

Photochemical Transformations of Tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene

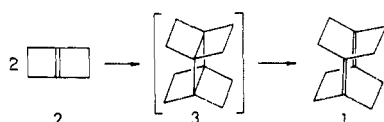
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The photolysis of tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (1) in an argon matrix at 15 K leads to 1,2,5,6-tetramethylenecyclooctane (5) and 2,5-dimethylenetricyclo[4.2.2.0^{1,5}]decane (4) as the primary photoproducts. The latter diene is formed in the less stable boat conformation. The photolysis of 1 in solution leads to polymer along with a compound that appears to be the Diels-Alder adduct between 1 and 5.

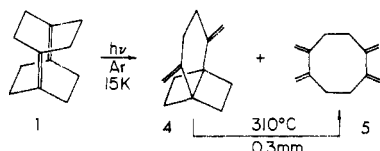
Tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (1) is formed from bicyclo[2.2.0]hex-1(4)-ene (2), probably via the pentacyclic propellane 3 as an intermediate.¹ In view of the thermal



instability of [2.2.2]propellane,² 3 would be expected to rearrange rapidly to 1 under the conditions used for the dimerization (~50 °C). We would like to examine the properties of 3, and therefore we have explored the possibility of forming it via photolysis of 1.

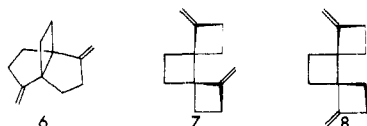
When 1 was irradiated in a pentane solution with a medium-pressure mercury lamp, only polymer was formed. In order to minimize bimolecular reactions, the photolysis of an argon matrix containing 1 was examined at 15 K. A relatively rapid reaction occurred as shown by the loss of characteristic infrared bands of 1. They were replaced by bands at 890 and 3090 cm⁻¹ which are characteristic of C=CH₂ groups.

The products were characterized by transferring the material and examining its NMR spectrum in CDCl₃ solution. The presence of 2,5-dimethylenetricyclo[4.2.2.0^{1,5}]decane (4), the thermal Cope rearrangement



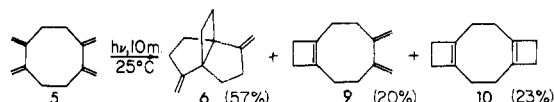
product of 1,¹ was easily demonstrated. Two other major products were observed. One appeared to be 1,2,5,6-tetramethylenecyclooctane (5) and was confirmed by comparison with the spectrum of an authentic sample prepared by the vacuum pyrolysis of 4 at 310 °C.

The other major product was found to have 4 olefinic and 12 aliphatic protons and to have a degree of symmetry consistent with structures 6, 7, and 8. The first of these



compounds has been reported by Borden et al.³ to be formed via the photolysis of 5. A comparison with an authentic sample showed that the propellane 6 was the

third major product. Both 9 and 10³ were found as minor products of the photolysis of 1.

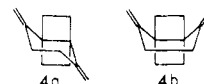


Although the products of the photolysis have been identified, some questions remain. Do the reactions proceed via the propellane 3 as an intermediate? Is tetramethylenecyclooctane 5 a primary photoproduct, or is it formed from the diene 4 in a secondary photochemical step? In order to examine these questions, the photolysis was repeated under different conditions, giving the data shown in Table I.

Photolysis of 1 for a short time (5 min vs. 50 min) gave essentially the same product composition except that less 6, 9, and 10 were formed. The latter products are then formed via photolysis of 5. However, the ratio of 4 to 5 was constant, suggesting that both are formed as primary photoproducts.

When 4 was photolyzed either in a matrix at 15 K or in pentane solution at room temperature, only a slow reaction was observed leading to the formation of 5 and its photoproducts. The photolysis of 5 in a matrix led to 6 and 9 but no 4 or 10. Photolysis in pentane solution at room temperature gave a comparable result except that 10 was also formed.

Although the above results suggest that both 4 and 5 are primary photoproducts, it must be recognized that 4 may exist in two conformers, 4a and 4b. The chair conformer,



4a, presumably has the lower energy and would be the species that is deposited in the argon matrix at 15 K. However, it is likely that the material formed in the photolysis of 1 would be the boat conformer, 4b. It is known that the twist-boat conformer of cyclohexane is a stable species below 70 K.⁴ Evidence for the formation of 4b was obtained by examining the infrared spectrum of the photolysis products formed from 1 in the matrix. Some strong bands observed in the matrix spectrum of 4a were absent in the photolysis products. However, when the latter were transferred to a CDCl₃ solution and the NMR spectrum was examined, the bands due to 4a were observed. It seems clear that the photolysis of 1 initially gave 4b, which then was converted to 4a when removed from the matrix.

Irradiation of 1 in pentane solution gives mainly a polymer, along with a small amount of another compound













(1) Wiberg, K. B.; Maturro, M. G.; Okarma, P. J.; Jason, M. E. *J. Am. Chem. Soc.* 1984, 106, 2194.

(2) Eaton, P. E.; Temme, G. H., III. *J. Am. Chem. Soc.* 1973, 95, 7508.

(3) Borden, W. T.; Reich, I. L.; Sharpe, L. B.; Weinberg, R. B.; Reich, H. J. *J. Org. Chem.* 1975, 40, 2438.

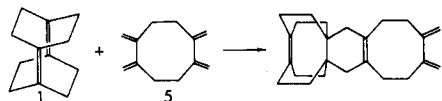
(4) Squillacote, M.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* 1975, 97, 3244.

Table I. Products of the Photolysis of Tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene and Related Compounds

reactant	conditions	products, %				
						
	15 K, 50 min, Ar	24	37	31	8	<i>b</i>
	12 K, 5 min, Ar	27	43	27	3	<i>c</i>
	15 K, 30 min, Ar	88	4	5	3	<i>c</i>
	15 K, 20 min, Ar		46	35	19	<i>c</i>
	25 °C, 5 min, C ₆ H ₁₂	<i>b</i>				
	25 °C, 30 min, C ₆ H ₁₂	62	6	22		<i>b</i>
	25 °C, 10 min, C ₆ H ₁₂ ^a			57	20	23

^a97% conversion. ^bTrace. ^cNone.

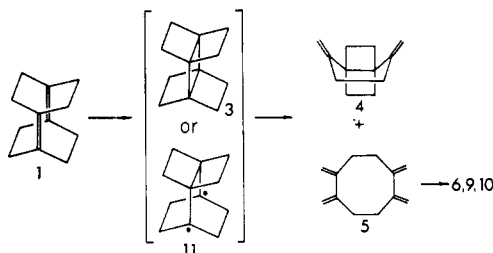
which was identical with the product formed when 1 and 5 were mixed as a pentane solutions. This is presumably



a Diels-Alder adduct. Thus, 5 is formed rapidly on photolysis of 1. If 4 were formed first and then was converted to 5, 4 should readily give 5 in an independent photolysis. However, the photolysis of 4 in solution proceeds very slowly. Since there is no conformational problem in solution, one must conclude that 5 is a primary photoproduct. The Diels-Alder adduct may react with itself to form polymer, but this reaction was found to be relatively slow. The origin of the polymer found in the solution photolysis of 1 is not clear at this time.

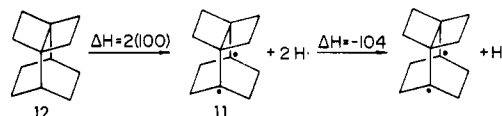
In a final matrix photolysis, 1 was irradiated in an argon matrix at 12 K and the infrared spectrum was recorded after 30 s, 2, 12, and 30 min. The bands due to 1 disappeared, and those of the products increased as the photolysis was continued. No other bands were observed. Therefore, no significant concentration of 3 was developed during the photolysis.

The photolysis of 1 may proceed through a vibrationally excited 3 which rapidly goes to products or may proceed via the diyl 11. Both 4b and 5 are initial photoproducts, and 6, and 9, and 10 are secondary photoproducts.



The photochemical intramolecular cyclization of dienes has been examined by Osawa et al.,⁵ who found that good

yields were generally found when the strain increase in the reaction was less than ~70 kcal/mol but that the reactions generally failed when the strain increase was larger than this value. In the present case, the strain increase on going from 1 to 3 may be estimated to be 123 kcal/mol,⁶ and therefore it is likely that it proceeds via the diyl 11. An estimate of ΔH_f for 11 may be obtained from the MM2⁷ ΔH_f for 12 of 44 kcal/mol and by using ~100 kcal/mol for the dissociation of the CH bonds which will lead to 11.



Since the combination of the two hydrogen atoms will be exothermic by 104 kcal/mol⁸ for 11, $\Delta H_f = 44 + 200 - 104 = \sim 140$ kcal/mol. This is close to the estimated $\Delta H_f = 131$ for 3. Although these estimates may not be very accurate, they again suggest that the photolysis of 1 could lead to 11 rather than 3.

Experimental Section

1,2,5,6-Tetramethylenecyclooctane (5). A 12-in. 10-mm glass tube was packed with stainless steel mesh and heated to 310 °C. A flask containing 175 mg of 2,5-dimethylenetricyclo[4.2.2.0]-dodecane (4) was attached at one end and cooled in liquid nitrogen, and a liquid nitrogen cooled trap was attached at the other end. The system was evacuated to 0.25 torr, and the diene was slowly distilled through the tube as it allowed to come to room temperature. The crude pyrolysate was shown by ¹H NMR spectroscopy to contain essentially only 5. Pure 5 was obtained by preparative gas chromatography using a 10 ft × 1/4 in. 5% Carbowax 20M column at 126 °C. The ¹H NMR spectrum (250 MHz, CDCl₃) had bands at δ 2.40 (s, 8 H), 4.81 (d, *J* = 2 Hz, 4H, and 4.90 (d, *J* = 2 Hz, 4H).

Matrix Isolation. The cryostat consisted of an Air Products Displex closed-cycle refrigerator which was capable of reaching

(6) The ΔH_f of 3 has been estimated to be 131 kcal/mol,¹ leading to a strain energy of 167 kcal/mol. The ΔH_f of 1 has been estimated to be 54 kcal/mol, leading to a strain energy of 44 kcal/mol.

(7) Allinger, N. L. *J. Am. Chem. Soc.* 1977, 99, 8127.

(8) Cottrell, T. L. "The Strengths of Chemical Bonds"; Butterworths: London, 1958.

a temperature of 12 K. The sample was deposited on a cesium iodide cold window (5 mm × 25 mm). It was contained in a vacuum shroud which had four ports. One port was attached to a 2.5-L manifold having an argon inlet and a trap containing the sample to be deposited. A second port had a quartz window which was used during irradiation. The other two ports were fitted with 5 mm × 37.5 mm potassium bromide plates.

In a typical deposition, the system was evacuated until the pressure dropped below 2×10^{-5} torr. The refrigerator was turned on, and the window was cooled to 20 K. The valve between the manifold and shroud was closed, and the manifold was filled with argon to 640 torr. The sample trap was maintained at an appropriate temperature, the valve was opened, and argon was bled over the sample at a rate of about 6.3×10^{-6} mol/s. The mixture of argon and substrate was allowed to collect on the cesium iodide plate. Typically, 100–200 torr of argon was deposited over the course of 1–2 h.

The shroud was rotated 90°, and the spectrum of the matrix was obtained with a FT-IR spectrometer. Rotation of the shroud so that the sample faced the quartz window allowed irradiation to be effected. The IR spectrum was again obtained. The products could be removed from the window by turning off the refrigerator and pumping the volatiles out through a U-tube cooled in liquid nitrogen (6–12 h).

Matrix Photolysis of Tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (1). A sample of the diene was deposited as described above. Because of the low volatility of 1 the sample was maintained at room temperature during the deposition. The infrared spectrum had bands at 572 (s), 644 (s), 941 (w), 1201 (m), 1216 (s), 1465 (w), 1478 (m), and 1480 (m) cm^{-1} , in addition to CH stretching bands. The matrix was photolyzed at 15 K for 50 min with a 450-W Hanovia medium-pressure mercury lamp. After photolysis the IR spectrum had bands at 887 (m), 888 (m), 889 (m), 893 (v s), 983 (w), and 1216 (w) cm^{-1} in addition to broad weak bands at 1430–1460 and 1590–1650 cm^{-1} .

The products were collected, and the NMR spectrum was determined in CDCl_3 (250 MHz). The composition was as follows: 2,5-dimethylenetricyclo[4.2.2.0]decane (4), 24%; 1,2,5,6-tetramethylenecyclooctanes (5), 37%; 4,5-dimethylenebicyclo[6.2.0]dec-1(8)-ene (9), 8%; 2,6-dimethylenetricyclo[3.3.2.0]decane (6), 31%. Photolysis for only 5 min gave 92% conversion and essentially the same product distribution (Table I).

Matrix Photolysis of 2,5-Dimethylenetricyclo[4.2.2.0]decane (4). A sample of the diene was deposited as described above with the sample at room temperature. The IR spectrum of 4 had bands at 527 (w), 697 (m), 892 (s), 1440 (m), 1444 (m), and 1646 (s) cm^{-1} in addition to CH bands. After photolysis for 30 min, the IR spectrum was virtually unchanged. The material was collected from the plate and the NMR spectrum showed 88% unchanged 4, 4% 5, 5% 6, and 3% 9.

Matrix Photolysis of 1,2,5,6-Tetramethylenecyclooctane (5). A sample of the tetraene was deposited as described above with sample trap cooled to -23°C . The IR spectrum had bands at 578 (w), 892 (s), 896 (s), 899 (s), 1589 (m), 1607 (m), 1611 (m), and 1630 (m) cm^{-1} along with CH stretching bands. It was photolyzed for 20 min. The IR spectrum of the products showed that the 578- cm^{-1} band had disappeared and the 890- cm^{-1} region

was much more complex. Prior to photolysis, the 890- cm^{-1} region was much more intense than the 1600- cm^{-1} region, but after photolysis the relative intensities were reversed. After removal from the window, the NMR spectrum of the products showed 46% starting material, 35% 6, and 19% 9.

Solution Photolysis of Tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (1). A solution of 6 mg of 1 in 8 mL of degassed pentane was placed in a quartz tube and was irradiated by a 450-W Hanovia lamp for 5 min. A white polymeric precipitate formed during the photolysis. The pentane solution was examined by ^1H NMR spectroscopy and was found to contain some 1, a very small amount of 4, and another compound characterized by very broad resonances. The tube was allowed to stand until no further polymer precipitated. The NMR spectrum showed that the remaining 1 had been converted to its bis(epoxide). In addition to the bands of the epoxide and of 4, there were olefinic bands at δ 4.77 (br s) and 4.63 (d, $J = 2$ Hz) in addition to broad upfield bands.

Solution Photolysis of 2,5-Dimethylenetricyclo[4.2.2.0]decane (4). A solution of 25 μL of 4 in 4 mL of degassed pentane was placed in a quartz tube under nitrogen. The course of irradiation with a 450-W Hanovia lamp was monitored by gas chromatography using a 10 ft × $1/4$ in. 5% Carbowax 20M column at 130°C . The reaction was found to proceed slowly. After 30 min, only 38% of 4 had undergone reaction. Analysis by NMR (250 MHz) indicated the formation of 22% 6, 10% 9, and 6% 5.

Reaction of Tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (1) with 1,2,5,6-Tetramethylenecyclooctane (5). A solution of 3 mg of 5 in 0.5 mL of pentane was added to a stirred solution of 10 mg of 1 in 4 mL of pentane. The solution was stirred for a few minutes, and the solvent was removed under reduced pressure. The ^1H NMR spectrum of the residue showed the presence of 1 and 5 in addition to new olefinic bands at δ 4.77 (br s) and 4.63 (d, $J = 2$ Hz) and a series of broad bands from δ 1.6–2.9. The spectrum of this material was the same as that obtained from the above photolysis.

Solution Photolysis of 1,2,5,6-Tetramethylenecyclooctane (5). A solution of 10 mg of 5 in 2 mL of degassed pentane was placed in a quartz tube and was irradiated with a 450-W Hanovia lamp for 10 min. Examination of the products by GC showed only a small amount of starting tetraene along with the two previously observed products: 2,6-dimethylenetricyclo[3.3.2.0]decane (6) and 4,5-dimethylenebicyclo[6.2.0]dec-1(8)-ene (9). A third product, tricyclo[8.2.0.0^{4,7}]dodeca-1(10),4(7)-diene (10) also was found. The four alkenes were separated by GC using a 10 ft × $1/4$ in. 5% Carbowax 20M column at 130°C . The NMR spectrum of 6 had bands at β 2.16 (s, 8 H) and 2.28 (s, 8 H).

Acknowledgment. This investigation was supported by NSF Grant CHE81-21421. P.O. thanks the Dox Foundation for a fellowship. We appreciate the assistance of Professor Weston Borden in supplying spectral data for compounds 6, 9, and 10.

Registry No. 1, 77422-56-1; 1:5 Diels–Alder adduct, 97521-75-0; 4, 60123-41-3; 5, 27567-69-7; 6, 28547-76-4; 9, 97521-76-1; 10, 6788-95-0.