eluent, yield 0.70 g. Crystallization from ethyl acetate-petroleum ether (bp 60-68°) gave a melting point of 58-60°; ir (Nujol) 2.85, 2.89 (NH), 5.56 (COOC₂H₅), 5.82, 5.86, 6.04 μ (CON).

Anal. Calcd for $C_{17}H_{22}N_4O_9$: C, 47.89; H, 5.20; N, 13.14. Found: C, 47.61; H, 4.92; N, 13.05.

Registry No.—1a, 38215-61-1; 1b, 33628-81-8; 2a, 38229-27-5; 2b, 38215-63-3; CAMA, 38215-64-4; 3a, 38215-65-5; 3b, 38215-66-6; 4a, 38215-67-7; 4b, 38215-68-8; 5, 38215-69-9; 6, 38215-70-2; 7, 38215-71-3; 8,

38215-72-4; alaninemethylamide (HCl), 38215-73-5; N-carbobenzoxy-N'-methyloxamide, 38215-74-6; 1methyl-3-ethylhydantoin, 36650-99-4; polymeric Nbenzoylaminoacrylmethylamide, 38193-79-2; Nbenzoyl-O-methylserinemethylamide, 38215-76-8; carbobenzoxyalanylserine methyl ester, 38660-05-8; Ncarbobenzoxyalanyl-O-nitroserine methyl ester, 38660-06-9; N-carbobenzoxyglycylserylglycine ethyl ester, 33660-07-0; N-carbobenzoxyglycyl-O-nitroserylglycine ethyl ester, 38660-08-1.

A Kinetic Study of the Thermal Decomposition of 1,1-Diphenylpropyl Hydrogen Phthalate Ester in Solution

RAPHAEL M. OTTENBRITE, *1 JAMES W. BROCKINGTON,² AND KENNETH G. RUTHERFORD

Department of Chemistry and Pharmaceutical Chemistry, Virginia Commonwealth University, Richmond, Virginia 23220

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The rate of thermal decomposition of 1,1-diphenylpropyl hydrogen phthalate ester, using nmr techniques, was determined in DMSO solution over temperatures ranging from 65 to 92°. The pyrolysis reaction followed first-order kinetics. Values for the activation energy and the entropy of activation were calculated to be 30.2 kcal/mol and 7.3 eu, respectively. This positive entropy is indicative of a heterolytic or homolytic type cleavage and precludes a cyclic transition state for this decomposition. A decrease in rate was observed when the acid ester was converted to the corresponding methyl diester. Further, the reaction was completely curtailed when the acid ester was converted to the sodium salt. It seems evident that the proton of the orthocarboxylate acid function is playing a significant role in the mechanism of the decomposition of tertiary hydrogen phthalate esters, probably by intramolecular hydrogen bonding.

Ester pyrolyses have received a considerable amount of attention, both for their utility in the formation of olefinic compounds as well as for their mode of decomposition.³ In general, the presently accepted mechanism for the decomposition of acetate esters, xanthate esters, and related esters involves a concerted six-membered cyclic transition state.



The above mechanism can only account for ciselimination products, even though there have been instances of varying amounts of trans-elimination products reported.⁴ Briggs and Djerassi⁵ have recently found in their pyrolysis studies of epimeric *cis*- and *trans*-9-methylcyclohexyl-S-methyl xanthates and acetates that the cis isomers yield considerable transelimination product. Kinetic deuterium isotope studies led these authors to propose an ionic mechanism for the net trans-elimination process. This is in agreement with Sixma and coworkers,⁶ who reported predominantly positive entropies of activation for a number of tertiary acetate pyrolyses. In contrast, recent vaporphase ¹⁸O studies by Smith, *et al.*,⁷ with ethyl acetate

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and Kwart and Slutsky⁸ with *tert*-butyl N,N-dimethyl carbamate esters showed an absence of randomization of the ¹⁸O label in the unreacted ester after pyrolysis, thus supporting a concerted transition state in these cases.

Recently, Rutherford⁹ reported the pyrolyses of a new ester system, tertiary hydrogen phthalate esters, which decompose at low temperatures (less than 150°) to yield exclusively olefinic products and phthalic acid. On decomposition of *trans*-1,2-dimethylcyclohexyl hydrogen phthalate, 19% of trans-elimination product was obtained. It was, therefore, suggested that carbonium ion character was evident (at least in part) in the transition state during the pyrolysis. It was further found that *trans*-2-methyl-1-phenylcyclohexyl hydrogen phthalate ester yielded 6% trans product on pyrolysis¹⁰ as well.

We later showed that partial decomposition of ¹⁸Oenriched carbonyl oxygen of the *trans*-1,2-dimethylcyclohexyl hydrogen phthalate ester resulted in the enrichment of ¹⁸O in the alkyl portion of the undecomposed ester.¹¹ This increase in ¹⁸O abundance represents a 17% exchange, which was explained by invoking an ionic intermediate state in the decomposition.

More recently,¹⁰ a detailed kinetic study was made of the decomposition of *cis*- and *trans*-1,2-dimethylcyclohexyl hydrogen phthalate esters and *cis*- and *trans*-2methyl-1-phenylcyclohexyl hydrogen phthalate esters. Pyrolysis of these compounds, both neat and in DMF, showed that the rate-determining step involved ion pair formation.

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1,1-Diphenylpropyl Hydrogen Phthalate Ester



Figure 1.—Nmr spectra showing the decrease in methyl hydrogens (A) of the ester and the increase in methyl hydrogens (B) of the olefin with reaction time.

Simultaneously in our laboratory, a program was carried out to further substantiate ionic character in the low-temperature decomposition of the hydrogen phthalate ester of a tertiary alicyclic system. A system was designed in which a study of the rate of decomposition could be made over a much wider temperature range than previously recorded and which would employ a more effective means than titrimetry to follow the course of reaction. Thus, we wish to report a kinetic study of the thermal decomposition of 1,1-diphenylpropyl hydrogen phthalate ester in DMSO solution, using nmr techniques to determine the rate of decomposition.

Results

The decomposition of 1,1-diphenylpropyl hydrogen phthalate ester in DMSO at moderately low temperatures produces 1,1-diphenylpropene and phthalic acid, nearly quantitatively (98%).



This particular structure was employed for two reasons: first, the two phenyl groups on the alkyl-oxygen carbon should enhance the stability of any carbonium ion character that may be involved in the reaction mechanism; and secondly, the rate of the decomposition could be followed conveniently by nmr techniques. In the latter case, we were able to clearly distinguish between the triplet peak of the methyl group of the ester and the doublet peak of the olefin methyl group of



Figure 2.—Decomposition of 1,1-diphenylpropyl hydrogen phthalate in dimethyl sulfoxide: 65° (\bullet), 75° (\blacktriangle), 80° (\blacksquare), and 92° (\bigcirc).

the decomposition product (Figure 1). The sum of the integration values of these two peaks is always coequivalent to the amount of ester in the original sample, thus affording us with an internal standard to measure relative concentrations at all times during the experiment. The solvent, DMSO, was employed, as it readily dissolved both the reactants and the products, thus giving a homogeneous solution throughout the investigation.

Kinetics.—The rates of reaction were followed by measuring the integration curves for the disappearance of the methyl peak A (δ 0.82) of the hydrogen phthalate ester and the appearance of the methylene peak B (δ 1.7) of the 1,1-diphenylpropene (Figure 1). Stoichiometrically, the sum of the moles of olefin and ester at any time must be equal to the initial amount of ester (E_0) present in the solution. Therefore,

$$\frac{E}{E_0} = \frac{H_a}{H_a + H_b} \tag{1}$$

where E is the number of moles of ester at any time, t, and H_a and H_b are the height of the integrations of peaks A and B, respectively. As the decompositions were carried out under constant volume, the above equation was used to represent the concentration ratio of the solution. Application of this relationship to a first-order rate expression gives

$$\frac{\mathrm{d}E}{\mathrm{d}t} = -kE$$
$$\ln E = -kt + \ln E_0$$
$$\ln \frac{E}{E_0} = -kt$$
$$\ln \frac{H_a}{H_a + H_b} = -kt$$

Plots of $\log H_a/(H_a + H_b)$ vs. time for the decomposition of 1,1-diphenylpropyl hydrogen phthalate ester in DMSO at 65, 75, 80, and 92° (Figure 2) were obtained. It can readily be seen that first-order kinetics is followed in each case. The individual rate constants and averages for three separate runs at each of the four temperatures are listed in Table I.

The rate constants, k, were used in an Arrhenius plot to determine the activation parameters (Figure 3). The energy of activation was calculated to be 30.2 kcal/ mol, and the entropy of activation was determined to



Figure 3.—Arrhenius plot for the decomposition of 1,1-diphenylpropyl hydrogen phthalate in DMSO.

 TABLE I

 The Thermal Decomposition of 1,1-Diphenylpropyl

 Hydrogen Phthalate Ester in Dimethyl Sulfoxide-de

Rate constant				
Temp, °C	$10^{5} k$, sec $^{-1} a$	10^5 SD^b		
65.0	2.46	0.01		
75.0	8.65	0.10		
80.0	15.9	0.3		
92.0	68.0	1.1		

^a Average of three determinations. ^b Standard deviation.

be 7.3 eu. This positive entropy of activation clearly indicates that the mechanism of decomposition involves a heterolytic or homolytic type cleavage, rather than a cyclic transition state that has been generally reported for most ester pyrolyses.

The results of this solution decomposition study directly support the previously postulated ion-pair mechanism proposed for the neat decomposition of tertiary hydrogen phthalate esters.⁹⁻¹¹ It also supports the generalized reaction scheme¹² recently proposed for the



decomposition of these types of compounds in which reaction paths A and B were indicated, based on the per cent ¹⁸O in the reduced phthalic acid from which 2and 4-oxygen equilibration of the phthalate moiety was determined for *cis*- and *trans*-1,2-dimethylcyclohexyl hydrogen phthalate esters. It therefore appears that this decomposition is also occurring heterolytically. Homolytic decomposition of these esters has not been observed but cannot be entirely ruled out and further studies are presently being carried out.

Hydrogen Bond Effects.—Intramolecular hydrogen bonding has been suggested to have some influence on the rate of decomposition of hydrogen phthalate esters;¹³ however, no experimental evidence has been reported. To determine this effect, the acid ester of 1,1-diphenylpropyl hydrogen phthalate was converted to the corresponding sodium salt by reaction with sodium hydride. On heating this salt in DMSO for 40 hr at 65°, there was no indication that decomposition took place under these conditions (although it may be possible to effect decomposition at higher temperatures). There are two possibilities that could explain this inert behavior under our conditions. First, the decomposition may be impeded by the unavailability of the carboxylic hydrogen to stabilize the incipient anion of the ion pair through hydrogen bonding, as shown below, thus indicating that intramolecular hydrogen bonding could be significant.



Secondly, the carboxylate anion moiety is electron donating and consequently adversely affecting heterolytic cleavage of the alkyl-oxygen bond in the ester portion of the molecule.

In order to show that the anion inactivity was not totally due to the electrical effects of the carboxylic anion group, the acid portion of 1,1-diphenylpropyl hydrogen phthalate was methylated with diazomethane. The methyl ester group has similar electrical effects to an acid group but eliminates any hydrogen bonding. It was found that this diester compound did decompose on heating in DMSO but at a rate some 50-fold slower than the acid ester (Table II).

	TABLE II		
Compd	Solvent	Rate constant $10_{\delta} k$, sec $^{-1}$	Relative rate ^a
1,1-Diphenylpropyl hydrogen phthalate	DMSO	68.0	1
1,1-Diphenylpropyl methyl phthalate	DMSO	1.33	0.02
1,1-Diphenylpropyl hydrogen phthalate	Pyridine	15.0	1
1,1-Diphenylpropyl <i>p</i> -nitrobenzoate	Pyridine	1.01	0.07
1,1-Diphenylpropyl sodium phthalate	DMSO	No dec	

^a Relative rates were determined for various compounds in the same solvents.

To further determine the importance of hydrogen bonding and electrical effects, the decomposition of 1,1diphenylpropyl *p*-nitrobenzoate ester was studied. The decomposition again followed first-order kinetics. The reaction rate, compared to that of 1,1-diphenylpropyl hydrogen phthalate ester under the same conditions, was some 14 times slower (Table II). The nitro group is a much stronger electron-withdrawing group than the carboxylic acid group, and so one would expect a rate increase unless hydrogen bonding is in fact having

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1,1-DIPHENYLPROPYL HYDROGEN PHTHALATE ESTER

a decided influence on the course of hydrogen phthalate ester decomposition.

It seems evident from the rates of decomposition of the *p*-nitrobenzoate ester and the methyl phthalate diester of 1,1-diphenylpropanol that intramolecular bonding does play an important role in the decomposition of hydrogen phthalate esters in solution.

Experimental Section

All melting points are uncorrected and were determined in a Thomas-Hoover melting point apparatus. Infared spectra were obtained on a Perkin-Elmer 257. Kinetic studies were performed in a mineral bath, maintained at $\pm 0.1^{\circ}$ by means of a Haake E-51 temperature controller. Kinetic measurements were made on a Varian A-60 nmr spectrometer in precision nmr tubes (507-PP-7 and 504-PP-7) obtained from Wilmad Glass Co. The deuterated solvents were obtained from Merck Sharp and Dohme. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

General Kinetic Procedure.—Ester was analytically weighed and a 0.75 M solution was prepared in dimethyl sulfoxide- d_6 . At the beginning of each run, 0.4 ml of this solution was placed into each of six nmr tubes which immediately were sealed with pressure caps. The tubes were placed simultaneously in the constant-temperature bath. Tubes were withdrawn at appropriate intervals and quenched by plunging the tube into a beaker of crushed ice and water. The tube was allowed to return to room temperature and the nmr analysis was performed. Each nmr signal was integrated six times. The averaged value for $H_a/(H_a - H_b)$ had a mean deviation of less than 1%.

Preparation of 1,1-Diphenylpropanol.-Phenylmagnesium bromide was prepared by adding a solution of bromobenzene (94.2 g, 0.6 mol) and anhydrous ethyl ether (150 ml) to a stirred mixture of magnesium turnings in anhydrous ethyl ether. When reaction was complete, the flask was cooled in an ice-water bath and a solution of propiophenone (67 g, 0.5 mol) in anhydrous ether (100 ml) was added slowly over a period of 1 hr. After refluxing for an additional 30 min, the solution was cooled in an ice bath, and the Grignard complex was decomposed with a saturated aqueous solution of ammonium chloride. The ether layer was separated and the aqueous layer was extracted twice with 100-ml portions of ether. The combined ethereal solution was washed several times with water and then dried over anhydrous magnesium sulfate and filtered. The solution was then concentrated to approximately 200 ml with a rotary evaporator. The addition of petroleum ether (bp 30-60°) brought about the precipitation of a white, crystalline product which was collected by filtration. Recrystallization from ether-petroleum ether gave 97 g (91.5%) of 1,1-diphenylpropanol: mp 90–92° (lit.¹⁴ mp 91–92°); ir (KBr) 3530 (free OH stretch), 1358 (OH bend), and 1165 cm⁻¹ (CO stretch); nmr (CDCl₈, TMS) δ 0.88 (t, 3, J 7 Hz, CH₃CH₂), 2.32 (q, 2, J = 7 Hz, CH₂CH₃), 2.13 (s, 1, OH), and 7.1-7.7 ppm (complex multiplet, 10, aromatic); the peak at 2.13 ppm disappeared upon the addition of D_2O .

Preparation of 1,1-Diphenylpropyl Hydrogen Phthalate Ester.—A solution of methylsulfinyl carbanion in dimethyl sulfoxide¹⁵ was prepared in the following manner. A threenecked flask was fitted with an addition funnel, magnetic stirrer, and condenser, to which was attached a mercury pressure release trap. This apparatus was thoroughly dried and purged with nitrogen. Sodium hydride, 4.2 g (0.10 mol, as a 57% dispersion in oil), and 100 ml of dry dimethyl sulfoxide were added. The flask was heated to 55–65° in an oil bath until the evolution of hydrogen ceased (approximately 1 hr). This solution of methylsulfinyl carbanion was cooled to room temperature, and 1,1-diphenylpropanol (21.2 g, 0.10 mol) in 50 ml of dimethyl sulfoxide was added slowly with stirring. The mixture was stirred for 30 min at room temperature. Phthalic anhydride (14.8 g, 0.10 mol) was then added to the mixture as a solution in dimethyl sulfoxide. This addition produced considerable heat, and the flask was periodically cooled with cold tap water. After the addition of phthalic anhydride was completed, the solution was allowed to stir overnight. Formation of the desired hydrogen phthalate ester was accomplished by pouring the dimethyl sulfoxide solution of the sodium salt of the ester onto a crushed ice-water mixture containing concentrated hydrochloric acid (20 ml). In order to prevent the hydrolysis of the ester, a layer of ether was maintained over the ice-water mixture which was vigorously stirred. As the sodium salt was being poured, the ester was extracted rapidly into the ether layer. The ether layer was separated and the aqueous layer was extracted again with The combined extracts were dried over magnesium sulfate ether. and then concentrated to a small volume on a rotary evaporator. Careful addition of small portions of petroleum ether brought about the precipitation of a solid material (16.5 g, 46%). Recrystallization from benzene-petroleum ether gave a white material: mp 119° dec; ir (KBr) 3440 (broad peak, bonded OH stretch), 2660 and 2540 (OH stretch characteristic of hydrogenbonded carboxylic acids), 1733 and 1710 (CO stretch), and 1305, 1266, 1235, and 1070 cm⁻¹ (CO stretch); nmr (dimethyl sulf-oxide- d_6 , TMS) δ 0.81 (t, 3, J = 7 Hz, CH₃CH₂), 2.96 (q, 2, J =7 Hz, CH₂CH₃), and 7.1-7.9 ppm (m, 14, aromatic).

Anal. Calcd for C₂₃H₂₀O₄: C, 76.63; H, 5.60. Found: C, 76.55; H, 5.65.

Decomposition of Hydrogen Phthalate Esters. Characterization of the Products.—1,1-Diphenylpropyl hydrogen phthalate (1 g) was refluxed for 1 hr in chloroform. The phthalic acid which formed was collected, dried, and weighed (0.46 g, 98% of the theoretical yield), mp 211° dec (lit.¹⁶ mp 210–211° dec). The chloroform was removed *in vacuo* and the resulting solid residue was recrystallized from methanol, yielding 0.54 g (98% of the theoretical yield) of 1,1-diphenylpropene, mp 46–47° (lit.¹⁷ mp 48–48.5°). The olefin produced in the decomposition gave an ir spectra identical with that of a sample produced by the dehydration of 1,1-diphenylpropanol with acid: nmr (CDCl₃, TMS) δ 1.71 (d, 3, J = 7 Hz, CH₃CH), 6.07 (q, 1, J = 7 Hz, CHCH₃), and 7.1–7.6 ppm (m, 10, aromatic).

Preparation of 1,1-Diphenylpropyl-p-nitrobenzoate Ester.-Sodium hydride (2.1 g, 0.05 mol as a 57% dispersion in oil) was added to a reaction flask and the mineral oil was washed from the hydride with small portions of petroleum ether. The petroleum ether was removed by decantation and 150 ml of anhydrous benzene was added with 10.6 g of 1,1-diphenylpropanol. The mixture was allowed to react at refluxing temperature for 4 hr. A solution of p-nitrobenzoyl chloride (9.3 g, 0.05 mol) in anhydrous benzene (100 ml) was added slowly to the reaction flask with constant stirring. After the addition was completed, the contents were stirred for several hours and then filtered. The solution was washed with 5% sodium bicarbonate solution and then dried over anhydrous magnesium sulfate. After the solution was decolorized with charcoal, it was concentrated on a rotary evaporator. The addition of petroleum ether brought about the precipitation of light yellow crystals (11 g, 61%) which melted with decomposition at 135°: ir (KBr) 1735 (CO stretch), 1528 (NO asymmetric stretch), 1350 (NO symmetrical stretch), and 1272 and 1100 cm⁻¹ (CO stretch); nmr (dimethyl sulfoxideand 1212 and 1210 only (construction), min (dimetal) sufficiency d_{d_0} TMS) $\delta 0.82$ (t, 3, J = 7 Hz, CH₃CH₂), 2.96 (q, 2, J = 7 Hz, CH₂CH₃), 7.2–7.7 (m, 1, aromatic), and 8.5 (s, 4, aromatic).

Anal. Calcd for C₂₂H₁₉NO₄: C, 72.94; H, 5.39. Found: C, 73.12; H, 5.30.

Esterification of 1,1-Diphenylpropyl Hydrogen Phthalate.—A freshly prepared ethereal solution of diazomethane was placed in a 250-ml beaker. To this solution was added 7.2 g (0.02 mol) of 1,1-diphenylpropyl hydrogen phthalate dissolved in ether. The disappearance of the yellow color of the ether solution and cessation of effervescence indicated the end of the reaction. The solution was concentrated *in vacuo* and the product was precipitated with petroleum ether. Recrystallization from benzene-petroleum ether yielded 2.1 g (28%) of material: mp 92° dec; ir (KBr) 1753 and 1733 (CO stretch) and 1297, 1274, 1125, and 1072 cm⁻¹ (CO stretch); nmr (CDCl₃, TMS) δ 0.87 (t, 3, J = 7 Hz, CH₃CH₂), 2.95 (q, 2, J = 7 Hz, CH₃CH₂), 3.65 (s, 3, CH₃), and 7.1–8.0 ppm (m, 14, aromatic).

Anal. Caled for $C_{24}H_{22}O_4$: C, 76.77; H, 6.17. Found: C, 76.69; H, 6.03.

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Registry No.—1,1-Diphenylpropanol, 5180-33-6; phthalic anhydride, 85-44-9; 1,1-diphenylpropyl hydrogen phthalate ester, 37817-54-2; p-nitrobenzoyl chloride, 122-04-3; 1,1-diphenylpropyl-*p*-nitrobenzoate ester, 37816-59-4; 1,1-diphenylpropyl hydrogen phthalate methyl ester, 37816-61-8.

Thermolysis of Phenyl Glycosides

FRED SHAFIZADEH,* MAKRAM H. MESHREKI, AND RONALD A. SUSOTT

Wood Chemistry Laboratory, Department of Chemistry and School of Forestry, University of Montana, Missoula, Montana 59801

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Thermal analysis of several series of phenyl glycosides has shown that the pyrolytic cleavage of the glycosic group is facilitated by the participation of free hydroxyl groups in a transglycosidation reaction which releases the aglycone as a free phenol. The thermal stability of these compounds is considerably increased by complete acetylation of the molecule and is affected by the inductive effect of the substituents on both the phenolic aglycone and the sugar moiety.

Thermal cleavage of glycosidic bonds is of special interest in understanding the pyrolytic reactions of the carbohydrates and combustion of cellulosic materials.¹⁻⁷ In our previous studies of this subject, thermal analysis of analogous series of phenyl and substituted phenyl β -p-xylopyranosides,^{4,5} β -p-glucopyranosides, and 2-deoxy- α -D-arabino-hexopyranosides,⁶ selected as model compounds, has shown that the pyrolytic reactions proceed through the cleavage of the glycosidic group. In this process the aglycone group abstracts a proton to form free phenol, which evaporates, and the glycosyl group is condensed mainly as randomly linked oligosaccharides or an anhydro sugar which is decomposed on further heating. As in acid hydrolysis,⁸ thermal cleavage of the aryl glycosides is influenced by the electron-withdrawing effect of the substituent on the phenolic group.^{4,6} Furthermore, phenyl glucopyranoside is more stable than the corresponding 2-deoxyhexopyranoside or xylopyranoside.

These studies have been followed by thermal analysis of several phenyl and substituted phenyl 2-amino-2deoxy- β -D-glucopyranosides, 2-acetamido-2-deoxy- β -Dglucopyranosides, and a variety of acetylated phenyl glycosides to determine the influence of the substituents in the sugar molecule and the availability of free hydroxyl and amino groups.

Results

The thermal analysis of phenyl 2-amino-2-deoxy- β -D-glucopyranoside (**3a**) is shown in Figure 1. The differential thermal analysis (dta), thermogravimetric analysis (tga), and derivative thermogravimetry (dtg) reflect the sequence of physical transformations and chemical reactions as the sugar is heated at a constant rate. As in the case of phenyl- β -D-glucopyranoside,⁶ the first event at 80° is due to dehydration and the amount of water lost depends on previous treatment of the sample. Fresh crystals obtained from ethanolwater solution correspond to the dihydrate and contain 12% water that is lost at this temperature (see the tga curve in Figure 1). Storage in a dry atmosphere or under desiccation results in complete removal of the water. The endotherm at 178° is due to melting. At higher temperatures, these two physical transformations are followed by weight loss due to the cleavage of the glycosidic bond, evaporation of phenol, and decomposition of the sugar moiety. The tga and dtg curves show that the weight loss starts at about 225° and reaches a maximum rate at 284°. The dta curve shows only a slight thermal effect in this region due to the overlapping of endothermic and exothermic reactions. Following the rapid weight loss, there is a slow volatilization which leaves a fairly stable carbonaceous residue of 41% at 400° . This compares with 11% residue obtained from phenyl β -D-glucopyranoside.⁶ The high yield of charred residue is characteristic for amino sugars, O-glycosides, with an amino group either in the aglycone or the glycosyl moiety, and N-glycosides. This aspect of the amino compound will be discussed in a following communication.

The thermal analysis features of phenyl and pbromophenyl 2-amino-2-deoxy- β -D-glucopyranosides (**3a** and **3d**) are summarized in Table I. A comparison of these data with those obtained for the corresponding normal glycosides shows that the decomposition peaks for the amino compounds are about 15° lower and, as noted already, the residues are substantially higher.

The thermogram of phenyl 2-acetamido-2-deoxy- β p-glucopyranoside (2a) is shown in Figure 2. A comparison of this thermogram with Figure 1 shows that, after acetylation of the amino group, the melting point is shifted from 178° to 249° and is closely followed by a rapid decomposition indicated by the dtg peak at 261°.

Table I gives a summary of the dynamic thermal analysis data for a number of 2-acetamido glycosides (2a-g). For these compounds the melting process is accompanied or closely followed by decomposition. Consequently, the dta peak for decomposition is superimposed as a shoulder on the melting point endotherm or appears as an adjoining peak. The maximum rates of decomposition are still shown by distinct dtg peaks, but these show no discernible trend because the decomposition is controlled by physical transition of the crystalline materials to liquid rather than the

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