W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least Squares Program", USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965; C. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program", U.S. Atomic Energy Commission Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(8) P. A. Plattner and U. Nager, *Helv. Chim. Acta*, **31**, 665, 2192 (1948).
(9) T-s. Tō, *Hoppe-Seylers Z. Physiol. Chem.*, **260**, 175 (1939), reports the isolation of levorotatory *N,O*-dimethyltyrosine from the urine of rabbits which had been injected with racemic *N,O*-dimethyltyrosine. He assigns the D configuration to the excreted amino acid, but a plus sign appears to have been erroneously placed in front of the optical rotation, $[\alpha]^{20}D$ +21.9° (solvent and concentration not indicated).
(10) D. Eaker and J. Porath, *Sep. Sci.*, **2**, 518 (1967).
(11) H. Bertsch and H. Reinheckel, *Fette, Seifen, Anstrichm.*, **64**, 881 (1962).
(12) R. J. C. Kleipool and J. T. Heins, *Nature (London)*, **203**, 1280 (1964).
(13) V. du Vigneaud and C. E. Meyer, *J. Biol. Chem.*, **93**, 295 (1932).
(14) P. Karrer, M. Gisler, E. Horlacher, F. Locher, W. Mäder, and H. Thomann, *Helv. Chim. Acta*, **5**, 469 (1922).
(15) U. S. Corti, *Helv. Chim. Acta*, **22**, 681 (1949).

1,2-Diphenylmaleyl, a Protecting Group for Amino Functions

Uri Zehavi†

Chemistry Department, Imperial College, London SW7 2AY, United Kingdom

Received December 29, 1976

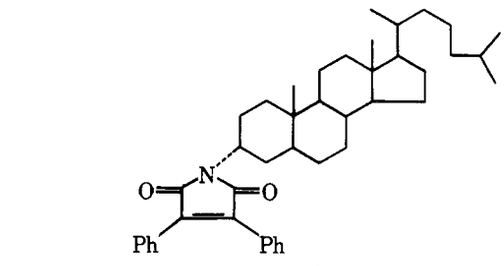
1,2-Diphenylmaleyl (DPM) is described as a protecting group for amino functions and was applied to carbohydrates and steroids. DPM derivatives are prepared through the condensation of the corresponding amines with 1,2-diphenylmaleic anhydride and removed by ethanolic hydrazine. DPM proves to be compatible with and a useful protecting group in glycoside synthesis.

Phthaloyl has been a particularly advantageous protecting group for amino functions in peptide chemistry,[1] penicillin chemistry,[2] and in many areas of natural product chemistry. Diphenylmaleyl (DPM) derivatives, introduced here as a protecting group for amino functions, bear many similarities to the corresponding phthaloyl derivatives, including, to some extent, the protection and deprotection steps; DPM derivatives differ, however, in that they are yellow and fluorescent and thus can be easily determined quantitatively and followed chromatographically; their increased volume compared to many other protecting groups for amino functions can affect adjacent functional groups and they can be conveniently modified into reactive protecting groups as will be described in the subsequent paper.

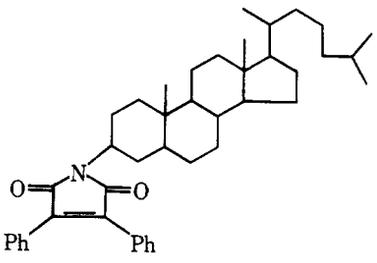
Compounds **1**, **2**, and **3** were conveniently prepared by heating 1,2-diphenylmaleic anhydride[3] and the corresponding amine in dimethylformamide or in dimethylformamide–toluene. Compound **3** in turn was acetylated in pyridine to give compound **4** ($J_{1,2}$ = 8 Hz) in a very good yield. The selective formation of the β-tetraacetate **4** could be explained by the possibility that compound **3**, owing to the steric effect of the DPM group, could be mostly the β anomer (this is supported by the low optical rotation) and by the less hindered approach of the acetylating reagent from the β (e) side. In the Fischer glycoside synthesis both the α and the β anomers (compounds **5**, and **6**, respectively) are formed, the β being the more abundant. It is pertinent to note that in this case the α anomer moves faster in TLC and is less polar than the β anomer. In addition, the NMR spectrum of compound **5** suggests that it might be present in chloroform solution as an equilibrium mixture of conformers rather than the $^4C_1$ chair conformer.

Compound **4** was treated with hydrobromic acid in acetic acid to yield the intermediate 1-bromo derivative (the DPM group appears to be unaffected even after 48 h under these conditions). Subsequent condensation of the bromo intermediate with methanol in the presence of mercuric cyanide afforded the β-glycoside **7** ($J_{1,2}$ = 9 Hz). A number of factors could govern the anomeric nature of compound **7**. At present, the anomeric composition of the bromo intermediate is not known and also it is not clear whether neighboring group participation of the DPM groups could take place; obviously, the easier approach for a nucleophile would be from the β side.

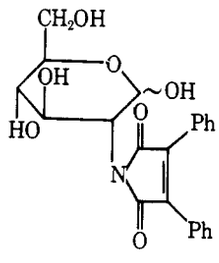
Compound **7** was correlated with compound **6** by deacetylation and by acetylation of compound **6**.



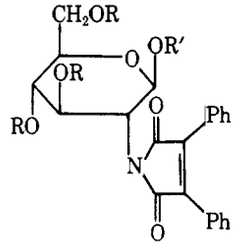
1



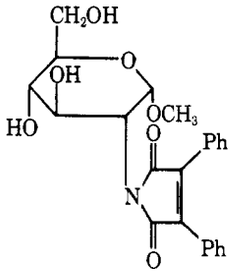
2



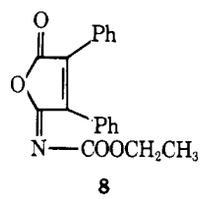
3



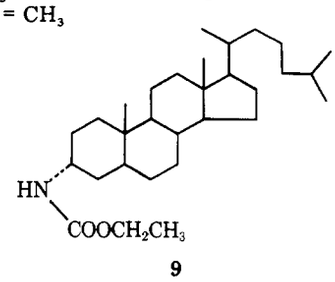
4, R = R′ = CH_3CO
6, R = H; R′ = CH_3
7, R = CH_3CO; R′ = CH_3



5



8



9

† Dr. Uri Zehavi, Research and Development Authority, Ben-Gurion University of the Negev, Beer-Sheva 84110, P.O. Box 1025, Israel.

A few methods designed to facilitate and improve the yields of formation of phthalimido derivatives are reported in the literature. Usually they aim at circumventing or activating the intermediate phthalamic acids. A useful reagent for phthaloylation is reported to be *N*-ethyloxycarbonyl phthalimide.[4] Since the author's early preparations gave rise to yields much lower than those reported here (33–87%) for DPM derivatives, a similar approach was tried in this series. Attempted preparation of *N*-ethyloxy-1,2-diphenylmaleimide gave rise, however, to the isoimide 8 (as apparent from the IR spectrum) that reacted with 3α-aminocholestane[5] to give some of the desired imide 1 but more significantly the ethyloxycarbonyl derivative 9. Hence employing compound 8 proved to be much inferior to the use of 1,2-diphenylmaleic anhydride in the preparation of DPM derivatives.

Removal of the DPM protecting groups and regeneration of the parent amines is effected by ethanolic hydrazine. Thus, compound 1 yielded, following hydrazine treatment and acetylation, 3α-acetamidocholestane[6,5] in 65% yield and compound 7, following the same treatment, gave methyl 2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-β-D-glucopyranoside[7] in 71% yield.

The yields of protection and deprotection employing DPM derivatives are thus similar to those reported for phthaloyl derivatives. The utility of the DPM protecting group in glycoside synthesis is particularly established for the Königs–Knorr synthesis where very conveniently a pure β-glycoside was formed (compound 7).

Experimental Section

Melting points were determined on a Reichert apparatus and are not corrected. ^{1}H NMR spectra were determined in deuteriochloroform with tetramethylsilane as an internal standard at 60 MHz, unless otherwise mentioned. IR, visible, and UV spectra and optical rotations are taken in chloroform, unless otherwise mentioned. TLC and preparative layer chromatography (PLC) were carried out with chloroform (unless otherwise mentioned) on silica gel GF (Merck) and all compounds described (unless otherwise mentioned) were pure by TLC. Column chromatography was performed on silica gel 60 (70–230 mesh, Merck). Evaporations were carried out with a rotary evaporator and in vacuo.

3α-(1,2-Diphenylmaleylimido)cholestane (1). Crude 3α-aminocholestane (0.787 g) and 1,2-diphenylmaleic anhydride (0.560 g) were refluxed in a mixture of dimethylformamide (10 mL) and toluene (2 mL) for 1 h. The reaction mixture was then evaporated, extracted with ether, washed with dilute hydrochloric acid, water, and saturated sodium hydrogen carbonate, dried over sodium sulfate, evaporated, and purified on a "dry" silica gel column (20 g, eluted with benzene–petroleum ether, 1:1). Compound 1 was isolated as a yellow glass (0.412 g, 33%) that was crystallized from acetone: mp 157–162 °C; $[\alpha]^{21}_D$ +43.3° (*c* 0.09); ν_{max} 3400, 3350, 1698, and 1345 cm^{-1}; λ_{max} 278 nm (ε 1.04 × 10^4) and 357 (3.84 × 10^3); ^{1}H NMR τ 2.68 (m, 10, narrow, aromatic), 5.60 (m, 1, H-3e, half-height width 15 Hz), 7.9–9.5 (steroid "envelope" including CH_3 signals at 9.12, 9.18, and 9.37).

Anal. Calcd for $C_{43}H_{57}NO_2$: C, 83.31; H, 9.27; N, 2.26. Found: C, 83.18; H, 9.30; N, 2.22.

3α-(1,2-Diphenylmaleylimido)cholestane (1) and 3β-(1,2-Diphenylmaleylimido)cholestane (2). A mixture of 3α- and 3β-aminocholestane[5] (326 mg) and 1,2-diphenylmaleic anhydride (413 mg) in dimethylformamide (6 mL) was kept in a 160 °C bath for 6 h. The reaction mixture was then evaporated and applied to a "dry" silica gel column (20 g, 1 cm in diameter). Fractions (8 mL each) were collected as soon as the yellow color started to emerge. Fractions 9–13 contained compound 1 (124 mg, 24%) and fractions 2–6 contained compound 2 (155 mg, 30%). Compound 2 was recrystallized from acetone to give yellow needles: mp 238–239 °C, $[\alpha]^{21}_D$ +14.6° (*c* 0.26); ν_{max} 2900, 2850, 1690, 1600, and 1330 cm^{-1}; λ_{max} 277 nm (ε 1.10 × 10^4) and 357 (3.75 × 10^3); ^{1}H NMR τ 2.53 (narrow m, 10, aromatic), 5.95 (38 Hz half-height width m, H-3a, measured at 100 MHz), 7.5–9.4 (steroid "envelope" including CH_3 signals at 9.02, 9.06, 9.17, 9.33).

Anal. Calcd for $C_{43}H_{57}NO_2$: C, 83.31; H, 9.27; N, 2.26. Found: C, 83.27; H, 9.31; N, 2.31.

2-Deoxy-2-(1,2-diphenylmaleylimido)-D-glucose (3). 2-Amino-2-deoxy-D-glucose hydrochloride (1.5 g) was dissolved in methanol (20 mL) and treated with sodium methoxide in methanol (40 mL, 0.15 M). The methanol was subsequently evaporated at 30 °C, 1,2-diphenylmaleic anhydride (1 g), dimethylformamide (35 mL), and toluene (15 mL) were added, and the reaction mixture was kept at reflux for 2 h. Considerable decomposition was apparent (browning). The reaction mixture was evaporated, extracted with chloroform, and washed with dilute hydrochloric acid, water, and saturated sodium hydrogen carbonate, dried over sodium sulfate, evaporated, and applied to a column of silica gel (30 g, 2 cm in diameter and eluting with ethyl acetate at 10 mL per fraction). Collection started when the yellow color began to emerge. Compound 3 (fractions 6–16) was isolated as a yellow glass: mp 85–95 °C (0.265 g); $[\alpha]^{19}_D$ +23.4° (3 min) → 18.3° (18 h, final, *c* 0.21); ν_{max} 3430 (wide), 1695, 1600, 1350 cm^{-1}.

2-Deoxy-2-(1,2-diphenylmaleylimido)-1,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (4). The compound was prepared under conditions that caused less browning from 2-amino-2-deoxy-D-glucose without the intermediate isolation of compound 3. 2-Amino-2-deoxy-D-glucose hydrochloride (108 mg) and 1,2-diphenylmaleic anhydride (125 mg) were stirred in dimethylformamide and triethylamine (0.1 mL) was added. The reaction mixture was then placed in a bath of 105 °C for 15 min whereby it was transformed to a clear yellow solution. The solution was evaporated, dissolved in a mixture of pyridine (1 mL) and acetic anhydride (0.5 mL), and kept at room temperature overnight. Ice was added to the reaction mixture and after 1 h it was evaporated, extracted with ether, washed with dilute hydrochloric acid, water, and saturated sodium hydrogen carbonate, dried over sodium sulfate, evaporated, and purified by PLC. Compound 4 was isolated as a yellow oil (197 mg, 87%) or glass: mp 88–93 °C; $[\alpha]^{30}_D$ +46.7° (*c* 0.66); ν_{max} 1770, 1730, 1700 (shoulder), and 1400 cm^{-1}; λ_{max} 274 nm (ε 7.44 × 10^3), 370 (4.02 × 10^3); 100-MHz ^{1}H NMR τ 2.46 (narrow m, 10 aromatic), 3.39 (d, 1, H-1, $J_{1,2}$ = 9.0 Hz, and no sign of a narrow d), 4.05 (q, 1, *J* = 11, 9.5 Hz), 4.70 (t, 1, *J* = 9.5 Hz), 5.4–6.1 (multiplets, 4), 7.90 (s, 3, $COCH_3$), 7.93 (s, 3, $COCH_3$), 7.96 (s, 3, $COCH_3$), and 8.08 (s, 3, $COCH_3$).

Anal. Calcd for $C_{30}H_{29}NO_{11}$: N, 2.42. Found: N, 2.57.

Methyl 2-Deoxy-2-(1,2-diphenylmaleylimido)-α-D-glucopyranoside (5) and Methyl 2-Deoxy-2-(1,2-diphenylmaleylimido)-β-D-glucopyranoside (6). A. Compound 3 (0.252 g) and Amberlite IR 120 (H^+ form) were refluxed in methanol (20 mL) for 18 h, by which time compound 3 was partially converted, as evidenced by TLC (chloroform–ethyl acetate, 1:1), into compound 5 and the slower moving compound 6. The two products were greatly purified by PLC (in the same solvent). Compound 5 (46 mg) was isolated as a yellow oil, crystallized from ethanol–water as elongated leaflets: mp 128 °C $[\alpha]^{30}_D$ +51.2° (*c* 0.65); λ_{max} 278 nm (9.22 × 10^3) and 370 (5.43 × 10^3); 100-MHz ^{1}H NMR [same for a sample isolated from the mother liquor, $[\alpha]^{18}_D$ +46.6° (*c* 0.7)] τ 2.68 (m, 10), 4.67 (d, 0.6, H-1, $J_{1,2}$ = 5 Hz), 4.82 (d, 0.4, H-1, $J_{1,2}$ = 3.5 Hz), 5.10 (m, 1), 5.3–6.5 (multiplets), 6.58 (s, 1.8, OCH_3), 6.68 (s, 1.2, OCH_3), 6.58 (s, 1.8, OCH_3), and 6.68 (s, 1.2, OCH_3).

Anal. Calcd for $C_{23}H_{23}NO_7$: C, 64.93; H, 5.45; N, 3.29. Found: C, 64.74; H, 5.34; N, 3.16.

Attempted crystallization of compound 6 (97 mg, yellow oil) from the same solvent yielded a very small amount of solid, mp 107 °C, $[\alpha]^{30}_D$ +63.5 (*c* 0.6). Compound 6 was isolated from the mother liquor following PLC as a yellow oil: $[\alpha]^{18}_D$ +21.2° (*c* 0.8); ^{1}H NMR τ 2.48 (m, 10, aromatic), 4.8 (d, 1, H-1, $J_{1,2}$ = 8 Hz), 4.9–6.7 (multiplets), 6.54 (s, 3, OCH_3).

B. Compound 7 was dissolved in ethanolic ammonia (2%) and left at room temperature overnight. The product moved in TLC (chloroform–ethyl acetate, 1:1) like compound 6.

Methyl 2-Deoxy-(1,2-diphenylmaleylimido)-3,4,6-tri-*O*-acetyl-β-D-glucopyranoside (7). A. Compound 4 (3.0 g) was dissolved in 1,2-ethylene dichloride and hydrobromic acid in acetic acid (3 mL, 45%) was added. The reaction mixture was kept for 2 h at room temperature, evaporated from a bath of 30 °C, and extracted with ether and the intermediate 1-bromo derivative separated as an oil upon the addition of petroleum ether (faster moving than compound 4 and relatively clean by TLC): ν_{max} 1770, 1730, 1700 (shoulder), 1605, 1450, 1400, and 1250 cm^{-1}. The oily intermediate, mercuric cyanide (2.0 g), and crushed calcium sulfate (2.0 g) were stirred in chloroform (30 mL), washed with water, and dried. Methanol (3 mL) was added and the reaction mixture was refluxed overnight. Subsequently, it was filtered through a Celite filter, washed with water, dried over sodium sulfate, evaporated, and applied to a "dry" silica gel column (40 g, 2.0 cm in diameter, eluted with chloroform–ethyl acetate, 1:1, 5-mL fractions). Pure compound 7 (2.34 g, yellow glass) was present in fractions 11–32. It was crystallized from ethanol as yellow, elongated prisms: mp 194–195 °C; $[\alpha]^{20}_D$ +40.4° (*c* 0.2); ν_{max} 275 nm (ε 9.12 × 10^3) and 362 (4.83 × 10^3); ^{1}H NMR (100 MHz) τ 2.68 (m, 10, aro-

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.

References and Notes

(1) R. A. Boissonnas, *Adv. Org. Chem.*, **3**, 159 (1963).
(2) B. G. Ramsay and R. J. Stoodley, *J. Chem. Soc. C.*, 1319 (1969); S. Kukolja and S. R. Lammert, *J. Am. Chem. Soc.*, **97**, 5582 (1975).
(3) C. F. Koelsch and S. Wawzonek, *J. Org. Chem.*, **6**, 684 (1941).
(4) G. H. L. Nefkens, G. I. Tesser, and R. J. F. Nivard, *Recl. Trav. Chim. Pays-Bas*, **79**, 688 (1960).
(5) C. W. Shoppe, D. E. Evans, H. C. Richards, and G. H. R. Summers, *J. Chem. Soc.*, 1649 (1956).
(6) R. D. Haworth, L. H. C. Lunts, and J. McKenna, *J. Chem. Soc.*, 986 (1955).
(7) P. G. Walker, *J. Chem. Soc.*, 4754 (1957).

Photochemical Reactions of Phenylglyoxalyl Amides

Uri Zehavi†

Chemistry Department, Imperial College, London SW7 2AY, United Kingdom

Received December 29, 1976

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

† Address correspondence to Dr. Uri Zehavi, Research and Development Authority, Ben Gurion University of the Negev, Beer-Sheva 84110, P.O. Box 1025, Israel.