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Photo-induced iron-catalyzed allylic amination of unfunctionalized olefins with nitroarenes

Radhey S. Srivastava*

Department of Chemistry, University of Louisiana at Lafayette, LA 70504, USA

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Photochemical reactions between unfuctionalized olefins and nitroarenes under CO pressure, catalyzed by $[Cp^*Fe(CO)_2]_2$, form the corresponding allyl amines. The use of mechanistic probes containing 2-nitrobiphenyl, 2,3-dimethylbutadiene and pentafluoronitrobenzene suggest that neither aryl nitrene nor nitrosoarene is the active aminating agent in these transformations. Copyright © 2006 John Wiley & Sons, Ltd.

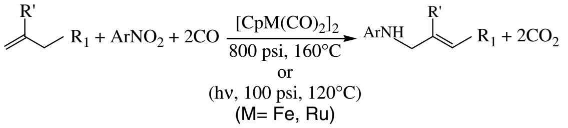
KEYWORDS: photoinduced; iron; allylic amination; unfunctionalized olefins; nitroarenes

INTRODUCTION

Ally amines and their derivatives are important organic intermediates, since they can be used as building blocks in several industrially important and useful transformations. Transition metal-promoted allylic aminations of alkenes and alkynes provide a fascinating route to functionalized amines via C–N bond formation. Unlike the nitrogenation of unsaturated hydrocarbons, considerable effort has been exerted towards studies of the oxidation of unsaturated hydrocarbons.[1,2] The direct nitrogenation of unsaturated hydrocarbons remains an attractive goal due to the commercial potential of the processes. The stoichiometric allylic amination of group 16 imido compounds ($R'N = X = NR'$; $X = S^{3,4}$, $Se^{5,6}$) and reactions of molybdooxaziridine complexes $[MoL_n(\eta^2\text{-RNO})]$ with alkenes have been reported.[7]

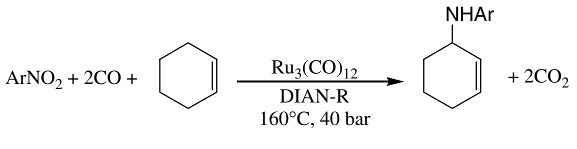
A few catalytic allylic amination schemes have also been reported using hydroxylamines, nitroso- and nitroarenes as N-source. The reactions catalyzed by redox-active Mo-[8–10], Fe-[11–15] and Cu-[16–19] species generally proceed with high ene-like regioselectivity, albeit via different and sometimes novel organonitrogen intermediates.

Recently, more readily accessible nitroarenes have been used as aminating agents, carbon monoxide as reductants and $[Cp^*Fe(CO)_2]_2$ as catalyst[20–22] in thermal and photochemical allylic aminations of olefins. These reactions proceed regioselectively with N-functionalization at the less substituted olefinic carbon [equation (1)].



(1)

Formation of the allylic amine typically requires the availability of prefunctionalized olefins under these processes. Although, a $Ru_3(CO)_{12}$/diimine-promoted allylic amination of unfunctionalized olefins using carbon monoxide as reductant has been reported recently[23,24] [equation (2)], the reaction requires strenuous reaction conditions (150–200 °C, 25–50 atm pressure of CO).



(2)

We report here, photo-induced nitroarene-based allylic aminations that proceed under much milder conditions. The reactions were carried out in glass vessels. The results of preliminary mechanistic probes are also presented.

RESULTS AND DISCUSSION

The near-UV irradiation (>300 nm) of dioxane solutions containing cyclohexene, nitroarene and $[Cp/Cp^*Fe(CO)_2]_2$

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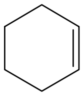
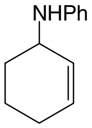
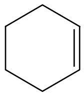
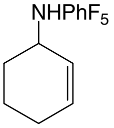
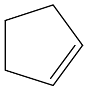
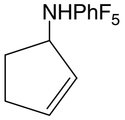
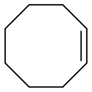
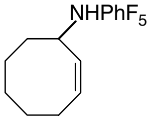
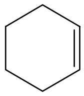
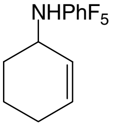
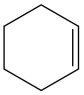
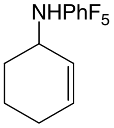
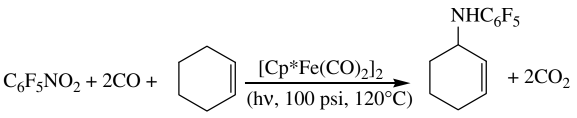
*Correspondence to: Radhey S. Srivastava, Department of Chemistry, University of Louisiana at Lafayette, LA 70504, USA.
E-mail: rss1805@louisiana.edu

Table 1. Allylic amination of unfunctionalized olefins catalyzed by $[Cp^*Fe(CO)_2]_2$ (1)

Run	Alkene	Nitroarene	Temperature (°C)	Pressure (psi)	Allyl amine	Yield (%)	N-selectivity (%)
1		$PhNO_2$	120	100		5	40
2		PhF_5NO_2	120	100		30	90
3		PhF_5NO_2	120	100		20	70
4		PhF_5NO_2	120	100		18	70
5		PhF_5NO_2	160	100		7	55
6		PhF_5NO_2	120	60		16	56

GC yield using sensitivity factor vs naphthalene internal standard.

at 100–120 °C and CO in a Fisher-Porter bottle[10] produced the corresponding allyl amine, with $[Cp^*Fe(CO)_2]_2$ being more effective [equation (3); Table 1]. Aniline, azo- and azoxybenzene were formed as byproducts in variable quantities. No allyl amine was produced in the absence of CO or catalyst. Other substrates such as cyclopentene and cyclooctene also yield the desired product under identical reaction conditions.

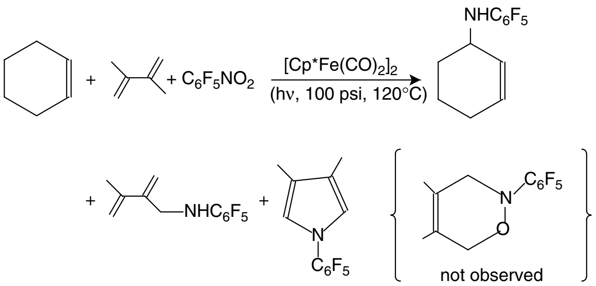
 (3)

The yields of ally amines and their selectivity increase with an increase in the electron withdrawing strength of the substituents on the nitroarene. This could be explained by the formation of a nitrosoarene complex, which contains an olefin and a CO group. In fact, the nitrosoarene acts as an electrophile in the coupling with an olefin, and electron-withdrawing groups accelerate these kinds of couplings on the aromatic ring.[25,26] The product formation appreciably decreases with an in increase in temperature and a decrease in pressure (Table 1, runs 5 and 6). The GC detected only aniline as a major product when 3,4-dichloronitrobenzene and pentachloronitrobenzene were employed as N-transfer agents.

The $ArNO_2$ to catalyst ratio was important. An $ArNO_2$: catalyst ratio of 20 gives a better yield and better selectivity of ally amine. However, when the $ArNO_2$: catalyst ratio was decreased by half, the yield of byproducts increased substantially. The higher yield of ally amine at an $ArNO_2$: catalyst ratio of 20 is probably caused by formation of the monomeric species [equation (4)]:

$$[Cp^*Fe(CO)_2]_2 \rightleftharpoons [Cp^*Fe(CO)_2] \qquad (4)$$

The thermal or photochemical[27–30] formation of an Fe–Fe bond is an important step to generate active catalyst. It was demonstrated by kinetic studies in thermal, $[Cp/Cp^*Fe(CO)_2]_2$-catalyzed allylic amination reactions that the active catalyst is the 17-electron monomer radical generated by homolytic fission of the Fe–Fe bond in $[Cp/Cp^*Fe(CO)_2]_2$.[31] In fact, the equilibrium (K_{eq} at 23 °C = 2×10^{-17}) has been well established through thermal and photochemical trapping studies.[32,33] Additional support for the involvement of the Fp radical in the present reaction is

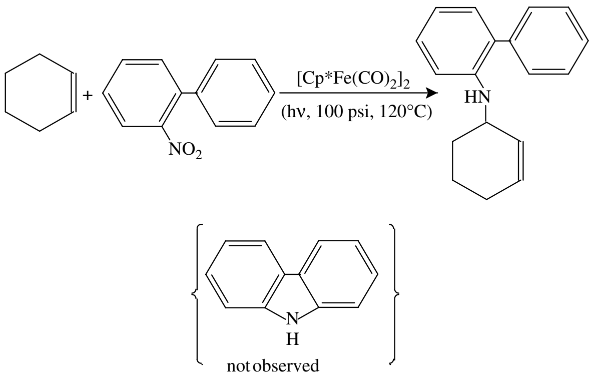


(5)

provided by the complete reaction inhibition in the presence of CCl_4.[34–37]

To explore intermediacy of ArNO, an established enophile, the allylic amination was initiated in the presence of 2,3-dimethylbutadiene (an established trapping agent for ArNO). The allyl amines derived from the olefin and diene were produced along with a substantial amount of *N*-phenyl-3,4-dimethylpyrrole, but none of the Diels–Alder adduct[38] [equation (5)] was formed. The pyrrole could be derived from photo-induced dehydration of the Diels–Alder adduct from the diene and free ArNO. However, when a solution of ArNO, cyclohexene and catalyst were irradiated under similar conditions little of the allyl amine was detected. This finding argues against the intermediacy of free ArNO in the reaction catalyzed by Fp-dimer and suggests that the pyrrol byproduct does not arise from the free ArNO.

Irradiation of 2-nitrobiphenyl with cyclohexene under catalytic conditions produced the corresponding *N*-biphenyl-*N*-allyl amine and 2-biphenylamine but no carbazole was produced in this reaction, which suggests the lack of intervention of a free aryl nitrene intermediate [equation (6)].[39,40]



(6)

EXPERIMENTAL

Photo-induced catalytic allylic amination

An 80 ml Pyrex Fisher-Porter bottle with a magnetic stirrer bar was charged with olefin (6.3 mmol), nitroarene (1.16 mmol), $[Cp^*Fe(CO)_2]_2$ (0.056 mmol), naphthalene (0.15 mmol) and 7 ml dry dioxane. The head was attached and the vessel was purged with carbon monoxide (toxic) three times in a fume hood. The vessel was pressurized with 100 psi of carbon monoxide and heated in a preheated oil bath at 120 °C. The apparatus was then irradiated while stirring in a Rayonett photoreactor with 300–350 nm lamps (16 × 16 W) for 30 h. The vessel was allowed to cool and, after the venting toxic CO in the fume hood, the product was analyzed by GC and GC-MS.

Reaction of $[Cp^*Fe(CO)_2]_2$ with mixture of 2-methyl-2-pentene and 2,3-dimethyl-1,3-butadiene

A dioxane solution (5 ml) containing 2-methyl-2-pentene (0.029 mmol) of 2,3-dimethylbutadiene (0.029 mmol) and 0.0032 mmol of $[Cp^*Fe(CO)_2]_2$ was heated and irradiated at 120 °C for 24 h. An aliquot was analyzed by GC and GC-MS and found to contain allyl amines from the alkene and diene. None of the hetero-Diels–Alder adduct was detected.

Reaction of $[Cp^*Fe(CO)_2]_2$ with 2-nitrobiphenyl and cyclohexene

A mixture of 2-nitrobiphenyl (0.035 mmol), cyclohexene (0.035 mmol) and $[Cp^*Fe(CO)_2]_2$ (0.040 mmol) in dioxane (5.0 ml) was irradiated for 24 h at 120 °C. GC and GC-MS analysis found to contain *N*-biphenyl-*N*-allyl amine and 2-biphenylamine, but no carbazole was detected.

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