matic), 4.31 (q, 1, H-3, $J_{2,3}$ = 11, $J_{3,4}$ = 9 Hz), 4.77 (d, 1, H-1, $J_{1,2}$ = 9 Hz), 4.86 (t, 1, H-4, $J_{4,5}$ = 9 Hz), 5.5–5.9 (multiplets, 3), 6.20 (wide m, ca. 20 Hz, 1, H-5), 6.54 (s, 3, OCH_3), 7.92 (s, 3, $COCH_3$), 8.00 (s, 3, $COCH_3$), 8.12 (s, 3, $COCH_3$). Irradiation at τ 4.31 changes the signal at τ 4.86 into a doublet. Irradiation at τ 4.86 changes the signal at τ 6.20 to a triplet (J = ca. 8 Hz) and affects the signal at τ 4.31.

Anal. Calcd for $C_{29}H_{29}NO_{10}$: C, 63.15; H, 5.30; N, 2.54. Found: C, 63.08; H, 5.12; N, 2.48.

B. Compound **6** (12 mg) was dissolved in a mixture of pyridine (2 mL) and acetic anhydride was kept at room temperature overnight. Ice was added to the reaction mixture and after 1 h it was evaporated. The product was crystallized as yellow prisms from ethanol (10 mg), mp 191–192 °C, and was identical by TLC (chloroform) and gave no depression in a mixture melting point with a sample prepared according to procedure A.

***N*-Ethyloxycarbonyl-1,2-diphenylmaleylisoimide (8).** 1,2-Diphenylmaleic anhydride (5 g) and ammonium hydroxide (4 mL, 35%) in dimethylformamide (5 mL) were refluxed for 1 h. The reaction mixture was cooled, another identical portion of ammonium hydroxide was added, and heating was continued after the condenser was removed, to let most of the water evaporate. The starting material was converted predominantly (TLC) into 1,2-diphenylmaleimide. The stirred reaction mixture was then cooled in an ice bath, and triethylamine (2.8 mL) in dimethylformamide was added following by ethyl chloroformate (2 mL). The reaction mixture was brought to room temperature for 1 h, poured into ether, dried over sodium sulfate, evaporated, and applied to a column of "dry" silica gel (100 g, 3 cm in diameter and eluted with chloroform at 15 mL per fraction). Fractions 3–7 contained 1,2-diphenylmaleic anhydride (0.482 g). Fractions 8–23 contained the slightly contaminated compound **9** (2.536 g) that was recrystallized from chloroform–petroleum ether as yellow prisms: mp 108 °C; ν_{max} 1800, 1755, 1715, and 1315 cm^{-1}.

Anal. Calcd for $C_{19}H_{15}NO_4$: C, 71.02; H, 4.71; N, 4.36. Found: C, 70.92; H, 4.72; N, 4.26. Compound **8** could be also crystallized from ethanol as yellow needles: mp 95 °C identical IR spectrum; ^1H NMR τ 2.58 (s, 10, aromatic), 5.52 (q, 2, J = 7 Hz), 8.59 (t, 3, J = 7 Hz, CH_3).

Anal. Calcd for $C_{19}H_{15}NO_4$: C, 71.02; H, 4.71; N, 4.36. Found: C, 71.22; H, 4.57; N, 4.20.

Reaction of Compound 8 with 3α-Aminocholestane. 3α-Aminocholestane hydrochloride (27.3 mg) and compound **8** were stirred in dimethylformamide at 0 °C, triethylamine (0.25 mL) was added, and the stirring was continued for 1 h. The reaction mixture was evaporated and separated by PLC. Compounds identified (in order of increased migration) were ethylurethane (TLC); 1,2-diphenylmaleimide (15.5 mg, TLC, IR, NMR); compound **8** (8.3 mg, TLC, IR); 3α-ethyloxycarbonylaminocholestane (**9**, 19.3 mg), recrystallized from ethanol as very thin needles [mp 125–126 °C $[\alpha]^{21}_D$ +29.5° (*c* 0.11); ^1H NMR τ 5.18 (1, NH), 5.90 (q, 2, J = 7.0 Hz, CH_2O), 6.16 (m, 1, H-3), 8–9.4 (steroid "envelope" containing CH_3 signals at 9.10, 9.20, and 9.38)].

Anal. Calcd for $C_{30}H_{53}NO_2$: C, 78.37; H, 11.62; N, 3.05. Found: C, 78.30; H, 11.46; N, 3.05.

Compound 1 (3.9 mg, TLC).

Removal of the 1,2-Diphenylmaleyl Protecting Groups. A. Compound 1 (106 mg) was left at reflux in a solution of hydrazine hydrate (0.2 mL) in ethanol (5 mL) whereby it gradually dissolved. After 4 h the reaction mixture was evaporated and the residue was dissolved in pyridine (2 mL) and acetic anhydride (1 mL) and left at room temperature overnight. Ice was added and after 1 h the reaction mixture was extracted with ether, washed with dilute hydrochloric acid, water, and sodium hydrogen carbonate, dried over sodium sulfate, evaporated, and purified by PLC to give 3α-acetamidocholestane (42.8 mg, 65%), mp 193–205 °C. The product recrystallized as needles from ethanol: mp 218 °C; $[\alpha]^{23}_D$ +35.3° (*c* 0.31) (lit.[6] mp 216 °C, $[\alpha]_D$ +33°); ν_{max} 3440, 2910, 2850, and 1660 cm^{-1}.

B. Compound **7** was refluxed for 1 h in an ethanolic hydrazine solution and then acetylated as above. TLC (ethyl acetate) showed only one compound that was charred by sulfuric acid. Methyl 2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-β-D-glucopyranoside was isolated from PLC (ethyl acetate, 46.1 mg, 71%). It was recrystallized as needles from ethanol, mp 162 °C (ethyl acetate–petroleum ether, mp 156 °C), $[\alpha]^{21}_D$ −20.9° (*c* 0.12, methanol) (lit.[7] mp 163 °C, $[\alpha]^{21}_D$ −22.2° in methanol).

Anal. Calcd for $C_{15}H_{23}NO_9$: C, 49.86; H, 6.42; N, 3.88. Found: C, 49.52; H, 6.17; N, 3.81.

Acknowledgment. The author is grateful to Professor Sir D. H. R. Barton, F.R.S., for his discussions and encouragement and would like to thank Dr. W. Motherwell for a gift of 3α-aminocholestane and Dr. S. Narang for a gift of a mixture of 3α- and 3β-aminocholestane.

Registry No.—**1**, 62460-40-6; **2**, 62493-02-1; **3**, 62461-73-8; **4**, 62461-74-9; **4** 1-bromo derivative, 62461-78-3; **5**, 62461-75-0; **6**, 62461-76-1; **7**, 62448-72-0; **8**, 62461-77-2; **9**, 62493-03-2; 3α-aminocholestane, 62560-52-5; 1,2-diphenylmaleic anhydride, 4808-48-4; 3β-aminocholestane, 62532-40-5; 2-amino-2-deoxy-D-glucose HCl, 66-84-2; ethyl chloroformate, 541-41-3; 3α-aminocholestane HCl, 62532-41-6; 1,2-diphenylmaleimide, 31295-36-0; 3-acetamidocholestane, 16356-49-3; methyl 2-acetamido-2-deoxy-3,4,6-triacetyl-β-D-glucopyranoside, 2771-48-4.

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Photochemical Reactions of Phenylglyoxalyl Amides

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Phenylglyoxalyl amides undergo a photochemical oxidation–reduction that, after acid hydrolysis, converts the amino residues of the amides to the corresponding carbonyl derivatives. The procedure is applied to the conversion of cyclohexylamine, amino sugars, and steroidal amines to the corresponding carbonyl compounds. A convenient synthesis of phenylglyoxalyl amides is through the ozonolysis and partial trans acylation of 1,2-diphenylmaleimides. This presents an example of utilizing the 1,2-diphenylmaleyl (DPM) derivative as a *reactive protecting group*.

Phenylglyoxalic acid esters undergo an intramolecular photochemical redox reaction in which the alcohol moiety of the ester is oxidized.[1,2] Phenylglyoxalic acid amides could be expected to undergo an analogous reaction, possibly through a similar $n \rightarrow \pi^*$ excited state as indicated in Scheme I.

This reaction could prove to be useful in polyfunctional molecules where acylation (and thus the formation of the corresponding phenylglyoxylic acid amide) may be directed

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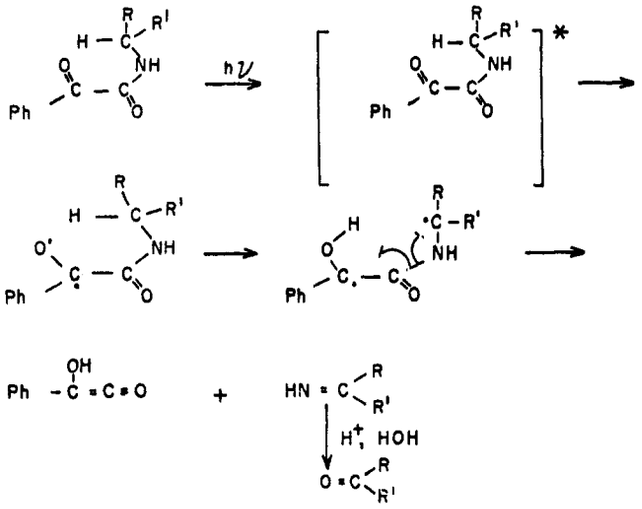
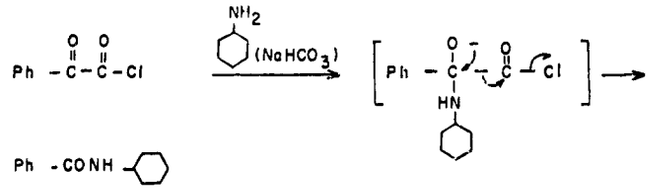
Scheme I



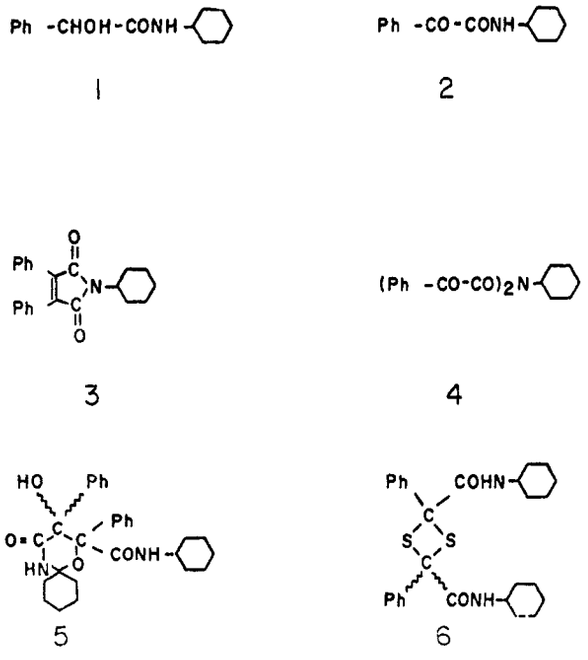
selectively to nitrogen. The net result would be the synthetic operation of converting primary amines to the corresponding carbonyl derivatives.[3]

In our first attempt to prepare phenylglyoxalyl-*N*-cyclohexylamide, starting from phenylglyoxalyl chloride[4] and cyclohexylamine under Schotten–Baumann conditions, decarbonylation took place and benzoyl-*N*-cyclohexylamide was isolated (Scheme II). Alternative routes to phenylglyoxalic

Scheme II



acid amides were sought and they have been prepared through (a) the oxidation of the mandelic acid amide (thus compound 1 was oxidized with permanganate[5] to compound 2); or (b)



through the ozonolysis[6] of 1,2-diphenylmaleyl imides and via bisphenylglyoxalylimides. Thus compound 3 was ozonolyzed to yield compound 4 which, in turn, could be selectively deacylated to give compound 2.

Table I. Irradiation of Compound 2 (0.066 M, Ambient Temperature) in Different Solvents

Solvent	Yield of cyclohexanone, %[a]	Solvent	Yield of cyclohexanone, %[a]
Acetone	25	*tert*-Butyl alcohol	10
Acetonitrile	14	Ethanol	25–46[c]
Benzene	16[b]	Ether	18

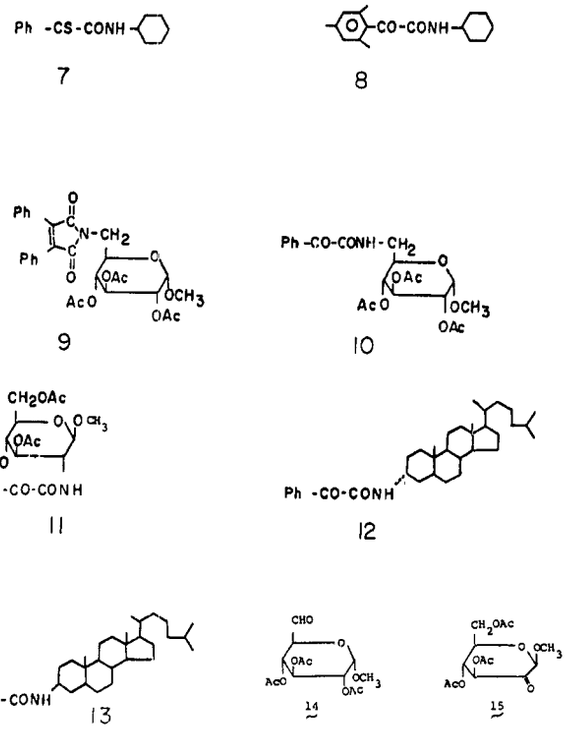
[a] Irradiation times were 100 or 120 min, longer than necessary for the disappearance of compound 2 (TLC) and with no noticeable difference. The solution was subsequently acidified with a drop of 3 N hydrochloric acid and cyclohexanone was determined a few minutes later by GC. [b] Benzaldehyde (3%) was also determined. [c] Irradiation at reflux temperature did not improve the yield; irradiation without the exclusion of air or even with bubbling oxygen did not alter the yield.

Irradiation of compound 2 in a variety of solvents provided cyclohexanone in low yields with ethanol being the choice solvent for the reaction (Table I). Examination of the nonvolatile products from a reaction in ethanol resulted in the isolation of three of them: compound 1 and two products (B and C) to which structure 5 is tentatively assigned.

In an attempt to obtain similar results but employing lower energy irradiations, compound 7 was made alongside the dimer 6 from the corresponding Bunte salt $PhCH(CONHC_6H_{11})S{-}SO_3Na$, by a procedure similar to the one described for thiobenzoylcarboxylic acid ethyl ester.[7] In distinction from the ester, compound 7 is stable in the solid state for months. In chloroform solution, however, it tends to dimerize to compound 6 (TLC). Irradiation of compound 7 with a tungsten lamp failed to yield more than traces of cyclohexanone and mostly led to dimerization.

Several routes were tried in order to improve the cyclohexanone yield from the irradiation of compound 2. Thus, compound 8 was designed to inhibit the extent of dimerization through steric hindrance. It was synthesized by a Friedel–Crafts reaction with mesitylene using (presumably) $(ClCOCO)_2NC_6H_{11}$ as an intermediate. Unfortunately, the substitution on the benzene ring inhibited also the photochemical reaction—no reaction was obtained. It was then considered that since, in the proposed mechanism for the photochemical reaction (Scheme I) a crucial step is the homolytic cleavage of the amide C–N bond and since, in distinction from the ester case, this should have had a partial double bond character that could be expected to retard such a homolytic cleavage, an appropriate electron-withdrawing substitution on the nitrogen could improve the yield. Compound 4 was an obvious choice where an additional (electron-withdrawing) phenylglyoxalyl group is situated on nitrogen and could also increase the probability of the required hydrogen abstraction in the photochemical reaction. This compound, however, presented no advantage over compound 2. An alternative approach was to include aqueous mineral acids in the irradiation mixture; this, in addition, should have hydrolyzed the intermediate imine to the desired ketone. In fact, including mineral acids proved to be very satisfactory and compound 2 was converted into cyclohexanone in 77% yield.

Encouraged by these results, we have prepared a few phenylglyoxalic acid amides, compounds 10–13, through the ozonolysis of the corresponding DPM derivatives and selective deacylation. Compound 10 was transformed in low yield to the 6-aldehydo intermediate 14 and identified (compare ref 8) after sodium borohydride reduction and acetylation as methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glycopyranoside or as the *p*-ni-



trophenylhydrazone. Compound **11** was converted by irradiation to the 2-keto derivative **15** that was not isolated (compare ref 9) but reduced and hydrolyzed to a mixture of D-glucose and mannose. More suitable conditions designed to circumvent side reactions and to isolate the carbonyl product are being considered.

Compounds **12** and **13** yielded, upon irradiation, 51 and 59% of 3-cholestanone demonstrating the synthetic usefulness of the photolysis of phenylglyoxalyamides in converting primary amines to carbonyl derivatives (at least in cases where complication is not expected).

Phenylglyoxalyl itself could serve as a protecting group for amines in certain synthetic operations. The DPM group, however, is much more suited for this purpose.[10] At the appropriate stage of synthesis it can be made reactive by converting it to phenylglyoxalyl, whose photochemistry is the subject of this paper.

Experimental Section

Experimental details are as described in the preceding paper.[10] In addition, GC was carried out employing a Perkin-Elmer F 11 instrument and a column of 8% Carbowax 1540 on Chromosorb W AW DMCS, 80–100 mesh, 0.125 in. in diameter and 2 m long. All irradiations, unless otherwise mentioned, were carried out at room temperature, under argon with a 250-W high-pressure mercury lamp through a Pyrex filter and irradiation times were longer than necessary for the complete conversion (TLC) of the starting material. Descending paper chromatography was carried out on Whatman No. 1 paper developed with 1-butanol–ethanol–water (4:1:1, I) or with 1-butanol–acetic acid–water (25:6:25, upper phase, II) and chromatographs were sprayed with an *m*-phenylenediamine reagent.[11]

Benzoyl-*N*-cyclohexylamide. A solution of cyclohexylamine (2.5 mL) and of sodium hydrogen carbonate (3.0 g) in water (50 mL) was stirred in an ice bath. Phenylglyoxalyl chloride[4] (3.0 g) was added slowly and the stirring was continued at room temperature overnight. The white, amorphous product was collected by filtration (4.4 g, mp 147–151 °C) and recrystallized from ethyl acetate to yield prisms, mp 151 °C (lit.[12] mp 153 °C).

Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.59; H, 8.22; N, 6.85.

α-Hydroxy-α-phenylacetyl-*N*-cyclohexylamide (1). This was prepared according to the general procedure of Shapiro, Rose, and Freedman[13] starting from mandelic acid ethyl ester (10 g) and cyclohexylamine (5.8 mL). The title compound **1** was crystallized from a mixture of ethanol and water to give leaflets: mp 95 °C (7.0 g); ν_{max} 1665 cm^{-1} (C=O); ^1H NMR τ 2.66 (narrow m, 5, aromatic), 5.01 (d, 1, benzylic, J = 4 Hz), 6.20 (d, 1, NH, J = 4 Hz), 6.28 (m, 1, cyclohexyl H), 7.8–9.2 (m, 10). The signal at τ 6.20 disappears upon the addition of D_2O and the one at τ 5.01 collapses to a singlet.

Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.20; N, 6.00. Found: C, 72.11; H, 8.11; N, 5.90.

Phenylglyoxalyl-*N*-cyclohexylamide (2). A. Compound **1** (9.2 g) in ether (300 mL) was stirred mechanically together with a solution of dihydrogen phosphate (dihydrate, 76 g) in a saturated aqueous solution of magnesium sulfate (48 mL) in an ice bath. Potassium permanganate (5.3 g) was added and the reaction mixture was allowed to reach room temperature. Following the disappearance of the purple permanganate color (checked by applying a drop to a filter paper), water (40 mL) and another portion of potassium permanganate were added. TLC indicated a partial reaction. The ether solution was separated, washed with water, dried over sodium sulfate, and evaporated. The residue was applied to a column of silica gel (100 g, 2.5 cm in diameter) and the crystalline product, pure by TLC (chloroform), was eluted with ethyl acetate–chloroform (3:2, 1.4 g), mp 75–80 °C. The title compound **2**, needles from chloroform–petroleum ether, had mp 112 °C; ν_{max} (carbon tetrachloride) 1670 and 1695 cm^{-1}; λ_{max} 253 nm (ϵ 1.10 × 10^4); ^1H NMR τ 1.2–1.9 (m, 2), 2.2–2.9 (m, 3), 6.18 (m, 1 cyclohexyl H), 7.6–9.1 (m, 10).

Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.69; H, 7.41; N, 6.06. Found: C, 72.79; H, 7.33; N, 5.96.

Further fractions from the column chromatography contained a mixture of compounds **1** and **2** (0.3 g) and pure compound **1** (5.9 g).

B. Sodium methoxide (10 mL, 0.15 M in methanol) was added to a methanolic solution (10 mL) of compound **4** (91 mg) at 0 °C. The reaction was stopped after 10 min by stirring and neutralizing with excess Amberlite IR 120 (H^+ form). The resin was removed, the solution was evaporated, and the residue was purified by PLC and the product crystallized as needles (49 mg, 84%), mp 111–112 °C (Found: C, 72.49; H, 7.50; N, 5.79). Compound **2** was alternatively prepared from compound **4** by dissolving the later in pyridine–water (5:1) and keeping it overnight at room temperature.

1,2-Diphenylmaleyl-*N*-cyclohexylimide (3). 1,2-Diphenylmaleic anhydride[14] (0.5 g) in toluene–dimethylformamide (3:1, 40 mL) and cyclohexylamine (0.2 mL) were left for reflux under nitrogen for 3 h. The solvents were evaporated and the residue was crystallized from ethanol to give the title compound as yellow, fluorescent needles: mp 160–161 °C (0.48 g, 72%); λ_{max} 278 nm (ϵ 9.80 × 10^3) and 365 (3.76 × 10^3); ^1H NMR τ 2.47 (narrow m, 10, aromatic), 8.20 (m, 11, cyclohexane).

Anal. Calcd for $C_{22}H_{21}NO_2$: C, 79.73; H, 6.39; N, 4.23. Found: C, 79.52; H, 6.15; N, 4.10.

Bisphenylglyoxalyl-*N*-cyclohexylimide (4). Compound **3** (0.55 g) was dissolved in acetone (20 mL) and propionaldehyde was added (5 mL). Ozone in oxygen was bubbled through the solution at −78 °C until the disappearance of the yellow color. The solution was then evaporated at room temperature and the title compound was crystallized as prisms (0.46 g, 77%) from ethanol: mp 98 °C; ν_{max} 2900, 2850, 1755 (low), and 1700 cm^{-1} (high); λ_{max} 260 nm (shoulder, ϵ 1.90 × 10^3) and 266 (shoulder, ϵ 1.56 × 10^3) increasing absorbance 240–200 nm; ^1H NMR τ 2.48 (m, 10, aromatic), 7.4–9.2 (m, 11).

Anal. Calcd for $C_{22}H_{21}NO_4$: N, 3.85. Found: N, 3.77.

Nonvolatile Products from the Irradiation of Compound 2. Compound **2** (186 mg) in ethanol (15 mL) was irradiated for 2 h. The reaction mixture was evaporated and separated by PLC (benzene) and three bands, in order of decreased polarity, were isolated: A, oil, 78 mg, impure component containing compound **1** (TLC and IR); B, oil, 38 mg (21%), that could be crystallized from methanol–water [mp 129–130 °C; ν_{max} 3500 (wide, OH), 3390 (sharp, NH), 3250 (CH), 1650 (CO), 1600, 1550 cm^{-1}; the ^1H NMR had no benzylic proton, τ 2.2–2.8 (m, aromatic), 2.81 (apparent s, aromatic), 6–7 (multiplets), 7.9–9.0 (cyclohexyl envelope)]; C, 31.4 mg (17%), elongated prisms [mp 189–190 °C; IR very similar to that of B with variation in the "fingerprint" area; the ^1H NMR had no benzylic proton, τ 1.9–2.8 (m, aromatic), 2.81 and 2.82 (apparent singlets, aromatic), 3.91 (wide m), 6.23 (wide m), 7.7–9.0 (cyclohexyl envelope)].

Anal. Calcd for $C_{28}H_{34}N_2O_4$: C, 72.69; E, 7.41; N, 6.06. Found: C, 72.70; H, 7.45; N, 5.97.

The mass spectra of compounds B and C were very similar: *m/e* 463 (M + 1), 462 (M), 338, 336 ($C_{21}H_{22}NO_3^+\cdot$, M − $C_6H_{11}NHCO$), 233 (PhCHOH − $CONHC_6H_{11}^+\cdot$), 105 ($PhCO^+$), 98 and 77 ($Ph^+\cdot$). Compounds B and C were stable in ethanol solution. Upon acidification and GC (as described in Table I) cyclohexanone was released at 25 and 28% yield, respectively (theory 50%).

2,4-Di(*N*-cyclohexyl)carbamyl-2,4-diphenyldithietane (6) and Thiobenzoylcarboxylic Acid *N*-Cyclohexylamide (7). Sodium

thiosulfate (pentahydrate, 3 g) was dissolved in water (30 mL). Dimethylformamide (100 mL) and α-phenyl-α-chloroacetyl-*N*-cyclohexylamide (2.51 g) were added to form a homogenous solution. The reaction mixture was left at reflux for 3 h. The solution was evaporated and the residue dissolved in water (300 mL) and washed with ether. Chloroform (300 mL) and sodium hydroxide solution (10%, 150 mL) were then added, the mixture was vigorously shaken, and the blue chloroform solution quickly separated. It was washed with water, dried over sodium sulfate, and evaporated at room temperature. The residue was extracted with benzene (15 mL) and a white precipitate (compound **6**, 0.125 g) formed upon the addition of petroleum ether (10 mL). Recrystallized from chloroform the amide **6** formed needles: mp 236 °C; ν_{max} 3300 (NH), 2910 and 2850 (CH), and 1660 cm^{-1} (CO); λ_{max} 315 nm (ϵ 3.58 × 10^2) and 250 (shoulder, 6.02 × 10^3); mol wt 446 (osmometry in chloroform) (required 494.70).

Anal. Calcd for $C_{28}H_{34}N_2O_2S_2$: C, 67.97; H, 6.93; N, 5.66; S, 12.96. Found: C, 67.76; H, 6.67; N, 5.57; S, 13.04. This compound is many times accompanied by a slower moving component that could represent a trimer. The benzene–petroleum ether solution described above was concentrated and compound **7** was allowed to crystallize as blue, elongated prisms: mp 106 °C (loses the color); ν_{max} (carbon tetrachloride) 3400 (NH), 2930 and 2850 (CH), 1670 (CO), 1500 (NH), and 1130 cm^{-1} (C=S, the only significant absorbance that does not have its equivalent in compound **2**); λ_{max} 615 nm (ϵ 45.5), 330 (6.29 × 10^3), and 264 (5.54 × 10^3).

Anal. Calcd for $C_{14}H_{17}NOS$: C, 67.97; H, 6.97; N, 5.66. Found: C, 67.66; H, 6.80; N, 5.33. Only part of compound **7** crystallized as described. Most of it stayed in the mother liquor. Attempted fractionation on silica gel, using benzene for elution, brought about the partial conversion to compound **2**. Yield 0.375 g (15%, compounds **7** and **2**).

A solution of compound **7** (λ_{max} 615 nm, A = 0.3) was left at room temperature for 18 h. As the result the absorbance went down by 35% and the formation of the dimer **6** was evident (TLC).

Irradiation of Compounds 6 and 7. Compound **6** (6.6 mmol) in chloroform was irradiated for 2 h with a 750-W tungsten lamp. No reaction was observed (TLC and GC). Similar irradiation (4 h) was carried out on a chloroform solution of compound **7** (λ_{max} 615 nm, A = 0.1). Only a trace amount of cyclohexanone was formed and compound **7** dimerized and produced also a slower moving compound that could be a trimer (TLC).

2,4,6-Trimethylphenylglyoxalyl-*N*-cyclohexylamide (8). Cyclohexylamine (2.88 mL) in carbon tetrachloride (20 mL) was added slowly to a stirred solution of oxalyl chloride (5 mL) in carbon tetrachloride (20 mL) at −10 °C. After the initial exothermic reaction, the reaction mixture was refluxed for a few hours and evaporated. Mesitylene (8.4 mL) and dichloromethane (30 mL) were added and the stirred solution was cooled in a salt–ice bath. Stannic chloride (5 mL) was added dropwise for 30 min and the reaction mixture was stirred for an additional 2 h at 0 °C. It was then poured into dilute hydrochloric acid, extracted with ether, washed with water, and dried over sodium sulfate. Following evaporation, the residue was applied to a column of silica gel (100 g, 2.5 cm in diameter) and eluted with benzene–chloroform (1:1). The title compound **8** (0.556 g) emerged after 450 mL and was further purified by PLC (benzene–chloroform, 1:1). Recrystallization from chloroform–petroleum ether gave elongated prisms (0.153 g): mp 173–174 °C; ν_{max} 3380 (NH), 2920 and 2850 (CH), 1710 and 1670 (CO), and 1600 cm^{-1}.

Anal. Calcd for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.47; N, 5.12. Found: C, 74.63; H, 8.36; N, 5.30.

Irradiation of Compound 8. The irradiation was carried out in ethanol under the conditions specified in Table I and up to 16 h. No reaction was observed by TLC or by GC.

Irradiation of Compound 4 and the Irradiation of Compound 2 in the Presence of Mineral Acids. The irradiations were carried out as specified in Table I; compound **4** in ethanol and compound **2** in ethanol–aqueous 3 M hydrochloric acid (5:1) or in ethanol–aqueous 10% sulfuric acid (4:1). Yields of cyclohexanone were 25–30, 61, and 77%, respectively.

Methyl 6-deoxy-6-(1,2-diphenylmaleylimido)-2,3,4-tri-*O*-acetyl-α-D-glucopyranoside (9) was prepared as described for 2-deoxy-2-(1,2-diphenylmaleylimido)-1,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside[10] but starting from crude methyl 6-amino-6-deoxy-α-D-glucopyranoside[15] (0.634 g). The product was purified by chromatography on a column of "dry" silica gel (20 g, 1 cm in diameter and eluted with chloroform at 6 mL per fraction). Collection started when a yellow color emerged and fractions 9–21 contained compound **9**: yellow glass (0.954 g, 52%); $[\alpha]^{20}_D$ +114.5° (c 0.13); ν_{max} 1745, 1705, 1600 (weak), 1360, 1105, and 1005 cm^{-1}; λ_{max} 273 nm (ϵ 9.19 × 10^3) and 365 (4.26 × 10^3); ^{1}H NMR τ 2.62 (m, 10, aromatic), 4.57, 5.84, and 6.17 (multiplets, 5), 5.03 (narrow m, 2), 6.66 (s, 3, OCH_3), 7.95 (s, 6, $COCH_3$), 8.00 (s, 3, $COCH_3$).

Anal. Calcd for $C_{29}H_{29}NO_{10}$: N, 2.57. Found: N, 2.30.

Methyl 6-Deoxy-6-phenylglyoxalamido-2,3,4-tri-*O*-acetyl-α-D-glucopyranoside (10). Compound **9** (0.771 g) was ozonolyzed as described in the preparation of compound **4** and the residue was dissolved in pyridine (7 mL)–water (4 mL). The reaction mixture was kept at room temperature overnight, evaporated from a 30 °C bath, and purified on a column as described for compound **9**. The product (0.630 g, quantitative yield) was a slightly contaminated oil. The title compound **10** crystallized as needles from ethyl acetate–petroleum ether: mp 119 °C; $[\alpha]^{20}_D$ +140.0° (c 0.23); ν_{max} 3400 (weak), 1740, 1670, 1600 (weak), and 1370 cm^{-1}; λ_{max} 266 nm (ϵ 1.24 × 10^4); ^{1}H NMR τ 1.79 (m, 2, aromatic), 2.60 (m, 3, aromatic), 4.63, 5.10, 5.17, 6.08, and 6.40 (multiplets, 8, including a 2 H narrow m at 5.10), 6.62 (s, 3, OCH_3), 7.92 (s, 3, $COCH_3$), 7.95 (s, 3, $COCH_3$), 8.03 (s, 3, $COCH_3$).

Anal. Calcd for $C_{21}H_{25}NO_{10}$: C, 55.87; H, 5.58; N, 3.10. Found: C, 55.81; H, 5.56; N, 3.07.

Methyl 2-Deoxy-2-phenylglyoxalylamido-3,4,6-tri-*O*-acetyl-β-D-glucopyranoside (11). This compound was prepared by ozonolysis and deacylation of methyl 2-deoxy-2-(1,2-diphenylmaleylimido)-3,4,6-tri-*O*-acetyl-β-D-glucopyranoside[10] as described for compound **10**. Evaporation of the pyridine solution and recrystallization from ethyl acetate–petroleum ether afforded the title compound as needles: mp 194 °C; $[\alpha]^{30}_D$ −2.6° (c 0.15); ν_{max} 3390 (wide), 1745, 1670, 1690 (shoulder), 1595, and 1365 cm^{-1}; λ_{max} 262 nm (ϵ 1.19 × 10^4); 100-MHz ^{1}H NMR τ 1.74 (m, 2, aromatic), 2.56 (m, 3, aromatic), 4.56 (q, 1, H-3, $J_{2,3}$ = 10 Hz, $J_{3,4}$ = 9 Hz), 4.91 (t, 1, H-4, $J_{4,5}$ = 9 Hz), 5.29 (d, 1, H-1, $J_{1,2}$ = 8.5 Hz), 5.6–6.3 (4 H, multiplets), 6.50 (s, 3, OCH_3), 7.93 (3 H, s, $COCH_3$), 8.00 (3 H, s, $COCH_3$), 8.04 (3 H, s, $COCH_3$). Assignments were made in analogy to the ones in the starting material.

Anal. Calcd for $C_{21}H_{25}NO_{10}$: C, 55.87; H, 5.58; N, 3.10. Found: C, 55.74; H, 5.55; N, 3.05.

3α-Phenylglyoxalylamidocholestane (12). 3α-(1,2-diphenylmaleimido)cholestane[10] (0.335 g) and propionaldehyde (10 mL) were dissolved in acetone (40 mL) and ozone in oxygen was bubbled through the solution at −78 °C. Since some of the starting material crystallized out the bubbling was stopped, the solution was brought to room temperature, the precipitate was dissolved, the reaction mixture was cooled again to −78 °C, and the bubbling was continued. This procedure had to be repeated four times before the yellow color disappeared. The solution was then evaporated at room temperature, and the residue was dissolved in pyridine (15 mL)–water (4 mL) and was kept overnight at room temperature. The reaction mixture was evaporated, extracted with ether, washed with dilute hydrochloric acid, water, and sodium hydrogen carbonate, dried over sodium sulfate, and evaporated. The oily residue (0.258 g, 92%) contained only traces of impurities and was crystallized to give the title compound **12** as an amorphous solid from ethanol–ethyl acetate: mp 163 °C; $[\alpha]^{21}_D$ + 35.9° (c 0.17); ν_{max} 3400, 2900, 2850, 1665, 1600, 1450 cm^{-1}; λ_{max} 260 nm (ϵ 1.44 × 10^4); ^{1}H NMR τ 1.68 (m, 2, aromatic), 2.60 (m, 3, aromatic), 5.67 (m, 1, H-3, 100 MHz, half-height width 18 Hz), 7.8–9.4 (steroid "envelope" containing CH_3 signals at 9.10, 4.17, and 9.37).

Anal. Calcd for $C_{35}H_{53}NO_2$: C, 80.87; H, 10.27; N, 2.69. Found: C, 81.08; H, 10.32; N, 2.60.

3β-Phenylglyoxalylamidocholestane (13). 3β-(1,2-Diphenylmaleylimido)cholestane[10] (59 mg) and propionaldehyde (2.0 mL) were dissolved in carbon tetrachloride (20 mL) and ozone in oxygen was bubbled through at 0 °C till the yellow color disappeared. The solution was evaporated and treated as described for compound **12**. The product was further purified by PLC (benzene–petroleum ether, 1:2) and was crystallized from ethanol–ethyl acetate to give the title compound as prisms (23.5 mg, 46%): mp 145–146 °C; $[\alpha]^{20}_D$ +27.2° (c 0.05); ν_{max} 3395, 2910, 2850, 1665, and 1600 cm^{-1}; λ_{max} 269 nm (ϵ 1.54 × 10^4); ^{1}H NMR τ 1.5–1.74 (m, aromatic), 2.2–2.64 (m, aromatic), 6.22 (m, H-3), 7.8–9.5 (steroid "envelope" including CH_3 signals at 9.10, 9.16, 9.35).

Anal. Calcd for $C_{35}H_{53}NO_2$: C, 80.87; H, 10.27; N, 2.69. Found: C, 80.92; H, 10.22; N, 2.59.

Irradiation of Compound 10. Compound **10** (63 mg) in ethanol (30 mL) containing aqueous hydrochloric acid (3 mL, 3 N) was irradiated for 2 h resulting in the complete disappearance of the starting material (TLC). The reaction mixture was neutralized with lead carbonate and filtered through a Celite filter and the filter washed with additional ethanol (total ca. 100 mL).

A. Sodium borohydride (250 mg) was added to the reaction mixture and kept at 4 °C overnight. It was then neturalized with acetic acid, evaporated, and dissolved in pyridine (30 mL)–acetic anhydride (10

mL) and kept overnight at room temperature. Ice was added to the mixture and after 2 h the solution was evaporated. The residue was dissolved in chloroform, washed with water, and purified by PLC. Methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (1.5 mg, 3%) was isolated, identical in TLC and IR with an authentic sample.[16] Two slower moving components (acetate signals but no *O*-methyl) were also isolated from the same PLC.

B. The solution was evaporated, and methyl 2,3,4-tri-*O*-acetyl-α-D-gluco-1,6-dialdohexo-1,5-pyranoside *p*-nitrophenylhydrazone was prepared[17] and purified by PLC (chloroform–methanol, 9.8:0.2) to give a yellow, crystalline product (6.4 mg, 10%), possessing the expected ^{1}H NMR, mp 126 °C (lit.[17] mp 126–128 °C).

Irradiation of Compound 11. Compound 11 was irradiated as described for compound **10**. Water (15 mL) and platinum oxide (40 mg) were added to the solution and the mixture was shaken overnight under hydrogen at room temperature and atmospheric pressure. The solution was neutralized with calcium carbonate, filtered, and evaporated. Barium methoxide (0.1 M, 25 mL in methanol) was added to the residue and the solution was left for 7 h at room temperature. It was then neutralized with carbon dioxide, filtered, and evaporated. Following this, the residue was extracted with water (10 mL), hydrochloric acid was added (3 N, 10 mL), and the acid solution was left under reflux overnight. It was then neutralized with a mixture of Amberlite IR 120 (H^+ form) and IR 4B (OH^- form), evaporated, and dissolved in water (3 mL). The solution gave a positive reaction with Clinistix (Ames laboratories, a glucose oxidase–peroxidase strip). Glucose and mannose were detected by paper chromatography (solvent systems I and II); they were isolated from preparative paper chromatography (solvent I and solvent II) and determined by the phenol–sulfuric acid test. Average yields follow: glucose, 6.9%; mannose, 4.0%.

Irradiation of Compound 12. Compound **12** (46 mg) was dissolved in benzene (4 mL)–ethanol (6 mL) and sulfuric acid (10%, 1 mL) was added. Irradiation was carried out for 3 h. The solution was diluted with ether (300 mL), washed with dilute hydrochloric acid, water, and saturated sodium hydrogen carbonate, dried over sodium sulfate, and evaporated. The product, 3-cholestanone, 17.2 mg (51%), a white solid, was isolated from PLC (chloroform) following detection with iodine. It was recrystallized from ethanol, mp 131–132 °C, $[\alpha]^{30}_D$ +41.0° (*c* 0.13) (lit.[18] mp 128–129 °C, $[\alpha]^{20}_D$ +43.7°). The product was identical with an authentic sample in TLC (chloroform), IR, and a mixture melting point.

Anal. Calcd for $C_{27}H_{46}O$: C, 83.87; H, 11.99. Found: C, 83.99; H, 12.11.

Irradiation of Compound 13. Compound **13** (46 mg) was treated as described for compound **12** yielding 3-cholestanone (20.3 mg, 59%) as prisms, mp 127–128 °C, $[\alpha]^{20}_D$ +40.5° (*c* 0.26), identical with an authentic sample by TLC, which gave no depression of a mixture melting point (Found: C, 83.98; H, 11.96).

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Registry No.—**1**, 62448-60-6; **2**, 724-92-5; **3**, 62448-61-7; **4**, 62448-62-8; **5**, 62448-63-9; **6**, 62448-64-0; **7**, 62448-65-1; **8**, 62448-66-2; **9**, 62448-67-3; **10**, 62448-68-4; **11**, 62448-69-5; **12**, 62448-70-8; **13**, 62448-71-9; benzoyl-*N*-cyclohexylamide, 1759-68-8; cyclohexylamine, 108-91-8; phenylglyoxalyl chloride, 25726-04-9; mandelic acid ethyl ester, 774-40-3; 1,2-diphenylmaleic anhydride, 4808-48-4; α-phenyl-α-chloroacetyl-*N*-cyclohexylamide, 40934-39-2; oxalyl chloride, 79-37-8; mesitylene, 10867-8; methyl 6-amino-6-deoxy-α-D-glucopyranoside, 5155-47-5; methyl 2-deoxy-2-(1,2-diphenylmaleylimido)-3,4,6-tri-*O*-acetyl-β-D-glucopyranoside, 62448-72-0; 3α-(1,2-diphenylmaleimido)cholestane, 62460-40-6; propionaldehyde, 123-38-6; 3-cholestanone, 15600-08-5.

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