# Singlet Photosensitization of Simple Alkenes. Part 4.† *cis-trans* Photoisomerization of Cycloheptene sensitized by Aromatic Esters. Some Aspects of the Chemistry of *trans*-Cycloheptene †

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Upon photosenstitization at −78 °C of *cis*-cycloheptene (1*c*) with methyl benzoate as sensitizer, *trans*-cycloheptene (1*t*) was produced in a high *trans*: *cis* photostationary ratio of 0.24. *trans*-Cycloheptene thus formed was entirely stable at −78 °C and, on warming to room temperature, regenerated the *cis*-isomer quantitatively, but was found to be trapped efficiently by methanol in acid and by diazomethane at low temperature. An anomalous enhancement of the rate of protonation was observed for (1*t*) compared with (1*c*) or even with *trans*-cyclo-octene, for which the constrained structure of (1*t*) must be responsible. The thermodynamic parameters for the thermal *trans–cis* isomerization of (1*t*) were also determined from a study of the lifetime at temperatures between −15.0 and +1.0 °C: $E_a$ 17.4 kcal mol$^{-1}$,‡ log *A* 11.1, $\Delta G^‡_{266}$ 19.4 kcal mol$^{-1}$, $\Delta H^‡_{266}$ 17.0 kcal mol$^{-1}$, $\Delta S^‡_{266}$ −9 cal K$^{-1}$ mol$^{-1}$. A potential energy curve for the ground-state cycloheptene was presented.

A novel singlet photosensitization of cyclo-octene by aromatic esters has recently been reported from these laboratories.[1] The reaction proceeds *via* a singlet-energy transfer process and gives a much higher *trans*: *cis* ratio in the photostationary state than that obtained from the usual triplet photosensitization. The mechanism involves the formation of a singlet exciplex of cyclo-octene with an excited aromatic ester. Rotation about the double bond of the cyclo-octene moiety in the exciplex gives rise to a twisted singlet ($^1p$) of cyclo-octene, which in turn decays into *cis*- and *trans*-cyclo-octene in the same ratio as obtained for direct irradiation at 185 nm. This high *trans*: *cis* photostationary state ratio prompted us to apply this singlet sensitization to the high-yield *cis–trans* isomerization of a smaller cycloalkene, cycloheptene.

Despite theoretical calculations on the strain energy and torsion angle of *trans*-cycloheptene,[2] few experimental data are available on its chemical and physical properties. *trans*-Cycloheptene (1*t*) was first generated by Corey *et al.*[3] in the reaction of *trans*-cycloheptane-1,2-diyl thiocarbonate with tri-iso-octyl phosphite and trapped by 2,5-diphenylisobenzofuran to afford a Diels–Alder adduct with *trans*-stereochemistry; attempts to isolate (1*t*) were unsuccessful. The photochemical generation of (1*t*) was first reported by Kropp[4] involving the xylene-sensitized *cis–trans* photoisomerization of cycloheptene (1*c*) in acidic methanol; methoxycycloheptane (2) was obtained as the major product through protonation of (1*t*). More recently Evers and Mackor have reported the attempted isolation of (1*t*) from a copper(I) trifluoromethanesulphonate complex of (1*t*) by a ligand-exchange treatment.[5] In these experiments, however, no convincing evidence was presented for *trans*-cycloheptene itself or against the possibility that any reactive intermediates such as 1,5-dipolar or electronically excited species were intercepted by the trapping agents. Our previous work on the direct photolysis at 185 nm of *cis*-cycloheptene at −78 °C gave definitive evidence for the existence of *trans*-cycloheptene in its ground electronic state,[6] although the properties of the *trans*-isomer have not been fully elucidated.

In this work we present a further example of singlet photosensitization and further evidence for *trans*-cycloheptene. The chemistry of *trans*-cycloheptene and the kinetics and thermodynamics of the *trans–cis* thermal isomerization are also reported.

**Table 1.** Benzoate-sensitized photoisomerization of cycloheptene (1*c*) in methanol at −78 °C[a]

| | Concentration (mM) | | | Yield (%)[b] | | Total recovery (%)[c] |
|---|---|---|---|---|---|---|
| Run | (1*c*) | $PhCO_2Me$ | $H_2SO_4$ | (1*c*) | (2) | |
| 1 | 9.1 | 11 | 0 | 89 | 0 | 89 |
| 2 | 9.1 | 11 | 27[d] | 76 | 15 | 91 |
| 3 | 9.1 | 11 | 27[e] | 74 | 16 | 90 |

[a] Irradiations by a 300-W high-pressure mercury lamp were conducted for 5 min for neutral (runs 1 and 3) or acidic (run 2) methanol solution (3 ml) in a quartz tube immersed in a dry ice–methanol bath. After irradiation, the solution was gradually warmed to room temperature without further treatment (runs 1 and 2) or with acidification (run 3). [b] Yield based on (1*c*). [c] Combined yield of (1*c*) and (2). [d] Acid was added before irradiation. [e] Acidic methanol (0.3 ml, 0.3M in $H_2SO_4$) was added to the neutral photolysate (3 ml) after irradiation.

## Results and Discussion

The presence of *trans*-cycloheptene in its ground state was first confirmed by photochemical generation of (1*t*) at low temperature and the subsequent addition of a trapping agent. Photoisomerization of (1*c*) was performed in neutral and acidic methanol solutions at −78 °C in the presence of methyl benzoate as sensitizer. As shown in Table 1, irradiation of (1*c*) in acidic methanol (run 2) gave methoxycycloheptane (2) (15% yield) and recovered (1*c*) (76%), while photolysis in neutral methanol (run 1) resulted in the recovery of (1*c*) in 89% yield. In run 3, the same solution as in run 1 was irradiated at −78 °C under identical conditions, allowed to stand in the dark for 10 min at this temperature after irradiation, and then acid was added.. Upon gradual warming of the solution, adduct (2) was obtained in 16% yield, which is comparable to that in run 2. In a similar experiment, no significant decrease was observed in the yield of (2) even after 24 h standing at −78 °C in the dark. These results clearly indicate that the precursor of (2) is not an electronically excited cycloheptene but a reactive ground-state molecule, *i.e.*

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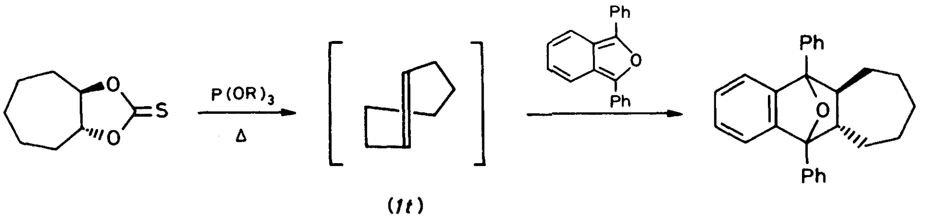
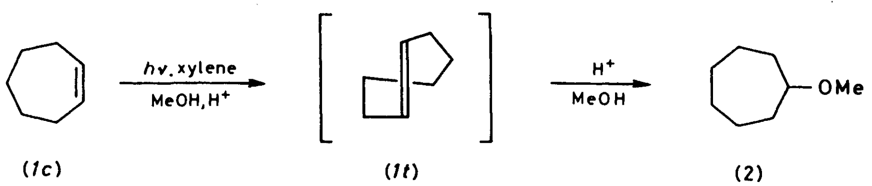
† Part 3, Y. Inoue, K. Nishida, K. Ishibe, T. Hakushi, and N. J. Turro, *Chem. Lett.*, 1982, 471. Preliminary report, Y. Inoue, T. Ueoka, T. Kuroda, and T. Hakushi, *J. Chem. Soc., Chem. Commun.*, 1981, 1031.

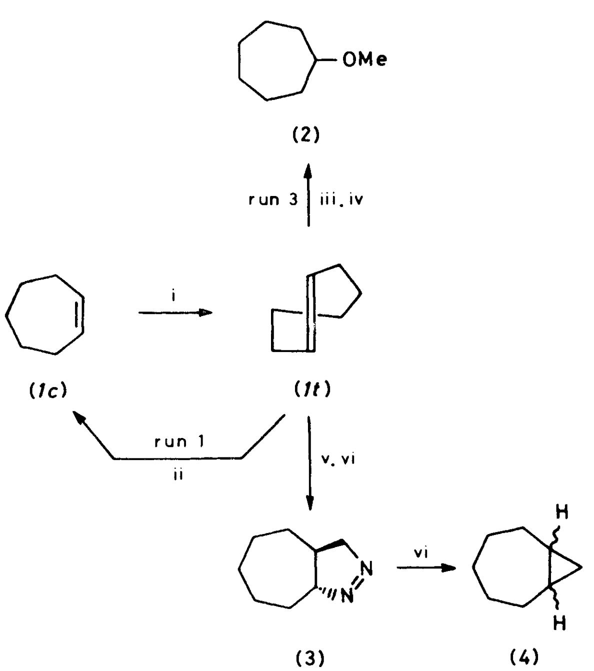
‡ 1 cal = 4.18 J.



**Scheme 1.**



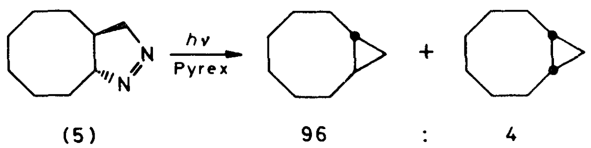
**Scheme 2.**



Scheme 3. Conditions: i, *h*ν, PhCO$_2$Me, −78 °C; ii, Δ (room temperature); iii, H$^+$, MeOH, −78 °C; iv, Δ (room temperature); v, CH$_2$N$_2$, −78 °C; vi, Δ (room temperature); vii, *h*ν, Pyrex

*trans*-cycloheptene (1*t*). The consistent total recoveries for runs 1—3 demonstrate: (1) that any excited state is not intercepted by acidic methanol, (2) that any *trans*-isomer generated suffers either thermal *trans–cis* isomerization under neutral conditions (run 1) or, in acidic methanol, protonation to give the addition product (2) (run 3), and (3) that no other channels, *e.g.* cyclodimerization, are open to (1*t*) under the conditions employed.

Diazomethane was also examined as a trapping agent. The photosensitization of (1*c*) (0.01M) was carried out likewise in pentane solution at −78 °C, and after irradiation an excess amount of diazomethane in diethyl ether (−78 °C) was added to the irradiated solution. The mixture was warmed to 0 °C and the excess of diazomethane was purged with nitrogen flow until its characteristic u.v. absorption disappeared completely.



**Scheme 4.**

Direct injection of the mixture into the g.l.c. column did not give any trace of new products. The first attempt to isolate the product pyrazoline (3) from the residue obtained upon evaporation of the solvent, by column chromatography over silica gel, was successful, but, later, similar treatment with silica gel or with activated alumina resulted in decomposition of the pyrazoline (3). Therefore, most analyses of (3) were performed *in situ*. A satisfactory spectroscopic characterization of (3) was, however, still possible because it showed a characteristic structureless u.v. absorption at 330 nm and an i.r. band at 1 530 cm$^{-1}$, both of which are exclusively attributable to the N=N bond of a 1-pyrazoline; *cf.* the 1-pyrazoline derivative (5) produced in the reaction of diazomethane with *trans*-cyclo-octene: $\lambda_{max.}$ (hexane) 328 nm ($\varepsilon$ 470 l mol$^{-1}$ cm$^{-1}$); $\nu_{N=N}$ 1 538 cm$^{-1}$.[7a] Assuming the same extinction coefficient ($\varepsilon$ 470) for the pyrazoline (3), the product yield of (3) was estimated to be 16—20% by u.v. spectrometry. These yields are in good accord with those obtained for trapping with acidic methanol, and therefore diazomethane is considered to be a good trapping agent for highly strained *trans*-cycloalkenes.

The stereochemistry of the pyrazoline (3) is *trans*,* since the reactions of diazomethane with *trans*-cyclo-octene and other alkenes [7] have been shown to be stereospecific *syn*-additions and, under the conditions employed, diazomethane did not react with *cis*-cycloheptene after 24 h at room temperature. Nevertheless, irradiation at >300 nm of (3) gave *cis*- and *trans*-bicyclo[5.1.0]octanes (4) in a *ca.* 1 : 1 ratio, in contrast to the highly stereospecific denitrogenation of the higher homologue, *trans*-9,10-diazabicyclo[6.3.0]undec-9-ene (5).[7a]

This non-stereospecific denitrogenation of the pyrazoline (3) may be attributable to the higher strain of the *trans*-

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* In view of the anomalously high strain in (1*t*), the possibility of non-stereospecific addition of diazomethane cannot be ruled out absolutely.

**Table 2.** Lifetimes of some *trans*-cycloheptenes

| Compound | Solvent | Temperature (°C) | Lifetime |
|---|---|---|---|
| *trans*-Cycloheptene (1*t*) | MeOH | 1.0 ± 0.1 | 9.7 ± 0.3 min [a] |
| | | −3.0 ± 0.1 | 14.4 ± 0.6 min [a] |
| | | −5.4 ± 0.1 | 22.4 ± 1.0 min [a] |
| | | −7.0 ± 0.1 | 26.3 ± 0.9 min [a] |
| | | −10.0 ± 0.1 | 38.3 ± 1.5 min [a] |
| | | −15.0 ± 0.1 | 67.9 ± 1.5 min [a] |
| | Pentane | −10 ± 2 | 23 min [b] |
| | MeOH | 25 | 45 s [a,c] |
| 1-Phenyl-*trans*-cycloheptene | Cyclohexane | Ambient | 250 s [d] |
| *trans*-Cyclohept-2-enone | Cyclohexane | Ambient | 45 s<br>(>1 000 s) [e,f] |
| | MeOH | Ambient | 0.033 s [e,g] |

[a] This work. [b] Ref. 6. [c] Obtained by extrapolation of the Arrhenius plot. [d] Ref. 10. [e] Ref. 11. [f] Major decay process is the reaction with *cis*-cyclohept-2-enone, the lifetime being a function of the *cis*-isomer concentration. The extrapolated lifetime at zero *cis*-isomer concentration is given in parentheses. [g] Major decay process is the reaction with the solvent.

configuration of (3), which enhances bond rotation in the resulting 1,3-biradical intermediate.

*Studies of Lifetimes.*—The remarkable stability of (1*t*) at low temperature and the efficient trapping by acidic methanol enable us to perform an experiment to evaluate the lifetimes of (1*t*) at various temperatures. Neutral methanol solutions containing (1*c*) (0.01M), methyl benzoate (0.01M), and cyclo-octane (0.0005M) as an internal standard were irradiated at −78 °C for 10 min under identical photochemical conditons and each solution was then immersed in a bath maintained at a desired temperature in the range −15.0 to ±1.0 °C for a definite period, and chilled again to −78 °C. Subsequent addition of precooled acidic methanol to the treated solution and gradual warming to room temperature gave the adduct (2), the yield of which was determined by g.l.c.* A plot of ln[(2)] as a function of time gave a good linear relationship at each temperature, indicating unimolecular decay of (1*t*) to (1*c*). As can be seen from Table 2, the lifetimes thus obtained are unexpectedly long in view of the fairly high strain energy of 27 kcal mol$^{-1}$. The lifetime of (1*t*) at −10 °C, 38.3 min, is longer than our previously reported value for pentane solution, *i.e.* 23 min at −10 °C.[6] This discrepancy may be explained in terms of the high dipole moment which is characteristic of strained *trans*-cycloalkenes: the dipole moments of *cis*- and *trans*-cyclo-octenes are 0.4 and 0.8 D,[9] respectively. The strained *trans*-cycloheptene with a high dipole moment is much stabilized in polar solvents. Lifetimes of some related *trans*-cycloheptenes [10,11] at ambient temperature are also listed for comparison in Table 2. The lifetime of (1*t*) is almost comparable to those of the conjugated *trans*-cycloheptenes. However, most of these lifetimes should not be compared directly with the extrapolated lifetime of (1*t*) at 25 °C, since the major decay process of *trans*-cycloheptenes with conjugating groups is not a unimolecular *trans–cis* isomerization but a bimolecular reaction with the solvent or with the *cis*-isomer [11] or miscellaneous reactions giving rise to unidentified products.[10]

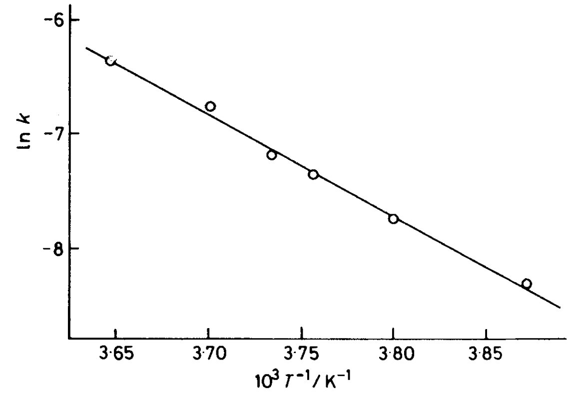

Figure 1. The Arrhenius plot for thermal *trans–cis* isomerization of *trans*-cycloheptene (1*t*)

The activation energy and the frequency factor for the thermal *trans–cis* isomerization were obtained from the Arrhenius plot shown in Figure 1:† $E_a$ 17.4 ± 0.7 kcal mol$^{-1}$; log $A$ 11.1 ± 0.6. This activation energy is fairly close to the reported $E_a$ of $\geqslant$17 kcal mol$^{-1}$ for *trans*-cyclohept-2-enone,[11] in spite of the absence of the conjugating carbonyl group in our compound. A plot of $\ln(k/T)$ *versus* $1/T$ afforded additional thermodynamic parameters: $\Delta G^{\ddagger}_{266}$ 19.4 ± 1.4 kcal mol$^{-1}$; $\Delta H^{\ddagger}_{266}$ 17.0 ± 0.7 kcal mol$^{-1}$; $\Delta S^{\ddagger}_{266}$ −9 ± 8 kcal K$^{-1}$ mol$^{-1}$. The high activation energy and the negative entropy of activation should be noted. Using Allinger and Sprague's calculation on the strain energy (27 kcal mol$^{-1}$) and torsion angle (*ca.* 125°) [2] and the present activation energy, a more precise potential curve for the ground-state cycloheptene is deducible. The result is shown in Figure 2 along with that for the next higher homologue, cyclo-octene.[12]

*Photostationary* trans : cis *Ratios.*—Upon photosensitized isomerization of cyclo-octene, a remarkable difference in the photostationary *trans* : *cis* ratio was observed between the singlet and triplet sensitizations in our previous work.[1] Thus

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* Throughout this work, the amount of adduct (2) detected by g.l.c. was taken as equal to that of (1*t*) present in solution. This assumption is not valid if any cycloheptyl cation, formed through protonation of (1*t*), undergoes deprotonation regenerating (1*c*). *trans*-Cyclo-octene indeed gave methoxycyclo-octane and *cis*-cyclo-octene in a ratio of 8 : 1, when treated with acidic methanol at room temperature.[8] However, in spite of this fact, the lifetimes derived from the measurement of adduct (2) are essentially correct, since the amount of (2) detected is still proportional to that of (1*t*) remaining in the treated solution.

† Inclusion of the additional lifetime data at −10 and −15 °C gave somewhat different activation parameters compared with those reported previously.

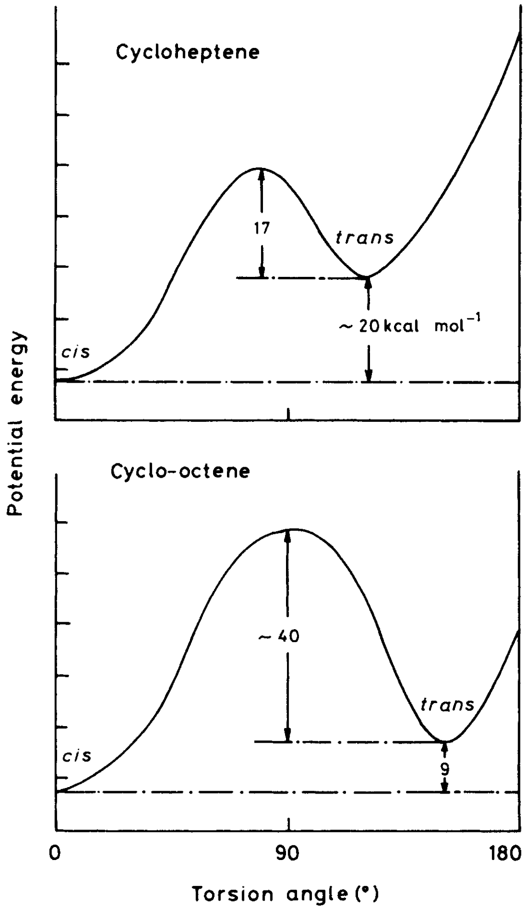

Figure 2. The potential energy curves for the ground states of cycloheptene (top) and cyclo-octene (bottom)

**Table 3.** The photostationary ' *trans* : *cis* ' ratio, $(t/c)_{pss}$, of cycloheptene and cyclo-octene upon photosensitization in methanol [a]

| Compound | Sensitizer (excited state) | $(t/c)_{pss}$ |
|---|---|---|
| Cycloheptene [b] | Methyl benzoate (singlet) | 0.24 [c] |
| | Toluene (triplet) | 0.065 [d] |
| | Xylenes (triplet) | 0.094 [d] |
| Cyclo-octene [e] | Methyl benzoate (singlet) | 0.36 |
| | Toluene (triplet) | 0.05 |

[a] Irradiations by a 300-W high-pressure mercury lamp were conducted with methanol solutions containing an alkene (0.01M) and a sensitizer (0.01M) in a quartz tube; see text for detailed procedures. [b] Irradiated at −78 °C. [c] The photostationary state was attained after 10—30 min irradiation. [d] The photostationary state was attained after 5—15 min irradiation. [e] Irradiated at room temperature; see ref. 1.

$$\mathrm{S} \xrightarrow{h\nu} {}^{*}\mathrm{S} \qquad \text{(i)}$$

$$ {}^{*}\mathrm{S} \longrightarrow \mathrm{S} \qquad \text{(ii)}$$

$$ {}^{*}\mathrm{S} + (1c) \longrightarrow \mathrm{Ex} \qquad \text{(iii)}$$

$$\mathrm{Ex} \longrightarrow {}^{*}p + \mathrm{S} \qquad \text{(iv)}$$

$$\mathrm{Ex} \longrightarrow \text{Cross-adducts} \qquad \text{(v)}$$

$$ {}^{*}p \longrightarrow (1c) \qquad \text{(vi)}$$

$$ {}^{*}p \longrightarrow (1t) \qquad \text{(vii)}$$

$$(1t) \longrightarrow (1c) \qquad \text{(viii)}$$

$$(1t) + \mathrm{H}^{+} \longrightarrow \text{Cycloheptyl cation} \qquad \text{(ix)}$$

$$\text{Cycloheptyl cation} + \mathrm{MeOH} \longrightarrow (2) + \mathrm{H}^{+} \qquad \text{(x)}$$

**Scheme 5.**

methyl benzoate as a sensitizer gives a *trans* : *cis* ratio as high as 0.25—0.36 : 1 while benzene, toluene, or xylenes afford an average value of 0.05 : 1; these results are accounted for in terms of a higher decay ratio for the twisted, excited singlet cyclo-octene than for the excited triplet.[1] Likewise, a high decay ratio and therefore a high photostationary *trans* : *cis* ratio are anticipated upon photosensitization of cycloheptene with methyl benzoate. Although the direct measurement of the *trans* : *cis* ratio is not applicable to cycloheptene photoisomerization, the amount of *trans*-cycloheptene (1*t*), generated photochemically, was estimated from that of methoxycycloheptene (2) produced in the low-temperature experiments described above. Irradiation of methanol solutions containing (1*c*) and a sensitizer were carried out at −78 °C for various periods. The addition of pre-cooled acidic methanol at −78 °C and subsequent warming gave various yields of adduct (2). The ratio of adduct (2) to the remaining (1*c*) increased with increasing irradiation time, reaching a plateau for each sensitizer employed. The photostationary (2) : (1*c*) ratio, tentatively represented as ' *trans* : *cis* ' ratios, are shown in Table 3, and may be compared with the photostationary *trans* : *cis* ratio of cyclo-octene upon methyl benzoate photosensitization. However, as a consequence of the above assumption, the (2) : (1*c*) ratios obtained are equal to or, more probably, somewhat smaller than the *real* (1*t*)/(1*c*) ratios attained at the low temperature. The photostationary ' *trans* : *cis* ' ratio of cycloheptene is much higher in the methyl benzoate sensitization than in the triplet sensitizations. This result coincides with those for the photosensitization of cyclo-octene,[1] and is attributable to the difference in the excited state involved: a singlet for the benzoate and a triplet for toluene and xylenes. According to our previous work on cyclo-octenes,[1,13] methyl benzoate in its excited singlet state transfers its singlet energy to cycloheptene *via* a singlet exciplex to give a twisted, excited singlet cycloheptene ($^1p$), which decays into *trans*- and *cis*-cycloheptene with higher *trans* : *cis* decay ratio than that for triplet cycloheptene ($^3p$).

*Kinetic Studies*.—The above discussion leads to Scheme 5 for the photosensitization of cycloheptene in acidic methanol where S, Ex, and *p* represent sensitizer, exciplex, and twisted cycloheptene, respectively, and the asterisk refers to electronic excitation. The participation of Ex may be eliminated for triplet photosensitizations. Process (v) is added since small amounts of cross-adducts were detected by g.l.c.-m.s. A steady-state treatment of the above sequence leads to expression (xi) for the inverse quantum yield of adduct (2). The equation requires a linear relationship between the inverse quantum yield of (2) *versus* the inverse acid concentration [equation (xi)].*

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* The acid, not proton, concentration was employed, since the acid-catalysed hydration of alkenes have been shown to proceed through general acid catalysis: A. J. Kresge, Y. Chiang, P. H. Fitzgerald, R. S. McDonald, and G. H. Schmid, *J. Am. Chem. Soc.*, 1971, 93, 4907.

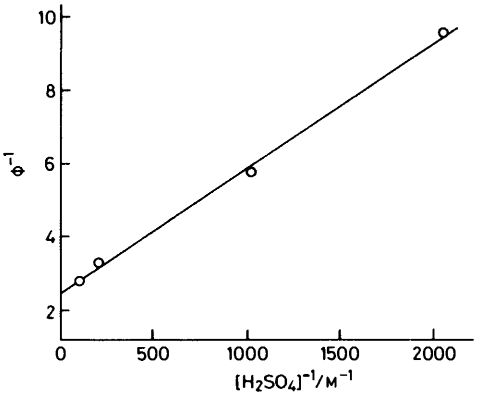


Figure 3. Plot of inverse quantum yield of the methanol adduct (2) *versus* inverse acid concentration upon photosensitization of *cis*-cycloheptene (1*c*)

Table 4. Rate constants of protonation ($k_{ix}$) and thermal *trans–cis*-isomerization ($k_{viii}$) upon photosensitization of (1*c*) in acidic methanol

| Sensitizer | Excited state involved | $k_{ix}/k_{viii}$/ l mol$^{-1}$ | $k_{ix}$/ l mol$^{-1}$ s$^{-1}$ [a] |
|---|---|---|---|
| Methyl benzoate | $^1p$ | 710 | 16 |
| Dimethyl isophthalate | $^1p$ | 890 | 20 |
| Toluene | $^3p$ | 810 | 18 |
| Xylenes | $^3p$ | 680 | 15 |
|  | Av. | 770 ± 80 | 17 ± 2 |

[a] Calculated from the $k_{ix}/k_{viii}$ value, $k_{viii}$ being assumed as 0.022 s$^{-1}$ (τ 45 s); see text.

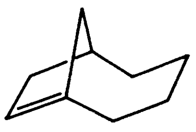
$$1/\Phi_{(2)} = (1 + k_v/k_{iv})(1 + k_{vi}/k_{vii})\left(1 + \frac{k_{viii}}{k_{ix}[\text{Acid}]}\right)\left(1 + \frac{k_{ii}}{k_{iii}[(1c)]}\right) \quad \text{(xi)}$$

The effect of acid concentration was examined in order to evaluate the protonation rate of (1*t*). Benzoate photosensitization of (1*c*) (0.01M) was performed in a merry-go-round apparatus at a variety of acid concentrations, and the inverse quantum yield of (2) was plotted as a function of inverse acid concentration to give a good straight line as shown in Figure 3. Equation (xi) and the intercept/slope ratio of Figure 3 give the ratio of rate constants of protonation against thermal *trans–cis* isomerization: $k_{ix}/k_{viii}$ = 710 l mol$^{-1}$. This indicates that, even at an acid concentration of 0.01M, 88% of *trans*-cycloheptene generated is trapped by the acid. Similar experiments were repeated on the photosensitization with dimethyl isophthalate, toluene, and xylenes as sensitizers to give good linear relationships between 1/Φ and 1/[acid] for all sensitizers. As shown in Table 4, similar treatment afforded comparable $k_{ix}/k_{viii}$ ratios of 680—890 l mol$^{-1}$ for all sensitizers employed, in spite of the different excited state involved. This finding may be taken as further support for the hypothesis that the immediate precursor of protonation is not an electronically excited singlet or triplet state but *trans*-cycloheptene (1*t*) generated as a common reactive species in both singlet and triplet photosensitization. The rate constant $k_{viii}$ is calculated as 0.022 s$^{-1}$ from the extrapolated lifetime at 25 °C shown in Table 2, and we obtain the $k_{ix}$ value for each sensitizer shown in Table 4. In Table 5, the average $k_{ix}$ value thus obtained is compared with the rate constants for the acid-catalysed solvation of some highly and less strained alkenes in water and in methanol. As can be seen from Table 5, strained bridgehead alkenes such as bicyclo[4.2.1]non-1(8)-ene (6) and bicyclo-[3.3.1]non-1-ene (7), both of which have a *trans*-cyclo-octene skeleton, are much more reactive by a factor of 10$^3$—10$^5$ toward acid than a normal trisubstituted cycloalkene.

Table 5. Rate constants for acid-catalysed addition of solvent to some alkenes at 25 °C [a]

| Compound (Solvent) | $SE$ [b] | $k$/l mol$^{-1}$ s$^{-1}$ |
|---|---|---|
| ($H_2O$) |  |  |
| Cyclohexene | 2.5 | 4.43 × 10$^{-8}$ [c] |
| 1-Methylcyclohexene | 1.7 | 3.05 × 10$^{-4}$ [c] |
| Bicyclo[4.2.1]non-1(8)-ene | — | 0.278 [d] |
| Bicyclo[3.3.1]non-1-ene | 23 | 31.4 [d] |
| (MeOH) |  |  |
| *cis*-Cyclo-octene | 7.4 | (1.7 ± 0.9) × 10$^{-8}$ [e] |
| *trans*-Cyclo-octene | 16.7 | (5.1 ± 0.1) × 10$^{-5}$ [e] |
| *cis*-Cycloheptene | 6.7 | (2.2 ± 0.3) × 10$^{-8}$ [e] |
| *trans*-Cycloheptene | 27 | 17 ± 2 [f] |
| 1-Phenyl-*trans*-cycloheptene | — | 10$^3$ [g] |

[a] Sulphuric acid was used. [b] Strain energy in kcal mol$^{-1}$; P. M. Lesko and R. B. Turner, *J. Am. Chem. Soc.*, 1968, **90**, 6888; refs. 2 and 14. [c] W. K. Chwang, V. J. Nowlan, and T. T. Tidwell, *J. Am. Chem. Soc.*, 1977, **99**, 7233. [d] Y. Chiang, A. J. Kresge, and J. R. Wiseman, *J. Am. Chem. Soc.*, 1976, **98**, 1564. [e] Ref. 8; temperature 25.0 ± 0.1 °C. [f] This work; temperature *ca.* 25 °C. [g] Ref. 10; ambient temperature.



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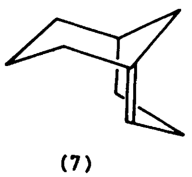

(7)

Similar enhanced reactivities were also observed for both *trans*-cyclo-octene and, to a much greater extent, *trans*-cycloheptene (1*t*). The observed enhancement, by a factor of 3 × 10$^3$, for *trans*-cyclo-octene is not unexpected from the results for the bridgehead alkenes carrying a *trans*-cyclo-octene structure. It should be noted, however, that *trans*-cycloheptene undergoes protonation at a rate 7.7 × 10$^8$ times faster than the *cis*-isomer and 3.3 × 10$^5$ times higher than its higher homologue, *trans*-cyclo-octene, whereas 1-phenyl-*trans*-cycloheptene, a trisubstituted *trans*-cycloheptene, gives a much faster rate of protonation under similar conditions.[10] These rate constants are well correlated with the strain energies [2,14] of the *trans*-cycloalkenes which are released upon protonation forming relaxed cycloalkyl cations.

Although we have only limited data, more quantitative treatment of the above results may give further insights into the strain energy–reaction rate relationship. From the Arrhenius equation, the relative rate ($k_{rel.}$) of protonation between highly and less strained cycloalkenes, *e.g.* (1*c*) and (1*t*), is expressed by equation (xii) where the subscript 0 refers to the

$$\log k_{rel.} = \log k/k_0 = \log A/A_0 + (E_{a0} - E_a)/2.303RT \quad \text{(xii)}$$

appropriate reference cycloalkene, *i.e.* (1*c*) in this case. As can be seen from Table 5, a higher strain gives a faster rate. We then assume that the activation energy difference ($\Delta E_a = E_{a0} - E_a$) is proportional to the strain energy difference ($\Delta SE = SE - SE_0$), *i.e.* $\Delta E_a = \alpha \Delta SE$. We now obtain

**Table 6.** Relative rates of protonation

| Cycloalkene | $\Delta SE$ | $\log k_{\mathrm{rel.}}$ |
|---|---|---|
| (1*c*) | ≡0 | ≡0 |
| *cis*-Cyclo-octene | 0.7 | −0.11 |
| *trans*-Cyclo-octene | 10 | 3.37 |
| (1*t*) | 20 | 8.89 |

equation (xiii). A plot of $\log k_{\mathrm{rel.}}$ *versus* $\Delta SE$ on (1*c*), (1*t*),

$$\log k_{\mathrm{rel.}} = \log A/A_0 + \alpha\Delta SE/2.303RT \qquad \text{(xiii)}$$

and *cis*- and *trans*-cyclo-octene (Table 6) gave a fairly good straight line (*r* 0.993) with a slope of 0.45 mol $\mathrm{kcal}^{-1}$ and we can calculate the $\alpha$ value to be 0.61; *ca.* 60% of the strain-energy difference contributes to reducing the activation energy. It is thus shown that the reaction rate is quantitatively related to the strain energy at least for the protonation of cycloalkenes. More data are apparently required in order to establish the general strain–reactivity relationship.

We may conclude that definitive evidence for the existence of *trans*-cycloheptene is presented by the low-temperature photosensitization of the *cis*-isomer by methyl benzoate, and some aspects of the chemistry and thermodynamics of the *trans*-isomer are also elucidated.

## Experimental

*Materials.*—Cycloheptene (Nakarai) was purified (>99%) by fractional distillation. The photosensitizers (Nakarai) were purified by distillation or repeated recrystallization. Pentane and cyclo-octane were stirred over sulphuric acid until the acid layer no longer turned yellow, washed with water, dried ($K_2CO_3$), and fractionally distilled. Methanol was fractionally distilled after refluxing overnight with magnesium turnings. ' Guarantee grade ' sulphuric acid (Nakarai) was used without further purification.

*Analyses.*—G.l.c. analyses of the reaction mixture were performed on a 1.5 m column of 10% Apiezon L; cyclo-octane was used as internal standard. After irradiation, the acidic reaction mixture was usually poured into an excess of aqueous potassium carbonate solution and its pentane extract was subjected to g.l.c. analysis. The results were consistent within experimental error with those from the direct injection onto a column of the acidic mixture.

*Photolyses.*—Throughout the work, a 300-W high-pressure mercury lamp and quartz tubings were employed and all irradiations were run under nitrogen. Kinetic studies were carried out in a merry-go-round apparatus at room temperature (*ca.* 25 °C).

The chemical actinometer used was the methyl benzoate sensitized *cis–trans* photoisomerization of cyclo-octene,[1] the quantum yield of which have been calibrated by potassium ferrioxalate actinometry.[15]

Low-temperature irradiations by the same light source were performed in a dry ice–methanol bath through a transparent quartz Dewar vessel. Although a merry-go-round could not be used at this temperature, the light intensity was checked frequently and was found to be constant within experimental error.

*Identifications.*—Photochemically produced methoxycycloheptane (2) in a preparative-scale irradiation of (1*c*) in acidic methanol was identical with an authentic specimen [6] prepared by the reaction of cycloheptanol with sodium hydride and the subsequent treatment with methyl iodide.

The pyrazoline (3) was identified by the characteristic N=N absorption bands in the i.r. and u.v. spectra. Upon irradiation through a Pyrex filter, the pyrazoline (3) gave *cis*- and *trans*-bicyclo[5.1.0]octane (4*c* and *t*). The authentic *cis*-bicyclooctane (4*c*) was synthesized independently by a modified Simmons–Smith reaction of cycloheptene with di-iodomethane in the presence of a zinc–copper couple.[16] The *trans*-bicyclooctane (4*t*) was identified only from its g.l.c. retention time on Apiezon L and PEG-6000 columns and the mass spectrum; the fragmentation patterns of (4*c* and *t*) resembled each other: g.l.c.-m.s. (15 eV), (4*c*), *m/e* 110(14%), 95(32), 82(60), 81(58), 69(34), 68(40), 67(100), 55(36), 54(90), 53(20), 41(78), and 39(40); (4*t*), *m/e* 110(10%), 95(27), 82(67), 81(71), 69(42), 68(36), 67(100), 55(47), 54(88), 53(24), 41(93), and 39(40). Furthermore, both (4*c* and *t*) were not hydrogenated over 5% Pd–C at a hydrogen pressure of 1 atm., indicating the absence of double bonds.

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## References

1 Y. Inoue, S. Takamuku, Y. Kunitomi, and H. Sakurai, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1672.
2 N. L. Allinger and J. T. Sprague, *J. Am. Chem. Soc.*, 1972, **94**, 5734.
3 E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Am. Chem. Soc.*, 1965, **87**, 934.
4 P. J. Kropp, *J. Am. Chem. Soc.*, 1969, **91**, 5783.
5 J. Th. M. Evers and A. Mackor, *J. R. Netherlands Chem. Soc.*, 1979, **98**, 423.
6 Y. Inoue, S. Takamuku, and H. Sakurai, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1635.
7 (*a*) E. J. Corey and J. I. Schulman, *Tetrahedron Lett.*, 1968, 3655; (*b*) T. V. Van Auken and K. L. Rinehart, jun., *J. Am. Chem. Soc.*, 1962, **84**, 3736.
8 Y. Inoue, T. Ueoka, and T. Hakushi, *J. Chem. Soc., Chem. Commun.*, 1982, 1076.
9 N. L. Allinger, *J. Am. Chem. Soc.*, 1958, **80**, 1953.
10 R. Bonneau, J. Joussot-Dubien, J. Yarwood, and J. Pereyre, *Tetrahedron Lett.*, 1977, 235.
11 R. Bonneau, P. F. de Violet, and J. Joussot-Dubien, *Nouv. J. Chim.*, 1977, **1**, 31.
12 Y. Inoue, S. Takamuku, and H. Sakurai, *J. Phys. Chem.*, 1977, **81**, 7.
13 S. Goto, S. Takamuku, H. Sakurai, Y. Inoue, and T. Hakushi, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1678.
14 P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Am. Chem. Soc.*, 1970, 92, 2377.
15 C. A. Parker, *Proc. R. Soc. (London), Ser. A*, 1953, 104.
16 R. J. Rawson and I. T. Harrison, *J. Org. Chem.*, 1970, **35**, 2057.

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