

Regioselective 1,4-addition of ammonia to 1-arylalka-1,3-dienes and 1-aryl-4-phenylbuta-1,3-dienes by photoinduced electron transfer

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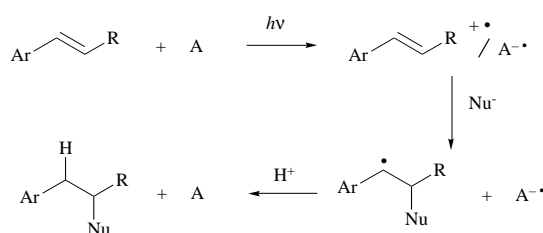
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The photoamination of 1-arylalka-1,3-dienes **1a–f** and 1-aryl-4-phenylbuta-1,3-dienes **1g–k** with NH₃ in the presence of *p*-dicyanobenzene (DCB) gives 4-amino-1-arylalk-2-enes **2a–f** and 1-amino-1,4-diarylbut-2-enes **2g–k**, respectively. The photoamination proceeds by nucleophilic addition of NH₃ to the cation radicals of **1**⁺ generated by photoinduced electron transfer to DCB. The regiochemistry of **2** is related to the distribution of the positive charge in **1**⁺ calculated by the PM3-UHF/RHF method, the stability of the aminated radicals formed by the addition of NH₃ to **1**⁺ and the stability of the aminated anion formed by the reduction of the aminated radicals by DCB^{•-}. The stabilities of these intermediates are estimated by the calculation of the heat of formation by the PM3-UHF/RHF method. Distributions of the positive charge in **1**⁺ and the stabilities of the aminated anion show a good agreement with the product analysis.

Photoinduced nucleophilic addition (PNA) to double bonds occurs through generation of the cation radicals of the substrates by photoinduced electron transfer to an electron acceptor and subsequent addition of nucleophiles to the cation radicals followed by electron-transfer and protonation steps (see Scheme 1). The PNA of alcohols have been applied to a



Scheme 1

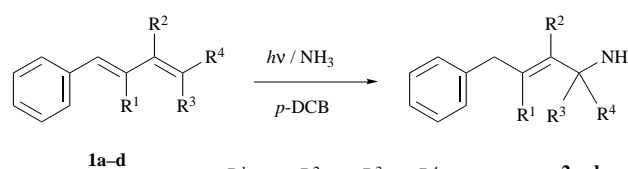
variety of substrates involving alkenes and strained molecules (e.g. cyclopropanes) from synthetic and mechanistic points of view.¹ However, PNA of alcohols to the delocalized cation radicals of arenes and stilbenes were unsuccessful because of the weak nucleophilicity of alcohols.² By use of stronger nucleophiles than alcohols, NH₃ and primary alkylamines, we have investigated extensively the PNA reactions to arenes³ and stilbenes⁴ as well as styrenes⁵ and 1,1-diarylalk-1-enes (photoamination).⁶ However, little is known about PNA to conjugated alkadienes. We are interested in the regiochemistry of the PNA reaction to conjugated dienes and the factors controlling the regiochemistry. Here we report on the photoamination of 1-arylalka-1,3-dienes **1a–f** and 1-aryl-4-phenylbuta-1,3-dienes **1g–k** with NH₃.

Results and discussion

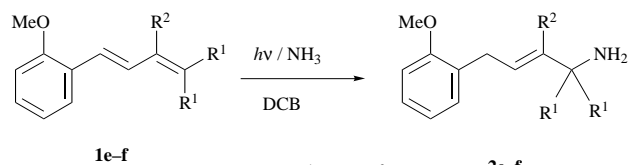
Photoamination

The substrates selected for the photoamination were 3-methyl-1-phenylbuta-1,3-diene **1a**, 2-methyl-, 3-methyl- and 4-methyl-1-phenylpenta-1,3-dienes **1b–d**, 1-(*o*-methoxyphenyl)-3-methyl-

buta-1,3-diene **1e**, and 1-(*o*-methoxyphenyl)-4-methylpenta-1,3-diene **1f**. 1-Arylbuta-1,3-dienes having no substituent on the terminal vinyl group could not be used for the photoamination, since they were rapidly polymerized and converted into intractable materials under the reaction conditions employed. Irradiation of an ammonia-saturated MeCN–H₂O (8:2, v/v) solution containing **1a–f** and *p*-dicyanobenzene (DCB) by a high-pressure mercury lamp gave 4-amino-1-arylalk-2-enes **2a–f** (Scheme 2). The aminated products were acetylated by Ac₂O



	R ¹	R ²	R ³	R ⁴	2a–d
a	H	Me	H	H	
b	Me	H	H	Me	
c	H	Me	Me	H	
d	H	H	Me	Me	



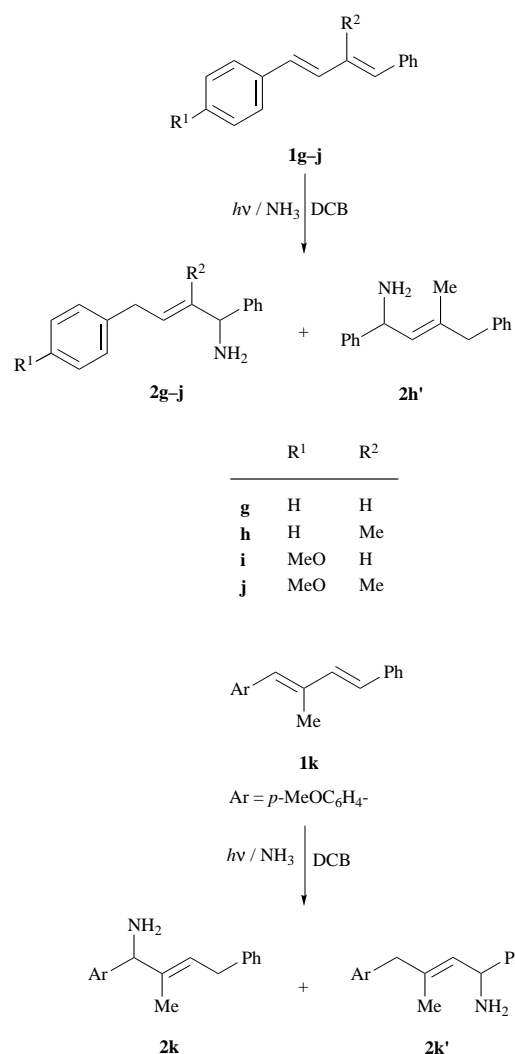
	R ¹	R ²	2e–f
e	H	Me	
f	Me	H	

Scheme 2

and then isolated by column chromatography on silica gel. The results are shown in Table 1. The photoamination of **1a** gave 4-amino-3-methyl-1-phenylbut-2-ene **2a**, resulting in a selective 1,4-addition of NH₃. Similarly, the photoamination

of **1b–d** gave exclusively the corresponding 1,4-addition products, 2-methyl-, 3-methyl- and 4-methyl-4-amino-1-phenylpent-2-enes **2b–d**, respectively. Although the yields of **2a–d** were low (26–37%), other isomers were not isolated. The photoamination of *o*-methoxyphenyl-substituted compounds **1e, f** gave the corresponding 1,4-addition products **2e, f** in relatively high yields (77–85%). These aminated products were isolated as one stereoisomer, the *E*-form, even though a mixture of *E*- and *Z*-stereoisomers of **1** were used as the starting materials.

Moreover, the photoamination was applied to 1-aryl-4-phenylbuta-1,3-dienes **1g–k** (Scheme 3). The photoamination



Scheme 3

of 1,4-diphenylbuta-1,3-diene **1g** gave 1-amino-1,4-diphenylbut-2-ene **2g**. The photoamination of 2-methyl-1,4-diphenylbuta-1,3-diene **1h** gave 1-amino-2-methyl-1,4-diphenylbut-2-ene **2h** (58%) predominantly over 1-amino-3-methyl-1,4-diphenylbut-2-ene **2h'** (11%). The photoamination of 1-(*p*-methoxyphenyl)-4-phenylbuta-1,3-diene **1i** and 1-(*p*-methoxyphenyl)-3-methyl-4-phenylbuta-1,3-diene **1j** gave exclusively 4-amino-1-(*p*-methoxyphenyl)-4-phenylbut-2-ene **2i** and 4-amino-1-(*p*-methoxyphenyl)-3-methyl-4-phenylbut-2-ene **2j**, respectively, thus resulting in selective amination at the benzylic position (C-4) of the unsubstituted phenyl group. On the other hand, the photoamination of 1-(*p*-methoxyphenyl)-2-methyl-4-phenylbuta-1,3-diene **1k** gave 1-amino-1-(*p*-methoxyphenyl)-2-methyl-4-phenylbut-2-ene **2k** (58%) together with 4-amino-1-(*p*-methoxyphenyl)-2-methyl-4-phenylbut-2-ene **2k'** (13%), showing that the photoamination occurred mainly at the benzylic position (C-1) of the *p*-methoxyphenyl group.

Table 1 Photoamination of **1a–k** with NH₃^a

1	E_2^{ox}/V	Product	Yield (%)	Conversion (%)
1a	1.16	2a	26	95
1b	0.99	2b	28	100
1c	0.98	2c	30	82
1d	0.88	2d	37	100
1e	0.95	2e	77	96
1f	0.82	2f	85	100
1g	0.87	2g	89	97
1h	0.82	2h, 2h'	58, 11	90
1i	0.64	2i	60	93
1j	0.67	2j	50	50
1k	0.67	2k, 2k'	58, 13	71

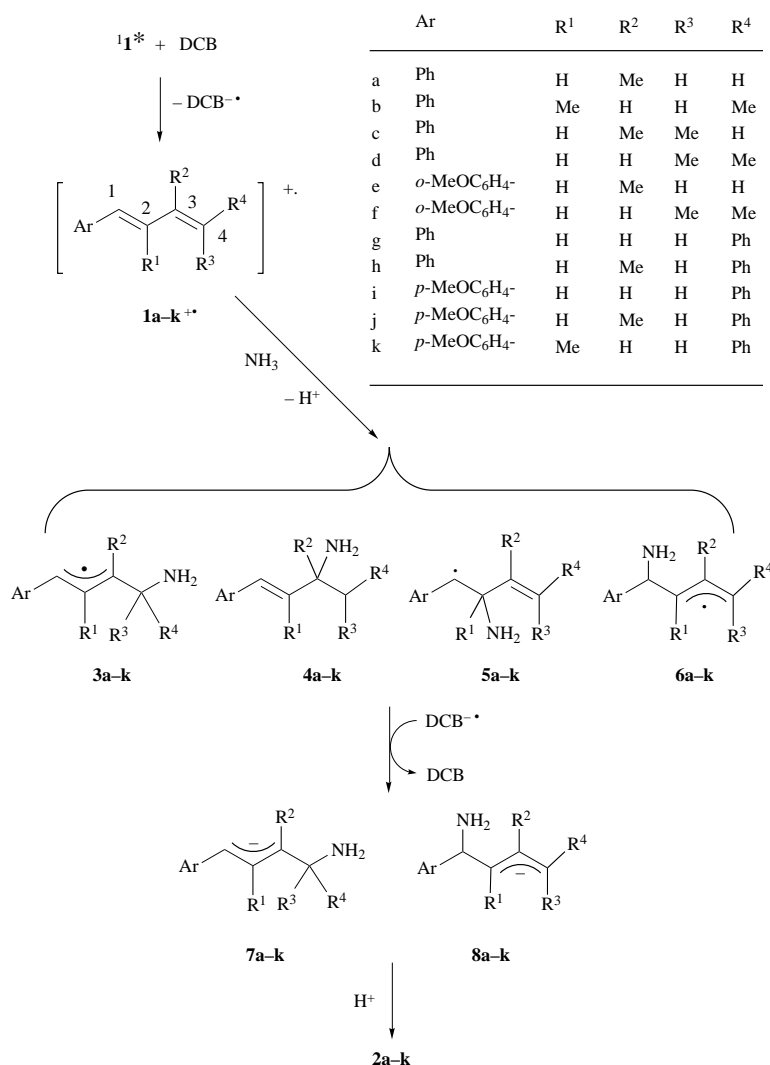
^a DCB was recovered >80% yield except for the cases of **1c** (63%).

Mechanism

The photoamination of **1g–k** was shown to be initiated by electron transfer from the excited singlet state of **1g–k** to DCB from the following results: (i) the fluorescence of **1g–k** was quenched by DCB at nearly diffusion-controlled rates; (ii) the free energy changes (ΔG) for electron transfer from the excited singlet state of **1g–k** to DCB were calculated to be negative by the Rehm–Weller equation⁷ using half peak of oxidation potentials (E_2^{ox}) and E^{B-0} values obtained from fluorescence spectra; (iii) the fluorescence of **1g–k** were not quenched by NH₃ at all. Similarly, the electron transfer from the excited singlet state of **1a–f** to DCB is responsible for the initiation process of the photoamination of **1a–f**, since the oxidation potentials of **1a–f** were relatively low (Table 1) and no photoamination occurred in the absence of DCB, although the fluorescence quenching experiments of **1a–f** by DCB failed because of the short fluorescence lifetimes of **1a–f**. The cation radicals of **1** thus formed allow the nucleophilic attack of NH₃ to give the aminated radicals after deprotonation. The aminated radicals are reduced by the anion radicals of DCB, followed by protonation to give final aminated products **2** (Scheme 4). The photoinduced electron transfer from **1** in the ground state to the excited singlet state of DCB could be safely excluded under the reaction conditions, since almost all incident light was thought to be absorbed by **1** from a comparison of the molar absorptivity (ϵ) of **1** with that of DCB at 300 nm, the shorter wavelength limit of light transmission of a Pyrex filter [*e.g.* ϵ (DCB) = 36, ϵ (**1e**) = 6.4×10^4 , ϵ (**1i**) = 2.5×10^4 mol⁻¹ dm³ cm⁻¹ at 300 nm].

Regiochemistry

Thus, the photoamination proceeds *via* three kinds of intermediates: the cation radicals of **1**, the aminated radicals and the aminated anion. If the regiochemistry of the photoamination is determined by the differences in rate for the nucleophilic addition of NH₃ to the cationic centres of **1⁺**, it is necessary to estimate the activation energies in the process from **1⁺** to the aminated radicals. However, estimation of the activation energy is not so easy. So we considered both the distribution of positive charge in **1⁺** and the stabilities of the aminated radicals as factors determining the rate of nucleophilic addition. The distribution of the positive charge in **1⁺** was calculated by PM3-UHF/RHF on a MOPAC program (see Table 2). For compounds **1a–g,i,j**, it is found that the highest positive charge distributed over C-4 where the photoamination actually occurred, shows good agreement for the distribution of the positive charge with the product analysis. In the cases of **1h** where the positive charge develops over C-1 slightly more than C-4, the photoamination occurred at both the C-1 and C-4 positions. The positive charge of **1k⁺**, to some extent, develops over C-4, while the photoamination occurred mainly at C-1 and slightly at C-4. Therefore, the positive charge distribution of **1k⁺** was not in agreement with the regiochemistry.



Scheme 4

Table 2 Calculation of the charge distribution in the cation radicals of **1a-k**^a

Entry	C-1	C-2	C-3	C-4	Δq^b	Y/N ^c
a	0.02	0.02	-0.12	0.11	0.09	Y
b	0.01	0.08	-0.19	0.10	0.09	Y
c	0.04	-0.03	-0.10	0.12	0.08	Y
d	0.05	-0.03	-0.15	0.14	0.09	Y
e	-0.01	0.02	-0.12	0.08	0.09	Y
f	0.03	-0.02	-0.16	0.12	0.09	Y
g	0.08	-0.09	-0.09	0.08	0	Y
h	0.08	-0.12	-0.01	0.06	-0.02	N
i	0.04	-0.06	-0.12	0.09	0.05	Y
j	0.04	-0.09	-0.04	0.07	0.03	Y
k	0.01	0.01	-0.15	0.08	0.07	N

^a The calculation was performed by the PM3 UHF-RHF method. ^b Difference in positive charge between C-4 and C-1. ^c Y and N refer to whether the calculated values meet (Y) or do not agree with (N) the regiochemistry.

The stabilities of the aminated radicals were estimated using the calculation by a PM3-UHF method for the heat of formation, H_a , of four kinds of aminated radicals, **3-6**, which were derived from the amination at C-1, C-2, C-3 and C-4 (Table 3), on the basis that the difference, ΔH_a , of H_a for compounds **3-6** is thought to be equal to the difference in their stabilities. One or both of the radicals **3** and **6** aminated at C-1 and C-4 (benzylic position) were $>17 \text{ kJ mol}^{-1}$ more stable than the radicals **4** and **5** aminated at C-2 and C-3. Therefore, the photo-

Table 3 Calculation of the heat of formation (H_a) for the aminated radicals **3-6**^a

Entry	3	4	5	6	ΔH_a^b	Y/N ^c
a	149	243	194	192	-43	Y
b	147	191	177	143	4	N
c	125	210	159	151	-26	Y
d	137	166	153	138	-1	N
e	-3	90	48	43	-46	Y
f	-15	16	2	-10	-5	N
g	306	328	328	306	0	Y
h	263	326	298	283	-20	Y
i	141	168	162	142	-1	N
j	109	172	136	126	-17	Y
k	121	138	149	107	14	Y

^a Calculated by the PM3-UHF method (kJ mol^{-1}). ^b Difference in the heat of formation between **3** and **6**. ^c Y and N refer to whether the calculated values meet (Y) or do not agree with (N) the regiochemistry.

amination of **1** occurred at C-1 and/or C-4. Since the H_a values for **3a,c,e,h,j** were $>17 \text{ kJ mol}^{-1}$ lower than those of **6a,c,e,h,j** and the H_a of **6k** is 14 kJ mol^{-1} lower than that of **3k**, the stabilities of the aminated radicals show good agreement with the product analysis in the photoaminations of **1a,c,e,h,j** and **1k** which occurred predominantly at C-4 and C-1, respectively. In the cases of **1b**, **1d**, **1f** and **1i**, however, the H_a of **3** is nearly equal to or slightly higher ($<5.0 \text{ kJ mol}^{-1}$) than that of **6**; this shows that there is no difference between **3** and **6** in terms of the stabilities of their aminated radicals. This is a case where regio-

Table 4 Heat of formation (H_b) of the aminated anions **7a–k** and **8a–k**^a

Entry	7	8	ΔH_b^b	Y/N ^c
a	35	137	-102	Y
b	18	63	-45	Y
c	4	92	-88	Y
d	1	53	-52	Y
e	-109	-4	-105	Y
f	-154	-99	-55	Y
g	178	178	0	Y
h	130	169	-39	Y
i	8	20	-12	Y
j	-36	-16	-20	Y
k	-5	-16	11	Y

^a Calculated by the PM3-RHF method (kJ mol⁻¹). ^b $\Delta H_b = H_b(7) - H_b(8)$. ^c Y and N refer to whether the calculated values meet (Y) or do not agree with (N) the regiochemistry.

chemistry cannot be interpreted in terms of aminated radicals stability.

The reduction process for the aminated radicals by DCB^{-•} can also be related to the regiochemistry. The stabilities of the aminated allyl anions **7** and **8** derived from the reduction of **3** and **6** by DCB^{-•} were deduced from the heat of formation (H_b) calculated by PM3-RHF (see Table 4). In the case of 1-aryllalka-1,3-dienes **1a–f**, the H_b of **7a–f** were >40 kJ mol⁻¹ lower than those of **8a–f**, probably as a result of the conjugation of the anion with the aryl group in the former. For the 1-aryl-4-phenylbuta-1,3-dienes **1h–k**, **7h–j** and **8k** were more stable than **8h–j** and **7k**, respectively, showing a good agreement with the product analysis. Moreover, the protonation occurred on the benzylic position of the aminated allyl anions **7g–j** and **8k**, resulting in the 1,4-addition of NH₃.

In conclusion, we have calculated for the title compounds the positive charge distribution of the cation radicals and the heat of formation of the reactive intermediates by a simple calculation using the PM3-RHF/UHF method. Although the regiochemistry can be predicted to some extent by a PM3-UHF calculation for the positive charge distribution of **1⁺**, the heats of formation (H_b) of the aminated anions clearly direct the regiochemistry. The PM3-RHF calculation shows that the photoamination proceeds predominantly through a reaction pathway *via* the most stable aminated anion. Therefore, it is suggested that the reduction process of adduct radicals with the anion radicals of electron acceptors, in general, plays an important step in determining the regiochemistry and the efficiency in the PNA reaction.

Experimental

Melting points were measured on a Shibata MEL 270 and were uncorrected. ¹H (250 MHz) and ¹³C NMR (62.9 MHz) spectra were taken on a Bruker AC 250P spectrometer in CDCl₃ using tetramethylsilane as an internal standard. *J* Values are given in Hz. Mass spectra were measured on a Hitachi 2000A spectrometer. The oxidation potentials were measured on a Hokuto Denko HA-501G and HB-105 as potentiostat and function generator for an MeCN solution *vs.* an Ag/AgNO₃ reference electrode.

Materials

Acetonitrile of spectral grade was distilled from CaH₂ before use. DCB were recrystallized from MeOH. Commercially available **1g** was used without further purification.

Compounds (*E*)- and (*Z*)-**1a,d–f** were prepared by Wittig reactions of benzaldehyde or *o*-methoxybenzaldehyde with 2-methylprop-2-enyl(triphenyl)phosphonium bromide or 3-methylbut-2-enyl(triphenyl)phosphonium bromide in the presence of BuLi. Wittig reaction of 2-methyl-3-phenylprop-2-enal with ethyl(triphenyl)phosphonium bromide gave (*E*)- and (*Z*)-

1b. Compounds (*E*)- and (*Z*)-**1c** were prepared by Wittig reaction of *trans*-2-methylbut-2-enal with benzyl(triphenyl)phosphonium chloride. Compound (*E,E*)-**1h** was prepared by Wittig reaction of 2-methyl-3-phenylprop-2-enal with benzyl(triphenyl)phosphonium chloride in the presence of BuLi. Wittig reactions of 3-phenylprop-2-enal and 2-methyl-3-phenylprop-2-enal with *p*-methoxyphenylmethyl(triphenyl)phosphonium bromide gave (*E,E*)-**1i** and (*E,E*)-**1j**, respectively. The preparation of (*E,E*)-**1k** was performed by reaction of 3-(*p*-methoxyphenyl)-2-methylprop-2-enal with benzyl(triphenyl)phosphonium bromide. A mixture of stereoisomers of **1a–f** was used for the photoamination without separation.

Typical procedure

To a THF solution (250 cm³) of 3-methylbut-2-enyl(triphenyl)phosphonium bromide (50 mmol) and BuLi (1.6 mol dm⁻³ of hexane solution; 25 cm³) was added *o*-methoxybenzaldehyde (50 mmol) in THF (50 cm³). The mixture was stirred at room temperature for 15 h and then quenched with water (50 cm³) and extracted with CHCl₃ (200 cm³) and saturated brine (50 cm³). The organic layer was dried (Na₂SO₄), filtered and concentrated under reduced pressure to give **1f**.

(E)-3-Methyl-1-phenylbuta-1,3-diene 1a.⁸ δ_H 1.95 (3 H, s), 5.05 (1 H, s), 5.09 (1 H, s), 6.51 (1 H, d, *J* 16.1), 6.86 (1 H, d, *J* 16.1) and 7.18–7.42 (5 H, m); δ_C 18.52, 117.28, 126.42, 127.34, 127.79, 128.53, 128.79, 131.61 and 137.31 [Found (HRMS): *m/z* 144.0896. Calc. for C₁₁H₁₂: *M*, 144.0938].

(E,E)-2-Methyl-1-phenylpenta-1,3-diene 1b. δ_H 1.71 (3 H, d, *J* 6.3), 1.95 (3 H, s), 5.69–5.83 (1 H, m), 6.23 (1 H, d, *J* 15.8), 6.39 (1 H, s) and 7.17–7.39 (5 H, m); δ_C 13.64, 18.28, 124.64, 126.13, 127.97, 129.09, 129.67, 134.31, 136.46 and 138.10 [Found (HRMS): *m/z* 158.1075. Calc. for C₁₂H₁₄: *M*, 158.1095].

(E,E)-3-Methyl-1-phenylpenta-1,3-diene 1c.⁹ δ_H 1.74 (3 H, d, *J* 6.8), 1.82 (3 H, s), 5.67 (1 H, q, *J* 6.8), 6.41 (1 H, d, *J* 16.1), 6.79 (1 H, d, *J* 16.1) and 7.12–7.38 (5 H, m); δ_C 11.91, 13.99, 125.19, 125.43, 126.04, 126.68, 127.62, 128.41, 128.83 and 133.77 [Found (HRMS): *m/z* 158.1078. Calc. for C₁₂H₁₄: *M*, 158.1095].

(E)-4-Methyl-1-phenylpenta-1,3-diene 1d.⁸ δ_H 1.84 (3 H, s), 1.85 (3 H, s), 6.00 (1 H, d, *J* 11.0), 6.29–6.39 (1 H, m), 6.42 (1 H, d, *J* 14.4) and 7.13–7.40 (5 H, m); δ_C 18.59, 26.23, 121.35, 125.43, 126.01, 126.84, 128.49, 128.98, 136.54 and 138.03 [Found (HRMS): *m/z* 158.1087. Calc. for C₁₂H₁₄: *M*, 158.1094].

(E,E)-3-Methyl-1-(*o*-methoxyphenyl)buta-1,3-diene 1e.¹⁰ δ_H 1.65 (3 H, s), 3.79 (3 H, s), 4.94 (1 H, br s), 4.99 (1 H, br s), 6.25 (1 H, d, *J* 12.3), 6.48 (1 H, d, *J* 12.3), 6.80–7.00 (3 H, m) and 7.08–7.39 (1 H, m); δ_C 21.70, 55.27, 110.03, 117.38, 119.81, 123.18, 125.43, 128.36, 130.57, 132.88, 142.06 and 156.76 [Found (HRMS): *m/z* 174.1046. Calc. for C₁₂H₁₄O: *M*, 174.1044].

(E)-4-Methyl-1-(*o*-methoxyphenyl)penta-1,3-diene 1f. δ_H 1.76 (3 H, s), 1.79 (3 H, s), 3.74 (3 H, s), 6.25–6.48 (2 H, m) and 6.74–7.37 (5 H, m); δ_C 18.10, 26.16, 55.11, 110.42, 120.10, 121.84, 122.81, 126.42, 126.85, 128.20, 137.50 and 156.88 [Found (HRMS): *m/z* 188.1197. Calc. for C₁₃H₁₆O: *M*, 188.1199].

(E,E)-4-Methyl-1,2-diphenylbuta-1,3-diene 1h.¹¹ δ_H 2.13 (3 H, s), 6.66 (1 H, d, *J* 17.9), 6.67 (1 H, s), 6.99 (1 H, d, *J* 17.9) and 7.22–7.48 (10 H, m); δ_C 13.93, 126.39, 126.61, 127.27, 127.96, 128.15, 128.62, 129.24, 132.24, 134.19, 135.93, 137.64 and 137.85 [Found (HRMS): *m/z* 220.1253. Calc. for C₁₇H₁₆: *M*, 220.1252].

(E,E)-1-(*p*-Methoxyphenyl)-4-phenylbuta-1,3-diene 1i. Mp 160–161 °C (lit.,¹¹ 160–162 °C); δ_H 3.82 (3 H, s), 6.63 (1 H, d, *J* 14.8), 6.83–6.89 (2 H, m) and 7.37–7.68 (10 H, m); δ_C 55.27, 114.07, 123.20, 126.83, 127.81, 128.31, 128.99, 129.19, 130.10, 130.55, 134.47, 137.83 and 159.18 [Found (HRMS): *m/z* 236.1211. Calc. for C₁₇H₁₆O: *M*, 236.1201].

(E,E)-3-Methyl-1-(*p*-methoxyphenyl)-4-phenylbuta-1,3-diene 1j. Mp 112–115 °C; δ_H 2.19 (3 H, s), 3.81 (3 H, s), 6.60 (1 H, s),

6.61 (1 H, d, *J* 16.0), 6.89 (2 H, d, *J* 8.5), 6.97 (1 H, d, *J* 16.0), 7.19–7.35 (5 H, m) and 7.45 (2 H, d, *J* 7.8); δ_{C} 13.90, 55.22, 113.60, 126.26, 127.08, 127.16, 128.58, 130.49, 131.91, 133.34, 134.40, 134.38, 137.73 and 158.28 (Found: C, 86.04; H, 7.26. Calc. for $\text{C}_{18}\text{H}_{18}\text{O}$: C, 86.36; H, 7.25%).

(*E,E*)-2-Methyl-1-(*p*-methoxyphenyl)-4-phenylbuta-1,3-diene 1k. Mp 110–112 °C (hexane); δ_{H} 2.09 (3 H, s), 3.75 (3 H, s), 6.59 (1 H, d, *J* 15.8), 6.61 (1 H, s), 6.84 (1 H, d, *J* 15.8), 6.85 (2 H, d, *J* 8.7) and 7.31–7.39 (7 H, m); δ_{C} 13.88, 55.14, 114.00, 126.37, 127.44, 127.50, 128.06, 129.16, 130.03, 131.18, 132.06, 135.09, 137.90 and 158.95 (Found: C, 86.15; H, 7.37. Calc. for $\text{C}_{18}\text{H}_{18}\text{O}$: C, 86.36; H, 7.25%).

General procedure for photoaminations

An MeCN–H₂O (8:2, v/v; 70 cm³) solution containing **1** (3.5 mmol) and DCB (3.5 mmol) was introduced into a Pyrex vessel. Gaseous NH₃ was bubbled through the solution for 20 min after which it was irradiated with an Eikosha PIH-300 high-pressure mercury lamp (300 W) for 8–20 h with water cooling. After this, the mixture was evaporated under reduced pressure. The photolysates were treated with acetic anhydride (10 cm³) for 20 h, and then quenched with saturated aqueous NaHCO₃ with ice cooling. The reaction mixture was then extracted with CHCl₃ and the extract was dried (Na₂SO₄) and concentrated under reduced pressure. The residue was chromatographed on silica gel using CHCl₃ as eluent. After the elution of **1** and DCB, the aminated products which showed one spot on TLC were isolated. ¹H NMR spectroscopy showed that the purity of the aminated products was >90% except for **1 h** and **1k**.

4-Acetylamino-1-phenyl-3-methylbut-3-ene 2a. Oil; δ_{H} 1.74 (3 H, s), 1.95 (3 H, s), 3.35 (2 H, d, *J* 7.2, H-1), 3.93 (2 H, d, *J* 5.6, H-4), 5.47 (1 H, t, *J* 7.2, H-2), 6.23 (1 H, br s, NH) and 7.13–7.27 (5 H, m); δ_{C} 14.43, 22.87, 33.80, 46.57, 124.81, 125.76, 128.12, 128.26, 132.38, 140.63 and 170.41 [Found (HRMS): *m/z* 203.1342. Calc. for $\text{C}_{13}\text{H}_{17}\text{NO}$: *M*, 203.1309].

4-Acetylamino-2-methyl-1-phenylpent-2-ene 2b. Oil; δ_{H} 1.18 (3 H, d, *J* 6.6), 1.62 (3 H, s), 1.91 (3 H, s), 3.26 (2 H, s, H-1), 4.70–4.76 (1 H, m, H-4), 5.12 (1 H, d, *J* 8.7, H-3), 5.93 (1 H, br s, NH) and 7.12–7.30 (5 H, m); δ_{C} 16.27, 21.66, 23.17, 43.54, 45.58, 125.97, 127.93, 128.13, 128.70, 137.11, 139.25 and 169.07 [Found (HRMS): *m/z* 217.1419. Calc. for $\text{C}_{14}\text{H}_{19}\text{NO}$: *M*, 217.1466].

4-Acetylamino-3-methyl-1-phenylpent-2-ene 2c. Oil; δ_{H} 1.27 (3 H, d, *J* 6.8), 1.73 (3 H, s), 2.09 (3 H, s), 3.33 (2 H, d, *J* 7.2, H-1), 4.46 (1 H, m, H-4), 5.56 (1 H, t, *J* 7.2, H-2), 6.33 (1 H, d, *J* 8.2, NH) and 7.11–7.26 (5 H, m); δ_{C} 13.46, 19.33, 22.95, 33.60, 50.73, 122.97, 125.58, 128.03, 128.13, 136.64, 140.69 and 169.25 [Found (HRMS): *m/z* 217.1423. Calc. for $\text{C}_{14}\text{H}_{19}\text{NO}$: *M*, 217.1466].

4-Acetylamino-4-methyl-1-phenylpent-2-ene 2d. Oil; δ_{H} 1.41 (6 H, s), 1.88 (3 H, s), 3.34 (2 H, d, *J* 6.6, H-1), 5.58–5.68 (1 H, m, H-2), 5.79 (1 H, d, *J* 15.7, H-3), 6.19 (1 H, br s, NH) and 7.14–7.40 (5 H, m); δ_{C} 23.90, 27.12, 38.30, 53.50, 125.69, 125.69, 128.05, 128.18, 137.14, 140.14 and 169.25 [Found (HRMS): *m/z* 217.1512. Calc. for $\text{C}_{14}\text{H}_{19}\text{NO}$: *M*, 217.1466].

4-Acetylamino-1-(*o*-methoxyphenyl)-3-methylbut-2-ene 2e. Oil; δ_{H} 1.70 (3 H, s), 1.93 (3 H, s), 3.33 (2 H, d, *J* 7.4, H-1), 3.77 (2 H, s, H-4), 3.79 (3 H, s), 5.46 (1 H, t, *J* 7.4, H-2), 6.31 (1 H, br s, NH), 6.80–6.89 (2 H, m) and 7.08–7.19 (2 H, m); δ_{C} 14.18, 22.75, 27.97, 46.61, 54.98, 110.00, 120.18, 124.36, 126.99, 128.84, 129.07, 132.16, 156.94 and 170.09 [Found (HRMS): *m/z* 247.1614. Calc. for $\text{C}_{14}\text{H}_{19}\text{NO}_2$: *M*, 247.1572].

4-Acetylamino-1-(*o*-methoxyphenyl)-4-methylpent-2-ene 2f. Oil; δ_{H} 1.41 (6 H, s), 1.89 (3 H, s), 3.33 (2 H, d, *J* 6.4, H-1), 3.76 (3 H, s), 5.53–5.68 (1 H, m, H-2), 5.77 (1 H, d, *J* 15.8, H-3), 6.44 (1 H, s, NH), 6.65–6.89 (2 H, m) and 7.10–7.29 (2 H, m); δ_{C} 24.08, 27.27, 32.54, 53.53, 55.14, 110.14, 120.38, 125.27, 127.14, 128.88, 129.49, 137.21, 157.07 and 169.55 [Found (HRMS): *m/z* 247.1614. Calc. for $\text{C}_{15}\text{H}_{21}\text{NO}_2$: *M*, 257.1572].

1-Acetylamino-1,4-diphenylbut-2-ene 2g. Oil; δ_{H} 1.85 (3 H, s), 3.34 (2 H, d, *J* 6.2, H-4), 5.56–5.80 (4 H, m) and 7.10–7.33 (10 H, m); δ_{C} 22.86, 38.31, 54.29, 125.89, 126.84, 127.09, 128.32, 128.46, 128.46, 130.59, 130.71, 139.64, 141.17 and 169.05 [Found (HRMS): *m/z* 265.1432. Calc. for $\text{C}_{18}\text{H}_{19}\text{NO}$: *M*, 265.1399].

1-Acetylamino-2-methyl-1,4-diphenylbut-2-ene 2h. Oil; δ_{H} 1.63 (3 H, s), 1.94 (3 H, s), 3.43 (2 H, d, *J* 6.4, H-4), 5.52 (1 H, d, *J* 8.0, H-1), 5.65 (1 H, t, *J* 6.4, H-3), 6.09 (1 H, br d, *J* 8.0, NH) and 7.16–7.30 (10 H, m); δ_{C} 14.71, 23.21, 33.84, 59.28, 124.56, 125.46, 127.26, 127.44, 128.26, 128.38, 128.59, 134.74, 140.32, 140.80 and 168.93 [Found (HRMS): *m/z* 279.1643. Calc. for $\text{C}_{19}\text{H}_{21}\text{NO}$: *M*, 279.1622].

1-Acetylamino-3-methyl-1,4-diphenylbut-2-ene 2h'. δ_{H} 1.69 (3 H, s), 1.95 (3 H, s), 3.32 (2 H, s, H-1), 5.37 (1 H, d, *J* 8.0, H-3), 5.84 (1 H, t, *J* 8.0, H-4), 6.09 (1 H, br d, *J* 8.0, NH) and 7.16–7.30 (10 H, m).

1-Acetylamino-4-(*p*-methoxyphenyl)-1-phenylbut-2-ene 2i. Oil; δ_{H} 1.88 (3 H, s), 2.78 (2 H, d, *J* 12.1, H-4), 3.67 (3 H, s), 5.54–5.77 (4 H, m), 6.78 (2 H, d, *J* 8.5) and 7.01–7.61 (7 H, m); δ_{C} 22.61, 38.11, 54.76, 54.76, 113.46, 125.67, 126.64, 127.86, 128.01, 128.11, 128.30, 131.45, 131.61, 158.33 and 169.12 [Found (HRMS): *m/z* 295.1615. Calc. for $\text{C}_{19}\text{H}_{21}\text{NO}_2$: *M*, 295.1571].

1-Acetylamino-2-methyl-4-(*p*-methoxyphenyl)-1-phenylbut-2-ene 2j. Oil; δ_{H} 1.60 (3 H, s), 1.88 (3 H, s), 3.40 (2 H, d, *J* 7.1, H-4), 3.68 (3 H, s), 5.46 (1 H, d, *J* 8.3, H-1), 5.63 (1 H, t, *J* 7.1, H-3), 6.74 (1 H, d, *J* 8.3, NH), 6.79 (2 H, d, *J* 8.7) and 7.14–7.27 (7 H, m); δ_{C} 14.38, 22.70, 33.63, 54.86, 58.53, 113.63, 124.04, 125.59, 128.02, 128.13, 128.22, 132.31, 135.04, 140.65, 158.54 and 169.00 [Found (HRMS): *m/z* 309.1759. Calc. for $\text{C}_{20}\text{H}_{23}\text{NO}_2$: *M*, 309.1727].

1-Acetylamino-2-methyl-1-(*p*-methoxyphenyl)-4-phenylbut-2-ene 2k. Oil; δ_{H} 1.62 (3 H, s), 1.94 (3 H, s), 3.35 (2 H, d, *J* 7.2, H-1), 3.75 (3 H, s), 5.51 (1 H, d, *J* 8.4, H-4), 5.63 (1 H, t, *J* 7.2, H-2), 6.50 (1 H, d, *J* 8.4, NH), 6.82 (1 H, d, *J* 8.3), 7.08 (1 H, d, *J* 8.3) and 7.23–7.30 (7 H, m); δ_{C} 14.55, 23.10, 32.84, 55.07, 59.24, 113.69, 124.95, 127.19, 127.53, 128.48, 129.06, 132.74, 134.37, 140.28, 157.65 and 168.98 [Found (HRMS): *m/z* 309.1687. Calc. for $\text{C}_{20}\text{H}_{23}\text{NO}_2$: *M*, 309.1726].

1-Acetylamino-3-methyl-4-(*p*-methoxyphenyl)-1-phenylbut-2-ene 2k'. δ_{H} 1.66 (3 H, s), 1.93 (3 H, s), 3.31 (2 H, s, H-4), 3.75 (3 H, s), 5.37 (1 H, d, *J* 7.3, H-2), 5.78 (1 H, t, *J* 7.3, H-1), 6.27 (1 H, br s, NH), 6.82 (1 H, d, *J* 8.4), 7.08 (1 H, d, *J* 8.4) and 7.23–7.30 (7 H, m).

Calculation by PM3

The calculation was performed on a Silicon Graphics Ingico 2 IRIS workstation using a Daikin MOL-MOLIS/CRYS ver. 2.0 and MOPAC ver. 6.¹² The calculation on **1⁺** was performed by PM3-UHF to give the structure with minimum energy and followed by one cycle of SCF on PM3-RHF to give the distribution of the positive charge. The calculations on **3–6** were performed by PM3-UHF to give the structures and the heat of formations. The calculations on **7** and **8** were performed by PM3-RHF to give the structures and the heat of formations.

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