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PHOTOCATALYSIS (III)[1]

PHOTOCHEMICAL ISOMERISATION OF CYCLOHEXENES AND CYCLOHEPTENE IN THE PRESENCE OF COPPER(I) TRIFLUOROMETHANESULPHONATE. IDENTIFICATION AND ACID-CATALYSED ISOMERISATION OF THE PRODUCTS

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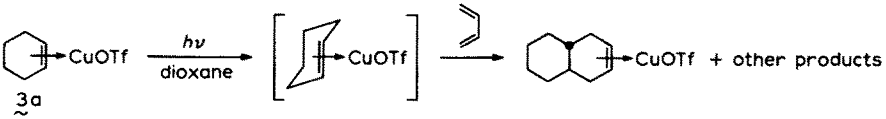
Under irradiation in the CT bands of complexes between Cu^I compounds and unsaturated substrates, catalytic photochemical (photocatalysed) transformations of the ligands take place at wavelengths $\geq$250 nm, at which the pure substrates do not absorb and consequently cannot react.

An example is the *cis*-*trans*-isomerisation of cyclo-octene, **1**, which occurs at 185 nm without a catalyst[3], whereas it can be performed at 254 nm with CuCl as a photocatalyst[4]. Similarly, following Salomon and Kochi[5] we have proposed the isomerisation of cycloheptene, **2**, and cyclohexenes, **3**, to their highly strained *trans*-isomers, when irradiated under photocatalytic conditions, using copper(I) trifluoromethanesulphonate (copper(I) triflate, CuOTf) as a catalyst.

In the presence of conjugated dienes these *trans*-isomers may undergo photocatalytic cycloaddition reactions[1], rather than a previously described photocatalytic dimerisation in the absence of diene[5].

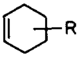
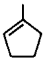
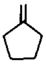
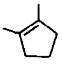
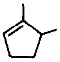
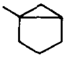
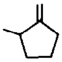
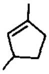
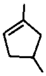
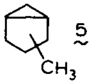
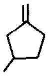


The identification of two minor side products as 1-methylcyclopentene, **4a**, and at least one similarly ring-contracted isomer of **3c** prompted us to reinvestigate the photoreaction of cyclo-olefins with CuOTf complexes as a catalyst, because for these cycloalkenes only a dimerisation has been reported[5].

In this paper we present preliminary data on the identification of the products which are obtained from compounds **2** and **3a-d** (*cf.* Table 1) at considerably lower cycloalkene concentration than used previously ($\geq$ 75 mol%)[5,6].

Table 1

Products obtained from cyclohexenes 3a-3d in their photochemical reaction at 254 nm, catalysed by CuOTf[a] (in 1,4-dioxane, at 20° C, irradiation time 40 h)

Starting compound	(Photo)products			
	1-Methyl-cyclopentenes	Bicyclo[3.1.0]-hexanes	Methylene-cyclopentanes	Dimers
3a; R = H	 4a	 5a	 6a[c]	7a-c
3b; R = 1-methyl	 4b  4c	 5b	not found	d
3c; R = 3-methyl	4b + 4c	5b	 6b	5 or more[e]
3d; R = 4-methyl	 4d  4e	 5c[b]	 6c	5 or more[e]

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[a] Using the solid complex of CuOTf with the cyclohexene under consideration as the catalyst.

[b] Non-identified, unresolved (GC), mixture of at least two out of five possible stereoisomers with the methyl group in the cyclopentane ring.

[c] Identification uncertain; the presence of 6a was indicated by the PMR spectrum of a GC--fraction of one run only.

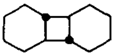
[d] Absence of dimers ascribed to the steric hindrance of dimerisation by the 1-methyl group.

[e] Unidentified mixture in minor yield.

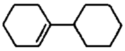
The irradiations were performed in purified 1,4-dioxane under nitrogen in quartz vessels at 254 nm using a Rayonet RPR 208 photochemical reactor. The cycloalkene concentration amounted to 0.25 mol/l and the CuOTf.cycloalkene complex (catalyst) concentration to 0.01 mol/l[1,2].

Under these reaction conditions the main products from 3a-3d were 1-methylcyclopentenes 4a-d, bicyclo[3.1.0]hexanes 5a-c and methylenecyclopentanes 6a-c, together with some dimeric products. The product ratios strongly depend on the reaction conditions.

From 3a the dimers 7a-c were obtained[5].


7a


7b


7c

In Table 1 we have listed all products found and identified sofar. Most of them were identified by comparison of their IR, NMR and mass spectra with those reported in the literature. The remaining compounds were identified by comparison of their spectra with those of the structures already assigned[2].

The major (photo)products found are 4a from 3a, 5b from 3b, 6b from 3c and 6c from 3d, for which inconsistency we have no explanation yet.

Similar to the recently found photocatalysed cycloaddition of cyclohexenes to butadienes[1], the photocatalysed isomerisations observed for cyclohexenes do neither occur with cyclopentene nor with norbornene, while with cycloheptene only a very slow isomerisation occurs, probably to 1-methyl cyclohexene, as was indicated by GCMS analysis (retention time and mass spectrum). Under our conditions we find the reported photocatalysed dimerisation of these ligands to be very slow.

Consecutive thermal reactions

The composition of the reaction mixtures was found to change in the dark after irradiation at ambient temperature. Therefore, it was suspected that part of the products are formed by thermal isomerisation of the primary photoproducts. This isomerisation could occur under the influence of traces of the very strong trifluoromethanesulphonic acid, 8, which may be present if the copper(I) triflate complex is not rigorously purified by repeated crystallisation. Such a thermal isomerisation was demonstrated by the formation of increased amounts of 1-methylcyclopentenes 4a-e in irradiated reaction mixtures, containing 8 in concentrations up to 0.01 mol/l. In particular the methylenecyclopentanes, 6, were found to be susceptible to the acid, while the isomerisation of the bicyclo[3.1.0]hexanes, 5, proceeded considerably slower.

The formation of products 4 during irradiation is strongly suppressed when the purified catalyst is used. From these experiments it appears that the primary isolable photoproducts from cyclohexenes 3 are bicyclo[3.1.0]hexanes 5 and methylenecyclopentanes 6. Recently these products were found to be the major products of the uncatalysed photolysis of 3a at 185 nm in pentane solution[7].

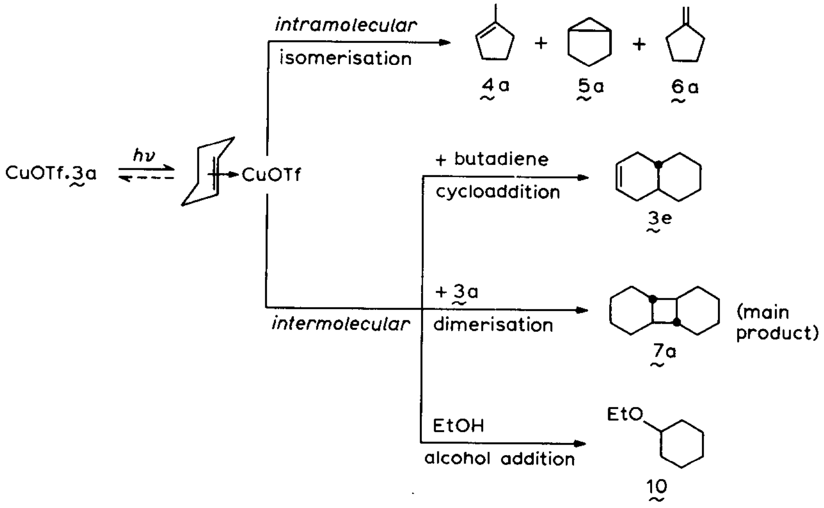
Our photocatalytic process, with wavelengths up to approximately 300 nm, provides a convenient synthesis of the bicyclo[3.1.0]hexene 5b and the methylenecyclopentanes 6b and 6c. However, in the presence of acid 8 the more stable 1-methyl-1-cyclopentenes 4a-d are obtained as the final products.

The intermediary of *trans*-cycloalkenes in photochemical reactions of six- to eight-membered cycloalkenes is now widely accepted[1-11]. *Trans*-cyclooctene has been isolated, but *trans*-cycloheptene, 9, and *trans*-cyclohexene have escaped isolation sofar. Inoue et al.[7] reported for 9 a lifetime of 23 min at -10° C.

In our work we expect the *trans*-cycloalkenes to be stabilised by complexation with CuOTf. We have recently obtained evidence by ^{13}C-NMR spectroscopy that the CuOTf·*trans*-cycloheptene complex is a stable compound at room temperature[2,8]. Presently, we are also attempting to observe the CuOTf *trans*-cyclohexene complex at 77 K[9]. For cyclopentene the π-orbitals cannot pass beyond orthogonality and therefore a "*trans*"-structure cannot be reached. The increase of ring strain in the order *trans*-cyclooctene < *trans*-cycloheptene < *trans*-cyclohexene is reflected by the photocatalytic reactivity of these cycloalkenes which increases in the same order.

Reaction pathways of *trans*-cyclohexene

In the scheme below we summarise the pathways by which complexed (or free) *trans*-cyclohexenes may react to products other than 3a.



The ratio of isomerisation to dimerisation products depends upon the concentration of 3a: at low [3a] the isomerisation prevails while in a 75% solution of 3a in THF dimerisation is predominant[5]. Alcohol solvent addition seems to be more important for free *trans*-cyclohexene[10] than for its complex with CuOTf since with ethanol as a solvent we have only obtained traces of 10 (identity by GCMS) in the photocatalysed reaction of 3a. Apparently the stabilised CuOTf *trans*-cyclohexene complex prefers isomerisation and cycloaddition reactions.

We are presently studying the scope and mechanism of the photocatalytic isomerisation of cyclohexenes. The photocatalytic nature of this reaction is proved by the absence of reaction when CuOTf is not present,independent of the absence or presence of a catalytic amount of HOTf. In the dark the catalyst is inactive at room temperature.

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References and notes

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9. In this compound "*trans*" signifies a stabilized state with a dihedral angle between the C-C bonds in the C-C=C-C fragment exceeding 90°.
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, 7058 (1973).
11. As an alternative, the intermediacy of the first singlet or Rydberg excited state of 3a without the involvement of *trans*-cycloalkene may be envisaged as proposed by Inoue et al.[7].