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Theoretical and experimental study on the reactions between 3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl chloride and alcohols

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ABSTRACT

The solvent effect on the reactions of 3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl chloride with alcohols has been studied with the help of density functional theory (DFT) method using the polarized continuum model (PCM). Moreover, the calculation allows a discussion of the solvent effect on the ratio of α- to β-anomer to compare with the experimental result. The results obtained by the present calculations are in excellent agreement with the experimental findings.

1. Introduction

3,5-Di-*O*-*p*-toluoyl-D-2-deoxyribosyl chloride (Scheme 1) is a common and important starting material for most syntheses of the nucleoside analogues [1,2]. Nucleoside analogues are of wide biological interest. For example, they can be used for site-directed modification of DNA/RNA fragments with respect to the studies of structures and functions of nucleic acids [3–5]. Additionally, many nucleoside analogs exhibit antiviral, antibiotic and anticancer activity [6]. Therefore, it should be of significance to study the nucleoside analogues.

From Scheme 1 we can see: 3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl chloride is a chiral compound and it has a stereogenic center on the position of C_1, hence when it reacts with the alcohol, the product afforded is commonly constituted by two diastereomers (α- and β-anomers), and the ratio of α- to β-anomer is related to the reaction conditions. However, only the β-anomer shows physiological activity [7,8]. Thus, in order to get more of the desired anomer, exploring the effect of the reaction conditions on the ratio of α- to β-anomer should be essential.

In our previous work, we explored the selectivity of the anomers in the reaction between 3,5-di-*O*-*p*-toluoyl-D-2-deoxyribofuranosyl chloride and bis-*O*-(trimethylsilyl)-5-S-benzyl-mercaptouracil [9]. Meanwhile, the nucleoside analogues can also be synthesized by the formation of O-nucleoside besides N-nucleoside [10–17] and C-nucleoside [18], to the best of our knowledge, few has synthesized the O-nucleoside by the reaction between 3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl chloride and alcohols neither to say under our optimized conditions. As a consequence, in this work, we synthesized a series of new O-nucleoside through the reaction of 3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl chloride with alcohols, meanwhile, the ratio of β- to α-anomer in different solvents were analyzed using High Performance Liquid Chromatography (HPLC). On the other hand, theoretical study of the solvent effect on the selectivity of this reaction and the reaction mechanism were also carried out.

2. Experiment

Methanol (0.0960 g, 3.0 mmol) was added to a solution of 3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl chloride (1.0734 g, 2.5 mmol) in tetrahydrofuran (20 ml), and the mixture was stirred at room temperature for several hours (Scheme 2). The reaction was monitored by thin layer chromatography (TLC). After the reaction, the mixture was evaporated in *vacuo*, the residue was then diluted with petroleum ether (20 ml) and the precipitation was filtrated. The filtrate was concentrated again in *vacuo* to give the product in 94.5% yield. The isomers were separated by silica gel column chromatography and a series of diastereomers as new compounds were obtained and identified by ^{1}H NMR and GC–MS. The ratio of β- to α-anomer in different solvents were analyzed using HPLC (Tables 1–7).

2.1. General

The ^{1}H NMR spectra was measured on a Bruker Avance-500 spectrometer operating at 500 MHz, and the chemical shifts are

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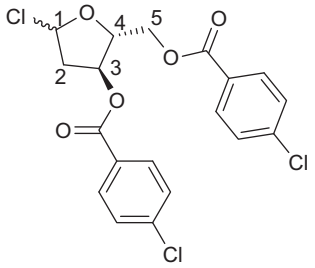


Scheme 1. 3,5-Di-*O*-*p*-toluoyl-D-2-deoxyribosyl chloride.

reported in parts per million on δ scale downfield from tetramethysilane (TMS) used as an internal standard and signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. All the solvents are analytical reagent.

2.2. Representative data

1-O-ethyl-3,5-di-O-p-toluoyl-α-D-2-deoxyribosyl: ^{1}H-NMR($CDCl_3$, 500 MHz): 7.94–7.99 (m, 4H, Ar–H); 7.39–7.42 (m, 4H, Ar–H); 5.39–5.42 (m, 1H, H-3); 5.30–5.31 (d, 1H, $^3J_{1,2}$ = 4.8, H-1); 4.59–4.61 (m, 1H, H-4); 4.52–4.54 (m, 2H, H-5); 3.80–3.83 (m, 1H, OCH_2CH_3); 3.43–3.53 (m, 1H, OCH_2CH_3); 2.48–2.54 (m, 1H, H-2); 2.18–2.21 (m, 1H, H-2); 1.22–1.25 (t, 3H, CH_2CH_3). Mp: 66–68 °C.

1-O-ethyl-3,5-di-O-p-toluoyl-β-D-2-deoxyribosyl: ^{1}H-NMR($CDCl_3$, 500 MHz): 7.94–8.03 (m, 4H, Ar–H); 7.39–7.42 (m, 4H, Ar–H); 5.59–5.62 (m, 1H, H-3); 5.35,5.36 (dd, 1H, $^3J_{1,2}$ = 2.0, $3J_{1,2'}$ = 5.6, H-1); 4.54–4.59 (m, 1H, H-4); 4.47–4.52 (m, 2H, H-5); 3.74–3.81 (m, 1H, OCH_2CH_3); 3.43–3.51 (m, 1H, OCH_2CH_3); 2.52–2.58 (m, 1H, H-2); 2.33–2.39 (m, 1H, H-2′); 1.15–1.18 (t, 3H, CH_2CH_3). Mp: 70–71 °C.

1-O-isopropyl-3,5-di-O-p-toluoyl-α-D-2-deoxyribosyl: ^{1}H-NMR-($CDCl_3$, 500 MHz): 7.95–8.03 (m, 4H, Ar–H); 7.39–7.42 (m, 4H, Ar–H); 5.42–5.43 (m, 1H, H-3); 5.40 (d, 1H, $^3J_{1,2}$ = 5.4, H-1); 4.58–4.60 (m, 1H, H-4); 4.51–4.54 (m, 2H, H-5); 3.96–3.98 (m, 1H, $OCH(Me)_2$); 2.46–2.51 (m, 1H, H-2); 2.15–2.31 (m, 1H, H-2′); 1.14–1.26 (m, 6H, $2CH_3$). Mp: 89–90 °C.

1-O-isopropyl-3,5-di-O-p-toluoyl-β-D-2-deoxyribosyl: ^{1}H-NMR-($CDCl_3$, 500 MHz): 7.94–8.03 (m, 4H, Ar–H); 7.38–7.42 (m, 4H, Ar–H); 5.57–5.61 (m, 1H, H-3); 5.48, 5.50 (dd, 1H, $^3J_{1,2}$ = 2.6, $3J_{1,2'}$ = 5.4, H-1); 4.54–4.55 (m, 1H, H-4); 4.49–4.52 (m, 2H, H-5); 3.91–3.97 (m, 1H, $OCH(Me)_2$); 2.47–2.53 (m, 1H, H-2); 2.34–2.40 (m, 1H, H-2′); 1.14–1.19 (m, 6H, $2CH_3$). Mp: 82–83 °C.

3. Calculation

The calculations were performed with the GAUSSIAN 98 program package [19], using DFT method. The geometries of all the stationary points were fully optimized at the B3LYP/6-31G* [20] level of theory. Before optimization, the BioMedCAche 5.02 program package [21] was used by means of CONFLEX [22] conformational search procedure to locate low-energy conformations of all the products. The B3LYP functional is composed of Becke's three-parameter hybrid exchange functional (B3) [23,24], as implemented in GAUSSIAN 98 [25], and the correlation functional of Lee, Yang, and Parr (LYP) [26]. The energy differences between products and solvation energies for products were computed using solvation model PCM with the permittivities of 36.64, 8.93, 7.58 and 4.9 for CH_3CN, CH_2Cl_2, THF and $CHCl_3$, respectively.

Table 1
1-*O*-methyl-3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl.[a]

Solvent[b]	Productivity (%)	β-anomer (%)	α-anomer (%)	β/α
CH_3CN	96.4	53.1	43.3	1.23
CH_2Cl_2	95.2	49.8	45.4	1.10
THF	94.5	48.4	46.1	1.05
$CHCl_3$	92.0	48.3	43.7	1.11

[a] The ratio of 3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl chloride to methanol was 1:1.2.
[b] For different solvents, the reaction was reacted for the same period of time.

Table 2
1-*O*-ethyl-3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl.[a]

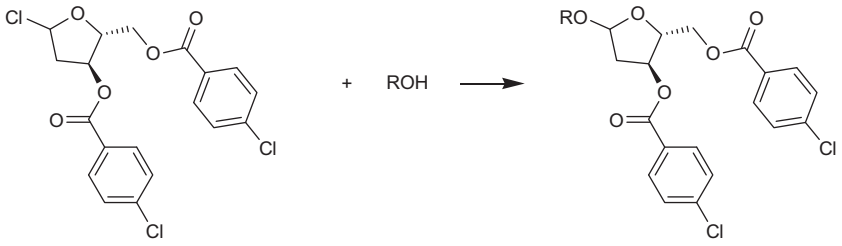
Solvent[b]	Productivity (%)	β-anomer (%)	α-anomer (%)	β/α
CH_3CN	96.5	57.5	39.0	1.47
CH_2Cl_2	90.9	50.6	40.3	1.25
THF	88.4	47.6	40.8	1.17
$CHCl_3$	86.3	45.4	40.9	1.11

[a] The ratio of 3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl chloride to ethanol was 1:1.2.
[b] For different solvents, the reaction was reacted for the same period of time.

Table 3
1-*O*-isopropyl-3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl.[a]

Solvent[b]	Productivity (%)	β-anomer (%)	α-anomer (%)	β/α
CH_3CN	92.4	86.4	6.0	14.4
CH_2Cl_2	91.4	48.6	42.8	1.13
THF	89.5	49.3	40.2	1.23
$CHCl_3$	89.1	52.0	39.1	1.33

[a] The ratio of 3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl chloride to isopropanol was 1:1.2.
[b] For different solvents, the reaction was reacted for the same period of time.



R=CH_3, CH_3CH_2, *i*-C_3H_7, C_3H_7, C_4H_9, C_6H_{11}, $C_{10}H_{19}$

1: R=CH_3; 2: R=CH_3CH_2; 3: R=*i*-C_3H_7; 4: R=C_3H_7

5: R=C_4H_9; 6:R=C_6H_{11}; 7:R=$C_{10}H_{19}$

Scheme 2. The reaction route.

4. Results and discussion

3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl chloride reacted with alcohols in acetonitrile, dichloromethane, tetrahydrofuran and chloroform, respectively, at room temperature for several hours, the products were analyzed by HPLC and the results were collected in Tables 1–7. The experimental outcomes show on one hand, of all the products studied, the ratio of β- to α-anomer is greater than one, that is to say, β-anomer could be more easily obtained than α-anomer and is the predominant product in the reaction, which is in accordance with what we concluded when exploring the selectivity of the anomers in the Hilbert–Johnson reaction [9]. In addition, the conformations of all the products were optimized and the energy differences between the two isomers are collected in Table 8. It was found that the energies of β-anomers are lower than that of α-anomers, so the β-anomer is more stable than the α-anomer and is the major product of the reaction, which conforms to the experimental results (Tables 1–7) very well.

Table 4
1-*O*-*n*-propyl-3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl.[a]

Solvent[b]	Productivity (%)	β-anomer (%)	α-anomer(%)	β/α
CH_3CN	88.8	58.6	30.2	1.94
CH_2Cl_2	85.3	46.1	39.2	1.18
THF	84.6	43.4	41.2	1.05
$CHCl_3$	83.3	43.3	40.0	1.08

[a] The ratio of 3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl chloride to *n*-propanol was 1.2:1.
[b] For different solvents, the reaction was reacted for the same period of time.

Table 5
1-*O*-*n*-butyl-3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl.[a]

Solvent[b]	Productivity (%)	β-anomer (%)	α-anomer (%)	β/α
CH_3CN	93.6	50.9	42.7	1.19
CH_2Cl_2	87.2	45.5	41.7	1.09
THF	84.7	45.0	39.7	1.13
$CHCl_3$	81.8	42.5	39.2	1.08

[a] The ratio of 3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl chloride to *n*-butanol was 1.2:1.
[b] For different solvents, the reaction was reacted for the same period of time.

Table 6
1-*O*-cyclohexyl-3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl.[a]

Solvent[b]	Productivity (%)	β-anomer (%)	α-anomer (%)	β/α
CH_3CN	95.0	52.3	42.7	1.22
CH_2Cl_2	92.9	52.8	40.1	1.32
THF	91.8	49.3	42.5	1.16
$CHCl_3$	91.5	64.2	27.3	2.35

[a] The ratio of 3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl chloride to cyclohexanol was 1.2:1.
[b] For different solvents, the reaction was reacted for the same period of time.

Table 7
1-*O*-menthyl-3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl.[a]

Solvent[b]	Productivity (%)	β-anomer (%)	α-anomer (%)	β/α
CH_3CN	90.8	61.4	29.4	2.09
CH_2Cl_2	87.5	47.8	39.7	1.21
THF	80.7	45.6	35.1	1.30
$CHCl_3$	69.4	41.0	28.4	1.44

[a] The ratio of 3,5-di-*O*-*p*-toluoyl-D-2-deoxyribosyl chloride to menthol was 1.2:1.
[b] For different solvents, the reaction was reacted for the same period of time.

On the other hand, when the reaction was carried out for the same period of time in the four different solvents we selected, with the increasing of the solvent polarity, the yields of the products increase, which means that the products can more easily be obtained in polar solvent than in apolar one. On the whole, the ratio of β-anomer to α-anomer increases with the increasing of solvent polarity except for a few one, this maybe for the reason that in the selected reaction time, this few reactions have not reached their equilibrium. Why polar solvent is preferred in the reaction? We suppose, this maybe related to the mechanism of the reaction.

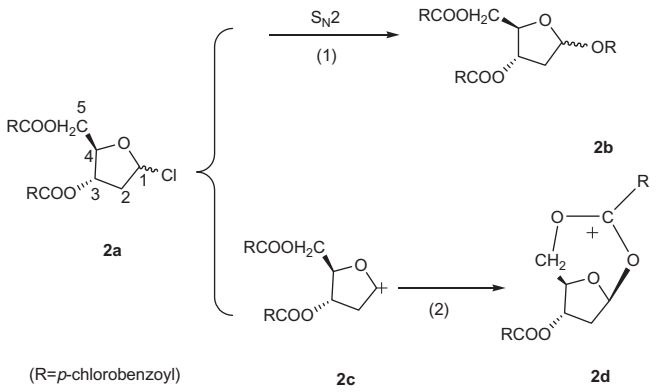
Concerning the mechanism of the Hilbert–Johnson reaction, two possible pathways were proposed in the literature works so far (Scheme 3). Path (1) is S_N2 mechanism [12], Path (2) is carbonium ion mechanism with a neighboring-group participation effect (the group of C(2) links to the carbonium ion, and the group of C(5) links to the carbonium ion if there are no groups on the C(2)) [12,27,28], which determines that the α-anomer is the predominant product in the reaction. However, in our previous study we proposed a different mechanism (Scheme 4) [9], in which a carbonium ion **3b** with a neighboring-group participation effect (the group of C(3) links to the carbonium ion instead of the group of C(5)) is formed.

The optimized conformation of the carbonium ion **3b** with minimal energy was obtained (Fig. 1). In this conformation, the distance between oxygen atom in carbonyl group of 5-(*p*-chlorobenzoyl) on C(3) and C(1) is 1.513 Å (within the range of a normal bond distance), but the distance between oxygen atom in carbonyl group of 5-(*p*-chlorobenzoyl) which links C(5) and C(1) is 5.215 Å, somewhat out of the normal bond distance. Meanwhile, we also calculated the minimal energy of **3b** and **2d**, the result shows that the energy of **3b** is about 5.02 kcal/mol lower than that of **2d**, it indicates that the conformation of **3b** is priority to **2d**, and the neighboring-group participation effect determines that the β-anomer is the predominant product in the reaction, which is in

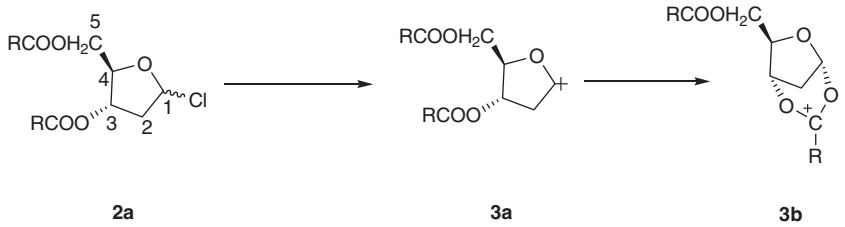
Table 8
Energy differences between α- and β-anomer (β-anomer – α-anomer) (kcal/mol).

Entry	CH_3CN	CH_2Cl_2	THF	$CHCl_3$
1[a]	−0.76	−0.65	−0.64	−0.69
2	−0.77	−0.75	−0.72	−0.70
3	−0.65	−0.58	−0.61	−0.63
4	−0.15	−0.13	−0.18	−0.17
5	−0.37	−0.38	−0.31	−0.44
6	−0.26	−0.31	−0.20	−0.27
7	−0.080	−0.089	−0.18	−0.26

[a] See Scheme 2 for the definition of 1–4.



Scheme 3. Two typical mechanism of the Hilbert–Johnson reaction.



Scheme 4. The proposed mechanism of the reaction.

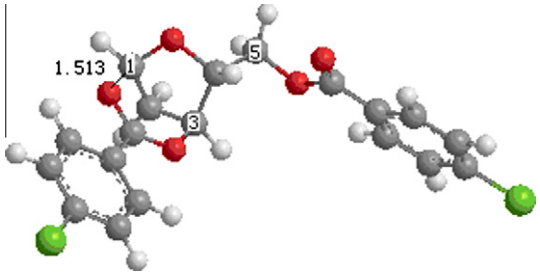


Fig. 1. Carbonium ion.

Table 9
Solvation energies of products (kcal/mol).

Products	CH_3CN	CH_2Cl_2	THF	$CHCl_3$
1 β-anomer[a]	−13.56	−11.32	−10.70	−9.32
1 α-anomer	−13.26	−11.11	−10.50	−9.04
2 β-anomer	−13.48	−11.32	−10.67	−9.28
2 α-anomer	−13.23	−11.07	−10.44	−9.06
3 β-anomer	−13.33	−11.17	−10.56	−9.21
3 α-anomer	−13.08	−10.96	−10.32	−8.93
4 β-anomer	−13.18	−10.99	−10.33	−8.94
4 α-anomer	−13.53	−11.32	−10.60	−9.20
5 β-anomer	−13.39	−11.15	−10.39	−9.05
5 α-anomer	−13.63	−11.34	−10.66	−9.15
6 β-anomer	−13.38	−11.16	−10.55	−9.11
6 α-anomer	−13.57	−11.36	−10.63	−9.25
7 β-anomer	−13.50	−11.23	−10.50	−9.07
7 α-anomer	−12.81	−10.69	−10.04	−8.67

[a] See Scheme 2 for the definition of 1–4.

good accordance with the experimental results (Tables 1–7) and our calculated outcomes (Table 8). Solvent with strong polarity can distribute the charges on the carbonium ion and will be favorable for the production of β-anomer.

The interaction between all the nucleosides and solvents were calculated and the results were collected in Table 9. As can be seen from the results: the interaction energies (absolute value) of solvents and products increase with the increasing of solvent polarity, that is to say, increasing polarity of the solvent could facilitate the formation of the products, which is in accordance with the experimental results in Tables 1–7.

5. Conclusion

The effect of solvent on the ratio of α-anomer to β-anomer was studied by both experimental and theoretical methods. The calculation was carried out with the GAUSSIAN 98 program package at the B3LYP/6-31G* level, and the solvent effect was investigated using PCM model. The experiment and calculation results both show that the β-anomer is the predominant product of the reaction, meanwhile, the increase of the solvent polarity facilitates the formation of the products.

A new possible reaction pathway is proposed by theoretical calculation, which is a carbonium ion mechanism with a neighboring-group participation effect. The mechanism determines that the β-anomer is the predominant product in the reaction. All the experimental results are in accord with the calculation outcomes very well.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2010.03.064.

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