Compatibility of Various Carbanion Nucleophiles with Heteroaromatic Nucleophilic Substitution by the $S_{RN}1$ Mechanism

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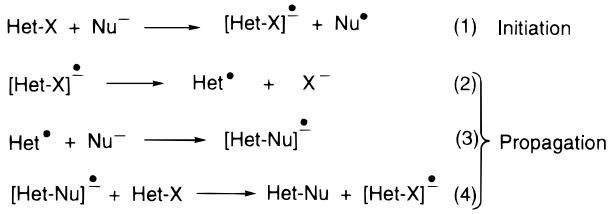
Carbanions generated from 2,4,4-trimethyl-2-oxazoline (**1a**), 2-benzyl-4,4-dimethyl-2-oxazoline (**1b**), 2,4-dimethylthiazole (**13a**), 2-benzyl-4-methylthiazole (**13b**), *N*,*N*-dimethylacetamide (**17a**), *tert*-butyl acetate (**17b**), ethyl phenylacetate (**17c**), *N*-methyl-*N*-phenyl-2-butenamide (**22**), *tert*-butyl 3-butenoate (**25**), and dimethyl methylphosphonate (**29a**) by means of KNH_2 in liquid NH_3 all reacted with 2-bromopyridine (**2**) via photoassisted reactions that exhibited characteristics of the $S_{RN}1$ mechanism. Similar results were obtained in reactions of these carbanions with other substrates, including 2-chloroquinoline (**6**), iodobenzene (**9**), bromobenzene (**10**), and bromomesitylene (**11**).

In connection with our continuing interest in the scope and synthetic utility of heteroaromatic $S_{RN}1$ reactions[1,2] (Scheme 1), we undertook a study of the participation of several synthetically useful but previously untested classes of carbanion nucleophiles as reactants in such radical chain processes involving π-deficient haloheterocycles. We were especially interested in nucleophiles in which the carbanion-stabilizing functional groups were readily amenable to synthetic transformations following attachment to the heterocylic substrate. Therefore, the nucleophiles chosen for study included carbanions derived from lateral deprotonation of the synthetically versatile 2,4,4-trialkyl-2-oxazolines **1a**,**b**[3] and 2,4-dialkylthiazoles **13a**,**b**,[4] as well as certain carboxamide and ester enolates and dienolates, along with the carbanion of dimethyl methylphosphonate (**29a**).

Owing to the established superiority of liquid NH_3 as a medium for $S_{RN}1$ reactions,[1,5] and in keeping with our aim to minimize the chemical complexity of the reaction mixtures, we limited our experiments to this solvent, using near-UV light (350 nm) to promote the substitution. The respective carbanions were generated with an alkali metal amide, usually KNH_2, which represents the strongest type of base available in liquid NH_3. The necessity for photoassistance in successful substitution reactions was tested by attempting analogous reactions in the dark, while the radical chain nature of productive reactions was probed using the radical scavenger, di-*tert*-butyl nitroxide (DTBN).[6] Since pyridyl halides generally represent the least reactive class of π-deficient substrates among typical heteroaromatic azines in both $S_{RN}1$ and S_NAr reactions,[7] 2-bromopyridine (**2**) was chosen as the model substrate. In cases where a particular nucleophile had not been tested previously for $S_{RN}1$ reactivity with carboaromatic substrates, iodobenzene (**9**), bromobenzene (**10**), and 1-bromomesitylene (**11**) were used as prototypical aryl halides.

Scheme 1



There have been no reports to date of carbanions derived from 2-alkyl-2-oxazolines and 2-alkylthiazoles participating in $S_{RN}1$ reactions. In addition, the extent to which such carbanions can be generated by means of alkali metal amides in liquid NH_3 is not well established.[8] When we began this study, examples of $S_{RN}1$ reactions of carboxamide and ester enolates with π-deficient heteroaromatic halides were rare, although Rossi had re-

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(8) Treatment of oxazolines **1a** and **1b** with KNH_2 or $NaNH_2$ in liquid NH_3 followed by propyl nitrate affords the corresponding 2-(α-nitroalkyl) derivatives in yields of 13 and 75−84%, respectively: Feuer, H.; Bevinakatti; Luo, X.-G. *J. Heterocycl. Chem.* **1986**, *23*, 825.

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Table 1. Reactions of 2,4,4-Trialkyl-2-oxazoline Carbanions Derived from 1a,b with Heteroaromatic and Carboaromatic Halides

expt	carbanion from	cation	substr	reaction time (min)	reaction conditions	products (yield, %)[a]
1	**1a**	K	**2**	5	*hν*	**3a** (26),[c] **4** (50),[c] **5** (1)[c]
2	**1a**	K	**2**	60	*hν*	**3a** (33), **4** (59)[d]
3	**1a**	Li	**2**	60	*hν*	**3a** (33), **4** (45)[d]
4	**1a**	K	**2**	5	dark	**3a** (4), **4** (64)
5	**1a**	K	**2**	5	*hν*, DTBN[b]	**3a** (<1), **4** (76)
6	**1a**	K	**6**	5	*hν*	**7** (41), **8** (16)
7	**1a**	K	**6**	5	dark	**7** (45), **8** (21)
8	**1a**	K	**6**	5	*hν*, DTBN[b]	**6** (37), **7** (13), **8** (22)
9	**1a**	K	**9**	5	*hν*	**1b** (56),[c] **12a** (28),[c] **5** (3)[c]
10	**1a**	K	**10**	120	*hν*	**1b** (63), **12a** (28)
11	**1a**	K	**9**	5	dark	**1b** (28)
12	**1a**	K	**9**	5	*hν*, DTBN[b]	**1b** (24)
13	**1a**	K	**11**	5	*hν*	**12b** (50)[d]
14	**1a**	K	**11**	60	*hν*	**12b** (94)
15	**1a**	K	**11**	5	dark	s.m.[e]
16	**1a**	K	**11**	5	*hν*, DTBN[b]	s.m.[e]
17	**1b**	K	**2**	5	*hν*	**3b** (70)
18	**1b**	K	**2**	120	*hν*	**3b** (88)
19	**1b**	K	**2**	5	dark	s.m.[e]
20	**1b**	K	**2**	5	*hν*, DTBN[b]	**1b** (66),[c] **3b** (34)[c]
21	**1b**	K	**9**	5	*hν*	**12a** (43)
22	**1b**	K	**9**	60	*hν*	**12a** (62)
23	**1b**	K	**9**	5	dark	s.m.[e]
24	**1b**	K	**9**	5	*hν*, DTBN[b]	**12a** (26)

[a] Unless indicated otherwise yields are those of isolated products. [b] 10 mol % based on substrate. [c] Yields determined by ^{1}H NMR. [d] Compound **5** was observed by ^{1}H NMR in the crude reaction mixture, but not isolated. [e] Only starting materials (s.m.) could be detected in the ^{1}H NMR spectrum of the crude reaction mixture.

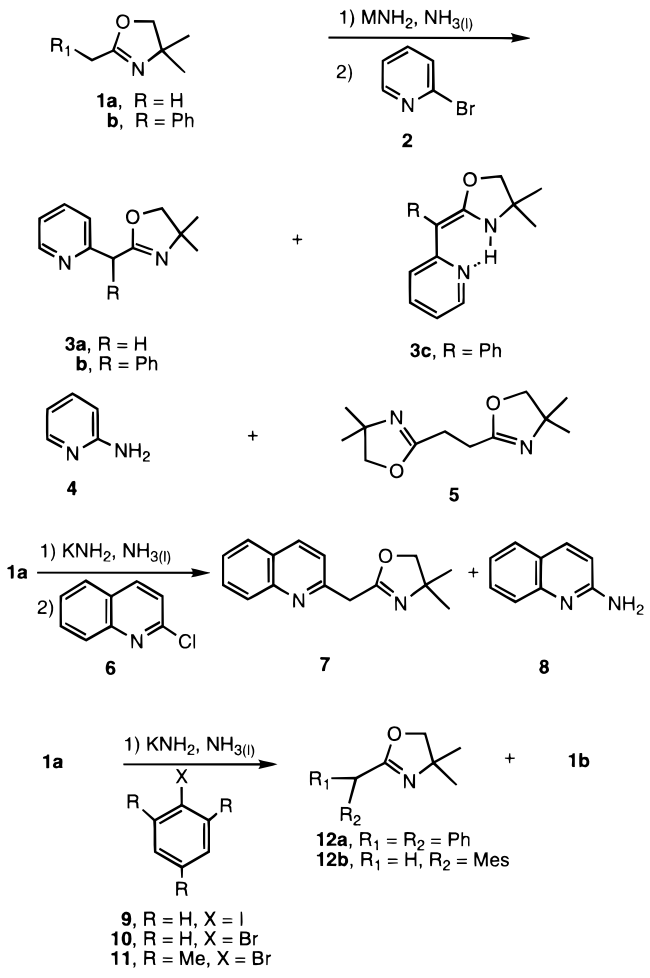
ported on the successful application of photostimulated, intermolecular $S_{RN}1$ reactions of amide[9] and lactam[10] enolates with several carboaromatic halides. Our report[11] of the intramolecular photocyclization of the α-enolate of 3-acetamido-2-chloropyridine was the only published example of a putative heteroaromatic $S_{RN}1$ reaction involving a carboxamide enolate. Reports[12] of reactions of ester enolates with carboaromatic halides were scarce as well, and the only example with a halogenated heterocycle involved the reaction of 2,6-dibromopyridine with the potassium enolate of ethyl phenylacetate.[13] More recently, McKillop and van Leeuwen published a thorough study of ferrous ion-promoted $S_{RN}1$ reactions of the sodium enolate of *tert*-butyl acetate with carboaromatic and heteroaromatic halides.[14] In the same paper, the sodium enolates of *N*-acylmorpholines were found to react with several carboaromatic substrates, but haloheterocycles were not studied. In spite of the synthetic versatility of phosphonate-stabilized carbanions,[15] there appear to be no literature examples of these or other phosphorous-stabilized carbanions participating in either carboaromatic or heteroaromatic $S_{RN}1$ reactions.

Results and Discussion

Carbanions Derived from 2,4,4-Trialkyl-2-oxazolines. These reactions are illustrated in Scheme 2, and the results of specific experiments appear in Table 1.

Treatment of 2,4,4-trimethyl-2-oxazoline (**1a**) with 1 equiv of KNH_2 in liquid NH_3 followed by addition of 2-bromopyridine (**2**) with irradiation of the reaction mixture for 5 min at −33 °C afforded substitution product **3a** (26%) along with 50% of 2-aminopyridine (**4**) and

Scheme 2



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oxazoline dimer **5** (1%). Similar results were obtained after 60 min of irradiation using either KNH_2 or $LiNH_2$ (Table 1 expts 1−3). Yields of **3a** declined dramatically after 5 min of illumination in the presence of 10 mol % of DTBN, or when the reaction was carried out in the dark. In both cases (expts 4 and 5) yields of **4** increased sharply, while dimer **5** could not be detected.

When 2-chloroquinoline (**6**) was employed as substrate with the carbanion of **1a** under illumination, a rapid reaction occurred to consume **6** and give 2-(2-quinolylmethyl)oxazoline **7** (41%) along with a 16% yield of 2-aminoquinoline (**8**) (expt 6). Similar yields of **7** and **8** were obtained from reactions conducted in the dark (expt 7). However, irradiation in the presence of 10 mol % of DTBN (expt 8) resulted in much lower yields (13%) of **7** and recovery of more starting materials when compared with both photostimulated and dark reactions conducted without DTBN.

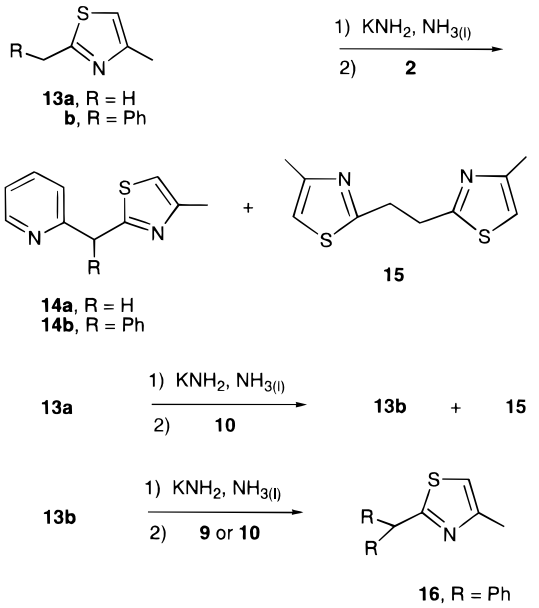
A series of photostimulated, dark, and DTBN-inhibited reactions of oxazoline **1a** in the presence of KNH_2 in liquid NH_3 with the carboaromatic substrates iodobenzene (**9**), bromobenzene (**10**), and 1-bromomesitylene (**11**) produced mono- (**1b** and **12b**) and diarylated (**12a**) products as summarized in Table 1 (expts 9−16).

The results obtained with **1a** and 2-bromopyridine (**2**) are consistent with photoinduced, radical chain pyridylation of the lateral carbanion of **1a** to give **3a**. Formation of 2-aminopyridine (**4**) in photostimulated reactions (expts 1−3), and to a greater extent in dark and in DTBN-inhibited reactions (expts 4 and 5), indicates that **1a** is incompletely deprotonated by KNH_2 in liquid NH_3. Thus, amide ion competes via an ionic S_NAr reaction for substrate **2** with the carbanion of **1a**, which appears to react with **2** mainly by the $S_{RN}1$ mechanism. When the $S_{RN}1$ pathway is impeded by conducting the reaction in the dark, or in the presence of DTBN, the ionic amination reaction dominates.[6c] In the reactions of the carbanion of **1a** with 2-chloroquinoline (**6**) the yield of **7** was diminished only in the presence of DTBN (expt 8), implicating the occurrence of a thermally initiated $S_{RN}1$ process in the dark reaction (expt 7).

In contrast to reactions involving 2-bromopyridine (**2**) (expts 4 and 5) when reactions of **1a** with iodobenzene (**9**) were conducted in the dark (expt 11) or with irradiation in the presence of DTBN (expt 12), appreciable (24−28%) amounts of the phenylated product **1b** were formed. It seems unlikely that the carbanion of **1a** would react with **9** by either an ionic S_NAr mechanism or by an $S_{RN}1$ pathway that was more resistant to inhibition or more prone to thermal initiation than the analogous radical chain process involving **2**. Instead, it is more reasonable to assume that amide ion in equilibrium with **1a** effects benzyne phenylation of the carbanion of **1a** to produce **1b**. When the possibility of aryne formation was precluded by using 1-bromomestiylene (**11**) as substrate, photostimulated reactions of the carbanion of **1a** to form substitution product **12b** proceeded quite well (expts 13 and 14), while dark and DTBN-inhibited reactions with **11** gave only recovered starting materials (expts 15 and 16).

Although it is tempting to assume that dimer **5** is formed by coupling of 2-oxazolinylmethyl radicals generated in the initiation step of the radical chain substitution involving the carbanion of **1a** (Scheme 1, step 1), this is not the only pathway available for dimerization. Thus, treatment of **1a** alone with KNH_2 in liquid NH_3 under near-UV irradiation for 1 h, followed by careful anaerobic quenching with solid NH_4Cl to avoid possible aerial oxidative dimerization of the carbanion (vide infra), afforded **5** in 30% yield. Without illumination, **5** was formed in only trace amounts under otherwise identical experimental conditions or when the dark reaction mixture was exposed to air during neutralization with NH_4Cl.

Scheme 3



2-Benzyl-4,4-dimethyl-2-oxazoline (**1b**) was readily converted to its lateral carbanion[8] by means of 1 equiv of KNH_2 in liquid NH_3 as evidenced by facile, photoinduced reactions with **2** to form 2-pyridyl derivative **3b** in yields of 70−88% (expts 17 and 18). When the reaction mixture was denied illumination, only starting materials were present after 5 min (expt 19) and DTBN exerted a strong inhibitory effect on the photostimulated substitution reaction (expt 20). None of these reactions produced detectable (^1H NMR) amounts of 2-aminopyridine (**4**) or the phenylated analog of dimer **5**. Iodobenzene (**9**) proved to be less reactive than **2** as an electron acceptor in photostimulated reactions (expts 21 and 22) and exhibited a complete lack of reactivity in the dark, along with diminished photoreactivity in the presence of DTBN (expts 23 and 24).

Carbanions Derived from 2,4-Dialkylthiazoles. Results of reactions of the carbanions derived from 2,4-dimethylthiazole (**13a**) and 2-benzyl-4-methylthiazole (**13b**) with 2-bromopyridine (**2**), iodobenzene (**9**), and bromobenzene (**10**) are illustrated in Scheme 3 and summarized in Table 2.

As with oxazoline **1a**, deprotonation at the 2-methyl group of **13a** by KNH_2 is incomplete as evidenced by competitive formation of 2-aminopyridine (**4**) when **2** was employed as substrate (expts 25−27). Amination of bromobenzene (**10**) was not observed, but this substrate, like **2**, displayed the dependency on near-UV irradiation and susceptibility to DTBN (expts 28−30) expected for a photostimulated $S_{RN}1$ reaction.

Reactions of the carbanion of **13a** with substrates **2** and **10** were accompanied by formation of thiazole dimer **15** in yields of 12−18% under photostimulation (with or without DTBN) and in the dark (expts 25 and 28−30). Dimer **15** was also produced from **13a** in 20% yield in

Table 2. Reactions of 2,4-Dialkylthiazole Carbanions Derived from 13a,b with Heteroaromatic and Carboaromatic Substrates

expt	carbanion from	cation	substr	reaction time (min)	reaction conditions	products (yield, %)[a]
25	**13a**	K	**2**	100	*hν*	**14a** (37), **4** (37), **15** (12)
26	**13a**	K	**2**	100	dark	**4** (89)
27	**13a**	K	**2**	100	*hν*, DTBN	**4** (89)
28	**13a**	K	**10**	100	*hν*	**13b** (59), **15** (14)
29	**13a**	K	**10**	100	dark	**13b** (12), **15** (14)
30	**13a**	K	**10**	100	*hν*, DTBN	**15** (18)
31	**13b**	K	**2**	100	*hν*	**14b** (94)
32	**13b**	K	**2**	100	dark	s.m.[b]
33	**13b**	K	**2**	100	*hν*, DTBN	s.m.[b]
34	**13b**	K	**9**	100	*hν*	**16** (39)
35	**13b**	K	**10**	100	*hν*	**16** (57)
36	**13b**	K	**10**	100	dark	**16** (9)
37	**13b**	K	**10**	100	*hν*, DTBN	s.m.[b]

[a] Unless indicated otherwise, yields are those of isolated products. [b] Only starting materials (s.m.) could be detected in the ^{1}H NMR spectrum of the crude reaction mixture.

the absence of substrate by irradiating a mixture of **13a** and KNH_2 in liquid NH_3 for 1 h, followed by an anaerobic quench with NH_4Cl. Without irradiation, <2% of **15** was formed under these conditions. Thiazole **13a** afforded 18% of dimer **15** when a similar dark reaction mixture was poured onto solid NH_4Cl, thereby exposing the carbanion to air. This is in contrast to oxazoline **1a**, which failed to yield dimer **5** upon similar treatment. Thus, while the carbanions of both **1a** and **13a** undergo photoinduced dimerization, only the latter is appreciably susceptible to aerobic oxidative dimerization. The anaerobic dimerization of these carbanions may result from a redox process involving photostimulated electron transfer from the carbanion to the respective neutral precursors, **1a** and **13a**, which are present owing to their incomplete deprotonation.

Deprotonation of 2-benzyl-4-methylthiazole (**13b**) with KNH_2 appears complete as evidenced by nearly quantitative, photoassisted 2-pyridylation of the resulting carbanion to afford **14b** (expt 31). This reaction, as well as the analogous phenylations with **9** and **10**, required irradiation and was strongly inhibited by DTBN (expts 32−37). The lower reactivity of the carbanion of 2-benzylthiazole **13b** toward carboaromatic halides **9** and **10** versus heterocyclic substrate **2** may be the result of the greater rate at which this more stable (lower pK_a) carbanion transfers an electron to the more easily reduced pyridyl halide **2** than to halobenzenes **9** and **10**.[7,16]

Carboxamide and Ester Enolates. As anticipated from earlier reports of carboxamide enolate ion reactivity toward carboaromatic halides under photostimulation[9] or in the presence of ferrous ion,[14] the potassium enolate, **17a**, of *N*,*N*-dimethylacetamide reacted smoothly with heterocyclic halides **2** and **6** under illumination to afford good yields of 2-pyridyl (**18a**) and 2-quinolyl (**20**) products, accompanied by minor amounts of disubstitution products **19a** and **21**, respectively (Scheme 4). These results are summarized in Table 3 (expts 38−46), where it may be seen that the radical chain character of the reactions was indicated by their relatively sluggish nature in the dark and the strong inhibitory action of catalytic amounts of DTBN. It appears that the dark reaction of amide enolate **17a** with 2-chloroquinoline (**6**) to give **20** (expt 44) is a thermally initiated $S_{RN}1$ process,

Scheme 4

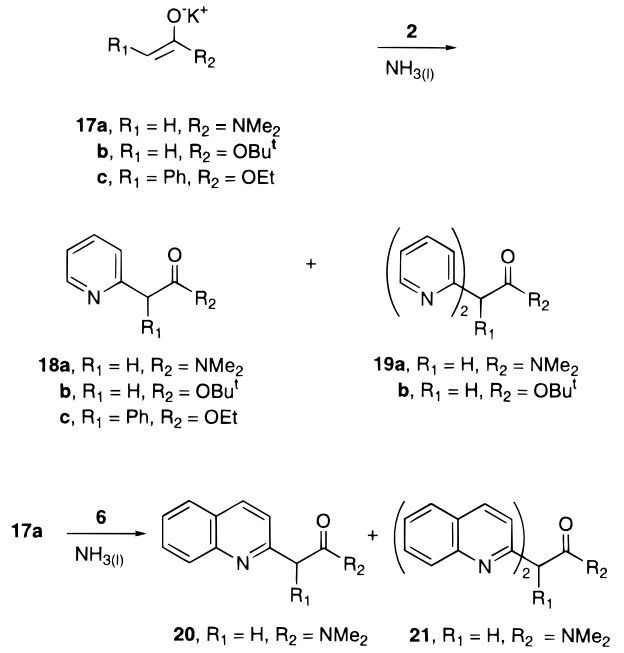


Table 3. Reactions of the Potassium Enolates of *N*,*N*-Dimethylacetamide (17a), *tert*-Butyl Acetate (17b), and Ethyl Phenylacetate (17c) with Substrates 2 and 6

expt	enolate	substr	reaction time (min)	reaction conditions	products (yield, %)[a]
38	**17a**	**2**	5	*hν*	**18a** (74),[b] **19a** (5)[b]
39	**17a**	**2**	20	*hν*	**18a** (84), **19a** (7)
40	**17a**	**2**	5	dark	**18a** (17)
41	**17a**	**2**	5	*hν*, DTBN	**18a** (2)
42	**17a**	**6**	5	*hν*	**20** (87)
43	**17a**	**6**	60	*hν*	**20** (80), **21** (14)
44	**17a**	**6**	5	dark	**20** (41)
45	**17a**	**6**	5	dark, DTBN	s.m.[c]
46	**17a**	**6**	5	*hν*, DTBN	s.m.[c]
47	**17b**	**2**	5	*hν*	**18b** (44), **19b** (21)
48	**17b**	**2**	5	dark	**18b** (5)
49	**17b**	**2**	5	*hν*, DTBN	s.m.[c]
50	**17c**	**2**	5	*hν*	**18c** (77)
51	**17c**	**2**	5	dark	s.m.[c]
52	**17c**	**2**	5	*hν*, DTBN	s.m.[c]

[a] Unless indicated otherwise, yields are those of isolated products. [b] Yields determined by GC. [c] Only starting materials (s.m.) could be detected in the ^{1}H NMR spectrum of the crude reaction mixture.

since DTBN, which would not be expected to inhibit an ionic S_NAr reaction, prevents formation of **20** in the dark (expt 45).

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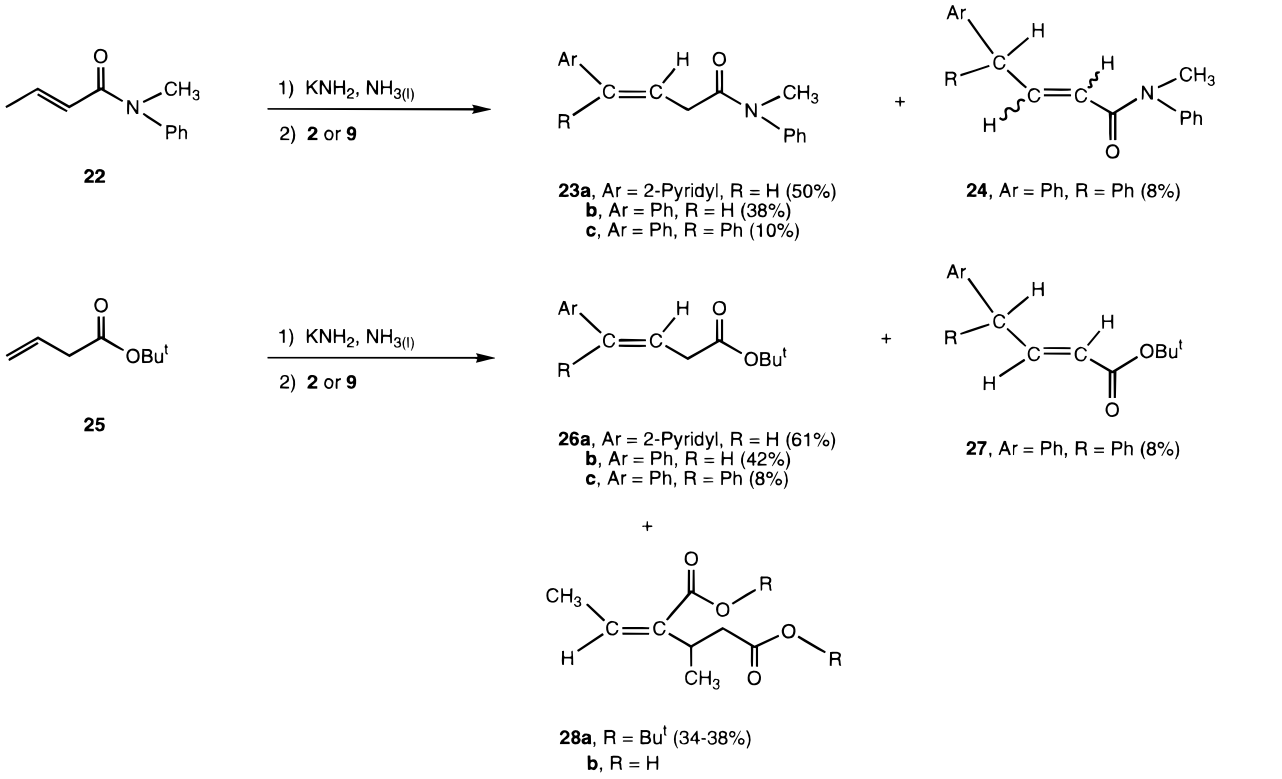
Scheme 5

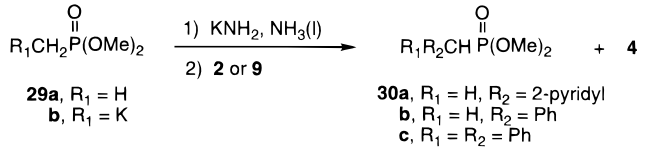


Reactions of the potassium enolates of *tert*-butyl acetate (**17b**) and ethyl phenylacetate (**17c**) with substrate **2** (expts 47−52) exhibited mechanistic features similar to those of the carboxamide enolates. Illumination facilitated the substitution process, while experiments involving near-UV light together with DTBN (expts 49 and 52), or those conducted in the dark (expts 48 and 51), failed to afford products **18b**,**c** and **19b**.

Although dienolate ions derived from α,*β*-unsaturated carbonyl compounds have not been unequivocally identified as participating nucleophiles in either carboaromatic or heteroaromatic $S_{RN}1$ reactions,[11,17] we have now found that the potassium dienolates of (*E*)-*N*-methyl-*N*-phenyl-2-butenamide (**22**) and *tert*-butyl 3-butenoate (**25**) both react smoothly and regioselectively with substrates **2** and **9** under photostimulation to give exclusively *γ*-substituted products (Scheme 5). Thus, reaction of the dienolate of amide **22** with **2** gave **23a** in 50% isolated yield, with no detectable (^{1}H NMR) amounts of products arising from pyridylation at the position α to the carbonyl group. The analogous reaction of this dienolate with **9** similarly resulted in exclusive *γ*-phenylation, but was complicated by formation of both mono- (**23b**) and diphenylated (**23c** and **24**) products.

Pyridylation of the dienolate from *β*,*γ*-unsaturated ester **25** gave **26a** (61%) unaccompanied by either α-coupled or α,*β*-unsaturated products. As in the case of amide **22**, phenylation of the ester dienolate mainly resulted in monosubstitution at the *γ*-position to produce both **26b** (42%) and diphenyl derivatives **26c** (8%) and **27** (8%). Photoassisted reactions of the potassium dienolate of ester **25** with both **2** and **9** were accompanied by formation of ester self-condensation product **28a**, the origin of which can be traced to a Michael addition of the original dienolate anion to the neutral α,*β*-unsaturated isomer of **25**, produced by proton−metal exchange between excess dienolate present in the reaction mixture and the acidic α-hydrogens of the $S_{RN}1$ product.[18] All of the substitution reactions shown in Scheme 5, including formation of diester **28a**, failed to proceed in the dark.

Carbanion of Dimethyl Methylphosphonate. Treatment of dimethyl methylphosphonate (**29a**) with 1 equiv of KNH_2 in liquid NH_3 generated α-carbanion **29b** in sufficient equilibrium concentration to afford α-(2-pyridyl) phosphonate **30a** in 68% yield after 1 h of illumination (expt 53). The accompanying formation of 2-aminopyridine (**4**) in 10% yield implicated competitive S_NAr amination of **2** (Table 4, expt 53). This was further



supported by the results of expts 54 and 55, where amination of **2** became the major substitution pathway when electron transfer was suppressed without a light source or by adding DTBN to the illuminated reaction mixture. Phenylation of carbanion **29b** with iodobenzene (**9**) to form **30b**,**c** responded to photostimulation (expt 56),

(17) (a) A report that the dienolate of cyclohex-2-en-1-one failed to react with bromobenzene under near-UV irradiation appears to be the only published example of an attempt to effect an intermolecular aromatic $S_{RN}1$ reaction with the dienolate of an α,*β*-unsaturated carbonyl compound: Bunnett, J. F.; Sundberg, J. E. *J. Org. Chem.* **1976**, *41*, 1702. (b) Our earlier finding[11] that carbanions from a series of α,*β*-unsaturated *o*-haloanilides underwent photoinduced cyclizations prompted us to intiate the present study of intermolecular reactions with dienolates from α,*β*-unsaturated anilides. (c) For a description of $S_{RN}1$ reactions involving carbanions from α,*β*-unsaturated nitriles, see: Alonso, R. A.; Austin, E.; Rossi, R. A. *J. Org. Chem.* **1988**, *53*, 6065.

(18) (a) Munch-Petersen, J. *J. Org. Chem.* **1957**, *22*, 170. (b) Shabtai, J.; Ney-Igner, E., Pines, H. *J. Org. Chem.* **1981**, *46*, 3795. (c) Shabtai, J.; Pines, H. *J. Org. Chem.* **1965**, *30*, 3854.

Table 4. Reactions of Dimethyl Methylphosphonate Carbanion 29b with Substrates 2 and 9

expt	K salt	substr	reaction time (min)	reaction conditions	products (yield, %)[a]
53	**29b**	**2**	60	*hν*	**30a** (68), **4** (10)
54	**29b**	**2**	25	dark	**2** (40), **4** (51)
55	**29b**	**2**	25	*hν*, DTBN	**30a** (4)[b]
56	**29b**	**9**	60	*hν*	**30b** (47), **30c** (18)
57	**29b**	**9**	25	dark	s.m.[c]
58	**29b**	**9**	25	*hν*, DTBN	**30b** (30)[d]

[a] Unless indicated otherwise, yields are those of isolated products. [b] The crude reaction mixture also contained **2** and **4** as determined by qualitative GC and ^{1}H NMR analysis. [c] Only starting materials (s.m.) could be detected in the ^{1}H NMR spectrum of the crude reaction mixture. [d] Unreacted **9** was also present.

failed to occur in the dark (expt 57), but was surprisingly resistant to inhibition by DTBN (expt 58).

Conclusion

Carbanions derived from alkyl oxazolines (**1a**,**b**), thiazoles (**13a**,**b**), and phosphonate **29a** by means of KNH_2 in liquid NH_3 are shown here for the first time to participate in photostimulated $S_{RN}1$ reactions with carboaromatic and heteroaromatic halides. These reactions proceed with sufficient generality and efficiency to be synthetically useful, with the caveat that incomplete, equilibrium deprotonation of the respective carbanion precursors may result in competitive S_NAr amination of certain heterocyclic substrates.

The present results involving the potassium enolates of *N*,*N*-dimethylacetamide (**17a**), *tert*-butylacetate (**17b**), and ethyl phenylacetate (**17c**) in $S_{RN}1$ reactions with heterocyclic substrates **2** and **6** complement the results of earlier studies of reactions of these and related carboxamide[9−11,14] and ester[12,14] enolates with carboaromatic halides and, in the process, establish these enolates as versatile nucleophiles in aromatic $S_{RN}1$ chemistry.

Successful $S_{RN}1$ reactions of dienolates derived from carboxamide **22** and ester **25**, respectively, represent the first examples of enolates of α,β-unsaturated carbonyl compounds participating in such radical chain processes with levels of reactivity and regioselectivity that make them preparatively useful and predictable.

Experimental Section

General. Photostimulated reactions were performed under N_2 using a Rayonet RPR-240 or Rayonet RPR-100 photochemical reactor equipped with lamps emitting maximally at 350 nm. Commercial anhydrous NH_3 (Matheson) was used directly from the tank. 2-Benzyl-4,4-dimethyl-2-oxazoline (**1b**) was prepared by the reaction of phenylacetic acid with 2-amino-2-methylpropanol.[19] 2-Benzyl-4-methylthiazole (**13b**) was obtained from the reaction of phenylthioacetamide and chloroacetone.[20] (*E*)-*N*-Methyl-*N*-phenyl-2-butenamide (**22**)[21] and *tert*-butyl 3-butenoate (**24**)[22] were synthesized via reactions of but-2-enoyl chloride with *N*-methylaniline and 2-methyl-2-propanol, respectively. All other reagents were obtained commercially and distilled or recrystallized before use. ^{1}H NMR spectra were determined using $CDCl_3$ as the solvent unless otherwise indicated. Medium pressure liquid chromatography (MPLC) was carried out with 230−400 mesh E. Merck silica gel. Elemental analyses were performed by either Galbraith Laboratories, Inc., Knoxville, TN, or by Atlantic Microlab, Inc., Norcross, GA.

General Procedure for Photostimulated Reactions. To a solution of KNH_2 (2 or 3 equiv) in liquid NH_3 (15 mL/mmol substrate) was added the nucleophile precursor (2 or 3 equiv) via syringe. After stirring at −33 °C for 15 min, the lights of the photoreactor were turned on and the haloaromatic substrate (1 equiv) was immediately added. Irradiation of the resulting solution was continued for the specified time (see tables) after which the reaction mixture was quenched by pouring onto excess solid NH_4Cl in a beaker. The reaction vessel was rinsed with 2 × 100 mL portions of ether, and the rinses were added *slowly* to the NH_3 solution. After evaporation of the NH_3 on a steam bath, the ethereal solution was decanted and the solid residue was washed with 2 × 50 mL portions of ether. The combined ethereal solutions were dried, filtered, and concentrated on a rotary evaporator to yield the crude product which was purified as further described in this section.

The same procedure was used in dark reactions except the reaction flask was wrapped in a black cloth before addition of the substrate. In inhibited reactions, 10 mol % of DTBN was added to the solution of the nucleophile just prior to the addition of the substrate. The results of photostimulated reactions are described below. In all cases the molar quantity of KNH_2 was the same as that of the carbanion precursor.

2-Benzyl-4,4-dimethyl-2-oxazoline (1b) and 2-Benzhydryl-4,4-dimethyl-2-oxazoline (12a). Irradiation of 2,4,4-trimethyl-2-oxazoline (**1a**) (3.39 g, 30.0 mmol) and **9** (2.04 g, 10.0 mmol) for 5 min afforded 1.54 g of a yellow oil, the ^{1}H NMR spectrum of which showed three components: monosubstitution product **1b**,[19] disubstitution product **12a**,[8] and oxazoline dimer, 1,2-bis(4′,4′-dimethyl-2′-oxazolin-2′-yl)ethane (**5**),[23] in a molar ratio of 15:4:1, respectively. Calculation of weight ratios gave 1.06 g (56%) of **1b**, 0.39 g (28%) of **12a**, and 0.09 g (3%) of **5** (based on total oxazoline **1a**). Separation of this mixture was accomplished by MPLC using EtOAc to elute first **12a** (0.34 g) followed by **1b** (0.98 g). Dimer **5** (0.06 g) was then eluted with 10% MeOH−EtOAc. The ^{1}H NMR spectra of these compounds, all of which were colorless oils, were in complete agreement with those reported earlier.

2-((4,4-Dimethyloxazolin-2-yl)methyl)pyridine (3a). Photostimulated reaction of **1a** (5.77 g, 51.0 mmol) and **2** (2.69 g, 17.0 mmol) after 5 min gave 1.64 g of a brown oil, ^{1}H NMR analysis of which indicated a 1:1.9 mixture of **3a** and 2-aminopyridine (**4**), respectively. Crude **3a**, 0.85 g, was isolated by MPLC using 10% MeOH−CH_2Cl_2 as eluent. GC-MS analysis of this colorless oil showed **3a** contaminated with ca. 12 mol %, 0.12 g, of dimer **5**. ^{1}H NMR for **3a**: δ 1.29 (s, 6H), 3.82 (s, 2H), 3.94 (s, 2H), 7.15−7.18 (m, 1H), 7.19−7.32 (m, 1H), 7.61−7.68 (m, 1H), 8.55 (m, 1H). MS(EI): *m*/*z* (relative intensity) 190 (M^+, 10), 189 (10), 175 (100), 118 (80), 93 (70), 78 (30). HRMS: calcd for $C_{11}H_{14}N_2O$ 190.1106. Found: 190.1097.

2-((4,4-Dimethyloxazolin-2-yl)benzyl)pyridine (3b). From the reaction of 2-benzyl-4,4-dimethyl-2-oxazoline (**1b**) (3.92 g, 20.7 mmol) and **2** (1.09 g, 6.90 mmol) after 2 h of irradiation was obtained 3.51 g of a crude product mixture which was chromatographed first with 1:1 hexane−ether to remove excess **1b** and then with ether to give 1.01 g of **3b** as a light yellow solid. The eluent was changed to 10% MeOH−ether, and 0.60 g of a mixture of **3b** and its enamine tautomer **3c** was eluted. Analysis of this mixture by GC indicated a 2:1 ratio of **3b**:**3c**. Preparative GC afforded **3c** as a white solid. The total yield of **3b**,**c** amounted to 1.61 g (88%). ^{1}H NMR for **3b**: δ 1.29 (s, 3H), 1.32 (s, 3H), 3.97 (s, 2H), 5.26 (s, 1H), 7.12−7.16 (m, 1H), 7.26−7.64 (m, 7H), 8.56 (m, 1H). MS(EI): *m*/*z* (relative intensity) 266 (M^+, 25), 251 (27), 167 (100). ^{1}H NMR for **3c**: δ 1.36 (s, 3H), 1.40 (s, 3H), 4.05 (s, 2H), 7.38 (m, 8H), 8.57 (m, 1H). Anal. (mixture **3b**,**c**). Calcd for $C_{17}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.52. Found: C, 76.41; H, 6.86; N, 10.39.

2-((4,4-Dimethyloxazolin-2-yl)methyl)quinoline (7). From **1a** (3.00 g, 26.6 mmol) and **6** (1.44 g, 8.86 mmol) was

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obtained 2.19 g of an orange oil which was chromatographed with 10% EtOH−EtOAc to give 0.21 g (16%) of 2-aminoquinoline (**8**) followed by 0.87 g (41%) of **7** as a yellow oil which solidified when triturated with hexane. Recrystallization from hexane afforded pure **7** as a pale yellow solid, mp 45 °C. ^{1}H NMR: δ 1.31 (s, 6H), 3.95 (s, 2H), 4.01 (s, 2H), 7.44−7.54 (m, 2H), 7.67−7.73 (m, 1H), 7.80 (d, 1H), 8.06−8.14 (m, 2H). Anal. Calcd for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.72; H, 6.70; N, 11.61.

2-Benzhydryl-4,4-dimethyl-2-oxazoline (12a). Irradiation of 2-benzyl-4,4-dimethyl-2-oxazoline (**16**) (3.83 g, 20.2 mmol) and **10** (1.06 g, 6.73 mmol) yielded after 1 h 1.11 g (62%) of **12a** as a light yellow oil, lit.[8] mp 57−58 °C, following MPLC with 2:1 hexane−ether to remove excess **16**. ^{1}H NMR: δ 1.29 (s, 6H), 3.96 (s, 2H), 5.10 (s, 1H), 7.24−7.31 (m, 10H). MS(CI): *m*/*z* (relative intensity) 265 (M^+, 100), 167 (80), 104 (30), 76 (30). HRMS: calcd for $C_{18}H_{19}NO$ 265.1466. Found: 265.1421.

2-(Mesitylmethyl)-4,4-dimethyl-2-oxazoline (12b). Irradiation of **1a** (2.44 g, 21.6 mmol) and **11** (1.43 g, 7.2 mmol) for 1 h gave 1.56 g (94%) of **12b** as a light yellow oil by MPLC with 1:1 hexane−ether. ^{1}H NMR: δ 1.23 (s, 6H), 2.23 (s, 3H), 2.32 (s, 6H), 3.59 (s, 2H), 3.84 (s, 2H), 6.83 (s, 2H). Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.71; H, 9.22; N, 6.06.

2-Benzyl-4-methylthiazole (13b). Reaction of 2,4-dimethylthiazole (**13a**) (3.61 g, 31.8 mmol) with **10** (1.67 g, 10.6 mmol) under photostimulation for 100 min afforded 3.76 g of a dark brown oil. Chromatography with 2:1 hexane−EtOAc gave, following elution of excess **13a**, 1.33 g of crude **13b** as an orange oil and 0.50 g (14%) of 1,2-bis(4-methylthiazol-2-yl)ethane (**15**) on the basis of **13a**, mp 64−66 °C, lit.[24] mp 68−69 °C. Distillation of the crude oil gave 1.19 g (59%) of **13b** as a pale yellow liquid, bp 105 °C/0.50 mm, lit.[20] bp 90 °C/0.20 mm. ^{1}H NMR spectral data for **13b** are in agreement with those reported.[25] ^{1}H NMR for **15**: δ 2.42 (s, 6H), 3.45 (s, 4H), 6.72 (s, 2H).

2-((4-Methylthiazol-2-yl)methyl)pyridine (14a). From **13a** (6.45 g, 57.0 mmol) and **2** (3.00 g, 19.0 mmol) was obtained 2.99 g of a dark brown oil after 100 min of irradiation. Column chromatography with 10:1 CH_2Cl_2−MeOH afforded 1.34 g (37%) of **14a** as a yellow oil, 0.66 g (37%) of **4**, and 0.77 g (12%) of dimer **15**. ^{1}H NMR for **14a**: δ 2.36 (s, 3H), 4.29 (s, 2H), 6.73 (s, 1H), 7.10−7.40 (m, 3H), 8.70 (d, 1H). MS(CI): *m*/*z* (relative intensity) 189 (M^+, 100), 145 (20), 118 (25). HRMS: calcd for $C_{10}H_{10}N_2S$ 190.0565. Found: 190.0565.

2-[α-(4-Methylthiazol-2-yl)benzyl]pyridine (14b). Irradiation of 2-benzyl-4-methylthiazole (**13b**) (3.19 g, 16.9 mmol) and **2** (0.89 g, 5.63 mmol) for 100 min gave 3.74 g of a dark red oil. After chromatographic separation of excess **13b** by elution with 2:1 hexane−EtOAc, 1.41 g (94%) of **14b** was obtained as a pale yellow solid. Recrystallization from hexane afforded an analytical sample, mp 69 °C. ^{1}H NMR: δ 2.43 (s, 3H), 5.93 (s, 1H), 6.81 (s, 1H), 7.13−7.39 (m, 7H), 7.60 (t, 1H), 8.31 (d, 1H). MS(CI): *m*/*z* (relative intensity) 265 (M^+, 100), 167 (80). Anal. Calcd for $C_{16}H_{14}N_2S$: C, 72.15; H, 5.30; N, 10.52. Found: C, 72.17; H, 5.33; N, 10.62.

2-Benzhydryl-4-methylthiazole (16). Reaction of **13b** (2.93 g, 15.5 mmol) and **10** (0.81 g, 5.16 mmol) after 100 min gave 2.36 g of a red oil from which 0.78 g (57%) of **16** was obtained by MPLC with 5:1 hexane−EtOAc as eluent. Crystallization from hexane gave white crystals of **16**, mp 60−63 °C, lit.[26] mp 63−65 °C. ^{1}H NMR: δ 2.49 (s, 3H), 5.80 (s, 1H), 6.79 (s, 1H), 7.27 (m, 10H).

Photostimulated Dimerization of the Carbanion of 2,4,4-Trimethyl-2-oxazoline (1a). To a solution of KNH_2 prepared from potassium (0.78 g, 20.0 mmol) in 200 mL of liquid NH_3 was added a solution of **1a** (2.26 g, 20.0 mmol) in 15 mL of anhydrous ether. After irradiation for 1 h, solid NH_4Cl (2.00 g, 37.0 mmol) was added under N_2 to the dark green reaction mixture. The resulting colorless solution was stirred for 15 min and then poured into a beaker. A 100 mL ether rinse of the reaction flask was added cautiously, and the NH_3 was evaporated. The ether solution was decanted, combined with an additional 100 mL of ether wash of the solid residue, and concentrated on a rotary evaporator to remove the solvent and unreacted **1a**. The pale yellow oily residue of dimer **5** solidified on standing, 0.68 g (30%). Similar reactions carried out in the dark followed by quenching of the reaction mixture either by the addition of NH_4Cl (anaerobic quench) or by pouring the reaction mixture onto NH_4Cl in a beaker (aerobic quench) gave only 0.02 g of a violet-colored residue, the ^{1}H NMR spectrum of which indicated the absence of **5**.

Dimerization of the Carbanion of 2,4-Dimethylthiazole (13a). Irradiation of a solution containing **13a** (2.26 g, 20.0 mmol) and 20.0 mmol of KNH_2 in 200 mL of liquid NH_3 for 1 h, followed by the anaerobic workup described previously for the dimerization reaction of **1a**, gave 0.60 g of crude dimer **15** as a dark red oil which solidified on standing. Purification of **15** by MPLC using 1:1 CH_2Cl_2−EtOAc as eluent yielded 0.45 g (20%) of **15** as a yellow solid, mp 65−67 °C. A similar dark reaction of **13a** gave only 0.08 g of a dark red oily mixture which contained **15** in ca. 50% purity by ^{1}H NMR. However, an aerobically quenched dark reaction of **13a** afforded 0.40 g (18%) of essentially pure **15** as an orange-red solid.

***N*,*N*-Dimethylpyridin-2-ylacetamide (18a) and *N*,*N*-Dimethyldipyridin-2-ylacetamide (19a).** *N*,*N*-Dimethylacetamide (**17a**) (1.31 g, 15.0 mmol) and **2** (0.79 g, 5.00 mmol) after photostimulation for 5 min gave 1.19 g of crude product whose GC analysis (I.S.: dimethyl phthalate) showed 74% of **18a** and 5% of **19a**.[27] Analytical samples of **18a** and **19a** were obtained as light yellow oils by preparative GLC. ^{1}H NMR for **18a**: δ 2.97 (s, 3H), 3.09 (s, 3H), 3.92 (s, 2H), 7.17 (t, 1H), 7.33 (d, 1H), 7.62 (t, 1H), 8.54 (d, 1H). Anal. Calcd for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.06. Found: C, 65.68; H, 7.50; N, 16.90. ^{1}H NMR for **19a**: 3.05 (s, 6H), 5.74 (s, 1H), 7.18 (t, 2H), 7.32 (d, 2H), 7.62 (t, 2H), 8.56 (d, 2H). Anal. (as HCl salt, mp 180 °C). Calcd for $C_{14}H_{16}N_3OCl$: C, 60.54; H, 5.81; N, 15.13. Found: C, 60.30; H, 5.85; N, 15.03.

***N*,*N*-Dimethylquinolin-2-ylacetamide (20) and *N*,*N*-Dimethyldiquinolin-2-ylacetamide (21).** Irradiation of the carbanion derived from **17a** (2.56 g, 29.3 mmol) and **6** (1.59 g, 9.78 mmol) for 60 min gave 2.20 g of a crude orange oily mixture which was separated on an acidic alumina column with EtOAc. Compound **20** was isolated as an orange oil, 1.68 g (80%) which crystallized upon trituration with ether, mp 99−100 °C, followed by **21** as a red solid, 0.45 g (14%). ^{1}H NMR for **20**: δ 2.98 (s, 3H), 3.13 (s, 3H), 4.11 (s, 2H), 7.52 (t, 2H), 7.69 (t, 1H), 7.82 (d, 1H), 8.03 (d, 1H), 8.12 (d, 1H). MS(EI): *m*/*z* (relative intensity) 214 (M^+, 35), 170 (30), 143 (100), 72 (65). Anal. Calcd for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07. Found: C, 72.90; H, 6.59; N, 13.09. ^{1}H NMR for **21**: 3.13 (s, 3H), 3.19 (s, 3H), 7.64 (bs, 1H), 7.97 (m, 2H), 8.09 (t, 4H), 8.24 (d, 2H), 8.32 (d, 2H), 8.95 (d, 2H). Anal. (as HCl salt, mp 111 °C). Calcd for $C_{22}H_{20}N_3OCl$: C, 69.93; H, 5.34; N, 11.12. Found: C, 70.14; H, 5.56; N, 11.14.

***tert*-Butyl Pyridin-2-ylacetate (18b) and *tert*-Butyl Dipyridin-2-ylacetate (19b).** From *tert*-butyl acetate (**17b**) (2.59 g, 22.4 mmol) and **2** (1.17 g, 7.45 mmol), 1.00 g of crude product was obtained, which by ^{1}H NMR analysis consisted of a 2:1 molar ratio of **18b**:**19b**. Column chromatographic separation using 2:1 hexane−ether led to the isolation of 0.64 g (44%) of **18b** as a colorless liquid and 0.21 g (21%) of **19b** as a colorless solid, mp 90−92 °C after recrystallization from hexane. The ^{1}H NMR and mass spectral data of **18b** are consistent with the values reported.[14,28] ^{1}H NMR for **19b**: δ 1.45 (s, 9H), 5.35 (s, 1H), 7.18 (m, 2H), 7.39 (d, 2H), 7.64 (t, 2H), 8.67 (d, 2H). MS(EI): *m*/*z* (relative intensity) 169 ($M^+ - CO_2Bu^t$, 70), 57 (100). Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.08, H, 6.71, N, 10.27.

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Ethyl Phenylpyridin-2-ylacetate (18c). Ethyl phenylacetate (**17c**) (3.83 g, 23.3 mmol) and **2** (1.23 g, 7.78 mmol) gave 1.45 g (77%) of **18c** as a light yellow oil after MPLC with 2:1 hexane−ether. ^{1}H NMR: δ 1.22−1.27 (t, 3H), 4.19−4.27 (q, 2H), 5.22 (s, 1H), 7.13−7.41 (m, 7H), 7.57−7.63 (m, 1H), 8.56 (d, 1H). Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.38; H, 6.24; N, 5.81. Found: C, 74.47; H, 6.26; N, 5.82.

(*E*)-*N*-Methyl-*N*-phenyl-4-(pyridin-2-yl)-3-butenamide (23a). Irradiation of *N*-methyl-*N*-phenyl-2-butenamide (**22**) (3.50 g, 20.0 mmol) and **2** (1.58 g, 10.0 mmol) for 1 h gave 4.4 g of a brown oil which was chromatographed using CH_2Cl_2 to remove 1.52 g (43%) of a mixture of **22** and its isomer, *N*-methyl-*N*-phenyl-3-butenamide. The eluent was changed to 10% MeOH−CH_2Cl_2, and 2.58 g of a yellow oil was collected. Trituration with ether afforded 1.25 g (50%) of **23a** as a light yellow solid, an analytical sample of which was obtained by recrystallization from ether−hexane as colorless crystals, mp 79−80 °C. ^{1}H NMR: δ 3.10 (d, 2H, J = 6.8 Hz), 3.30 (s, 3H), 6.37 (d, 1H, J = 16 Hz), 6.68−6.79 (dt, 1H, J = 16 Hz, J' = 6.8 Hz), 7.07−7.12 (m, 1H), 7.22−7.31 (m, 3H), 7.36−7.47 (m, 3H), 7.56−7.63 (m, 1H), 8.50 (m, 1H). MS(CI): *m*/*z* (relative intensity) 253 (M^+ + 1100), 174 (5), 160 (7), 146 (38). Anal. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 76.31; H, 6.46; N, 11.12.

(*E*)-*N*-Methyl-4,*N*-diphenyl-3-butenamide (23b). Reaction of **22** (3.50 g, 20.0 mmol) and **9** (2.04 g, 10.0 mmol) after photostimulation for 1 h gave 4.29 g of a yellow oil. Unreacted **22** and its isomer, total 1.66 g (48%), were removed by vacuum distillation at 70−75 °C/0.01 mm, and the residue was chromatographed using CH_2Cl_2 as the eluent. A 1.6:1 *E*:*Z* mixture of disubstitution product **24**, 0.13 g (8%), was eluted as the first major component. Further elution gave 0.17 g (10%) of disubstitution product **23c** and then crude **23b**, 1.14 g, as a pale yellow oil which was vacuum distilled at 144−145 °C/0.01 mm to afford 0.95 g (38%) of **23b**. ^{1}H NMR for **23c**: δ 2.96 (d, 2H, J = 7.2 Hz), 3.26 (s, 3H), 6.24 (t, 1H, J = 7.2 Hz), 7.00−7.35 (m, 15H). HRMS: calcd for $C_{23}H_{21}NO$ 327.1623. Found: 327.1630. ^{1}H NMR for **23b**: δ 3.05 (d, 2H, J = 6.1 Hz), 3.30 (s, 3H), 6.19 (d, 1H, J = 16 Hz), 6.21−6.32 (dt, 1H, J = 16 Hz, J' = 6.1 Hz), 7.19−7.47 (m, 10H). HRMS: calcd for $C_{17}H_{17}NO$ 251.1310. Found: 251.1305. ^{1}H NMR for **24**, (*E*) isomer: δ 3.29 (s, 3H), 4.38 (d, 1H, J = 8.8 Hz), 6.20 (d, 1H, J = 16 Hz), 6.63−6.69 (m, 1H), 6.97−7.43 (m, 15H). ^{1}H NMR for **24**, (*Z*) isomer: δ 3.21 (s, 3H), 4.42 (d, 1H, J = 10 Hz), 6.59 (d, 1H, J = 8.4 Hz), 6.63−6.69 (m, 1H), 6.97−7.43 (m, 15H).

(*E*)-*tert*-Butyl 4-(Pyridin-2-yl)-3-butenoate (26a). Following 1 h of irradiation, *tert*-butyl 3-butenoate (**25**) (2.84 g, 20.0 mmol) and **2** (1.58 g, 10.0 mmol) yielded 3.69 g of a reddish-orange liquid, the ^{1}H NMR of which indicated the complete absence of both **25** and **2**. Chromatography with CH_2Cl_2 resulted in the elution of a pale yellow liquid, subsequently identified as the dimer, *tert*-butyl 3-methyl-4-(*tert*-butoxycarbonyl)-4-hexenoate (**28a**), 1.07 g (38%). Further elution with 10% EtOAc-CH_2Cl_2 afforded 1.68 g of crude product as a yellow oil. Vacuum distillation at 98−100 °C/0.10 mm gave 1.34 g (61%) of colorless **26a**. For characterization, **26a** and **28a** were converted to the corresponding acids by refluxing their hexane solutions with 2.0 mol % of *p*-toluenesulfonic acid for 5 h. (*E*)-2-Ethylidene-3-methylglutaric acid (**28b**) was thus obtained in 88% yield from **28a** as colorless crystals from CH_2Cl_2, mp 128−128.5 °C, lit.[18c] mp 126−127 °C. (*E*)-4(Pyridin-2-yl)-3-butenoic acid, derived from **26a**, crystallized from ether as colorless tiny needles, mp 94−95 °C with CO_2 evolution. ^{1}H NMR: δ 3.34−3.37 (dd, 2H, J = 7.0 Hz, J' = 1.2 Hz), 6.63 (d, 1H, J = 16 Hz), 6.85−6.96 (dt, 1H, J = 16 Hz, J' = 7.0 Hz), 7.21−7.33 (m, 2H), 7.68−7.75 (m, 1H), 8.66−8.68 (m, 1H), 10.70 (br s, 1H). MS(EI): *m*/*z* (relative intensity) 163 (M^+, 34), 119 (34), 117 (100), 91 (51). Anal. Calcd for $C_9H_9NO_2$: C, 66.24; H, 5.56; N, 8.58. Found: C, 66.37; H, 5.61; N, 8.59.

(*E*)-*tert*-Butyl 4-Phenyl-3-butenoate (26b). From **25** (2.84 g, 20.0 mmol) and **9** (2.04 g, 10.0 mmol) after irradiation for 1 h was obtained 3.19 g of a yellow liquid, ^{1}H NMR analysis of which indicated mostly a mixture of monosubstitution product **26b**, disubstitution products **26c** and **27**, and dimer **28a**. MPLC using 1:1 hexane−benzene eluted 0.40 g of a crude 1:1 mixture of **26c** and **27** first as a colorless oil which crystallized on standing. Recrystallization from hexane afforded 0.22 g (15%) of a pure 1:1 mixture of **26c** and **27** as colorless crystals, melting range 80−98 °C.[29] Compound **25b** was eluted next as a colorless oil, 0.92 g (42%). The eluent was changed to benzene and dimer **28a**, 0.96 g (34%), was obtained as a nearly colorless liquid. The ^{1}H NMR spectrum of **26b** was consistent with that reported.[30] ^{1}H NMR for **26c**: δ 1.44 (s, 9H), 3.07 (d, 2H, J = 7.4 Hz), 6.24 (t, 1H, J = 7.4 Hz), 7.20−7.35 (m, 10H). ^{1}H NMR for **27**: δ 1.44 (s, 9H), 4.35 (d, 1H, J = 7.7 Hz), 6.46 (d, 1H, J = 16 Hz), 6.52−6.61 (dd, 1H, J = 16 Hz, J' = 7.7 Hz), 7.20−7.35 (m, 10H). Anal. (mixture of **26c**:**27**). Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.46; H, 7.57.

Dimethyl (Pyridin-2-ylmethyl)phosphonate (30a). Photostimulated reaction of dimethyl methylphosphonate (**29a**) (11.17 g, 90.0 mmol) and **2** (4.74 g, 30.0 mmol) after 1 h gave 12.49 g of a dark orange liquid. Unreacted **29a** was removed by distillation at 41−43 °C/1.0 mm leaving 5.66 g of a red-brown, more viscous oil which was chromatographed with EtOAc. A trace of **29a** was removed first, followed by 2-aminopyridine (**4**) 0.28 g (10%). The eluent was changed to 10% MeOH−EtOAc, and **30a** was eluted as a pale yellow liquid, 4.13 g (68%), which solidified when refrigerated. Compound **30a** was vacuum distilled at 100−103 °C/0.10 mm, lit.[31] bp 96−97 °C/0.2 mm. ^{1}H NMR: δ 3.43 (d, 2H, J = 22 Hz), 3.73 (d, 6H, J = 11 Hz), 7.22 (t, 1H), 7.38 (d, 1H), 7.65 (t, 1H), 8.54 (d, 1H). MS(EI): *m*/*z* (relative intensity) 201 (M^+, 35), 108 (55), 93 (100), 65 (36).

Dimethyl Benzylphosphonate (30b) and Dimethyl Benzhydrylphosphonate (30c). Reaction of **29a** (11.17 g, 90.0 mmol) and **9** (6.12 g, 30.0 mmol) under photostimulation for 1 h gave 12.48 g of a dark yellow liquid which was fractionally distilled. Excess **29a** distilled first at 40−42 °C/1.0 mm followed by substitution product **30b** as 2.57 g of a colorless liquid, bp 95−100 °C/0.10 mm, lit.[32] bp 85 °C/0.15 mm. Continued distillation afforded a third fraction, 1.12 g of a pale yellow oil, 120−140 °C/0.10 mm, whose ^{1}H NMR spectrum indicated it to be mostly a 1:3 mixture of **30b** and **30c**. Separation of this mixture was achieved with MPLC by gradient elution using CH_2Cl_2−EtOAc. Disubstitution product **30c** was eluted first as a colorless oil, 0.75 g (18%), which crystallized from ether−hexane, mp 96−97 °C, lit.[33] mp 96−97 °C. Further elution afforded 0.26 g of additional **30b**, total yield 2.83 g (47%). The ^{1}H NMR spectra were consistent with those reported for **30b**[32] and **30c**.[34]

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