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A Theoretical Analysis of the Regiochemistry in the Intramolecular Photocycloaddition of 1,5-Hexadien-3-ones and 2-Formyl-1,5-hexadienes

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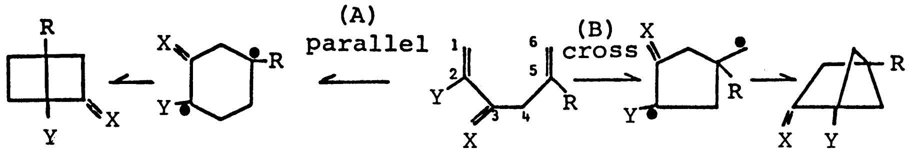
A regiochemistry of the photolysis of the substituted 1,5-hexadienes was analyzed by using an ab initio SCF MO procedure. The calculated total energies explained the observed product distributions.

During the last two decades photochemical intramolecular [2+2] cycloaddition reaction of the non-conjugate dienes has been investigated very extensively, and it is now well-known that this reaction occurs via the triplet state and leads to parallel (A) and/or cross (B) products.[1)] The product distribution depends on the number of the methylene groups existing between the double bonds or on the kind of substituted group. For example 1,4-pentadiene produces the A compound predominantly and 1a the B one. The 1c leads to only the B-closure.[2)] The 1d gives larger ratio of the A/B products. The 1e converts into the B compound. The 1f however, does not affect the regiospecific B-closure.[2)] This was first explained by the "rule of the five"[1)] and later by the concept of the "through-bond" interaction.[3)] More recently this has been explained by an ab initio MO procedure;[4)] the result showed that the B-closure took place from the envelope (Env) form and the A-closure from the trans-cis-trans (TCT) conformation around the C2-C3, C3-C4, C4-C5 bonds, e.g., for 1,5-diene. However the effect of the substitution at the C2, C3, and/or C5 has not yet been analyzed from a theoretical point of view.



3a-f 1a-f 2a-f

a:	R=Y=H, X=H_2	B/A=72/28	1)
b:	R=CH_3, X=H_2, Y=H	=68/32	
c:	R=Y=H, X=O	=100/0	2,6-8)
d:	R=CH_3, X=O, Y=H	=61/39	
e:	R=H, X=H_2, Y=CH_3CO	=100/0	9)
f:	R=CH_3, X=H_2, Y=CH_3CO	=100/0	

Scheme 1.

In order to clarify the substituent effects, the acyl group at C2, the C=O group at C3, and the methyl group at C5, the reaction was analyzed by an ab initio SCF MO procedure. The ground state molecule was optimized by the RHF method and the excited triplet state by the UHF one. The 1b,1d,1f' were calculated only by the single point calculations with the geometries transferred from those of 1a,1c,1e'. The geometry of the methyl part was adequately assumed: r(C-C) =1.501 Å, r(C-H)=1.09 Å, ϕ(CCH)=109.5°. The used program was GAUSSIAN 80[5] and the basis the STO-3G.

The experimental data of the reaction (from the triplet state) are summarized in Scheme 1. In the present study we have taken up six molecules 1a,1b, 1c,1d, and 1e',1f' as models for these reaction systems. The acetyl group of 1e,1f was simplified by the formyl group (1e',1f') for a computational convenience. Three conformers, trans zigzag (TTT), TCT, and Env forms of the skeleton, were assumed. For 1e', the C1-C2-C9-O17 was fixed as trans. The geometry at the excited state are summarized in Fig. 1 and the energies in Fig. 2.

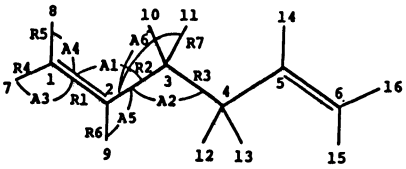
With 1c, the geometry in the excited state is fairly different from that for 1a. The R1 and R2 are considerably shorter than those of 1a. This implies that the R1 in 1c retains still fair amount of double bond character. The R3 of 1c is slightly shorter than that of 1a, and this does not vary much between the TTT and TCT forms. This is not the case of 1a. As for the skeletal valence angles, the A2 is different between 1c and 1a. Examining the internal rotation angles of the Env form between 1c and 1a, there are large differences on B1, B2, and B4.

With 1e', the bond lengths are very similar to those of 1a. This shows that the situation by the substitution at C2 (-CHO) in 1e' is entirely different from that in 1c. The skeletal valence angles obtained fairly differ from those of 1a. As for the internal rotation angles of the Env form, those for 1e' are very similar to 1a.

The energy difference between the TCT and Env forms in the excited state, ca. 10 kcal/mol, for 1a and 1c seems too much to allow the coexistence of these forms at the temperatures to 80 °C. However the STO-3G basis set used is known to overestimate the energy difference sometimes and the configuration interaction (CI) is not taken into account in the present calculation. The larger basis set and CI calculation may reduce the energy difference. In spite of that shortcoming the energy difference in 1e' both in the ground and excited states is much larger than that in 1a or 1c. This large difference supported well the exclusive B closure in 1e,1f;[2,9] B-closure comes from the Env form.

The features of the energy diagrams for the ground and excited states are very similar between 1a and 1e'. In the case of 1c the TTT form is calculated as the most stable form in the ground state, however in the excited triplet state the energies are in the order: Env < TTT < TCT. Anyway in all three species, 1a, 1c, 1e', the Env form was calculated as the most stable one in the excited state and this explains reasonably the experimental predominance of the B-closure for these molecules.

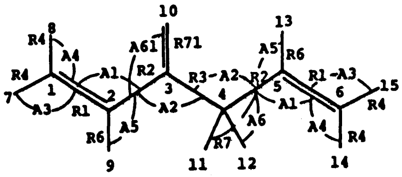
The energies of the 1b,1d,1f' are also summarized. In some cases the energies are underestimated because of single point calculation. The steric hindrance, therefore, is overestimated in such a case. Nevertheless the destabilization of the TCT form in 1d is much less than that of 1b or 1f'. This may combine to the



1a

B1	C4C3-C2C1
B2	C5C4-C3C2
B3	C6C5-C4C3
B4	H9C2-C3C4
B5	H10C3-C2C1
B6	H11C3-C2C1
B7	H12C4-C5C6
B8	H13C4-C5C6
B9	H14C5-C4C3

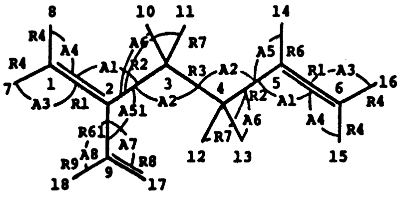
	TTT	TCT	Env
R1	1.470	1.471	(1.470)
R2	1.522	1.523	(1.522)
R3	1.552	1.581	(1.552)
R4	1.081	1.081	(1.081)
R5	1.081	1.081	(1.081)
R6	1.083	1.079	(1.083)
R7	1.090	1.089	(1.090)
A1	121.90	120.01	(121.90)
A2	111.68	118.02	(111.68)
A3	120.92	120.94	(120.92)
A4	120.93	120.96	(120.93)
A5	119.02	121.84	(119.02)
A6	110.19	108.62	(110.19)
B1	(180.)	(180.)	-75.61
B2	(180.)	(0.)	75.61b)
B3	(180.)	(180.)	-124.83
B4	(0.)	(0.)	69.98
B5	(60.)	(60.)	45.71
B6	(-60.)	(-60.)	163.72
B7	(60.)	(60.)	114.90
B8	(-60.)	(-60.)	-2.79
B9	(0.)	(0.)	55.95



1c

B1	C4C3-C2C1
B2	C5C4-C3C2
B3	C6C5-C4C3
B4	H9C2-C3C4
B5	O10C3-C2C1
B6	H11C4-C5C6
B7	H12C4-C5C6
B8	H13C5-C4C3

	TTT	TCT	Env
R1	1.374	1.376	(1.374)
R2	1.475	1.473	(1.475)
R3	1.541	1.542	(1.541)
R4	1.081	1.081	(1.081)
R6	1.084	1.081	(1.084)
R7	1.092	1.093	(1.092)
R71	1.462	1.461	(1.462)
A1	123.72	122.72	(123.72)
A2	117.20	122.01	(117.20)
A3	121.69	121.69	(121.69)
A4	121.28	121.23	(121.69)a)
A5	116.74	118.52	(116.74)
A6	110.01	109.17	(110.01)
A61	120.92	121.10	(120.92)
B1	(180.)	(180.)	-52.55
B2	(180.)	(0.)	52.55b)
B3	(180.)	(180.)	-123.44
B4	(0.)	(0.)	139.41
B5	(0.)	(0.)	162.83
B6	(60.)	(60.)	114.56
B7	(-60.)	(-60.)	-1.49
B8	(0.)	(0.)	58.43



1e'

B1	C4C3-C2C1
B2	C5C4-C3C2
B3	C6C5-C4C3
B4	C9C2-C3C4
B5	H10C3-C2C1
B6	H11C3-C2C1
B7	H12C4-C5C6
B8	H13C4-C5C6
B9	H14C5-C4C3
B10	O17C9-C2C1
B11	H18C9-C2C1

	TTT	TCT	Env
R1	1.463	1.464	(1.463)
R2	1.531	1.534	(1.531)
R3	1.552	1.591	(1.552)
R4	1.081	1.080	(1.081)
R6	1.083	1.075	(1.083)
R7	1.089	1.088	(1.089)
R61	1.385	1.377	(1.385)
R8	1.352	1.359	(1.352)
R9	1.092	1.081	(1.092)
A1	117.56	114.79	(117.56)
A2	113.72	125.23	(113.72)
A3	120.47	120.44	(120.47)
A4	121.36	121.18	(120.47)a)
A5	121.23	125.65	(121.23)
A6	109.00	106.50	(109.00)
A51	126.23	129.29	(126.23)
A7	127.07	120.99	(127.07)
A8	116.59	122.79	(116.59)
B1	(180.)	(180.)	-80.48
B2	(180.)	(0.)	80.48b)
B3	(180.)	(180.)	-124.87
B4	(0.)	(0.)	97.50
B5	(60.)	(60.)	41.23
B6	(-60.)	(-60.)	158.23
B7	(60.)	(60.)	114.86
B8	(-60.)	(-60.)	-2.06
B9	(0.)	(0.)	55.60
B10	(180.)	(0.)	(0.)
B11	(0.)	(180.)	(180.)

Fig. 1. Optimized geometries in the excited triplet state for 1a,[4] 1c, and 1e'. Figures in parentheses are assumed and a) A4=A3, b) B2=-B1.

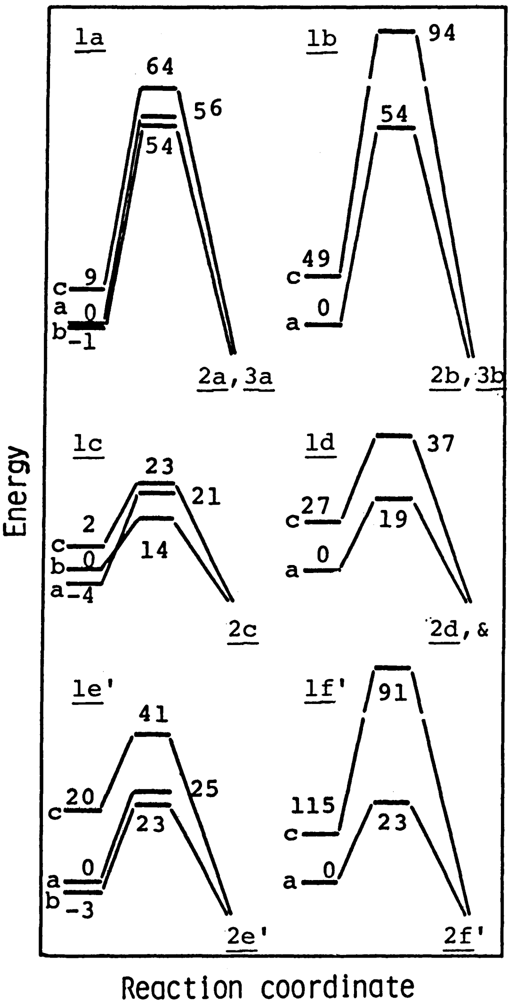


Fig. 2. Relative energies (kcal/mol) for the systems. Upper, 1a,1b--2a,3a,2b,3b. Middle, 1c,1d--2c,2d, and others. Lower, 1e',1f'--2e',2f'. a=TTT, b=Env, and c=TCT forms.

small hindrance and the increase ratio of the A-closure in 1d; A-closure comes from the TCT form.

We still have to mention about following two points: i) the more elaborate basis set, and ii) propriety of our model replacing the CH_3CO group by the HCO.

Some single point calculations using the 3-21G basis set with the optimized geometry by the STO-3G for 1a showed energies in the ground state: TTT; -145386.69, TCT; -145377.62, Env; -145388.69;; triplet state: TTT; -145313.31, TCT; 145304.99, Env; 145315.27 kcal/mol, seeing good agreement with those of the STO-3G calculation.$^{4)}$ Therefore the energy difference can be explained even by the small basis set in case which there are fair energy differences among the rotamers.

Further, the STO-3G single point calculations were performed for 1e by assuming the same geometry of the methyl part as mentioned above. Energies obtained in the ground state were: TTT; -238335.01 (O-cis, in relation to the skeletal C1-C2 bond), -238418.73 (O-trans);; TCT; -238159.74 (O-cis), -238405.32 (O-trans);; Env; -238435.43 (O-cis), -238422.79 (O-trans) kcal/mol; the stability among the three forms agrees excellently well with that of the formyl species. Therefore, it can be concluded that our model is reasonable.

In conclusion, the predominance of the B/A-closure of the substituted 1,5-hexadienes can be estimated from the total energies. The variation of the reactivity by the substituent of CHO at C2 or of C=O at C3 could be analyzed by their total energies with reference to that of parent molecule. The effect of the methyl group at C5 is explained qualitatively but difficult quantitatively at present.

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