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PAPER

Photoinduced decarboxylation of 3-(*N*-phthalimido)adamantane-1-carboxylic acid and radical addition to electron deficient alkenes†

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Direct and sensitized excitation of 3-(*N*-phthalimido)adamantane-1-carboxylic acid (**1**) leads to the population of the triplet state that, in the presence of a base, decarboxylates, giving *N*-(1-adamantyl)phthalimide (**2**) cleanly and efficiently ($\Phi = 0.11$). The radical initially formed by decarboxylation adds regiospecifically to electron deficient alkenes, whereas radical addition was not observed for electron rich alkenes. The radical addition can also be applied to molecules not bearing adamantanes wherein the electron donor (carboxylate) and the acceptor (phthalimide) are separated by a rigid spacer. The photodecarboxylation induced radical addition of phthalimide derivative **1** to alkenes takes place in good to excellent yields and represents a mild and efficient method for C–C bond formation.

Introduction

Phthalimide is a versatile chromophore that has been extensively used in different photochemical reactions with synthetic applicability.[1] Similar to simple carbonyl chromophores, excited state phthalimide abstracts H-atoms from suitable H-donors giving rise to addition and reduction products.[2] Recently, we reported the convenient photochemical formation of complex benzazepinone derivatives by a domino photochemical reaction of phthalimides that involves two consecutive intramolecular γ-H abstractions.[3] The second type of photochemical reaction of phthalimides is cycloaddition.[4] Mazzocchi *et al.* reported a number of formal $\sigma^2 + \pi^2$ cycloadditions that deliver benzazepinones.[5] Finally, imide derivatives undergo photoinduced single electron transfer (SET), and that probably represents the most widely used photochemical reaction of phthalimides in organic synthesis.[6]

The reduction potential of ground state *N*-methylphthalimide in DMF is −1.37 V *vs.* SCE (saturated calomel electrode).[7] Taking into account the energy for the excitation to the singlet and the triplet excited states (E_{00} = 3.8 eV and E_{00} = 3.1 eV, respectively), the reduction potentials in the excited states are estimated to be 2.4 V, and 1.7 V *vs.* SCE, respectively.[8] Consequently, phthalimides in the excited state are oxidants that react with electron-rich substrates. Intermolecular SET has been used in reactions of phthalimides with alkenes,[9] amines,[10] and thioethers.[11] Furthermore, intermolecular SET is involved in photoinduced decarboxylations.[12] Radicals that were formed on loss of CO_2 reacted with phthalimide giving addition products.[13] In addition, SET has been used in intramolecular reactions, inducing cyclizations to medium and large rings.[14] Particularly, SET promoted desilylations were applied in the synthesis of macrocyclic ethers,[15] whereas decarboxylations have found use in cyclizations of peptides.[16] However, photodecarboxylation induced addition to double bonds has not yet been reported in phthalimide photochemistry, although it is known in the photochemistry of carboxylic acids,[17] where it has been initiated by use of dicyanobenzenes as electron acceptors in the photoinduced electron transfer processes.[17]

In continuation of our research on synthesis of unnatural adamantyl amino acids,[18] and their transformations to more complex systems,[19] we turned our attention to the photochemistry of amino acids activated by a phthalimide moiety. Herein we report on synthesis of 3-(*N*-phthalimido)adamantane-1-carboxylic acid (**1**) and its photoinduced decarboxylation. Furthermore, for the first time, we describe photodecarboxylative radical addition of the phthalimide derivative to alkenes. The mechanism of the photochemical reaction was investigated by performing preparative irradiations and laser flash photolysis. Since this hitherto unknown photoinduced addition reaction of phthalimides represents a novel mild method for C–C bond formation it may find application in the functionalization of different molecules bearing phthalimide as a photoactivation group.

Results and discussion

3-(*N*-Phthalimido)adamantane-1-carboxylic acid (**1**) was prepared from 3-aminoadamantane-1-carboxylic acid[20] and phthalic

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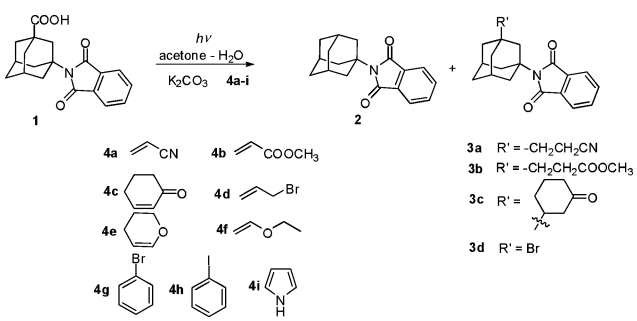
Table 1 Irradiation of **1** in the presence of alkenes and arenes[a]

Entry	Alkene/Arene	**2** (%)[b]	**3** (%)[b]
1	**4a**	5	(**3a**) 95
2	**4b**	8	(**3b**) 85
3	**4c**	30	(**3c**) 60
4	**4d**	40	(**3d**) 50
5	**4e**	20[c]	—
6	**4f**	30[c]	—
7	**4g**	80[c]	—
8	**4h**	100[c]	—
9	**4i**	100[c]	—

[a] Irradiation was carried out for 2 h in Ar-purged acetone–H_2O in the presence of K_2CO_3. [b] NMR ratio from the isolated mixture of products. [c] Isolated yield.

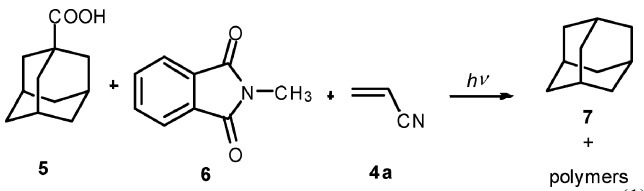
anhydride. The reaction was carried out in anhydrous refluxing DMF, yielding **1** in moderate yield (53%). Irradiation of **1** was performed under direct excitation and in the presence of acetone or benzophenone sensitizers. Both direct and sensitized excitation gave rise to decarboxylation, cleanly delivering *N*-(1-adamantyl)phthalimide (**2**). The photodecarboxylation was significantly more efficient in the presence of a protic solvent (H_2O) and base (K_2CO_3). The quantum yields of the photochemical decarboxylation of **1** in basic CH_3CN–H_2O (3 : 1) and acetone–H_2O (3 : 1) was determined by use of photodecarboxylation of 4-(*N*-phthalimidomethyl)cyclohexane-1-carboxylic acid (**8**, eqn (2)) as an actinometer (Φ_R = 0.3).[21] The quantum yields are Φ_R = 0.11 and Φ_R = 0.50, respectively. The estimated values for the quantum yield in the sensitized reaction (0.50), and on direct excitation (0.11), are in good agreement with the quantum yield of intersystem crossing (Φ_{ISC} = 0.22, *vide infra*). In order to induce the addition of the adamantylphthalimide to double bonds, or substitute the adamantyl moiety by an aryl group, irradiations of **1** were carried out in the presence of alkenes and arenes. Indeed, besides photodecarboxylation, for the first time addition of phthalimide derivatives to double bonds was achieved. Together with product **2**, novel 1,3-disubstituted adamantane derivatives **3** were obtained in good yields (Scheme 1). However, products **3** were obtained only with electron deficient alkenes. In the presence of electron rich alkenes or arenes, irradiation gave high-molecular weight products, or only decarboxlyation took place yielding **2** (Table 1). Irradiations were generally performed until the complete conversion of **1** was achieved. However, we have not observed formation of secondary photoproducts that would result from the intramolecular H-abstractions we have previously reported.[3] This is in accord with a much higher quantum yield of the photodecarboxylative addition to alkenes than that of the intramolecular H-abstraction, which is generally low.



Scheme 1

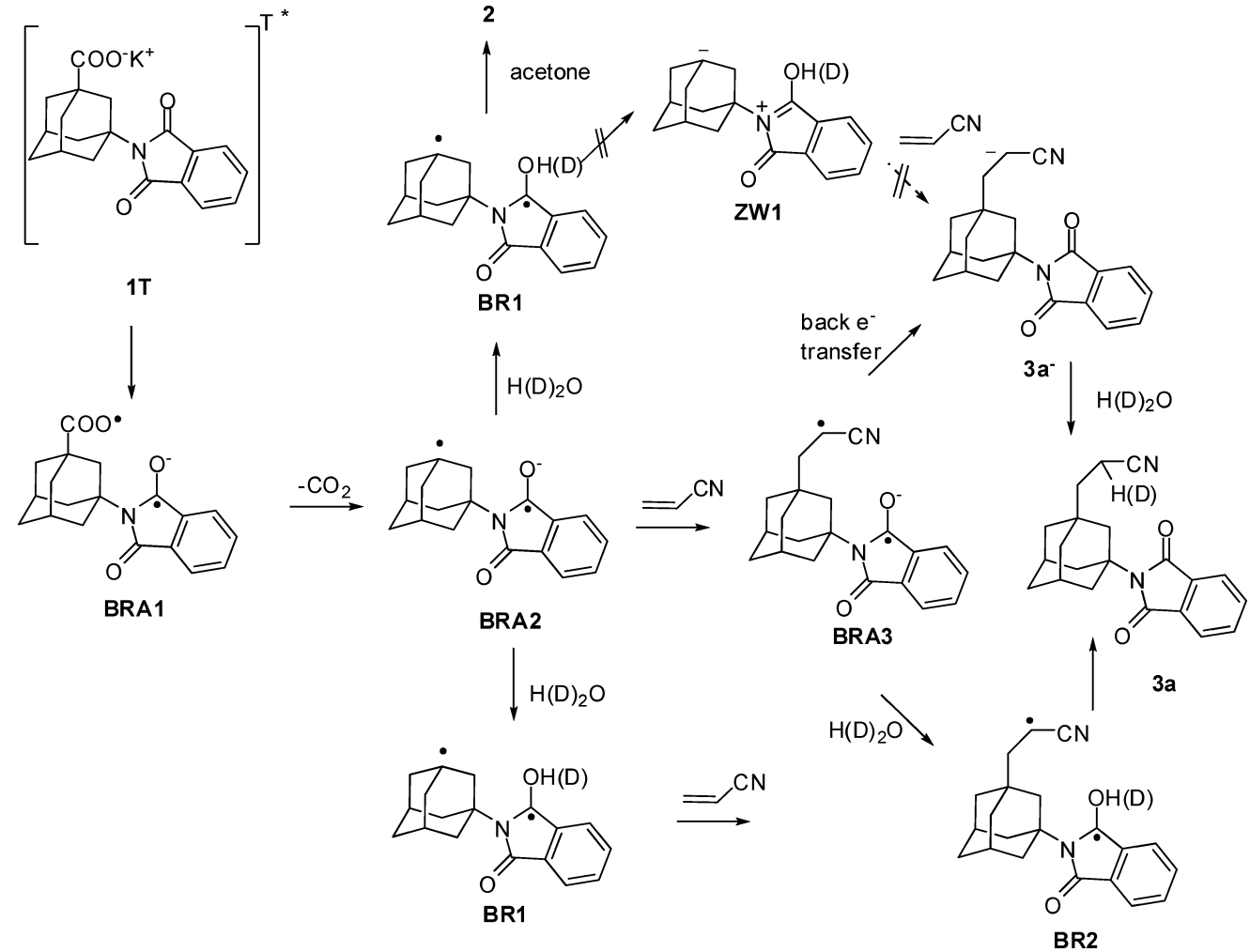
To get a deeper understanding of the mechanism of the decarboxylation and the addition to alkenes, we carried out irradiation of **1**, with and without acrylonitrile, in acetone–D_2O, or D_6-acetone–H_2O, in the presence of K_2CO_3. Detection of deuterated products in these experiments could indicate the presence of carbanion or radical intermediates in the mechanism. Irradiation of **1** in acetone–D_2O furnished **2** without deuterium being incorporated in the molecule (according to NMR and MS), whereas irradiation in D_6-acetone–H_2O gave rise to **2** with deuterium being incorporated at position 3 of the adamantane skeleton (65% D according to MS). Irradiation of **1** in acetone–D_2O in the presence of **4a** gave **3a** with one deuterium almost quantitatively incorporated (according to MS > 99% D) at the position alpha to the CN group (see ESI†). Isolation of the deuterated **2** indicates that the photodecarboxylation gives rise to an adamantyl radical that abstracts an H-atom from acetone giving **2**. On the other hand, formation of deuterated **3a** strongly suggests intermediacy of a carbanion in its formation (*vide infra*, Scheme 2).

To investigate the scope of the decarboxylative radical addition to alkenes we performed the intermolecular version of the reaction, that is, irradiation of admantane-1-carboxylic acid (**5**) and *N*-methylphthalimide (**6**) in the presence of acrylonitrile (eqn (1)). In accordance with previous findings, adamantane-1-carboxylic acid underwent decarboxylation.[12] However, no addition to the alkene took place. Presumably, the reason for the lack of the radical addition is slow intermolecular SET and decarboxylation, as well as competitive polymerization of acrylonitrile. Thus, whereas irradiation of **1** for 2 h gave complete conversion to **2** and **3**, acid **5** and phthalimide **6** were irradiated for 18 h to achieve complete conversion. During such a long irradiation, acrylonitrile polymerized and only decarboxylation took place without the addition products being observed by NMR or GC.

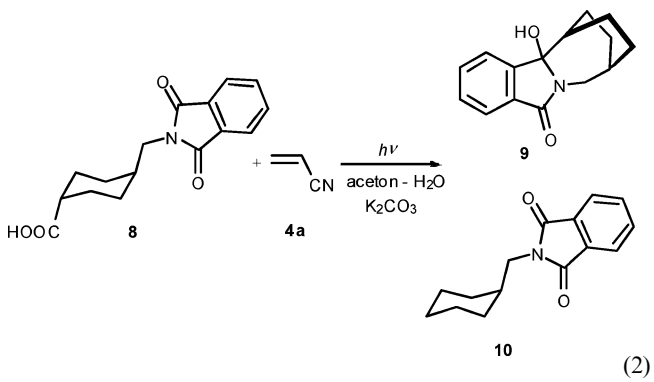


(1)

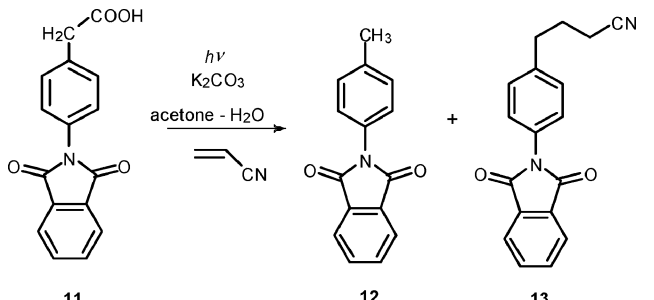
The scope of the reaction was also investigated for the derivatives without the adamantane skeleton. We performed irradiation of *trans*-4-(*N*-phthalimidomethyl)cyclohexane-1-carboxylic acid (**8**, used as an actinometer, *vide supra*) in the presence of acrylonitrile. However, under the irradiation conditions where **1** gave 95% yield of **3a**, intramolecular cyclization and decarboxylation of **8** took place and no intermolecular addition product was isolated (eqn (2)).



Scheme 2



(2)



(3)

The successful decarboxylative addition was achieved with the *N*-phenylphthalimide derivative **11**.[22] Irradiation of **11** in the presence of acrylonitrile gave decarboxylation product **12**[23] and addition product **13** (eqn (3)). This finding indicates that the decarboxylative addition principally can be used as a method for C–C bond formation in the synthesis of different compounds. However, the electron donor and the acceptor in the SET reaction have to be separated by a rigid spacer to prevent the cyclization.

Since photodecarboxylation of **1** takes place with sensitized or direct excitation, it is reasonable to assume that it is a triplet excited state process. However, the decarboxylation reaction is not quenched by O_2, suggesting that it is not a reaction taking place from the T_1 state. To get more insight into the photochemical reaction mechanism and characterize the triplet excited state we carried out laser flash photolysis (LFP). The LFP of the CH_3CN solution of **1** gave rise to transient absorption with the maximum at 340 nm (Fig. 1a) decaying with the rate constant $k = 7.7 \times 10^4$ s^{-1} ($\tau = 13$ μs). Comparison with the reported similar transient absorptions of the phthalimide chromophore[24] indicated the transient can be assigned to the T_1 state of **1**. The quantum yield of the intersystem crossing was estimated from the comparison of the intensity of the transient absorption with the optically matched solution of *N*-methylphthalimide

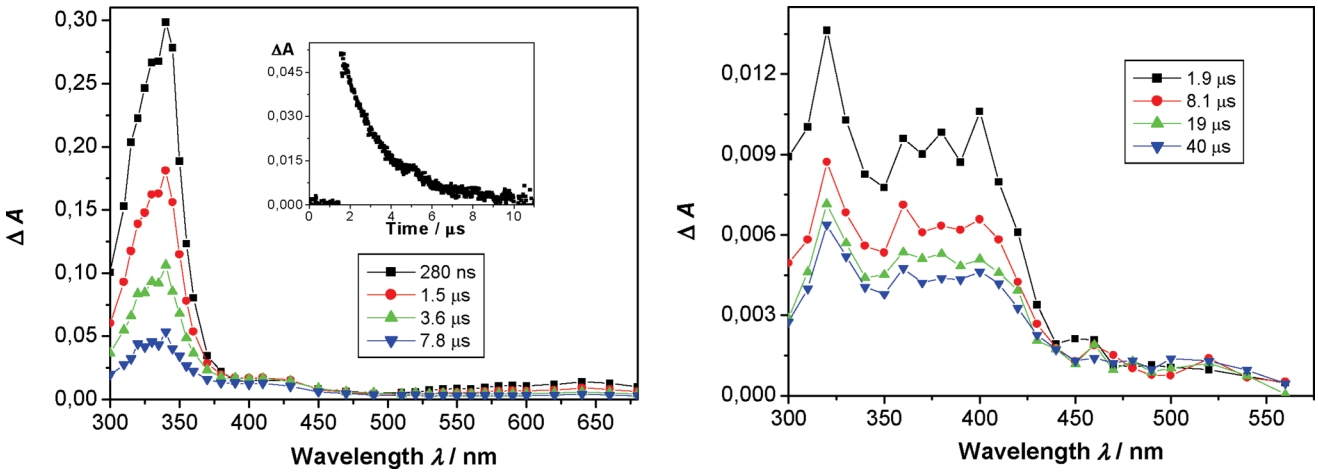


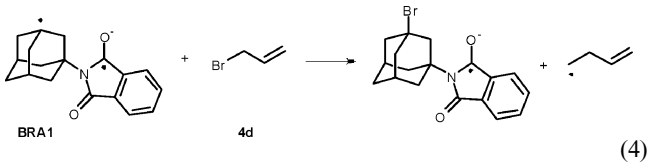
Fig. 1 Transient absorption spectra of **1** in N_2-purged CH_3CN (left), and N_2-purged CH_3CN–H_2O (1 : 1) in the presence of K_2CO_3 (right). Inset: decay at 340 nm in CH_3CN.

($\Phi_{ISC} = 0.8$), $\Phi_{ISC} = 0.22$.[24c] LFP experiments were also carried out under benzophenone sensitization (excitation 355 nm). We found that **1** quenches the triplet state of benzophenone. However, due to the overlapping of the transient absorption signals, quantitative analysis was difficult. The transient assigned to the phthalimide triplet (T_1) can be quenched by O_2 and ethyl vinyl ether (EVE) with the quenching rate constants $k_q = 2 \times 10^9$ M^{-1} s^{-1} and $k_q = 3 \times 10^9$ M^{-1} s^{-1}, respectively. In CH_3CN–H_2O solution in the presence of a base, more persistent transients were observed with a maximum at 400 nm. The latter were assigned to the phthalimide radical anion that is formed *via* intramolecular SET from the deprotonated carboxyl group (donor) to the phthalimide in the triplet excited state.

From the above findings, a mechanism for the photochemical reaction of **1** can be proposed (Scheme 2). On excitation (direct or sensitized) the T_1 state of the phthalimide, detectable by LFP, is populated. However, the T_1 is probably not the reactive state that delivers products, as suggested from the inability of oxygen to quench the decarboxylation reaction. Probably, the reaction takes place from an upper excited triplet state, in accordance with previous findings.[3b,24c,d] However, singlet excited state reactivity cannot be excluded. In the basic solution the upper triplet state of **1** undergoes intramolecular SET and gives biradical anion **BRA1** that rapidly and irreversibly decarboxylates, giving **BRA2**. Probably, the phthalimide radical anion detected by LFP (Fig. 1b) corresponds to **BRA2**, and is characterized by a relatively long lifetime. **BRA2** reacts as a radical with alkenes giving **BRA3**, or becomes protonated by H_2O to give **BR1**. Although the pK_a value of the phthalimide radical anion is not known, its protonation and formation of the ketyl radical species in protic solvents has been reported.[25] The reaction of **BRA2** with H_2O, followed by an H-atom transfer from acetone, ultimately delivers the decarboxylation product **2**, particularly in the absence of alkenes. The isolation of deuterated **2** on irradiation in D_6-acetone and finding that **2** without deuterium is formed on irradiation in D_2O shows that H-transfer from acetone delivers **2**, and not the intermolecular H-transfer from the OH(D) ketyl radical. **BRA3** formed in the reaction with electron deficient alkenes (R = CN, $COOCH_3$) most probably undergoes back electron transfer to deliver stabilized anion **3a**$^-$ and regenerate the phthalimide moiety. The protonation of anion **3a**$^-$ by H_2O yields the isolated addition products **3a**. Although, to the best of our knowledge, such a mechanism of photochemical reaction of phthalimides involving back electron transfer is not known, formation of the deuterated **3a** on irradiation in D_2O strongly indicates the intermediacy of the anion **3a**$^-$. In addition, back electron transfer after addition is the ubiquitous process in photo-NOCAS[26] and photo-ROCAS reactions.[27] The other less likely option for **BRA3** may be protonation of the radical anion moiety to **BR2**, followed by an intra- or an intermolecular H (D)-transfer yielding **3a**. In principle, formation of products **3** can also take place *via* a radical addition of alkene to **BR1** giving **BR2**, or a back electron transfer on **BR1** giving zwitterion **ZW1** that would react with alkene in a mechanism of Michael addition. However, since we have not detected deuterium in phthalimide **2**, the latter mechanism of back electron transfer prior to the addition to the double bond can be disregarded. Probably, the presence of the electron withdrawing group is essential for the back electron transfer.

Radical addition of **BRA2** to double bonds was only observed with electron deficient alkenes. The absence of the addition reaction with electron rich alkenes (entry 5 and 6, Table 1) is in accordance with the nucleophilic character of the adamantyl radical.[28] In addition, the lack of the addition reaction can be explained by quenching of the triplet state of **1** by these alkenes *via* intermolecular electron transfer. The T_1 state is quenched by EVE (*vide supra*). However, the Stern–Volmer quenching (see ESI†) is not indicative if EVE interacts with the upper triplet excited states. Quenching of the phthalimide excited state by electron rich alkenes *via* electron transfer, ultimately leading to the cycloaddition products, has been reported, wherein the triplet excited state reactivity has been precluded.[29] Consequently, in the presence of electron rich alkenes decarboxylation probably does not take place and the radical-cation of the alkene ultimately initiates formation of high-molecular weight material. Furthermore, if **BRA3** was formed by an addition to an alkene bearing an electron donating group, back electron transfer giving **3**$^-$ would not take place. The **BRA3** would then probably undergo cleavage to yield **2**, or initiate polymerization of the alkene.

Although adamantyl radicals have nucleophilic character, **BRA2** reacts with allyl bromide as a typical radical resulting in abstraction of a Br-atom and formation of a stable allyl radical that eventually forms polymers (eqn (4)). Such a reaction wherein the adamantyl radical abstracts bromine from the allyl bromide has been reported.[30] We cannot rule out, however, that **BRA2** adds to the double bond of the allyl bromide and gives a Br-radical. The latter reaction would give an adamantylalkene that is probably unstable and easily undergoes polymerization under irradiation conditions. The inability of arenes to react with **1** to give arylation products (entry 7–9, Table 1) may be explained by quenching of the triplet state of **1** by energy transfer to arenes. The other plausible reason may be too low radical-like reactivity of the adamantyl radical **BRA2** with arenes, and/or too high energy for the C–X bond cleavage.



(4)

Conclusion

After direct or sensitized excitation of phthalimide **1**, the triplet state is populated, and in the presence of a base undergoes decarboxylation (Φ = 0.11). The adamantyl radical formed by decarboxylation reacts with electron deficient alkenes giving addition products. The hitherto unreported addition reactions represent mild and efficient route to C–C bond formation. Since functionalization of the alkene allows for further derivatizations, this reaction could be applied in the synthesis of more complex adamantane derivatives and cage molecular structures, bearing phthalimide as a photoactivating group. In addition, the decarboxylative addition can be applied in the synthesis of molecules not bearing adamantanes providing that the phthalimide and the carboxylic acid are separated by a rigid spacer.

Experimental

Irradiation of 3-(*N*-phthalimido)adamantane-1-carboxylic acid (1) in the presence of alkenes and arenes, general procedure

A solution of 3-(*N*-phthalimido)adamantane carboxylic acid (**1**) (100 mg, 0.307 mmol), K_2CO_3 (21 mg, 0.1535 mmol) and alkene or arene **4** (3.070 mmol) in 200 mL acetone–H_2O (3 : 1) was irradiated at 300 nm in a Rayonet reactor (8 lamps) over 2 h and continuously purged with argon and cooled with an internal cold finger condenser (tap water). After irradiation, most of the acetone was removed on a rotary evaporator and the residue extracted with CH_2Cl_2 (3 × 50 mL). After the extraction, the aqueous phase was acidified to pH 3 by addition of HCl (0.1 M), and extraction with EtOAc was carried out (3 × 50 mL). The organic extracts were dried over anhydrous $MgSO_4$. After filtration and evaporation of the solvent photochemical products were obtained from the CH_2Cl_2 solution, whereas unreacted **1** was recovered from EtOAc. The ratio of the photoproducts **2** and **3** was determined by NMR.

Alternatively, after irradiation, the solvent (acetone and H_2O) was removed on a rotary evaporator and the residue chromatographed on a column filled with silica gel using 0–10% MeOH–CH_2Cl_2 as eluent. Pure photochemical products **3a–3d** were obtained by preparative TLC using CH_2Cl_2–Et_2O (9 : 1), or CH_2Cl_2–EtOAC–CH_3OH (8.5 : 1 : 0.5).

3-(*N*-Phthalimido)-1-(2-cyanoethyl)adamantane (3a). 92 mg (89%); yellowish oil; IR (KBr) ν_{max}/cm^{-1} 3457.6, 2911.5, 2852.9, 2245.4, 1769.1, 1706, 1368.8, 1314.4, 1078.6, 718.8; ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm) 7.76–7.73 (m, 2H), 7.69–7.66 (m, 2H), 2.47 (d, 2H, J = 11.7 Hz), 2.44 (d, 2H, J = 11.7 Hz) 2.35–2.31 (m, 2H), 2.27–2.25 (m, 2H), 2.24 (s, 2H), 1.79–1.74 (m, 1H), 1.63–1.58 (m, 3H), 1.56 (dd, 2H, J = 1.2 Hz, J = 12.2 Hz), 1.49 (dd, 2H, J = 1.2 Hz, J = 12.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 169.5 (s, 2C, C═O), 133.6 (d, 1C), 131.7 (s, 2C), 122.4 (d, 2C), 120.3 (s, 1C, CN), 60.3 (s, 1C), 43.8 (t, 1C), 40.1 (t, 2C), 39.2 (t, 2C), 38.6 (t, 1C), 35.2 (t, 1C), 34.3 (s, 1C), 29.4 (d, 2C), 11.0 (t, 1C); HRMS, calcd for $C_{21}H_{22}N_2O_2$+H$^+$ 335.1749; obsd 335.1749.

3-(*N*-Phthalimido)-1-(3-methoxy-3-oxopropyl)adamantane (3b). 40 mg (33%); light yellow oil; ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm) 7.75–7.74 (m, 2H), 7.67–7.66 (m, 2H), 3.67 (s, 3H, OCH_3), 2.46–2.44 (m, 4H), 2.33–2.30 (m, 2H), 2.23 (br s, 4H), 1.73 (d, 1H, J = 12.4 Hz), 1.59 (d, 1H, J = 12.4 Hz), 1.56–1.53 (m, 4H), 1.45 (d, 2H, J = 12.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm) 174.6 (s), 169.6 (s, 2C), 133.5 (d, 2C), 131.8 (s, 2C), 122.4 (d, 2C), 60.7 (s), 51.4 (q), 44.2 (t), 40.4 (t, 2C), 39.5 (t, 2C), 38.1 (t), 35.4 (t), 34.2 (s), 29.6 (d, 2C), 27.8 (t); IR (KBr) ν_{max}/cm^{-1} 3452.2, 2913.3, 1718.3, 1447.5, 1356.3, 1312.1, 1172.3, 1076.1, 718.7; HRMS, calcd for $C_{22}H_{25}NO_4$+Na$^+$ 390.1676; obsd 390.1676.

3-(*N*-Phthalimido)-1-(3-oxocyclohexyl)adamantane (3c). 36 mg (29%); colorless oil, ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.77–7.72 (m, 2H), 7.70–7.65 (m, 2H), 2.52–2.44 (m, 5H), 2.43–2.36 (m, 1H), 2.36–2.32 (m, 1H), 2.31–2.17 (m, 4H), 2.16–2.05 (m, 2H), 2.00 (d, 1H, J = 12.7 Hz), 1.76 (d, 1H, J = 12.5 Hz), 1.64–1.56 (m, 3H), 1.53–1.30 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 212.6 (s), 169.6 (s, 2C), 133.6 (d, 2C), 131.7 (s, 2C), 122.4 (d, 2C), 61.0 (s), 49.0, (d), 42.0 (t), 41.8 (t), 41.3 (t), 39.7 (t), 39.6 (t), 38.3 (t), 37.6 (t), 36.9 (s), 35.6 (t), 29.6 (d), 29.6 (d), 25.4 (t), 24.6 (t); IR (KBr) ν_{max}/cm^{-1} 2909.8, 2854.7, 1769.3, 1702.1, 1466.9, 1450.9, 1702.1, 1364.6, 1313.7, 1076.4; HRMS, calcd for $C_{24}H_{27}NO_3$+Na$^+$ 400.1883; obsd 400.1866.

3-(*N*-Phthalimido)-1-bromadamantane (3d). 10 mg (9%); colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.80–7.73 (m, 2H), 7.71–7.64 (m, 2H), 2.51 (br s, 2H), 2.48–2.33 (m, 6H), 1.83–1.65 (m, 5H), 1.56 (ddd, 1H, J = 8.0 Hz, J = 10.7 Hz, J = 12.6 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm) 169.4 (s, 2C), 133.7 (d, 2C), 131.7 (s, 2C), 122.6 (d, 2C), 69.2 (s), 68.2 (s), 47.8 (t), 43.8 (t, 2C), 38.8 (t, 2C), 34.6 (t), 30.7 (d, 2C); IR (KBr) ν_{max}/cm^{-1} 3447.4, 2915.1, 2855.6, 1769, 1704.3, 1354.8, 1308.7, 1121.3, 1100.2, 1077.5, 719.27; HRMS, calcd for $C_{18}H_{18}BrNO_2$+H$^+$ 360.0594; obsd 360.0594.

3-(*N*-Phthalimido)-1-(2-cyano-2-deuterioethyl)adamantane (3a-D)

A solution of 3-(*N*-phthalimido)adamantane carboxylic acid (**1**) (10 mg, 0.031 mmol), K_2CO_3 (2.1 mg, 0.015 mmol) and acrylonitrile **4a** (20 μL, 0.31 mmol) in 20 mL acetone–D_2O (3 : 1) was irradiated at 300 nm in a Rayonet reactor (8 lamps) for 45 h and continuously purged with argon and cooled with an internal cold finger condenser (tap water). After irradiation, the solvent

was removed on a rotary evaporator and the residue dissolved in $CDCl_3$ to record its NMR spectra. Yellowish oil, ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm) 7.76–7.73 (m, 2H), 7.69–7.66 (m, 2H), 2.47 (d, 2H, J = 11.7 Hz), 2.44 (d, 2H, J = 11.7 Hz) 2.33–2.29 (m, 1H), 2.27–2.25 (m, 2H), 2.24 (s, 2H), 1.80–1.76 (m, 1H), 1.61–1.59 (m, 3H), 1.56 (dd, 2H, J = 1.2, J = 12.2 Hz), 1.49 (dd, 2H, J = 1.2 Hz, J = 12.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm) 169.6 (s, 2C), 133.6 (d, 2C), 131.8 (s, 2C), 122.3 (d, 2C), 120.3 (s), 60.4 (s), 43.9 (t), 40.2 (t, 2C), 39.4 (t, 2C), 38.6 (t), 35.3 (t), 34.4 (s), 29.5 (d, 2C), 10.8 (dt, J_{HD} = 20.1 Hz); MS (ESI, m/z), 337 (25, M+H$^+$), 336 (100, M+H$^+$).

N-(3-Deuteroadamantyl)phthalimide (D–2)

A solution of 3-(*N*-phthalimido)adamantane carboxylic acid (**1**, 10 mg, 0.031 mmol) and K_2CO_3 (2.1 mg, 0.015 mmol) in 3 mL d_6-acetone–H_2O (3 : 1) was divided in three quartz NMR tubes. Each solution was purged with argon and irradiated at the same time in a Rayonet reactor (8 lamps) for 7 min at 300 nm. After irradiation, samples were combined and solvent was removed on a rotary evaporator. Pure product was isolated on preparative TLC with 5% MeOH–CH_2Cl_2 as eleunt and characterized by NMR and MS spectra.

5 mg, colorless crystals, ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.78–7.71 (m, 2H), 7.69–7.62 (m, 2H), 2.51 (s, 6H), 2.16 (s, 2H) 1.84–1.66 (m, 6H); MS (ESI, m/z), 283.2 (100, M+H), 284.2 (21).

Irradiation of 4-(*N*-phthalimido)phenyl acetic acid (11) in the presence of acrylonitrile

4-(*N*-Phthalimido)phenyl acetic acid (**11**) (56 mg, 0.2 mmol), K_2CO_3 (13.8 mg, 0.1 mmol) and acrylonitrile **4a** (131 μL, 2 mmol) were dissolved in acetone–H_2O (3 : 1, 20 mL) in a quartz cuvette. The solution was purged with argon for 15 min and then irradiated in a Rayonet reactor (8 lamps) for 4 h at 300 nm. After irradiation, the solvent was removed on a rotary evaporator and photoproducts **12** and **13** were isolated on a preparative TLC with 10% MeOH–CH_2Cl_2, and 60% hexane/15% ethyl acetate/15% CH_2Cl_2 as eluents.

***N*-(4-Methylphenyl)phthalimide (12).** 43 mg (77%), colorless crystals, mp 204–206 °C (lit. 204–205 °C);

***N*-[4-(3-Cyanopropyl)phenyl]phthalimide (13).** 8 mg (13%), colorless crystals, mp 145–147 °C; ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm) 7.99–7.89 (m, 4H), 7.40–7.34 (m, 4H), 2.75 (t, 2H, J = 7.9 Hz), 2.53 (t, 2H, J = 7.1 Hz) 1.91 (dd, 2H, J = 7.1, J = 7.9 Hz); ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm) 167.1 (s, 2C), 140.5 (s, 2C), 134.7 (d, 2C), 131.6 (s, 2C), 128.8 (d, 2C), 127.4 (d, 2C), 123.4 (d, 2C), 120.4 (s), 33.6 (t), 26.4 (t), 16.0 (t); IR (KBr) ν_{max}/cm^{-1} 2933, 2856, 2244, 1717, 1516, 1395, 1121, 1099, 1083, 715; HRMS, calcd for $C_{18}H_{14}N_2O_2$+H$^+$ 291.1128; obsd 291.1135.

Laser flash photolysis (LFP)

All LFP studies were conducted at the University of Victoria LFP facility employing a YAG laser, with a pulse width of 10 ns and excitation wavelength 266 nm or 355 nm (benzophenone experiments). Static cells (0.7 cm) were used and solutions were purged with nitrogen or oxygen for 20 min prior to measurements. Optical densities of **1** at 266 nm were ~0.4–0.6.

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