An Anomalously High *trans*:*cis* Photostationary Ratio on the Direct Photoisomerization of Cyclo-octene

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Summary On direct photoisomerization of cyclo-octene, a *trans* : *cis* photostationary ratio of 49 : 51 was observed, which is anomalously high for a strained cycloalkene, whereas the *trans* : *cis* ratios on toluene photosensitization in the liquid and vapour phase were 5 : 95 and 13 : 87, respectively.

Photochemical behaviour of simple alkenes following direct excitation has not been investigated extensively;[1,2] particularly lacking are studies on the direct *cis-trans* photoisomerisation of these compounds. Although the calculated potential curves for the excited singlet and triplet states of ethylene[3] can be used as models for those of acyclic alkenes, the geometry and the energetics of the excited states of cycloalkenes with steric restrictions have not been discussed. We now report a study on the direct *cis-trans* photoisomerization of cyclo-octene in connection with the photosensitized isomerization.[†]

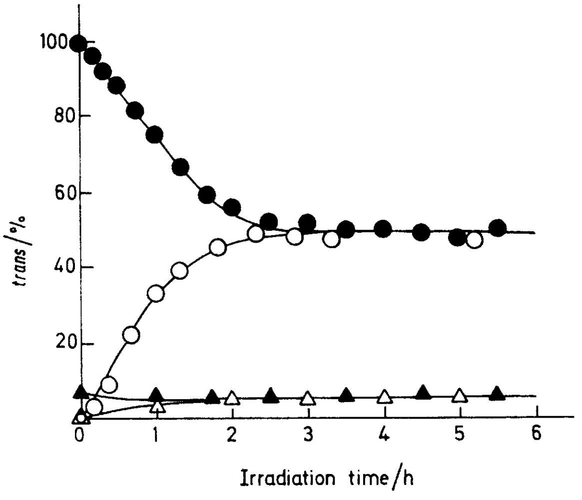

Figure. Plot of % *trans vs.* irradiation time: direct photolysis; ● (initial composition, 0·4% *cis*: 99·6% *trans*), ○(100 : 0); sensitized photolysis; ▲ (92 : 8), △ (100 : 0).

A pentane solution containing 0·01 M *cis*- or *trans*-cyclo-octene, *cis*- or *trans*-(**1**), was irradiated at 184·9 nm (as the effective resonance line of mercury) by a 30 W U-shaped low pressure mercury lamp (immersion-well type) at 17 °C under nitrogen. Toluene photosensitization of pentane solution containing 0·5 M toluene and 0·08 M cyclo-octene was carried out under similar conditions in a quartz tube using a 500 W high pressure mercury lamp.[‡] G.l.c. analysis on $\beta\beta'$-oxydipropiononitrile column revealed that both the direct and sensitized photolyses effect *cis–trans* isomerization as a major photochemical reaction.[§] The percentage of the *trans*-isomer in cyclo-octene is plotted as a function of the irradiation time in the Figure.

Table. The *trans* : *cis*-cyclo-octene photostationary ratio toluene photosensitized in the vapour phase[a]

Pressure/Torr			Irradiation time/h	*trans* : *cis*
cis-(**1**)	*trans*-(**1**)	Toluene		
3·0	0	3·0	1·5	0·154 (13·3% *trans*)
3·0	0	3·0	2·5	0·150 (13·0% *trans*)
2·5	0·5	3·0	1·5	0·153 (13·3% *trans*)

[a] Bicyclo[4.2.0]octane and octa-1,7-diene were also obtained, although the major photochemical reaction was *cis–trans* isomerization.[5]

We observed that the direct and sensitized photolyses gave quite different photostationary states after prolonged irradiation (the ratios of *trans* : *cis* are 49 : 51 and 5 : 95, respectively). It is worth noting that, in spite of the strain in the *trans*-form (9·3 kcal mol^{-1}),[4] an anomalously high *trans* : *cis* ratio, *i.e.* 49 : 51, was observed only upon direct irradiation.[¶] The electronically excited states involved are considered to be an excited singlet (S_1) state for direct photolysis and a triplet (T_1) state for photosensitization. Assuming that the extinction coefficients of *cis*-(**1**) and *trans*-(**1**) do not differ too greatly[**] and that the rates of energy transfer from the toluene triplet to *cis*-(**1**) and *trans*-(**1**) are approximately equal, the above phenomenon can be related to the difference in the decay ratio ($k_t : k_c$) from the S_1 and T_1 states into each isomer. The calculated potential curves for the excited states of ethylene,[3] which suggest the same decay ratio for S_1 and T_1 states, are

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[†] The xylene-sensitized photoisomerization of *cis*-cyclo-octene has been reported as a preparative procedure of the *trans*-isomer; J. S. Swenton, *J. Org. Chem.*, 1969, **34**, 3217.

[‡] No photoisomerisation was observed in the absence of the sensitizer in significant yield.

[§] Slow disappearance of cyclo-octenes was observed; after 1 h irradiation *ca.* 7 and 4% of cyclo-octenes disappeared on the direct and sensitized photolysis, respectively.

[¶] This will provide a convenient one-step method for preparing *trans*-cyclo-octene in good yield. In a preliminary experiment, the work-up procedure described in *Org. Synth.*, Col. Vol. V, 315, for the products from the direct irradiation of 0·5 M pentane solution of *cis*-cyclo-octene gave the *trans*-isomer in more than 10% yield, although prolonged irradiation of the high concentration solution results in the formation of polymers on the lamp surface together with uncharacterized products, which may act as sensitizers to prevent the reaction mixture reaching a 1 : 1 photostationary ratio.

[**] The reported extinction coefficient for *trans*-(**1**) is 5500 l mol^{-1} cm^{-1} at 185 nm, while the coefficient of *cis*-(**1**) is estimated to be 5000—10000 l mol^{-1} cm^{-1} from that of acyclic disubstituted alkenes;[8] M. G. Mason and O. Schnepp, *J. Chem. Phys.*, 1973, **59**, 1092.

evidently unsuitable for the present system. The extremely low *cis* → *trans* isomerisation efficiency when (**1**) is photosensitized may be attributable to the torsional conversion barrier from vibrationally relaxed triplet state into the *trans*-form.

Toluene photosensitization in the vapour phase will afford additional information on the decay ratio, since the triplet state generated in vapour-phase photosensitization is considered to have some excess vibrational energy in the absence of the fast collisional deactivation by solvent molecules. Vapour-phase photolysis of (**1**) sensitized by toluene vapour was carried out in a 100 ml cylindrical quartz cell using a 30 W spiral low pressure mercury lamp under the conditions described previously.[5] The results are shown in the Table. The *trans* : *cis* photostationary ratio of 0·15 was obtained in the vapour-phase photosensitization, while the ratio in the liquid phase was 0·05. It is, therefore, obvious that the vibrational activation in the T_1 state markedly enhances the rate of *trans* formation (k_t) from the triplet state, resulting in a higher decay ratio ($k_t : k_c$) and *trans* : *cis* photostationary ratio. Thus, the high *trans* : *cis* ratio obtained upon direct irradiation, may also be accounted for in terms of the higher internal energy of the S_1 state.

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[1] T. R. Fields and P. J. Kropp, *J. Amer. Chem. Soc.*, 1974, **96**, 7759.
[2] Y. Inoue, S. Takamuku, and H. Sakurai, *J.C.S. Chem. Comm.*, 1975, 577.
[3] A. J. Merer and R. S. Mulliken, *Chem. Rev.*, 1969, **69**, 639.
[4] P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, 1970, **92**, 2377.
[5] Y. Inoue, K. Moritsugu, S. Takamuku, and H. Sakurai, *J.C.S. Perkin II*, in the press.

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