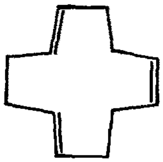
Tetrahedron Letters No.26, pp. 2161-2166, 1965 Pergamon Press Ltd.
Printed in Great Britain.

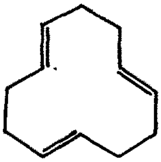
THE PHOTO-SENSITIZED ISOMERIZATION OF *cis,trans,trans*-1,5,9-CYCLODODECATRIENE

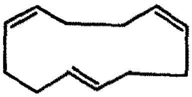
H. Nozaki, Y. Nisikawa, Y. Kamatani and R. Noyori
Department of Industrial Chemistry, Kyôto University
Kyôto, Japan

(Received 3 May 1965)

The *cis-trans* isomerization of *cis,trans,trans*-1,5,9-cyclododecatriene (I) by free radicals has recently been described by Duck and Locke (1) to afford the all-*trans* triene (II) in 43% yield (2). The present communication is concerned with the photosensitized isomerization of I to II in improved yields as well as with the transformation of I to its *cis,cis,trans*-isomer (III), the direction of the isomerization depending on the sensitizers used. This photo-isomerization technique would probably constitute the easiest preparative approach to the *cis,cis,trans*-triene (III) at present (3).


I


II


III

Experimental results have been summarized in Table I. The

TABLE I. THE PHOTO-SENSITIZED ISOMERIZATION OF I

Sensitizer	% Recovery of the Triene Fraction	% Content of		
		I	II	III[a]
None	95	93	4	3
None[b]	81	91	3	6
Acetone[c,d]	92	41	12	47
Cyclododecanone[c]	100	65	9	26
Cyclohexanone[e]	86	78	7	15
Dicyclopropyl ketone[c]	93	64	11	25
Camphor[e]	95	87	5	8
Acetophenone[e]	96	52	39	9
Benzophenone[e]	85	79	15	6
Benzaldehyde[e]	93	85	11	4
Anthraquinone[e]	53	53	40	7
1,4-Naphthoquinone[e]	82	72	26	2
p-Benzoquinone[e]	85	79	19	2
Biacetyl[e]	86	83	8	9
Benzil[e]	85	88	17	5
9,10-Dibromoanthracene[c]	100	76	22	2
Acridine[c]	100	94	6	tr.
Fluorenone[c]	100	96	4	tr.
Michler's ketone[c,f]	100	97	3	0
Dibenzalacetone[c,f]	100	97	3	0
Triphenylene[c,f]	100	97	3	0
Cuprous chloride[g]	95	64	10	26

a. These values were calculated based on the peak areas in the gas chromatogram.

b. In this particular experiment 0.1 molar benzene solution of I was irradiated with an immersion-type low pressure mercury arc (12W) for 300 hrs.

c. After 200 hrs. irradiation the presence of the sensitizer was indicated by gas chromatography and/or infrared spectroscopy.

d. This ratio reached practically constant after 100 hrs. irradiation.

e. The sensitizer could not be detected after the irradiation.

f. No reaction.

g. In this particular experiment 0.1 molar solution of I in ether containing catalytic amount of cuprous chloride was irradiated with an immersion-type low pressure mercury arc (12W) for 100 hrs. During this period the lamp wall was covered by metallic copper, which was scaled off after each 10 hrs. irradiation. For the photochemical reactions of olefins in the presence of cuprous chloride, see ref. 4.

triene I used had the purity of 97% and contained 3% of II. One molar solutions of I in benzene initially containing 0.2 mole equivalent each of sensitizers were placed in Pyrex glass test tubes and were irradiated externally with a 200W high pressure mercury arc at 10-15° under nitrogen atmosphere for 200 hrs. Other irradiation conditions, <u>i.e.</u>, the absence of the solvent or the filter, resulted in poorer recovery of the triene fraction and/or lower conversion. The mixtures were analyzed by gas chromatography with polyethylene glycol (PEG-6000) treated with silver nitrate as a stationary phase. Relative retention times of I, II and III were 1.00, 0.75 and 1.10, respectively. Every component was isolated by preparative gas chromatography and its infrared spectrum was found to be completely superimposable on the one of the corresponding authentic sample (3). In the absence of the sensitizers the triene I remained practically unchanged after 200 hrs. irradiation of the neat liquid with the same light source and Pyrex filter. It proved also stable towards γ-ray irradiation (1.2×10^7 r. total dosis during 170 hrs.) (6).

Data in Table I clearly indicate that aliphatic ketones (acetone and cyclohexanone, _etc._) give higher contents of the isomer III, whereas aromatic ketones (acetophenone and benzophenone) or quinones give mainly the isomer II. Notably, the isomerization does occur to a slight extent upon irradiation of the benzene solution of I in the absence of any added sensitizers. This benzene-sensitized (7) slow isomerization affording the isomer III predominantly appears to be inhibited by Michler's ketone, dibenzalacetone or triphenylene.

Some sensitizers were found to be consumed progressively during the irradiation. The formation of benzopinacol was observed in the benzophenone-sensitized reaction, but other by-products arising from sensitizers have not been characterized yet. Renewed addition of sensitizers naturally improves the conversion in these cases. Irradiation of 1 molar benzene solution of I in the presence of acetophenone (totally 0.8 mole equivalent added in portions) for 300 hrs. followed by careful fractional distillation (_ca._ 30 theoretical plates) gave about 70% yield of pure all-_trans_ isomer (II), m.p. 30-32°.

The cis-trans isomerization of non-conjugated double bonds of 1,5,9-cyclododecatriene would probably involve an endothermic triplet energy transition as proposed by G. S. Hammond et al. (8) for the isomerization of 2-pentene (8d). No definite correlation between the triplet energy (E_T) (9) and the product composition can, however, be drawn at present.

REFERENCES

1. E. W. Duck and J. M. Locke, Chem. and Ind. 507 (1965).
2. For thermal and catalytic cis-trans isomerization of I, see G. Wilke, Angew. Chem. 75, 10 (1963).
3. All three isomers, I, II and III have been recorded. See H. Breil, P. Heimbach, M. Kröner, H. Müller and G. Wilke, Makromol. Chem. 69, 18 (1963).
4. (a) R. Srinivasan, J. Amer. Chem. Soc. 85, 4045 (1963); (b) idem, ibid. 85, 3048 (1963); (c) idem, ibid. 86, 3318 (1964).
5. The sample was kindly supplied by Mr. H. Takahasi, Government Industrial Research Institute, Osaka, Japan.
6. The authors are indebted to Professor S. Okamura for this irradiation experiment.
7. For benzene-sensitized photochemical isomerization in solutions, see (a) V. A. Krongauz, Dokl. Akad. Nauk S.S.S.R. 155, 658 (1964); Chem. Abstr. 61, 5481 (1964); (b) H. Morrison, J. Amer. Chem. Soc. 87, 932 (1965).
8. (a) J. Saltiel and G. S. Hammond, J. Amer. Chem. Soc. 85, 2515 (1963); (b) G. S. Hammond and J. Saltiel, ibid. 85, 2516 (1963); (c) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt and C. Dalton, ibid. 86, 3197 (1964); (d) G. S. Hammond, N. J. Turro and P.

A. Leermakers, *J. Phys. Chem.* **66**, 1144 (1962); (e) For benzophenone-sensitized photo-equilibration between oleic acid and elaidic acid, see A. C. Testa, *J. Org. Chem.* **29**, 2461 (1964).

9. W. G. Herkstroeter, A. A. Lamola and G. S. Hammond, *J. Amer. Chem. Soc.* **86**, 4537 (1964).