column to remove solvent and to afford 4.5 g (56%) of diene **12**, bp 115 °C.

[2,4-$^2H_2$]-3-Methylcyclohexa-1,4-diene (13). Diene **13** was purchased from Isomet Crop., NJ. The route of synthesis consisted of Birch reduction of [2,6-$^2H_2$]benzoic acid followed by a sequence of steps analogous to those above to convert the carboxyl group into a methyl group (cf. ref, 11). The resultant methylcyclohexadiene (**13**) had 90% deuterium incorporated at C-2 and at C-4.

[4-^{2}H]-1-Methylcyclohexa-1,4-diene (15). Diene **15** (80% ^{2}H) was prepared by Birch reduction of [4-^{2}H]toluene[9] (80% ^{2}H) as described previously.[18]

Deuterated Toluene Oxides (1, 8, 14). Toluene 1,2-oxides **1** and **8** were prepared from dienes **12** and **15**, respectively, as described previously for the preparation of toluene 1,2-oxide[13] except that dehydrobromination of the dibromo epoxide was effected with 1,5-diazabicyclo[4,3.0]non-5-ene (DBN) in ether at room temperature. Toluene 2,3-oxide **14** was prepared from diene **13** as described for the unlabeled compound.[11] Oxide **8** had 80% ^{2}H at C-4 (^{1}H NMR), oxide **1** had 99% ^{2}H at C-2, and oxide **14** had 90% ^{2}H at C-2 and C-6.

Aromatization of 8. *o*-Cresol from **8** was brominated to afford 4,6-dibromo-2-methylphenol,[19] and the deuterium content at C-5 was determined from the 60-MHz ^{1}H NMR spectrum [δ 7.32 (H_3), 7.49 (H_5)]. The deuterium content at C-5 of the dibromo compound from aromatization at different pH's was 78% (pH 1.1), 79% (pH 4.0), 79% (pH 7.0), and 80% (pH 10.0).

Acknowledgment. We are grateful to the National Institutes of Health, Grant 1 RO1 GM 26388, and the North Atlantic Treaty Organization, Grant 1807, for financial support. We are also pleased to acknowledge the assistance of Dr. H. Fales and Mr. W. Comstock of the NIH in obtaining mass spectra.

Registry No. **1**, 76758-22-0; **8**, 76758-23-1; **9**, 76758-24-2; **10**, 76758-25-3; **11**, 76900-74-8; **12**, 76900-73-7; **13**, 76900-72-6; **14**, 76758-26-4; **15**, 76758-27-5.

---

(18) Jerina, D. M.; Daly, J. W.; Witkop, B. *J. Am. Chem. Soc.* **1968**, *90*, 6523–6525.

(19) Shriner, R. L.; Fusion, R. C.; Curtin, D. Y. "The Systematic Identification of Organic Compounds", 5th ed.; John Wiley and Sons: New York, 1964; pp 298, 374.

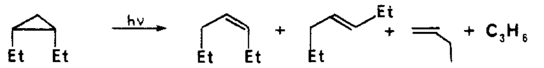
Organic Photochemistry with 6.7-eV Photons: *cis*- and *trans*-Bicyclo[6.1.0]nonanes

R. Srinivasan,* Jose A. Ors, and Thomas Baum

IBM, Thomas J. Watson Research Center,
Yorktown Heights, New York 10598

Received November 7, 1980

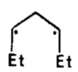
It had been reported previously[1] that photolysis of 1,2-dialkylcyclopropanes in solution with 185-nm radiation gave both one- and two-bond cleavage, typically as shown in eq 1. *cis*-1,2-Diethylcyclopropane (**1**) gave the products



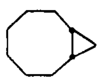
(1)

shown in eq 1 which were visualized to arise via the intermediates **1a** and **1b**. The unanswered questions from

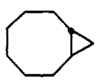
1a



1b



2



3

this study were (i) the failure to detect *trans*-1,2-diethylcyclopropane from the cis isomer by the reversal of the processes by which **1a** and **1b** were formed and (ii) the varying ratio of *cis*- to *trans*-3-heptene that was observed to depend on the starting material, which did not fit the idea of common intermediate(s) or agree with results by other workers[2] on the gas-phase photolysis of other 1,2-dialkylcyclopropanes.

A significant part of the problem in the study of 1,2-diethylcyclopropane was the meager yield of products from a one-bond cleavage and the formation of two small fragment molecules from a two-bond cleavage. In order to overcome these difficulties, an investigation of the photochemistry of the bicyclo[6.1.0]nonanes **2** and **3** was undertaken. The homologous relationship of these compounds to cyclooctene, the stereoisomerization of which is a successful reaction at 185 nm,[3] suggested that stereoisomerization may be observed in this instance as well.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer and/or a Beckman Acculab-6 spectrometer. The solvent was CCl_4 in all instances. NMR spectra were recorded on a Varian T60-1A spectrometer with CCl_4 as solvent and tetramethylsilane as internal reference. Mass spectra were recorded on a Du Pont 21-490B mass spectrometer.

Apparatus. The equipment for photolyses on both preparative (0.1–0.5 g) and quantitative scales has been described.[4] Irradiation at 214 nm was conducted in a cylindrical quartz cell of 50-mL volume the center of which was placed a Phillips Zn resonance lamp. The useful radiation was the Zn resonance line at 214 nm.

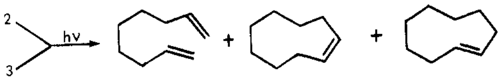
Materials. Compounds **2** and **3** were prepared by using methods described in the literature.[5] *trans*-Cyclononene was obtained from the photoisomerization of *cis*-cyclononene[6] on a preparative scale. All reactants were purified by GLC and their purities checked on two different columns.

Procedure. A solution of the reactant (~10^{-2} M) in pentane was placed in a cylindrical cell (volume 9.3 mL) with a Suprasil window and flushed with nitrogen. Photolyses were carried to conversions of <20%, and the initial, linear portion of the rate curve was extrapolated to zero time.

The products were analyzed on a Perkin-Elmer 3920B gas chromatograph fitted with a Carbowax column (14 ft × $^1/_8$ in.) or a gum rubber column of the same dimensions.

Results

Photolyses of both **2** and **3** gave rise to mixtures of 1,8-nonadiene (major product) and *cis*- and *trans*-cyclononenes (eq 2). There was no evidence for the formation



(2)

of **2** in the photolysis of **3** or of **3** from the photolysis of **2**. The limit of detection was 4% of the reactant that had disappeared.

The rates of formation of the products in the photolysis of either **2** or **3** are shown as a composite plot in Figure 1. The uncertainty in the determination which is principally in the analysis for the products is indicated by

---

(1) R. Srinivasan and J. A. Ors, *J. Org. Chem.*, **44**, 3426 (1979).

(2) J. H. Vorachek and R. D. Koob, *J. Phys. Chem.*, **76**, 9 (1972); K. Dees and R. D. Koob, *ibid.*, **77**, 759 (1973).

(3) Y. Inoue, S. Takamuku, and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, 423 (1976); *J. Phys. Chem.*, **81**, 7 (1977); R. Srinivasan and K. H. Brown, *J. Am. Chem. Soc.*, **100**, 2589 (1978); H.-P. Schuchmann, C. von Sonntag, and R. Srinivasan, *J. Photochem.*, **15**, 159 (1981).

(4) R. Srinivasan and L. S. White, *J. Am. Chem. Soc.*, **101**, 6389 (1979).

(5) S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 2225 (1961); A. C. Cope and J. Hecht, *ibid.*, **85**, 1780 (1963).

(6) *cis*-Cyclononene was prepared by the following procedures. 9,9-Dibromobicyclo[6.1.0]nonane was prepared by the method of W. v. E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **76**, 6162 (1954). 1,2-Cyclononadiene was prepared by the method of Skatteböl [*Tetrahedron Lett.*, **167** (1961)] and was mildly hydrogenated over palladium/carbon to give *cis*-cyclononene and cyclononane, which were GLC separated (24-ft, ucw-98 column).

0022-3263/81/1946-1950$01.25/0 © 1981 American Chemical Society

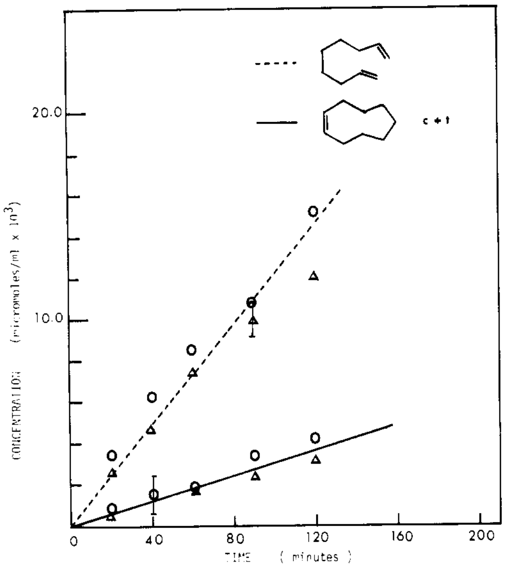


Figure 1. Composite plot of product concentration vs. time in the photolysis of bicyclo[6.1.0]nonanes: ○, *trans*-bicyclo[6.1.0]nonane; △, *cis*-bicyclo[6.1.0]nonane; reactions in pentane solution; 185-nm radiation.

vertical bars on two of the points. Within the experimental uncertainty, the rates are seen to be the same whether the starting material is 2 or 3. But the ratio of *trans*- to *cis*-cyclononene was not the same in both instances, the values being 0.45 and 0.80 from the cis and trans isomers. Since all of the useful radiation (185 nm) was totally absorbed by the reactant (at least at zero time) in these experiments, the rates may be considered to be proportional to the quantum yields. The apparent curvature for the yield of 1,8-nonadiene in the photolysis of the cis isomer is not only within the experimental uncertainty but is also at conversions at which the product must be absorbing the incident light to undergo secondary decomposition.

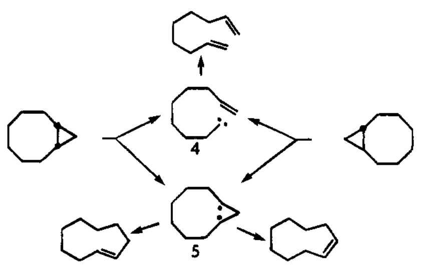
The photolysis of 2 in pentane solution at 214 nm was also studied. In this instance also, the products were the same (eq 2) as those in photolysis at 185 nm. The ratio of 1,8-nonadiene to cyclononene (cis plus trans) was 5.0 compared to the value of 4.3 at 185 nm. There was no indication of the isomerization of 2 to 3.

The photolysis of cyclononene in pentane solution at 185 nm was also investigated. Initially there was a rapid stereoisomerization reaction from either the cis or trans isomer to the other stereoisomer. The photostationary ratio may be considered to be quite close to a value of 0.90 although the formation of side products became noticeable well before this ratio was reached.

Discussion

The striking points in the present work are (i) the total similarity in the photochemistry of 2 to that of 3 in all but one detail and (ii) the absence of a stereoisomerization induced by light from 2 to 3 (or vice versa) in contrast to the ease with which this reaction occurs in cyclooctene.[3] These points will be discussed in order.

Scheme I



The similarity between 2 and 3 in their photochemical behavior is both qualitative and quantitative. It is best explained in terms of common intermediates as in Scheme I. This picture is consistent with earlier results[1,7] on the photochemistry of cyclopropanes in solution. But the single inexplicable feature that was found earlier, viz., the different ratios of trans to cis olefins that were obtained from the cis and trans reactants, persists in the present system. It may be observed that these ratios are not identical with the value at the photostationary state of cyclononene itself.

It is possible that the two-bond break *follows* the one-bond break as proposed by Rossi[8] from a theoretical analysis of the excited state of cyclopropane. In this instance, Scheme I should be rearranged to show 5 as the precursor to 4. The fact that 1,8-nonadiene is the major product further indicates that there is a strong tendency for 5 to go to 4 and then to 1,8-nonadiene, much less of a tendency to rearrange to cyclononene, and virtually no tendency to reclose to the starting material. This would rationalize the failure to detect any stereoisomerization of 2 to 3 or 3 to 2. It is tempting to view the two-bond cleavage as a reaction which would require more (activation) energy than the one-bond cleavage but the use of 214-nm radiation shows that in this instance there is more, not less, 1,8-nonadiene relative to cyclononene! Many of these uncertainties may be related to an emerging view[9] that the decomposition pathways in organic photochemistry in the far-ultraviolet are quite sensitive to small changes (1–2 kcal/mol) in the energy of the photon and hence to the level of excitation of the reacting molecule. These ideas are currently under investigation.

It is relevant to mention here that the photolysis of cyclononene with 185-nm radiation *in the vapor phase* has been studied before.[10] The products that were observed were 1,8-nonadiene and vinylcycloheptane in the ratio of 2:1. Since, in this work, *cis*- and *trans*-cyclononene were not separated from each other, it was not possible to observe any stereoisomerization. The present results show that the vapor-phase reaction bears little relationship to the reaction in solution.

Registry No. 2, 13757-43-2; 3, 39124-79-3.

---

[7] R. Srinivasan and J. A. Ors, *J. Am. Chem. Soc.*, 100, 7089 (1978).

[8] A. R. Rossi, *J. Phys. Chem.*, 83, 2554 (1979).

[9] R. Srinivasan and A. R. Rossi, to be submitted for publication.

[10] Y. Inoue, S. Takamuku, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, 49, 1147 (1976).

Aromatic Substitution: Regiospecific Synthesis of Highly Substituted Diphenyl Sulfones

James A. Kloek

Monsanto Agricultural Products Company, Research Department, St. Louis, Missouri 63166

Received September 17, 1980

The preparation of specifically substituted aromatic rings ranks as one of the oldest and most continually studied problems of organic synthesis. Although many general, efficient, highly workable methods have been developed, there remain specific areas where these classical

0022-3263/81/1946-1951$01.25/0