Photochemical addition of secondary alcohols to maleimides

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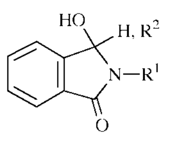
Under UV irradiation, propan-2-ol adds to the C=C bond of maleimides **4** to give 2-(1-hydroxy-1-methylethyl)succinimides **5** in 25–70% yield. Cyclohexanol adds in the same way to give 2-(1-hydroxycyclohexyl)succinimides **6**. Several trace by-products are identified by GC-MS analysis and their formation accounted for.

Introduction

Imides possess a diverse photochemistry. Phthalimides undergo a variety of inter- and intramolecular addition reactions at a carbonyl group.[1] Many such reactions involve first abstraction of hydrogen from a C–H bond by oxygen of the imide n,π* excited state. In alcoholic or ether solvents products such as **1** are obtained; tricyclic or tetracyclic products **1** (R^1–R^2 connected) are formed following intramolecular H-abstraction from within the *N*-substituent R^1. On the other hand, photochemical reaction with alkenes gives spiro oxetane adducts **2** and products derived from them or alternatively ring-expanded products resulting from addition to the C(O)–N bond. Some similar reactions are known for succinimides and glutarimides,[2] but not for maleimides. On the contrary, photochemical dimerisation[3] of maleimides and maleic anhydride and their [2 + 2] cycloaddition to alkenes,[4] alkynes,[5] and to benzene[6] involve reaction at the C=C bond instead. Novel examples of inter- and intramolecular reactions of alkenes with maleimides have attracted recent attention.[7]

Reduction of *N*-phenylmaleimide **4c** with sodium borohydride gave a complex mixture of products from which **3** was isolated only in poor yield.[8] As an alternative approach, we examined the possibility of photochemical reduction of **4c** by alcohols, according to precedents of phthalimides undergoing this type of reaction.[9] In so doing, we have observed the photochemical addition of secondary alcohols to the C=C bond of maleimides **4a–c**.



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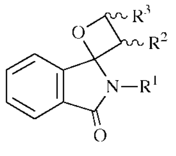

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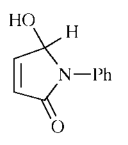

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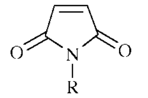
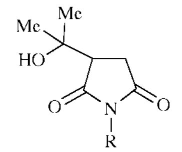
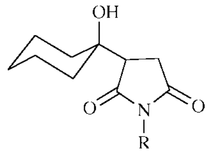


4 a; R = H
b; R = Me
c; R = Ph



5 a; R = H
b; R = Me
c; R = Ph

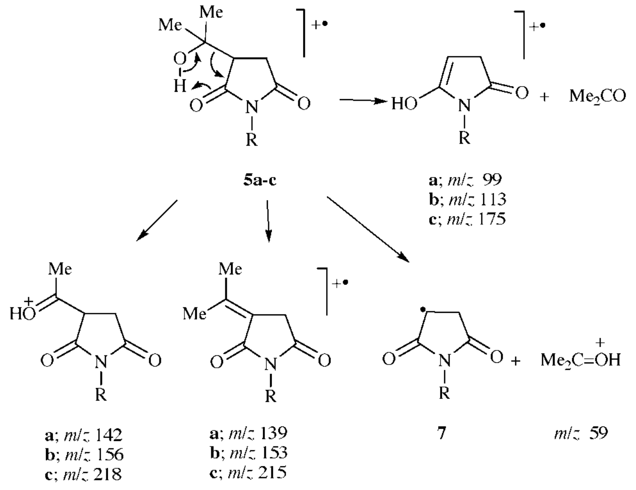


6 a; R = H
b; R = Me

Results and discussion

The major product from UV irradiation through Pyrex of maleimide **4a** in propan-2-ol was the 1 : 1 adduct **5a**, which was isolated in 60% yield by chromatography and identified by elemental analysis and IR, NMR and mass spectra. The corresponding adducts **5b,c** were obtained in the same way from maleimides **4b,c** (see below).

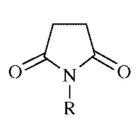
^{1}H NMR spectra of these compounds **5a–c** and of the related cyclohexanol adduct **6a** showed an ABX pattern for CH_2CH of the succinimide ring, with J_{trans}, J_{cis} and J_{gem} values *ca.* 5, 9 and 18 Hz, respectively. Mass spectra of **5b,c** obtained by electron impact showed no peak for the molecular ion, and the peak with highest *m*/*z* value corresponded to $[M - CH_3]^+$ in each case. Fragmentation of the molecular ion for each of **5a–c** is dominated by loss of acetone (McClafferty rearrangement) and by loss of the succinimidyl radical **7** leaving the daughter ion $Me_2C{=}OH^+$, *m*/*z* 59. These and competing fragmentation pathways are shown in Scheme 1. The cyclohexanol adducts **6a,b** showed the corresponding fragmentation patterns, losing either cyclohexanone or **7** from the molecular ion. Coincidentally, for **6a** the daughter ions $C_4H_5NO_2^+$ and $C_6H_{11}O^+$ from these two processes are isobaric with *m*/*z* 99. The same fragmentation pathways were important features of the mass spectra of all the higher order adducts **10a–c**, **11** and **15** recognised in the present work.



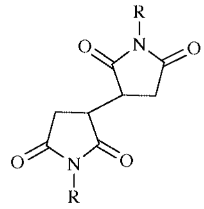
Scheme 1

Other products formed in small amounts from maleimide **4a** in propan-2-ol were succinimide **8a**; the 2 : 1 adduct **10a** from **4a** and propan-2-ol; and the 2,2′-bissuccinimide **9a**. After methylation of **9a**, the two diastereoisomers of **9b** were separated by GC and characterised by GC-MS. Additionally, when irradiation of **4a** in propan-2-ol was done in quartz apparatus, pinacol **19** was also formed.

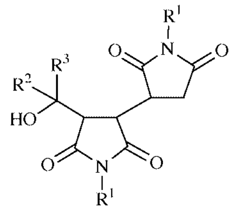
UV irradiation of maleimide **4a** in dichloromethane in the presence of cyclohexanol afforded the 1 : 1 adduct **6a**, but this was isolated in only 7% yield after chromatography. The same product **6a** was formed on irradiation of **4a** in cyclohexanol as



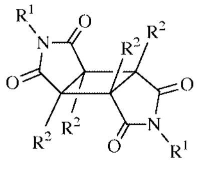
8a; R = H
b; R = Me
c; R = Ph



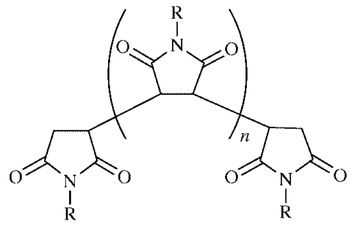
9a; R = H
b; R = Me



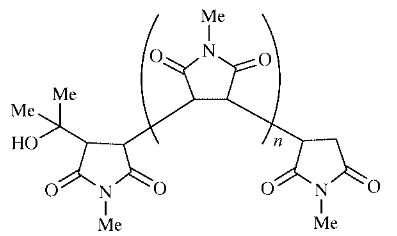
10a; R^1 = H, R^2 = R^3 = Me
b; R^1 = R^2 = R^3 = Me
c; R^1 = Ph, R^2 = R^3 = Me
11; R^1 = H, R^2–R^3 = $(CH_2)_5$
12a; R^1 = R^2 = H, R^3 = Ph
b; R^1 = Me, R^2 = H, R^3 = Ph



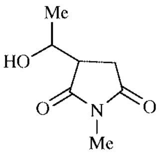
13a; R^1 = R^2 = H
b; R^1 = Me, R^2 = H
c; R^1 = Ph, R^2 = H
d; R^1 = H, R^2 = Me



14 a; R = H, *n* = 1, 2
b; R = Me, *n* = 1 – 5



15; *n* = 1, 2



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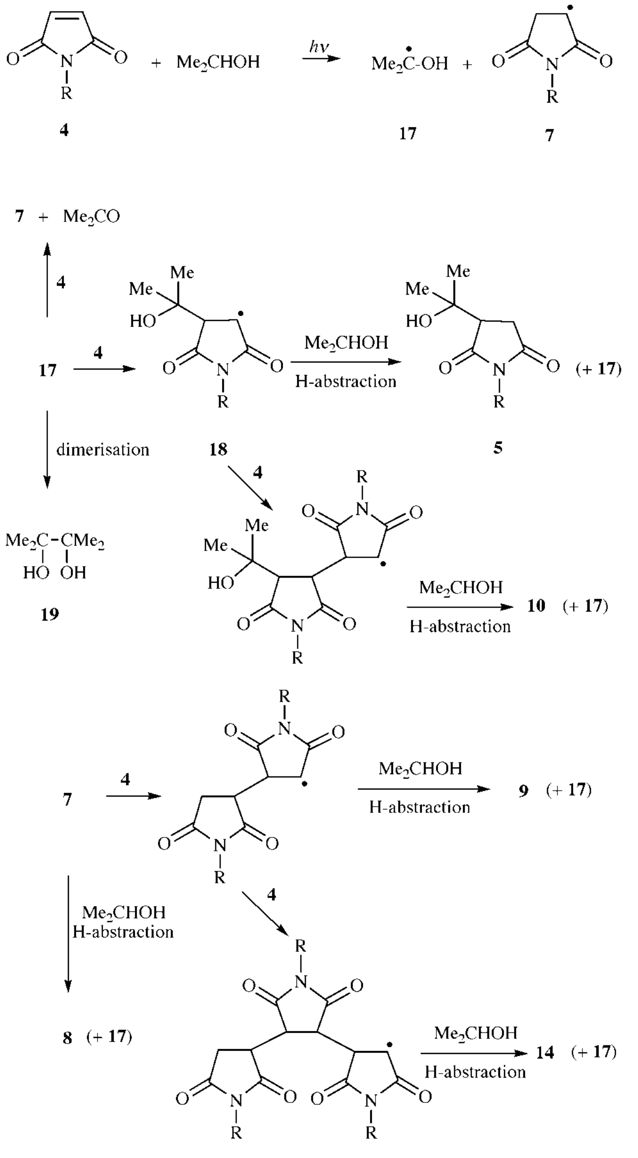
solvent, but in this case separation of **6a** from unreacted cyclohexanol was more difficult. By-products characterised by GC-MS included the 2,2′-bissuccinimides **9a** and **11**, and the trissuccinimide **14a** (*n* = 1). Irradiation of **4a** in chloroform in the presence of benzophenone gave the cyclobutanebisimide **13a** analogous to known photodimers **13c,d** of other maleimides.[3]

UV Irradiation of *N*-methylmaleimide **4b** in propan-2-ol gave the 1 : 1 adduct **5b**, isolated in 70% yield, and very small amounts of by-products **8b**, **9b** (2 diastereoisomers), **10b** and **13b**; the rest was polymeric material, in which **14b** (*n* = 1) and **15** (*n* = 1, 2) were recognised by GC-MS analysis. The adduct **5b** was also prepared, as reported for the *N*-ethyl analogue,[10] from **4b** and acetone with zinc and 2-iodopropane. Irradiation of *N*-methylmaleimide in dichloromethane in the presence of cyclohexanol led to formation of the cyclohexanol adduct **6b** (major product) alongside small amounts of **8b**, **9b**, **13b** and **14b** (*n* = 1). Irradiation of *N*-phenylmaleimide **4c** in propan-2-ol gave the corresponding succinimide derivative **5c** in 25% yield together with pinacol **19**, 2,2′-bissuccinimide **10c** and polymeric material.

An earlier EPR study[11] of the pulsed radiolysis of maleimides **4b,c** in propan-2-ol identified the radicals **7** and **18**, but the authors did not look for any end-products of the reaction. Moreover, the spectra of these radicals showed strong CIDEP effects. Under conditions of continuous UV irradiation of *N*-phenylmaleimide **4c** in propan-2-ol, we have observed only the EPR spectrum of the ketyl radical **17**,[12] the steady-state concentration of which is clearly much greater than that of **7** or **18**. Irradiation of the same concentration of **4c** in propan-2-ol through quartz instead of through Pyrex resulted in a much more intense EPR signal, and the higher steady state concentration of **17** is consistent with the appearance of pinacol **19** among the products under these conditions.

The primary photochemical reaction step required to account for formation of the radicals **7** and **17** is H-abstraction from propan-2-ol by the maleimide, most likely its n,π* triplet excited state. Formation of all the identified products can then be accounted for in terms of secondary reactions of radical addition, H-abstraction or radical–radical combination outlined in Scheme 2. Radical **17** can react with imide **4** in two ways: by H-atom transfer to give succinimidyl radical **7** and acetone, or by addition to give radical **18**. Formation of the main product **5** as shown is then accompanied by formation of another radical **17**, so that a chain mechanism converts **4** into **5** *via* **18**. Indeed, the chain carrier **17** is reformed in every step in Scheme 2 involving H-abstraction from propan-2-ol. Combination of radicals **7** and **17** could also account for formation of **5**, although the contribution of this pathway is likely to be very unimportant. Irradiation of a mixture of maleimide **4a** and succinimide **8a** in dichloromethane produced only the maleimide dimer **13a** and none of the cross-addition product **9a**, showing that H-abstraction from **8a** by the excited state of **4a** is unimportant. Likewise, irradiation of a mixture of maleimide **4a** and adduct **5a** in dichloromethane produced only the maleimide dimer **13a** and none of the cross-addition product **10a**. Radical polymerisation of maleimides initiated by



Scheme 2

AIBN and anionic polymerisation initiated by butyllithium have been studied,[13] but without any direct observation of smaller oligomers of the type of **14**.

Our results are complementary to those of the EPR investigation.[11] Photochemical addition of propan-2-ol (and, in some cases, methanol) in the same way as **4**→**5** is known for oct-1-ene,[14] norbornene (in competition with alkene dimerisation, sensitised by benzophenone),[15] maleic and fumaric acids,[16] and the C=C bond of cyclic enones[17] and unsaturated lactones.[18] In further experiments with maleimides **4a**,**b**, we observed the photochemical addition of ethanol or benzyl alcohol to give products **12a**,**b** and **16**, but none of these was formed in preparatively useful amounts. Surprisingly, when **4b** was irradiated with benzhydrol in dichloromethane, the dimer **13b** was formed rather than an adduct analogous to **5b**. Thus, although the photochemical addition of propan-2-ol to maleimides provides a route to **5a**–**c** which is more convenient than alternative approaches,[10,19] the method is not generally applicable to other alcohols.

Experimental

^{1}H NMR Spectra were recorded at 270 MHz and ^{13}C NMR spectra at 67.9 MHz (JEOL EX270 spectrometer) for solutions in $CDCl_3$ (or other solvents specified) with Me_4Si as internal standard. GC analyses were done on Carbowax stationary phase temperature programmed for 2 min at 120 °C, then rising by 8° min^{-1} to 240 °C. Mass spectra were recorded by electron impact at 70 eV or by chemical ionisation with ammonia (VG Autospec). For UV irradiation a 110 W Hanovia medium-pressure mercury lamp in a water-cooled Pyrex (or quartz) jacket was immersed in the solution of reactant(s), through which a stream of nitrogen was bubbled to exclude air.

Photochemical products 5a, 6a, 8a, 9a, 10a, 11a, 12a and 13a from maleimide 4a

Maleimide **4a** (980 mg) in propan-2-ol (150 ml) was irradiated for 12 h. After evaporation of the solvent *in vacuo*, the residue was chromatographed on silica. Elution with dichloromethane–acetone (9:1→7:3 v/v) afforded the 1:1 adduct **5a** (950 mg, 60%); mp 99.5–100.5 °C (from chloroform) (Found: C, 53.58; H, 7.22; N, 8.87. $C_7H_{11}NO_3$ requires C, 53.50; H, 7.05; N, 8.90%); δ_H 1.30 and 1.34 (each 3H, s, 2 × CH_3), 2.60 (1H, dd, *J* 5.2 and 18.3 Hz), 2.82 (1H, dd, *J* 9.3 and 18.3 Hz), 2.97 (1H, dd, *J* 5.2 and 9.3 Hz) and 8.24 (1H, s, NH); δ_C 24.5 and 26.2 (2 × CH_3), 32.9 (CH_2), 51.6 (CH), 71.5 (COH), 175.8 and 179.1 (2 × C=O); EIMS M^+ absent, *m*/*z* 142 (M − CH_3, 26%), 139 (M − H_2O, 11), 125 (10), 100 (31), 99 (M − Me_2CO, 78), 71 (60), 59 ($Me_2C{=}OH^+$, 100) and 43 (48); CIMS *m*/*z* 175 (M^+ + NH_4) and 158 (MH^+).

Further elution of the column with acetone–THF gave another 470 mg of a mixture. Fractional crystallisation from acetone–ether afforded the 3-(1-hydroxy-1-methylethyl)-2,2′-bissuccinimide **10a** (25 mg) as a mixture of diastereoisomers (^{13}C NMR spectrum); EIMS M^+ absent, *m*/*z* 239 (M − CH_3, 11%), 236 (7), 222 (6), 196 (M − Me_2CO, 60), 125 (21), 99 (69), 59 (Me_2COH^+, 68), 54 (100) and 43 (49).

Another fraction was the 2,2′-bissuccinimide **9a** (11 mg); *m*/*z* 196 (M^+, 21%), 99 (53) and 54 (100). This was heated for 1 h under reflux with methyl iodide and potassium carbonate in acetone; the solution was cooled and filtered, and the filtrate concentrated *in vacuo*. Two diastereoisomers of the *N*,*N*′-dimethyl derivative **9b** were then resolved by GC (28.6 and 35.9 min retention times) and identified by GC-MS (HREIMS Found: M^+ 224.08056 and 224.08000. $C_{10}H_{12}N_2O_4$ requires 224.07971); EIMS were identical apart from small differences in relative intensities *m*/*z* 224 (M^+, 31 or 47%), 139 (11), 113 (94 or 67), 82 (20) and 54 (100).

Analysis by GC-MS of the crude photolysate from **4a** in propan-2-ol, before chromatography to separate **5a**, **9a** and **10a**, showed the presence of small amounts of succinimide **8a** (eluted before **5a**), *m*/*z* 99 (M^+, 100%), 56 (74) and 42 (9), identical with an authentic sample in respect of GC retention time and mass spectrum.

Maleimide **4a** (970 mg) in dichloromethane (140 ml) with cyclohexanol (10 ml) was irradiated for 20 h, during which time a white solid separated. This solid was separated by filtration, extracted with hot chloroform, and the extract afforded the 2,2′-bissuccinimide **9a** (2 mg), MS as above. The chloroform-insoluble residue was a mixture of trissuccinimide **14a** ($n = 1$), *m*/*z* 293 (M^+, 2%), 196 (18), 195 (24), 178 (13), 99 (62), 55 (100), 54 (64) and 42 (75), tetramer **14a** ($n = 2$), *m*/*z*, 390 (M^+, 1%), 291 (15), 271 (21), 230 (18), 195 (58), 194 (62), 99 (100), 80 (57), 54 (87) and 52 (95), and higher oligomers of **14a**, which were separated in MS by gradually raising the temperature of the probe.

The filtered photolysate was evaporated *in vacuo* and the residue chromatographed on silica. Elution with acetone–cyclohexane (3:7 v/v) afforded the 2-(1-hydroxycyclohexyl)succinimide **6a** (140 mg, 7%) as a viscous oil (HREIMS Found M^+ 197.10519. $C_{10}H_{15}NO_3$ requires 197.10614); δ_H (CD_3OD) 1.32 (10H, m), 2.68 (1H, dd, *J* 8.7 and 18.1 Hz), 2.76 (1H, dd, *J* 5.0 and 18.4 Hz), 2.92 (1H, dd, *J* 5.3 and 8.7 Hz) and 7.56 (1H, s, NH); δ_C (CD_3OD) 22.1 (CH_2), 26.0 (CH_2), 33.4 (CH_2), 36.4 (CH_2), 53.8 (CH), 72.9 (COH), 178.2 (C=O) and 180.0 (C=O); *m*/*z* 197 (M^+, <1%), 179 (M − H_2O, 12), 154 (M − HNCO, 13), 141 (19), 99 (M − $C_6H_{10}O$, 100), 81 (34) and 55 (94). A later fraction eluted with acetone afforded the 3-(1-hydroxycyclohexyl)-2,2′-bissuccinimide **11** (5 mg), *m*/*z* 294 (M^+, 5%), 276 (M − H_2O, 9), 196 (M − $C_6H_{10}O$, 40), 178 (31), 99 (100), 81 (30), 55 (55) and 54 (65).

Additionally, the presence of the cyclobutanebisimide **13a** in the filtered photolysate from **4a** was shown by GC-MS and by comparison with a sample of **13a** prepared by UV irradiation of **4a** in chloroform in the presence of benzophenone; *m*/*z* 194 (M^+, 52%), 151 (38), 123 (25), 80 (48) and 52 (100) (HREIMS Found M^+ 194.03227. $C_8H_6N_2O_4$ requires 194.03276).

Photochemical products 5b, 6b, 8b, 9b, 10b, 12b, 13b, 14b, 15 and 16 from *N*-methylmaleimide 4b

N-Methylmaleimide **4b** (113 mg) in propan-2-ol (20 ml) was irradiated until, after 1 h, conversion of **4b** was almost complete. After evaporation of solvent *in vacuo*, the residue was chromatographed on silica. Elution with cyclohexane–acetone (4:1 v/v) afforded the 1:1 adduct **5b** (122 mg, 70%) as a colourless oil [HRCIMS Found (M^+ + NH_4) 189.12340. $C_8H_{17}N_2O_3$ requires 189.12392. HREIMS Found (M^+ − CH_3) 156.06666. Calc. for $C_7H_{10}NO_3$ 156.06607]; δ_H 1.21 and 1.34 (each 3H, s, 2 × CH_3), 2.51 (1H, dd, *J* 4.8 and 18.0 Hz), 2.91 (1H, dd, *J* 9.3 and 18.0 Hz), 2.93 (1H, dd, *J* 4.8 and 9.3 Hz), 3.00 (3H, s, NCH_3) and 3.42 (1H, s, OH); δ_C 24.6 (CH_3), 26.0 (CH_3), 27.1 (CH_3), 31.5 (CH_2), 50.1 (CH), 71.4 (COH), 176.3 (C=O) and 179.0 (C=O); EIMS M^+ absent, *m*/*z* 156 (M − CH_3, 24%), 153 (M − H_2O, 18), 113 (M − Me_2CO, 100), 85 (26), 71 (45), 59 (Me_2COH^+, 79) and 43 (43) in fair agreement with that reported previously.[19] Another sample of **5b** was prepared (17% yield) from **4b** with acetone, 2-iodopropane and zinc by the method described for the *N*-ethyl analogue;[10] the GC retention time and MS matched those of **5b** obtained in the photochemical reaction.

GC-MS analysis of the crude photolysate from **4b** showed, in addition to **5b**, the presence of small amounts of other products: in order of increasing retention time, *N*-methylsuccinimide **8b**, identified by comparison of retention time and mass spectrum with an authentic sample; two diastereoisomeric 2,2′-bissuccinimides **9b** (2:1 ratio) identified from mass spectra (as above for **9a**→**9b**): and two diastereoisomeric 2:1 adducts of **4b** and propan-2-ol (3:2 ratio) **10b** [HRCIMS Found (M^+ + H) 283.12993. $C_{13}H_{19}N_2O_5$ requires 283.12940]; CIMS *m*/*z* 300 (M^+ + NH_4) and 283 (M^+ + H); EIMS M^+ absent, *m*/*z*

267 ($M - CH_3$, 24 or 23%), 264 ($M - H_2O$, 8 or 21), 224 ($M - Me_2CO$, 60 or 79), 153 (30 or 5), 139 (16 or 22), 113 (100), 59 (Me_2COH^+, 93) and 43 (43). None of these by-products was isolable in substance from the chromatography which gave **5b**.

More prolonged irradiation of *N*-methylmaleimide **4b** in propan-2-ol led to the formation of a precipitate which was separated and extracted with hot chloroform. The extract was concentrated and analysed by GC-MS, which revealed the presence of more complex products: the trissuccinimide **14b** ($n = 1$), *m*/*z* 335 (M^+, 8%), 223 (100), 113 (70) and 80 (25); the 3:1 adduct **15** ($n = 1$), CIMS, *m*/*z* 411 ($M^+ + NH_4$) and 394 ($M^+ + H$); EIMS M^+ absent, *m*/*z* 378 ($M - CH_3$, 18%), 335 ($M - Me_2CO$, 42), 263 (13), 223 (96), 113 (100), 59 (Me_2COH^+, 50) and 43 (52); the 4:1 adduct **15** ($n = 2$), *m*/*z* 504 (M^+, 1%), 489 ($M - CH_3$, 13), 446 ($M - Me_2CO$, 38), 334 (79), 223 (91), 113 (100), 58 (33) and 43 (41).

Prolonged irradiation of *N*-methylmaleimide **4b** in propan-2-ol, and particularly irradiation through quartz instead of through Pyrex, resulted in formation of pinacol **19**, identified by comparison of GC retention time and mass spectrum with an authentic sample.

N-Methylmaleimide **4b** (250 mg) in dichloromethane (100 ml) with cyclohexanol (10 ml) was irradiated for 4 h. The solvents were evaporated *in vacuo* and the residue analysed by GC-MS showing, in order of elution: *N*-methylsuccinimide **8b**, *m*/*z*, 113 (M^+, 100%), 56 (80) and 42 (13); 2-(1-hydroxycyclohexyl)-*N*-methylsuccinimide **6b**, *m*/*z* 211 (M^+, 1%), 193 ($M - H_2O$, 15), 168 (13), 155 (12), 113 ($M - C_6H_{10}O$, 100), 99 ($C_6H_{11}O^+$, 21), 81 (20), 55 (43) and 41 (20); two diastereoisomers of the bissuccinimide **9b** (as before); the cyclobutanebisimide **13b**, *m*/*z* 222 (M^+, 53%), 137 (48), 80 (100) and 52 (95); and the trissuccinimide **14b** ($n = 1$) (as before). Although **6b** was the major product, attempts to isolate it by chromatography on silica gave only a very small sample which was still contaminated with cyclohexanol.

After UV irradiation of *N*-methylmaleimide **4b** (111 mg) in ethanol (100 ml) for 20 h, the solution was filtered, the filtrate was evaporated *in vacuo* and the residue analysed by GC-MS: 2-(1-hydroxyethyl)-*N*-methylsuccinimide **16** as two diastereoisomers (1:1 ratio), *m*/*z* 157 (M^+, 3 or 7%), 142 ($M - CH_3$, 5 or 6), 139 ($M - H_2O$, 11 or 5), 113 ($M - C_2H_4O$, 100), 85 (36 or 34), 57 (36 or 35), and 45 (CH_3CHOH^+, 36 or 48). The solid by-product was analysed by MS by gradually raising the probe temperature in the ion source; the resulting spectra provided evidence for the presence of **14b** ($n = 1$), *m*/*z* 335 (M^+); **14b** ($n = 2$), *m*/*z* 446 (M^+); **14b** ($n = 3$), *m*/*z* 557 (M^+); **14b** ($n = 4$), *m*/*z* 668 (M^+); and **14b** ($n = 5$), *m*/*z* 779 (M^+).

After irradiation of *N*-methylmaleimide **4b** in benzyl alcohol, analysis by GC-MS showed the formation of small amounts of the 2:1 adduct **12b**, as two diastereoisomers with similar mass spectra *m*/*z* 330 (M^+, 10%), 224 ($M - PhCHO$, 3), 281 (8), 189 (4), 128 (5), 113 (100), 107 ($PhCHOH^+$, 22) and 77 (Ph^+, 20). Attempted isolation by chromatography was unsuccessful.

After irradiation of *N*-methylmaleimide **4b** in chloroform with benzhydrol, analysis by GC-MS showed the photodimer **13b**, CIMS *m*/*z* 240 ($M^+ + NH_4$), EIMS *m*/*z* 222 (M^+, 72%), 1376 (51), 80 (100) and 52 (85), as the only product.

Photochemical products 5c, 8c and 10c from *N*-phenylmaleimide 4c

N-Phenylmaleimide **4c** (173 mg) in propan-2-ol (180 ml) was irradiated through quartz for 12 h. The solution was filtered from a small amount of polymeric solid, the solvent was evaporated *in vacuo* and the residue chromatographed on silica, from which ethyl acetate eluted colourless semi-solid (199 mg). This was shown by GC-MS analysis to be a mixture of 1:1 adduct **5c** and pinacol **19**. The pinacol was removed by fractional sublimation *in vacuo* and by repeated washing with water leaving 2-(1-hydroxy-1-methylethyl)-*N*-phenylsuccinimide **5c** (59 mg, 25%) as a viscous oil (HREIMS Found M^+ 233.10579. $C_{13}H_{15}NO_3$ requires 233.10519); ν_{max} ($CHCl_3$) 3506 (OH), 1774 and 1735 (CO) cm^{-1}; δ_H 1.33 and 1.37 (each 3H, s, $2 \times CH_3$), 2.71 (1H, dd, *J* 4.7 and 18.1 Hz), 2.95 (1H, dd, *J* 9.3 and 18.1 Hz), 3.06 (1H, dd, *J* 4.7 and 9.3 Hz), and 7.23–7.54 (5H, m, ArH); δ_C 26.0 (CH_3), 27.4 (CH_3), 31.9 (CH_2), 50.2 (CH), 71.8 (COH), 126.5 (aryl CH), 128.7 (aryl CH), 129.1 (aryl CH), 131.5 (aryl C), 175.1 (C=O) and 178.2 (C=O); *m*/*z* 233 (M^+, 32%), 218 ($M - CH_3$, 13), 215 ($M - H_2O$, 6), 175 ($M - Me_2CO$, 100), 147 (20), 119 (43), 93 (49), 71 (221), 59 (Me_2COH^+, 85), 55 (43) and 43 (36).

Analysis by GC-MS of the photolysate before work-up showed the formation of small amounts of *N*-phenylsuccinimide **8c**, *m*/*z* 175 (M^+), GC retention time and mass spectrum identical with those of an authentic sample; and the 2,2′-bissuccinimide **10c**, *m*/*z* 406 (M^+, 8%), 348 ($M - Me_2CO$, 24), 175 (75), 93 (61), 59 (Me_2COH^+, 100) and 43 (70).

Irradiation of *N*-phenylmaleimide **4c** in propan-2-ol through Pyrex produced the 1:1 adduct **5c** more slowly, but was accompanied by less pinacol **19**.

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