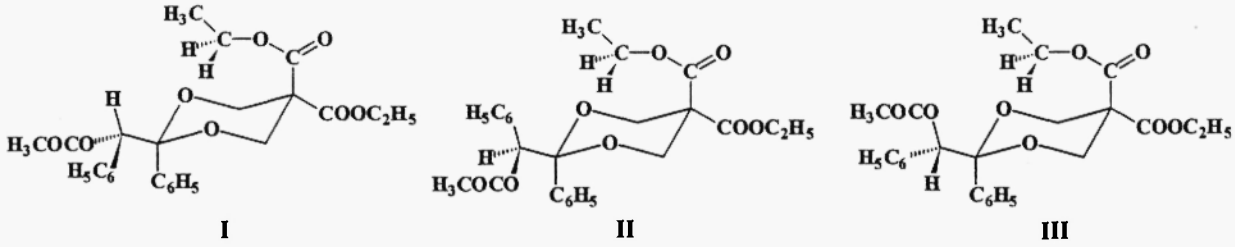


Figure 2. ^{1}H-NMR spectrum of compound **8** (fragment).

A remarkable feature is the recording in the ^{1}H NMR spectrum of compound **8** (Figure 2) of different signals (δ=4.009 and δ=4.018 ppm) for the diastereotopic methylene protons of the axial ester group. The pattern shows for these protons two overlapped doublets of quartets (due to the geminal coupling between the diastereotopic protons and to the coupling of these ones with the protons of the vicinal methyl group). The influence of the chiral carbon atom (at a distance of 8 lengths) is transmitted through space. The missing of the same differentiation for the similar protons of the equatorial ester group (also located at 8 lengths distance of the chiral carbon atom, but showing a usual quartet) can be considered as a proof for this supposition.

This conclusion is suggested by the rotameric behaviors of the axial ester group of position 5 and of the chiral substituent located in the acetal part of the heterocycle. The conformer displaying the axial substituent located to C^5 towards the 1,3-dioxane ring is the most representative (this orientation determines by means of the influence of the oxygen atoms of the ring the observed deshielding of the protons and carbon atoms of this group).

The three rotamers (Scheme 6, I-III) of the chiral group located in position 2 exhibit different populations. They generate for the two methylene protons (of the axial ester group) enough different average magnetic environments for permitting the recording of different signals (in the NMR spectrum) for each of them. The distance between the chiral group located in position 2 and the equatorial ester group of position 5 is too high (the differences between the magnetic environments of the diastereotopic methylene protons are too small) for being possible to observe the diastereotopicity of the methylene protons of this group, too.



I II III

Scheme 6

A variable temperature experiment showed there are not significant differences among the ^{1}H NMR spectra of compound **8** recorded at room, high (85 °C) and low (-55°C) temperatures (only a fading of resolution at low temperature was observed). This experiment shows there are not hindrance of the rotation (at room temperature) of the substituents located in positions 2 and 5 and the influences observed by means of the diastereotopicity of the methylene protons of the axial ester group are due to different mean magnetic environments (for these two kind of protons) generated by the different populations of the conformers I-III.

CONCLUSIONS

The investigated compounds exhibit anancomeric structures. A unique aromatic substituent in the acetal part of the 1,3-dioxane ring prefers the equatorial position, whereas in 2,2-disubstituted compounds the phenyl group prefers the axial position. The NMR spectra of the compounds (**5**-**8**) allow to observe the hindrance of the rotation of the gonal rotamer of the axial phenyl group and the influence of the chiral carbon atom belonging to the equatorial substituent of position 2.

EXPERIMENTAL

^{1}H-and ^{13}C-NMR spectra were recorded at room temperature, using C_6D_6 as solvent, in 5 mm tubes, on a Bruker AM 400 Fourier transform NMR spectrometer, equipped with a dual ^{13}C-^{1}H head, operating at 400 MHz for protons and 100 MHz for carbon atoms.

M.ps were measured with Electrothermal melting point apparatus and are uncorrected.

*Compounds **1-6**, general procedure.* - Equimolecular amounts of 1,3-diol and carbonyl compound (0.1 mol) with catalytic amounts of p-toluenesulphonic acid (0.1 g) were solved in 200 ml benzene. The mixture was refluxed and the water resulted in the reaction was removed using a Dean-Stark trap. When 80 % of the theoretical water was separated, after cooling at room temperature, the catalyst was neutralized (under stirring 0.5 h) with CH_3-COONa powder in excess (0.2 g). The reaction mixture was washed twice with 100 ml water. After drying (with Na_2SO_4) the benzene was removed and the 1,3-dioxane compounds were purified by crystallization from ethanol.

*Compounds **7** and **8**, general procedure.* - Equimolecular amounts of 1,3-dioxane **5** or **6** and acetic anhydride were refluxed for three hours in 20 % excess of pyridine. After the neutralization of pyridine with HCl 10 %, the solution was poured upon 50 g mixture of water and ice and the dioxanes **7** and **8** crystallized. After separation the compounds were purified by crystallization from ethanol.

5,5-Dimethyl-2-(2'-thiophenyl)-1,3-dioxane 1. Solid, m.p. 70-71 °C. Yield 74%. Anal. Calcd. for $C_{10}H_{14}O_2S$: C, 60.58, H, 7.12. Found: C, 60.36, H, 7.21. ^{1}H NMR δ (C_6D_6) 0.32[3H, s, 5-CH_3 (eq)], 1.18[3H, s, 5-CH_3 (ax)], 3.23(2H, d, J=11.1 Hz, 4,6-H_{ax}), 3.50(2H, d, J=11.1 Hz, 4,6-H_{eq}), 5.50(1H, s, 2-H_{ax}), 6.76(1H, dd, J=5.0, J'=3.5 Hz, 4'-H), 6.80(1H, dd, J=5.0,

J'=0.8 Hz, 3'-H) and 7.22 ppm (1H, dd, J=3.5, J'=0.8 Hz, 5'-H). ^{13}C NMR δ (C_6D_6) 21.18[5-CH_3(eq)], 22.67[5-CH_3(ax)], 29.58 (C^5), 76.89($C^{4,6}$), 98.42(C^2), 124.71($C^{4'}$), 125.21(C^3), 126.71(C^5) and 131.86 ppm (C^2).

5,5-Dimethyl-2-(2'-naphtyl)-1,3-dioxane 2. Solid, m.p. 96-97 °C. Yield 71%. Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79,31, H, 7.49. Found: C, 79.50, H, 7.36. ^{1}H NMR δ (C_6D_6) 0.42[3H, s, 5-CH_3 (eq)], 1.27[3H, s, 5-CH_3 (ax)], 3.38(2H, d, J=10.8 Hz, 4,6-H_{ax}), 3.63(2H, d, J=10.8 Hz, 4,6-H_{eq}), 5.45(1H, s, 2-H_{ax}), 7.24-7.29(2H, m, 3'-H, 4'-H), 7.63-7.65(1H, m, 5'-H), 7.70-7.73(2H, m, 6'-H, 7'-H), 7.88(1H, d, J=8.6 Hz, 8'-H) and 8.19 ppm (1H, s, 1'-H). ^{13}C NMR δ (C_6D_6) 21.33[5-CH_3(eq)], 22.83[5-CH_3(ax)], 29.74(C^5), 77.21($C^{4,6}$), 101.51(C^2), 124.42, 125.70, 125.90, 125.99, 127.81, 128.35 (aromatic tertiary carbon atoms) and 136.74, 137.75, 137.81 ppm (quaternary aromatic carbon atoms).

2-(p-Dimethylaminophenyl)-5,5-dimethyl-1,3-dioxane 3. Solid, m.p. 96-97 °C. Yield 67%. Anal. Calcd. for $C_{14}H_{21}O_2N$: C, 71.46, H, 8.99, N, 5.95. Found: C, 71.22, H, 9.12, N, 5.80. ^{1}H NMR δ (C_6D_6) 0.41[3H, s, 5-CH_3 (eq)], 1.29[3H, s, 5-CH_3 (ax)], 2.50[6H, s, $N(CH_3)_2$], 3.39(2H, d, J=10.7 Hz, 4,6-H_{ax}), 3.63(2H, d, J=10.8 Hz, 4,6-H_{eq}), 5.42(1H, s, 2-H_{ax}), 6.66 (2H, d, J=8.6 Hz, aromatic protons) and 7.74(2H, d, J=8.6 Hz, aromatic protons). ^{13}C NMR δ (C_6D_6) 21.43[5-CH_3(eq)], 22.94[5-CH_3(ax)], 29.70(C^5), 39.87 [$N(CH_3)_2$], 77.18($C^{4,6}$), 102.12(C^2) and 111.90, 127.27, 150.76 ppm (aromatic carbon atoms).

5,5-Bis(ethyloxycarbonyl)-2-(p-dimethylaminophenyl)- 1,3-dioxane 4. Solid, m.p. 95-96 °C. Yield 62%. Anal. Calcd. for $C_{18}H_{25}O_6N$: C, 61.52, H, 7.17, N, 3.99. Found: C, 61.29, H, 7.40, N, 4.10. ^{1}H NMR δ (C_6D_6) 0.84[3H, t, J=7.1 Hz, 5-$COOCH_2CH_3$ (eq)], 0.98[3H, t, J=7.1 Hz, 5-$COOCH_2CH_3$(ax)], 2.48[6H, s, $N(CH_3)_2$], 3.82(2H, q, J=7.1 Hz, 5-$COOCH_2CH_3$ (eq)], 4.09(2H, q, J=7.1 Hz, 5-$COOCH_2CH_3$ (ax)], 4.10(2H, d, J=11.6 Hz, 4,6-H_{ax}), 5.15(2H, d, J=11.6 Hz, 4,6-H_{eq}), 5.40(1H, s, 2-H_{ax}), 6.60(2H, d, J=6.9 Hz, aromatic protons) and 7.62(2H, d, J=8.6 Hz, aromatic protons). ^{13}C NMR δ (C_6D_6) 13.48[5-$COOCH_2CH_3$(eq)], 13.68[5-$COOCH_2CH_3$(ax)], 39.74[$N(CH_3)_2$], 53.44(C^5), 61.27[5-$COOCH_2CH_3$(eq)], 61.43[5-$COOCH_2CH_3$ (eq)], 69.55($C^{4,6}$), 102.77(C^2), 111.80, 126.50, 127.30, 150.76 (aromatic carbon atoms), 166.91[5-COO-CH_2CH_3(eq)], and 167.67 ppm[5-$COOCH_2CH_3$(ax)].

5,5-Dimethyl-2-phenyl-2-(phenyl-hydroxymethyl)-1,3-dioxane 5. Solid, m.p. 116-117 °C. Yield 60 %. Anal. Calcd. for $C_{19}H_{22}O_3$: C, 76.48, H, 7.43. Found: C, 76.28, H, 7.25. ^{1}H NMR δ (C_6D_6) 0.10[3H, s, 5-CH_3 (eq)], 1.15[3H, s, 5-CH_3 (ax)], 3.09[1H, d, J=2.5 Hz, -CH(OH)C_6H_5], 3.22(2H, d, J=11.0 Hz, 4,6-H_{ax}), 3.32(1H, d, J=11.0 Hz, 4-H_{eq}), 3.33(1H, d, J=11.0 Hz, 6-H_{eq}), 4.95(1H, d, J=2.5 Hz, -CH(OH)C_6H_5] and 7.00-7.15 ppm (10H, overlapped peaks, aromatic protons). ^{13}C NMR δ (C_6D_6) 21.09[5-CH_3(eq)], 22.67[5-CH_3(ax)], 29.67(C^5), 71.19(C^4), 71.28(C^6), 80.64[2-CH(OH)C_6H_5] 102.36(C^2), 126.83, 127.24, 127.73, 128.01, 128.68, 128.94 (tertiary aromatic carbon atoms) and 135.46. 138.43 ppm (quaternary aromatic carbon atoms).

5,5-Bis(ethyloxycarbonyl)-2-phenyl-2-(phenyl-hydroxymethyl)-1,3-dioxane 6. Solid, m.p. 88-89 °C. Yield 61 %. Anal. Calcd. for $C_{23}H_{26}O_7$: C, 66.65 H, 6.32. Found: C, 66.88, H, 6.57. ^{1}H NMR δ (C_6D_6) 0.67[3H, t, J=7.1 Hz, 5-$COOCH_2CH_3$ (eq)], 1.06[3H, t, J=7.1 Hz, 5-$COOCH_2CH_3$ (ax)], 3.63[2H, q, J=7.1 Hz, 5-$COOCH_2CH_3$ (eq)], 4.14[2H, q, J=7.1 Hz, 5-$COOCH_2CH_3$ (ax)], 3.26[1H, s, 2-CH(OH)C_6H_5], 4.06(1H, d, J=11.5 Hz, 4-H_{ax}), 4.13 (1H, d, J=11.5 Hz, 6-H_{ax}), 4.80[1H, dd (overlapped), J=11.5, J'=2.9 Hz, 4-H_{eq}), 4.83[1H, dd [overlapped), J=11.5, J'=2.9 Hz, 6-H_{eq}], 4.90(1H, s, -CH(OH)C_6H_5] and 7.00-7.20 ppm (10H, overlapped peaks, aromatic protons). ^{13}C NMR δ (C_6D_6) 13.71[5-$COOCH_2CH_3$(eq)], 13.76[5-$COOCH_2CH_3$(ax)], 53.20(C^5), 61.29[5-COO-CH_2CH_3(eq)], 61.76[5-$COOCH_2CH_3$(ax)], 63.72(C^4), 63.95(C^6), 80.38[2-CH(OH)-C_6H_5] 103.01(C^2), 126.86, 127.33, 128.01, 128.42, 128.57, 128.64, 129.66 (tertiary aromatic carbon atoms) 134.24. 137.93 (quaternary aromatic carbon atoms), 166.26[5-$COOCH_2CH_3$(eq)] and 167.85 ppm[5-$COOCH_2CH_3$(eq)].

5,5-Dimethyl-2-phenyl-2-[phenyl (oxycarbonylmethyl)methyl]- 1,3-dioxane 7. Solid, m.p.107-108 °C. Yield 81 %. Anal. Calcd. for $C_{21}H_{24}O_4$: C, 74.09 H, 7.11. Found: C, 74.28, H, 7.20. ^{1}H NMR δ (C_6D_6) 0.10[3H, s, 5-CH_3 (eq)], 1.03[3H, s, 5-CH_3 (ax)], 1.71[3H, s, -CH(OCOCH_3)C_6H_5], 3.26(2H, d, J=11.0 Hz, 4,6-H_{ax}), 3.343(1H, d, J=11.0 Hz, 4-H_{eq}), 3.350(1H, d, J=11.0 Hz, 6-H_{eq}), 6.36(1H, s, -CH(OCOCH_3)C_6H_5] and 7.00-7.22 ppm (10H, overlapped peaks, aromatic protons). ^{13}C NMR δ (C_6D_6) 21.07[5-CH_3(eq)], 22.30[5-CH_3(ax)], 29.66(C^5), 71.18 ($C^{4\,6}$), 79.62[2-CH(OCOCH_3)C_6H_5] 101.16(C^2), 127.12, 128.90, 129.40 (tertiary aromatic carbon atoms), 136.30, 136.46 (quaternary aromatic carbon atoms) and 168.39 ppm[2-CH(OCOCH_3)C_6H_5].

5,5-Bis(ethyloxycarbonyl)-2-phenyl-2-[phenyl-(oxycarbonylmethyl)methyl]-1,3-dioxane 8. Solid, m.p.128.129 °C. Yield 79 %. Anal. Calcd. for $C_{25}H_{28}O_8$ C, 65.78 H, 6.18. Found: C, 65.90, H, 6.27. ^{1}H NMR δ (C_6D_6) 0.63[3H, t, J=7.1 Hz, 5-COOCH_2CH_3 (eq)], 1.02[3H, t, J=7.1 Hz, 5-COOCH_2CH_3 (ax)], 1.71[3H, s, 2-CH(OCOCH_3)C_6H_5], 3.59[2H, q, J=7.1 Hz, 5-COOCH_2CH_3 (eq)], 4.009[1H, dq, J=7.1 Hz, 5-COOCH(H)CH_3 (ax)], 4.018[1H, dq, J=7.1 Hz, 5-COOCH(H)CH_3 (ax)], 4.11(1H, d, J=11.5 Hz, 4-H_{ax}), 4.17(1H, d, J=11.5 Hz, 6-H_{ax}), 4.85[1H, dd (overlapped), J=11.5, J'=2.4 Hz, 4-H_{eq}), 4.88[1H, dd (overlapped), J=11.5, J'=2.4 Hz, 6-H_{eq}], 6.30[1H, s,-CH(OCOCH_3)C_6H_5] and 7.00-7.20 ppm (10H, overlapped peaks, aromatic protons). ^{13}C NMR δ (C_6D_6) 13.24[5-COOCH_2CH_3(eq)], 13.71[5-COOCH_2CH_3(ax)], 20.15[2-CH(OCOCH_3)-C_6H_5] 53.41(C^5), 61.29[5-COO-CH_2CH_3(eq)], 61.50[5-COOCH_2CH_3 (ax)], 63.61(C^4), 63.71(C^6), 79.06[2-CH(OCOCH_3)-C_6H_5] 101.67(C^2), 127.16, 128.19, 128.62, 129.32(tertiary aromatic carbon atoms), 134.88, 135.90(quaternary aromatic carbon atoms), 166.38[5-COOCH_2CH_3(eq)], 167.13 [5-COOCH_2CH_3(ax)] and 168.33 ppm [2-CH(OCOCH_3)C_6H_5].

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