

PHOTOCHEMICAL VALENCE ISOMERIZATION*

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INTRODUCTION

The intensive investigation of organic photochemical systems that has taken place in the past fifteen years has resulted in the discovery of dozens of valence isomerization reactions, many of which were found to give novel and interesting products. Attention in this area has recently focused on the predictions made by Woodward and Hoffmann¹ on the basis of the conservation of orbital symmetry, concerning the stereochemistry of these reactions. The experimental study of the stereochemistry of a photochemical reaction contains a complication that is not to be found in thermal systems. Invariably, in a photochemical system, all that is known is that a molecule, A, in its electronic ground state is, on irradiation, transformed to a product, B, also in its electronic ground state. But in order to apply the orbital symmetry rules, it is imperative that all the intermediate steps be sorted out and the exact identity of the precursor to B be defined. In most organic molecules, at room temperature, it takes times of the order of only microseconds for initial electronic excitation, crossover to a second electronic state of a different multiplicity, internal conversion from either state to the ground state, and photochemical reaction so that the origin of the product is not readily discernible. In this lecture, we shall examine one of the systems for which a considerable amount of data are available, namely, the photochemical isomerization of a 1,3-diene to a cyclobutene and a bicyclo[1.1.0]butane.

1,3-BUTADIENE

Some time ago it was observed² that on exposure of 1,3-butadiene in solution in various solvents to 2537 Å radiation, a mixture of cyclobutene and bicyclo[1.1.0]butane was obtained in essentially quantitative yield. The ratio of cyclobutene to bicyclo[1.1.0]butane was between 7 and 14



under these conditions³. In view of the deceptive simplicity of these two valence isomerizations, we attempted to calculate from purely kinetic considerations what the relative importance of the two pathways should be.⁴ Since the calculation indicated that the ratio of cyclobutene to

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bicyclo[1.1.0]butane would be < 1 , it is merely of historic interest. But it is worth examining why it failed so completely. One of the assumptions made in it was that bicyclo[1.1.0]butane would be formed only from the transoid excited state of 1,3-butadiene and cyclobutene only from the cisoid excited state, and further both these isomerizations would proceed at comparable rates. There is evidence now to indicate that these two photo-reactions may proceed by entirely different mechanisms. We shall detail these here.

From orbital symmetry considerations, it was predicted¹ that the concerted photochemical closure of 1,3-butadiene to cyclobutene should proceed by a disrotatory mechanism. That the reaction did take place in this fashion was shown by Crowley⁵, and by Dauben and his coworkers⁶. More recently, we were able to demonstrate the occurrence of the same disrotatory mechanism, in a quantitative way, in a simple system with a minimum of stereochemical constraints on it⁷.

Irradiation of 2,4-hexadiene was shown to give *cis*-3,4-dimethylcyclobutene (I) and 1-ethyl-3-methylcyclopropene (II) in 33 and 5 per cent yields,

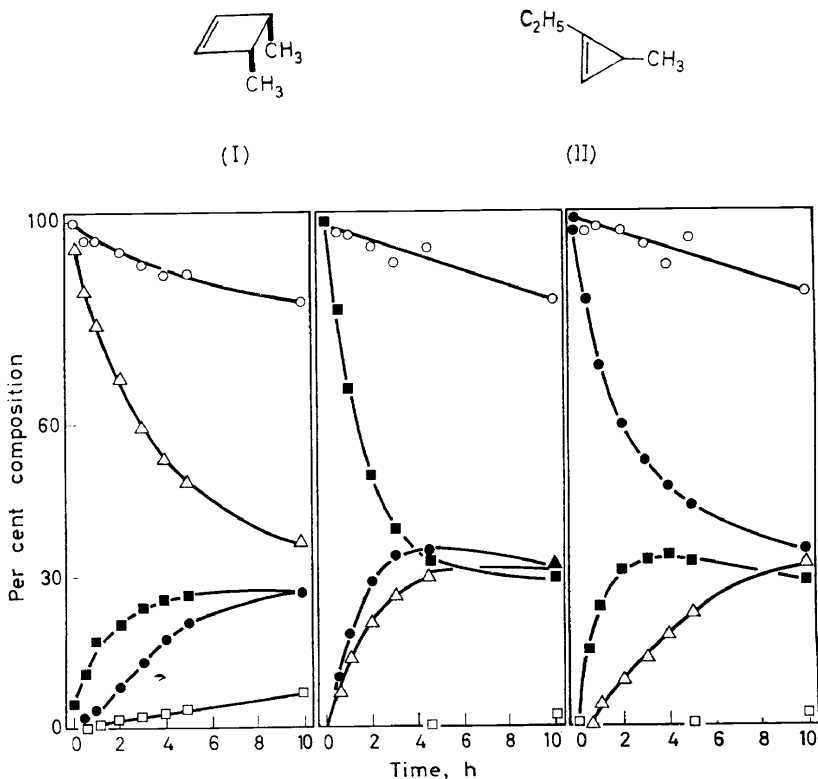
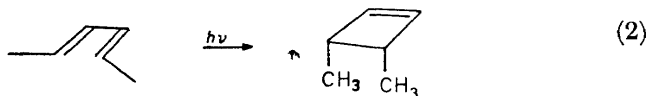


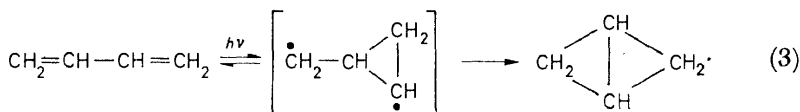
Figure 1. Formation of isomeric products from various 2,4-hexadienes as a function of time. \triangle *trans,trans*-2,4-hexadiene; \blacksquare *trans,cis*-2,4-hexadiene; \bullet *cis,cis*-2,4-hexadiene; \square *cis*-3,4-dimethylcyclobutene; \circ total C_6 compounds in system.

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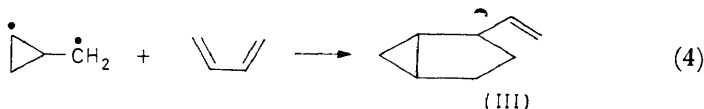
respectively. The rate data for the formation of *cis*-3,4-dimethylcyclobutene starting from pure *trans,trans*-, *trans,cis*-, and *cis,cis*-2,4-hexadienes are given in Figure 1. It can be seen that only with the pure *trans-trans*-isomer as the starting material is *cis*-3,4-dimethylcyclobutene formed in detectable amount even at zero time. Starting with either of the other two 2,4-hexadienes, the formation of I could be detected only when at least 20 per cent of the *trans,trans*-2,4-hexadiene had accumulated in the system. It was hence concluded that the cyclization proceeds according to Eq. (2) which verifies the predictions of Woodward and Hoffmann¹.



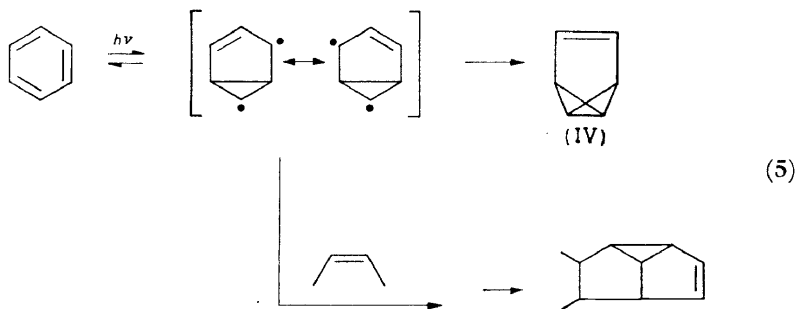
There are no data as yet to demonstrate the stereochemistry of the photochemical isomerization of a 1,3-butadiene to a bicyclo[1.1.0]butane. The process may not be conrotatory as it would lead to a *trans*-fused product, but a disrotatory process can lead to the right geometry⁸. However, whether the process is concerted or not is a debatable point. Experimental evidence can be adduced to support the view that the reaction may proceed by the following mechanism:



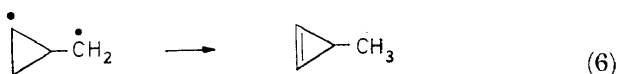
The presence of the diradical intermediate and its subsequent reaction with another molecule of 1,3-butadiene would readily explain the isolation of (III) as the most important dimeric product from the direct irradiation



of butadiene⁹. The dimers account for only about 10 per cent of the butadiene that is photolyzed, but a more important example of this reaction is the photochemical addition of benzene to olefins¹⁰. The isomerization of benzene to benzvalene (IV) is similar to reaction (1b) but the addition reaction is more successful in this instance possibly because the diradical intermediate can be stabilized by allylic resonance.



The intermediate in reaction (3) can also rearrange to a cyclopropene by the migration of a hydrogen:



A cyclopropene (II) has actually been isolated in the irradiation of *trans,trans*-2,4-hexadiene⁷. The photochemistry of 1,3-butadiene-1,1,4,4-d₄¹¹ suggests that butadiene itself may also rearrange according to Eq. (6), but the product is vibrationally hot and therefore unstable towards dissociation. It readily yields a methyl and a C₃H₃ fragment which, in turn, leads to secondary products. From 1,3-butadiene-1,1,4,4-d₄, both C₃H₂D and C₃D₂H radicals were shown to be formed¹¹. The distribution of the deuterium atoms in the products derived from these radicals can be qualitatively explained by the intermediacy of a cyclopropenyl radical.

It should be emphasized that there is no experimental result that rules out a concerted mechanism for the formation of bicyclo-[1.1.0]butane. Both concerted and radical pathways may also cross so that, depending on the reaction conditions, one or the other of the two mechanisms may be favoured. Along the diradical pathway [reaction (3)] a fairly large (>10 kcal/mole) activation energy could be expected to apply to the closure of the second cyclopropyl ring in bicyclo[1.1.0]butane. There is no obvious way to estimate the activation energy for a concerted closure to the bicyclo[1.1.0]butane.

CIS-3,4-DIMETHYLCYCLOBUTENE

The rules proposed by Woodward and Hoffman¹ may be used to identify the precursor for a given (concerted) process in a photochemical system from the stereochemistry of the transformation, provided it is known that the rules are obeyed in that system. This method is superior to the alternatives such as emission spectroscopy, or the use of quenchers for the identification of an electronically excited state because the information is obtained without replacing or destroying the photochemical reaction.

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The utility of this approach can be illustrated by an example: it is known that in their electronic ground states both *cis*- and *trans*-3,4-dimethylcyclobutenes undergo isomerization to a 2,4-hexadiene exclusively by a conrotatory mechanism¹². In the electronically excited state, it has already been pointed out that the cyclization of *trans,trans*-2,4-hexadiene also obeys the prediction based on orbital symmetry consideration⁷. It is, therefore, reasonable to expect that the stereochemistry of the electrocyclic reactions that are observed on electronically exciting the 3,4-dimethylcyclobutenes can be sorted out according to their stereochemistry by the application of these rules.

The decomposition of *cis*-3,4-dimethylcyclobutene sensitized by mercury (³P₁) atoms was studied in the gas phase over a range of pressure¹³. The products that were observed were 1,3-hexadiene, *trans,trans*-2,4-hexadiene, and *cis,trans*-2,4-hexadiene. There was only one isomer of 1,3-hexadiene present and this was most probably the *cis* compound. At low pressures, a trace of *cis,cis*-2,4-hexadiene was also formed.

Since the products were all conjugated dienes, it was probable that secondary photochemical reactions were also taking place. In order to minimize this complication, quantitative data were obtained from experiments in which a constant low pressure (20 Torr) of *cis*-3,4-dimethylcyclobutene was decomposed in the presence of varying pressures (0-480 Torr) of an inert gas (diethylether). The results are summarized in Figure 2.

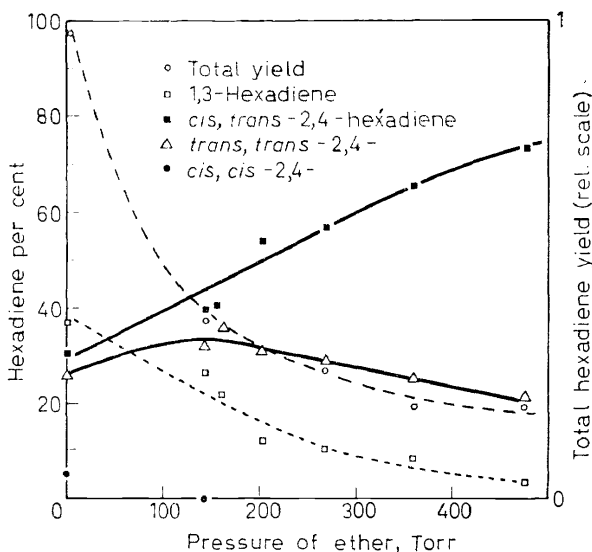
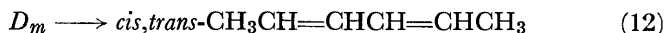
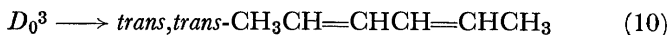
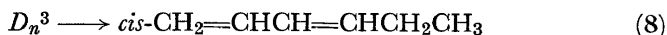
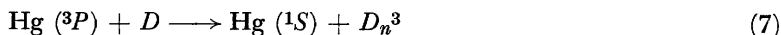


Figure 2. Isomerization of *cis*-3,4-dimethylcyclobutene sensitized by mercury (³P₁) atoms. Quencher: diethylether.

With an increase in the total pressure in the system, the total yield of the products is seen to decrease. This can be attributed mostly to the deactivation of the Hg (³P₁) atoms which sensitize the reaction, and in part to the deactivation of the excited molecules of *cis*-3,4-dimethylcyclobutene. Of

greater importance are the relative yields of the products. The yield of *cis,cis*-2,4-hexadiene is small even at low pressure and is entirely eliminated at about 130 Torr. It is probably formed in a secondary reaction. The primary isomerization products can be accounted for by the following mechanism wherein *D* stands for *cis*-3,4-dimethylcyclobutene and *M* for a molecule of the inert gas:



The superscripts and the subscripts refer to the multiplicities and the vibrational levels, respectively. The evidence for the mechanism is as follows: the data show that an increase in pressure favours the formation of *cis,trans*-2,4-hexadiene over *trans,trans*-2,4-hexadiene and the latter over *cis*-1,3-hexadiene. This suggests that quenching reactions such as (9) and (11) are important. Reactions in which the deactivation of Hg (3P_1) atoms and independently of D_n^3 take place should also be included, but are not shown here. The identities of the precursors for the products follow from the application of the Woodward-Hoffmann rules¹. The isomerization of *cis*-3,4-dimethylcyclobutene to *cis,trans*-2,4-hexadiene is a conrotatory process which can occur only in the ground electronic state. The isomerization to *trans,trans*-2,4-hexadiene is a disrotatory process which can occur only in the electronic excited state. The formation of *cis*-1,3-hexadiene appears to proceed only under conditions such that the formation of the 2,4-hexadienes is not favoured. Its precursor must, therefore, be the electronically excited state of *cis*-3,4-dimethylcyclobutene.

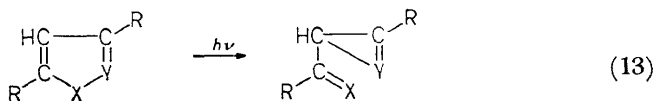
A discussion of the valence isomerization reactions in the 2,4-hexadiene system in terms of the orbital symmetry correlation diagram which was proposed by Longuet-Higgins and Abrahamson¹⁴ will be found elsewhere¹³.

5-MEMBERED HETEROCYCLIC COMPOUNDS

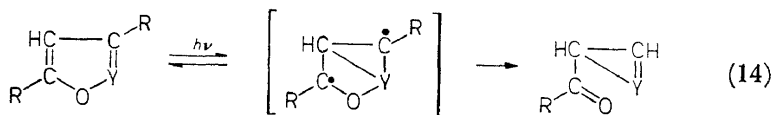
The photochemical valence isomerizations of a number of 5-membered heterocyclic compounds have been investigated. All of these molecules possess a conjugated diene chromophore which is modified to a varying degree by the presence of one or more hetero atoms. The ultraviolet spectrum of furan strikingly resembles that of 1,3-butadiene, that of thiophene less so, while the spectrum of pyrrole is considerably modified¹⁵. If 1,3-cyclopentadiene is also included in this group, it is seen that its spectrum does resemble 1,3-butadiene but is shifted towards red.

The photoisomerizations in many of these molecules can be related to the two reactions (1a, 1b) seen in 1,3-butadiene. The principal reaction in furan¹⁶ and isoxazole¹⁷ is:

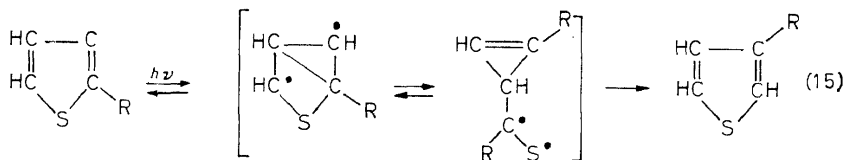
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By analogy with 1,3-butadiene the following mechanism which is related to (3) can be postulated:



In this view, the formation of the C=X bond is seen to act as a driving force to give a ring-contracted product from the intermediate diradical. When X = S, this driving force no longer exists, but the transient formation of a thioaldehyde or ketone, presumably in an excited state, would lead to the observed product which is the 3-substituted thiophene¹⁸:

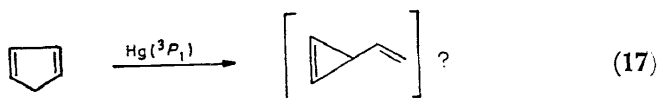


It is noteworthy that the over-all transformation from the 2-substituted to the 3-substituted compound is one that was first reported in isoxazoles¹⁷ and is also observed in furans^{19, 20}, and pyrazoles²¹.

An interesting case is that of 1,3-cyclopentadiene. If the photoreactions in the 5-membered heterocyclics are viewed as primarily those initiated by the conjugated diene chromophore, then these reactions can be expected to occur in the isoelectronic carbocyclic system. In solution, it has been reported²² that the photoisomerization of 1,3-cyclopentadiene gives bicyclo[2.1.0]-pent-2-ene which is a reaction analogous to (1a). The reaction



corresponding to (14) should give 3-vinylcyclopropene. Attempts to isolate this compound as a photoproduct were not successful²³. An alternative



route to the preparation of 3-vinylcyclopropene led to 1,3-cyclopentadiene as a major product which suggests that the photochemical ring contraction as in Eq. (17) can be readily reversed in a thermal process.

The thermochemistry of this reaction seems to support the idea. The thermal rearrangement of 3-vinylcyclopropene to 1,3-cyclopentadiene would probably have an activation energy which would be equal to the activation energy for the pyrolysis of cyclopropene (35 kcal/mole²³) less the difference in activation energies between the thermal isomerization of cyclopropane (65.0 kcal/mole²⁴) and of vinylcyclopropane (49.7 kcal/mole²⁵). The value of 20 kcal/mole thus obtained indicates that 3-vinylcyclopropene would have only limited stability at room temperature unless the pre-exponential factor in the Arrhenius expression is abnormally low.

One peculiar feature of the photoisomerization of 5-membered heterocycles is the strong directive influence that alkyl substituents have been shown to have on reactions such as (13) and (15). The effect seems to be quite general and has been well-documented in simple furans¹², highly-substituted furans²⁰ as well as in thiophenes¹⁸. A parallel situation exists in the photoisomerization of 1,3-butadienes to bicyclo[1.1.0]butanes in that even a single methyl substituent on the 1- or 2-position appears to reduce the yield to less than the point of detection. No rational explanation for these substitution effects has hitherto been put forward.

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