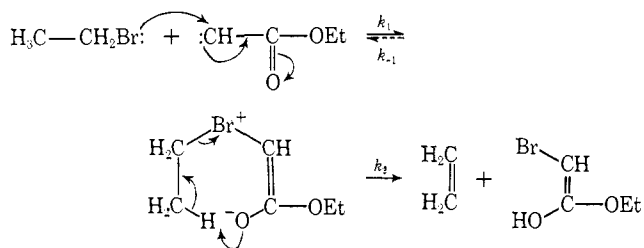


We envision the mechanism of the elimination reaction as involving the formation of an intermediate bromonium ylide.¹² If the ylide once formed does not



often regenerate carbene (*i.e.*, $k_2 \gg k_{-1}$), then within the limits of applicability of the steady-state approximation we would expect to see *no* primary kinetic isotope effect, as is indeed the case. In terms of the above mechanism, the observed absence of a primary kinetic isotope effect requires that k_1 (or the sequence of reactions represented by k_1) be rate determining. The observed stereoselectivity (but not stereospecificity) of the elimination reaction suggests a further breakdown of the ylide, perhaps to a diradical intermediate which can then collapse rapidly to give predominantly but not exclusively *cis* elimination product.¹³

We have extended our study to include the reaction between neopentyl bromide (no β hydrogens) and carbethoxycarbene. Here, direct carbon-hydrogen or carbon-bromine bond insertion might occur. Alternatively, abstraction of bromide ion by the carbene might occur, followed by rearrangement to a tertiary carbonium ion which might then either eliminate to form olefin or recombine with the BrC-HCOOEt moiety to give a "rearranged insertion product" (ethyl 2-bromo-3,3-dimethylvalerate). In our hands, the reaction gave only unrearranged insertion products; the C-Br bond insertion product (ethyl 2-bromo-4,4-dimethylvalerate) predominated over that arising *via* primary C-H bond insertion (ethyl 3,3-dimethyl-4-bromovalerate) by a factor of 4, despite the 9:1 statistical predominance of primary C-H bonds in the substrate!

In view of the observed predisposition of the carbene to insert into the C-Br bond in neopentyl bromide, we are currently examining the reaction of carbethoxycarbene with other suitably substituted alkyl halides which cannot directly react *via* β elimination with an eye toward the possible synthetic utility of this reaction. We shall communicate the results of our study shortly.

(11) Mass spectral deuterium analyses were performed in the laboratory of Mr. Seymour Meyerson, American Oil Co., Whiting Ind. We thank Mr. Meyerson for rendering his facilities and guidance in this connection.

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(13) We gratefully acknowledge the suggestions of a referee, which are embodied in our formulation of the elimination reaction mechanism.

(14) National Aeronautics and Space Administration Predoctoral Trainee, 1965-1968.

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Orbital Symmetry Control in the Photochemistry of 1,3,5-Hexatrienes

Sir:

The photoisomerization of a 1,3,5-hexatriene to a bicyclo[3.1.0]hex-2-ene is a well-documented photoreaction.¹⁻¹³ If concerted, this intramolecular photo-Diels-Alder reaction can be viewed as a 4 + 2 cycloaddition, in which case it should be either a ($\pi^4_s + \pi^2_a$) or a ($\pi^4_a + \pi^2_s$) process.¹⁴ Alternatively, it could be viewed as a 2 + 2 + 2 cycloaddition which would be photochemically allowed if antarafacial on all three components or on one. It is interesting to note that, in the few cases where the hexatriene is sufficiently labeled to provide a test of these conclusions,^{10,10-12} the gross observations made are not in accord with orbital symmetry predictions. In the hope of providing some data for understanding the stereochemical course of this reaction, we have investigated the photochemistry of a series of 1,2,6-triphenyl-1,3,5-hexatrienes. The result of our studies appears to be compatible with the theoretical predictions.

1,2,6-Triphenyl-(*Z,Z,E*)-hexa-1,3,5-triene¹⁵ (**1**; mp 78-80°), prepared by the Wittig reaction of triphenyl-*trans*-cinnamylphosphonium bromide and *cis*-2,3-diphenylacrolein,¹⁶ upon irradiation¹⁷ rearranges stereospecifically to give an isomeric species (76%; mp 104-106°) to which we have assigned the structure of *exo,exo*-3,4,6-triphenylbicyclo[3.1.0]hex-2-ene (**2**).¹⁸ The stereochemical assignment was based on the following nmr (CCl₄) data: δ 1.71 (t, 1, C₆H), 2.02 (dd, 1, C₅H), 2.31 (m, 1, C₁H), 4.41 (t, 1, C₄H), 6.80 (t, 1, C₂H), and 7.25 (m, 15, aromatic). Appropriate spin-decoupling experiments were performed which allowed

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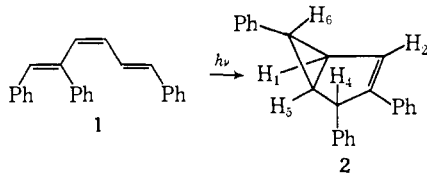
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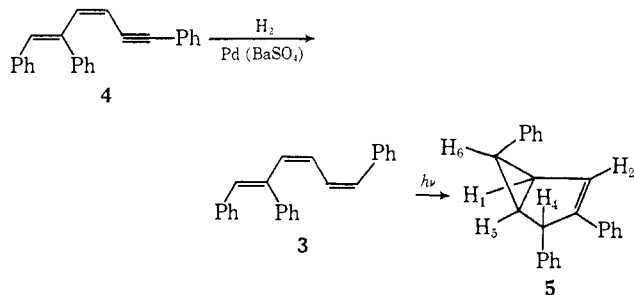
(17) All irradiations were done in cyclohexane using a 450-W Hanovia lamp fitted with a Pyrex filter.

(18) All compounds analyzed satisfactorily. Complete spectroscopic and degradative details will be given in our full publication. No other stereoisomers could be detected ($\pm 5\%$) by nmr spectroscopy.



the determination of the following coupling constants; $J_{1,5} = 6.3$ Hz, $J_{1,6} = 2.3$ Hz, $J_{5,6} = 3.6$ Hz, $J_{1,4} = 2.4$ Hz, $J_{2,4} = 1.6$ Hz, and $J_{1,2} = 1.9$ Hz. The magnitude of the coupling implies *trans*-cyclopropyl vicinal coupling^{19,20} and thus requires that the C₆-phenyl group be *exo*. The absence of coupling between H₄ and H₅ implies *trans* vicinal coupling and fixes the C₄-phenyl group in the *exo* position.^{1c,2b,7a}

Bicyclo[3.1.0]hexene **2** is not the expected product from orbital symmetry considerations but is the thermodynamically most favored isomer. In order to determine whether the photoisomerization of a triphenyl-substituted hexatriene is subject to orbital symmetry interpretation, we have investigated the photochemistry of the isomeric 1,2,6-triphenyl-(*Z,Z,Z*)-hexa-1,3,5-triene (**3**). This material was obtained from the catalytic hydrogenation of 1,2,6-triphenyl-(*Z,Z*)-hexa-1,3-dien-5-yne (**4**). Dienenne **4** was in turn synthesized from the Wittig reaction of *cis*- α -phenylcinnamyltriphenylphosphonium bromide and phenylpropargyl aldehyde followed by fractional crystallization of the two isomeric dienyne. Irradiation of **3** in cyclohexane gave a new



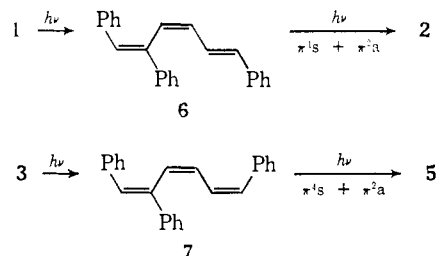
photoisomer (mp 132–133°) whose structure is assigned as 4-*exo*,6-*endo*-3,4,6-triphenylbicyclo[3.1.0]hex-2-ene (**5**) on the basis of its nmr spectrum:¹⁸ δ 2.01 (dd, 1, C₅H), 2.50 (m, 2, C₁H and C₆H), 3.78 (t, 1, C₄H), 6.32 (m, 1, C₂H), and 6.8–7.3 (m, 15, aromatic). Appropriate spin-decoupling experiments showed that $J_{1,2} = J_{1,4} = J_{2,4} = 2.0$ Hz, $J_{1,5} = 6$ Hz, and $J_{5,6} = 8.0$ Hz. The magnitude of the *cis*-cyclopropyl vicinal coupling requires that the C₆-phenyl group be *endo*. In accord with this assignment is the observation that H₆ is no longer shielded by the anisotropy of the double bond and appears 0.8 ppm downfield from C₆H in the *exo,exo* isomer **2**. Again, $J_{4,5} = 0$ Hz, requiring that the C₄-phenyl group be *exo*.

The fact that only **5** was isolated from the irradiation of **3** implies that the stability of the final product is not the major factor governing the photoisomerization in the triphenylhexatriene system. These results indicate that orbital symmetry control must be important in these systems. It should be pointed out, however, that **5** is not the isomer that would be predicted to be formed from the irradiation of **3**. The above observa-

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tions can be rationalized if it is assumed that the above reactions are consecutive photoreactions involving initial *cis*-*trans* photoisomerization followed by bond reorganization to the bicyclic isomer.



In order to gain further evidence for the above scheme, trienes **6** and **7** were independently synthesized.²¹ When subjected to irradiation, **6** gave only **2** and **7** afforded **5** as predicted. Furthermore, in the partial photolysis of **1**, the presence of **6** could be detected by nmr spectroscopy.

It appears that photoisomerization about the 1,2 double bond to relieve *cis*-diphenyl nonbonded interactions is rapid relative to symmetry-allowed concerted cyclization. In both cases the cyclization is observed to occur only *via* the $\pi^*1s + \pi^*2a$ route.²² This perhaps is a reflection of the somewhat greater steric requirements of the $\pi^*4a + \pi^*2s$ path. Closure by the $\pi^*4s + \pi^*2a$ route would also be expected from consideration of the nodal structure of the lowest π^* level of the *transoid* conformer of the hexatriene. Further work on the importance of orbital symmetry control in 1,3,5-hexatriene photochemistry in related systems is currently under way and will be the subject of future reports.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant GP-9385).

(21) Triene **6** was synthesized from the Wittig reaction of *trans*- α -phenylcinnamyltriphenylphosphonium bromide and *trans*-cinnamyl aldehyde. Triene **7** was obtained from the catalytic hydrogenation of 1,2,6-triphenyl-(*E,Z*)-hexa-1,3-dien-5-yne. The dienyne was obtained from the Wittig reaction of *trans*- α -phenylcinnamyltriphenylphosphonium bromide and phenylpropargyl aldehyde followed by chromatographic separation of the two isomers.

(22) It should be pointed out that even though the photoreaction is stereospecific it is not necessarily concerted, even though it is allowed to be so. The concertedness of the reaction still has to be experimentally verified.

(23) Alfred P. Sloan Fellow, 1968–1970; to whom correspondence should be addressed.

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The Photolysis of Sulfur Ylides. Diphenylsulfonium Allylide

Sir:

The utility of sulfur ylides in organic synthesis depends upon a definition of their reactivity and the availability of diverse ylides. In our work directed toward these goals, we have examined the thermal, photochemical, and catalyzed decomposition of dimethylsulfonium phenacylide¹ as well as the properties