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Effect of Cu(I) on Cyclic Enone Photodimerizations

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Cu(I) can complex with either a nonbonded electron pair on oxygen or with the C═C π bond in enones and might act as a template to arrange the 2:1 enone–copper complex into the preferred head-to-head regiochemistry. Upon excitation of either the n,π^* or π,π^* band of the resulting metal complexes of cyclopentenone or of isophorone, however, the proportion of head-to-tail regioisomer observed in the dimeric products increases. This shift in isomer distribution is caused by metal quenching of the preferentially formed head-to-head 2:1 enone–metal complex.

Metal catalysis of photoredox reactions of organic ligands has been recognized for some time, although mechanistic details of the requisite electron exchange are sketchy.[1] Even less is known, however, concerning the possible role of metal ions as templates for photochemical reactions. We report here our study of the use of Cu(I) to control the regiochemistry of a synthetically important reaction, the (2 + 2) photodimerization of enones.

The choice of cyclopentenone **1**[2] and isophorone **2**[3] as substrates for our initial investigation was based on well-established reports that photoexcitation of either compound led to high yields of photodimerization products in which the regioisomeric ratio (head-to-head:head-to-tail) was a sensitive function of the solvent polarity and of the heterogeneity in the immediate environment of the excited state.[4,5] These substrates were also easily available and could, we reasoned, be used as models for enone dimerizations of five- and six-membered cyclic enones, respectively.

Copper(I) salts have been shown to accelerate the rates of a wide variety of photoreactions.[6] Although Cu(I)–olefin complexes have been most extensively studied, a recent report shows that analogous complexes can form also with α,β-unsaturated nitriles.[7] Photolysis of these complexes led to selective photodimerization.

Results

Spectral Evidence of Cu(I) Complexation with Enones. The absorption spectra of enones are characterized by an intense π,π^* band at approximately 230 nm and a much weaker n,π^* band at about 310 nm. Specific absorption maxima for compounds **1** and **2** in the absence and presence of copper triflate are shown in Table I. The negligible shift of the π,π^* band and the significant red shift of the n,π^* band show a clear preference for complexation of the copper with the nonbonded electrons. The long wavelength band in the **1**–CuOTf complex tails into the visible, causing an intense blue coloration, a phenomena which is often characteristic of charge-transfer absorption bands. Optimum shifts at a 2:1 molar ratio of enone–copper suggest formation of a stable complex in which one copper coordinates with two enone molecules.

Table I. Effect of Cu(I) on Absorption Spectra[a] of Cyclopentenone (1) and Isophorone (2)

	absorption maxima, nm	
solvent system	1	2
MeOH	233, 304	234, 306
MeOH/CuOTf	239, 315	233, 336
CH_2Cl_2	235, 308	228, 316
CH_2Cl_2/CuOTf	238, 338	232, 332

[a] 1:1 CuOTf:enone ratio at room temperature.

Regiochemistry of Enone Photodimerizations. The photolyses of deoxygenated solutions of the enones in the presence and absence of copper triflate was accomplished in a Rayonet photochemical reactor equipped with low-pressure mercury arcs (254 nm) for formation of the π,π^* excited states and with phosphor-coated low-pressure mercury arcs for long wavelength excitation (λ_{max} = 350 nm) for generation of the n,π^* excited states. The ratio of head-to-head:head-to-tail isomers was determined by gas–liquid chromatography. Our assignments of product structure were consistent with those made in the original photochemical studies of **1** and **2**.[2,3] Only the cis-syn-cis and cis-anti-cis dimers were found, and the originally reported product ratios were produced,[8] within experimental error, in each solvent system examined, eq 1 and 2.

A summary of the effect of Cu(I) on the regiochemistry of the photodimerization of **1** and **2** in a protic (MeOH) and an aprotic (CH_2Cl_2) solvent is given in Table II. The reported fraction of head-to-head isomers were those observed at about 10% conversion of starting material and therefore represent initial product branching ratios. In each case, the fraction of head-to-tail dimer increased in the presence of copper, although the stereochemical preference was far from complete. In fact, alteration of solvent polarity induced a more profound effect.

A kinetic profile for the photodimerization of **2** was obtained to determine whether Cu(I) affected the observed kinetic partitioning of the excited state by selective quenching of the transition state leading to the head-to-head dimer or by selective enhancement of that producing the head-to-tail isomer. When the progress of the reaction was monitored in the presence and absence of Cu(I), a significant decrease in the relative rates of both reactant disappearance and product appearance was observed, Figure 1. The fivefold decrease in the slopes of the pseudo-first-order rate profiles requires quenching of both the head-to-head and head-to-tail transition states.

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[2] (a) Eaton, P. E. *J. Am. Chem. Soc.* **1962**, *84*, 2344, 2454. (b) Eaton, P. E.; Hurt, W. S. *Ibid.* **1966**, *88*, 5038. (c) Ruhlen, J. L.; Leermakers, P. A. *Ibid.* **1966**, *88*, 5671. (d) Wagner, P. J.; Bucheck, D. J. *Ibid.* **1969**, *91*, 5090. (e) Wagner, P. J.; Bucheck, D. J. *Can. J. Chem.* **1969**, *47*, 713.

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[7] Bolte, M.; Lemaire, J. *Nouv. J. Chim.* **1980**, *4*, 461.

[8] Under our analytical conditions, stereoisomeric resolution of the cis-syn-cis dimer of **2** proved to be possible so that four dimers were obtained rather than the three reported by Chapman and co-workers.[3] The sum of the fraction of the two head-to-head dimers corresponded closely to that reported earlier for the single head-to-head dimer. Overall yields corresponded exactly to those reported earlier.[3]

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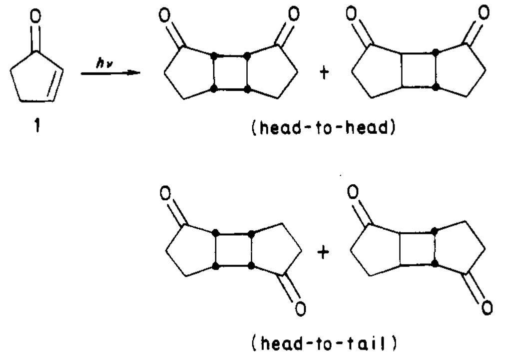
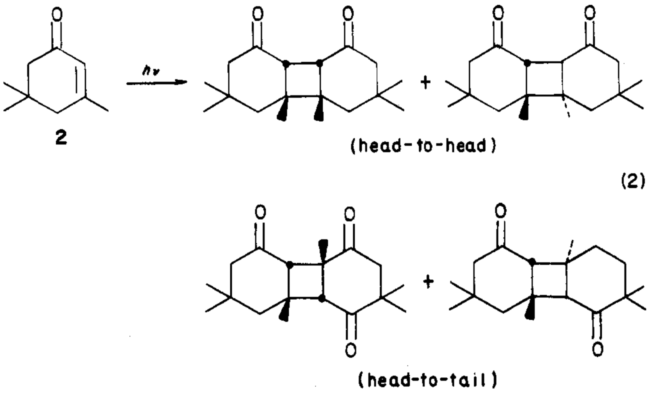


(1)



(2)

Product analysis shows a greater retardation in the formation of the head-to-head product than in that of the head-to-tail product.

Perturbation of the Photophysics of Enones 1 and 2 by Cu(I). Both 1 and 2 exhibited weak fluorescence with excitation in either the n,π* or π,π* bands. Addition of increasing concentrations of CuOTf induced fluorescence quenching. Table III summarizes the extent of fluorescence quenching of 2 when excited in the n,π* band.

Laser flash excitation (λ_{max} = 355 or 266 nm) of enones 1 or 2 led to transients with absorption at about 295 nm. These species were assigned as the first excited triplets by virtue of their sensitivity to oxygen as well as the close correspondence of their observed lifetimes and spectral features with typical solution phase ketone triplet states. Addition of increasing concentrations of copper triflate led to diffusion-controlled quenching, nearly completely obviating detection of these transients at the concentrations employed in the preparative experiments. Lifetimes for the observed triplets in oxygenated and deoxygenated solution, with and without copper triflate, upon excitation into either the n,π* or π,π* bands are summarized in Table IV.

Discussion

The red shift observed when copper triflate is added to a solution of 1 or 2, resulting in the observed coloration often ascribed to charge-transfer bands, suggests the formation of an enone–copper complex. Since a much more pronounced effect is observed on the band position of the n,π* absorption band, we infer that copper preferentially complexes with the nonbonding electrons of the enone. In parallel to this inference, Lewis acid enhancement of photochemical trans-to-cis isomerization of α,β-unsaturated esters is thought to occur via coordination with the carbonyl nonbonding electrons.[9] If n complexation is preferred, such a complex would probably exist in head-to-head regiochemistry, Figure 2, where the metal can interact spatially with lone pairs from each carbonyl.

Table II. Effect of Cu(I) on Regiochemistry. Product Distribution in Some Enone Photodimerizations[a]

system/excitation	λ, nm	fraction of head-to-head dimer, % (±2%) neat	reactn with 0.1 M CuOTf
1/MeOH	254	67	40
1/CH_2Cl_2	254	35	7
2/MeOH	254	60	39
2/MeOH	350	70	66
2/CH_2Cl_2	350	11	8.5

[a] Concentration of enones ≃0.5 M.

Table III. Fluorescence of Isophorone in MeOH

system	excitation λ, nm	emission λ, nm	rel Φ (±0.05)
2	305	345	1.00
2/CuOTf[a]	335	373	0.21

[a] Concentration: 2 = 4×10^{-3} M, CuOTf = 2×10^{-3} M.

Table IV. Effect of Cu(I) on the Excited Triplet Lifetimes of 1 and 2

system[a]	excitation λ, nm	τ, ns
1/N_2	355	56.2
1/O_2	355	15.6
1/N_2/CuOTf	355	<0.1
1/N_2	266	~10[b]
2/N_2	355	103
2/O_2	355	42.2
2/N_2/CuOTf	355	<0.1
2/N_2	266	83.7

[a] Solvent was methanol. [b] Signal quenching was qualitatively observed upon the addition of CuOTf; interference of the excitation band (266 nm) with transient absorption (295 nm) affected the experimental resolution.

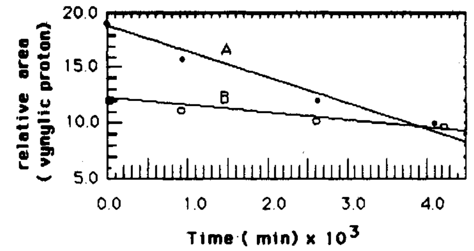


Figure 1. Disappearance of 2 upon ultraviolet irradiation without (A) and with (B) Cu(I).

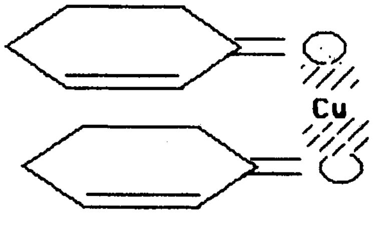


Figure 2.

Although this complex might reasonably arrange the transition state for favorable head-to-head dimer formation, no such preference was observed. Instead, the yield of the head-to-head dimer decreased in the presence of copper triflate relative to the alternate regioisomer.

Rate studies indicate a kinetic retardation of the photodimerization in the presence of copper(I). Specifically, a greater inhibition of dimerization by the pathway leading to head-to-head dimer is observed in the presence, rather than in the absence, of copper.

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Since these enone dimerizations are thought to proceed through the triplet excited state,[3] quenching of the excited states of 1 and 2 was studied. The importance of the excited singlet state in these photoreactions could be determined by observing the fluorescence yield in the presence and absence of copper. When excited into the n,π^* band at 335, however, the fluorescence of 2 is somewhat reduced, but not completely quenched, by the presence of Cu(I). We conclude that either Cu(I) can quench the n,π^* singlet state or can facilitate intersystem crossing to the triplet state.

The transient enone triplets, generated by laser flash spectroscopy, were sensitive to oxygen in methanolic solution and were nearly completely quenched if precomplexed with copper triflate. Thus, the observed shift in regiochemistry toward the head-to-tail dimer may be attributed to more efficient quenching of the preferentially formed Cu(I)–head-to-head dimer complex.

Although the enhanced quenching of the head-to-head complex provides partial stereocontrol of these reactions, a mixture of regioisomers is still obtained. The shift in regiochemical preference obtained with copper closely resembles that observed in these systems upon alteration of solvent polarity. Comparable chemical yields are observed in the presence and the absence of the copper salt, and the quantum yield of photodimer is greatly reduced when copper is present. We, therefore, find no clear synthetically useful advantage in pre-complexation with copper salts as a means for regiocontrol in enone (2 + 2) cycloadditions.

Experimental Section

Commercial (Aldrich) samples of cyclopentenone and isophorone were distilled to 99% gas chromatographic purity. Solvents employed here were reagent grade, distilled before use.

Photodimerizations. In a typical experiment, enone (2 g, 15 mmol) was diluted to a solution volume of 20 mL with either methanol or dichloromethane. The resulting solution, having been purged by a nitrogen stream for 30 min and sealed into a glass test tube, was irradiated for 2 h at 254 or 350 nm. Quartz vessels were used for irradiations at 254 nm and Pyrex vessels were employed at 350 nm.

Irradiations conducted in dichloromethane were analyzed directly by GC. Those conducted in methanol were stripped of solvent and redissolved in diethyl ether. Having been washed with water, the solutions were dried over $MgSO_4$, filtered, and concentrated for analysis. Products were identified by comparison of ^1H and ^{13}C NMR spectral data and mass spectral fragmentation patterns with authentic samples.[1,2]

Photodimerizations in the Presence of Copper Triflate. To a 5-mL solution of enone prepared as above was added 1 mL of a saturated solution of CuOTf[10] (2 g in 10 mL solvent). The resulting dark blue-green solution was irradiated as above for 24 h at 254 or 350 nm. Products were worked up, analyzed, and identified as in the uncomplexed irradiations. Rates of reaction were determined by monitoring the absolute rates of appearance of product by GC and by observing the rate of disappearance of the vinyl proton of the starting material by proton NMR.

Fluorescence Quenching Studies. Solutions of isophorone (optical density of approximately 0.2) were excited by a source passing a beam from a high-pressure mercury arc through a monochromator blazed at 305 or 335 nm. Emission intensity, monitored at a right angle to the incident beam, was scanned from 325 to 400 nm, and the area under the emission curves was compared electronically. A solution containing a 1:1 ratio of enone to copper triflate was similarly scanned.

Phosphorescence Quenching Studies. Solutions (CH_2Cl_2 or CH_3OH) of 1 or 2 containing varying quantities of copper triflate were adjusted in concentration so that the resulting mixtures had an optical density between 0.1 and 0.2 at 355 or 265 nm. The resulting solutions were purged by a slow stream of nitrogen. Laser flash excitation with a N_2 laser or with the second harmonic of a Nd-YAG laser produced a transient with absorption at 295 nm. Transient decay rates were analyzed with a Biomation 8100 digitizer, coupled with either a PDP 11/34 or a PDP 11/70 computer, as previously described.[11]

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Registry No. 1, 930-30-3; 2, 78-59-1; CuOTf, 42152-44-3.

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Asymmetric Electrophilic Substitution on Phenols. 1. Enantioselective Ortho-Hydroxyalkylation Mediated by Chiral Alkoxyaluminum Chlorides

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A method has been developed for the asymmetric ortho-specific hydroxyalkylation of phenols with trichloroacetaldehyde in the presence of chirally modified aluminum chloride derivatives. Enantiomeric excesses of up to 80% were obtained by using (−)-menthoxy(ethyl)aluminum chloride in toluene at room temperature. A chelate transition state involving the chiral Lewis acid promoter and the reactants is proposed to account for both regio- and enantioselection.

The electrophilic aromatic substitution represented by Friedel–Crafts reaction is one of the most efficient procedures for formation of carbon–carbon bonds to aromatic rings.[1] Along this route we have been developing, in the