

PHOTOCATALYSIS—VII¹

PHOTOCHEMICAL CYCLODIMERISATION OF CYCLOALKENES CATALYSED BY COPPER(I) TRIFLATE. FORMATION AND IDENTIFICATION OF TWO CYCLOHEPTENE AND FIVE CYCLOOCTENE DIMERS

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Abstract—The photochemical cyclodimerisation of cycloheptene and cyclooctene has been studied under irradiation at 254 nm, using copper(I) triflate as catalyst. Two cycloheptene dimers cis-anti-cis- and trans-syn-trans-tricyclo [7.5.0.0^{2,8}] tetradecane and five cyclooctene dimers (all stereoisomeric tricyclo [8.6.0.0^{2,9}] hexadecanes) have been obtained. The ¹H and ¹³C NMR spectra of the cyclooctene dimers show an upfield shift (from 2.4 to 1 ppm) of the cyclobutyl hydrogens due to cyclobutane ring puckering and a downfield shift of the cyclobutyl carbon resonances. Their GC retention times decrease upon increased ring puckering.

The photocatalysed dimerisation of cycloheptene is exceptional in that no trans-anti-trans or cis-trans isomers are formed as is the case for cyclohexene or cyclooctene. Thermally, the trans-cycloheptene ligand in the copper(I) triflate complex cyclotrimerizes exclusively, via *R,R,R*- or *S,S,S*-combinations.

Stable trans-isomers are known for cyclooctene and larger cycloalkenes. For cyclopentene and smaller unsaturated rings it is assumed that the double bond cannot pass through the orthogonal state and consequently, a trans-form is impossible. We have become interested in the intermediate situation of C₇- and C₆-trans-cycloalkenes, where an increasing ring-strain occurs. These compounds can be generated by photochemical cis→trans isomerisation of cyclohexene and cycloheptene, coordinated to copper(I) triflate (trifluoromethanesulphonate, OSO₂CF₃), at 254 nm. In solutions of cycloalkenes, containing CuOTf, the presence of CuOTf-(cycloalkene)_n complexes (n = 1–3) has been demonstrated and a number of these complexes have been isolated.^{1,2}

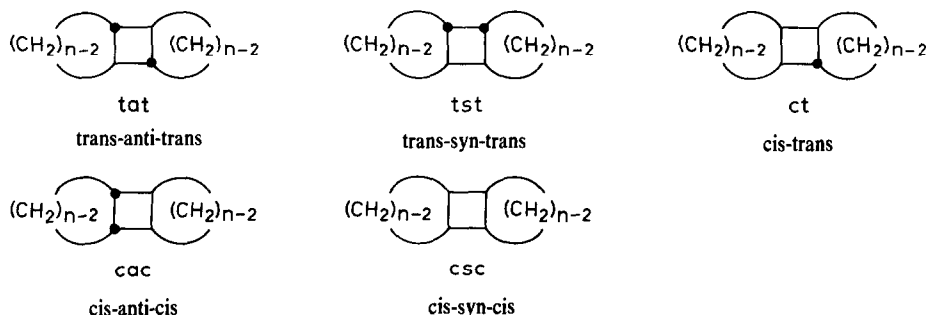
Trans-cycloalkenes have been found to be strong ligands for Cu(I) and the use of the non-coordinating triflate anion promotes the coordination of cycloolefins. By this coordination the trans-cycloalkenes are stabilised. We have recently isolated a stable CuOTf-trans-cycloheptene complex,³ while the existence of a CuOTf-trans-cyclohexene complex in solution has been demonstrated by various reactions of the ligand, e.g.

isomerisation (ring-contraction),⁴ cycloaddition of 1,3-butadiene,⁵ methanol addition² or its cyclodimerisation.⁶

In the cyclodimerisation reaction of C₆–C₈ cycloalkenes, theoretically five different stereoisomeric products may be obtained, as depicted below, two of which are chiral compounds (tat and ct).

The major product of the CuOTf-catalysed cyclodimerisation of cyclohexene is tat-C₁₂, together with some ct-C₁₂.⁶ For cycloheptene, Salomon, Kochi *et al.*⁶ assigned the tat-C₁₄ structure to the product of the photocatalysed reaction. However, we have recently established the trimeric tatat-C₂₁ structure with a central cyclohexene ring having C₃ symmetry, for this compound.¹⁸ This places cycloheptene in an exceptional position since neither for cyclohexene nor for cyclooctene cyclotrimers are formed. We have also observed that the trimer is formed in a thermal reaction from three trans-cycloheptene ligands at slightly elevated temperatures (≥50°C), possibly in a template mechanism.¹

For mixtures of CuOTf and cyclooctene, Salomon, Kochi *et al.*⁶ reported cis-trans photoisomerisation, but no cyclodimerisation was observed. Cyclopentene can-



n = 6; tricyclo [6.4.0.0^{2,7}] dodecane^{7a}
n = 7; tricyclo [7.5.0.0^{2,8}] tetradecane^{7b}
n = 8; tricyclo [8.6.0.0^{2,9}] hexadecane^{7c}

not give a trans-isomer, but it undergoes the CuOTf-catalysed photochemical cyclodimerisation reaction to give cac-C₁₀ as the major product, together with some csc-C₁₀. On the other hand, cyclohexene forms the highest-strained trans-cycloalkene upon photolysis in the presence of CuOTf. In both C₁₂-cyclodimers the trans-structure is present.

A priori there is no reason to assume that the C₇- and C₈-cycloalkenes, for which stable CuOTf-cis- and trans-cycloalkene complexes are known, do not give [2+2] cycloadducts by photocatalysed dimerisation of cis- and trans-isomers. Therefore, we were puzzled by the absence in the literature of authentic data on the formation of dimers in these cases and we have reinvestigated the CuOTf-catalysed photodimerisation of cycloheptene and cyclooctene. In this paper we wish to describe the formation, isolation and identification of two cycloheptene and all five cyclooctene cyclic dimers. For a full assignment, we had to reconsider criteria, based mostly on ¹H and ¹³C NMR spectroscopy.

In the literature only limited spectroscopic data have been given for cyclooctene and especially for cycloheptene cyclodimers. We have reviewed these data in search of suitable criteria for assignment of configuration to each compound.

RESULTS

Cycloheptene dimers

We have previously observed^{2,8} the photochemical, CuOTf-catalysed formation of two dimers from (neat) cycloheptene at 254 nm, together in 5% yield, accompanying trimer formation (≥85% yield) at slightly elevated temperatures. The dimers were identified by GC/MS (parent peak at *m/e* 192) and they were isolated by preparative GC. Their ¹H and ¹³C NMR spectra did not allow an unambiguous assignment so far. However, in the following we have now assigned the cac- and tst-structures on the basis of comparison with the cyclohexene and cyclooctene dimers.

At low temperatures, the trimer formation is largely, but not completely suppressed, as illustrated by the following relative yields of dimers and trimer: 1:20 (20°); 2:3 (-20°); 2:1 (-50°). Neither the absolute yield nor the relative amounts of dimers (GC peak ratio ~1:1) changed much over this temperature range. These results suggest that the thermal formation of the trimer can be suppressed, certainly at -50°, but at this point we do not completely exclude a photochemical pathway to the trimer.

Cyclooctene dimers

When neat cyclooctene is irradiated at ambient temperatures in the presence of CuOTf-cyclooctene, the dimerisation process is very slow. However, upon dilution with hexane (1/8 by volume), dimer formation is accelerated and by GC/MS four dimers C₁₆H₂₈ (*m/e* 220) have been observed in substantial amounts, together with a trace of the fifth dimer. Following Salomon, Kochi *et al.*,⁶ who separated and identified cyclohexene dimers, these cyclooctene dimers were separated on a Carbowax GC column. In the order of increasing retention time, their ratio is approximately 30:15:45:10:2.

DISCUSSION

Assignment of configurations to cyclooctene dimers

For a long time, only scattered data existed on cyclooctene dimers, mostly melting points, and structures were assigned, based on their chemical origin only, not always without ambiguity. Later, the compounds were characterised by IR and mass spectra, and ¹H NMR spectra helped in deriving their configurations. Very recently, Leitich^{9a} completed a study and assignment of all five isomeric tricyclo [8.5.0.0^{2,9}]hexadecanes. We have come to the same conclusions on the basis of ¹H and ¹³C NMR spectra, which we have used for a better understanding of the factors, governing the spectral differences in the various stereoisomers, and also for

Table 1. Literature data on the tricyclo [7.5.0.0^{2,8}] tetradecanes and tricyclo [8.6.0.0^{2,9}] hexadecanes.

Compound ^a	M ₀ P. (°C) ^a	IR spectra (μ)	¹ H NMR spectra (270 MHz) Chemical shifts δ ^b	GC ret. order ^c	Remarks
Tricyclotetradecane					
tat	Unknown				
cac	64-5 ^d	liq.	0.9-2.3 ^{d,e}	1 ^a	
ct	liq. ^f	-	0.67-2.4 ^{e,f}		B ₀ P. 67°/0.01 mm; n _D ²⁰ = 1.4999 ^f
tst	-	66-8		2 ^a	
csc	53 ^f	-	0.6-2.1 (20 H; m); 2.17-2.7 (4H; m) ^{e,f}		
Tricyclohexadecane					
tat	liq. ^c	liq.	1.19-1.24 (16 H), 1.75 (8 H) ^c ; 1.18, 1.69 ^{e,g}	1	
cac	58-9 ^g	57-8	1.20-1.66 (24 H), 1.66 (4 H) ^c	2	
ct	55-6 ^{c,g} 56-7 ^f	53-4	1.10-1.73 (26 H), 1.98 (1 H), 2.16 (1 H) ^c	3	¹³ C NMR spectrum (16 resonances) ^e
tst	68.5 ^h	62 ⁵ -64	1.26-1.77 (24 H), 2.21 (4 H) ^c	4	
csc	117-8 ⁱ 115-6 ^f	<95	1.15-1.59 (24 H), 2.32 (4H) ^c	5	

^aIn italics, when obtained from samples in this study by GC. ^bδ (mC₆) underlined. ^cRef. 9a. ^dRef. 10.

^e60 MHz ¹H NMR spectrum. ^fRef. 11. ^gRef. 12. ^hRef. 13. ⁱRef. 14.

assigning the two cycloheptene dimers. As an introduction we have summarised the present situation in the literature on cycloheptene and cyclooctene dimers in Table 1.

¹H NMR spectra

300 MHz ¹H NMR spectra were run for the pure cycloheptene dimers and for pure cyclooctene dimer-1 (GC order), dimer-2 (containing 12% of dimer-1), dimer-3 (containing 15% of dimer-1 and 30% of -2) and dimer-4 (containing 30% of dimer-2 and 15% of -3), as obtained by preparative GC. By combination of GC analysis with the ¹H and ¹³C NMR spectra of these fractions a consistent qualitative and quantitative analysis of the photodimers was obtained. The fifth cyclooctene dimer (m.p. 116-8°¹⁴) has been characterised by Leitich.^{9a} It was present in trace amounts in the photolysis mixture and it is eluted in glc as the last dimer. Its GC/MS spectrum is consistent with those of the other stereoisomers and it showed the expected cyclobutyl doublet hydrogen

resonance at 2.33 ppm.^{9a} The ¹H NMR spectra, together with the 75.5 MHz ¹³C NMR spectra, the GC/MS data, IR spectra and some melting points (see Table 1), allowed a complete assignment of the various products as stereoisomeric cyclobutane compounds.

Rather surprisingly it was found that ¹H NMR spectra provide a straightforward identification of these cyclobutane compounds with two cis- and/or trans-fused C₅-C₈ rings. Previously, Salomon and Kochi *et al*⁶ based their assignments for cyclohexene dimers mainly on ¹³C NMR spectroscopy. We will now concentrate on the configuration of the laterally fused rings.

In four out of five isomers for each dimeric cycloalkene, a fourfold symmetry is present and assignments have to be done on the basis of chemical evidence and mutual comparison of the spectra. The fifth isomer, *ct*, is asymmetric and it can be identified directly on the basis of ¹H and ¹³C NMR resonances, see Tables 2 and 3.

The simplest model system for the formation of 1,2,3,4-tetra-substituted cyclobutanes by [2+2] cyclo-

Table 2. 300 MHz ¹H NMR spectra of the tricyclo [7.5.0.0^{2,8}] tetradecanes and tricyclo [8.6.0.0^{2,9}] hexadecanes, obtained by photocatalysed dimerisation of cycloheptene and cyclooctene, in CDCl₃.

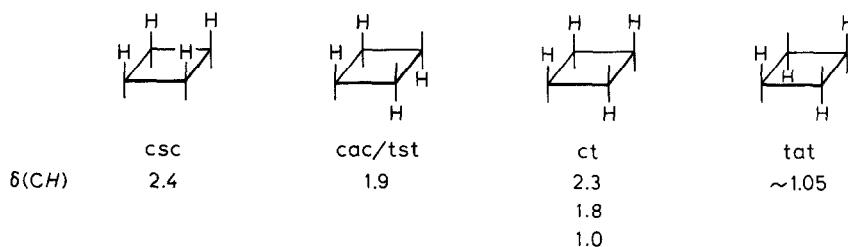
Compound	GC peak	Chemical shifts δ (ppm)		Coupling constants J (H,H), (H,z) ^a
		Cyclobutyl H	Other H	
<u>Tricyclotetradecane</u>				
cac	1	1.77 m,br	1.60 (4H,m,br); 1.43 (12H,m); 1.15 (4H,m,br)	
tst	2	1.89 d	1.40, 1.68 (H _{3,7}); 1.02, 1.77 (H _{4,6}); 1.19, 1.77 (H ₅)	~10 (1a,7a); 13 (3-gem); 11 (3a,4a); 7 (3e,4e); 12 (4-gem); 11 (4a,5a); 12 (5-gem)
<u>Tricyclohexadecane</u>				
tat	1	b	1.19 (12H); 1.26 (4H); 1.76 (12H) ^b	
cac	2	1.66 (8H,m,br)	1.55 (4H,m,br); 1.38 (12H,m); 1.19 (4H,m,br)	
ct	3	2.16 (Ha); 1.96 (Hb)	0.95-1.87 (26H)	a: 2 (1H), 8.5 (2H), 11.5 (1H) b: 3.5 (1H), 9 (2H), 11 (1H)
tst	4	2.23 (4H,d)	~1.2-1.77 (24H)	7 (H ₁ -H ₇)
csc	5	2.33 (4H,d)		

^aApproximate values, taken directly from the spectra. ^bδ (=CH) probably around 1.2 ppm, cf. Figure 1.

Table 3. 75.5 MHz ¹³C NMR spectra of tricyclo [7.5.0.0^{2,8}] tetradecanes and tricyclo [8.6.0.0^{2,9}] hexadecanes, obtained by photocatalysed dimerisation of cycloheptene and cyclooctene, in CDCl₃.

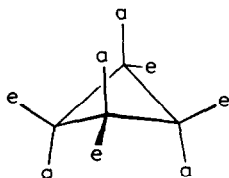
Compound	Cyclobutyl resonances (ppm)	Other resonances (ppm)
<u>Tricyclotetradecane</u>		
cac	46.47 (4C)	32.66 (4C); 29.63 (4C); 26.33 (2C)
tst	42.00 (4C)	32.79 (4C); 29.77 (4C); 32.35 (2C)
<u>Tricyclohexadecane</u>		
tat	47.57 (4C)	35.54 (4C) ^b ; 28.33 (4C); 27.82 (4C)
cac	43.45 (4C)	30.32 (4C); 28.75 (4C); 25.75 (4C)
ct	46.49; 43.64; 42.70; 41.24 (all: 1C)	35.56 ^b ; 31.64; 30.77; 28.78; 28.56; 28.14; 27.88; 27.80; 25.91; 25.78; 25.44; 23.72 (all: 1C)
tst	40.70 (4C)	30.53 (4C); 28.53 (4C); 28.17 (4C)
csc ^c	41.3 (4C)	30.3 (4C); 25.7 (4C); 23.8 (4C)

^aδ (CDCl₃) taken as 76.95 ppm from TMS. ^bAssigned to the =CH-CH₂ resonance. ^cData kindly supplied by Dr. J. Leitich.



dimerisation of (cyclo) alkenes is that of 2-butene.¹⁵ Four products have been found, having cyclobutyl H resonances at ~ 2.4 ppm (csc and ct), ~ 1.9 ppm (cac, tst and ct) and ~ 1.0 ppm (tat and ct).

The large differences between these hydrogen resonances reflect the ring-strain in the cyclobutyl ring, which is most easily interpreted in terms of the number of vicinal cis-H,H-interactions, causing steric compression and downfield shifts.¹⁶ Cyclobutane itself has a puckered conformation inducing axial and equatorial positions, as in cyclohexane.¹⁷



Apparently in the strongly puckered tat-tetrasubstituted cyclobutane,⁶ the axial hydrogens resonate at high field (~ 1 ppm). Both in dimeric cyclohexene⁶ and cyclooctene having the tat-configuration, two narrow regions of resonance are found, at ~ 1.2 and ~ 1.7 ppm, the former probably containing the cyclobutyl hydrogens. Four cis-positioned alkyl groups force the cyclobutyl ring in a flat conformation and the cyclobutyl hydrogens appear at ~ 2.4 ppm. This argument holds consistently for csc-C₁₀: 2.66⁶; -C₁₂: 2.37⁶; -C₁₄: ~ 2.4 ¹¹ and -C₁₆: 2.32 ppm^{9a}.

An intermediate situation occurs in the cis-anti-cis, trans-syn-trans- and cis-trans-dimers of these cycloalkenes, where intermediate resonances are expected. Among these isomers, the asymmetric cis-trans compound can be identified unambiguously by its ¹H and ¹³C NMR spectra, as found for ct-C₁₆. The difference between the remaining tst-(highest strained) and cac-(lowest strained) isomers is more subtle and it requires a closer consideration of a puckering of the cyclobutane ring.

Upon ring enlargement from 5- to 8-membered rings, the puckered situation becomes more favourable for the cac dimers (two ae junctions). We find cyclobutyl H

resonances at 1.94,⁶ 2.00,⁶ 1.77 and 1.66 ppm, respectively.

A puckered tst-isomer with a larger fused ring still would have one strained ring with an aa-junction, therefore an unfavourable situation. Its conformation can be described as a flat one. The cyclobutyl H resonance in tst-C₁₆ is at 2.23 ppm (see Ref. 9a and Table 1) and we assign the tst structure to the C₁₄-isomer with cyclobutyl H resonance at 1.89 ppm.

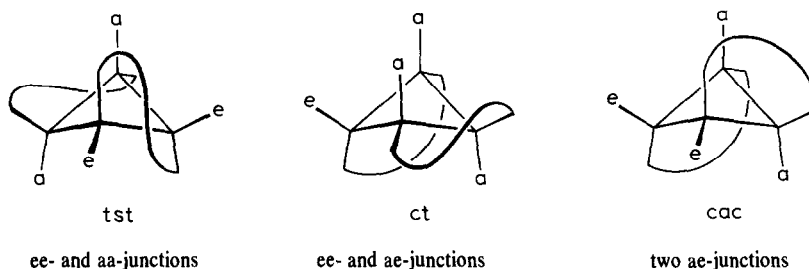
We have assigned the two cycloheptene dimers on the basis of chemical shift considerations as cac-C₁₄ (dimer-1) and tst-C₁₄ (dimer-2), because they lack an absorption at 2.4 ppm (no csc), they have four-fold symmetry in ¹H and ¹³C NMR spectra (no ct) and the spectra are more complicated than those of tat-C₁₂⁶ and -C₁₆ and they differ considerably in chemical shifts (see Table 2 and Fig. 1). The absence of tat-C₁₄ among our products is a striking conclusion, to which we will return.

Also, the cyclobutyl resonances in tst-C₁₄ and -C₁₆ have a similar doublet appearance. In cac-C₁₄ and -C₁₆ four blocks of resonances appear in the same spectral regions, having a similar appearance with a poorly-structured broad cyclobutyl H signal for the former compound.

¹³C NMR spectra

As already noted, all but one cycloheptene and cyclooctene dimers in this study give four carbon resonances, see Table 3. The asymmetric ct-cyclooctene dimer has 16 carbon resonances. The cyclobutyl carbons (δ 40–50 ppm) and some of the adjacent methylene carbons b ($\delta < 36$ ppm) have been assigned.

Upon comparing all available ¹³C data⁶ for the C₅–C₈ dimers, we find consistency in flat cyclobutyl rings in csc compounds, resonating at 35–41 ppm and puckered rings in tat-C₁₂ and -C₁₆ near 50 ppm including the resonances in the strongly puckered tricyclo[3.3.0.0^{2,6}]-octane. Salomon, Kochi *et al.*⁶ have furthermore successfully used a criterion for assigning b resonances in the cyclohexene dimers, which originates from the work of Grant and Cheney.¹⁶ It is based on the observation that every 1,2-cis-H,H-interaction at the a and b carbons results in an upfield shift of over 4 ppm for the b resonances, while the a resonances move to lower field.



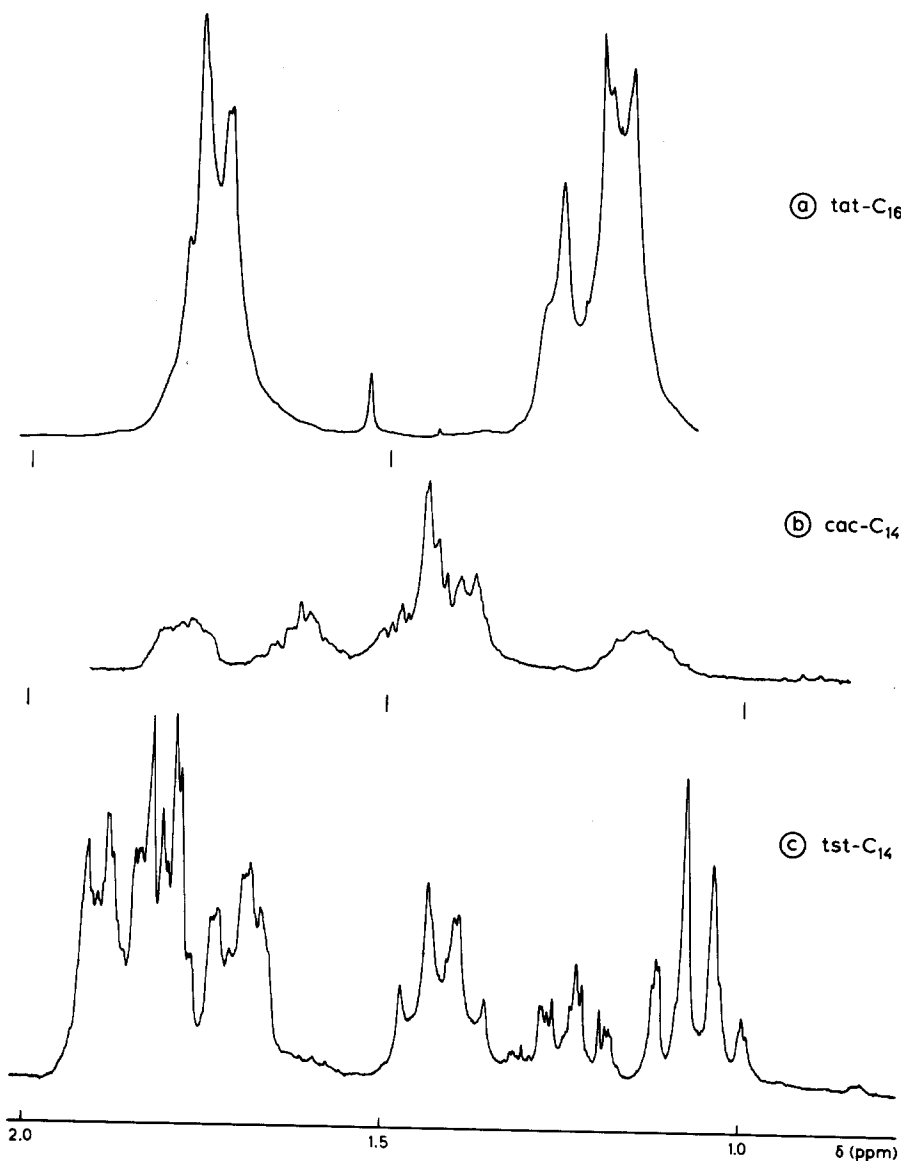


Fig. 1. 300 MHz ^1H NMR spectra of trans-anti-tricyclo [8.6.0.0^{2,9}] hexadecane (a), as compared to cis-anti-cis- (b) and trans-syn-trans-tricyclo [7.5.0.0^{2,8}] tetradecane (c), in CDCl_3 .

This makes clear why in *csc*-C₁₂ the *b* resonances are at 23 ppm, in *cac*-C₁₂ at 27 ppm and in *tat*-C₁₂ at 41 ppm. The same holds for *csc*- and *cac*-C₁₀ (27 and 33 ppm, respectively). We find *b* resonances in *tat*- and *ct*-C₁₆ at 35.5 ppm and ≤ 30.5 ppm in *tst*- and *cac*-C₁₆. When the cyclobutyl H resonance reflects the ring puckering, the expected order of puckering in cyclooctene dimers is *tat* > *cac* \approx *ct* > *tst* > *csc*. The cyclobutyl carbon resonances in the first four compounds are 47.5, 43.5, 46.5–41.2 and 40.7 ppm, therefore they are roughly in the same order. In our two cycloheptene dimers, *cac* and *tst*, we find accordingly cyclobutyl H signals at 1.66 and 1.89 ppm, and ^{13}C signals at 46.5 and 42.0 ppm. Upfield shifts of the cyclobutyl hydrogen resonances and downfield shifts of the cyclobutyl carbon resonances reflect an increased *p* character at the carbon atom upon puckering.

In conclusion, we find an internal consistency in the ^1H and ^{13}C NMR spectra of our cycloheptene and cyclooctene dimers and we can offer a plausible explanation for it, based on interactions by substituents at neigh-

boring cyclobutyl carbons and cyclobutyl ring puckering. The results on cyclohexene dimers⁶ can be treated in the same way. It should be realised, however, that other interactions, e.g. 1,3-diaxial interactions, in chair-shaped cyclohexene compounds, may play a disturbing role in these simple considerations.

Mass spectral and IR data are given in the Experimental Part.

GC data

Considering the foregoing conclusions on the influence of ring puckering on chemical shifts, it is striking to find that cyclooctene dimers are eluted from various GC columns in the same order, which is possibly due to a decreased size or varying shape for puckered molecules. Our two cycloheptene dimers (*cac* and *tst*) are eluted in the same order. When measured, together with an *n*-alkene mixture on a Carbowax column, relative retention times were found, as given in Table 4. For cyclohexene dimers, Salomon, Kochi *et al.*⁶ reported the following

Table 4. Relative retention times of cycloheptene and cyclooctene dimers, in mixtures with n-alkanes on a 10% Carbowax column (cf. Experimental Part).

n-C ₁₆	0.068
cac-C ₁₄	0.080
tst-C ₁₄	0.093
n-C ₁₈	0.19
n-C ₁₉	0.29
tat-C ₁₆	0.32 ⁵
cac-C ₁₆	0.41
n-C ₂₀	0.44
ct-C ₁₆	0.52
n-C ₂₁	0.66
tst-C ₁₆	0.71
csc-C ₁₆	0.80
n-C ₂₂	1.00

retention order: $tat < ct < cac < csc$, therefore a reversal of *cac* and *ct*, possibly related to the stronger deformation in the trans-fused ring of *ct*-C₁₂.

Under our conditions, *tst*-C₁₆ remained contaminated with over 50% of *ct*-C₁₆, even upon repeated preparative GC, followed by GC analysis. We assume that *tst* → *ct* epimerisation has taken place in the GC detector, another indication that C₈-dimer-4 is the most strained one.

Mechanisms of photocatalysed dimerisation

Having assigned in a conclusive way all cycloheptene and cyclooctene dimers, obtained in the photocatalytic reaction with CuOTf upon irradiation at 254 nm, we will now discuss the significance of these results for the mechanisms of photochemical cyclodimerisation in relation with the results for cyclohexene. We wish to emphasise that at this stage we can only stipulate certain points of interest, which we will investigate further.

Photocatalysed dimerisation and isomerisation of cyclohexene

When cyclohexene is irradiated at low concentrations with CuOTf in dioxane solution, the *tat*- and *ct*-C₁₂ dimers are formed in addition to isomerisation products, together with 1-cyclohexenyl-cyclohexene⁶ (1-cc). We find that the mutual ratio of these dimers strongly depends on the concentration of the solution and on the presence of added compounds. For example in very dilute solution or in the presence of tert-butylallene the ratio of *tat*:*ct*:1-cc is 88:4:8. In concentrated solution this ratio is 58:10:32, close to Salomon and Kochi's results⁶ (49:8:24). Since 1-cc has been found to be susceptible to further photocatalysed reactions, the ratio of *tat*/*ct* is significant only.

When a saturated solution of CuOTf·*c*-C₆ in hexane is irradiated at -20° at 254 nm, a mixture of cyclohexene dimers is obtained in which the *tat*-dimer predominates strongly.

The rates of formation of *tat*-C₁₂ and that of the main isomerisation product, 1-methylcyclopentene, are dependent on the concentration of cyclohexene at ambient temperature, as shown in Fig. 2.

There is a maximum in the formation of *tat*-C₁₂, which apparently is related to the composition of the mixture of CuOTf complexes in solution, a CuOTf·(C₆)₂ complex probably being the reactive species for dimerisation. In any case, the lifetime of a CuOTf·*t*-C₆ complex must be considerable and this point deserves further attention.

From these results it can be concluded that the cyclohexene dimers are formed by different routes.² For the formation of *tat*-C₁₂, Salomon, Kochi *et al.*⁶ have proposed a thermal [$\pi_2s + \pi_2a$] cycloaddition of trans-cyclohexene with *cis*-cyclohexene in a suprafacial-antarafacial reaction. A trans-trans template reaction could similarly lead to *ct*-C₁₂.

Photodimerisation of cyclooctene

This is the simplest of the three cases, where all five

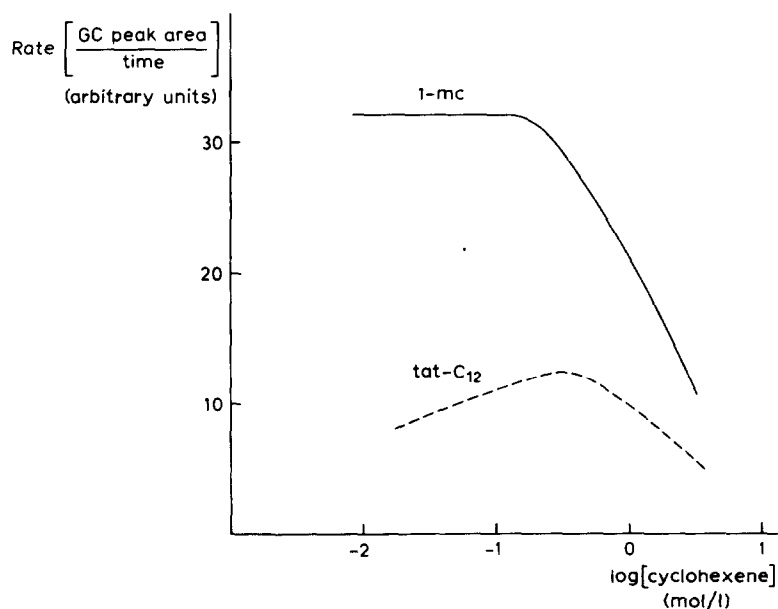


Fig. 2. Photocatalysed isomerisation to 1-methylcyclopentene (1-mc) and dimerisation to *tat*-C₁₂ as a function of cyclohexene concentration in 1,4-dioxane solution.

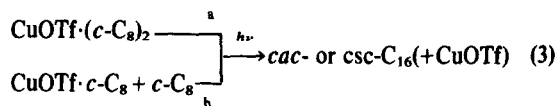
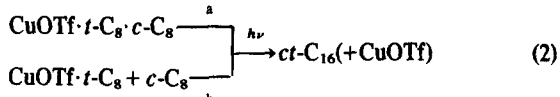
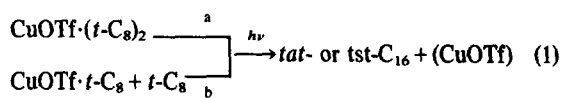
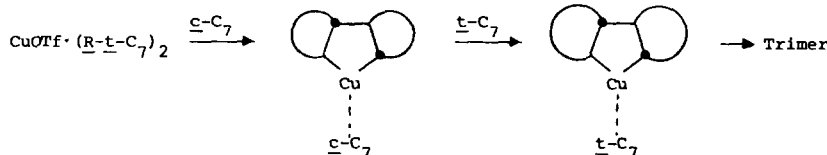
configurational isomers have been obtained and identified. First, the photochemical process starts with the cis-trans isomerisation of a cyclooctene ligand, leading to a steady-state of unknown composition, e.g. $\text{CuOTf} \cdot c\text{-C}_8 \rightleftharpoons \text{CuOTf} \cdot t\text{-C}_8$. The trans-cyclooctene, being a better ligand for Cu(I), will be coordinated preferably. Preponderance of trans-structures in the photo-products reflects a strong participation of $t\text{-C}_8$ in dimer formation. Since both cis- and trans-cyclooctene (as free compounds or in the presence of copper(I) triflate) are stable, at least up to 80°, the formation of the dimers may take place in photochemical, suprafacial-suprafacial [$\pi_2s + \pi_2s$] processes.

A priori we do not know whether the products are formed from CuOTf complexes having two trans- and/or cis-ligands in a template reaction (1,2,3-a) or in a bimolecular process (1,2,3-b) with a monocoordinated copper ion.

Photocatalytic dimerisation and trimerisation of cycloheptene

The formation of *cac*- and *tst*- C_{14} and particularly the absence of the *tat*-isomer, a main product of the photocatalytic dimerisation of cyclohexene and cyclooctene, needs a rationalisation. We can offer one, relatively simple, explanation. First, one should realise that, contrary to trans-cyclooctene, there is no free and stable trans-cycloheptene in solution at ambient temperatures. Our previous attempts² to liberate and isolate trans-cycloheptene from its CuOTf complex by triphenylphosphine at -20° have failed, only the cis-isomer being obtained. So all trans-cycloheptene in solution, being a strong ligand, is coordinated to CuOTf.

Secondly, the major product of the photocatalysed reaction of cycloheptene is the cyclic *tatat*- C_{21} trimer. This is the thermal product of the *R,R,R*- or *S,S,S*-combinations of three trans-cycloheptene ligands.¹ The trans-cycloheptene ligand will give a thermal cyclo-trimerisation, while trans-cyclohexene possibly gives the *ct*- C_{12} dimer in a thermal reaction and no trimer. The higher ring-strain of trans-cyclohexene may account for this difference in reactivity. It appears therefore that the *R,R*- or *S,S*-combinations at CuOTf, which can be formed by ligand exchange between two CuOTf- $t\text{-C}_7$ molecules, do not dimerise, but instead the CuOTf- $(R\text{-}t\text{-C}_7)_2$ complex(s) or its *S*-counterparts will accept a third *t*- C_7 ligand of the same chirality to form a trimer. Again, the possibility of a cupracyclopentane intermediate as an alternative to a template process around copper, is considered:¹

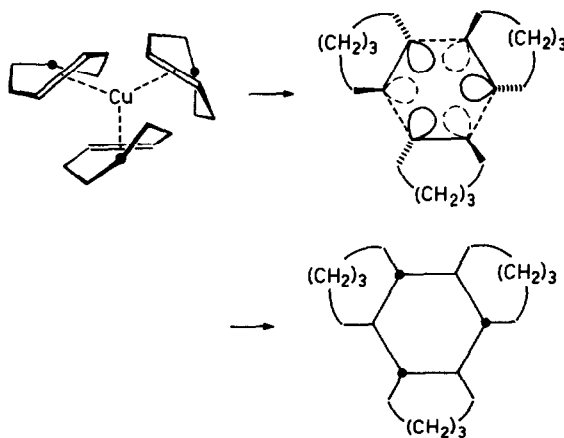


The major products are in italics. Theoretically, even a $\text{CuOTf} \cdot (\text{C}_8)_3$ complex could lead to dimeric products. However, the fact that in neat cyclooctene photocatalytic dimerisation is a very slow process, while the concentration of these complexes should be highest, argues against such a possibility.

Interestingly, a considerable amount of *tst*- C_{16} is formed, apparently from one *R*-trans-cyclooctene molecule and one *S*-molecule, around one copper ion or in a bimolecular process. The *tat*-isomer is formed from an *R,R*- or *S,S*-combination. Leitich⁹ has studied the thermal dimerisation of *R*-trans-cyclooctene at $T > 100^\circ$, where initially no *tst*- C_{16} is formed. However, in the thermal dimerisation racemisation of the *R*-compound occurs,^{9a,17} while in the photocatalytic reaction cis-trans-isomerisation will eventually lead to racemisation.

We suppose that a $\text{CuOTf} \cdot R\text{-}t\text{-C}_7 \cdot S\text{-}t\text{-C}_7$ complex must exist in solution and it may give the *tst*- C_{14} dimer in a photochemical process.

The absence of any *tat*-dimer is another indication that trimerisation is a very favourable process for *R,R,R*- and *S,S,S*-combinations. We have therefore no indication for the occurrence of a cupracyclopentane intermediate from $\text{CuOTf} \cdot (R\text{-}t\text{-C}_7)_2$ or its *S*-stereoisomer, which might escape to give *tat*- C_{14} dimers. In combination with previously obtained evidence,¹ we now more strongly prefer the template mechanism:



A final point here is the formation of *cac*- C_{14} and the absence of *ct*- C_{14} dimers. Although the presence in solution of mixed complexes $\text{CuOTf} \cdot t\text{-C}_7 \cdot (c\text{-C}_7)_n$ ($n = 1$ or 2) has been demonstrated by microwave and NMR titrations² and the complex $\text{CuOTf} \cdot t\text{-C}_7 \cdot (c\text{-C}_7)_2$ has been isolated,¹ we must assume that the formation of the *ct*-dimer has a high activation barrier or a low quantum efficiency.

For the formation of cac-C₁₄, inter- and intramolecular pathways are open, (*vide supra*).

EXPERIMENTAL

The photochemical experiments were carried out as in Ref. 1 and they are described below. After GC separation of the products, melting points were determined with a Reichert melting point microscope. 300 MHz ¹H and 75.5 MHz ¹³C NMR spectra were run on a Varian SC 300 spectrometer at the Central Laboratory of TNO (Delft). Decoupling experiments helped us to assign the resonances and coupling constants as given in Table 2. Also ¹³C NMR spectra of crude mixtures of dimers were run on a Bruker WH 90 spectrometer.

The identity of the products was further established by GC/MS on a Finnigan 3100 D mass spectrometer, coupled to a Finnigan-6100 MS data system;¹ later analyses were performed on a Finnigan 4100 mass spectrometer with an INCOS data system, using a capillary column Carbowax HP (WCOT; 25 m), injection temperature 225°, column temperature 50-230°.

Infrared spectra were taken at the Central Laboratory TNO in Delft on a Bruker 113V FT-IR spectrometer for the cyclooctene dimers and on a Perkin-Elmer 283 IR spectrophotometer for the cycloheptene dimers.

Dimerisation of cyclooctene

150 mg CuOTf·t-C₈¹ was dissolved in 12 ml *c*-C₈. This solution was diluted with 228 ml of *n*-hexane and irradiated in a Rayonet RPR 208 photochemical reactor with 254 nm lamps for seven days in a nitrogen atmosphere. After the irradiation 60 ml of concentrated ammonia were added. The hexane layer was separated and the aqueous layer washed twice with 20 ml of ether. Hexane and ether were evaporated to yield a residue, which solidified upon standing at 4°. Total yield 2.2 g (20%). According to a ¹³C NMR spectrum, it consisted of four dimers, which were then separated by preparative gas chromatography on a Perkin-Elmer Sigma 1 system. Column: 10% Carbowax 20 M on Chromosorb WHP 100-120; 1.2 m glass $\frac{1}{4}$ " OD, 4 mm ID. Programme: injector 190°, detector 235°, oven 125° (5'), rising to 185° (10') by 4°/min. The results are given in the text.

Irradiations at low temperature were performed in a cooled alcohol bath, which was kept at the correct temperature by means of a cryostat. As a light source a Hanau VG/NN15-32 low-pressure mercury immersion lamp was used.

Dimerisation of cycloheptene

The same procedure was followed as for cyclooctene, except that no *n*-hexane was used for dilution. The reaction products were purified by gas chromatography, in which a dimer/trimer

separation was carried out, using a SE-30 column (3.8% on Diazoport S 60/80), 1.3 m, $\frac{1}{4}$ " OD, 4 mm ID. Programme: injector 235°, detector 285°, oven 60° (1'), rising by 12°/min to 200° (10'). The crude mixtures of dimers and trimer, obtained at -20° and -51°, were characterised before by a ¹³C NMR spectrum. The dimers were separated on a Carbowax column as for cyclooctene. Programme: injector 190°, detector 200°, oven 90° (5'), rising by 5°/min to 140° (10'). Further details are given in the text and below.

Mass spectra

The 70 eV mass spectra of the cycloheptene and cyclooctene dimers are very much the same within each group. They do not (easily) allow an identification of the various isomers. Probably, at an early stage of ionisation and fragmentation a similar or common hydrocarbon ion occurs. The prominent peaks appear at *m/e* 29, 41, 54, 55, 67, 81, 82, 95, 96 (in C₁₄ only), 110 (in C₁₆ only), 121, 135, 149, 163, 177 and 192 for C₁₄- (and C₁₆-) dimers, moreover for C₁₆-dimers a parent peak is present at *m/e* 220.

Infrared spectra

The spectra of cycloheptene and cyclooctene dimers are typical for saturated hydrocarbons, i.e. they show that strongest peaks in the stretch region (2955s, 2920vs, 2850s) and C-H binding modes around 1450 cm⁻¹. Furthermore a number of weak bands are present, which in the case of the cycloheptene dimers have not been very helpful for assignment, the only available reference being the IR spectrum of the cac-C₁₄ isomer,[†] which does not allow a definite identification of our cac-C₁₄ compound. For the cyclooctene dimers the results are complicated further by the isomeric contamination. However, this problem was largely solved by using FT-IR spectra, which were corrected for contributions by impurities. In this way a number of characteristic peaks for each of the four major cyclooctene dimers were positively identified, as listed in Table 5.

Dimerisation of cyclohexene²

20 ml of a dioxane solution with [cyclohexene] = 0.25 mol/l and [CuOTf-cyclohexene] = 0.01 mol/l are irradiated in a Rayonet RPR 208 reactor at 254 nm for 62 hr. GC analyses have been performed after 2, 6, 14, 30 and 62 hr of irradiation, using *n*-nonane as an internal standard on a Hewlett-Packard 5750 gas chromatograph with a glass column, containing 15% Carbowax 20 M on Diat. S 60-80, 1.2 m, $\frac{1}{4}$ " OD, 4 mm ID (on column injection). When tert-butylallene was present, its concentration was equal to that of cyclohexene.

[†]Ref. 10. We are grateful to Prof. K. G. Taylor for sending us the IR and 60 MHz ¹H NMR spectra of this compound.

Table 5. Characteristic peaks in the infrared spectra of the tricyclo [7.5.0.0^{2,8}]tetradecanes and tricyclo [8.6.0.0^{2,9}]hexadecanes,^a isolated in this study.

Compound	State	IR bands (cm ⁻¹)
<u>Tricyclotetradecane</u>		
cac	Film ^b	2956s, 2920vs, 2850s, 1450w, 1120m,br, 990m,br
tst	Film ^b	2955s, 2920vs, 2850s, 1448w, 1125m,br, 1000m,br
<u>Tricyclohexadecane</u>		
tat	CS ₂	1450s, 1358w, 1331w, 1306w, 1287vw, 1264vw, 1224vw, 992vw, 829w, 705vw
cac	CS ₂	1461s, 1442m, 1354mw, 1287w, 1268w, 1247vw, 1182vw, 1143w, 1052w, 1027w, 956w, 873w, 849w, 745m
ct	CS ₂	1358mw, 1288w, 1181vw, 1066w, 1016w, 812w
tst	CS ₂	1451s, 1267w, 1183vw, 1121vw, 999vw, 829vw

^aObtained for the products for which the purities are given in the Section on ¹H NMR spectra; only those peaks are given which were positively identified as appearing in the spectrum of the compound under examination. These assignments were assisted by FT-IR spectral correction for contributions by impurities. ^bThin film on a KBr disk.

The experiments described in Fig. 2 were carried out with a stock solution, prepared from 369 mg of CuOTf·C₆ in 12 ml of dioxane. 1 ml of this solution was placed in a 40 ml quartz tube under N₂ and 100 μl of nonane was added. Then the solution was made up to 10 ml by adding various amounts of cyclohexene (varying from 10 μl to 9 ml) and dioxane.

GC analyses were performed after 0.5, 1.5, 3, 6 and 12 hr of irradiation. Peak areas were determined by a weighing method.

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