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On a Preliminary Theoretical Approach to the Investigation of the Mercury ($^3P_1$) Photosensitized Internal Cycloaddition in 1,4-Pentadiene and 1,5-Hexadiene

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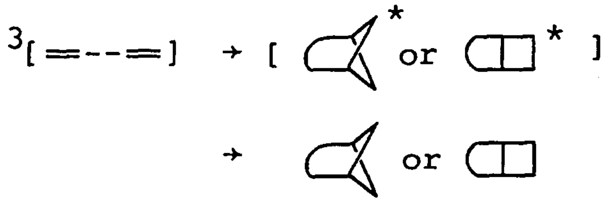
A preliminary theoretical calculation was performed on the photosensitized internal cycloaddition in non-conjugate dienes by using an ab initio SCF MO procedure. The result explains very reasonably the experiments; predominant parallel compound from 1,4-diene, cross compound from 1,5-diene, and the ratios of these parallel/cross products in both cases.

It is well known that a series of non-conjugate aliphatic dienes are converted into bicyclo-alkanes on sensitization by the mercury ($^3P_1$) atom,[1] as shown in eqs (1) - (4).

$$Hg(^1S_0) + h\nu \rightarrow Hg(^3P_1) \qquad (1)$$

$$=\!=\!-\!-\!=\!= + Hg(^3P_1) \rightarrow {}^3[=\!=\!-\!-\!=\!=] + Hg(^1S_0) \qquad (2)$$


(3)

(4)

These reactions have been extended to identify photochemistry of the substituted 1,5-hexadienes and 1,5-hexadien-3-ones.[2] Most of dienes change into mixtures of parallel and cross compounds. In the case of 1,4-pentadiene the parallel compound, bicyclo[2.1.0]pentane, is prevailing, while the cross compound, bicyclo[2.1.1]hexane, prevails in the case 1,5-hexadiene.[1] For these reaction systems several explanations were attempted up to now.[1-3] Srinivasan et al. proposed "the rule of the five",[1] Wolff et al. insisted "the effect of substitution" at C(5) and "the ring effect" in 1,5-dienones,[2] and Gleiter et al. discussed the effect of "the through-bond interaction".[3] However there are still some unclear points in the course of the reaction. In the present communication, we have attempted to investigate this type of reaction by taking up 1,4-pentadiene and 1,5-hexadiene as examples.

It is indeed very important to estimate the geometry of the 1,4- and 1,5-dienes in the ground state at the first step. The ground state molecule is excited by the triplet state Hg and the molecule instead may become triplet excited state.[4] Therefore only the triplet state is taken into account for the excited state for these dienes. The geometry optimizations were performed for several probable forms by using the GAUSSIAN 80 program package.[5] The used basis is STO-3G. The results are shown in Figs. 1 and 2, for 1,4- and 1,5-dienes, respectively. The ground state is calculated by the RHF method and the excited state by the UHF one.

1,4-Diene

Ground state. The trans-trans (TT), trans-cis (TC), and envelope forms were taken up. In the TT and TC forms all of the atoms except two hydrogens in the central methylene group are assumed planer. The central carbon in the envelope form is not on the co-plane of both-end double bonds. The most stable form estimated is the envelope form and there is only a little energy difference between the TT and TC forms. The energy difference between the envelope and TT forms estimated is ca. 4 kcal/mol.

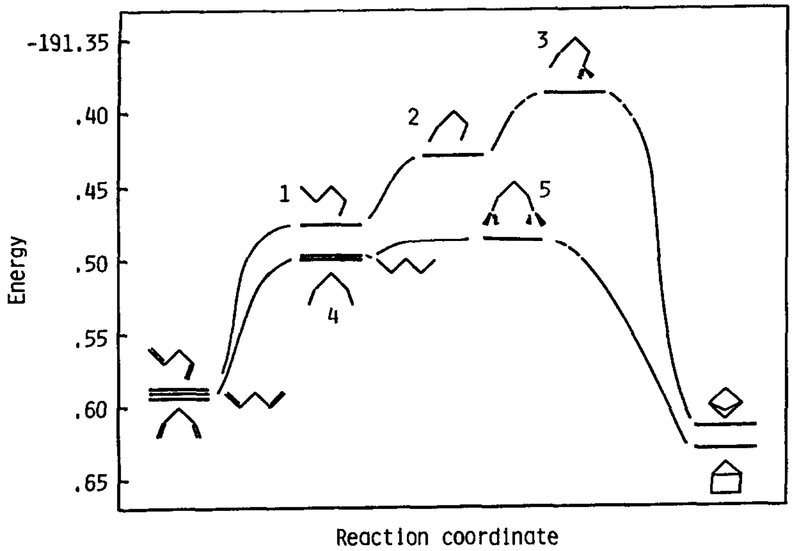


Fig. 1. Relative energies (a.u.) for the system 1,4-pentadiene -- bicyclopentane.

Triplet state. The geometries of the triplet state were also optimized in three conformational forms mentioned above at first. The most stable form estimated is the envelope structure, which is destabilized by 61 kcal/mol from the ground state, and the TC form is the most unstable one. The TT and envelope forms have nearly the same energies. It is very reasonable to consider here that the parallel compound comes from the envelope structure and the cross one from the TC form. The geometry optimizations were performed moreover at two and one points in the TC and envelope forms, respectively. The form 2 is the one in which the left-hand vinyl group rotates by a right angle around the CC-CCC bond from the form 1. The form 3 is the one in which the right-hand methylene group rotates by a right angle around the CCCC-C bond from the form 2. For these steps from 1 to 2 and from 2 to 3, ca. 29 and 26 kcal/mol are destabilized, respectively. The form 5 is the one in which both-end methylene groups rotate 90° from the form 4. From the step 4 to 5, ca. 8 kcal/mol was destabilized.

1,5-Diene

Ground state. The ground state of this species was geometrically optimized by assuming the three conformational forms. The most stable form estimated is the envelope one. The trans zigzag (TTT) is next stable and the trans-cis-trans (TCT) is most unstable. The difference between the envelope and TCT forms is ca. 11 kcal/mol. The single point calculation is performed on the structure in which the left-hand group is in a trans conformation and the rest has the same geometry as the envelope one as a test case. The energy calculated shows nearly the same as that of the envelope one.

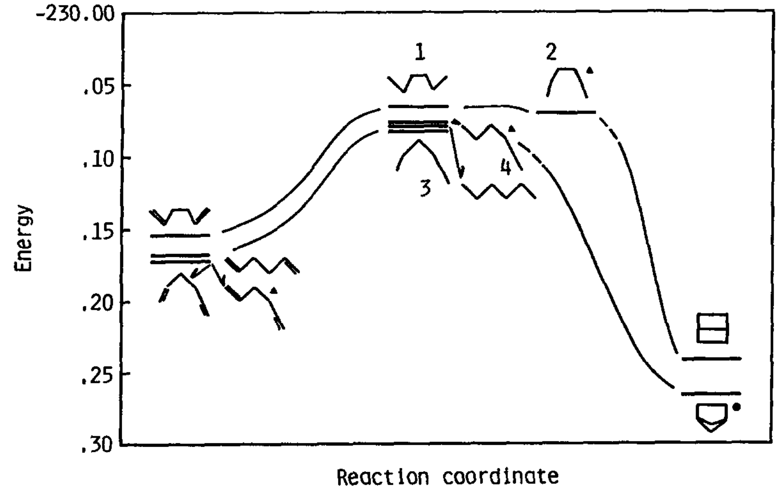


Fig. 2. Relative energies (a.u.) for the system 1,5-hexadiene -- bicyclohexane.
▲: single point calculation.
●: from Ref. 6).

Triplet state. The geometries of the triplet state were optimized for the three forms; TTT, TCT, and the envelope forms. The envelope form is destabilized ca. 58 kcal/mol by the triplet excitation, while the TCT form ca. 57 kcal/mol. The single point calculation on 4, in which the conformation of the left-hand vinyl group is different from the 3, shows destabilization of ca. 3 kcal/mol from that of 3. The form 2 is the one in which both-end methylene groups rotate 90° around two single bonds in a contrarotatory way from 1. By this rotation the energy lowers ca. 3 kcal/mol. The TCT form may change into bicyclo[2.2.0]hexane, while the envelope structure may reasonably be converted into bicyclo[2.1.1]hexane.

The smallest triplet state energy of 1,4-diene in the envelope form supports the experimental result that in this diene main product is the parallel species. The TC form 1 is less stable by ca. 15 kcal/mol than the envelope form 4 in the triplet state. The energy difference between the forms 5 and 3 is estimated to be ca. 62 kcal/mol. In the case of the triplet state of 1,5-diene, the envelope form has the smallest energy and this explains reasonably the dominant product of the cross compound and the energy difference between the envelope 3 and TCT 1 forms is ca. 10 kcal/mol. In a previous paper the ratios of cross/parallel products were reported for 1,4- and 1,5-dienes to be 0.10 and 2.53, respectively.1) The energy difference between the forms 3 and 1 in 1,5-diene is (much) less than that between the forms 4 and 1 or between 5 and 3 in 1,4-diene. This result explains remarkably well the difference of the ratio of the products.

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