An attempt to prepare an allene by this method proved unsuccessful. Upon reaction with methyllithium, cinnamaldehyde tosylhydrazone gave a mixture of 14 products, none of which has, as yet, been completely identified. Thus, it appears that, in order for the elimination reaction to be successful, the α-hydrogen atom must be attached to a saturated carbon atom. Also, when the tosylhydrazone of piperitone was allowed to react under the described conditions, no diene was found. Thus, the α-hydrogen atom must be a methylene or methyl group for the reaction to proceed under these conditions; a similar restriction has been noted for the preparation of alkenes.[3b]

The following procedure is representative. A 250-ml, three-necked flask was fitted with a condenser and a magnetic stirring bar. In the flask was placed 7.5 g (0.05 mol) of carvone and 9.3 g (0.05 mol) of *p*-toluenesulfonylhydrazine. Sufficient tetrahydrofuran (~25–50 ml) was added to bring the reactants into solution, three drops of concentrated HCl was added, and the solution was refluxed for 6 hr. Benzene was added and tetrahydrofuran was distilled at atmospheric pressure from the reaction mixture, bp 66–67°. The temperature of the distillate then rose to 70° and the benzene–water azeotrope was allowed to distil. The distillation was continued until the temperature was near 80°. The reaction mixture was then cooled in an ice bath and 0.11 *M* of methyllithium in ether was added, dropwise, over a 40-min period with stirring. The ice bath was removed and water was slowly added to the slurry. The mixture was extracted with pentane, the extract dried, and the solvent removed to yield 5.15 g of 2-methyl-5-isopropenyl-1,3-cyclohexadiene.

(7) National Institutes of Health Postdoctoral Fellow, 1967–present.
(8) NDEA Predoctoral Fellow, 1965–present.
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The Photochemical Conversion of Cyclooctatetraene to Semibullvalene. Mechanistic and Exploratory Photochemistry. XXXVII[1]

Sir:

A goal of considerable interest is the delineation of the excited-state pathways interrelating the C_8H_8 hydrocarbons and extension of the study to the benzo derivatives.[2] In the course of these studies we have been investigating the photochemistry of cyclooctatetraene. Although cyclooctatetraene (**1**) has been obtained photochemically from barrelene and semibullvalene (**2**), and similar behavior has been found for the benzo derivatives,[2] such transformations have not been found to be photochemically reversible. Thus, benzene and acetylene[3] and the valence tautomer bicyclo[4.2.0]-octa-2,4,7-triene (**3**)[4] have been reported as being formed on photolysis of cyclooctatetraene, but no semibullvalene (**2**) has been noted. We now wish to report the formation of semibullvalene from cyclooctatetraene as the major product at low temperature from sensitized photolysis. The reaction is of both preparative and theoretical value.

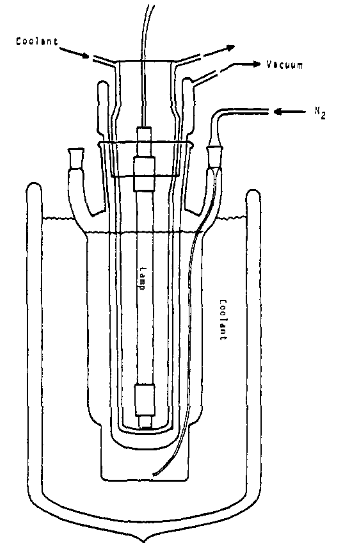


Figure 1.

In initial semimicro scale runs in a low-temperature infrared cell at −78°, irradiation of a 0.387 *M* solution of cyclooctatetraene in THF–*n*-propyl ether (2:1 v/v) led to a decrease of the 12.4- and 14.7-μ bands of reactant **1** and the appearance of peaks at 6.82, 12.68, and 14.6 μ which are characteristic of semibullvalene (**2**). Furthermore, this absorption remained upon warming the sample to room temperature. Preparative irradiation of cyclooctatetraene at low temperature was carried out in the apparatus depicted in Figure 1. Irradiation of 11.4 g of cyclooctatetraene in 500 ml of isopentane and 16.6 g of acetone at −60° with a 450-W medium-pressure lamp with a Vycor filter for 50 hr afforded a mixture which was shown by nmr and vpc to contain 9.27 g of cyclooctatetraene, 0.845 g of semibullvalene (**2**), and 0.340 g of benzene. Semibullvalene was separated from cyclooctatetraene (**1**) by crystallization of **1** from the mixture followed by aqueous silver nitrate–ether liquid–liquid partition chromatography. Final isolation was by preparative vpc. Separate experiments, including some in sealed quartz tubing attached to the medium-pressure lamp, showed: (1) that in the absence of acetone the reaction proceeded slowly, (2) that a stationary state of ~88% cyclooctatetraene and 12% semibullvalene could be reached by extended photolysis, and (3) that benzophenone and acetophenone were ineffective as sensitizers.

Prior to concerning ourselves with molecular details of the reaction mechanism, two points are of interest. First, the reaction clearly proceeds *via* the triplet, since without acetone the conversion is inefficient. Second,

(1) For paper XXXVI see H. E. Zimmerman and D. S. Crumrine, *J. Am. Chem. Soc.*, in press.

(2) (a) H. E. Zimmerman and G. L. Grunewald, *ibid.*, **88**, 183 (1966); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); (c) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 4191 (1968).

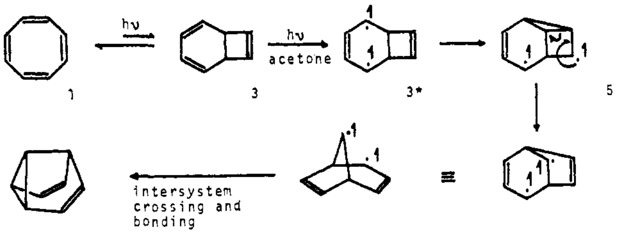
(3) (a) I. Tanaka, S. Miyakawa, and S. Shida, *Bull. Chem. Soc. Japan*, **24**, 119 (1951); (b) I. Tanaka and M. Okuda, *J. Chem. Phys.*, **22**, 1780 (1954).

(4) (a) E. Migirdicyan and S. Leach, *Bull. Soc. Chim. Belges*, **71**, 845 (1962); (b) G. J. Fonken, *Chem. Ind.* (London), 1625 (1963).

the present reaction is the reverse of the previously observed[2a,b] conversion of semibullvalene (**2**) to cyclooctatetraene (**1**).

Two molecular pathways seem reasonable possibilities for the reaction. One is based on the presumption that there is an appreciable concentration of bicyclo[4.2.0]octa-2,4,7-triene (**3**).[4–6] A di-π-methane rearrangement[7] of the type noted by us earlier[2b] as being general, when applied to this bicyclic intermediate (*i.e.*, **3**),[8] leads to semibullvalene (**2**) (note Chart I).

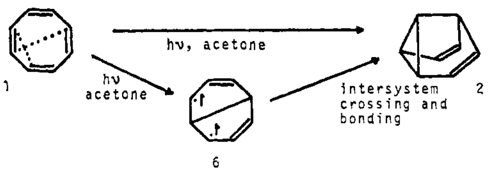
Chart I. Di-π-methane Route from Cyclooctatetraene to Semibullvalene



Interestingly, this mechanism proceeds *via* the same triplet biradical **4** that was demonstrated[2b] in the photolysis of barrelene to lead to semibullvalene.

The second pathway available is by 1,5 and 2,8 (or 4,6) bonding as depicted in Chart II.[9] However, the correct mechanism need not be the reverse of that utilized in the semibullvalene (**2**) to cyclooctatetraene reaction[2a] since, as has been pointed out,[12] microscopic reversibility is not easily invoked in photochemistry.

Chart II. Direct Route from Cyclooctatetraene to Semibullvalene



We are presently pursuing the mechanistic ramifications of this unusual new reaction.

Acknowledgment. Appreciation is expressed to the National Institutes of Health for support of this research by Grant GM07487.

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(5) It is possible that **3**, available thermally (R. Huisgen and F. Mietzsch, *Angew. Chem.*, **76**, 36 (1964)), is utilized in the reaction.

(6) In the present study no direct evidence was adduced for photochemical formation of **3**. Further studies on this point, the photochemistry of **3**, and detailed mechanistic investigations of the conversion are in progress.

(7) We now prefer the term di-π-methane rearrangement for this transformation since aryl-substituted methanes undergo the process as well as divinylmethanes, as has been noted.[2b]

(8) This compound has been independently synthesized by E. Vogel, H. Keifer, and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964).

(9) Such 1,5 bonding, as well as bonding of 1,3 related atoms in a π system, has been noted by us earlier[10] to be energetically favorable photochemically. More recently this has been considered by Woodward and Hoffmann.[11]

(10) H. E. Zimmerman, *J. Am. Chem. Soc.*, **88**, 1566 (1966).

(11) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(12) H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *J. Am. Chem. Soc.*, in press.

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Book Reviews

Catalytic Hydrogenation over Platinum Metals. By Paul N. Rylander, Research and Development Division, Engelhard Industries, Inc., Newark, N. J. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1967. xii + 550 pp. 16 × 23.5 cm. $22.50.

Catalytic hydrogenation is now a classical procedure for reducing a wide variety of functional groups, but few chemists are aware of the many different catalysts available or the most advantageous way to carry out a particular reduction. This information is widely scattered throughout the literature, and much of it has been published during the past 15 years. The object of this book is to collect, summarize, and interpret this information. The emphasis is on recent literature and on the practical side of the art; historical aspects are barely mentioned, and there is little mechanistic speculation. Only the platinum metals and their oxides are considered. The reader will have to look elsewhere for a discussion of other metal oxide catalysts and of sulfide catalysts which are competitive with the platinum metals and are preferable in certain situations. Nickel catalysts are mentioned only occasionally.

After a 50-page discussion of general matters (types of catalysts, certain of their properties, reactors, and reaction conditions), the work is organized according to the nature of the functional group to be reduced: acetylenes, olefins, imines, hydrazones, aldehydes, etc. A few of the interesting new catalytic procedures in the book are described below in order to give some idea of the newer material included. Iridium catalysts are especially useful in stereospecific hydrogenation of certain 16-methylene steroids to the β-methyl derivatives. Rhodium on alumina is superior to platinum and palladium for hydrogenation of vinyl or allylic halides to haloalkanes; the latter catalysts cause extensive hydrogenolysis. Certain optically active olefins are hydrogenated over platinum oxide with almost no racemization, but over palladium on carbon considerable racemization occurs; this indicates that double bond migrations during hydrogenations are more likely with palladium than with platinum. Reduction of oximes over a rhodium-on-carbon catalyst gives largely primary amines, whereas over platinum or palladium under similar conditions, secondary amines may be the principal products. Both the aromatic ring and the nitro group of aromatic nitro compounds can be hydrogenated in a single operation over a ruthenium catalyst. A trace of stannous chloride is a superior promotor for the reduction of aldehydes over platinum oxide, but it acts as a poison with a prereduced platinum catalyst. Palladium is often ineffective as a catalyst for the hydrogenation of ketones whereas platinum is usually satisfactory. Protonation of a ketone by hydrogenating in an acid medium greatly increases the rate of reduction over platinum catalysts, but rhodium and ruthenium catalysts are more active in neutral or basic solution. These are only some of the examples which show that organic chemists who employ catalytic hydrogenation have a wide variety of useful catalysts at hand, and that this book will be a source of many new ideas about how to carry out practical hydrogenations.

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