Photoaccelerated Reductive Coupling of Acid Chlorides with Conjugate Dienes and Styrenes by Use of Neodymium Metal in *N*,*N*-Dimethylacetamide

Zhi-fang Li,[1,2] Yuri Tomisaka,[1] Akihiro Nomoto,[1] Yongmin Zhang,*[3] and Akiya Ogawa*[1]
[1]*Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University,*
1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531
[2]*Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education,*
Hangzhou Normal University, Hangzhou 310012, P. R. China
[3]*Department of Chemistry, Zhejiang University, Xi-xi Campus, Hangzhou 310028, P. R. China*

(Received September 24, 2008; CL-080917; E-mail: ogawa@chem.osakafu-u.ac.jp)

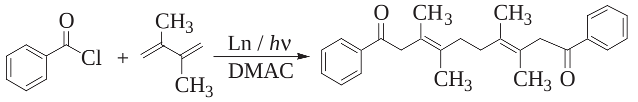
Upon photoirradiation, neodymium metal powder in *N*,*N*-dimethylacetamide (DMAC) exhibits excellent reducing ability for the reductive coupling of benzoyl chlorides with conjugate dienes and styrenes.

Recently lanthanoid metal salts and organolanthanoid compounds have been widely employed in organic synthesis. Among them, divalent lanthanoid salts, especially samarium diiodide, work as useful reducing agents in synthetic organic reactions. Zero-valent lanthanoid metals also bear potential reducing ability. However, the use of zero-valent lanthanoid metals themselves directly in organic synthesis is still rare. The advantages of the use of lanthanoid metals are the electron economies compared with divalent lanthanoid species, because lanthanoid metals can afford three electrons from the zero-valent state to the stable trivalent state. In addition, another advantage of the use of lanthanoid metals is easy operation. However, the problems of the use of lanthanoid metals are the heterogeneous nature in organic solvents and lower reactivity. In order to increase the reducing ability of lanthanoid metals, some additives are employed. For example, Nishiyama et al. found that iodoalkanes could be reduced with lanthanum metal in the presence of a catalytic amount of iodine.[1] Samarium metal[2a,2b] and cerium metal[2c] have been reported to promote pinacol coupling reactions by using iodine as the activating reagent. The silylative coupling reaction mediated by ytterbium/Me_3SiBr in hexamethylphosphoramide has also been reported by Fujiwara et al.[3] Talukdar and Fang described the coupling reaction of aromatic aldehydes mediated by samarium in the presence of aqueous hydrochloric acid.[4]

Recently, we have found that photoirradiation dramatically enhances the reducing ability of some rare earth metals (e.g., Ce, Nd, Sm, and Eu) toward the reductive deiodation of iodoalkanes.[5] In this paper, we wish to report that neodymium metal upon photoirradiation (Nd/$h\nu$) acts as an electron-economical reducing agent for the reductive coupling of aroyl chlorides with conjugate dienes and styrenes with easy operation.[6,7]

When a mixture of benzoyl chloride (1 mmol) and 2,3-dimethyl-1,3-butadiene (2 mmol) in DMAC (*N*,*N*-dimethylacetamide) (5 mL) was treated with lanthanoid metals powder (0.5 mmol) such as samarium, cerium, neodymium, and europium under photoirradiation conditions for 2 h,[8] the cross coupling product was obtained in good yield. It should be noted that when the reaction was performed in the dark, the yield was low. When the reaction was performed in THF, acetonitrile, or DME, no reaction took place at all (Table 1).

Table 1. Reductive coupling of benzoyl chloride with a 1,3-diene[a]



Ln	Condition	Sovent	Time/h	Yield/%[b]
Sm	$h\nu$	THF	5	0
Sm	$h\nu$	CH_3CN	5	0
Sm	$h\nu$	DME	5	0
Sm	dark	DMAC	6	58
Sm	$h\nu$	DMAC	2	94
Ce	dark	DMAC	6	20
Ce	$h\nu$	DMAC	2	83
Nd	dark	DMAC	6	42
Nd	$h\nu$	DMAC	2	95
Eu	dark	DMAC	6	55
Eu	$h\nu$	DMAC	2	78

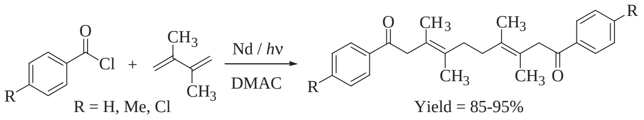
[a]Reaction conditions: Benzoyl chloride (1 mmol), 2,3-dimethyl-1,3-butadiene (2 mmol), Ln (0.5 mmol), $h\nu$ (Xe lamp), DMAC. [b]Isolated yield based on benzoyl chloride used.

By using neodymium metal powder under photoirradiation, 4-toluoyl chloride and 4-chlorobenzoyl chloride can also react with 1,3-diene smoothly to give the corresponding coupling products in high yields (Scheme 1).

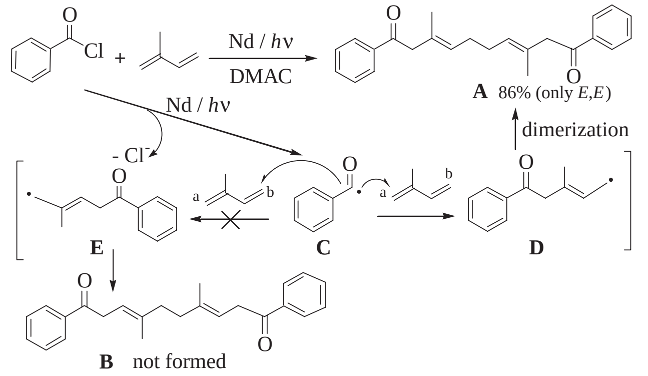
Under the same reaction conditions, the cross coupling of benzoyl chloride with isoprene was also examined. The benzoyl radical **C** selectively attacks the isoprene *a* position to give the coupling product **A**[9] in good yield. The product **B** formed through *b* attack was not obtained at all (Scheme 2). This regioselectivity can be explained by the difference in stability between allylic radical intermediates **D** and **E**.

Next, we examined the reductive coupling by using a cyclic diene. When the photoirradiated reaction of benzoyl chloride (1 mmol) with 1,3-cyclohexadiene (1.1 mmol) was conducted in the presence of neodymium metal powder (0.5 mmol), another type of coupling product **F** was obtained in 65% yield (Scheme 3). In this case, the allyl radical **G** formed in situ from aroyl radical and 1,3-cyclohexadiene is a secondary radical, and does not homocouple, most probably owing to steric factors. The allyl radical **G** undergoes single electron transfer from low-valent Nd species, generating allyl anion species **H**, which is aroylated with aroyl chloride to give the coupling product **F**.

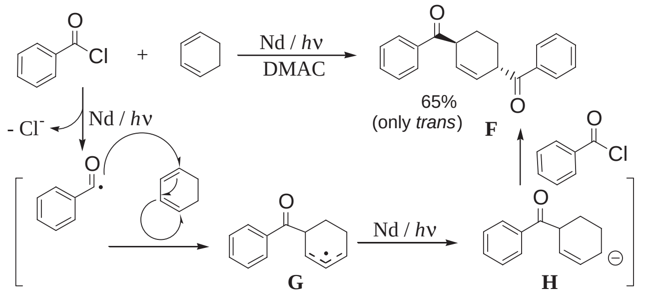
Furthermore, the present photoinduced coupling reaction of aroyl chlorides with conjugated dienes using Nd metal powder can be applied to reductive coupling with styrene derivatives



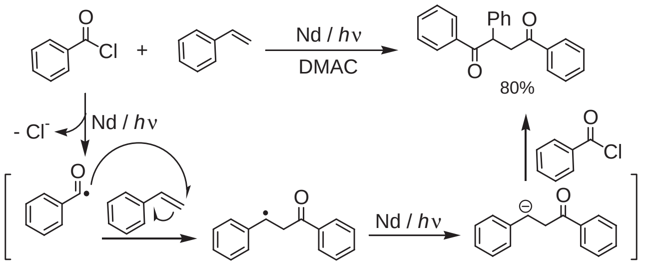
Scheme 1.



Scheme 2.



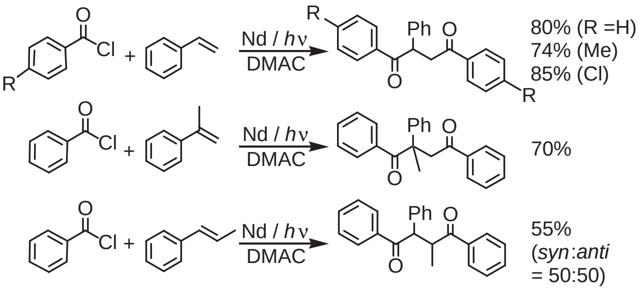
Scheme 3.



Scheme 4.

(Scheme 4).[10] In this case, the reductive coupling reaction proceeded similarly to the case of cyclic dienes, providing the corresponding coupling product derived from two molecules of benzoyl groups and one molecule of styrene. Representative results of the reductive coupling of aroyl chlorides with styrenes using a Nd/$h\nu$ system are shown in Scheme 5.

In summary, under photoirradiation, lanthanoid metals, such as cerium, neodymium, samarium, and europium metals indicate higher reducing abilities toward the reductive transformation of acid chlorides. By using these novel photoinduced reduction systems of rare earth metals, benzoyl chloride reacts with dienes and styrenes, giving the corresponding coupling products in good yields.



Scheme 5.

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8 In the stoichiometric reaction, Ln metals were changed to $LnCl_3$, and the resulting solution was homogeneous.

9 Only E,E isomer was obtained, and no formation of Z isomers were confirmed (see ref. 6): **E,E isomer**: ν_{max}(KBr)/cm^{-1}: 3062, 2949, 1686, 1596, 1580, 1448. ^{1}H NMR δ_H($CDCl_3$): 8.01–7.96 (4H, m), 7.58–7.55 (2H, m), 7.48–7.44 (4H, m), 5.31 (2H, d, $J = 1.2$ Hz), 3.64 (4H, s), 2.13–2.11 (4H, t, $J = 3.2$ Hz), 1.68 (6H, s). ^{13}C NMR δ($CDCl_3$): 182.4, 120.6, 116.6, 113.4, 112.7, 112.1, 112.0, 49.3, 33.0, 11.7. MS(EI) m/z(%): 347 ($M^+ + 1$, 0.72), 346 (M^+, 1.56), 241 (0.68), 226 (2.17), 173 (5.11), 105 (100.00), 77 (50.93).

10 Benzoyl chloride (1 mmol), styrene (1.1 mmol), and Nd powder (0.5 mmol) were usually employed for the reductive coupling reaction with styrenes. Similar results were obtained when benzoyl chloride (2 mmol), styrene (1.1 mmol), and Nd (0.8 mmol) were used.