Tetrahedron Letters No. 26, pp 2317 - 2320, 1978.

0040-4039/78/0622-2317$02.00/0

PHOTOCATALYSIS (II)[1]

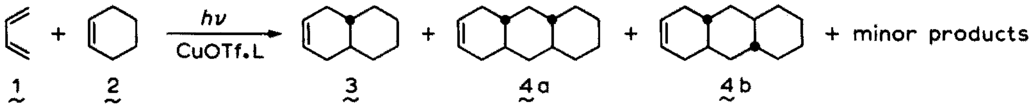
PHOTOCHEMICAL CYCLOADDITIONS OF CYCLOHEXENES AND CYCLOHEPTENE WITH CONJUGATED DIENES CATALYSED BY COPPER(I) TRIFLUOROMETHANE SULPHONATE

J.Th.M.Evers[2a] and A.Mackor*
Institute for Organic Chemistry TNO, P.O. Box 5009, Utrecht, The Netherlands

(Received in UK 20 January 1978; accepted for publication 4 May 1978)

Upon irradiation in the charge-transfer absorption band of $Cu^{I}X\cdot$cycloalkene complexes (X = trifluoromethane sulphonate = triflate = OTf) in organic solvents in the presence of a large excess of the cycloalkene, catalytic transformations of the cycloalkene occur. At high concentrations or with neat cycloalkene a photocatalysed dimerisation has been reported[3]. The dimerisation can be suppressed by irradiation in dilute solution. Under the latter condition, new reaction types are found, especially with cyclohexenes and cycloheptene as substrates. These reactions are still under investigation[2b].

The work described in the present paper was initiated by the report of Srinivasan[4] that copper(I) chloride catalyses the photochemical conversion of 1,3-butadiene to cyclobutene in ether solution at 254 nm. Despite numerous efforts under a variety of reaction conditions, including other possible catalysts (CuOTf, AgOTf, $ZnCl_2$ and $PtCl_2$) and solvents, we have been unable to confirm this result. In all cases the rate of ring closure to cyclobutene was found to be smaller than that of the uncatalysed reaction. *Therefore we conclude that* Cu^{I} *salts do not catalyse the photochemical ring closure of 1,3-butadiene to give cyclobutene*[5]. In fact, using CuOTf·butadiene as a catalyst, the cyclobutene formation is very slow. It seemed attractive to perform a photocatalytic experiment with a mixture of the unreactive substrate butadiene and a more reactive cycloalkene. This reaction was performed by irradiating a solution of butadiene, **1**, and cyclohexene, **2**, (both 0.25 mol/l) with a CuOTf complex as catalyst (0.01 mol/l) in thoroughly purified 1,4-dioxane in a Rayonet RPR-208 photochemical reactor under an atmosphere of nitrogen at 254 nm, using quartz vessels. Under these conditions a reaction was found, which can be formally classified as a photochemical Diels-Alder (PDA) addition. The products are *trans*-Δ^2-octalin, **3**, (*trans*-1,2,3,4,4a,5,8,8a-octahydronaphthalene) in > 50% yield, together with its PDA products with butadiene, **4**, and some minor products[2b].



L = butadiene or cyclohexene

The structure of **3** was determined by comparison of its IR, Raman, NMR and mass spectra with those of an independently synthesised sample of **3**[7]. Mixture **4** was identified by GCMS and by the similarity of its NMR and IR spectra with those of **3**.

At short irradiation times **3** is found exclusively, whereas upon prolonged irradiation **4** is formed as well. The formation of **4** can be either promoted or suppressed by choosing appropriate reaction conditions, *viz.* by using an excess of butadiene or cyclohexene, respectively. The photocatalytic nature of the reaction was confirmed by the following experiments:

- No reaction takes place when the irradiation is performed without CuOTf in the presence of HOTf, this acid being a possible contamination of CuOTf.
- No reaction is found with the catalyst under thermal conditions and without catalyst under photochemical or thermal conditions[8].

As a catalyst both CuOTf·**1** and CuOTf·**2** can be used. The choice of catalyst is non-essential since we have observed by NMR and UV spectroscopy and by microwave titrations that a rapid exchange of ligands **1** and **2** takes place in dioxane solutions. The microwave titrations also show that a mixed complex of CuOTf with **1** and **2** can exist in dioxane solution.

The photo reaction is not catalysed by AgOTf (which decomposes at 254 nm), Cu^0 or $Cu^{II}(OTf)_2$; with CuCl as a catalyst only a very slow reaction occurs to give mainly cyclohexene dimers. Because the reaction is rather slow under the conditions employed ($\simeq$ 50% conversion of the reactants in $\simeq$ 100 h), we tried to increase the rate of the PDA reaction by increasing the concentrations of catalyst and/or reactants. Increase of the catalyst concentration appeared to be impossible, since its concentration of 0.01 mol/l almost corresponds to a saturated solution in dioxane. A tenfold increase in the concentration of both **1** and **2**, keeping the ratio constant, did not have an appreciable effect on the reaction rate. However, the reaction is significantly accelerated when the ratio **2** : **1** is increased at a constant concentration of **1** of 0.25 mol/l. At a ratio **2** : **1** of 2 and 8 the yield increases by a factor of 1.6 and 2.9, respectively.

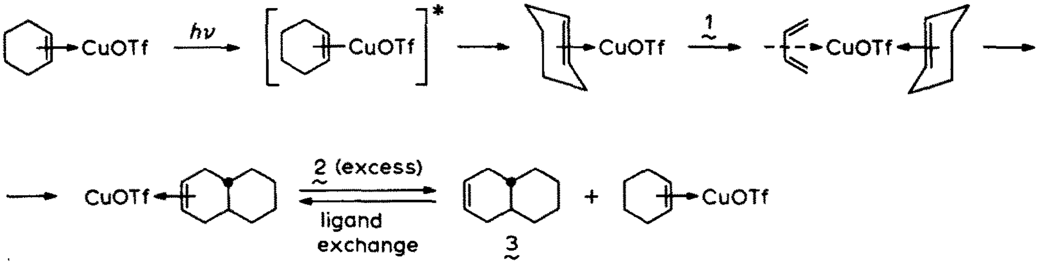
From this observation we conclude that the active catalyst in solution contains at least one molecule of cyclohexene. When the irradiations are performed at 300 nm only little **3** is formed, while at 360 nm no reaction occurs. This behaviour is in accordance with the UV spectra of complexes of CuOTf with either **1** or **2** (CuOTf·**1**; λ_{max} (nm): 213, 252, 315; CuOTf·**2**, λ_{max} (nm): 228, 260 sh).

Cyclopentene, cyclooctene and norbornene do not give this PDA reaction with butadiene; with cycloheptene the addition is very slow: after 100 h of irradiation a rather small amount of a product with the correct mass (GCMS: m/e = 150) was formed. It is remarkable that the order of reactivity of cyclopentene and cyclohexene in the PDA reaction is reversed to the reported order of reactivity of these cycloalkenes in thermal DA reactions[8].

The reactivity of the diene increases with increasing number of electron-releasing substituents: butadiene < isoprene < 2,3-dimethyl-1,3-butadiene. Other compounds which were tested as diene, *viz.* 2-methyl-1-buten-3-yne and 1,3-cyclohexadiene, did not react with cyclohexene under our photocatalytic conditions.

Mechanism of the photocatalytic Diels-Alder reaction

In view of the high specificity of cyclohexenes as a dienophile for the PDA reaction, which is comparable to previous results with cyclohexene(s)[3,9,10], we propose that the key step in this photochemical reaction is a *cis* → *trans* isomerisation of cyclohexene, which occurs in the ligand sphere of the copper(I) complex:



The *cis* → *trans* isomerisation of the complexed cyclohexene is a reaction now well-documented for uncomplexed cycloalkenes[11,12]. The *trans*-cyclohexene remains coordinated to CuOTf in agreement with the behaviour of *trans*-cyclooctene, which forms more stable complexes with Cu^I than the *cis*-compound[13]. Preliminary results show that CuOTf·*trans*-cycloheptene is stable at room temperature[2]. Because cyclopentene cannot give a *cis* → *trans* isomerisation no PDA reaction occurs.

The experimentally determined order of reactivity for the cycloalkenes, cyclohexene > cycloheptene > cyclooctene, corresponds to the decreasing ring strain in this order of the *trans*-cycloalkenes.

In the mechanism proposed for the formation of **3**, the CuOTf·*trans*-cyclohexene complex reacts thermally with butadiene, possibly in a template reaction to give products with the correct stereochemistry for a $(\pi^s_4 + \pi^s_2)$ thermal reaction. The electrophilic character of coordinated *trans*-cyclohexene by π-electron-donation to empty Cu^I 4 s orbitals may explain its enhanced reactivity towards electron-rich dienes.

At the start of the reaction no cyclohexene dimers are formed, even at a **2** / **1** ratio as high as 20. This is ascribed to the higher reactivity of **1** towards *trans*-cyclohexene as compared to the reactivity of **2**. Also the complex-forming ability of CuOTf with butadiene is somewhat better than with cyclohexene. In this respect it is interesting to note the difference between the triflate anion in CuOTf and the chloride ion in CuCl. The chloride ion is the better ligand and competes with **1** and **2** for coordination sites at copper. This property may be responsible for the fact that CuCl is a catalyst with low efficiency for the PDA reaction, by making a template process less probable.

Presently, we are studying the stability of coordinated *trans*-cyclohexene and -cycloheptene and the scope and mechanism of their reactions in more detail.

Acknowledgements: The authors thank Prof.Dr. W.Drenth, Dr. H.J.T.Bos and Mr. P.van Meurs for stimulating discussions.

The investigations were supported (in part) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

REFERENCES AND NOTES

1. Part I. J.Th.M.Evers and A.Mackor, submitted for publication in Tetrahedron Letters.
2. a. Part of the forthcoming thesis of J.Th.M.Evers, where further details will be given.
   b. J.Th.M.Evers and A.Mackor, to be submitted for publication in *Tetrahedron Letters*.
3. R.G.Salomon, K.Folting, W.E.Streib and J.K.Kochi, *J.Amer.Chem.Soc.*, 96 (1974) 1145.
4. R.Srinivasan, *J.Amer.Chem.Soc.*, 85 (1963) 3048.
5. Afterwards we learned that Dr. Srinivasan has withdrawn his original conclusion; R.Srinivasan, personal communication. See ref.6 for a recent citation of ref.4.
6. R.G.Salomon and M.F.Salomon, *J.Amer.Chem.Soc.*, 98 (1976) 7454.
7. W.S.Johnson, V.J.Bauer, J.L.Margrave, M.A.Frisch, L.H.Dreger and W.N.Hubbard, *J.Amer.Chem. Soc.*, 83 (1961) 606.
8. F.Bergmann and A.Weizmann, *J.Org.Chem.*, 9 (1944) 352.
9. J.A.Marshall, *Science*, 170 (1970) 137.
10. P.J.Kropp, E.J.Reardon Jr., Z.L.F.Gaibel, K.F.Williard and J.H.Hattaway Jr., *J.Amer.Chem.Soc.*, 95 (1973) 7058.
11. Y.Inoue, S.Takamuku and H.Sakurai, *J.Phys.Chem.*, 81 (1977) 7.
12. Y.Inoue, S.Takamuku and H.Sakurai, *J.Chem.Soc.Perkin II*, (1977) 1635.
13. R.G.Salomon and J.K.Kochi, *J.Amer.Chem.Soc.*, 96 (1974) 1137.