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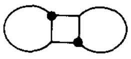
PHOTOCATALYSIS (VIII)[1]

(STEREO)SELECTIVE PHOTOCHEMICAL CO-DIMERIZATION OF CYCLOHEXENE AND CYCLOHEPTENE, CATALYZED BY COPPER(I) TRIFLATE[1]

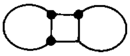
P.J.J.A. Timmermans, G.M.J. de Ruiter, A.H.A. Tinnemans and A. Mackor*
Institute of Applied Chemistry TNO, P.O. Box 5009, 3502 JA Utrecht, The Netherlands

Summary. Upon irradiation by 254 nm light of a mixture of cyclohexene and cycloheptene in the presence of copper(I) triflate (= trifluoromethanesulfonate), a very selective co-dimerization takes place to give *trans-transoid-trans*-tricyclo[7.4.0.0^{2,8}]tridecane.

The photochemical cyclodimerization of cycloalkenes in the presence of copper(I) triflate (Cu^IOTf = trifluoromethanesulfonate) may produce five different cyclobutane-type stereoisomers.


ttt


tct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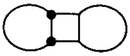
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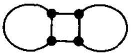

ccc

ttt = *trans-transoid-trans*; tct = *trans-cisoid-trans*; ct = *cis-trans*; ctc = *cis-transoid-cis* and ccc = *cis-cisoid-cis*.

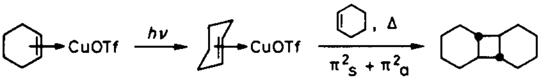
Thus, irradiation of cyclohexene yields ttt-C_{12} and ct-C_{12} in addition to 1-cyclohexylcyclohexene (1-cc). Irradiation of cyclopentene leads to ctc- and ccc-C_{10}[2] and irradiation of cyclooctene to all five stereoisomers, albeit in varying yields[1].

A special case forms cycloheptene, where the major product of irradiation in the presence of Cu^IOTf at room temperature or slightly above is the trimer **1**, having an all-*trans* cyclic structure

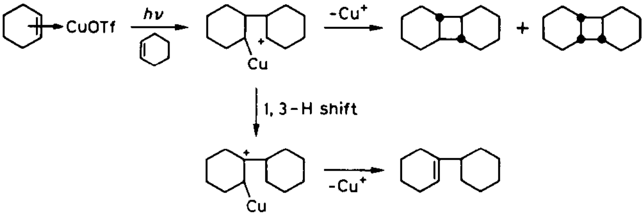
Trimer **1** has been shown to be formed in a thermal, probably concerted, reaction of three molecules of *trans*-cycloheptene, coordinated around copper(I)[3]. As side products, two photo-dimers, *viz.* tct- and ctc-C_{14}, have been obtained[1,3].

As to the mechanism of this photocatalyzed dimerization, Salomon and Kochi *et al.*[2,4] have proposed two possibilities for cyclohexene:

Mechanism A: thermal concerted reaction of *trans*-cyclohexene with *cis*-cyclohexene (around copper) produces ttt-C_{12}:

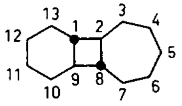


Mechanism B: involves the stepwise formation of the dimers, via a copper carbocation intermediate:



For a better understanding of the mechanisms of these reactions we have now carried out mixed irradiations of cyclohexene and CuOTf with either cyclopentene, cycloheptene or cyclooctene. Whereas the yield of mixed cyclobutane-type products from cyclohexene and either cyclopentene or cyclooctene is very low, to our surprise we find the C_{13}-compound **2** as the major product (15-37% yields, based on starting materials) in the reaction of cyclohexene with cycloheptene ([cyclohexene] = 0.05-0.25 M; [cycloheptene] = 0.1-0.75 M; [CuOTf·cycloheptene] = 10^{-2} M; in 1,4-dioxane). In addition small quantities ($\leq$ 0.5%) of other dimers (C_{12}, C_{13} and C_{14}) were found, and even smaller quantities of two C_{20}-trimers. Without the CuOTf catalyst a range of products in low yields were formed.

The identification of the major product as *trans-transoid-trans*-tricyclo[7.4.0.$0^{2,8}$]tridecane **2** (ttt-C_{13}; colourless liquid) has been done by:



2

1. GCMS analysis: the peak of **2** appears between the C_{12}- and C_{14}-peaks and its mass spectrum is similar in appearance to other cyclobutane-type dimers, with a parent peak at m/z 178.1724 (calcd. 178.1723).
2. NMR spectra of a sample, obtained by preparative GLC, showed the presence of 7 carbon resonances[5], thereby excluding the asymmetric ct-structure. Recently, Leitich[6] and our group[1] have established, mainly by NMR spectroscopy, the structures of the five cyclooctene dimers. It has been shown[2] that low-field resonances (at appr. 50 ppm) are connected with the ttt-structure. In contrast, the ccc-C_{12} and -C_{16} resonate at 34.8 and 41.3 ppm, respectively, and ctc-C_{12}, -C_{14} and -C_{16} at 34.3, 46.5 and 43.5 ppm, respectively. The cyclobutyl ^{13}C resonances of **2** are found at

48.43 and 48.91 ppm and they clearly point to a ttt-structure.

As to the ^{1}H NMR criterion, the most puckered cyclobutyl ring (ttt) should have its ^{1}H resonances at the highest field (≃1 ppm), and the least puckered ring (ccc) at the lowest field (≃2.5 ppm). In dimer 2 the cyclobutyl ^{1}H resonances appear at 0.92 and 1.60 ppm as determined by selective decoupling experiments and simultaneous observation of the cyclobutyl ^{13}C resonances[7] (*cf.* Figure 1). The former value is very characteristic for ttt-structures[1], while the latter value is more ambiguous and is probably related to steric effects in the cycloheptyl ring.

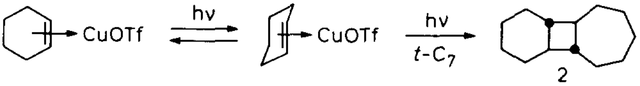
As to the mechanism of its formation, it is at first sight surprising to find such a preference for the formation of a mixed compound, when coordination behaviour and light absorption of the CuOTf complexes of cyclohexene and cycloheptene are so similar. Supposedly, the photodimerization takes place, involving a 2/1 cycloolefin/CuOTf complex in which at least one *trans*-cycloalkene ligand is present (mechanism A) or it could participate in a multi-step process (mechanism B).

Although at this point no final conclusions can be drawn on the mechanism of formation of co-dimer 2, several points are clear:

1. We have previously established the presence of substantial amounts of CuOTf-*trans*-cycloheptene complexes in irradiated solutions and we have isolated the stable 1/1 CuOTf/t-C_7 complex[8].
2. It is likely that similarly *trans*-cyclohexene is formed as a highly strained, highly reactive short-lived intermediate by photochemical isomerization of a *cis*-cyclohexene ligand of copper(I).
3. The selective formation of 2 is hard to reconcile with mechanism A in which *trans*-cyclohexene (at Cu^I) attacks a *cis*-cycloalkene, since under our conditions both cyclohexene and cycloheptene are available as a second ligand. Apparently, the *trans*-cyclohexene ligand strongly prefers reaction with a cycloheptene molecule, presumably a coordinated *trans*-isomer at the same Cu^I ion. The formation of the ttt-dimer 2 then is an indication of a different, photochemical, mechanism (C).
4. The low yields of C_{14} dimers from cyclohexene/cyclooctene mixtures, from which C_{12} and C_{16} dimers are found in comparable amounts and in the usual ratios of stereoisomers, point to different mechanisms for the photocatalyzed dimerizations of cyclohexene and cyclooctene.

Thus, we propose that for cycloheptene, mixed with cyclohexene, and for cyclooctene a different mechanism, C, is active in the formation of the ttt-dimer.

Mechanism C: photochemical concerted reaction of two coordinated *trans*-cycloalkene molecules, both with R- or S-configuration, in a simplified way presented here for the formation of 2:



2

Acknowledgements

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2. R.G. Salomon, K. Folting, W.E. Streib and J.K. Kochi, *J.Am.Chem.Soc. 96,* 1145 (1974).
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4. R.G. Salomon, *Adv.Chem.Ser. 168,* 174 (1978) and private communication.
5. At 48.91 (C-2,8), 48.43 (C-1,9), 32.41 (2C), 30.99 (2C), 29.69 (2C), 26.67 (2C) and 26.35 (1C) ppm, using δ $^{13}CDCl_3$ (solvent) = 76.91 ppm from TMS. See also ref. 7.
6. J. Leitich, *Tetrahedron 38,* 1303 (1982).
7. ^{1}H resonances were observed at 0.92 (H-1,9), 1.22 (6H, m, br), 1.39-1.54 (4H, m), 1.60 (2H and H-2,8), 1.71 (4H, m) and 1.79 ppm (2H, m, br). Spectra were taken with a Varian SC 300 spectrometer.
8. J.Th.M. Evers and A. Mackor, *Recl.Trav.Chim.Pays-Bas 98,* 423 (1979).

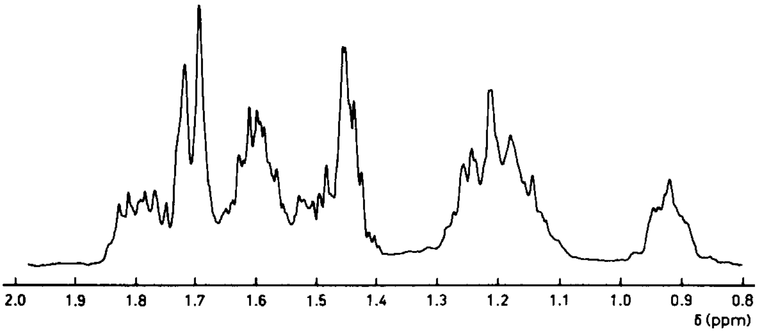

Figure 1. 300 MHz ^{1}H NMR spectrum of *trans-transoid-trans*-tricyclo[7.4.0$0^{2,8}$]tridecane, in $CDCl_3$, at ambient temperature.

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