

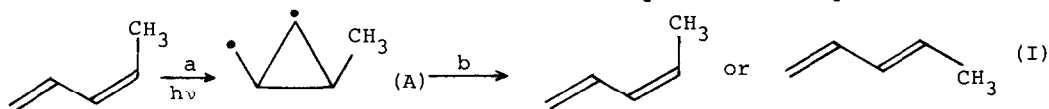
ON THE DECAY AND THE ISOMERIZATION OF EXCITED SINGLET 1,3-PENTADIENES

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It has been previously proposed¹ that a conrotatory 1,3 overlap of p_{π} orbitals leading to the diradical A could be responsible for the decay of S_1 dienes as well as for *cis* \rightleftharpoons *trans* isomerization [equation (I)²].



The low quantum yields for *cis* \rightleftharpoons *trans* isomerizations³ in S_1 would however require that the conrotatory ring opening (Ib) be highly stereospecific and this can hardly be assumed. The proposal was later improved⁴, following Oosterhoff's treatment of the 1,4-cyclomerization⁵, by considering that the S_1 and S_0 states might be degenerate (or close to that) along the coordinate of reaction (Ia); the decay would not then need completion in the C_2-C_4 bond formation and would therefore preserve the configuration whereas the isomerization would arise only from those molecules having achieved the ring closure, according to (Ib). However, this mechanism, which is sketched in figure 1, has been disputed⁶. We report here experimental data which bear out its validity.

In an attempt to trap the intermediate radicals arising from the S_1 1,3-pentadienes it was accidentally observed that photolysis of neat dienes in the presence of Me_3SnH ⁷ increases $\phi_{C \rightarrow T}$ up to 0.15 and decreases $\phi_{T \rightarrow C}$ down to \sim zero (vs. 0.10 and 0.08 respectively in dilute cyclohexane solution³). It was thus desirable to investigate on the possible influence of a very high diene concentration on the behavior of their singlet excited states⁸.

Neat *cis* and *trans* 1,3-pentadienes were irradiated at 253.7 nm in quartz tubes

and the quantum yields determined for all the observed processes. The data, which are collected in the table, suggest some important conclusions.

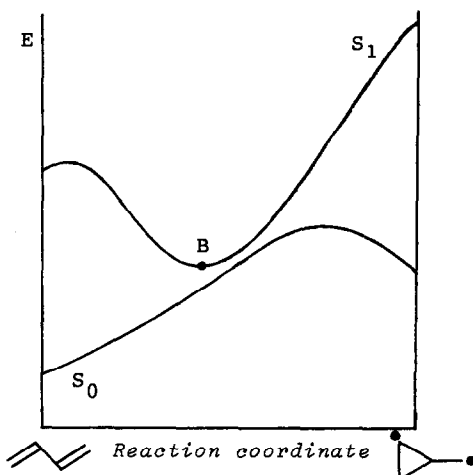


Figure 1. Hypothetical energy diagram proposed for the diene + methylenecyclopropyl diradical interconversion in the ground and the excited singlet states.

Table. Direct photolysis of 1,3-pentadienes in quartz cells at 253.7 nm; room temperature; ϕ measured at conversions < 5%.

Concentration	$\phi_{C \rightarrow T}$	$\phi_{T \rightarrow C}$	$\phi_{T \rightarrow \square}$	$\phi_{C \rightarrow \text{dimers}}$	$\phi_{T \rightarrow \text{dimers}}$	$[T]/[C]$ Photostationary
$5 \times 10^{-1} \text{ Ml}^{-1}$ in cyclohexane	0.10	0.08	0.03	-	-	0.75 ^a
Neat	0.12	0.05	0.03	0.15 ^b	0.06 ^b	1.43

a. This ratio emphasizes that the $\epsilon_{253.7}$ values reported in the literature are erroneous. Our values, determined in cyclohexane on dienes freshly purified by VPC and using a Carry 14 spectrophotometer, are: $\epsilon_{253.7}^{\text{cis}} = 31$ and $\epsilon_{253.7}^{\text{trans}} = 50.6$.

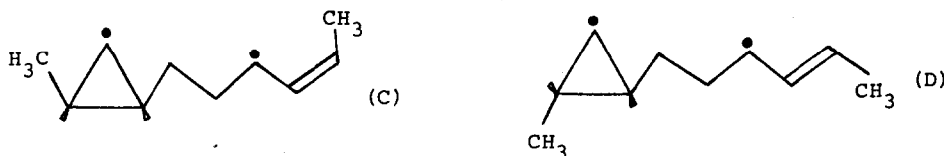
b. In contrast to the triplet case⁹ the pattern of dimers, as seen by VPC, is qualitatively and quantitatively different for the cis and for the trans diene, which shows that the configurations are retained in the course of dimerization. Polymerization did not make a significant contribution as checked by the mass balance.

The 1,4 cyclomerization is definitely an unquenchable process (even in the presence of Me_3SnH ⁷). Therefore the lifetime of the excited *s-cis* conformer from which it derives must be extremely short and distinctly different from that of the *s-trans* conformers. This in turn means that any conclusion which was based on the production of cyclobutenes does not apply to the majority of molecules since they lie in the *s-trans* configuration.

The absolute figures for the initial isomerization quantum yields are but little affected; their ratio however differs significantly from that obtained in dilute solution and moreover $\phi_{C \rightarrow T} \cdot \epsilon_C / \phi_{T \rightarrow C} \cdot \epsilon_T$ is virtually equal to the photostationary ratio $[T]/[C]$. This rules out the possibility that changes in ϕ_{isomer} merely reflect an independent contribution of dimerization and strongly suggests that geometrical isomerization involves a quenchable intermediate with respect to which *cis* and *trans* ground states are equally good traps. That the quantum yields for isomerization and dimerization parallel each other may well mean that the same intermediate is responsible for the two processes.


The increase in $\phi_{C \rightarrow T}$ requires that the quenching produces a reversible intermediate. The diallyl diradical is not a likely structure for enhancing isomerization since (i) it has a frozen configuration which is too long-lived¹⁰ - the dimers yielded by *cis* and *trans* 1,3-pentadienes being accordingly different - and (ii) a major contribution to the dimers is that of the vinyl-[3,1,0]-bicyclohexane skeleton¹¹.

Hence these results are best rationalized by postulating that the major decay to the ground state proceeds *via* an unquenched path, presumably involving a quasi-degenerate conformer of type B (see figure) which preserves the geometrical integrity of the isomer while the remainder of the excited molecules achieve the $\text{C}_2\text{-C}_4$ bond making and produce the quenchable methylene-cyclopropyl diradical. Then the adducts (C from *cis* ; D from *trans*) either react to give dimers or undergo a concerted reverse reaction to give, according to their particular stereospecificity, two molecules of diene.



Interestingly, the conformer B might be regarded as a distorted (relaxed) non spectroscopic singlet whose lifetime is possibly much longer than has been estimated for S_1 dienes¹²; this would have two important consequences which can be probed:

(i) an interaction between this state and a ground state molecule (diene or Me_3SnH e.g.) could provide a driving force for the 1,3 electrocyclization and improve its yield, thus justifying the fact that $\phi_{C \rightarrow T}$ increases in neat diene or in the presence of Me_3SnH .

(ii) by increasing the vibrational energy content of B one should favor the production of  over internal conversion. We have indeed observed that when *trans*-1,3-pentadiene is irradiated with 253.7 nm light in the vapor phase, $\phi_{T \rightarrow C}$ increases as the pressure of a cooling gas (ethane) is decreased¹³.

Finally our strongest evidence for a distorted long-lived singlet excited state came from the Stern-Volmer treatment of the 1,3-pentadiene \rightarrow 1,4-pentadiene photoinduced conversion at variable pressure: a lifetime of $\sim 10^{-7}$ sec has been found for the species giving rise to the hydrogen shift¹³.

Thus the data on quenching of the excited singlet 1,3-pentadienes neat and in the vapor phase consistently support the mechanism described by figure 1 for electronic demotion and for *cis* \rightleftharpoons *trans* isomerization.

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