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PHOTOINDUCED, ELECTRON-TRANSFER REACTIONS OF ARYL GLYCOSIDES*

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ABSTRACT

Photoinduced, electron-transfer (e.t.)-sensitized cleavage of phenyl β-D-glucopyranoside in acetonitrile brought about by irradiation at 350 nm, with sensitization with 1,4-dicyanonaphthalene (DCN) in the presence of methanol, proceeds rapidly, to produce 60% of the theoretical yield of the methyl D-glucosides within 6 h. Incorporation of water, instead of methanol, provides a means of conversion of the aryl D-glucoside into free D-glucose in comparatively high yields. Irradiation of the reaction system at 300-nm wavelength, with sensitization by DCN, produced, despite the higher energy, slightly lower levels of monosaccharide or methyl glycosides than are obtained from sensitized irradiations at 350 nm, concurrent with increased complexity in product composition. At 350-nm irradiation, levoglucosan is as equally favored as D-glucose as the reaction product from the cleavage of phenyl β-D-glucopyranoside in acetonitrile. Solubility of the materials and conformational interconversions are cited as contributing to anomeric and epimeric differences in the product yields reported. Secondary, and competitive, side-reaction products derived from u.v. irradiation in the presence of the sensitizer DCN are attributed to generation, from methanol in the acetonitrile solvent-system, of formic acid, which enhances degradation of the carbohydrates.

INTRODUCTION

Photochemical reactions have been employed in carbohydrate chemistry for syntheses, cleavages, removal of protecting groups, and cycloadditions to unsaturated carbohydrate derivatives[2]. For example, Zehavi and co-workers[3,4] reported the use, in synthesis, of photochemical, glycoside cleavage, whereby a light-sensitive polymer formed by attaching nitrovanillin to a copolymer served, for condensation with carbohydrate groups, as the solid support which, after appropriate

*Part II. For Part I, see ref. 1.

chemical reactions, was irradiated to release the desired, debenzylated oligosaccharide, isomaltose. Our research objective addressed here is to determine the application of the new area of photoinduced, electron-transfer (e.t.) sensitization to the field of carbohydrate chemistry in the hope of expanding the synthetic repertoire.

Earlier, we reported[1] that photoinduced, e.t.-sensitization reaction-conditions were effective in cleaving aryl D-glucopyranosides to monosaccharides and phenolic components. Anomeric phenyl D-gluco- and D-galacto-pyranoside solutions in acetonitrile saturated with oxygen, air, or nitrogen, and containing 1,4-dicyanonaphthalene (DCN), were irradiated at 350 nm for extended periods, with the reaction products monitored by 7-MPa liquid chromatography (l.c.) after 24, 48, and 72 h of irradiation[1]. Cleavage of the radical cation formed by e.t. proceeds spontaneously to the pyranosyl cation and the phenoxy radical. Upon hydration, the former affords the simple monosaccharide, and reduction of the latter gives phenoxide which, on protonation, yields phenol. The mechanism was examined experimentally by laser flash-photolysis, which confirmed the electron-transfer process and the intermediates involved[5].

The study has now been extended to sampling of the reaction products during the first 6 h of irradiation in the presence of methanol, in order to monitor more closely the progress of the reaction. Next, we incorporated water (10%) in the reaction mixture, instead of methanol, to intercept the cationic species as the unsubstituted sugar, and evaluated the irradiation of these reactions at a higher energy, *i.e.*, at 300 nm, with a view to possibly increasing the yields, or decreasing the time of irradiation needed to achieve the desired yields, or both.

Identification of the other components among the reaction products (after irradiation in the original study[1]) was undertaken. Phillips and Moody[6] had reported that, on direct u.v. irradiation at 254 nm, D-glucose in aqueous solution is degraded to D-arabinose, three- and two-carbon aldehydic fragments, formaldehyde, formic acid, and carbon dioxide, which were the main products detected by paper chromatography and isotope-dilution analysis, and possibly D-glucosone. Throughout the course of irradiation, it was noted that hydrogen was continuously evolved. During the overall irradiation time-period, which was >160 h, a linear decrease in the concentration of D-glucose was observed with increasing time of irradiation, concurrent with simultaneous increase in the concentration of degradation or secondary-reaction products. Near 100 h, a sharp decline in the concentration of products was observed, until all of the organic materials were transformed into carbon dioxide after 172 h of irradiation. In study[1] of the irradiation of aryl D-glycosides at 350 nm, low yields of the glycosides were obtained in acetonitrile solution, with high levels of conversion of the starting material. As was reported[1], control reaction-mixtures irradiated under otherwise identical experimental conditions, except for the presence of the sensitizer DCN, indicated that presence of the sensitizer was essential in order to effect reactions. This prompted us to pursue the characterization and identification of the other reaction-products obtained under

these conditions, in order to determine if the glycosidic products underwent u.v. degradation after their formation, thereby preventing higher yields from being obtained. Also, Kagan *et al.*[7] reported that, in some systems, photoaddition of the solvent methanol may occur from metal-ion (charge-transfer) or "photoacid" catalysis, despite the lack of chromophores in the reactants. Study of the effects on the reaction system of the sensitizer in combination with u.v. irradiation, and of the products formed, was thus deemed necessary.

EXPERIMENTAL

Materials and methods. — The materials and techniques were as described previously[1]. Suspensions (mM) of D-glucose were prepared in (*a*) acetonitrile, (*b*) 10:1 acetonitrile–methanol, and (*c*) 10:1 acetonitrile–water. Irradiations were conducted as indicated previously[1]. In the study using 300-nm irradiation, sixteen 8-W, 300-nm lamps were used in a Rayonet* reactor.

The 7-MPa liquid-chromatographic analysis-procedure was the same as described in the previous work[1]. Data acquisition by on-line computer allowed further callup of chromatographic peaks for integration and comparison of multiple-detector outputs. The following materials were employed as standards against which the experimental sample peaks were compared: D-glucose, D-galactose, D-xylose, L-arabinose, D-mannose, D-fructose, melezitose, cellobiose, D-gluconic acid, D-glucuronic acid, D-galacturonic acid, D-*arabino*-2-hexulosonic ("2-keto-D-gluconic") acid, levoglucosan, 2-furaldehyde, oxalic acid, acetic acid, levulinic acid, fumaric acid, malic acid, D-glucitol, D-ribitol, D-mannitol, formaldehyde, formic acid, phenyl α-D-glucopyranoside, phenyl β-D-glucopyranoside, phenyl β-D-galactopyranoside, phenol. Levoglucosan was prepared by pyrolysis of starch[8] by D. Stanonis, purified by F. W. Parrish, and furnished by W. Franklin. The formaldehyde standard was prepared by dilution of formalin (Baker, 37% formaldehyde; stabilized by methanol).

Retention times of peaks, obtained by refractive index (r.i.), u.v. at 210- and at 254-nm absorption detection, and u.v. scan-patterns (from 190–700 nm) were matched. Calculation of the quantity present in the irradiated sample was made from refractive-index response-curves (concentration *versus* area under peak). Reports had indicated that verification of an unknown can be achieved by matching the retention times of peaks and the u.v. scan of those peaks with known standards, in that no two compounds will completely correlate with the multiple-detector outputs, particularly the u.v. scan over a range of wavelengths, unless they are identical[9]. In monitoring carbohydrate separations, a wide range of linear, r.i.-detector response related to concentration of the components in solution is observed. Also,

*Names of companies or commercial products are given solely for the purpose of providing specific information; their mention does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.

it has been reported that saccharides ranging from D-fructose and D-glucose to maltose and maltotriose have essentially identical response factors, *i.e.*, the peak heights or integrated areas under the peak for saccharides, as determined by r.i., at the same concentration levels (weight)[10].

Carbohydrates lack suitable chromophores to render detection by u.v. detectors efficient at wavelengths >200 nm. In the case of formic acid, addition of methanol was made to the standard solution to check for the presence of its methyl ester under these conditions, but no u.v.-absorbing peak was detected. A mixture of formaldehyde and formic acid was prepared and analyzed; separate chromatographic peaks were detected, with a u.v.-absorption peak (at 210 nm) corresponding to formic acid. Averages were calculated for peak areas at the various retention times, based on replicate l.c. analyses for each sample.

RESULTS AND DISCUSSION

Production of methyl D-*glucopyranosides related to time of irradiation.* — A study of the production of methyl D-glucopyranosides relative to irradiation exposure was undertaken. Solutions of phenyl β-D-glucopyranoside in 10:1 acetonitrile–methanol were irradiated at 350 nm under conditions designed to achieve photoinduced, e.t. sensitization with DCN. Aliquots were taken hourly for the first 6 h of irradiation, and the reaction progress was monitored by l.c. The plot shown in Fig. 1 indicates a rapid buildup in the total amount of methyl α- and β-D-glucosides. After only 1 h of irradiation, 24% of the theoretical yield of methyl D-glucosides was observed. After 6 h, the yield of methyl D-glucosides was 61%, which approaches the yield (66%) obtained after 24 h of irradiation. These data demonstrate that the reaction proceeds rapidly during the first 6 h of irradiation at 350 nm with DCN sensitization, and levels off thereafter with increasing irradiation time.

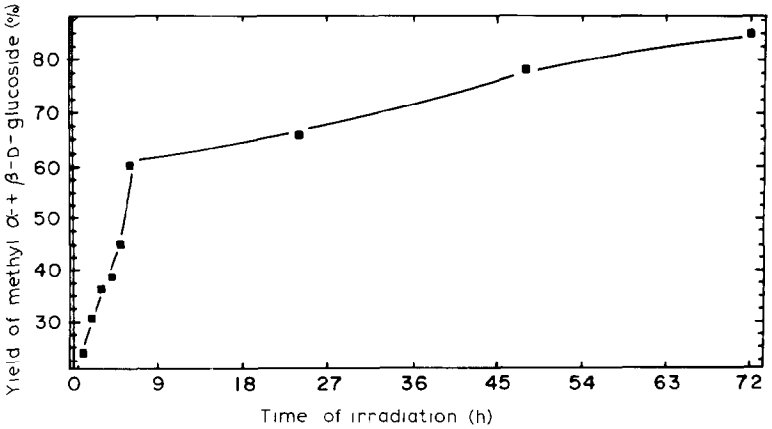

Fig. 1. Formation of methyl D-glucopyranosides (total of α + β) from DCN-sensitized cleavage of phenyl β-D-glucopyranoside irradiated at 350 nm in 10:1 MeCN–MeOH.

TABLE I

PHOTOINDUCED ELECTRON-TRANSFER OF PHENYL β-D-GLUCOPYRANOSIDE IN 10:1 MeCN–H_2O, WITH 1,4-DICYANONAPHTHALENE AS SENSITIZER, IRRADIATED AT 350 nm

Time of irradiation (h)	D-*Glucose (% of theoretical)*	*Starting material consumed (%)*
18	56	80
24	61	86
48	67	94
72	70	96

Incorporation of water for production of unsubstituted monosaccharides. — Because the methyl D-glucoside is produced in the presence of methanol, it was projected that the free sugar should be produced by corresponding incorporation of water for trapping of the presumed cationic species. D-Glucose is, indeed, the product when samples of phenyl β-D-glucopyranoside in 10:1 acetonitrile–water are irradiated under the conditions employed with methanol. The yields (% of the theoretical) of D-glucose and the amount of starting material consumed after exposure to 350-nm radiation are given in Table I. The yields correspond to those of total methyl D-glucopyranosides obtained with methanol, to within 5% after 24 h, within 11% after 48 h, and within 15% after 72 h. D-Glucose, as observed previously, is labile under photoinduced, e.t.-sensitized reaction-conditions, and is not as stable as the product methyl D-glucosides. These changes with time are discussed later.

Photoinduced, electron-transfer-sensitized reactions at 300 nm. — The u.v. absorption spectrum of DCN displays a broad absorption band that extends from 260 to 380 nm. The potential advantages of irradiation at higher energy were investigated by exchanging the broad-spectrum source having a maximum emission wavelength at 350 nm ("black lamp"), used in a Rayonet RPR-100 Photoreactor in all irradiations previously described, for a corresponding source having a maximum emission wavelength at 300 nm. Irradiation of phenyl β-D-glucopyranoside at 300-nm wavelength under conditions otherwise similar to those previously employed (DCN, acetonitrile–methanol, compressed air) was conducted. The yields of methyl D-glucosides, given in Table II were slightly lower than those obtained at 350 nm, with much more complexity in the mixture of the reaction products, as determined by the u.v.-absorbing components detected in l.c. analysis. Although conversion of the aryl into the methyl D-glucosides is observed at 300-nm irradiation sensitized with DCN, the production of methyl D-glucosides was diminished, with concurrent enhancement of undesirable byproducts. Thus, it appears that, for practical reasons, it is more advantageous to utilize the "black lamps" (350 nm) for photoinduced, electron-transfer cleavage of aryl glycosides, to avoid byproduct formation and to maximize the yield of the desired products.

TABLE II

PHOTOINDUCED, ELECTRON-TRANSFER REACTIONS OF PHENYL β-D-GLUCOPYRANOSIDE WITH 1,4-DICYANONAPHTHALENE (DCN) AS SENSITIZER IN VARIOUS SOLVENT-SYSTEMS IRRADIATED AT 300 nm

Time of irradiation (h)	*Solvent system*	*Product (% of theoretical)*	*Starting material (% remaining)*
		methyl D-glucosides	
1	MeCN–MeOH (10:1)	18	
2		27	
5		43	
9		41	
9 (no DCN)		9	
		D-glucose	
9	MeCN–H_2O (10:1)	48	31
9 (no DCN)		5	85

Secondary and competitive side-reaction products derived from photosensitized, electron-transfer reactions of aryl glycosides. — In order to establish the origins and structures of the additional products obtained from aryl glycosides in e.t.-sensitized reactions, an attempt was made to differentiate the contributions arising from photochemical and possible "photoacid"-catalyzed reactions[7]. A comprehensive study was made by examining the effects of the sensitizer DCN, with illumination at 350 nm, on all aspects of the reaction, namely, the solvent system, the glycosidic products, and the cleavage of the aryl glycosides. Throughout these studies, control experiments were conducted in the absence of the sensitizer (under otherwise identical conditions), and, except where previously reported, irradiation alone at 350-nm wavelength produced no detectable chemical changes in the starting materials.

To evaluate changes in the solvent brought about by the sensitizer in conjunction with irradiation, acetonitrile, 10:1 (v/v) acetonitrile–methanol, and 10:1 (v/v) acetonitrile–water containing 0.1mM DCN were photolyzed after purging with compressed air. No change was detected in the acetonitrile after irradiation for 72 h at 340 nm. In acetonitrile–methanol–DCN, formic acid (0.15 mg/mL) and formaldehyde (0.06 mg/mL) were detected after irradiation for 72 h. A formalin standard consisting of formaldehyde in aqueous solution, stabilized with methanol to prevent polymerization, was used for identification. (In alcohols, the dissolved aldehyde is apparently in the form of the simple hemiacetal and, according to Walker[11], evidence indicates that the hemiacetals or alcohols of formaldehyde are more stable than the corresponding hydrates.) In the case of the acetonitrile–water, a trace of formic acid (0.06 mg/mL) was produced. Thus, despite the apparent absence of chromophores in the solvent systems, the presence of the sensitizer and methanol, or water, may produce acidic conditions in acetonitrile by the formation of formic acid. Such "photoacid" formation has been reported in other cases, in which transparent oxiranes undergo acid-catalyzed addition-reactions of nucleophiles[7,12].

To examine the effects of e.t. conditions on the carbohydrate products, suspensions of D-glucose (mM) in acetonitrile, in 10:1 acetonitrile–methanol, and in 10:1 acetonitrile–water that had been purged with compressed air in the presence of DCN (0.1mM) were irradiated at 350 nm. (The solubility of the carbohydrate varies with the solvent composition.) Samples were evaluated prior to, and after, 3, 24, 48, and 72 h of irradiation. No color changes were observed during the course of the irradiation.

The measured amount of D-glucose in acetonitrile solution increased from 5% (of the amount actually added in the original suspensions in the solvent) to 13% after 72 h of irradiation in the absence of the sensitizer. Continued exposure of the sample in a Rayonet Photoreactor operated at 40° could possibly account for the increase in solubility. Similarly, after 72 h of irradiation in the presence of DCN, the peak measured for D-glucose acquired a u.v.-absorbing peak, indicating that a portion of the D-glucose had been converted into the co-eluted D-glucono-1,5-lactone. Additionally, "2-ketogluconic" acid was detected by the appearance of a u.v. peak at 210 nm. Traces of formic acid were noted after 48 h of irradiation, and the concentration attained 0.04 mg/mL after 72 h. Therefore, the presence of formic acid provided evidence that degradation of the carbohydrate had occurred.

For the solvent system of acetonitrile–methanol, the suspension of D-glucose was measured to have 12% of dissolved material initially, with an increase to 35% after irradiation, compared to the higher solubility of D-glucose in water. The sensitized solutions of carbohydrate had, after 72 h of irradiation, generated twice the levels of formic acid and formaldehyde detected after irradiation (sensitized) of the free solvent system. Aside from formic acid and formaldehyde, no other components were detected. A contribution to the levels of formic acid and formaldehyde obviously arises from degradation of the D-glucopyranosides, as Phillips and Moody[6] reported, but the amounts produced when methanol is used as a co-solvent with acetonitrile are significantly greater than those generated during carbohydrate degradation by photoinduced e.t. (DCN-sensitized) in neat acetonitrile. In summary, the photogenerated acid derived from methanol (with DCN present) catalytically accelerates the decomposition of the carbohydrate, permitting complete degradation of the D-glucose to single-carbon fragments.

In order to ascertain whether the "photoacid" effects proposed are, indeed, responsible for the enhanced decomposition of the carbohydrate by ground-state "dark reactions", a control experiment was performed. To an aliquot of acetonitrile–methanol DCN that had been irradiated at 350 nm for 72 h was added a sample of D-glucose immediately upon removal of the solvent from the photoreactor. The suspension was thoroughly stirred overnight at ambient temperature, and then analyzed. The proportion of D-glucose that had dissolved was 12%, as with the other starting samples, but traces of D-gluconic and levulinic acids had been generated. The proportion of formic acid was equivalent to that measured for the solvent system alone, whereas that of formaldehyde had increased slightly. The levulinic acid is a degradation product of hexoses, and is produced concurrently with formic

acid. Thus, these results indicated that the acidic conditions generated by the sensitized solvent exposed to irradiation had initiated degradation of the D-glucose.

Acetonitrile–water was, of those tested, the best solvent system for the glycopyranosides. The amount of D-glucose dissolved was 75% of that added initially, with total solubility after 72 h of irradiation for the control. In the presence of DCN, the proportion rose to 96% after 24 h of irradiation, but began to decrease to 85% after 72 h, concurrent with buildup of traces of D-arabinose. Again, a formic acid level twice that of the solvent system alone was detected, as in the acetonitrile–methanol system after 72 h of sensitized irradiation. A small proportion of D-gluconic acid was also present.

As discussed earlier[1], 17% yields of D-glucose were obtained from cleavage of phenyl β-D-glucopyranoside by irradiation of solutions in acetonitrile sensitized with DCN and purged with compressed air. The irradiation time (24, 48, or 72 h) did not affect the yield, despite increased conversion (decreasing proportions) of starting material. The results indicated that only 75% of the amount of added phenyl β-D-glucopyranoside is soluble in acetonitrile, compared to its solubility in water, as determined by response factors (areas) by liquid chromatography. In addition to D-glucose, levoglucosan (1,6-anhydro-β-D-glucopyranose) is detected as the other major product of photoinduced e.t. reactions, at yield levels of 15% of the theoretical, again regardless of the length of the irradiation period. A small amount of mannose was detected; based upon isomerization of D-glucose, or the carbonium ion formed in the reaction, the yield was calculated to be ~4% of the theoretical. A trace of formic acid was noted after 72 h of irradiation, but no evidence of a gluconolactone or "ketogluconate" was seen. For the corresponding sample purged with nitrogen prior to irradiation, the proportion of D-glucose was slightly higher (20%) and was maintained throughout exposure to additional irradiation. In this case, 12% of levoglucosan was formed after 24, 48, and 72 h of sensitized irradiation. After 72 h of irradiation, ~5% of D-mannose was formed, with formic acid at 0.1 mg/mL. There was evidence for conversion into a gluconolactone, and a trace of arabinose was detected. For both the aerated and nitrogen-purged systems, it was noted that the solutions were cloudy after 48 and 72 h of irradiation, which presumably reflects the insolubility of the products, as well as of the starting material. The level of D-glucose of 17% of the theoretical was measured in several instances among the reaction products in acetonitrile; calculations based on the reaction stoichiometry would give 0.15 mg/mL for the solubility of D-glucose in acetonitrile. The limited solubility of D-glucose and the aryl glycosides in acetonitrile accounts for the previous lack of materials-balance for the system. There are subtle differences in the products obtained from reactions that had been purged with nitrogen instead of compressed air, in that those deaerated with nitrogen gave more degradation-derived and u.v.-absorbing components.

The presence and stability of the levoglucosan in the final products of photoinduced, e.t. cleavage of phenyl β-D-glucopyranoside was tested by separate addi-

tion of water (10%) and of methanol (10%) to aliquots of the 72-h-irradiated product mixtures. The samples were stirred overnight, and then analyzed. No significant changes were detected in either case, indicating the stability of the levoglucosan product; its formation would logically proceed from the carbonium ion formed on the carbohydrate ring following the electron-transfer interaction. Further study of the stability of the reaction products, and of the post-irradiation effects, was conducted by reanalyzing samples that had been irradiated in acetonitrile and stored in the laboratory for ~12 months without any special precautions. A control sample (no DCN) that had been irradiated for 72 h did not demonstrate any further cleavage to the D-glucoside than had previously been determined. The sensitized, irradiated sample had the same level of levoglucosan as in the original sample, but the proportion of glucose had decreased, with concomitant buildup of mannose, arabinose, and formic acid. Apparently, levoglucosan is very stable.

Phenyl α-D-glucopyranoside in acetonitrile gave much lower yields of glucose after irradiation under sensitized conditions. Examination of the data indicated that the solubility of the starting material in acetonitrile was only 25% of that in water. For the samples purged with compressed air, formation of arabinose (5%) was noted after 24 h of irradiation, with buildup to 7% of arabinose and a trace of levoglucosan, and 0.09 mg of formic acid/mL after 72 h of irradiation. For the nitrogen-purged sample, the results were similar.

The solubility of phenyl β-D-galactopyranoside in acetonitrile was 83% of that in water. As earlier reported[1], galactose was formed in high yield under sensitized cleavage. After 24 h of irradiation, the galactose was accompanied by chromatographic patterns of products very like those already discussed for D-glucose in acetonitrile irradiated under sensitized conditions, with the presence of formic acid and the presumed lactone and "ketogalactonic" acid. Although authentic standards were not available, the mechanisms of separation occurring under these chromatographic conditions strongly suggest formation of these products. After 48 h of irradiation, the samples showed marked shifts in composition. The amount of galactose decreased, and the solutions were cloudy. The "ketogalactonic" acid peak decreased by 75%; the proportion of lactone doubled, with generation of 2.5 times the amount of formic acid and traces of acetic and levulinic acids. After 72 h of sensitized irradiation, the degradation of the galactose apparently proceeded further, with buildup of formic (0.2 mg/mL), acetic, and levulinic acids. The patterns of degradation were the same for samples oxygenated with compressed air or deoxygenated with nitrogen, differing only in the amounts of material, not the composition.

In the solvent system of acetonitrile–methanol, which was employed in order to intercept the carbonium ion as the methyl glycosides, phenyl β-D-glucopyranoside produced both anomers of methyl D-glucopyranoside and slight traces of formic acid and formaldehyde. No other components were detected, and no differences were observed beween the differently purged samples.

Cleavage of phenyl α-D-glucopyranoside in acetonitrile–methanol produced

both anomers, but with favored (4:1) production of the α over the β in the first 9 h of irradiation in the presence of the sensitizer. The levels of formic acid/formaldehyde were identical to those generated in the solvent system exposed to irradiation with the sensitizer, as already discussed.

Irradiation of phenyl β-D-galactopyranoside in acetonitrile–methanol, with sensitization, elicited sharply contrasting results according to the sparging gas used. With compressed air, the results were as expected, *i.e.*, formation of the methyl galactosides, and the same levels of formic acid/formaldehyde. With nitrogen, a 3% level of galactose was detected after 48 h of irradiation; this then proceeded to undergo the degradation patterns already seen, with three times as much formaldehyde and 2.5 times as much formic acid generated.

Finally, study of phenyl β-D-glucopyranoside in acetonitrile–water as herein reported showed the same profiles of changes as with glucose exposed to irradiation in this solvent, sensitized with DCN. It had been reported[1] that phenethyl β-D-galactopyranoside does not undergo photoinduced, electron-transfer-sensitized cleavage, although low levels of conversion of the starting material were reported. Evaluation of the data showed that the same level of formic acid was obtained as from sensitized irradiation of the solvent system, and approximately half the level of formaldehyde. The conversion observed is probably the result of acid hydrolysis.

From the results discussed, it seems clear that the photochemical, electron-transfer reactions sensitized by DCN take place in acetonitrile, but that additional, acid-catalyzed reactions may occur from generation of acid when methanol or water are incorporated into the system. Our main interest lies in elucidation of the photochemical mechanisms involved, and explanation of differences that have been observed. Photoinduced, electron-transfer reactions sensitized by DCN proceed in acetonitrile to cleave aryl glycosides into the sugar and phenol.

The chief differences between the products from cleavage of the phenyl D-glucopyranoside anomers are the amount of D-glucose produced, and the equivalent production of levoglucosan and D-glucose from cleavage of the β anomer. An explanation of the formation of levoglucosan from the β but not the α anomer through a common carbonium ion intermediate is best addressed by conformational considerations. The formation of 1,6-anhydroglycoses is assumed to proceed in two stages. *Step 1.* The $^4C_1$ conformer of the α anomer, that is, the form present at equilibrium, is converted into the $^1C_4$ conformer of the β-D anomer. *Step 2.* The 1,6-anhydride is formed[13]. Phenyl β-D-glucopyranoside is already in the required $^1C_4$ conformation prior to formation of the carbonium ion, eliminating Step 1 in the formation of levoglucosan, whereas phenyl α-D-glucopyranoside requires energy to convert it from the $^4C_1$ into the $^1C_4$ conformer required before the anhydride can be formed. Therefore, production of the anhydride from the β anomer would be a very favorable reaction, in competition with the formation of D-glucose. Supporting this approach is the favored formation of methyl α-D-glucoside from cleavage of phenyl α-D-glucopyranoside. The sharply differing solubilities in acetonitrile could explain the various levels of products formed. On comparing the β anomers

containing different glycosyl groups, the question then arises (concerning the greater production of glycoside from the D-galactopyranoside than from the β-glucopyranoside) does the 4-hydroxyl group play a role in the reaction? Initially, it was considered that the data would support that possibility, but careful examination of two factors eliminated the differences. First of all is the solubility, the β-glucopyranoside being less soluble than the D-galactopyranoside by at least 10%. Second, the yield of levoglucosan added to the yield of D-glucose gives a total product comparable with the level of D-galactose. Therefore, the results demonstrate that cleavage of the β anomers of the D-gluco- and D-galacto-pyranosides gives the same yield level, regardless of the glycosyl group present.

CONCLUSIONS

Study of the early stages of the photoinduced, electron-transfer-sensitized reactions of phenyl β-D-glucopyranoside in acetonitrile–methanol revealed that the cleavage takes place rapidly in the first 6 h of irradiation at 350 nm, to produce 60% of methyl D-glucopyranosides. Incorporation of water, instead of methanol, correspondingly produces D-glucose at almost the same levels as those of the methyl D-glucopyranosides at equivalent times of sensitized irradiation. Irradiation at a lower wavelength (for greater energy in the reaction) leads to slightly lower yields of glycosides, with more-complex byproducts, or degradation of the products. Photoinduced, e.t.-sensitized conditions when methanol or water is present in the acetonitrile solvent generate acidic conditions that can cause degradation of the carbohydrate products.

Levoglucosan is produced in competition with D-glucose, presumably from the pyranosyl cation generated from cleavage of phenyl β-D-glucopyranoside in acetonitrile–DCN. Conformational-energy requirements, and solubilities of the aryl glycosides, are primary factors in the levels of yields of products obtained from photoinduced, electron-transfer-sensitized reactions in acetonitrile.

Photoinduced, e.t. sensitization provides a readily accessible route to a reactive, oxocation carbohydrate intermediate under very mild conditions. Extension of this approach offers potential advantages, not only in selective cleavages, but also in synthetic applications.

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