

Copper(I) Catalysis in Photocycloadditions. I. Norbornene

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Abstract: The photodimerization of norbornene and related olefins is examined with copper(I) triflate as catalyst. Copper (I) triflate shows marked superiority in yield and other practical advantages over other copper(I) complexes for olefin photodimerization. Quantum yield studies of the CuOTf catalyzed photodimerization of norbornene are consistent with a mechanism involving photoexcitation of a 2:1 norbornene-CuOTf complex. The requirement for coordination of Cu(I) with both of the reacting C=C bonds is also apparent from a comparison of the photoreactions of *endo*-dicyclopentadiene catalyzed by CuOTf and that sensitized by acetone. The first example of a mixed photodimerization catalyzed by a metal salt is reported.

There are few clear-cut examples of catalysis by metal salts of olefin photocycloaddition reactions. The first example of copper(I) catalysis of olefin photocycloaddition was reported by Srinivasan for photolysis of 1,5-cyclooctadiene in the presence of cuprous chloride.¹ The role of Cu(I) in this reaction is not clear,² though it was proposed that CuCl merely acts as a catalyst for the isomerization of photoexcited 1,5-cyclooctadiene.¹ An alternative mechanism involving light-induced rearrangement of a preformed CuCl-olefin complex was dismissed. A closely related mechanism was subsequently favored³ for copper(I) halide catalyzed photodimerization of norbornene.⁴

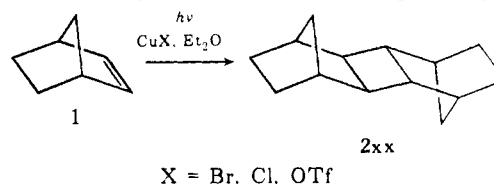
We recently reported the preparation of a variety of cationic copper(I)-olefin complexes which are readily derived from the benzene adduct of copper(I) trifluoromethanesulfonate.⁵ Trifluoromethanesulfonate (OTf = triflate) like perchlorate is an exceptionally weakly coordinating anion, and the binary metal salts such as those of copper(I) are extensively ionized (as ion pairs) even in nonaqueous solutions.⁶ The highly electrophilic metal ion under these conditions is capable of multiple coordination. If metal-olefin coordination is a factor in the Cu(I) catalyzed photocycloaddition reactions of olefins, CuOTf is expected to be a superior catalyst for olefin photodimerization. With this catalyst, photodimerization may not be limited to strained olefins such as norbornene derivatives.⁷ Thus, with previous studies of olefin-CuOTf coordination as a background,⁸ we have undertaken the present investigation of the scope and mechanism of Cu(I)-catalyzed photodimerization of olefins. In addition, for the sake of comparison we have examined some aspects of the related high energy triplet sensitized photodimerization of olefins.

Results and Discussion

Photodimerization of Norbornene Catalyzed by Cop-

- (1) R. Srinivasan, *J. Amer. Chem. Soc.*, **86**, 3318 (1964).
- (2) G. M. Whitesides, G. L. Goe, and A. C. Cope, *J. Amer. Chem. Soc.*, **91**, 2608 (1969).
- (3) D. J. Trecker, R. S. Foote, J. P. Henry, and J. E. McKeon, *J. Amer. Chem. Soc.*, **88**, 3021 (1966).
- (4) D. J. Trecker, J. P. Henry, and J. E. McKeon, *J. Amer. Chem. Soc.*, **87**, 3261 (1965).
- (5) (a) R. G. Salomon and J. K. Kochi, *J. Chem. Soc., Chem. Commun.*, 559 (1972); (b) M. B. Dines and P. H. Bird, *ibid.*, 12 (1973).
- (6) C. L. Jenkins and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 843 (1972).
- (7) A preliminary partial account of this work was given in: R. G. Salomon and J. K. Kochi, *Tetrahedron Lett.*, 2529 (1973).
- (8) R. G. Salomon and J. K. Kochi, *J. Amer. Chem. Soc.*, **95**, 1889 (1973).

per(I) Triflate. Irradiation of norbornene (**1**) in the presence of CuOTf as catalyst, with ultraviolet (uv) light from a medium-pressure mercury vapor lamp, afforded dimer in 88% isolated yield, which is a substantial improvement on the 38% yield reported for the same reaction catalyzed by CuBr.⁹ The product is the almost pure *exo-trans-exo* isomer² with either catalyst. The Cu(I) halide catalysts are unstable and partially trans-



formed under uv irradiation into an opaque insoluble deposit. The solid must be repeatedly removed from the walls of the reaction vessel and additional Cu(I) halide replenished during the course of photodimerization. Norbornene-Cu(I) triflate is thermally stable and soluble in various organic solvents as an undissociated monomeric species. Furthermore, the reaction mixture after irradiation remained light and clear, and the photomerization under these conditions is well suited for a mechanistic investigation.

To resolve the mechanism, the question of special interest is which Cu(I)-olefin complex, 1:1 or 1:2 or both, is catalytically active. In previous mechanistic studies of the CuBr catalyzed dimerization, it was concluded on the basis of uv spectral evidence that there is but a single complex in solution, which is probably the same as the 1:1 complex which is isolable. The presence of a second absorbing species, such as a 1:2 complex, was doubted. Thus, over a wide range of norbornene concentrations there was no detectable variation in either the position of the λ_{\max} or the essential shape of the curve with ϵ_{\max} remaining constant over the range of olefin concentrations.³ We find similar behavior with solutions of CuOTf in the presence of various concentrations of norbornene as shown in Figure 1. However, these observations are misleading, since we have recently demonstrated by nmr spectroscopy the presence in solution of several different complexes, which are most likely the 1:1 and 1:2 Cu(I)-norbornene complexes.⁸ The apparent disagreement between the uv and nmr results would be resolved if the uv spectra of all the Cu(I)-norbornene complexes were essentially the same. Indeed, the latter is not unreasonable since all

(9) D. J. Trecker and R. S. Foote, *Org. Photochem. Syn.*, **1**, 81 (1971).

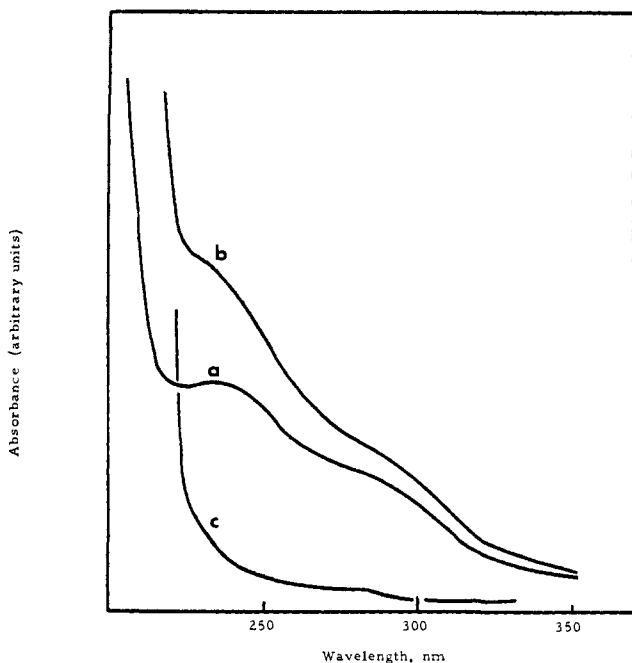


Figure 1. (a) The absorption spectrum of CuOTf-norbornene complex in methanol. (b) The spectrum of (a) in the presence of a tenfold excess of norbornene with norbornene in the reference cell for balancing. (c) The end absorption spectrum of norbornene. The vertical scale is arbitrary in (a)-(c).

the CuOTf-olefin complexes we have recently isolated as crystalline compounds exhibit two strong uv absorption bands in a narrow range, one at 233–241 nm (ϵ_{\max} 2500–3600) and one at 272–282 nm (ϵ_{\max} 1500–2100).⁸ These spectral studies included complexes with one, two, three, and even four C=C bonds coordinated to Cu(I) triflate.

Quantum Yields for Cu(I)-Catalyzed Photodimerization. The quantum yields for the photodimerization of norbornene catalyzed by Cu(I) triflate were examined at 254 nm as a function of olefin concentration. The solutions always contained sufficient catalyst to ensure essential complete absorption of the incident light. The quantum yields in Table I were measured at conversions which never exceeded 6%.

Mechanisms for the Cu(I)-Catalyzed Photodimerization of Norbornene. The mechanism shown in Scheme

Table I. Quantum Yields for the Photodimerization of Norbornene Catalyzed by Copper(I) Triflate^a

Norbornene (M)	Φ_{xx}^b	$1/\Phi_{xx}$	Φ_{nx}^c	$1/\Phi_{nx}$	$1/[nb]^d$	$1/[nb]^2$
0.10	0.060	16.7	0.012	83.3	10.00	100.00
0.15	0.091	11.00	0.017	58.8	6.67	44.49
0.20	0.103	9.71	0.019	52.6	5.00	25.00
0.30	0.138	7.25	0.026	38.5	3.33	11.09
0.40	0.162	6.17	0.031	32.3	2.50	6.25
0.60	0.178	5.62	0.036	27.8	1.67	2.79
0.80	0.255	3.92	0.051	19.6	1.25	1.56
1.20	0.323	3.10	0.065	15.4	0.83	0.69
1.60	0.370	2.70	0.068	14.7	0.63	0.40
5.00	0.610	1.64	0.102	9.80	0.20	0.04

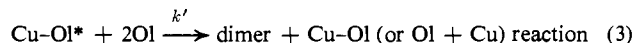
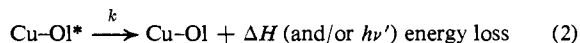
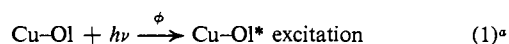
^a In ethereal solutions containing 3.0×10^{-2} M CuOTf at 25°.

^b Overall quantum yield for the formation of *exo-trans-exo*-norbornene dimer, 2xx. ^c *endo-trans-exo*-norbornene dimer, 2nx.

^d nb = norbornene.

I was previously suggested for the photodimerization of

Scheme I



Cu = CuCl, CuOTf; OI = olefin (norbornene)

^a The triflate counterion will not be included hereafter except where necessary for the discussion.

norbornene catalyzed by Cu(I) halides.³ This mechanism assumes only a single light-absorbing Cu(I)-olefin complex and predicts a linear relationship between $1/\Phi$ and $1/[\text{OI}]^2$ according to expression 4 in which Φ

$$\frac{1}{\Phi} = \frac{1}{\phi} + \frac{k}{\phi k' [\text{OI}]^2} \quad (4)$$

is the observed quantum yield and ϕ is the quantum efficiency for production of the photoactivated complex, Cu-OI*.

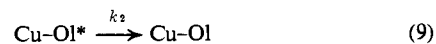
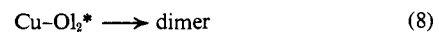
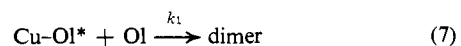
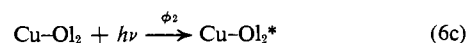
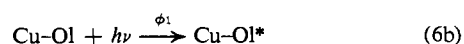
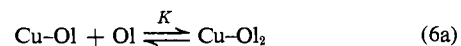
Due to the high solubilities of olefin-Cu(I) triflate complexes, the Cu(I) triflate catalyzed photodimerization could be studied over a much wider range of norbornene concentrations than was possible with Cu(I) halide. A plot of $1/\Phi$ vs. $1/[\text{OI}]^2$ shown in Figure 2a for the CuOTf catalyzed dimerization at varying norbornene concentrations failed to reveal the linear relationship in eq 4, which was presented previously for Cu(I) halide.³ The data replotted in Figure 2b, however, show an excellent linear relationship with $1/[\text{OI}]$, *i.e.*

$$\frac{1}{\Phi} = \frac{1}{\phi} + \frac{C}{[\text{OI}]} \quad (5)$$

where C is an experimental constant.

The foregoing discrepancy is not unexpected since there are more than one light-absorbing Cu(I)-olefin complexes in solutions of CuOTf in the presence of norbornene (*vide supra*). A general mechanism taking into account the presence of two light-absorbing Cu(I)-olefin complexes, a 1:1 and a 1:2 complex, and the possibility of dimer production *via* photoexcitation of either complex is outlined in Scheme II. In this

Scheme II



scheme, dimer production *via* a photoexcited 1:1 complex results from a bimolecular interaction with a single uncomplexed and unactivated, ground-state norbornene molecule, as shown in eq 7, rather than by the unusual termolecular interaction depicted in eq 3 of Scheme I above. Dimer production *via* a photoexcited 1:2 complex, as shown in eq 8, is an obligatory rapid unimolecular process.

If all of the processes in Scheme II are taken into

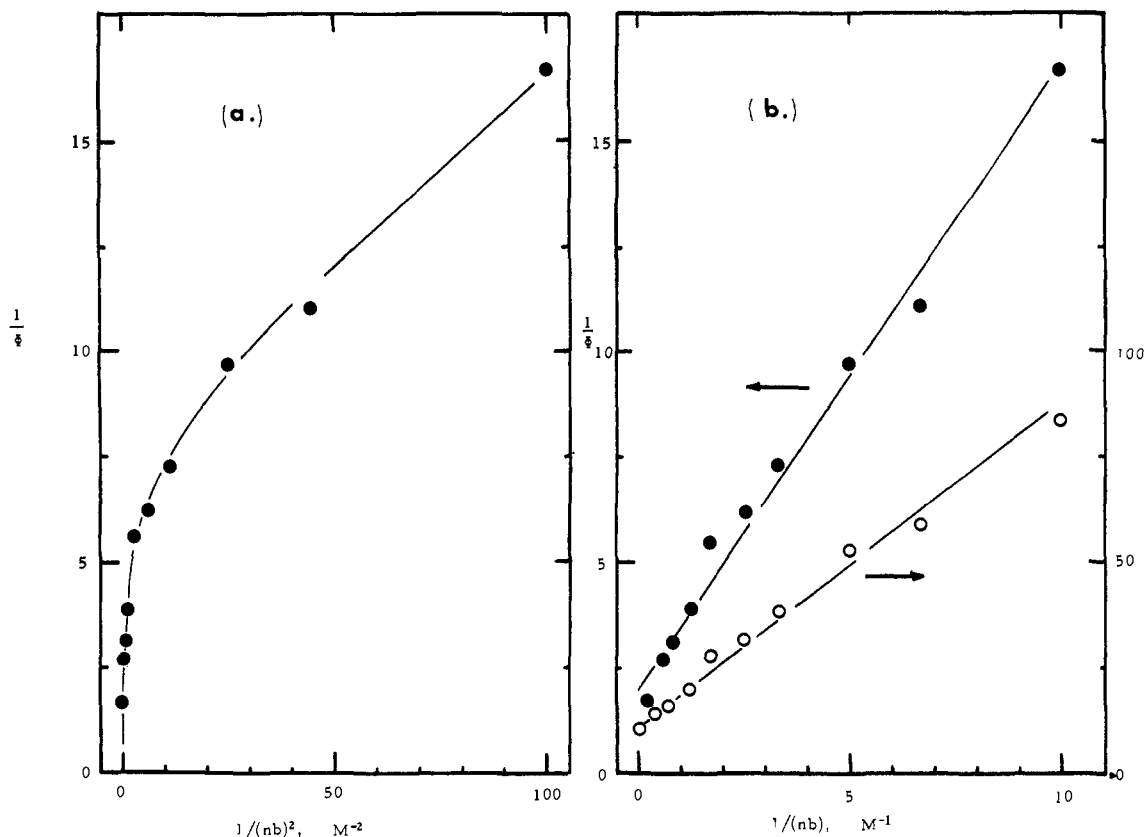


Figure 2. Plot of the quantum yields of norbornene cyclodimers at varying concentrations of norbornene keeping [CuOTf] constant at $3.0 \times 10^{-2} M$: (●) exo-trans-exo isomer, **2xx**. (○) endo-trans-exo isomer, **2nx**.

account, Φ , the observed quantum yield of dimer, can be expressed as eq 10. Φ may also be expressed as a func-

$$\Phi = \phi_1 \left[\frac{k_1[\text{OI}]}{k_1[\text{OI}] + k_2} \right] \left[\frac{[\text{Cu-OI}]}{[\text{Cu-OI}] + [\text{Cu-OI}_2]} \right] + \phi_2 \left[\frac{[\text{Cu-OI}_2]}{[\text{Cu-OI}] + [\text{Cu-OI}_2]} \right] \quad (10)$$

tion of olefin (norbornene) concentration as in eq 11.

$$\Phi = \left[\phi_1 \left(\frac{k_1}{k_1[\text{OI}] + k_2} \right) + \phi_2 K \right] \left[\frac{[\text{OI}]}{K[\text{OI}] + 1} \right] \quad (11)$$

The first term of eq 10 is the product of ϕ_1 , the quantum efficiency for production of the photoactivated complex Cu-OI*, a factor for that fraction of light absorbed by the 1:1 complex, and a factor for the partitioning of the photoactivated complex Cu-OI* between dimer production and deactivation to Cu-OI. The second term of 10 is the product of ϕ_2 , the quantum efficiency for production of the photoactivated complex Cu-OI₂* and a factor for that fraction of light absorbed by the 1:2 complex. These equations assume that the 1:1 and 1:2 Cu(I)-olefin complexes have the same or quite similar uv absorption spectra.

Since eq 11 predicts a complex dependence of Φ on [OI], the results of various simplifying assumptions are expressed in eq 12-14. If $k_1 \ll k_2$, then

$$\frac{1}{\Phi} = \frac{1}{\phi_2} + \frac{1}{\phi_2 K[\text{OI}]} \quad (12)$$

If $K \ll 1$, then

$$\frac{1}{\Phi} = \frac{1}{\phi_2} + \frac{k_2}{\phi_1 k_1 [\text{OI}]} \quad (13)$$

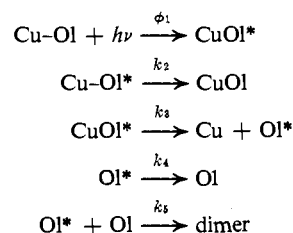
If photoexcitation of the 1:2 complex does not result in dimer formation, *i.e.*, $\phi_2 = 0$, then

$$\frac{1}{\Phi} = \frac{1}{\phi_1} \left[\left(\frac{Kk_2}{k_1} + 1 \right) + K[\text{OI}] + \frac{k_2}{k_1[\text{OI}]} \right] \quad (14)$$

The last assumption does not result in as simple a relationship between ϕ and [OI] as do the first two. It should be noted that eq 12 and 13 have the same functional form as the phenomenological relationship given in eq 5.

A plot of $1/\Phi$ as a function of $1/[\text{OI}]$ in Figure 2b for the CuOTf-catalyzed dimerization at varying norbornene concentrations reveals an excellent linear relationship as demanded by eq 12 or 13. Since K is not $\ll 1$ for CuOTf in the presence of norbornene (*vide supra*), it is likely that $k_1 \ll k_2$ or $\phi_1 = 0$.¹⁰ That is, photoactivation of the 1:1 Cu(I)-olefin complex (3) does

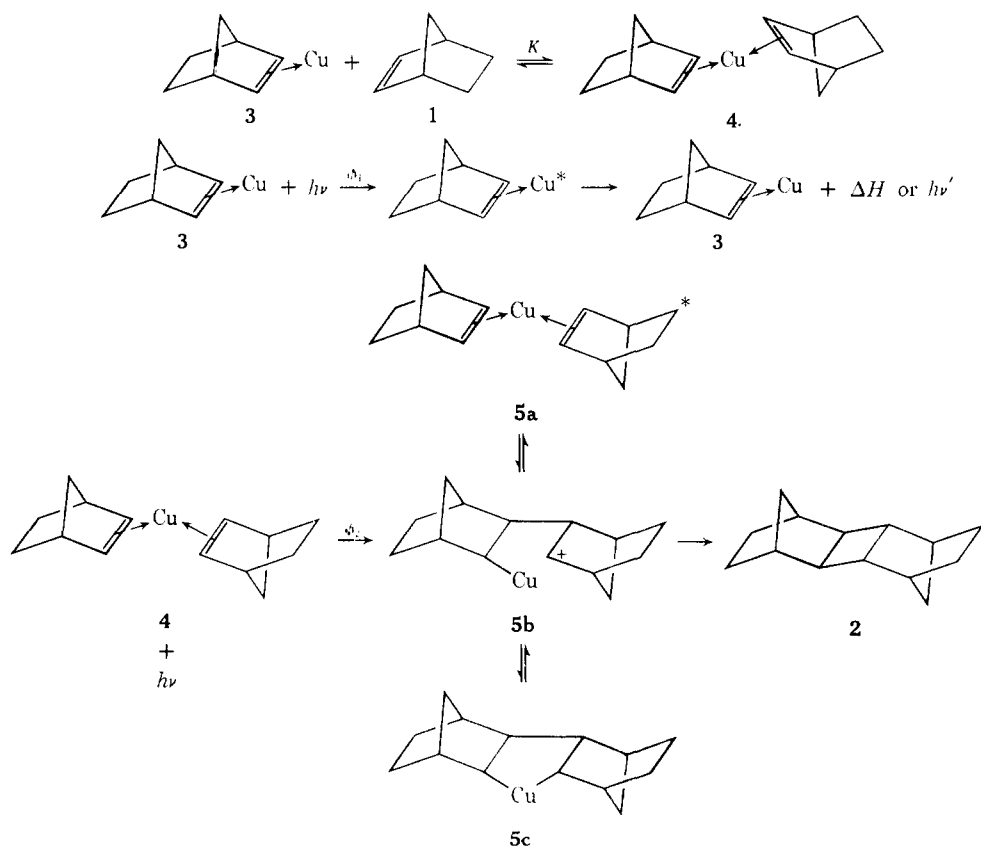
(10) A referee has suggested an additional mechanism which predicts the observed relationship expressed in eq 5



for which

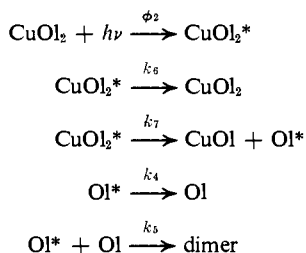
$$\frac{1}{\Phi} = \left(\frac{k_2 + k_3}{k_5} \right) \left[\frac{1}{\phi_1} + \frac{k_1}{\phi_1 k_5 [\text{OI}]} \right]$$

However, this mechanism, which is related to that giving rise to eq 13, can be excluded for the same reason, since it requires $K \ll 1$ for eq 6a.



not result in dimer production, and deactivation is much faster than the bimolecular association with a ground-state norbornene. Dimer 2 is produced exclusively by photoexcitation of a 1:2 Cu(I)–norbornene complex (4) and subsequent unimolecular collapse to products as shown in Scheme III.¹¹

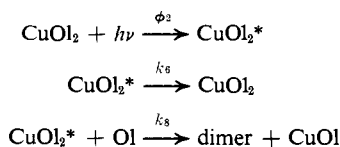
(11) (a) In the event that $K \gg 1$, the equilibrium in eq 6a lies entirely to the right, and several mechanisms can be formulated which predict the behavior observed as expressed in eq 5



for which

$$\frac{1}{\Phi} = \left(\frac{k_6 + k_7}{k_7} \right) \left(\frac{1}{\phi_2} + \frac{k_4}{\phi_2 k_5 (\text{Ol})} \right)$$

or



for which

$$\frac{1}{\Phi} = \frac{1}{\phi_2} + \frac{k_6}{k_8 \phi_2 (\text{Ol})}$$

In deriving these equations we have assumed that $[\text{Cu}-\text{Ol}_2]$ is essentially a constant, and have included this constant in ϕ_2 . We disfavor these mechanisms since only a 1:1 complex is isolated from a mixture of CuOTf and a large excess of norbornene. We believe that a 2:1 olefin–Cu complex is formed but that one of the olefin ligands is easily lost

Formulation of 4 with exo-coordinated ligands is in accord with the established tendency for norbornene to coordinate with Cu(I) in this manner.¹² Furthermore, the structurally related (*endo*-dicyclopentadiene)₂–CuOTf (9) has been isolated, and the olefinic ligands in 9 have been shown to be coordinated to Cu(I) in an exo-monodentate fashion.⁸

The mechanistic details of the collapse of the photoexcited species are not provided by these studies. It is possible that the copper ion in 4 facilitates the required absorption of uv light by an otherwise weakly absorbing olefin, and may merely act as a template which promotes a concerted orbital-symmetry allowed photochemical $[2\pi_s + 2\pi_s]$ cycloaddition.¹³ An analogous mechanistic possibility has been advanced for the related *thermally* induced metal catalyzed $[2 + 2]$ cycloaddition reactions.¹⁴

The metal may alternatively participate in a stepwise process in which a σ -bonded intermediate¹⁵ is

during isolation which involves washing the complex. This suggests that K in eq 6a is not *very* large. However, the above mechanisms cannot be definitely excluded without an accurate independent determination of K . (b) Partitioning of the photoactivated complex CuOl_2^* between dimer production and deactivation to CuOl_2 would introduce a constant which can be considered a part of ϕ_2 .

(12) N. C. Baenziger, H. L. Haight, and J. R. Doyle, *Inorg. Chem.*, **3**, 1535 (1964).

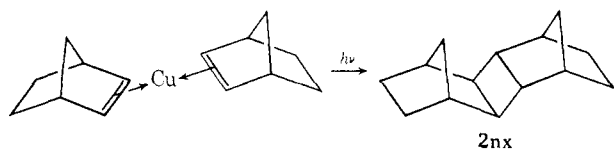
(13) (a) G. N. Schrauzer, P. Glochner, and S. Eichler, *Angew. Chem., Int. Ed. Engl.*, **3**, 183 (1964); (b) G. N. Schrauzer, B. N. Bastian, and G. A. Fosselius, *J. Amer. Chem. Soc.*, **88**, 4890 (1966); (c) G. N. Schrauzer, *Advan. Catal.*, **18**, 373 (1968); (d) R. B. Woodward and R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(14) (a) F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **89**, 2484 (1967); (b) F. D. Mango, *Advan. Catal.*, **20**, 291 (1969); (c) N. Calderon, *Accounts Chem. Res.*, **5**, 127 (1972); (d) G. S. Lewandos and R. Pettit, *Tetrahedron Lett.*, 789 (1971).

(15) The intermediate (6), though produced differently, has previously been suggested for the copper(I) halide catalyzed photodimerization of norbornene: E. K. v. Gustorf and E.-W. Greveis, *Photochemistry*, **13**, 366 (1969); see especially pp 413–415.

formed in a light-induced oxidative metalocycloaddition. In this process, the Cu(I)-bisolefin complex undergoes oxidation to a dialkylcopper intermediate (5), which collapses to product by reductive elimination. Formation of intermediates like 5c during thermally induced metal catalyzed [2 + 2] cycloaddition¹⁶ and related reactions¹⁷ has been proposed. Recently, metalocyclic "stabilized intermediates in the metal-promoted dimerization" of norbornadiene have been isolated and shown to have a structure analogous to 5c.¹⁸

The quantum yields of the minor photodimer, the endo-trans-exo isomer (2nx), were also measured as a function of olefin concentration (Table I). The inverse of the quantum yield $1/\Phi_{nx}$ for production of 2nx is also linearly related to $1/[\text{norbornene}]$ (Figure 2b). The mechanism for formation of this minor dimer must, therefore, be quite similar to that for the major dimer, and most likely involves photoexcitation of an endo,exo-bisnorbornene-copper(I) triflate complex.

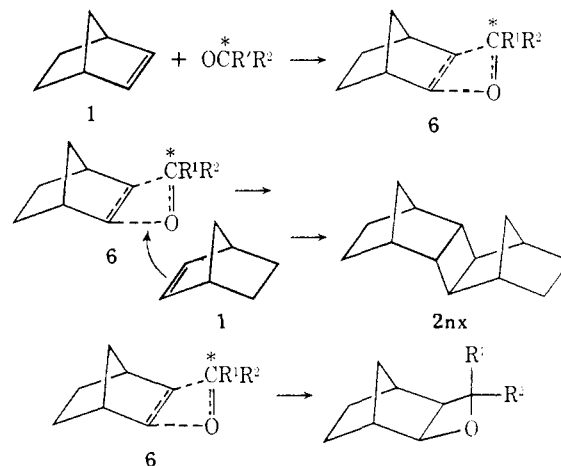


A different mechanism shown in Scheme I was previously suggested³ for the same photodimerization catalyzed by CuCl on the basis of an apparent linear relationship between $1/\Phi$ and $1/[\text{OI}]^2$. However, we find that the same data can be reinterpreted as a relatively good linear relationship between $1/\Phi$ and $1/[\text{OI}]$. Indeed, the difference between these two functions (*i.e.*, eq 4 and 5) is not readily distinguishable over a limited range in concentrations examined in the earlier study. For example, they only studied a threefold concentration range between 2.90 and 7.93 M norbornene, which merely represents the *initial* linear portion of the 50-fold range of concentrations spanned in Figure 2a or 2b. The problem is not resolved, however, since $1/[\text{OI}]$ from the earlier data³ extrapolates to a rather unlikely negative value for the quantum efficiency of photoactivation, Φ_2 . We feel that a decision between various mechanistic possibilities for the CuCl catalyzed reaction should await either more accurate data or data over a wider range of norbornene concentrations.¹⁹

It is noteworthy that the observed quantum yield with CuOTf as catalyst is at least an order of magnitude greater than that observed with CuCl as catalyst. These higher quantum yields can be explained by the much greater tendency of CuOTf compared with CuCl to form the 1:2 Cu(I)-olefin complex. The smaller values of the formation constants for 1:2 CuCl-olefin complexes result from the effective competition experienced by olefins for coordination sites on Cu(I) by the strongly associating halide ligands.⁸

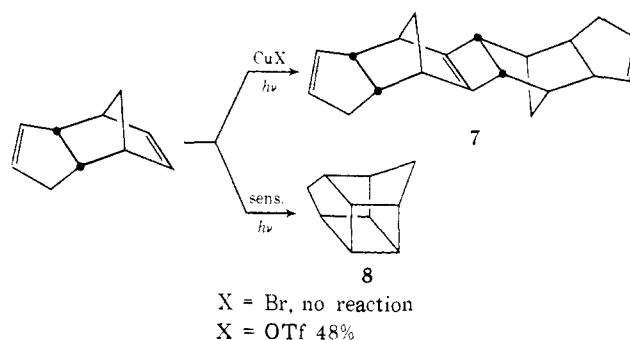
The stereospecificity of the Cu(I)-catalyzed photodimerization is a reasonable consequence of the ge-

ometries of the intermediates like 4 or 5 and the implicit requirement for coordination with Cu(I) of both of the reacting C=C bonds. It is interesting and significant that the acetone-sensitized photodimerization of norbornene stereospecifically gives 2nx (22%) and only 2% of 2xx.²⁰ A possible explanation²¹ for the steric course of the triplet sensitized reaction involves exo interaction of the sensitizer with norbornene in an activated complex (6). With the exo face of C=C thus blocked, attack on a free, unactivated, ground-state norbornene molecule is directed toward the endo face of the "excited complex" (excimer) (6). Collapse of 6



would lead to oxetane, always a minor reaction product.

Copper(I) Triflate Catalyzed Photodimerization of endo-Dicyclopentadiene. Irradiation of endo-dicyclopentadiene with 254-nm light in the presence of catalytic amounts of CuOTf afforded dimer 7 in 48% isolated yield. The cis-anti-cis structure (7), analogous to the



norbornene dimers 2xx and 2nx, is suggested by the ir and pmr spectra of the photodimer. In free endo-dicyclopentadiene, $\nu_{\text{C}=\text{C}}$ at 1615 and 1570 cm^{-1} have been assigned to the double bonds in the cyclopentene and norbornene rings, respectively.²¹ In the photodimer the absorption band associated with the double bond in the cyclopentene ring is observed but that associated with the norbornene ring is absent. Also, endo-dicyclopentadiene exhibits vinylic pmr absorptions at δ 5.95 due to protons of the norbornene double bond and at 5.45 due to protons of the cyclopentene double bond. In the pmr spectrum of the photodimer, no absorption is observed in the vicinity of δ 5.95, and only those associated with the vinyl protons of the cyclopentene double bond are present.

(20) D. Scharf and F. Korte, *Tetrahedron Lett.*, 821 (1964).

(21) B. W. Cook, R. G. J. Miller, and P. F. Todd, *J. Organometal. Chem.*, 19, 421 (1969).

(16) T. J. Katz and N. Acton, *Tetrahedron Lett.*, 27, 3515 (1967).

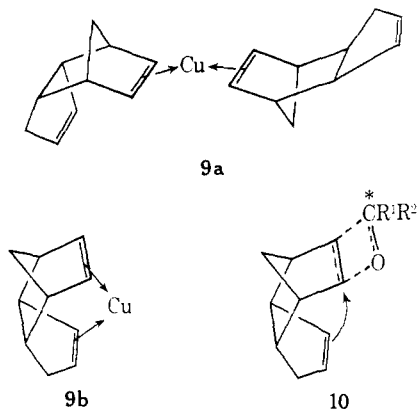
(17) (a) T. J. Katz and S. Cereface, *J. Amer. Chem. Soc.*, 91, 2405 (1969); (b) L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, 92, 3515 (1970); (c) R. H. Grubbs and T. K. Brunck, *ibid.*, 94, 2538 (1972).

(18) A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White, and J. A. Osborn, *J. Amer. Chem. Soc.*, 95, 597 (1973).

(19) It is not clear what effect the reported³ use of an actual minor product of the reaction as an internal standard has on the accuracy of these data.

It has been reported³ that *endo*-dicyclopentadiene underwent no detectable reaction upon uv irradiation in the presence of CuCl in contrast to our observations with CuOTf. Even more striking is the totally different course of the photoreaction of this olefin in the presence of acetone, a high triplet energy sensitizer, which yields only the intramolecular photocycloaddition product (8). Only traces of this product are found with CuOTf as catalyst. The strong preference for the formation of 7 in the CuOTf catalyzed reaction may arise from the requirement, as depicted in Scheme III, for the coordination of both reacting C=C bonds with Cu(I).

endo-Dicyclopentadiene forms an isolable 1:2 Cu(I)-olefin complex 9a with CuOTf. *endo*-Dicyclopentadiene is an *exo*-monodentate ligand in this complex and shows little tendency to act as an *endo*-tetrahapto chelating ligand as in 9b.⁸ On the other hand,

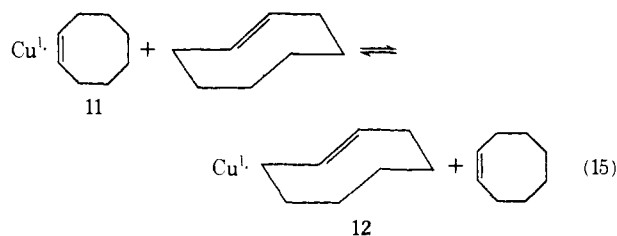


the acetone-sensitized exciplex 10 (which is analogous to 6) is constrained to undergo intramolecular addition since the free side of the coordinated C=C bond is sterically inaccessible to intermolecular attack. Intramolecular capture of the excited C=C bond by the ground-state C=C bond in an intermediate like 10 should be a facile process. Nevertheless, the analogous photoexcited intermediate derived from 9a is reluctant to undergo a similar reaction. Thus, Cu(I) does not merely serve as a template which facilitates capture of an excited C=C bond by a ground-state C=C bond in an orbital symmetry allowed [$2\pi_s + 2\pi_s$] concerted cycloaddition.

Copper(I) Triflate Catalyzed Mixed Photodimerization of Norbornene and Cyclooctene. *cis*-Cyclooctene did not dimerize upon irradiation at 254 nm in the presence of CuOTf. *Cis*-*trans* isomerization was the only reaction observed, and traces of *trans*-cyclooctene were detected in the recovered olefin. A heterogeneous copper halide catalyzed photoisomerization of cyclooctene was reported previously.²² It is significant that only traces of *trans* isomer are produced with CuOTf as catalyst.

trans-Cyclooctene coordinates exceptionally well with copper(I), as a consequence of its high torsional strain. Indeed, a 3:1 *trans*-cyclooctene-CuOTf complex has been isolated,⁵ and the equilibrium shown in eq 15 lies far to the right. Since photoisomerization must involve the olefin complexes 11 and 12, the *cis*-*trans* isomerization will depend on the position of this equilibrium. High concentrations of *trans*-cyclooctene can-

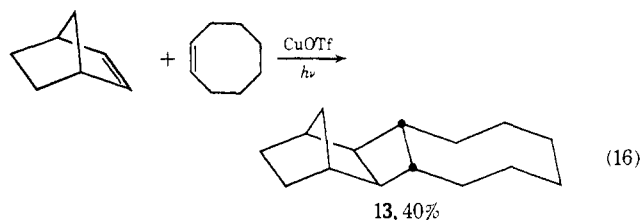
(22) J. A. Deyrup and M. Bethouski, *J. Org. Chem.*, **37**, 3561 (1972).



not build up when CuOTf is present in catalytic amounts in solution.

The heterogeneous photoisomerization catalyzed by copper halide, however, is carried out with relatively large quantities of "catalyst." Under these conditions, *trans*-cyclooctene forms an insoluble complex with the copper halide, and it is actually isolated from the insoluble complex after treatment with KCN.

Irradiation of a mixture of *cis*-cyclooctene and norbornene in the presence of CuOTf gives the mixed photodimer (13) as a major product. The cmr spec-



trum of 13 shows eight chemically nonequivalent carbon atoms, in accord with a *cis*-*anti*-*cis* structure present in the analogous norbornene photodimers (2xx and 2nx). The formation of additional photodimers was indicated by gas chromatographic analysis, but they were not identified further.^{23a}

Metal catalysis in the cross photodimerization of olefins represented in eq 16 is unique and has not been previously observed, although there are recent examples²⁴ of reactions carried out thermally. The cross photodimerization probably involves photoexcitation of the mixed complex of the catalyst and two reacting olefins, in analogy with the norbornene photodimerization discussed earlier.

Conclusion

The photodimerization of norbornene is catalyzed efficiently by copper(I) triflate. The mechanism in Scheme II involving the photoexcitation of a 2:1 olefin-CuOTf complex and subsequent unimolecular collapse to products is supported by quantum yield studies. An alternative mechanism in Scheme I, involving photoexcitation of a 1:1 olefin-Cu(I) complex and subsequent termolecular interaction with two ground-state olefins to form dimer, is not supported by our data. The latter mechanism was suggested³ previously for CuCl catalyzed photodimerization of norbornene on the basis of quantum yield data, which we find is also consistent with the mechanistic scheme similar

(23) (a) For example, small amounts of homodimer from norbornylene are also formed. The preferential formation of cross dimer is probably the result of the presence of a vast excess of cyclooctene and only 1 equiv of norbornene relative to Cu(I). (b) R. G. Salomon, K. Foltling, W. E. Streib, and J. K. Kochi, *J. Amer. Chem. Soc.*, **96**, 1145 (1974).

(24) L. G. Cannell, *J. Amer. Chem. Soc.*, **94**, 6867 (1972); R. Noyori, T. Ishigami, N. Hayashi, and H. Takiya, *ibid.*, **95**, 1674 (1973); *Tetrahedron Lett.*, 1691 (1973); D. R. Coulson, *J. Amer. Chem. Soc.*, **94**, 1253 (1972); A. Takahashi and T. Inukai, *Chem. Commun.*, 1473 (1970).

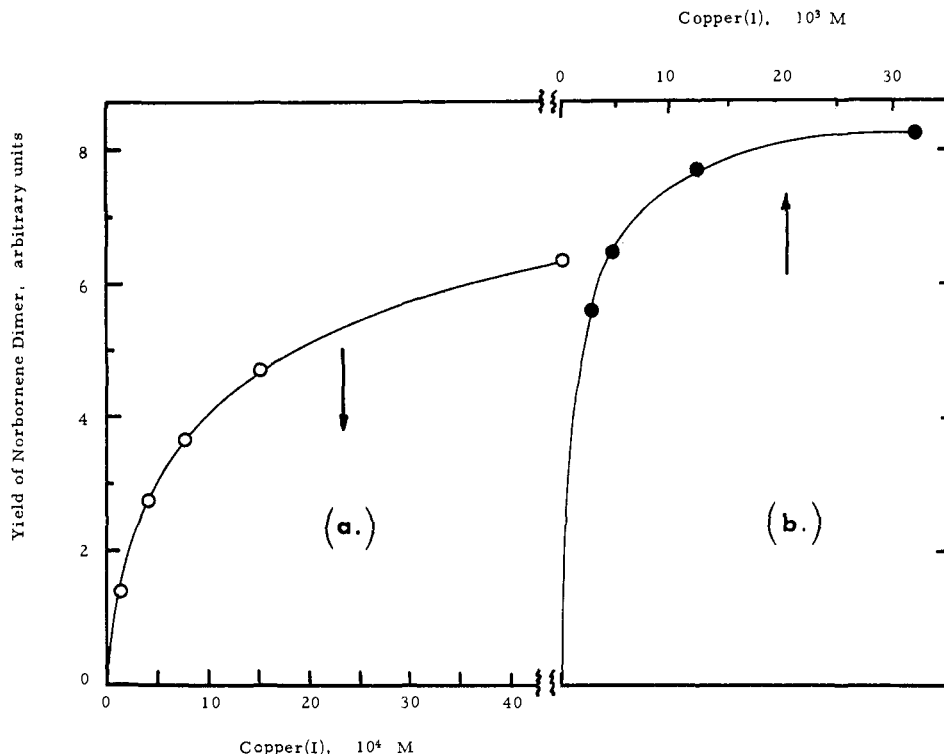


Figure 3. Relative quantum yields for norbornene dimerization with varying concentrations of CuOTf in the presence of constant norbornene concentrations at 0.4 M. Note difference in concentration scales.

to that proposed above for catalysis by CuOTf. The observed quantum yields for CuOTf are greater than those for CuCl by at least an order of magnitude due to the higher formation constants for the relevant 2:1 olefin-Cu(I) complexes. CuOTf also catalyzes the novel cross photodimerization of norbornene and cyclooctene.

Copper(I) triflate catalyzes the photodimerization of *endo*-dicyclopentadiene, while the triplet sensitized photolysis of *endo*-dicyclopentadiene results in an intramolecular photocyclization. These contrasting reactions indicate that both C=C bonds must be coordinated to the same Cu(I) to effect photodimerization.

Photodimerizations catalyzed by CuCl have only been observed with strained cycloolefins such as norbornene involved in strong coordination with Cu(I). Copper(I) triflate, in comparison, is an efficient catalyst for the photodimerization of even such simple cycloolefins as cyclopentene, cyclohexene, and cycloheptene as described in the following report.^{23b}

Experimental Section

Elemental microanalysis was performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Proton magnetic resonance spectra were obtained on a Varian HR220 or A-60 spectrometer. Carbon magnetic resonance spectra were obtained on a Varian DP-60 Fourier transform spectrometer with proton decoupling. In addition, off-resonance decoupled spectra were recorded to aid in the differentiation of carbon resonances due to methylene and methine carbons. All cmr spectra are reported in ppm upfield from CS₂, and were measured in CCl₄ solution taking the CCl₄ resonance at 96.7 as an internal standard. All pmr spectra are reported in ppm downfield from tetramethylsilane, and were measured in CCl₄ solution with TMS as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 137G spectrometer using neat liquids between KBr disks or solids fused into KBr disks. Ultraviolet spectra were recorded with a Cary 14 spectrophotometer. All reactions with copper trifluoromethanesulfonate complexes or other sensitive organometallics as well as all photoreac-

tions were conducted in an atmosphere of dry nitrogen. Vapor phase chromatography (vpc) was performed on Varian A90 or Aerograph Hi Fy chromatographs.

Preparative Copper(I) Triflate Catalyzed Photodimerization of Norbornene. A solution of (CuOTf)₂·C₆H₆ (1.2 g) in norbornene (30 g, used as received from Aldrich Chemical Co. without further purification) and tetrahydrofuran (THF, 15 ml, freshly distilled under nitrogen from sodium benzophenone ketyl) was irradiated for 6 days in a quartz vessel with a medium-pressure 450-W Hanovia mercury vapor lamp. The reaction mixture remained light and clear. Pentane (30 ml) was added and the mixture was washed with aqueous KCN to remove the catalyst. Distillation afforded dimer (26.4 g) in 88% yield. The product was mostly *exo-trans-exo* isomer (about 90%) with minor amounts of *endo-trans-exo* isomer by vpc analysis and comparison of spectra of isolated samples with reported spectra.²⁵

Quantum Yield of Norbornene Photodimers with Copper(I) Triflate Catalysis. The apparatus consisted of a quartz-spiral low-pressure mercury arc (Mr. Charles Schott, Department of Chemistry, University of Alberta, Edmonton) in the center of a precision merry-go-round apparatus (F. Moses Co., Wilmington, Del.). Norbornene was purified by stirring with molten sodium in a stoppered flask for several hours at 115–120°, cooling, followed by distillation from the resulting suspension of powdered sodium under a blanket of dry nitrogen. Ether was freshly distilled from LiAlH₄. Potassium ferrioxalate was prepared for actinometry by the method of Hatchard and Parker.²⁶

Four samples were prepared, each 0.4 M in norbornene and 0.004 M in hexadecane (internal standard) with varying concentrations of CuOTf-norbornene.⁸ The samples were irradiated for 6 hr in the precision merry-go-round apparatus with 254-nm light. The resulting solutions were analyzed by vpc with a 6 ft × 1/8 in. column containing 20% PDEAS on 60–80 Chromosorb W-HMDS at 160°. The total conversion to dimer under these conditions was 5–7%. Under the prevailing conditions of light intensity, norbornene dimerization is independent of catalyst concentration, that is, all of the incident light is absorbed, for concentrations of CuOTf above 2.5 × 10⁻² M (Figure 3a). About 90% of the incident light is absorbed with a CuOTf concentration of 1.0 × 10⁻²

(25) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Amer. Chem. Soc.*, **87**, 2596 (1965).

(26) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

M. The variation of quantum yield with catalyst concentration was examined for another range (lower) of catalyst concentrations in a 19-hr irradiation of five similar samples. The quantum yield drops sharply for Cu(I) at concentrations less than $1.5 \times 10^{-3} M$ as shown in Figure 3b.

Solutions of various concentrations of norbornene with CuOTf and hexadecane in ether were prepared. All samples except that 5 *M* in norbornene were prepared by combining 8.0 ml of a standard solution of CuOTf–norbornene and hexadecane in ether with various volumes of an 8 *M* standard solution of norbornene in ether, and sufficient ether to give 10 ml total volume in a volumetric flask. The 5 *M* norbornene sample was prepared by combining 91.8 mg of CuOTf–norbornene, 6.25 ml of 8 *M* norbornene in ether, 15 μ l of hexadecane, and sufficient ether to give a total volume of 10 ml. Each sample was $3.0 \times 10^{-2} M$ in CuOTf and contained 1.5 μ l of hexadecane per ml., and various concentrations of norbornene as indicated in the table below. An actinometer solution of 0.075 *N* $K_2Fe(C_2O_4)_3$ in aqueous 0.1 *N* H_2SO_4 was prepared. Two or three 3-ml aliquots of each concentration of norbornene solution and actinometer solution were irradiated simultaneously in the merry-go-round apparatus for a total of 2 hr. The aliquots were contained in quartz test tubes which were sealed with rubber caps lined with a Teflon sheet. The irradiation was interrupted frequently and the sample tubes shaken to mix the contents. The actinometer tube was replaced with a fresh one every 20 min. At the end of the total irradiation time, all actinometer solutions were combined and analyzed for total Fe(II), and the quantum yield for the dimerization was determined assuming a quantum yield of 1.25 of ferrous ion from $K_2Fe(C_2O_4)_3$.²⁶

Yields of norbornene dimers were determined by analysis of the irradiated solutions by vpc on a 7 ft \times 1/8 in. column containing 20% PDEAS on 60–80 Chromosorb W-HMDS at 160°. Each sample was analyzed two or three times. Relative yields were determined by cutting out the respective peaks and weighing them with an analytical balance. The quantum yields were averaged for each sample. These values were then averaged with those found for other samples of the same norbornene concentration. These quantum yields as well as their inverse are listed in Table I.

Plots of $1/\Phi_{xx}$ vs. $1/[nb]$ and of $1/\Phi_{nx}$ vs. $1/[nb]$ reveals two good linear correlations (see Figure 2). The apparently random variations of the experimental data from linear correlations for the two sets of data seem to be coupled. That is, random errors of similar relative magnitude and direction occur in both Φ_{xx} and Φ_{nx} for a particular value of $[nb]$. This observation indicates that the vpc analytical method used to measure the quantum yields is highly precise. The apparent random errors probably arose in the preparation of the solutions. The precision of the relative values of quantum yields of dimers for samples of different $[nb]$ is probably better than $\pm 5\%$. On the other hand, it is possible that the accuracy of the absolute quantum yields of dimers is not as high.

Copper(I) Triflate Catalyzed Photodimerization of *endo*-Dicyclopentadiene. A solution of (*endo*-dicyclopentadiene)₂-CuOTf (0.4 g) and *endo*-dicyclopentadiene (13 g) in THF (7 ml) was irradiated for 1 week in a quartz tube at 254 nm in a Rayonet RPR-100 photochemical reactor. Cyclohexane (300 ml) was added and the resulting mixture washed with aqueous KCN. Solvents and unreacted olefin were removed under reduced pressure by distillation and the residue triturated with pentane to give dimer (6.3 g) in 48% yield. Recrystallization from ethanol gave white flakes: mp 180–184°; exact mass, 264.1877 (calcd for $C_{20}H_{24}$, 264.1878); pmr (60 MHz) δ 5.57 [2 H, d, $J = 7.5$ Hz], 5.38 [2 H, d, $J = 7.5$ Hz], 1.2–3.0 (20 H); ir 3065, 2900, 1615, 1460, 1435, 1210, 940, 910, 817, 795 cm^{-1} .

The recovered dicyclopentadiene (5.7 g) was analyzed by vpc on a 6 ft \times 0.25 in. column containing 15% Carbowax on 30–60 Chromosorb P. The sample contained 1% of an impurity which corresponded in retention time to that of an authentic sample of pentacyclo[5.2.1.0^{2,6}.0^{4,8}]decane.²⁷ Thus, the yield of this product was at most 2%.

Copper(I) Triflate Catalyzed Mixed Photodimerization of Norbornene and Cyclooctene. A solution of (CuOTf)₂-C₆H₆ (1.03 g, 0.41 mequiv) and norbornene (0.39 g, 0.41 mequiv) in *cis*-cyclooctene (6 ml) and THF (1 ml) was irradiated at 254 nm in a sealed quartz tube for 4 days in a Rayonet Photochemical Reactor. The reaction was worked up as for the norbornene dimerization above. Unreacted cyclooctene (4.5 g, 89%) was recovered by distillation under reduced pressure (100 mm). The recovered cyclooctene was shown by vpc analysis to contain a trace of the trans isomer. The presence of traces of the trans isomer was also strongly in evidence by the characteristic obnoxious odor of this olefin. The residual oil contained a multitude of products (dimers) according to vpc analysis on a 6 ft \times 0.25 in. column containing 20% FFAP on Chromosorb W at 200°. The major product was isolated by preparative vpc on the same column. This product (0.33 g, 40% yield based on norbornene), a cross dimer, an isomer of tetracyclo[10.2.1.0^{2,11}.0^{3,10}]pentadecane (**13**) was characterized as follows: cmr 146.5, 152.6, 154.7, 160.1, 162.5, 163.0, 165.1, 166.8.

Anal. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.32; H, 11.99.

Photolysis of *cis*-Cyclooctene in the Presence of Copper(I) Triflate. A solution of (CuOTf)₂-C₆H₆ (0.2 g) in *cis*-cyclooctene (4 ml) and THF (1 ml) was sealed in a quartz tube and irradiated at 254 nm for 4 days. The reaction was worked up as above for the mixed photodimerization. No dimer was found and only cyclooctene was recovered. The recovered cyclooctene was found to contain a trace of the trans isomer as discussed above.

Acknowledgment. We thank the National Science Foundation for financial support of this work.

(27) G. O. Schenck and R. Steinmetz, *Chem. Ber.*, **96**, 522 (1963).