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Tin(II) chloride catalyzed reactions of diazodiphenylmethane with vicinal diols in an aprotic solvent. The reactions with *cis*- and *trans*-1,2-cyclohexanediols and 1,2-propanediol

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Abstract

The paper reports the tin(II) chloride catalyzed reactions of diazodiphenylmethane with the *cis*- and *trans*-1,2-cyclohexanediols and *R*,*S*-1,2-propanediol in 1,2-dimethoxyethane and the identification of the monodiphenylmethyl ethers formed. The catalyst is shown to work for both the *cis*- and *trans*-cyclohexanediols, but the catalyst is unstable at high reagent concentrations, especially in the case of the trans-isomer. Conditions where catalyst destruction is negligible show that the rate of the reaction with the trans-isomer is larger than with the cis-isomer. The reactions with 1,2-propanediol show small difference between the selectivity for the primary and secondary hydroxyl groups. This is in contrast with the tin(II) chloride catalyzed reactions of diazomethane and diazophenylmethane in methanol with carbohydrates, glycerol and ribonucleosides, where the primary hydroxyl group does not react. © 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Diazodiphenylmethane; Diols; Tin(II) chloride; 1,2-Cyclohexanediol; Monoetherification; 1,2-Propanediol

1. Introduction

During the earlier study of the tin(II) chloride catalyzed reactions of diazodiphenylmethane with carbohydrate vicinal diols, an attempt was made to react the diazo compound with methyl 4,6-*O*-benzylidene-α-D-glucopyranoside.[1] It was considered likely that the tin(II) chloride would also be a catalyst for the *gluco* system since both methyl 4,6-*O*-benzylidene-α-D-mannopyranoside and methyl 4,6-*O*-benzylidene-α-D-glucopyranoside have close to a perfect $^4C_1$ conformations in these relatively rigid bicyclic compounds, and the dihedral angles between the 2- and 3-hydroxyl groups in the *manno* and *gluco* configurations are of similar magnitude (see Fig. 1).

The result from the attempted reaction with the glucopyranoside was that no reaction seemed to take place. The likely explanation of this result was considered to be that any transitional conformational change is less likely for the *trans*-gluco than the *cis*-manno configuration. It was therefore of interest to try the same reaction with the model *cis*- and *trans*-1,2-cyclohexanediols that are not as rigid as the carbohydrate 4,6-acetals. The two cyclohexanediols are available commercially. The *cis*-diol is a *meso*-compound, but the *trans*-diol used was a racemic (*R*/*S*) mixture. On producing monoethers two enantiomers can theoretically be produced in each case, giving a racemic mixture as shown in Fig. 2.

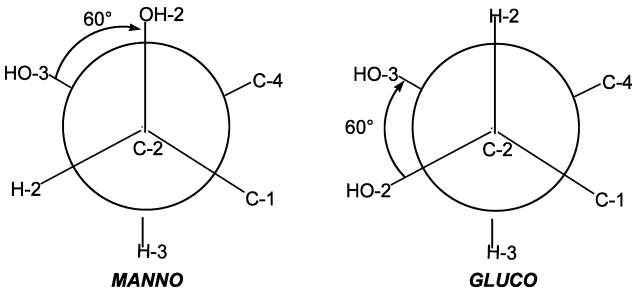

Fig. 1. Newman projections for the C-2–C-3 systems in manno- and glucopyranosides in the $^4C_1$ conformations.

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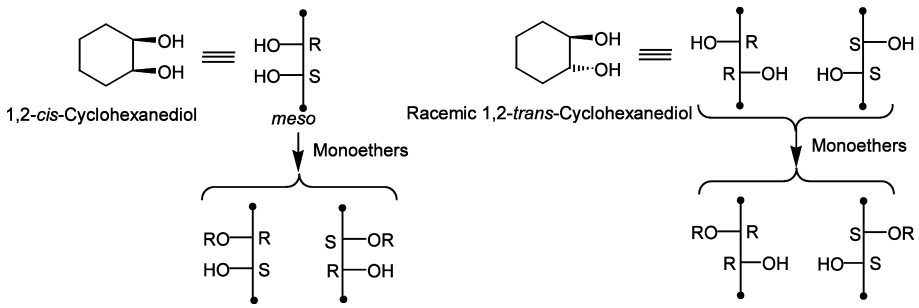


Fig. 2. Theoretical results from monoetherification of *meso*-1,2-cyclohexanediol and racemic (*R*/*S*)-1,2-cyclohexanediol.

There is interest in the optically active 1,2-cyclohexanediols as chiral auxiliaries and for crown ethers, and Sakai and co-workers have shown that esters of the racemates are efficiently resolved by *Pseudomonas fluorescencs* lipase.[2–6] Resolution has also been achieved on the diols themselves by enzymatic acyl transfer.[7] 1,2-Cyclohexanediol ethers are also of interest as herbicides.[8]

2. Results and discussion

2.1. Reactions with 1,2-cyclohexanediols

The initial reactions of diazodiphenylmethane–tin(II) chloride with the isomeric cyclohexanediols used about 0.2 M concentration of the diols. Identical reactions of the *cis*- and *trans*-cyclohexanediols were started with 1 mmol of each diol, 1 mmol of diazodiphenylmethane and 5.0 mg, (0.026 mmol), of tin(II) chloride in 5 mL of 1,2-dimethoxyethane. Since the catalyst was destroyed during the reaction, an additional 10 mg in the case of the cis-isomer and 20 mg in the case of the trans-isomer were needed to bring the reaction of the diazo compound to conclusion. When the reactions were repeated with 1.05 mmol of each diol, about 1.23 equiv of the diazo compound and 0.1 equiv of tin(II) chloride in 25 mL of DME (concentration of diol 0.042 M) the monoether products were isolated in 94 and 72% yields, respectively. Both these compounds are syrups, which were identified by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. The 3,5-dinitrobenzoyl derivatives of both compounds were also made, and the racemic (*R*,*S*/*S*,*R*)-1-(3,5-dinitrobenzoyloxy)-2-diphenylmethoxycyclohexane, which was a non-crystalline glassy compound, gave correct elemental analysis. Following these results the tin(II) chloride catalyzed reaction of diazodiphenylmethane with methyl 4,6-*O*-benzylidene-α-D-glucopyranoside was repeated using similar reaction condidtions. This time a mixture of the 2- and 3-monoethers was obtained in reasonable yield. These results have already been published.[9]

Since kinetic experiments with ethylene glycol had shown that the catalyst is unstable in the presence of high concentrations of either the diol or the diazodiphenylmethane reagent (see Ref. 9) and the above results indicate the same behaviour for the cyclohexanediols, it was decided to follow the reaction of the diazo compound with both diols, with, in the first place, high reagent concentration of Ph_2CN_2 approx 0.2 M, which is similar to the preparative conditions originally used, and secondly, at about quarter of that concentration. The results presented by $\ln[Ph_2CN_2]$ versus time plots in Fig. 3 show very clearly that the rate of the reaction dropped rapidly, from a value of the pseudo first-order rate constant, k', of about 0.02 min^{-1} in the early stage of the reaction (from 6 to 11 min) to 0.009 min^{-1} in the period 11–40 min for the cis-isomer. A similar experiment for the trans-isomer showed an even more dramatic drop in k', from about 0.01 min^{-1} in a period of 3–20 min to 0.0009 during 20–40 min. When the reactions were run with about a quarter of the preparative concentration of the diazo compound, there was a dramatic change in the behaviour of the system, especially in the case of the *trans*-diol. For the *cis*-diol the average value for k' in the first 15 min was about 0.098 min^{-1}, which dropped by about 40%, down to about 0.046 in the period of 15–87 min. More interestingly the rate for the trans-isomer was larger under these conditions with a value of k' of about 0.16 in the first 6 min, which had only dropped by about 12% in the period of 6–27 min. The average value of k' for the whole period was 0.146. Graphs A and B in Fig. 3 are for the cis-isomer and C and D for the trans-isomer. At this stage we can only draw qualitative conclusions from these results, but it is clear that stereochemical characteristics of the diol substrates have large effects on the rate of the reactions and that the higher rate for the trans-isomer is accompanied by a much reduced stability of the catalyst.

The results presented in Fig. 3 show very clearly the influence of the configurational characteristics of the diol system on the stability of the catalyst. Even if both hydroxyl groups are secondary in these compounds, the high diol concentrations used here may affect the cata-

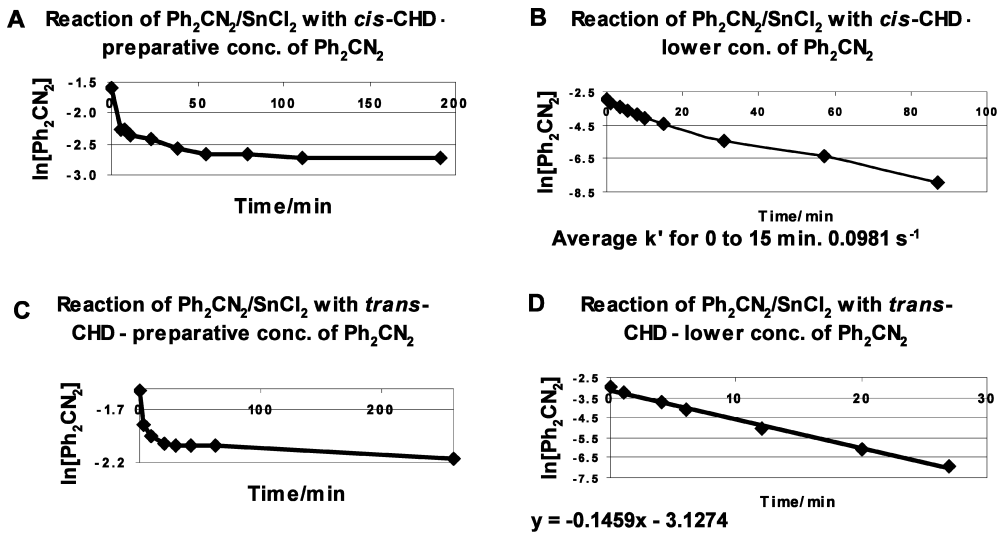


Fig. 3. Kinetic results from reactions of diazodiphenylmethane–tin(II) chloride with *cis*-1,2-cyclohexanediol (A and B) and *trans*-1,2-cyclohexanediol (C and D).

lyst stability as was observed in the case of ethylene glycol. To confirm the difference between the values of k' for the two diols, experiments were conducted for both diols using conditions of low concentrations for both reagents where the catalyst destruction can be assumed to be negligible. The results from these experiments are shown in Table 1. Both sets of experiments show the same trend as observed for ethylene glycol at concentrations below about 0.06 M (see Ref. 9), that is an increasing apparent k' with the diol concentration.

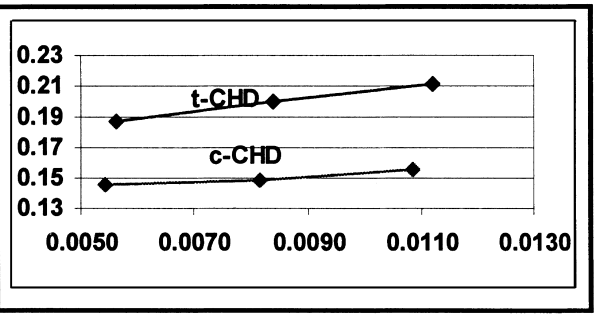
These results confirm that the rate for the tin(II) chloride catalyzed reactions is in fact larger for the *trans*-diol, of about 30% in this case.

2.2. Reactions with 1,2-propanediol

There is considerable interest in 1,2-propanediol as a chiral building block, for example, for optically active liquid crystals. Various protecting groups for the hydroxy functions have beeen used.[10–13] It was therefore decided to investigate the tin(II) chloride catalyzed reaction of diazodiphenylmethane with 1,2-propanediol, containing a primary and a secondary hyroxyl groups. From simple steric consideration one would predict a preferential reaction with the primary hydroxyl group. It must, however, be kept in mind that the tin(II) chloride catalyzed reactions of both diazomethane and diazo(phenyl)methane with vicinal primary/secondary diol systems in carbohydrate derivatives and in glycerol, using methanol as a solvent, gave a preferential reaction at the secondary group, and the primary ether was not detected.[14,15] Similar results had been reported earlier for nucleosides where the primary 5′-OH group was shown not to react at all, wheras the combined yield of the 2′- and 3′-monoethers was good to quantitative. These results are interesting, even if the primary hydroxyl group is not part of a vicinal diol system in these ribofuranosides.[16,17] The reaction of 1.25 molar equiv of diazodiphenylmethane with a 0.13 M solution of recemic propanediol in 1,2-dimethoxyethane in the presence of 0.05 equiv of tin(II) chloride went to completion at room tempera-

Table 1
Results from reactions of diazodiphenylmethane/tin(II) chloride with *cis*- and *trans*-1,2-cyclohexanediols with low reagents concentrations

			cis-CHD		*trans*-CHD	
	[TC]/M	[DA]/M	[DIOL]/M	k'/s^{-1}	[DIOL]/M	k'/s^{-1}
Expt. 1	0.00180	0.00240	0.0054	0.1413	0.0056	0.1822
Expt. 2	0.00180	0.00240	0.0082	0.1458	0.0084	0.1957
Expt. 3	0.00180	0.00240	0.0109	0.1505	0.0112	0.2058



ture in about 2 h. The main product, which appeared as one spot on TLC, turned out to be an inseparable non-crystalline mixture of the primary and secondary ethers (53:47), which was identified by ^{1}H and ^{13}C NMR spectroscopy. The 3,5-dinitrobenzoyl esters of the two isomers were prepared, which were also inseparable by the chromatography systems available. A crystalline product was obtained from ether (mp 94–95 °C) which was a 67:33 mixture of the racemic 1-ester-2-ether and the 2-ether-1-ester. Complete separation of the isomers has, however, not been achieved. The mother liquor yielded 61% of (*R*,*S*)-2-(3,5-dinitrobenzoyloxy)-1-diphenylmethoxypropane and 39% of (*R*,*S*)-1-(3,5-dinitrobenzoyloxy)-2-diphenylmethoxypropane (by NMR). These results for tin(II) chloride catalyzed reactions in the aprotic 1,2-dimethoxyethane, together with the earlier results for similar reactions with ethylene glycol (see Ref. 9), show that the lack of reactions with primary hydroxyl groups, as discussed above for reactions of diazomethane and diazo(phenyl)methane in methanol, does not apply here. The results support therefore a mechanism for these reactions that is different from the cyclic 1,3,2-dioxastannolane mechanism suggested by Shugar and co-workers.[18] The results reported here do not allow the proposal of a complete mecahnism for the reactions, but they support a mechanism involving a catalytically active tin(II) chloride-diol intermediate complex in equilibrium with the tin(II) chloride and the diol as discussed in Ref. 9.

3. Experimental

3.1. General methods

The absorption spectrometers used were an LKB-Ultraspec II and a Varian Carey 100BIO UV–Vis spectrometers. ^{1}H and ^{13}C NMR spectra were run on a Bruker AC 250 or a Bruker AV400 instrument with Me_4Si as the external standard. Diazodiphenylmethane was prepared using a published method.[19] *meso*-1,2-*cis*-Cyclohexanediol and racemic (*R*,*R*/*S*,*S*)-1,2-*trans*-cyclohexanediol, 99 and 98% pure, respectively, were from Aldrich Chemical Co. and used without further purification. The solvent used for the reactions was E. Merck 1,2-dimethoxyethane (DME) distilled from and stored over sodium. Anhydrous tin(II) chloride was prepared from the dihydrate by treatment with Ac_2O according to *Vogel's Textbook of Practical Organic Chemistry*.[20]

3.2. Spectroscopic experiments

The reactions for the kinetic studies were carried out in 3-mL quartz spectrometric cells in a total volume of 3.0 mL. The temperature in the cell compartment was 30 °C, which is the temperature used. The reactions under preparative conditions were run at room temperature in a separate reaction vessel. At different intervals 0.250 mL samples were withdrawn, quenched in 2.750 mL of EtOAc, and the absorbance at 523 nm was measured. The pseudo first-order rate constant was determined by plotting $\ln(A_{523})$ against time using the Microsoft Excel® software.

3.3. Racemic (*R*,*S*/*S*,*R*)-2-diphenylmethoxycyclohexanol

meso-1,2-*cis*-Cyclohexanediol (122 mg, 1.05 mmol) and tin(II) chloride (20 mg, 0.10 mmol) were dissolved in 1,2-dimethoxyethane (25 mL). Diazodiphenylmethane (250 mg, 1.29 mmol) was added, and a drying tube was fitted to the reaction flask. At the end of the reaction the product was purified on a column of silica gel, using a gradient of 4:1 → 7:3 hexane–EtOAc to give a syrup (280 mg, 94.4%). ^{1}H NMR ($CDCl_3$): δ 1.22–1.88 (8 H, m, H-3 to H-6), 2.1 (1 H, broad, OH), 3.51–3.56 (1 H, m, H-1), 3.86–3.89 (1 H, m, H-2), 5.57 (1 H, s, Ph_2CH), 7.2–7.4 (10 H, m, aromatic H). ^{13}C NMR ($CDCl_3$): δ 20.99 and 20.42 (C-4 and C-5), 26.72 and 30.44 (C-3 and C-6), 68.79 (C-1), 76.56 (C-2), 80.49 (Ph_2CH), 126.51–128.55 (nine peaks, aromatic C-2 to C-6, conformers), 142.25 and 142.65 (aromatic C-1, conformers). Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.7; H, 7.7.

3.4. Racemic (*R*,*S*/*S*,*R*-1-(3,5-dinitrobenzoyloxy)-2-diphenylmethoxycyclohexane

Racemic (*R*,*S*/*S*,*R*)-2-diphenylmethoxycyclohexanol (224 mg, 0.793 mmol) was treated with Et_3N (0.13 mL, 0.95 mmol) and 3,5-dinitrobenzoyl chloride (201 mg, 0.87 mmol) in CH_2Cl_2 (4 mL). The excess acid chloride was quenched on about 1 g of silica gel, and the product was purified on a silica gel column using hexane–EtOAc as eluent to give a non-crystalline glassy product (190 mg, 50.5% yield). ^{1}H NMR ($CDCl_3$): δ 1.26–2.00 (8 H, m, H-3 to H-6), 3.77–3.83 (1 H, dt, $J_{2,1}$ 2.8, $J_{2,3}$ 5.8 Hz, H-2), 5.3–5.4 (1 H, m, H-1), 5.52 (1 H, s, Ph_2CH), 7.1–7.4, 9.05 and 9.21 (13 H, m, aromatic H). ^{13}C NMR ($CDCl_3$): δ 21.59 and 22.07 (C-4 and C-5), 27.65 and 27.98 (C-3 and C-6), 73.81 (C-1), 75.11 (C-2), 81.05 (Ph_2CH), 122.08, 126.67–129.32 (10 peaks), 142.23, 142.50 and 148.47 (aromatic C-2 to C-6, conformers), 161.96 (carbonyl C). Anal. Calcd for $C_{26}H_{24}N_2O_7$: C, 65.5; H, 5.1; N, 5.9. Found: C, 65.46; H, 5.04; N, 5.74.

3.5. Racemic (*R*,*R*/*S*,*S*)-2-diphenylmethoxycyclohexanol

Racemic (*R*,*R*/*S*,*S*)-1,2-*trans*-cyclohexanediol (122 mg, 1.05 mmol) and tin(II) chloride (20 mg, 0.10 mmol) were dissolved in 1,2-dimethoxyethane (25 mL). Diazodiphenylmethane (250 mg, 1.29 mmol) was added,

and a drying tube was fitted to the reaction flask. At the end of the reaction the product was purified on a column of silica gel using a gradient of 4:1 → 7:3 hexane–EtOAc to give a syrup (214 mg, 72.2%). ^{1}H NMR ($CDCl_3$): δ 1.15–1.35 (4 H, m, H-4 and H-5), 1.66–1.72 (2 H, m, H-3), 1.96–2.08 (2 H, m, H-6), 2.46 (1 H, br s, OH), 3.21–3.31 (1 H, m, H-1), 3.54–3.64 (1 H, m, H-2), 5.60 (1 H, s, Ph_2CH), 7.3–7.4 (10 H, m, aromatic H). ^{13}C NMR ($CDCl_3$): δ 23.82 and 24.17 (C-4 and C-5), 29.66 and 31.98 (C-3 and C-6), 73.97 (C-1), 81.23 (C-2), 81.90 (Ph_2CH), 126.51–128.64 (seven peaks, aromatic C-2 to C-6, conformers), 142.19 and 143.06 (aromatic C-1, conformers). Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.9; H, 7.3.

3.6. Racemic (*R*,*R*/*S*,*S*)-1-(3,5-dinitrobenzoyloxy)-2-diphenylmethoxycyclohexane

Racemic (*R*,*R*/*S*,*S*)-2-diphenylmethoxycyclohexanol (180 mg, 0.637 mmol) was treated with Et_3N (0.14 mL, 1.0 mmol) and 3,5-dinitrobenzoyl chloride (220 mg, 0.96 mmol) in CH_2Cl_2 (2 mL). The excess acid chloride was quenched by pouring it onto ~1 g of silica gel, and the product was purified on a silica gel column using hexane–EtOAc as eluent to give a non-crystalline glassy product (190 mg, 62.3% yield). ^{1}H NMR ($CDCl_3$): δ 1.25–158 (4 H, m, H-4 and H-5), 1.75–1.80 (2 H, m, H-3), 2.11–2.17 (2 H, m, H-6), 3.59–3.68 (1 H, dt, $J_{2,1}$ 4,6, $J_{2,3}$ 8.6 Hz, H-2), 5.21–5.29 (1 H, m, H-1), 5.51 (1 H, s, Ph_2CH), 7.0–7.4, 8.95–8.96 and 9.17–9.22 (13 H, m, aromatic H). ^{13}C NMR ($CDCl_3$): δ 23.41 and 23.57 (C-4 and C-5), 30.12 and 30.39 (C-3 and C-6), 78.08 (C-1), 78.27 (C-2), 82.06 (Ph_2CH), 121.99, 126.50–129.28 (eight peaks), 142.25, 142.50 and 148.38 (aromatic C-2 to C-6, conformers), 162 (carbonyl C).

3.7. Reaction of diazodiphenylmethane–tin(II) chloride with (*R*,*S*)-1,2-propanediol

(*R*,*S*)-1,2-Propanediol (152 mg, 2.00 mmol), and tin(II) chloride (19 mg, 0.10 mmol), were dissolved in 1,2-dimethoxyethane (15 mL). Diazodiphenylmethane (485 mg, 2.50 mmol), was added, and the flask was fitted with a drying tube. The red colour of the diazo compound had disappeared after about 2 h, and a TLC examination showed one major spot. The product was purified on a column of silica gel giving a syrup (326 mg, 67.3%). NMR spectroscopy showed this to be a 47:53 mixture of (*R*,*S*)-2-diphenylmethoxypropanol (**1**) and (*R*,*S*)-1-diphenylmethoxy-2-propanol (**2**). The isomers had identical mobility on TLC, and further attempts at chromatographic separation of these non-crystalline compounds were unsuccessful. ^{1}H NMR ($CDCl_3$): The Ph_2CH-proton integral for **1** is 6.35 and for **2**, 7.27. δ 1.17 (integral 41.23, apparent triplet, $J_{3,2}$ 6.3 Hz, **1**/**2** H-3), 2.2 (integral 15.26, br s, **1**/**2** OH), 3.27–3.50 (2 H, ABX (**1**), $J_{1(A),1(B)}$ 9.4, $J_{1(A),2}$ 8.0, $J_{1(B),2}$ 3.2 Hz, H-2(A/B) (**1**)), 3.51–3.65 (2 H, ABM (**2**), $J_{1(A),1(B)}$ 11.4, $J_{1(A),H2}$ 6.4, $J_{1(B),2}$ 3.5 Hz, H-2(A/B) (**2**)), 3.67–3.74 (1 H, m (**2**), H-2 (**2**)), 4.02–4.09 (1 H, m (**1**), H-2 (**1**)), 5.41 (1 H, s (**1**), Ph_2CH (**1**)), 5.56 (1 H, s (**2**), Ph_2CH (**2**)), 7.3–7.4 (10 H, m (**1**/**2**), aromatic H (**1**/**2**)).

3.8. (*R*,*S*)-1-(3,5-dinitrobenzoyloxy)-2-diphenylmethoxypropane (3) and (*R*,*S*)-2-(3,5-dinitrobenzoyloxy)-1-diphenylmethoxypropane (4)

The 47:53 mixture of (*R*,*S*)-2-diphenylmethoxypropanol (**1**) and (*R*,*S*)-1-diphenylmethoxy-2-propanol (**2**) (445 mg, 1.84 mmol), was treated with Et_3N (0.380 mL, 2.71 mmol) and 3,5-dinitrobenzoyl chloride (598 mg, 2.59 mmol) in CH_2Cl_2 (10 mL). The excess acid chloride was quenched on about 1.5 g of silica gel, and the product was purified on a silica gel column using hexane–EtOAc as eluent to give an inseparable mixture (760 mg, 94.6% yield). The earlier fractions containing about 57% of the total amount were used for NMR spectroscopy. These contained 39% of 1-(3,5-dinitrobenzoyloxy)-2-diphenylmethoxypropane (**3**) and 61% of 1-diphenylmethoxy-2-(3,5-dinitrobenzoyloxy)-propane (**4**) based on the H-3 integrals. The mixture was dissolved in hot ether, and a crystalline product was obtained on cooling (mp 94–95 °C), which was a 67:33 mixture of the racemic 1-ester-2-ether and the 2-ether-1-ester. The mother liquor yielded 61% (*R*,*S*)-2-(3,5-dinitrobenzoyloxy)-1-diphenylmethoxypropane and 39% (*R*,*S*)-1-(3,5-dinitrobenzoyloxy)-2-diphenylmethoxypropane (by NMR). ^{1}H NMR ($CDCl_3$) (mixture of **3** and **4**): (*R*,*S*)-1-(3,5-Dinitrobenzoyloxy)-2-diphenylmethoxypropane (**3**): δ 1.34 (2 H, d, $J_{3,2}$ 6.2 Hz, H-3); 3.99–4.06 (1 H doublet of quintets (due to the three H-3 protons and one H-1), $J_{2,3/1A}$ 6.2, $J_{2,1B}$ 3.6 Hz, H-2), 4.43–4.56 (2 H, ABM, $J_{1(A),1(B)}$ 11.6, $J_{1(A),2}$ 4,0, $J_{1(B),2}$ 6.8 Hz, H-1(A/B); 5.58 (1 H, s, Ph_2CH). (*R*,*S*)-2-(3,5-dinitrobenzoyloxy)-1-diphenylmethoxypropane (**4**): δ 1.465 (2 H, d, $J_{3,2}$ 6.4 Hz, H-3); 3.67–3.74 (2 H, ABX, $J_{1(A),1(B)}$ 10.4, $J_{1(A),2}$ 4.0, $J_{1(B),2}$ 2.0 Hz, H-1); 5.42 (1 H, s, Ph_2CH); 5.50–5.57 (1 H doublet of quintets (due to the three H-3 protons and one H-1), $J_{2,3/1A}$ 6.4, $J_{2,1B}$ 4.4 Hz, H-2). Aromatic protons of **3** and **4**, 7.2–7.4 (10 H) and 9.08–9.23 (3 H). Anal. Calcd for $C_{23}H_{20}N_2O_7$: C, 63.30; H, 4.62; N, 6.42. Found: C, 63.19; H, 4.59; N, 6.64.

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