

PHOTOCATALYSIS (V)¹
CYCLOTRIMERISATION OF CYCLOHEPTENE

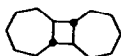
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ABSTRACT

When copper(I) triflate·*cis*-cycloheptene is irradiated in solution, a complex copper(I) triflate·*trans*-cycloheptene is formed. From the latter compound an all-*trans* cyclic trimer is formed in 80% yield in a thermal reaction. The mechanism of this cyclotrimerisation is discussed.

When neat *cis*-cycloheptene, 1, is irradiated in the presence of a catalytic amount of copper(I) trifluoromethanesulphonate (copper(I) triflate,



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CuOTf), a white precipitate is formed as described before³. On the basis of NMR and IR spectral data Salomon, Kochi et al.³ suggested the product to be *trans-anti-trans*-tricyclo-[7.5.0.0^{2,8}]tetradecane, 2.

Upon reinvestigation of this reaction we have obtained a crystalline product with the same spectral data and melting point (129° C). However, the mass spectrum of the product shows a parent peak at *m/e* = 288.2818 (calculated for C₂₁H₃₆: 288.2817). Therefore we conclude that this product is a *trimer* of cycloheptene instead of a *dimer*.



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The NMR data demonstrate that structure 3 with D₃ symmetry⁴ is the most probable one for the trimer.

a. The ¹³C NMR spectrum contains four carbon resonances only, in agreement with structure 3, while other geometrical isomers of 3 would have more magnetically different carbon atoms. E.g. the all-*cis*-isomer of the trimer has C₃ symmetry⁴ and therefore would show seven magnetically different carbon atoms provided that no fast ring-flip of the central six-membered ring occurs.

b. The ¹H NMR spectrum (Fig. 1) of the trimer contains six magnetically different hydrogens, in agreement with structure 3, while the position and shape of the resonance due to the axial hydrogens of the six-membered ring closely resemble that of the all-*trans*-isomer of perhydrotriphenylene⁵ (one broad signal at about 0.9 ppm).

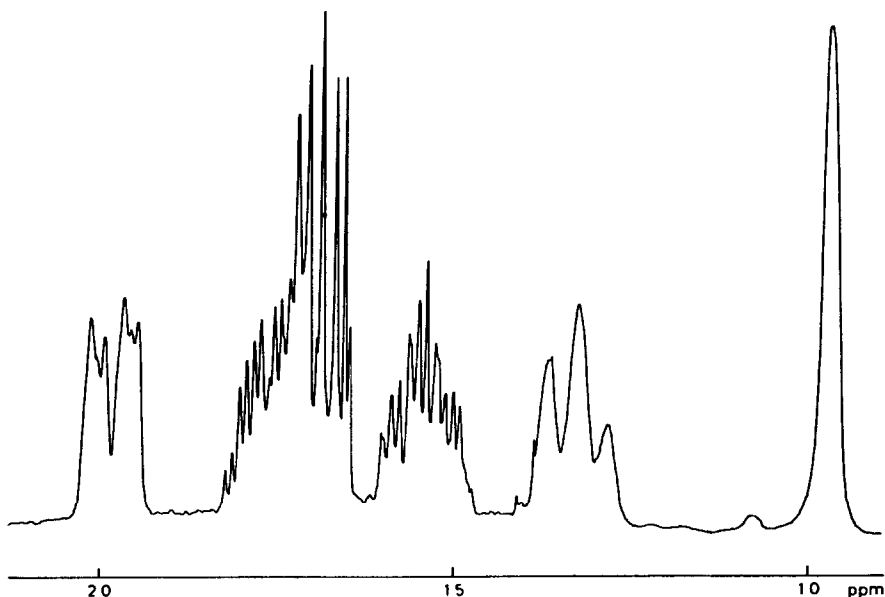
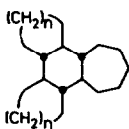


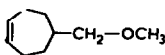
Fig. 1. 300 MHz ^1H NMR spectrum of cycloheptene trimer 3, in CDCl_3

In a previous communication we have reported the preparation of $\text{CuOTf}\cdot\text{trans-cycloheptene}$ ($\text{CuOTf}\cdot\text{t1}$)¹. The reactivity of this compound towards various unsaturated compounds is low. However, when $\text{CuOTf}\cdot\text{t1}$ is heated at 50°C in neat cycloheptene for a short period of time, a fast reaction occurs to yield mainly one product. This product is the same trimer of c1 as has been obtained in the photocatalytic experiment (vide supra). From this we conclude that the trimer is formed in a thermal reaction of

$\text{CuOTf}\cdot\text{t1}$. When $\text{CuOTf}\cdot\text{t1}$ is heated in neat cyclopentene, cyclohexene or cyclooctene, the same trimer is formed and no mixed trimer 4, ($n = 1, 2$ or 4) is obtained. Similarly, 1-methylcycloheptene does not cotrimerise with $\text{CuOTf}\cdot\text{t1}$. Since in this case steric hindrance may be involved, a better model system is cycloheptene, substituted in the 5-position. For this purpose we have studied 5-(methoxymethyl)cycloheptene, 5⁶. When neat 5 is irradiated in the presence of its CuOTf complex, analogous to experiments performed with c1, a mixture of products is obtained, among which we have identified a trimer by GCMS (parent peak at $m/e = 420$).



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When $\text{CuOTf}\cdot\text{t1}$ is thermally trimerised in the presence of a large excess of $\underline{5}$ in dioxane solution or in neat $\underline{5}$, again no mixed trimers have been found by careful GCMS analysis. Compound $\underline{3}$ is the sole trimeric product formed in 80% yield, as determined by GC.

These results can be explained in the following way. It is known that a complex exists between CuOTf and *trans*-cyclooctene with a metal-to-ligand ratio of 1:3⁷. For cycloheptene we have found evidence for the existence of a mixed complex $\text{CuOTf}\cdot(\underline{\text{c1}})_2\cdot\underline{\text{t1}}$ by NMR titration experiments². Since *trans*-cycloalkenes are very strong ligands for Cu(I) ⁸, we may assume that also $\text{CuOTf}\cdot(\underline{\text{t1}})_3$ can exist. This complex may be formed by exchange of $\underline{\text{t1}}$ ligands between $\text{CuOTf}\cdot(\underline{\text{c1}})_2\cdot\underline{\text{t1}}$ molecules to yield $\text{CuOTf}\cdot\underline{\text{c1}}\cdot(\underline{\text{t1}})_2$ and finally $\text{CuOTf}\cdot(\underline{\text{t1}})_3$. Within this complex $\text{CuOTf}\cdot(\underline{\text{t1}})_3$ the trimer is formed in a thermal reaction without direct involvement of $\underline{\text{c1}}$. The role of $\underline{\text{c1}}$ is then to replace the $\underline{\text{t1}}$ ligand at those CuOTf molecules from which $\underline{\text{t1}}$ is removed.

This mechanistic picture is in line with all observed facts. Experiments between either $\text{CuOTf}\cdot\underline{\text{t1}}$, deuterated in the ligand and cycloheptene $\underline{\text{c1}}$ or unlabelled $\text{CuOTf}\cdot\underline{\text{t1}}$ and deuterated $\underline{\text{c1}}$ should be conclusive.

We wish to emphasize that the formation of trimer $\underline{3}$ is the first example of a cyclotrimerisation of cycloalkenes with Cu(I) as the metal catalyst. The only other example of a cyclotrimerisation of cycloalkenes which is known to us, is that of cyclopropene in the presence of a Pd(O) catalyst⁹. In both cases it appears that the release of ring strain is the driving force for the cyclotrimerisation.

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REFERENCES

1. Part IV: J.Th.M. Evers and A. Mackor, *Recl.Trav.Chim.Pays-Bas*, 98 (1979) 423.
2. The major part of this work has been described in the Ph.D. thesis of J.Th.M. Evers, Utrecht, 1979.
3. R.G. Salomon, K. Folting, W.E. Streib and J.K. Kochi, *J.Am.Chem.Soc.*, 96 (1974) 1145.
4. D.S. Schonland, *Molecular Symmetry*, D. van Nostrand Company, London, 1965.
5. M. Farina and G. Audisio, *Tetrahedron*, 26 (1970) 1827.
6. a. Preparation of the alcohol: H.L. Goering and G.N. Fickes, *J.Am.Chem.Soc.*, 90 (1964) 2848.
b. Methylation: C.D. Hurd and W.H. Saunders Jr., *Ibid.*, 74 (1952) 5324.
7. S. Komiya and J.K. Kochi, *J.Organomet.Chem.*, 135 (1977) 65.
8. a. J.M. Harvilchuck, D.A. Aikens and R.C. Murray, *Inorg.Chem.*, 8 (1969) 539.
b. M.A. Muhs and F.T. Weiss, *J.Am.Chem.Soc.*, 84 (1962) 4697.
9. P. Binger, G. Schroth and J. McMeecking, *Angew.Chem.*, 86 (1974) 518.
10. Careful analysis of the reaction liquid of the photochemical reaction of $\text{CuOTf} \cdot \underline{\text{C}_1}$ in neat $\underline{\text{C}_1}$, from which the trimer was removed, revealed the formation of two cycloheptene dimers in very low yield. One of these was isolated in sufficient amount to obtain a melting point (66-68° C) and spectral data (^{13}C NMR: four carbon resonances; ^1H NMR: six hydrogen resonances; IR: no olefinic absorption). We have not yet assigned one of the possible structures to this dimer. However, structure 2 seems to be the most likely one.

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