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New evidence for the mechanism of the tin(II) chloride catalyzed reactions of vicinal diols with diazodiphenylmethane in 1,2-dimethoxyethane

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Abstract

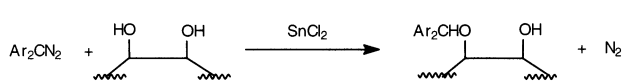
A kinetic study of the tin(II) chloride catalyzed reaction of diazodiphenylmethane with ethylene glycol in dimethoxyethane is reported. The preparation and characterization of ethylene glycol monodiphenylmethyl ether, the main product from this reaction, is also reported as well as the preparation of the two diphenylmethyl monoethers of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside. An unexpected relationship between the concentration of ethylene glycol and the pseudo first-order rate constant, k', was observed in these reactions. For low concentrations of ethylene glycol (below 0.06 M), k' increases with increasing concentration of the diol. This trend is reversed for high concentrations of ethylene glycol (from about 0.06 to about 0.2 M). The apparent rate constant was also inversely related to the initial concentration of diazodiphenylmethane for the concentrations investigated. These results make the previously proposed involvement of a 1,3,2-dioxastannolane intermediate very unlikely [Petursson, S.; Webber, J.M. *Carbohydr. Res.* **1982**, *103*, 41–52]. The results suggest that more likely intermediates for these reactions involve tin(II) chloride complexes in a dynamic equilibrium with the diol.

Keywords: Diazodiphenylmethane; Diols; Tin(II) chloride; Ethylene glycol; 1,2-Ethylene glycol monodiphenylmethyl ether; Monoetherification; Methyl 4,6-*O*-benzylidene-2-*O*-diphenylmethyl-α-D-glucopyranoside; Methyl 4,6-*O*-benzylidene-3-*O*-diphenylmethyl-α-D-glucopyranoside

1. Introduction

Protecting groups for carbohydrate hydroxyl groups have a long history, and their uses have played a vital role in the study of biologically important compounds and in syntheses.[1] Diazo compounds of the type R_2CN_2, where R can be hydrogen, alkyl, or more commonly, an aryl group have attracted considerable attention as mild hydroxyl protecting reagents in carbohydrate and nucleoside chemistry.[2–10] The reactions of diazomethane with hydroxyl groups are catalyzed by Lewis acids, notably by boron trifluoride and tin(II) chloride. Both these catalysts can result in interesting, albeit poorly explained, selectivities.[11–22]

The tin(II) chloride catalysis of reactions of diaryldiazomethanes has been found to depend on the presence of a diol, especially a cis-vicinal diol in a furanose ring, but both cis- and trans-vicinal diols in a pyranose ring have been shown to react and to result in the formation of a monoether as shown in Scheme 1.



Scheme 1. Monoetherification of a vicinal diol with a diaryldiazomethane in the presence of tin(II) chloride.

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Reactions of a series of diaryldiazomethanes with methyl 4,6-*O*-isopropylidene-α-D-mannopyranoside and methyl 4,6-*O*-benzylidene-α-D-mannopyranoside, in the presence of tin(II) chloride showed unexpected and varied selectivities.[23] Shugar and co-workers studied the tin(II) chloride catalyzed reaction of diazomethane with nucleosides in methanol. They found that diazomethane reacts with tin(II) chloride in methanol to form chloromethane and dimethoxystannane, $Sn(OMe)_2$. They further proposed that dimethoxystannane would react with 1,2- or 1,3-diols to give 5- or 6-membered cyclic tin 1,3-dioxygen structures, which were the likely active intermediates, rather than tin(II) chloride itself, in reactions of many nucleoside and glycoside diols with diazomethane in methanol. Reaction (1) shows the overall reaction of diazomethane with an alcohol to form dialkoxy stannane.[24]

$$2ROH + SnCl_2 + 2CH_2N_2 \rightarrow Sn(OR)_2 + 2CH_3Cl + 2N_2 \quad (1)$$

If the two alcohol groups belong to a vicinal diol, a 1,3,2-dioxastannolane would be formed. This reaction probably involves an intermediate between the diazo carbon, followed by a nucleophilic attack by chloride on this carbon atom. The formation of a dialkoxylate or 1,3,2-dioxastannolane would then involve such a sequence of reactions being repeated.

Shugar's mechanism has been presented as a possibility for the tin(II) chloride catalyzed reactions of diaryldiazomethanes with diol systems in nonhydroxylic 1,2-dimethoxyethane.[23] In an attempt to gain further understanding of these reactions, it was decided to study the kinetics of the reaction between the model diol, ethylene glycol ($HOCH_2CH_2OH$), and diazodiphenylmethane (Ph_2CN_2) in 1,2-dimethoxyethane (DME) in the presence of tin(II) chloride ($SnCl_2$). The visible absorption of diazodiphenylmethane at 523 nm was used to follow the progress of the reaction in the present study. Two series of kinetic experiments are presented here. Firstly the initial concentration of ethylene glycol was varied, and secondly the initial concentration of diazodiphenylmethane was varied. Experiments conducted with varying concentration of tin(II) chloride have also been undertaken. These showed a direct relationship between the concentration of tin(II) chloride and the rate constant, as expected, and are not discussed further. In all these experiments the temperature was 30 °C.

2. Results and discussion

Series I. Reactions with varying initial concentrations of ethylene glycol.—Seven experiments were conducted with an initial concentration of diazodiphenylmethane about 0.01 M and tin(II) chloride 0.0026 M, and the initial concentration of ethylene glycol ranged from 0.010 to 0.21 M. The reactions were run for 10 min, and the A_{523} readings were taken at 1-min intervals. The results are presented in Table 1 where the pseudo first-order rate constant is obtained directly from the $\ln(A_{523})$ versus time plots.

Table 1 shows that in experiments 1–4 the pseudo first-order rate constant increases with increasing concentration of ethylene glycol, but at $[HOCH_2CH_2OH]_0$ above 0.063 M, this trend is reversed. The increase in the rate constant in experiments 1–4 is consistent with a dynamic system where there is an equilibrium between ethylene glycol and tin(II)

Table 1
Results from reactions with increasing initial concentration of ethylene glycol

Experiment number	1	2	3	4	5	6	7
$[EG]_0$ (mol L^{-1})[a]	0.010	0.015	0.021	0.063	0.10	0.15	0.21
k'^* [b] (min^{-1})	0.158	0.175	0.200	0.278	0.245	0.227	0.197
R^2	0.998	0.999	0.999	0.999	0.999	0.999	0.999

[a] EG: ethylene glycol.
[b] k'^* is the pseudo first-order rate constant.

chloride on the one hand and an intermediate rate-determining complex on the other. Such an equilibrium would mean an increase in the active species with increasing concentration of ethylene glycol and consequently an increase in k'. The effect on the linearity of the $\ln(A_{523})$ versus time plots is only observed for low initial concentrations of ethylene glycol. The inverse relationship between the rate constant and the concentration of ethylene glycol in experiments 4–7 could be explained by a non-productive complex between the catalyst and ethylene glycol being formed in significant amount at the higher concentrations of ethylene glycol. This effect could also be caused by the catalyst being partially destroyed in a reaction involving the alcohol. Preparative experiments using still higher reagent concentrations have resulted in the preciptation of a catalytically inactive tin compound showing that the second explanation is more likely.

Series II. Reactions with varying initial concentrations of diazodiphenylmethane.—Four experiments were conducted with an initial concentration of ethylene glycol 0.021 M and tin(II) chloride 0.0026 M, and the initial concentration of diazodiphenylmethane ranged from 0.003 to about 0.01 M. The results are presented in Table 2.

The excellent linear relationship between $\ln(A_{523})$ and time shown by the R^2 values from the graphs used to obtain the pseudo first-order rate constants show that the reaction is first-order with respect to the concentration of diazodiphenylmethane. The most interesting aspect of these results are that also here there is an inverse relationship between the rate constant and the initial concentration of one of the reagents, that is the diazodiphenylmethane. This is again consistent with the partial destruction of tin(II) chloride in a reaction which must also involve diazodiphenylmethane.

Table 2
Results from reaction with decreasing initial concentration of diazodiphenylmethane

Experiment number	1	2	3	4
$[DA]_0$ (mol L^{-1})[a]	0.0030	0.0050	0.0070	0.0099
k'^* [b] (min^{-1})	0.379	0.370	0.294	0.246
R^2	0.994	0.997	0.997	0.998

[a] DA: diazodiphenylmethane.
[b] k'^* is the pseudo first-order rate constant.

The results discussed above do not justify the suggestion of a complete mechanism for the reaction, but if the inverse relationship between the initial concentration of the two reagents and k', shown for high concentrations, is due to a partial destruction of the catalyst, this cannot be happening during the whole course of the reaction. The kinetic study does in fact show a faster initial rate, for between one and two minutes, which then settles down to a steady rate represented in the above data. This could be due to the formation of an intermediate complex that takes the reaction along its main course only, while initially a different reaction is taking place as well, involving both reagents partly destroying the catalyst.

The chemistry of tin is fairly complex and dimers and oligomers of 1,3,2-dioxastannolanes and 1,3,2-dioxastannanes, similar to tin(IV) derivatives, can be formulated.[25] A prerequisite for the involvement of such complexes in the reactions discussed here is the transformation of the tin(II) chloride into the 1,3,2-dioxastannolanes. If this happens according to reaction 1, there is no inorganic chloride present, since that has been tied up in the chloromethane formed. It is also possible that tin(II) chloride reacts with only one of the diol hydroxyl groups according to reaction 1 and the second hydroxyl group displaces the second chloride by a nucleophilic attack. This would release hydrogen chloride. This mechanism can be discounted since it is known that strong acids, e.g., *p*-toluenesulfonic acid and perchloric acid, or even Lewis acids (BF_3 and $CuCl_2$) catalyzed reactions of diaryldiazo compounds with an equivalent of an alcohol or a diol in an inert solvent, while leading to decomposition of the diazo compound, give insignificant amounts of the ether product.[3] Inorganic chloride remaining at the end of the reaction can therefore be taken to indicate the presence of intact tin(II) chloride. The amount of inorganic chloride has been determined for the tin(II) chloride catalyzed reaction of diazodiphenylmethane with ethylene glycol according to the method of Lisensky and Reynolds.[26] In the same way the amount of

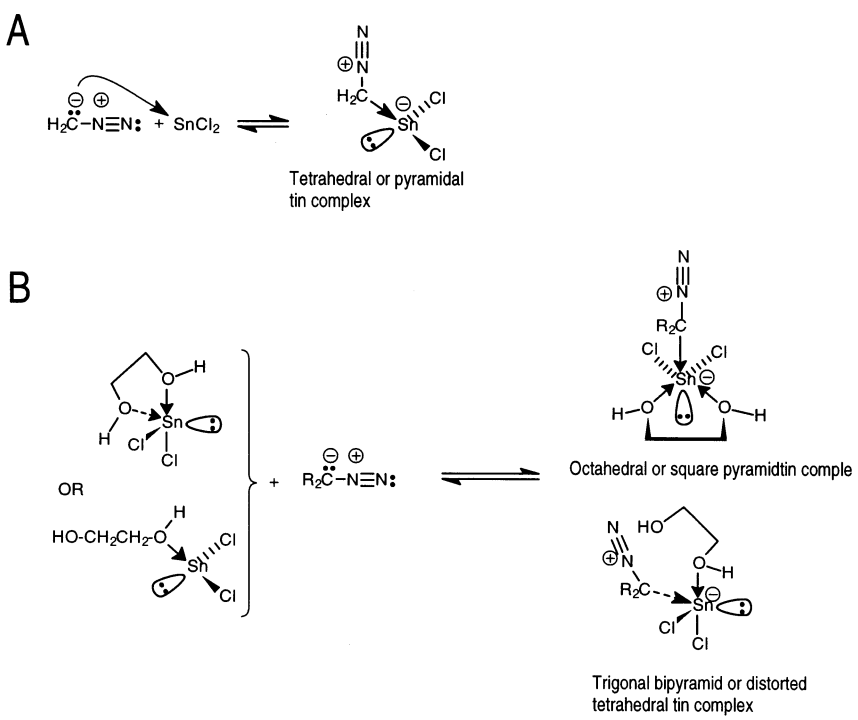
Table 3
Inorganic chloride remaining at the end of the tin(II) chloride catalyzed reactions of diazodiphenylmethane with ethylene glycol and methanol

Alcohol	Chloride remaining (%)
Ethylene glycol	68.2
Diazodiphenylmethane–$SnCl_2$–CH_3OH	77.5
Tin(II) chloride (no reaction)	100

chloride was determined for the reaction mixture between diazodiphenylmethane and tin(II) chloride in methanol, similar to the reaction of diazomethane with tin(II) chloride in methanol as described by Shugar and coworkers (reaction 1). The results from these reactions are given in Table 3.

The kinetics of the decompositions of diazodiphenylmethane and diazofluorene catalyzed by zinc halides have been explained by an initial electrophilic attack by the metal on the diazo carbon atom resulting in a simultaneous or subsequent loss of nitrogen.[27] A similar reaction involving a pyramidal tin(II) chloride complex could initially be taking place here (see Scheme 2(A)), while the main reaction takes place following the formation of a complex of tin(II) chloride having the diazo carbon as one ligand and with the diol in a dynamic equilibrium providing at least one additional ligand as shown in Scheme 2(B). The kinetic data presented in this paper suggest that while the complex in B is being formed, which can only be taking place after the addition of the diazo compound, the complex in A is causing a side reaction and partially destroying the catalyst. The reason why a complex such as the one shown in A would cause the destruction of the catalyst, whereas those in B would not, is not certain, but it is worth pointing out that the angle between the tin lone pair of electrons and the diazo carbon ligand in A is close to the tetrahedral angle, whereas in B it is much wider, or 180° in the square pyramid and over 120° in the distorted tetrahedral complex.

Experiments are being conducted with other model diols. The reactions with *meso*-1,2-*cis*-cyclohexanediol and racemic *R*,*R*/*S*,*S*-1,2-*trans*-cyclohexanediol have already given particularly interesting and relevant results. The former compound has the manno-structure and the latter a gluco-structure. In the earlier studies it was unexpected to find that



Scheme 2. Suggested complex intermediates in the tin(II) chloride catalyzed reactions of diazodiarylmethanes with a vicinal diol.

methyl 4,6-*O*-benzylidene-α-D-glucopyranoside, where the dihedral angle between the 2- and 3-OH groups is the same as it is in the manno-compound, did hardly react at all under exactly the same conditions as used for methyl 4,6-*O*-benzylidene-α-D-mannopyranoside (sugar, 0.12 M; Ph_2CN_2, 0.27 M; $SnCl_2$, 0.021 M).[23] Preparative reactions (both reagents 0.20 M) with the two model compounds showed a ready reaction with *meso*-1,2-*cis*-cyclohexanediol in the presence of tin(II) chloride giving the racemic monodiphenylmethyl ether in 82% yield. The *trans*-compound, on the other hand, appeared to react much less readily. The reason for this is the formation of a noncatalytic tin derivative, which precipitates out of the solution (this has also been observed for reactions with ethylene glycol). The addition of more tin(II) chloride gave eventually a 46% yield of the raecemic monodiphenylmethyl ether of 1,2-*trans*-cyclohexanediol. Interestingly a kinetic study of these reactions with an initial concentration of diazodiphenylmethane of 0.0024 M and of the diols of 0.011 M and less, gave in fact a higher pseudo first-order rate constant for the *trans*-cyclohexanediol. These results demonstrate very clearly the subtle steric effects, both on the reaction rate and particularly on the stability of the catalyst. Following these results with the *cis*- and *trans*-cyclohexanediols, the reaction of 3.5 equiv of diazodiphenylmethane with methyl 4,6-*O*-benzylidene-α-D-glucopyranoside was repeated in a dilute 1,2-dimethoxyethane solution (0.02 M) in the presence of 0.003 M tin(II) chloride. Contrary to the results from the same reaction with higher reagent concentrations (0.12 M), the reaction was now over in about 5 h, and the 2- and 3-monoethers were isolated in 20 and 69% yields, respectively. Methyl 4,6-*O*-benzylidene-2-*O*-diphenylmethyl-α-D-glucopyranoside is a crystalline compound with mp 160–161 °C. Methyl 4,6-*O*-benzylidene-3-*O*-diphenylmethyl-α-D-glucopyranoside was isolated as a glass. Satisfactory elemental analysis was obtained for this compound and the crystalline 2-(3,5-dinitrobenzoyl ester) was also prepared and characterized, mp 228–229 °C.

3. Conclusions

The conclusion from the results presented here is that the 1,3,2-dioxastannolane intermediate proposed for the reactions of diazomethane with vicinal diols in methanol cannot be the only species at work in the reactions of diazodiphenylmethane in a non-hydroxylic solvent like 1,2-dimethoxyethane, and is probably not involved in the catalysis at all.[24] Further experiments will be needed to explain the mechanism in more detail, but it is easier to rationalize the formation of monoethers by an intermediate involving tin(II) chloride itself, with diazo carbon and hydroxyl groups providing ligands around the electron-deficient tin atom. A careful analysis of such an intermediate will be undertaken using ^{119}Sn NMR spectroscopy and other appropriate methods, and it is hoped that such a study will lead to the explanation of the unexpected regioselectivities observed in the reaction of the diaryldiazomethanes with the mannopyranoside derivatives, especially methyl 4,6-*O*-isopropylidene-α-D-mannopyranoside.[1]

4. Experimental

General methods.—The absorption spectrometers used were LKB-Ultraspec II and Varian Carey 100BIO UV–Vis spectrometers. ^1H and ^{13}C NMR spectra were run on Bruker AC 250 and Bruker DPX 200 instruments with Me_4Si as an external standard. Optical rotations were determined with Schmidt and Haensch universal polarimeter. Diazodiphenylmethane was prepared using a published method, $\varepsilon(523\ nm) = 98\ L\ mol^{-1}$.[28] Ethylene glycol was E. Merck reagent grade. The solvent used for the reactions was E. Merck 1,2-dimethoxyethane (DME) distilled from and stored over sodium. Anhydrous tin(II) chloride and methyl 4,6-*O*-benzylidene-α-D-glucopyranoside were prepared according to textbook methods.[29]

Spectroscopic experiments.—The reactions for the kinetic studies were all done in 3-mL quartz spectrometric cells in a total volume of 3.0 mL. The temperature in the cell compart-

ment was 30 °C, which is the temperature used for both series. The solutions used for the experiments were stored inside the cell compartment between runs. At 1-min intervals the A_{523} was recorded. The pseudo first-order rate constant was determined by plotting $\ln(A_{523})$ against time using the Microsoft EXCEL software.

Ethylene glycol diphenylmethyl ether.—Ethylene glycol (0.25 g, 4.0 mmol) and anhydrous tin(II) chloride (0.023 g, 0.12 mmol) were dissolved in 1,2-dimethoxyethane (10 mL). Diazodiphenylmethane (0.971 g, 5.00 mmol) was then added, and the reaction was allowed to proceed at rt for about 5 h. TLC (4:1 hexane–EtOAc) showed the ether product, R_f 0.13, and a faster yellow component, R_f 0.50. The main product was purified on a column of silica gel to give 0.74 g, 65% yield, of the monoether product, which solidified on standing and was recrystallized from hexane: mp 60–61 °C. ^{1}H NMR ($CDCl_3$): δ 2.17 (1 H, s, OH), 3.46–3.51 (2 H, m, CH_2–OH), 3.67 (2 H, t, $J_{1,2}$ 4.6 Hz, Ph_2CHOCH_2), 5.31 (1 H, s, Ph_2CH), 7.15–7.29 (10 H, m, Ar H). ^{13}C NMR ($CDCl_3$): δ 61.94, 70.30 (2 C, negative in DEPTCP, –CH_2CH_2–), 84.01 (1 C positive in DEPTCP, Ph_2CH), 126.88, 127.54, 128.41 (4 C, 2 C, 4 C, all positive in DEPTCP, Ar C-2 and C-6, C-4, C-3 and C-5), 141.82 (2 C, disappear in DEPTCP, Ar C-1). MS: 228.1 (50%) M^+; 183.1 (8%), Ph_2CHO; 67.1 (100%) Ph_2CH. Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.9; H, 7.1. Found: C, 78.5; H, 7.1.

Reaction of diazodiphenylmethane and tin(II) chloride with methyl 4,6-O-benzylidene-α-D-glucopyranoside.—Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (1.00 g, 3.54 mmol) and tin(II) chloride (0.106 g, 0.559 mmol) were dissolved in 1,2-dimethoxyethane (180 mL). Diazodiphenylmethane (1.38 g, 7.10 mmol) was then added, and a drying tube was fitted onto the flask. After about 4 h the red color had disappeared, but a TLC examination (3:2 hexane–EtOAc) showed a substantial amount of unreacted diol. More diazodiphenylmethane (1.00 g 5.15 mmol) was added and the reaction was left stirring overnight. The ether products were isolated from a column of silica gel using a gradient of 95:5–3:2 hexane–EtOAc.

Methyl 4,6-*O*-benzylidene-2-*O*-diphenylmethyl-α-D-glucopyranoside (0.312 g 19.6%) was crystallized from ether–hexane, mp 160–161 °C, $[\alpha]_D^{22}$ +22.4° (*c* 3.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 2.26 (1 H broad, –OH), 3.33 (3 H, s, –OCH_3), 3.48 (1 H, t, $J_{H3,\,H2\text{ and }H3,\,H4}$ 9.3 Hz, H-3), 3.58 (1 H, dd, $J_{H2,\,H1}$ 3.6, $J_{H2,\,H3}$ 9.3 Hz, H-2), 3.68 (1 H, t, $J_{H4,\,H3\text{ and }H4,\,H5}$ 10.2 Hz, H-4), 3.78–3.84 (1 H, dd, $J_{H6a,\,H6b}$ 14.2, $J_{H6a,}$ H5 4.5 Hz, H-6a), 4.19–4.28 (2 H, m, H-5 and H-6b), 4.49 (1 H, d, $J_{H1,\,H2}$ 3.6 Hz, H-1), 5.51 (1 H, s, Ph_2CH), 5.66 (1 H, s, PhC*H*), 7.3–7.5 (15 H, m, Ar H). ^{13}C NMR ($CDCl_3$): δ 55.31 (–OCH_3), 61.97 (C-3), 68.98 (C-2), 70.32 (C-5), 79.37 (C-4), 81.25 (C-6), 84.42 (C-1), 98.77 (Ph_2CH), 101.89 (Ph*C*H), 126.29, 127.02, 127.49, 127.68, 127.89, 128.28, 128.46, 129.16 (Ar C-2 to C-6), 137.07 (PhCH Ar C-1), 141.54, 142.07 (Ph_2C Ar C-1 conformers). Anal. Calcd for $C_{27}H_{28}O_6$: C, 72.3; H, 6.3. Found: C, 72.09; H, 6.24.

Methyl 4,6-*O*-benzylidene-3-*O*-diphenylmethyl-α-D-glucopyranoside (1.10 g, 69.1%) glass $[\alpha]_D^{22}$ +78.2° (*c* 11, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 3.39 (3 H, s, –OCH_3), 3.7–3.9 (6 H, m, OH and H-2 to H-6a), 4.25–4.28 (1 H, m, H-6b), 4.77 (1 H, d, $J_{H1,\,H2}$ 1.7 Hz, H-1), 5.53 (1 H, s, Ph_2CH), 6.05 (1 H, s, PhC*H*), 7.2–7.4 (15 H, m, Ar H). ^{13}C NMR ($CDCl_3$): δ 55.29 (–OCH_3), 62.36 (C-3), 69.00 (C-2), 72.75 (C-5), 76.79 (C-4), 81.84 (C-6), 83.78 (C-1), 99.88 (Ph_2CH), 101.37 (Ph*C*H), 126.08, 127.09, 127.20, 127.63, 128.11, 128.19, 128.45, 128.97 (Ar C-2 to C-6), 137.28 (PhCH Ar C-1), 142.06, 142.33 (Ph_2C Ar C-1 conformers). Anal. Calcd for $C_{27}H_{28}O_6$: C, 72.3; H, 6.3. Found: C, 72.39; H, 6.28.

Methyl 4,6-O-benzylidene-2-O-(3,5-dinitrobenzoyl)-3-O-diphenylmethyl-α-D-glucopyranoside.—Methyl 4,6-*O*-benzylidene-3-*O*-diphenylmethyl-α-D-glucopyranoside (300 mg, 0.669 mmol) was treated with triethylamine (0.132 mL, 1.02 mmol) and 3,5-dinitrobenzoyl chloride (220 mg, 0.954 mmol) in CH_2Cl_2 (5 mL). The excess acid chloride was quenched with silica gel (1.5 g), and the product was purified on a silica gel column using hexane–EtOAc as eluent to give pure 2-(3,5-dinitrobenzoyl ester) (300 mg, 69.8%). The ester was recrystallized from heptane–EtOAc: mp 228–229 °C. ^{1}H NMR ($CDCl_3$): δ 3.37 (3 H, s, –OCH_3), 3.8–3.9 (3 H, m, H-4,

H-5, H-6a), 4.33–4.37 (2 H, m, H-3, H-6b), 4.98 (1 H, d, $J_{H1,\ H2}$ 3.9 Hz, H-1), 5.34 (1 H, dd, $J_{H2,\ H1}$ 3.9, $J_{H2,\ H3}$ 9.5 Hz, H-2), 5.54 (1 H, s, Ph_2CH), 5.82 (1 H, s, PhC*H*), 6.9–7.0 and 7.1–7.3 (15 H, m, PhCH and Ph_2C Ar H's), 8.85 (2 H, d, $J_{Ho,\ Hp}$ 2.1, dinitrobenzoyl *o*-H), 9.18 (1 H, t, $J_{Hp,\ Ho}$ 2.1, dinitrobenzoyl *p*-H). Anal. Calcd for $C_{34}H_{30}N_2O_{11}$: C, 63.5; H, 4.7; N, 4.4. Found: C, 63.40; H, 4.69; N, 4.12.

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