Tetrahedron Letters No. 9, pp 821 - 824, 1978. Pergamon Press. Printed in Great Britain.

PHOTOCATALYSIS (I)[1]

COPPER(I) TRIFLUOROMETHANE SULPHONATE CATALYSED PHOTOCHEMICAL REACTIONS OF UNSATURATED ETHERS AND ALCOHOLS

J.Th.M.Evers[2] and A.Mackor*

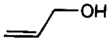
Institute for Organic Chemistry TNO, P.O. Box 5009, Utrecht, The Netherlands

(Received in UK 8 December 1978; accepted for publication 9 January 1978)

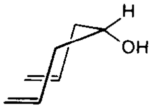
Recent research in the literature[3] and in our laboratory has shown that photochemical reactions of unsaturated compounds, under the catalytic influence of copper(I) trifluoromethane sulphonate (triflate) CuOTf, gives an entry to a field of fascinating novel synthetic possibilities.

The catalyst is formed beforehand or *in situ* by coordination of CuOTf with the unsaturated compounds to give complexes, which show in the UV spectrum one or more CT absorption bands at 250 nm or above. Irradiation in these CT bands makes olefinic photochemistry possible at longer wavelengths than before.

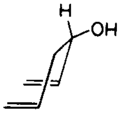
As a part of our study, which is aimed at exploring scope and mechanism of photocatalysed reactions, we investigated the behaviour of compounds 1 - 4 under photocatalytic conditions.



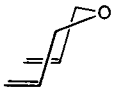
1



2



3



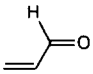
4

The complex nCuOTf.L (L = 1, 2, 3 or 4) was prepared from 2 CuOTf.benzene by ligand exchange, the number n being determined by elemental analysis of the solid complex, *cf.* below and ref. 2.

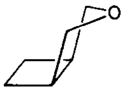
All irradiations were carried out in quartz vessels under a nitrogen atmosphere in a Rayonet RPR-208 photochemical reactor with 254 nm lamps, using purified 1,4-dioxane as a solvent. The substrate to solvent molar ratio was 0.025; also the Cu(I) triflate complex (catalyst) to substrate molar ratio was 0.025.

From the irradiation of allyl alcohol 1 four products (4 - 7) have been identified.

5



6



7

While the amounts of propene 5, acroleine 6 and 3-oxabicyclo[3.2.0] heptane 7[6] steadily increased during the irradiation, the amount of diallyl ether 4 after initial increase, remained approximately constant. The intermediacy of 4 in the formation of 7 is supported by a separate photocatalytic experiment, in which there was found a rapid and nearly complete conversion of 4 into 7, with no detectable formation of other products. Compound 7 was stable under our photocatalytic reaction conditions. In the absence of light neither 1 nor 4 were converted under these conditions. Also the possibility could be excluded that CuOTf.1 was converted thermally into CuOTf.4, without the liberation of free ligand, by comparison of the IR spectra of the catalyst before and after exposure to thermal reaction conditions. No changes were found.

From these experiments we conclude, that 4, 5 and 6 are formed directly from 1 via a photocatalytic reaction and that the formation of 7 proceeds by two photocatalytic steps, through 4.

Formally propene and acroleine are formed from two molecules of allyl alcohol, with the removal of one molecule of water. The same holds for the formation of diallyl ether from allyl alcohol. Although it has been reported in the literature[7], that Cu(I) compounds easily disproportionate under the influence of water to give Cu(0) and Cu(II), we have found that the water formed in our reaction has no appreciable effect. After 100 h of irradiation the conversion of olefin 1 was over 50%, whereas we would expect only a minor conversion if the Cu(I) complex was destroyed by water.

In this connection it is interesting to mention, that we previously used mixtures of Cu(0) and Cu(II)X_2 (X = ClO_4, BF_4) in organic solvents together with olefins, to generate Cu(I)X.olefin complexes thermally at room temperature[8].

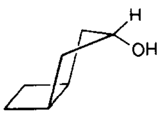
It is also possible, that the Cu(I) complex is regenerated photochemically from a Cu(II) compound, since it was found that Cu(II)X_2 in the presence of cis,cis-1,5-cyclooctadiene (COD) is reduced photochemically in dioxane containing a little water to give Cu(I)X.$(COD)_2$ complexes[9].

The detailed mechanism for the formation of 4, 5 and 6 from 1 remains to be clarified, while we assume that the formation of 7 from 4 occurs in a way analogous to the conversion of 2, which is described below.

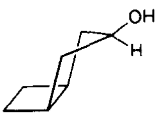
Under photocatalytic conditions allyl amine 8 was not converted, although 8 gives a 2 : 1 complex with CuOTf. It is not clear, whether this unreactivity is due to the different composition of the complex, or to an as yet unknown factor.

Irradiation of 1,6-heptadiene-4-ol 2

After 40 h 2 is completely isomerised to exo- and endobicyclo[3.2.0]heptane-3-ol 9 and 10 in a ratio 3 : 2, as determined by GLC.



9



10

The structures of these products were determined by IR, MS and NMR spectroscopy, using Eu(Hfod)$_3$[5] as shift reagent and by comparison with the literature[10]. No reaction was found in the absence of light, neither for 2 nor for 3. 1,5-Hexadiene-3-ol 3 was inactive under the photocatalytic conditions.

To obtain further information on the mechanism of the formation of 9 and 10 we studied the ^{13}C NMR spectra of 2 and CuOTf.2.

TABLE I. Carbon-13 chemical shifts in 2 and in CuOTf.2*

Compound	C-2,5	C-1,7	C-4	C-3,5
2:	134.9	115.9	69.7	41.6
CuOTf.2:	119.0	99.3	70.4	40.3

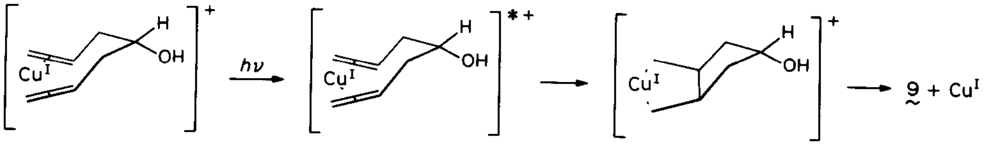
*Shifts measured with respect to dioxane resonance (taken as 66.6 ppm from TMS).

From these data two conclusions may be drawn:

a) Ligand 2 is symmetrically coordinated to CuOTf via its double bonds. The upfield shifts for C-1 and C-2 are nearly the same, *viz.* about 16 ppm.

b) There is no indication of OH-participation in the complexation as judged from the comparable chemical shift of C-4 in the complex and in the free ligand. It also follows from the ratio of products 9 and 10.

For the reaction of 2 to give 9 (and 10), the following mechanism may now be envisaged:



11

By this two-step mechanism, where the intermediacy of 11 is still hypothetical[12], we may understand why 2 and 4 react, whereas 3 does not. From 2 and 4 a five-membered ring is formed, while from 3 a strained four-membered ring has to be closed first.

Acknowledgements: The authors thank Mr. M.J.E.Fischer for carrying out part of the experimental work and 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 Organisation for the Advancement of Pure Research (ZWO).

REFERENCES AND NOTES

1. Following ref.3, p.114, we define photocatalysis as a catalytic photoreaction in which the catalyst is formed and/or activated photochemically *in situ* bringing about a thermal conversion of more than one substrate molecule per catalyst molecule. We do not follow the restriction, given by the cited authors, that the quantum yield must be greater than one per photon absorbed, for a reaction to be photocatalytic (see also ref.11).
2. Part of the forthcoming thesis of J.Th.M.Evers, where further details will be given as in later papers of this series.
3. E.A.Koerner von Gustorf, L.H.G.Leenders, I.Fischler and R.N.Perutz, *Adv.Inorg.Chem.Radiochem.,* 18 (1976) 65.
4. R.G.Salomon and J.K.Kochi, *J.Chem.Soc.Chem.Commun.,* (1972) 559.
5. Hfod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-octane-4,6-dionate.
6. Identified by its IR, NMR and mass spectrum; *cf.* also: V.I.Gol'mov and Z.P.Malevannaya, *Zh.Obshch.Khim.SSSR.,* 31 (1961) 1440.
7. F.A.Cotton and G.Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Wiley-Interscience, New York, N.Y. 1972, p.905.
8. A.Mackor and E.Ch.Th.Gevers, unpublished results.
9. A.Mackor, unpublished results.
10. J.Meinwald, P.Andersen and J.J.Tufariello, *J.Amer.Chem.Soc.,* 88 (1961) 1301.
11. M.S.Wrighton, D.S.Ginley, M.A.Schroeder and D.L.Morse, *Pure Appl.Chem.,* 41 (1975) 671.
12. Alternatively a Cu(III) intermediate may be envisaged: *cf.* H.Westmijze, J.Meijer, H.J.T.Bos and P.Vermeer, *Rec.Trav.Chim.,* 95 (1976) 299.