The Photochemistry of cis,trans-1,3,5-Hexatriene[1]

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The photolysis of cis,trans-1,3,5-hexatriene in the vapor phase led to the formation of hydrogen, benzene, 1,3-cyclohexadiene, 1,2,4-hexatriene and a liquid polymer. The structure of 1,2,4-hexatriene, which has hitherto not been described, was based on physical data, particularly the infrared spectrum. In quantitative studies, the rates of production of hydrogen and 1,2,4-hexatriene were measured as functions of the initial pressure of 1,3,5-hexatriene and of added foreign gases. The results may be best explained if it is postulated that from a single electronically excited state of 1,3,5-hexatriene, benzene and hydrogen or 1,2,4-hexatriene may be formed according to the vibrational energy possessed by the molecule. The relationship between the photochemistry of cis,trans-1,3,5-hexatriene and 1,3-cyclohexadiene is discussed. This relationship is similar to the one between precalciferol:tachysterol and ergosterol.

In a recent study of the photochemistry of 1,3-cyclohexadiene,[2] it was reported that at 4 mm. pressure the important products were hydrogen, benzene, 1,2,4-hexatriene[3] and a polymer. It has since been found that both in the vapor phase[4] and in condensed phases,[5,5a] 1,3,5-hexatriene is also formed. These results will be discussed later.

There is considerable evidence[6] that the formation of 1,3,5-hexatriene from 1,3-cyclohexadiene is one example of a very general photochemical reaction. The reverse reaction also occurs under the influence of light in at least one instance.[7] The main objective in the present study of the photochemistry of 1,3,5-hexatriene was to establish the relationship of this compound to the photochemistry of 1,3-cyclohexadiene.

Experimental

1,3,5-Hexatriene was made[8] from 1,5-hexadiene-3-ol by the method of Hwa, et al.[9] It was purified by distillation through a spinning-band column of 23 theoretical plates. A middle cut of 2–3 ml., b.p. 80.0° (uncor.), was collected, dried over Drierite and admitted into the vacuum system. It was degassed and stored at −78°. By vapor phase chromatography, it was found that this sample had a trace of water as the only impurity and that it was made up of about 17% cis and the rest trans-1,3,5-hexatriene. The infrared spectrum of the sample was in agreement with the published one[9] and also indicated that the trans isomer predominated over the cis isomer.

The apparatus and methods used were exactly as detailed in a previously study.[2] A clean cell was used in each experiment. Conversions ranged from 10 to 20%.

Hydrogen and the C₂ products were identified by mass spectrometry. The fraction non-volatile at −158° was introduced into a Perkin–Elmer 154-B vapor fractometer fitted with an 'A' column. The C₆ products were collected separately and identified by their infrared spectra in solution (solvent: CCl₄). 1,3-cyclohexadiene which was one of the products underwent further photolysis if it was allowed to build up in the system. Since it could not be separated cleanly from 1,3,5-hexatriene with the equipment that was available, its infrared spectrum could be obtained only as a

(1) The author wishes to thank the National Science Foundation for a grant to the Department of Chemistry, University of Rochester in support of this work.

(2) R. Srinivasan, J. Am. Chem. Soc., 82, 5063 (1960).

(3) In ref. 2, this product was incorrectly referred to as 1,3,4-hexatriene.

(4) R. Srinivasan, unpublished results.

(5) R. J. De Kock, Ph.D. Thesis, Rijksuniversiteit Te Leiden, 1959.

(5a) R. J. De Kock, N. G. Minnaard and E. Havinga, Rec. trav. chim., 79, 922 (1960).

(6) D. H. R. Barton, Helv. Chim. Acta, 42, 2604 (1959).

(7) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Co., New York, N. Y., 1959, p. 148.

(8) The author wishes to thank Mr. Edward Caress for the supply of a sample made in this way.

(9) J. C. H. Hwa, P. L. De Benneville and H. J. Sims, J. Am. Chem. Soc., 82, 2537 (1960).

mixture, and its identification is based on the intense absorption at 15.3 μ.

Results

The major products in the photolysis of 1,3,5-hexatriene were hydrogen, benzene, 1,3-cyclohexadiene, an oily liquid polymer and an unknown compound. By mass spectrometry this last product was found to have a molecular weight of 80 and hence isomeric to 1,3,5-hexatriene. Its vapor pressure at 29.3° (uncorr.) was 140.5 mm. Its infrared spectrum (Fig. 1) indicated the presence of an allenic group (5.18 μ) presumably monosubstituted as there was a strong band at 11.82 μ. The ultraviolet spectrum in the vapor phase showed a broad and intense absorption with a maximum close to 2200 Å. (molar absorption coefficient >2300). The instability of the product in solution made it difficult to obtain a clear nuclear magnetic resonance spectrum. It was nevertheless possible to conclude from the spectrum (CCl₄ solution: benzene as internal standard) that there were three aliphatic protons (8.25 τ-doublet) and five olefinic protons (band centered at 4.7 τ and ~1 τ wide). The product must therefore contain one double bond in addition to the allenic group. The absence of a strong absorption at 11.05 μ in the infrared excluded the possibility of a terminal double bond, while the presence of peaks at 6.1 μ and 10.4 μ indicated an internal double bond.[10] The structure 1,2,4-hexatriene would best fit all these observations.

In quantitative studies which were carried to low conversion it was not possible to separate by gas chromatography the benzene and 1,3-cyclohexadiene that were formed, from the (unreacted) 1,3,5-hexatriene. Hence, hydrogen and 1,2,4-hexatriene were the only products that were measured quantitatively, the former by the usual volumetric method and the latter by the area under the peak in the gas chromatogram. There was always a small amount of a C₂ fraction which consisted of ethylene and acetylene. These were not estimated separately.

The infrared spectrum of 1,3,5-hexatriene, after a portion of it had been photolyzed, indicated a decrease in the trans/cis ratio and at high conversions there was more cis than trans isomer left behind.

At 10 mm. pressure of 1,3,5-hexatriene, the observed C₂-C₆ products accounted for only about 30%

(10) The author wishes to thank Dr. J. H. Wotiz of the Diamond Alkali Company for his help in the deduction of the structure of this compound.
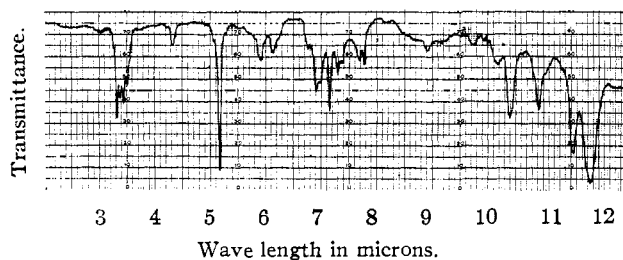
Fig. 1.—Infrared spectrum of 1,2,4-hexatriene; solvent, CCl_4; concn. 6%.

Fig. 2.—Effect of pressure of 1,3,5-hexatriene on formation of products. Unfiltered medium pressure Hg arc; path length 4.2 cm.; time 30 min.; temperature 27°: ●, hydrogen; □, C_2 hydrocarbons; O, 1,2,4-hexatriene.

of the reactant that was photolyzed. The rest probably went to form the polymer (compare 1,3-cyclohexadiene[2]). At a lower initial pressure there was a greater yield of volatile products, while at higher pressures the yield was lower. But even at 80 mm. initial pressure, all of the C_2 to C_6 products as well as hydrogen were observed to be formed, although the polymer was far more important than any of these. The ultraviolet transmission of the cell after photolysis merely showed a general absorption from 2000-3000 Å. which did not give any indication of the structure of the polymer (compare 1,3-cyclohexadiene[2]).

TABLE I

PHOTOLYSIS OF 1,3,5-HEXATRIENE IN THE PRESENCE OF FILTERS AND ADDED GASES

Room temperature; P = 10.3 mm.; t = 30 min. (except[b])

Filter	Gas added	Pressure, mm.	H_2	C_2	1,2,4-Hexatriene
None	None		2.39	0.36	2.83
Corex[a,b]	None		0.83	0.34	2.72
None	Oxygen	5.6	Present	?	2.95
None	Nitric oxide	12.5	Present	..	2.30
None	CO_2	16.7	2.26	..	2.67

[a] Corning clear glass filter which transmitted 60% at 3000 Å., 16% at 2800 Å. and 0.1% at 2500 Å. [b] t = 1070 min.

In Table I the influence of added gases and filter on the formation of hydrogen, C_2 hydrocarbons and 1,2,4-hexatriene are presented. In one experiment in which a Pyrex filter was used, no measurable decomposition was observed in 975 min. In Fig. 2 the effect of pressure of the formation of these products is shown.

Discussion

The ultraviolet absorption spectrum of 1,3,5-hexatriene above 2000 Å. consists of a banded region of intense absorption which stretches from 2300 to 2800 Å.[11] At longer wave lengths the absorption is weak. At the pressures used in this study, for a path length of 4.2 cm. (length of the cell used) absorption of the incident radiation would have ranged from 5-90% below 2800 Å. and less than 5% above this wave length. With the use of a Corex filter[12] the irradiation time had to be increased by a factor of 36 to obtain the same degree of decomposition as with an unfiltered light source, while with a pyrex filter no reaction was observed

(11) G. F. Woods and L. H. Schwartzman, *J. Am. Chem. Soc.*, **70**, 3394 (1948).
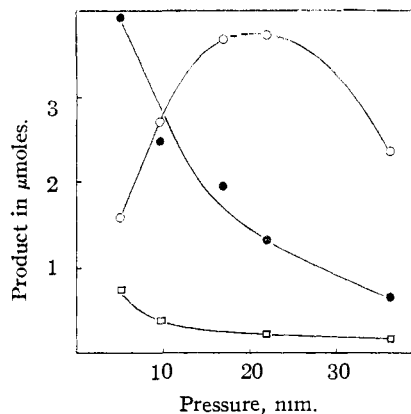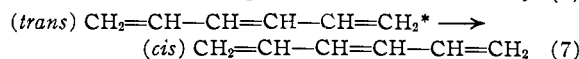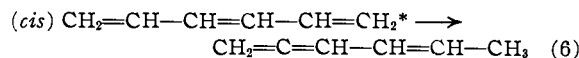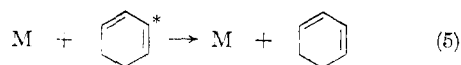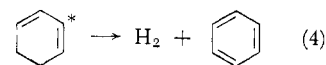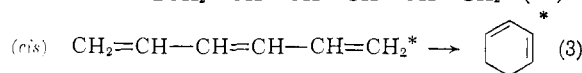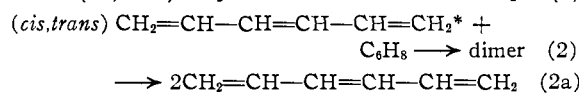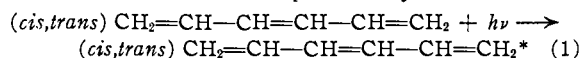
(12) See Table I for characteristics.

even with a 32-fold increase in irradiation time. From these observations it would appear that the photochemically useful radiation was confined to wave lengths shorter than 2800 Å.

In view of the poor mass balance that was obtained, the results of this study do not seem to have absolute quantitative significance. For this reason, quantum yields were not determined. But the relative yields of the products, which were found to be reproducible, show interesting trends.

The results can be explained by the mechanism

$$(cis,trans)\ CH_2=CH—CH=CH—CH=CH_2 + h\nu \longrightarrow$$
$$(cis,trans)\ CH_2=CH—CH=CH—CH=CH_2^* \quad (1)$$

$$(cis,trans)\ CH_2=CH—CH=CH—CH=CH_2^* +$$
$$C_6H_8 \longrightarrow dimer \quad (2)$$

$$\longrightarrow 2CH_2=CH—CH=CH—CH=CH_2 \quad (2a)$$

$$(cis)\ CH_2=CH—CH=CH—CH=CH_2^* \longrightarrow \quad (3)$$

$$\longrightarrow H_2 + \quad (4)$$

$$M + \quad \longrightarrow M + \quad (5)$$

$$(cis)\ CH_2=CH—CH=CH—CH=CH_2^* \longrightarrow$$
$$CH_2=C=CH—CH=CH—CH_3 \quad (6)$$

$$(trans)\ CH_2=CH—CH=CH—CH=CH_2^* \longrightarrow$$
$$(cis)\ CH_2=CH—CH=CH—CH=CH_2 \quad (7)$$

Since the total pressure of 1,3,5-hexatriene affected the relative yields of the various products, it is probable that the absorption of light initially leads to an excited state of the molecule. These excited molecules may be destroyed by deactivating collisions (2a), dimerization (2) or decomposition (3-7). Step 2 is pictured as the first in a series of reactions which lead to the formation of the polymer that was observed.

The formation of 1,2,4-hexatriene (6) may be an intramolecular process, as it is unaffected by the addition of oxygen or nitric oxide. The reaction would involve the transfer of a hydrogen atom *via* a six-membered ring intermediate which would be possible only if the central double bond is in the *cis* conformation. The analogous formation of 1,2-

butadiene from 1,3-butadiene is endothermic by 12.8 kcal.,[2] and the carryover of photochemical energy from this step in turn leads to the decomposition of 1,2-butadiene. Although step 6 may be endothermic by about the same energy, there is no reason to believe that the 1,2,4-hexatriene undergoes further decomposition.
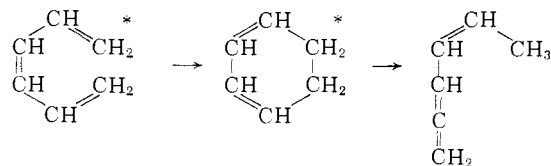
The formation of 1,3-cyclohexadiene from 1,3,5-hexatriene (3) would be endothermic by 10 kcal. if average values of C–C and C=C are assumed, and the molecules are "cold." Undoubtedly the cis isomer is the reactant in this step, as the central double bond is predisposed to ring closure. If the average energy of the photons is 124 kcal./mole (about 2300 Å.), there should be at least 100 kcal. left over in the cyclohexadiene molecule when it is formed in step 3. Hence, sufficient activation energy may be available for further decomposition of the 1,3-cyclohexadiene to benzene and hydrogen. As this would happen everytime unless the excited 1,3-cyclohexadiene is deactivated, step 5 is postulated to account for the presence of 1,3-cyclohexadiene in the products.[13]

The small amount of C_2 hydrocarbons in the products is probably from a split of 1,3-cyclohexadiene formed in step 3 to two acetylenes and an ethylene. This reaction is relatively more important in the photolysis of 1,3-cyclohexadiene.

Step 7 is postulated to account for the presence of more cis than trans isomer at the end of the photolysis. Such an isomerization under the influence of light is well known in other molecules.[14]

The effect of pressure on this system may be attributed to a competition between steps 3 and 6 for excited 1,3,5-hexatriene molecules. If absorption of radiation initially produces an electronically excited molecule with considerable amount of vi-

brational energy, then the rate of loss of this vibrational energy through collisions will be a function of pressure. For this reason, the process with a greater activation energy (presumably 3 followed by 4) will become less important as pressure increases (Fig. 2). Again, at 10 mm. pressure, if the shorter wave lengths are filtered out the effect is the same as an increase in pressure, which supports the idea that the vibrational energy (in the excited state) is the determining factor in the course of the reaction. The decrease in the yield of all the volatile products above 25 mm. may be due to a relative increase in dimerization (2) and deactivation of the electronically excited molecules (2a).

The great similarity in the products,[2] the effect of added gases[2] and of pressure[4] in the photochemistry of 1,3,5-hexatriene and 1,3-cyclohexadiene suggests that the two systems are related as shown
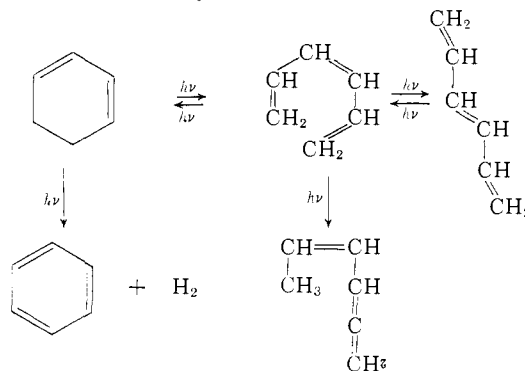
The obvious relationship of this system to the steroid system

$$\text{Ergosterol} \underset{h\nu}{\overset{h\nu}{\rightleftarrows}} \text{precalciferol} \underset{h\nu}{\overset{h\nu}{\rightleftarrows}} \text{lumisterol}$$

$$h\nu \uparrow \downarrow h\nu$$

tachysterol

may be mentioned. It has been deduced[15] that in the steroid system the photoisomerizations occurred from a singlet state of the molecule. The same conclusion may be reached in the C_6H_8 system too from the fact that oxygen has no effect on any of these processes.

(13) It is possible that the formation of 1,2,4-hexatriene (step 6) also goes through the intermediate formation of a "hot"-1,3-cyclohexadiene. Then the hydrogen transfer would be a four-center process as in 1,3-butadiene


Since 1,2,4-hexatriene appears to be a more important product in the photolysis of 1,3,5-hexatriene than of 1,3-cyclohexadiene, this mechanism need not be considered further.
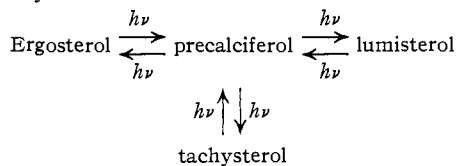
(14) A. Schönberg, "Präparative Organische Photochemie," Springer-Verlag, Berlin, 1958, p. 13.

(15) Ref. 5, p. 66.