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Photodecarboxylative additions of N-protected α-amino acids to *N*-methylphthalimide

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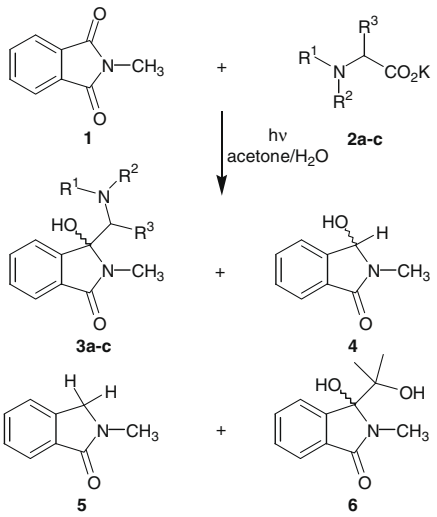
ABSTRACT

Photoreactions involving N,N-dimethylated α-amino acid salts and *N*-methylphthalimide are dominated by photoreduction and acetone trapping. Only, *N*-phenyl glycinate underwent photodecarboxylative addition in a moderate yield of 30%. In contrast, N-acylated α-amino acid salts readily gave addition products in fair to high yields of 20–95%. Comparison experiments with *N*,*N*-dimethylacetamide and amino-/amido-containing phthalimides revealed the origin of the crucial electron-transfer step and the reactivity order $NR_3 \gg RCO_2^- \geqslant RCONR_2$ was established.

The photochemistry of phthalimides has attracted considerable attention over the last two decades, and a number of efficient and selective transformations have been realized.[1] Photodecarboxylative additions of carboxylates, α-keto carboxylates and heteroatom-substituted carboxylates to phthalimides, for example, have been developed as versatile alternatives to Grignard additions.[2] To explore further the scope of this attractive application, we became interested in using amino acid derivatives as starting materials. Three nitrogen-containing carboxylates **2a–c** were thus irradiated at 300 nm in aqueous acetone in the presence of *N*-methylphthalimide (**1**, Scheme 1).[3] With N,N-dimethylated amino acids **2a** and **2c**, only photoreduction to **4** and **5**, and acetone trapping to **6** was observed (Table 1). Conversion rates and product ratios varied depending on the irradiation time as demonstrated for *N*,*N*-dimethylglycine (**2a**). The desired photoaddition product **3** could only be obtained when the potassium salt of *N*-phenyl glycine (**2b**) was used as the starting material.[4] The reaction was sluggish, but the addition product **3b** was isolated in a yield of 30% after column chromatography. Due to the low oxidation potentials of tertiary amines (NR_3: E_{Ox} = 0.7–1.3 vs SCE[5]), photoinduced electron transfer (PET) reactions involving phthalimides are highly exergonic. This suggests that electron transfer is followed by rapid photoreduction through hydrogen abstraction, a commonly observed side reaction of amines. In fact, photoaddition products similar to **3** were only obtained in low yields with simple amines as reaction partners.[6,7]

Photoreductions by amines are known to be sensitive towards the presence of water.[8,9] The reaction involving 2-(dimethylamino)acetic acid was thus carried out using dry acetonitrile as solvent. The reaction again proceeded rather sluggishly, but after 2 h the photoreduction product **4** was identified as the main prod-



Scheme 1. Photoreaction of **1** with nitrogen-containing carboxylates **2a–c**.

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Table 1
Product compositions and experimental details for photoadditions of **1** with **2a–c**

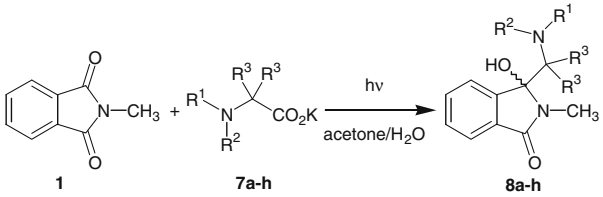
2	R^1	R^2	R^3	Time (h)	Product composition[a] (%)				
					1	3	4	5	6
a	Me	Me	H	1	—	—	37	34	29
a	Me	Me	H	18	—	—	4	45	51
b	Ph	H	H	4	25	41[b]	19	5	10
c	Me	Me	Bn	3	33	—	36	21	10

[a] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture.
[b] Isolated yield 30%.

uct. Hence, the outcome of the photoreactions involving nitrogen-containing carboxylic acids or carboxylates predominantly depends on the structure of the acid, in particular the substituents at the nitrogen, and not necessarily on the presence of water.

Likewise, a set of N-acylated glycine salts **7a–h** was irradiated in the presence of **1** under the conditions of the photodecarboxylative addition (Scheme 2; Table 2).[10] In contrast to their N-alkylated counterparts all the experiments proceeded readily and the corresponding addition products **8a–h** were collected in moderate to excellent yields of 20–95% after just 1–4 h of irradiation.[11] Only in the case of Fmoc-protected glycine **7f** were larger amounts of unidentified by-products detected in the crude NMR spectrum, but no attempt was made to isolate these products.

Since phthalimides are known to react via H-abstraction reactions,[1a] *N*-methylphthalimide (**1**) was furthermore irradiated in the presence of 5 equiv of *N*,*N*-dimethylacetamide (**9**) (Scheme 3). After irradiation for 5 h, no addition (**8b**) or photoreduction products (**4**/**5**) were observed. Instead, **1** was reisolated in 81% yield. Hence, photoadditions via H-abstraction do not contribute to the formation of the addition products **8**.

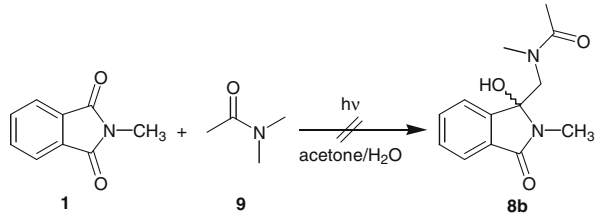


Scheme 2. Additions of N-protected glycine salts **7a**–**h** to **1**.

Table 2
Yields and experimental details for photoadditions of **1** with **7a–h**

8	R^1	R^2	R^3	Time (h)	Yield (%)
a	Ac	H	H	2	71 (75[a])
b	Ac	Me	H	1	73
c	Ac	Ph	H	1	95
d	Boc	H	H	1	74
e	Cbz	H	H	4	56
f	Fmoc	H	H	2	20[b]
g	Ac	H	Me	4	83
h	Ac	H	$(CH_2)_5$	3	80

[a] Yield based on a conversion of **1** of 95%.
[b] Larger amounts of unknown by-products detected.

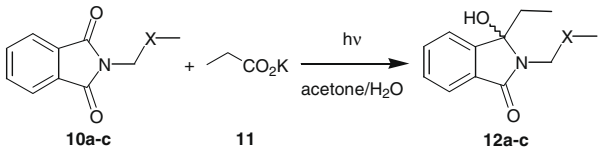


Scheme 3. Attempted addition of *N*,*N*-dimethylacetamide (**9**) to **1**.

For related photocyclizations of phthaloyl peptides, different scenarios for the crucial photoinduced electron transfer (PET)[12] step have been proposed. Whereas Yoon and Mariano suggested an electron transfer from the amide linker,[13] Griesbeck and Oelgemöller postulated an electron transfer from the carboxylate function instead.[14] The latter scenario is supported by successful macrocyclization of dipeptides with terminal ω-amino acids. In order to establish the origin of the crucial photoinduced electron transfer step, the phthalimides **10a–c** carrying potential donor substituents on the *N*-side chain were irradiated in the presence of potassium propionate **11** (Scheme 4; Table 3).

The amine-derived phthalimide **10a** completely prevented photodecarboxylative addition and showed extensive photodecomposition, as noticeable from its poor recovery of 23%. Unselective photodegradation of **10a** was also observed in the absence of **11**. In contrast, the incorporation of an amide group into the *N*-side chain had no influence on the ethylation and the corresponding addition products **12b** and **12c** were obtained in moderate yields of 43% and 51%, respectively.[15] Cyclization products arising from competing *intramolecular* CH activations or PET reactions were not detected.[16,17]

The general mechanistic scenario for photoreactions of amino acids with *N*-methylphthalimide is depicted in Scheme 5. For the amino-carboxylates **2**, electron transfer from the nitrogen gives the corresponding radical ion pair (path **A**). For phenyl glycinate, subsequent α-decarboxylation and carbon bond formation yields the addition product **3b**. For the dialkylated amino acids, stepwise photoreduction is observed instead.[18] N-acylation of the amino acids **7** restored photoreactivity. This suggests that the crucial electron transfer step now occurs primarily from the carboxylate func-

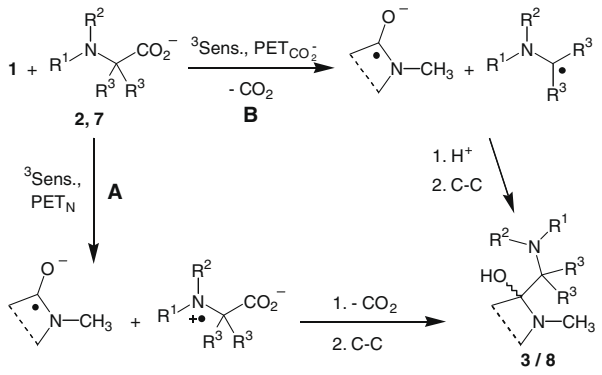


Scheme 4. Addition of propionate **11** to phthalimides **10a**–**c**.

Table 3
Yields and experimental details for photoadditions of **10a–c** with **11**

12	X	Time (h)	Conversion[a] (%)	Yield (%)
a	NMe	4	—	(23[b])
b	CONH	4	95	43 (45[c])
c	CONMe	4	95	51 (54[c])

[a] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture.
[b] Reisolated **10a**.
[c] Yields based on conversion.



Scheme 5. Mechanistic scenario.

tion (path **B**) as supported by the oxidation potentials of the competing electron donors (E_{Ox} $RCONR_2 \geqslant E_{Ox}$ RCO_2^-).[19] Subsequent decarboxylation of the resulting carboxy radical to the corresponding carbon-centred radical and carbon bond formation furnish the observed addition products **8**.[20]

An additional argument for the mechanistic scenario comes from the attempted photoaddition of dimethylacetamide to **1**. Since no addition product could be detected, electron transfer from the amide function (similar to path **A** in Scheme 5) appears energetically not feasible.[21,22] Likewise, amide groups within the *N*-side chain, as in compounds **10b** and **10c**, did not prevent photodecarboxylative ethylation. If electron transfer would operate from the amide-linker, complete deactivation could be expected as, for example, is known for thioether-derived phthalimides (**10**; X = S).[23]

In conclusion, N,N-dialkylated amino acid salts only undergo unselective photoreductions and acetone trapping. In contrast, *N*-phenyl glycine and N-acylated α-amino acid salts undergo photodecarboxylative addition to **1**. The simple protocol makes this transformation interesting for 'micro-photochemistry', that is, photochemistry in micro-structured reactors.[24]

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3. *General procedure for irradiation*: *N*-methylphthalimide (1.5 mmol) was dissolved in acetone (50 mL). A solution of the potassium carboxylate (4.5 mmol) in H_2O (50 mL) was added, and the mixture was irradiated (Rayonet Photochemical Reactor RPR-200; $\lambda = 300 \pm 20$ nm) at 15–20 °C in a Pyrex tube ($\lambda \geqslant 300$ nm) while purging with a slow stream of nitrogen. The progress of the reaction was monitored by TLC analysis or by passing the departing gas stream through a saturated barium hydroxide solution until precipitation of barium carbonate had ceased. Most of the acetone was evaporated and the remaining solution was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was washed with 5% $NaHCO_3$ (50 mL) and brine (50 mL), dried over $MgSO_4$ and evaporated. The products were purified by column chromatography (eluent: *n*-hexane/EtOAc = 1:1). In some cases, the pure product precipitated upon evaporation of acetone and was isolated by vacuum filtration and drying in vacuo instead. Selected physical and spectral data for *3-hydroxy-2-methyl-3-[(phenylamino)methyl] isoindolin-1-one* (**3b**): colourless solid, mp 152–155 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.02 (s, 3H, NCH_3), 3.67 (dd, ^2J = 12.8, ^3J = 6.2 Hz, 1H, CH_2), 3.90 (dd, ^2J = 12.8, ^3J = 6.2 Hz, 1H, CH_2), 4.60 (dd, ^3J = 6.2, ^3J = 6.2 Hz, 1H, NH), 5.54 (s, 1H, OH), 6.58 (m, 1H, H_{arom}), 6.68 (d, ^2J = 7.6 Hz, 2H, H_{arom}), 7.06 (m, 2H, H_{arom}), 7.51 (dd, ^3J = 7.2, ^4J = 1.0 Hz, 1H, H_{arom}), 7.59 (dd, ^3J = 7.2, ^4J = 1.0 Hz, 1H, H_{arom}), 7.66 (d, ^3J = 7.6 Hz, 1H, H_{arom}), 7.79 (d, ^3J = 7.6 Hz, 1H, H_{arom}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 23.9 (s, 1C, NCH_3), 49.0 (s, 1C, CH_2), 90.2 (s, 1C, COH), 113.9 (s, 2C, CH_{arom}), 117.8 (s, 1C, CH_{arom}), 123.3 (s, 1C, CH_{arom}), 123.7 (s, 1C, CH_{arom}), 129.8 (s, 2C, CH_{arom}), 130.4 (s, 1C, CH_{arom}), 130.7 (s, 1C, CH_{arom}), 133.4 (s, 1C, Cq), 147.7 (s, 1C, Cq), 149.6 (s, 1C, Cq), 167.5 (s, 1C, C=O). IR (KBr): ν = 3393, 2925, 1670, 1601, 1529, 1498, 1070, 741, 691 cm^{-1}.
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10. *N*-Acylated amino acids, if not commercially available, were synthesised according to: Paulmann, W. *Arch. Pharm.* **1894**, *232*, 601.
11. Selected physical and spectral data for *N-[(1-hydroxy-2-methyl-3-oxoisoindolin-1-yl) methyl]-N-phenylacetamide* (**8c**): yellowish solid, mp 158–160 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.63 (s, 3H, CH_3), 2.57 (s, 3H, NCH_3), 4.18 (d, ^2J = 14.5 Hz, 1H, CH_2), 4.51 (s, 1H, OH), 4.66 (d, ^2J = 14.5 Hz, 1H, CH_2), 6.69 (dd, ^3J = 7.8, ^4J = 2.3 Hz, 2H, H_{arom}), 7.19 (m, 3H, H_{arom}), 7.36 (m, 2H, H_{arom}), 7.44 (m, 1H, H_{arom}), 7.56 (m, 1H, H_{arom}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.9 (s, 1C, CH_3), 23.9 (s, 1C, NCH_3), 52.5 (s, 1C, CH_2), 90.0 (s, 1C, COH), 122.9 (s, 1C, CH_{arom}), 123.6 (s, 1C, CH_{arom}), 127.6 (s, 2C, CH_{arom}), 128.1 (s, 1C, CH_{arom}), 129.8 (s, 2C, CH_{arom}), 130.0 (s, 1C, CH_{arom}), 131.7 (s, 1C, CH_{arom}), 132.0 (s, 1C, Cq), 143.1 (s, 1C, Cq), 145.5 (s, 1C, Cq), 167.7 (s, 1C, C=O), 172.2 (s, 1C, C=O). IR (KBr): ν = 3249, 2935, 2345, 1656, 1691, 1631, 703 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 310 (M^+, 4), 292 (M^+-H_2O, 35), 77 (C_6H_5, 51). MS (ESI, positive ions): *m*/*z* = 311 $(M+H)^+$, 621 $(M_2+H)^+$. HR-MS (ESI, positive ions): Calcd $[M+H]^+$: 311.13902 for $C_{18}H_{18}N_2O_3 + H^+$. Found $[M+H]^+$: 311.13944. Calcd $[M+Na]^+$: 333.12096 for $C_{18}H_{18}N_2O_3 + Na^+$. Found $[M+Na]^+$: 333.12141.
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15. Selected physical and spectral data for *2-(1-ethyl-1-hydroxy-3-oxoisoindolin-2-yl)-N-methylacetamide* (**12b**): yellow solid, mp 95–97 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.46 (t, ^3J = 7.3 Hz, 3H, CH_3), 2.15 (m, 2H, CH_2), 2.72 (br s, 3H, CH_3), 3.81 (d, ^2J = 16.4 Hz, 1H, CH_2), 4.35 (d, ^2J = 16.4 Hz, 1H, CH_2), 5.67 (s, 1H, OH), 7.02 (br s, 1H, NH), 7.46 (ddd, ^3J = 7.3, ^3J = 7.3, ^4J = 1.0 Hz, 1H, H_{arom}), 7.53 (d, ^3J = 7.3 Hz, 1H, H_{arom}), 7.57 (ddd, ^3J = 7.3, ^3J = 7.3, ^4J = 1.0 Hz, 1H, H_{arom}), 7.70 (d, ^3J = 7.3 Hz, 1H, H_{arom}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 8.1 (s, 1C, CH_3), 26.7 (s, 1C, NCH_3), 29.6 (s, 1C, CH_2), 42.7 (s, 1C, CH_2), 92.1 (s, 1C, COH), 122.3 (s, 1C, CH_{arom}), 123.5 (s, 1C, CH_{arom}), 129.7 (s, 1C, CH_{arom}), 130.7 (s, 1C, Cq), 133.2 (s, 1C, CH_{arom}), 147.5 (s, 1C, Cq), 169.0 (s, 1C, C=O), 170.6 (s, 1C, C=O). IR (KBr): ν = 3291, 2929, 2346, 1690, 1663, 1617, 1260, 760 cm^{-1}.
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