

Novel Copper(II)-mediated Photocyclization of Methoxynaphthyl Analogues of Chalcone: Unusual Electron Transfer from Excited Vinyl Arenes

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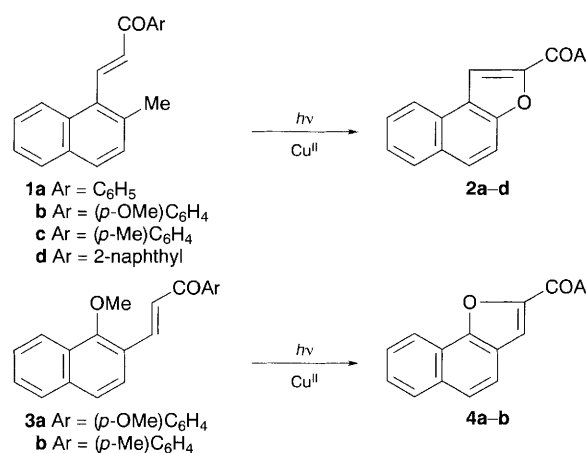
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Copper(II)-mediated photocyclization of the title compounds to naphthofurans *via* an electron-transfer process is reported.

Complexation of alkenes to electrophilic transition metals in the ground as well as in excited states is known to increase the reactivity of the double bond.¹ Cu^I and Pd^{II} have been extensively used as homogeneous metal catalysts in organic photochemical transformations, although Cu^{II} salts are also known to catalyse *cis-trans* isomerizations,^{1b} for instance dimerizations, cycloisomerizations and oxidations. Vinyl radicals, generated from vinyl halides, are known to undergo preferential photooxidation to vinyl cation in the presence of Cu^{II} salts.² However, metal-catalysed photocyclization of vinyl arenes is not common in the literature. We report here novel Cu^{II}-mediated photocyclizations of vinylnaphthalenes **1a-d** and **3a-b**, to naphtho[2,1-*b*]- and naphtho[1,2-*b*]-furans **2a-d** and **4a-b** (Scheme 1).

These vinylnaphthalenes may be considered as 1- and 2-naphthyl analogues of chalcones, which, like chalcones, generally tend to dimerize on direct irradiation.³ When the irradiation was carried out in presence of Cu^{II} acetate, respective naphthofurans **2a-d** and **4a-b** were obtained in moderately good yields from **1a-d** and **3a-b** (Table 1). Both the yield and the rate of this photocyclization were found to be enhanced when oxygen was bubbled through the reaction mixture. This observation suggests involvement of a reactive singlet state in this photoreaction. Since Cu^{II} acetate did not alter the UV spectra of these ketones, the catalytic influence of Cu^{II} appears to be operative only in the photoexcited state of the

reacting molecules. The reactive excited state of an enone has generally been assumed to be a charge polarized n,π^* state with higher electron density at C _{β} than at C _{α} .⁵ Since these naphthyl analogues of chalcone have an enone part, their reactive excited states were also assumed to have similar characteristics. We suggest that such a charge polarized excited state NC* of system



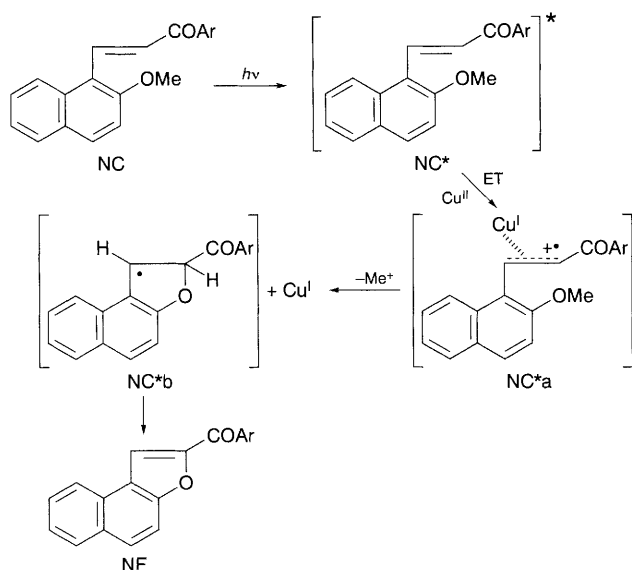
Scheme 1

Table 1

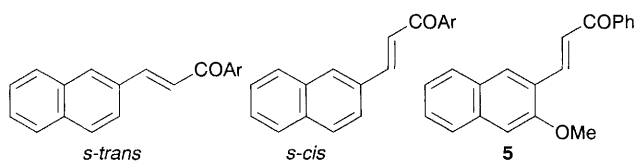
Starting compound ^a	Reaction time/h ^b	Product ^c (mp/°C)	Yield (%)	UV (EtOH) ^d λ_{\max}/nm (log ϵ)	NMR (CDCl ₃) ^e δ
1a	5	2a (135)	70	213 (4.48) 274 (4.26) 315 (4.09) 340 (sh, 3.72)	7.04 (s, 1H)
1b	6	2b (158)	64	223 (4.59) 292 (4.29) 322 (4.37) 342 (sh, 4.21)	7.0 (s, 1H)
1c	5	2c (187)	54	215 286 315 340 (sh)	6.83 (s, 1H)
1d	5	2d (186)	66	226 243 316 339 (sh)	7.1 (s, 1H)
3a	5	4a (177)	59	222 (4.64) 285 (4.39) 301 (4.37) 325 (sh, 4.31)	6.96 (s, 1H)
3b	7	4b (168)	58	223 (4.54) 284 (4.36) 315 (4.05) 344 (sh, 3.63)	6.85 (s, 1H)

^a These were prepared following a reported procedure.⁴ ^b In a typical run 1 mmol of reactant was irradiated in 170 ml of dry MeOH with 0.55 mmol of Cu(OAc)₂ using a 450 W medium-pressure mercury lamp. The product was eluted from a silica-gel (60–120 mesh) column with 20% mixture of EtOAc in petroleum ether (60–80 °C). ^c All compounds were characterized from their analytical and spectral data. ^d **2c** and **2d** being sparingly soluble in EtOH, their absorption patterns were only recorded. ^e Only the characteristic furyl proton signals have been reported.

NC would then, by electron transfer to Cu^{II} , give an organo-copper intermediate NC^*a . Such electron transfer between an excited organic molecule and metal have been suggested in many cases.^{1b} In a geometrically favourable situation, a tandem photocyclization of the resulting radical cation by intramolecular nucleophilic attack of the *o*-methoxy group would then give NC^*b which by H-elimination gave the resulting naphthofuran derivative NF (Scheme 2). In oxygenated medium a facile reoxidation of Cu^{I} to Cu^{II} took place. The probability of



Scheme 2



a vinyl radical being involved in our photocyclization process was discarded since that did not follow the octet rule. Similar photocyclizations of β -(*o*-methoxyphenyl)vinyl bromides to benzofurans have been reported to occur *via* vinyl cation by Taniguchi and coworkers.⁶

This photocyclization process appeared to have an addition selectivity. In the case of vinyl naphthalenes where the 1-vinyl derivatives are known to exist only as *s-cis* rotamers (as in NC), an equilibrium is known to exist between the *s-cis* and *s-trans* rotamers in the case of 2-vinyl derivatives.⁷ Since the vacant p-orbital of the carbenium ion and the lone pair on the oxygen atom should be in the close vicinity for final cyclization⁶ of **3a–b**, it is obvious that the *s-cis* form would then be the required geometry. On the other hand, for 3-methoxy-2-vinyl derivative **5**, the required conformation for cyclization should be *s-trans*. As is reported for 3-methyl-2-styrylnaphthalene,⁸ the 3-methoxy-2-vinyl derivative **5** would also be expected to exist in a *s-cis* form and, as expected according to the above proposition, no photocyclization was observed in this case.

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