***trans*-Cycloheptene. Photochemical Generation and Thermal *trans-cis* Isomerization**

By YOSHIHISA INOUE,* TOSHIHIKO UEOKA, TAKAYUKI KURODA, and TADAO HAKUSHI
(*Department of Applied Chemistry, Himeji Institute of Technology, Shosha* 2167, *Himeji, Hyogo* 671—22, *Japan*)

Summary *trans*-Cycloheptene was prepared at −78 °C by a singlet-sensitized photoisomerization of the *cis*-isomer, and its lifetime was measured at temperatures between −7·0 and +1·0 °C to give thermodynamic parameters

for the thermal *trans–cis* isomerization: $E_a = 18{\cdot}7$ kcal mol^{-1}, $\log A = 12{\cdot}2$.

---

trans-Cycloheptene has long been postulated in synthetic and photochemical reactions,[1–3] and is believed, on the basis of trapping experiments, to exist briefly at room temperature. However, there still remains some doubts about the existence of *trans*-cycloheptene in its ground state,[4] since most experiments have been conducted in the presence of trapping agents such as isobenzofuran[1] or acidic methanol,[2,3] which would react with the other reactive intermediates or electronically exicted states formed in the course of the reaction.

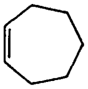
In the present work, *trans*-cycloheptene (**1*t***) was prepared at −78 °C by a singlet-sensitized photoisomerization of the *cis*-isomer (**1c**), and its lifetime was measured at temperatures between −7·0 and +1·0 °C to give the thermodynamic parameters for thermal *trans–cis* isomerization. The potential curve for the ground state of cycloheptene is also discussed quantitatively.

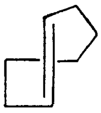
Table 1. Benzoate photosensitization of (**1c**) at −78 °C.[a]

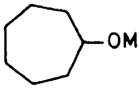
Run	[H_2SO_4] /mM	Yield[b]/% (**1c**)	 (**2**)
1	0	89	0
2	27[c]	76	15
3	27[d]	74	16

[a] Irradiations by a 300 W high pressure mercury lamp were conducted (for 5 min) of neutral (runs 1 and 3) or acidic (run 2) methanol solution [containing 9·1 mM (**1c**) and 11 mM $PhCO_2Me$] in a quartz tube which is immersed in a dry ice–methanol bath. After irradiation, the solution was gradually warmed up to room temperature without further treatment (runs 1 and 2) or with acidification (run 3). [b] Yield based on (**1c**) used. [c] Added *before* irradiation. [d] Added *after* irradiation.

The photosensitized isomerizations of (**1c**) were carried out in neutral and acidic methanol solutions at −78 °C under a nitrogen atmosphere in the presence of methyl benzoate as a sensitizer. The conditions and the results are shown in Table 1. The sensitized irradiation of (**1c**) in acidic methanol (run 2) gave methoxycycloheptane (**2**) in 15% yield along with recovered (**1c**) (76%),† while photolysis in neutral methanol (run 1) resulted in recovery of the starting material (**1c**) in 89% yield.‡ Although *trans*-cycloheptene (**1*t***) is an attractive candidate for the precursor of the adduct ether (**2**) as has been proposed previously,[2] an electronically excited state of (**1c**) is an alternative precursor. In order to rule out this possibility (run 3) the same solution as in run 1 was irradiated at −78 °C under the identical conditions, allowed to stand for 10 min at this temperature after irradiation, and then the acid was added. Upon gradual warming of the solution, the adduct (**2**) was obtained in 16% yield, which is comparable to that for run 2. This result clearly indicates that the precursor of (**2**) is not an electronically excited state but a reactive ground-state molecule, *i.e.* *trans*-cycloheptene (**1*t***). Since the total recoveries [combined yields of (**1c**) and (**2**)] are comparable for runs 1—3, the *trans*-cycloheptene 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).


(1c)


(1*t*)



(2)

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

Compound	Temp./°C	Lifetime
(**1*t***)[a]	1·0±0·1	9·7±0·3 min[c]
(**1*t***)[a]	−3·0±0·1	14·4±0·6 min[c]
(**1*t***)[a]	−5·4±0·1	22·4±1·0 min[c]
(**1*t***)[a]	−7·0±0·1	26·3±0·9 min[c]
(**1*t***)[a]	20	47 s[c,d]
1-Phenyl-*trans*-cycloheptene[b]	Ambient	250 s[e]
trans-Cyclohept-2-enone[b]	Ambient	45 s[f,g]
trans-Cyclohept-2-enone[a]	Ambient	0·303 s[f,h]

[a] Methanol solution. [b] Cyclohexane solution. [c] This work. [d] Obtained by extrapolation of the Arrhenius plot. [e] Ref. 4a. [f] Ref. 4b. [g] Major decay process is reaction with *cis*-cyclohept-2-ene. [h] Major decay process is reaction with the solvent, methanol.

The lifetime of (**1*t***) was measured at a variety of temperatures utilizing the reaction of (**1*t***) with acidic methanol. Several methanol solutions (3 ml) of (**1c**) (0·01 M) and methyl benzoate (0·01 M) were irradiated at −78 °C for 10 min under identical conditions; each irradiated solution was then kept at the desired temperature of −7·0 to +1·0 °C for a definite period and then chilled again to −78 °C. Subsequently, pre-cooled methanol (0·3 ml) containing an excess of sulphuric acid (0·3 M) was added to the treated solution, and the mixture was gradually warmed up to room temperature and subjected to analysis on g.l.c. (Apiezon Grease L) for the adduct (**2**).§ A plot of log [(**2**)] as a function of time gave a good linear relationship at each temperature employed, indicating unimolecular decay of (**1*t***) to (**1c**). The lifetimes thus obtained are shown in Table 2 and are unexpectedly long for the highly strained compound (strain energy 27 kcal mol^{-1}).[5] An extrapolated lifetime of (**1*t***) at 20 °C is compared with that of 1-phenyl-*trans*-cycloheptene and of *trans*-cyclohept-2-enone in Table 2.

† In the absence of u.v. light, no (**2**) was formed even after leaving the solution at room temperature for 24 h.

‡ In all runs, four cross-adducts (*m*/*e* 232) of (**1c**) with the sensitizer were also obtained in *ca.* 3% combined yield. The adducts would account for a part of the unrecovered (**1c**). The irradiation in neutral methanol also give three cyclodimers of (**1c**) (*m*/*e* 192, not hydrogenated on Pd/C), in *ca.* 1% yield, although these dimers disappeared under acidic conditions (runs 2 and 3).

§ Throughout this work, the amount of (**2**) detected on g.l.c. was taken as equal to that of (**1*t***) present in the solution. This assumption is not valid if any cycloheptyl cation, formed through protonation of (**1*t***), undergoes deprotonation regenerating (**1c**). However, the lifetimes derived from the measurement of the adduct (**2**) are essentially correct, since the amount of (**2**) detected will still be proportional to that of (**1*t***) remaining in the treated solution.

Plot of log k and log (k/T) *vs.* $1/T$ gave the following thermodynamic parameters for the thermal *trans–cis* isomerization: E_a 18·7 ± 1·2 kcal mol^{-1}; log A 12·2 ± 0·9; $\Delta G^{\ddagger}_{270}$ 19·4 kcal mol^{-1}; $\Delta H^{\ddagger}_{270}$ 18·2 ± 1·2 kcal mol^{-1}; $\Delta S^{\ddagger}_{270}$ −4·4 ± 4·4 cal K^{-1} mol^{-1}.¶ The fairly high activation energy and the negative entropy of activation should be noted. The present activation energy (18·7 kcal mol^{-1}) and the previously calculated strain energy (27 kcal mol^{-1}) and torsion angle (*ca.* 125°) of (**1*t***)[5] enables us to visualize more precisely the potential curve for the ground state of cycloheptene.

The authors thank the Ministry of Education of Japan for partial support of this research.

(*Received*, 6*th July* 1981; *Com.* 781.)

¶ 1 cal = 4·18 J.

[1] E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Am. Chem. Soc.*, 1965, **87**, 934.

[2] P. J. Kropp, *J. Am. Chem. Soc.*, 1969, **91**, 5783.

[3] Y. Inoue, S. Takamuku, and H. Sakurai, *J. Chem. Soc., Perkin Trans.* 2, 1977, 1635.

[4] Spectroscopic and kinetic properties of 1-phenyl-*trans*-cycloheptene and *trans*-2-cycloheptenone are now well established; (a) R. Bonneau, J. Joussot-Dubien, J. Yarwood, and J. Pereyre, *Tetrahedron Lett.*, 1977, 235; (b) R. Bonneau, P. Forner de Violet, and J. Joussot-Dubien, *Nouv. J. Chim.*, 1977, **1**, 31; (c) R. Bonneau, *J. Am. Chem. Soc.*, 1980, **102**, 3816; (d) P. E. Eaton, *Acc. Chem. Res.*, 1968, **1**, 50. However, these results are not sufficient to confirm the existence of *trans*-cycloheptene itself, since these *trans*-cycloheptene derivatives contain conjugated chromophores and are greatly stabilized through conjugation.

[5] N. L. Allinger and J. T. Sprague, *J. Am. Chem. Soc.*, 1972, **94**, 5734.