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74. Photoenolisation. X.¹)
An *ab initio* SCF-CI Study

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Summary

The processes involved in photoenolisations are theoretically simulated by an *ab initio* SCF-CI method, using *cis*-2-butenal as a prototype structure. The prominent role of the hydroxyl group conformation in the resulting transient (**2a**) is emphasized; its rotation 'out of the reaction site' allows the next reaction paths to proceed exothermally. The equilibration of the different types of twisted biradicals in the triplet manifold, which only involves a low energy barrier, is thus possible, populating in quite equal weights the precursors of both *E*- and *Z*-dienols. In the singlet state, the formation of the *Z*-isomer is expected to be kinetically dominant. An examination of the role of the substituents suggests that, in related systems, the steric crowding induces important structural relaxation of the dienol geometries.

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¹) Parts VIII and IX, see [2 l, m].

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Since *Yang & Rivas'* [1] discovery of the reversible photoenolisation process occurring with 2-substituted aromatic carbonyl compounds, a number of related investigations were undertaken by different groups [2]. In spite of the considerable work devoted to this topic, no definitive answers have been given to the complex set of questions arising from the experimental facts. In particular, are both dienols *Z* and *E* or is only one formed? What are the nature and characteristics of the reactive excited species and of any other transient in the reaction?

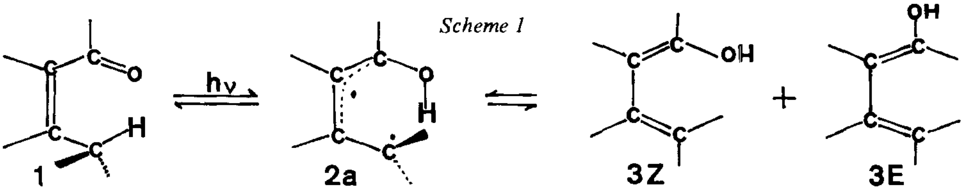
In an attempt to solve the first problem, suitable dienophiles were used under continuous irradiation, in order to trap the photodienols. In all instances, only adducts were obtained whose configuration showed that they came from the *E*-dienols, but at any rate these experiments did not prove that *Z*-dienols were not also formed [2 l] [2 m] [3].

Both problems have been approached by flash photolysis techniques [2 f] [2 i] [4]. Most of these studies were controversial, particularly concerning the assignment of the observed transients.

Recently, an exhaustive study - mainly based on flash photolysis experiments by *Haag et al.* [2j] - has clearly established the simultaneous formation of both dienols. With the help of semiempirical calculations these authors have proposed a scheme for the overall sequence of reactions.

We propose here a complete reaction scheme based on the theoretical study of photoenolisation processes. For practical reasons we had to restrict ourselves to a model structure - *cis*-2-butenal - which, nevertheless, allows a reasonable description of the complex chemical events and conformational rearrangements involved in the parent aromatic systems.

Scheme 1



Description of the Model. - The reaction pathway drawn in *Scheme 1* deserves some comment. Three distinct processes are involved: the first consists in photochemical excitation of the molecule; during the next step, a hydrogen atom is abstracted by the excited carbonyl group from the γ-position, leading to an open form here depicted as a biradical **2a**; then, through conformational rearrangements, intermediates **2a** yields two stable dienol specie *Z*-**3** and *E*-**3**. In this scheme, the hydrogen abstraction and the dienol formation are somewhat arbitrarily separated to emphasize that, in our proposal, the whole molecule remains frozen during hydrogen-atom transfer, while a substantial reorganization of the system (such as bond rotations) must occur during dienol formation.

This sequence of distinct paths will be used as a framework for our theoretical study of the reactive processes.

Methodology. - The reaction paths under scrutiny were simulated by an *ab initio* SCF-CI method already described [5] using the *Gauss* 70 series of programs [6] in its STO-3G minimal basis set option [7]. The CI step was carried out by mixing the first hundred mono- and bi-excited configurations (singlet and triplet), built on the six highest occupied and the four lowest empty molecular orbitals (MO's).

The large size of the various structures renders their complete optimization very tedious, and standard bond lengths and angles [8] were therefore chosen for the different geometrical parameters. Then, linear variation was assumed along the reaction coordinate, from the starting moiety to the final target. It is obvious that, due to our minimal basis set and limited CI-calculations, in the absence of optimization, we cannot pretend to reach precise quantitative information, especially regarding the potential barriers encountered by the various excited states during a given process. Nevertheless, this type of calculation allows a good qualitative description of the phenomena of chemical significance, since it describes correctly the relative variation of the low energy excited states, and thus provides a good basis for a rationale of the overall reactivity, based on simple concepts such as symmetry, various types of allowed or avoided crossings and an approximation of the energetics [9].

Table. *Calculated energies of the lowest states*[a])

Compound	S_0	S_1	T_1
		-6168.9584 (n,π^*)	-6169.4520 (n,π^*)
1	-6173.0234 (GS)	-6165.0068 (π,π^*)	-6168.8490 (π,π^*)
2a	-6169.0398 (Z_1)	-6168.9900 ($D_{\sigma\pi}$)	-6169.0979 ($D_{\sigma\pi}$)
2b	-6169.5400 (Z_1)	-6169.5422 ($D_{\sigma\pi}$)	-6169.5600 ($D_{\sigma\pi}$)
2c	-6169.5329 ($D_{\sigma\pi}$)	-6169.5100 (Z_1)	-6169.5515 ($D_{\sigma\pi}$)
2d	-6169.5057 ($D_{\sigma\sigma}$)	-6162.0020 ($D_{\sigma\pi}$)	-6169.3598 ($D_{\sigma\sigma}$)
Z-**3**	-6171.8516 (GS)	-6163.6035 (π,π^*)	-6168.7039 (π,π^*)
E-**3**	-6172.2604 (GS)	-6163.9617 ($\pi.\pi^*$)	-6169.1217 (π,π^*)
E-**3**[b])	-6170.5373	-6165.3847	-6169.8192

[a]) All values are in eV, after CI; in parentheses is given the dominant biradical character.

[b]) Without bond relaxation.

To illustrate these points let us consider *cis*-2-butenal in its s-*cis*-conformation (the most stable s-*trans* conformation is not reactive [2c,k]). The first calculated vertical triplet state, $^3(n,\Pi^*)$, is found at 3.52 eV; this value lies satisfactorily within the range of the experimental determinations made for similar compounds [10]. The corresponding singlet $^1(n,\Pi^*)$ appears at 4.06 eV [10]. These calculated energies and the singlet-triplet separation are slightly overestimated in the absence of optimization; a relaxation of the Π-system would allow the charge effect in the singlet to be minimized.

In parent aromatic systems, a very efficient intersystem crossing with $^3(n,\Pi^*)$ takes place, indicating that the singlet-triplet separation may be less. The important mass effect of the phenyl ring also intervenes to enhance the efficiency of this process through *Russel-Saunders* coupling [11].

The next excited state is $^3(\Pi,\Pi^*)$ at 4.17 eV. The corresponding singlet state lies at higher energy (8.02 eV); since these states do not play any significant role during the reaction, they are just described here as a reminder (see *Table*).

Hydrogen Transfer. - In our model calculation, the hydrogen atom was transferred from the γ-carbon- to the oxygen-atom in the plane of the molecule facilitates the state assignments which belong to the A'- or A''-symmetry - *i.e.* symmetric or antisymmetric respectively - in the C_s point-group. Even though this molecular geometry suffers from steric congestion5), it has the merit to allow a very (σ-plane)4). This symmetry plane is preserved during the process and thus greatly simple description of the photochemical reaction. Obviously the real process is very likely to begin in a slightly twisted geometry, the determination of which is beyond the scope of this study.

State Correlation Diagram. - The MO-scheme corresponding to this type of hydrogen transfer is already familiar [9] [12]. In our model reaction the Π- and σ-frameworks behave independently. Nevertheless, the modifications of the Π-system are important since they involve changes in the bonding pattern and stabilization by resonance of the positive charge which is created, formally speaking, on the oxygen atom during the overall process. Hence, the very simple state correlation diagram of *Figure 1* follows.

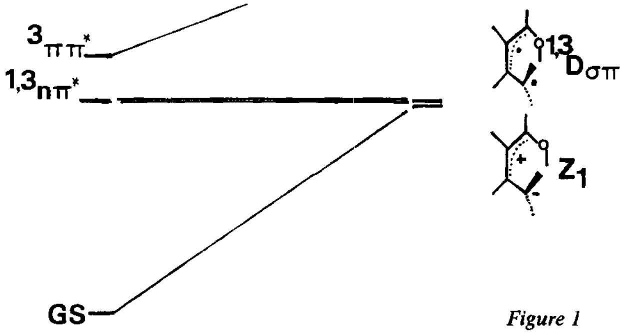


Figure 1

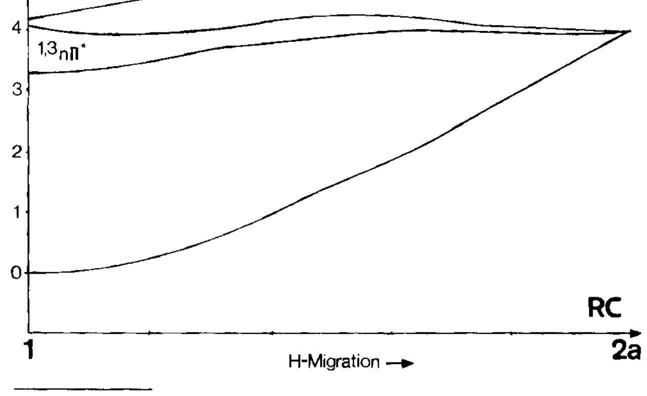


Figure 2

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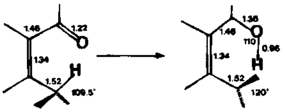
4) The corresponding geometries are:



All other angles = 120°.
All C-H bonds = 1.09 Å.

5) In this planar arrangement, the interatomic distance between oxygen and the migrating hydrogen is inferior to the sum of their *Van der Waals* radii, thus providing the initial ground state (GS) with a neat destabilization. A release of strain results in the transition state, and the energy barriers of the (GS) and the excited states are thus underestimated. We will see later on that in reality the hydrogen atom of concern, indeed tends to avoid this defavourable situation to yield a more stable species (**2b**) *(vide infra)*.

According to the MO-scheme, the ground state (GS) of the conjugated system is linked to the zwitterionic form Z_1 [13], where an electron pair is located on the methylene end; the $^{1,3}(n,\Pi^*)$ duo is correlated with $^{1,3}D_{\sigma\pi}$, of same symmetry, where an electron is promoted from the σ- to the Π-plane. The next excited state, $^3(\Pi,\Pi^*)$, intends to reach an excited form of Z_1, which is not specified here since the corresponding potential energy curve (PEC) is monotonously ascending, and therefore does not play a role in the reaction pathway.

Thermal and Photochemical Reactivity. - In *Figure 2*, only the low energy PEC's (among a hundred of calculated singlets and triplets) have been drawn. They are in full agreement with this analysis. The final drawing is quite similar to the ones obtained in previous studies of *Norrish*-type-II reaction [5a] [9], with the important difference that here Z_1 and $^{1,3}D_{\sigma\pi}$ are degenerate in energy. The energy lowering of Z_1 is provided by resonance of the positive charge delocalized in the allylic linkage, assisted by the HO-group which is a good stabilizer *via* its lone pairs. This result differs from the assignment by *Haag et al.* [2j] who place this state at high energy in the parent system 2-methylacetophenone. In this case, the resonance possibilities are even greater than in our model, and possibly Z_1 may be lower in energy than $^1D_{\sigma\pi}$.

In a thermal enolisation, the GS must overcome a monotonous destabilization before reaching Z_1.

Upon photochemical excitation, the $^{1,3}(n,\Pi^*)$ couple, directly leads to the biradicals $^{1,3}D_{\sigma\pi}$. Along the corresponding PEC's, energy barriers remain as 'souvenirs' of the avoided crossings already found at the MO-stage [12]. Both singlet and triplet can thus react, the difference in reaction efficiency coming from their intrinsic lifetimes. Reaction through $^1(n,\Pi^*)$ is easier than through $^3(n,\Pi^*)$ since this state is 'handicapped' of its initial separation with $^1(n,\Pi^*)$.

In the related aromatic systems, the intersystem crossing $^1(n,\Pi^*)\rightarrow{}^3(n,\Pi^*)$ is very efficient in the starting molecule; this fact prevents the singlet from reacting efficiently. Nevertheless, some singlet reactivity has been experimentally established in the aromatic series [2j], and for aliphatic derivatives - to which our model is better fitted - the singlet reaction is predominant [14].

The reverse transfer is very easy, especially in the singlet manifold. Thermally, it is spontaneous from Z_1. From $^1D_{\sigma\pi}$ an internal conversion (involving a symmetry change) is also possible. The initial structure is thus reformed, liberating a large excess of energy. In this way, an important part of the singlet reactivity may be masked. This is not the case in the triplet state since the final $^3D_{\sigma\pi}$ form, due to the electronic separation in perpendicular planes, rather looks like a true biradical.

From this situation, the triplet can reform the initial excited $^3(n,\Pi^*)$ state, passing through an energy barrier, or, more likely, return to the GS after an intersystem crossing from $^3D_{\sigma\pi}$ to Z_1, in the open form. Of course this provides the triplet - owing to its relatively long lifetime - with the possibility of undergoing further transformation and clearly explains that, in reality, only the triplet reaction is able to yield detectable transformations of the initial system.

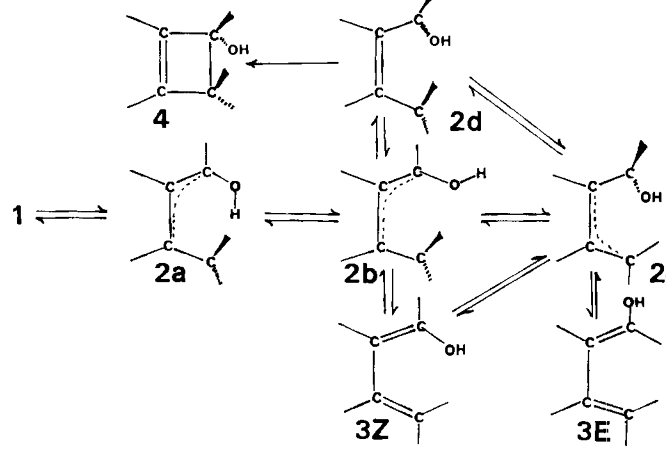
These findings are in close agreement with a previous dynamical study by *Leforestier* [15] who has shown that to be efficient, the proton transfer in the singlet state must be somewhat 'out of plane', to avoid the re-formation of the initial linkage.

To conclude, let us recall that hydrogen-atom transfer is very easy and completely reversible if the initial geometry is preserved. From a theoretical point of view this reaction is similar to the classical *Norrish*-type-II abstraction, in its first step. A question arises regarding the particular role of the Π-system. It doesn't play a significant perturbing role at the beginning of the cleavage since the bond to be broken, in the plane of the n electrons, 'ignores' the Π-framework. But the latter soon intervenes as the reaction proceeds. The (n,Π^*) state possesses one electron, located on the oxygen-atom, in the σ-plane and another in the Π-plane, mainly located between C(1) and C(2) where the lobes, in the first antibonding MO (Π_3) are in-phase [10b, g]. The Π-system therefore acts as a 'flexible' host for the extra electron and by smooth rearrangements it will allow a constant lowering of the energy barrier along the (n,Π^*)$\leftrightarrow D_{\sigma\pi}$ PEC's, thus rendering this reactive pathway extremely easy (it should be recalled that this optimization was not achieved here). On the other hand, during the thermal process [16] (GS-PEC), a charged species is created; here again the Π-linkage allows the delocalization of the positive charge and considerably lowers the corresponding energy barrier, as compared to the parent saturated system. Thus, both photochemical and thermal reactivity are facilitated by the presence of the Π-system. It is clear that in aromatic compounds, the delocalization possibilities are even greater since in the first step the overall aromaticity is preserved, and, as a whole, once the molecule is excited, the hydrogen atom can migrate back and forth without passing through significant energy barriers, thus acting like an *excited hydrogen bond.* This situation will remain as long as the system rests in this particular geometry.

We shall now examine the further transformation of the open form, leading to the dienols or to cyclobutenol.

Evolution of the Primary Product 2a. - Once it is formed, transient **2a** can undergo several possible transformations. We have already pointed out that reverse hydrogen-atom transfer is very easy. But one must first notice that the initial conjugated molecule is not in its most stable conformation (s-*trans*) [17], and this situation remains in the **2a** form. The calculated energy difference between **2a** and **2b** (see *Scheme 2* and *Figure 4*) is not less than 0.5 eV in favour of **2b**, indicating

Scheme 2



that in **2a** a noticeable steric congestion exists, in both the singlet and triplet states. This is in very good agreement with the results of dynamical studies that the migrating hydrogen-atom tends to move out of the plane during its transfer. In all the following discussion we shall therefore consider **2b** as the stable form of the primary product.

It is clear that intermediate **2b** cannot be the precursor of the stable products obtained after reaction without substantial rearrangements; it is therefore useful to examine the interconversions between different typical conformations of the open form. We have selected a certain number of them (**2b**, **2c** and **2d**), which are *a priori* suited to lead to dienols *Z*-**3** and *E*-**3** and to cyclobutenol **4**, respectively *(Scheme 2)*. In these conformers, the double bond was frozen to its standard value and the extremities left free to rotate, without bond relaxation (this last effect will be examined later). The complete study of the potential surfaces connecting all these structures is beyond the scope of this study, and we shall restrict ourselves to elementary motions of the rotating groups. The principal energetic data are collected in the *Table.*

Role of Allylic Conjugation: Cyclobutenol Formation. - Allylic conjugation exists in structures **2b** and **2c**, while, following the MO-scheme *(Fig. 1)*, OH only acts as a perturbating group. In both structures, the conjugative effects are of the same magnitude, and this is illustrated by the fact that the first singlet and triplet states (quasi degenerate in energy) lie at the same energy in both cases, in agreement with *Haag et al.* [2j] determinations[6]. The conjugative interactions can be roughly estimated by comparison with **2d**, where they do not exist. Indeed **2d** appears as an energy maximum separating **2b** and **2c**; the destabilization is rather high for the triplet (0.20 eV) and negligible for the singlet (0.05 eV). In our calculation, the **2b** and **2c** singlets are disfavoured since the system is not relaxed. This situation conversely favours the triplet form where longer bond lengths are expected [10g, h]. Transient **2d**, where no interactions between the ends and the double bond are possible, is close to its optimal structure; in those conditions the energy separation in the triplet manifold is significant while in the singlet state it is accidentally too low.

From **2d**, in the singlet state, cyclobutenol formation can take place without any further activation energy as is usually the case for singlet biradical collapse in a favourable geometry [13] [18]. Cyclobutenol can thus be formed from **2b** or **2c** without passing through a high energy barrier, but the reaction suffers from two important restrictions:

a) in **2b** (singlet state) competitive reverse hydrogen-atom transfer cannot directly occur, but if the OH position changes, it can take place even before reaching a fully planar conformation [15]; thus the corresponding energy barrier is less than the energy difference between **2b** and **2a**;

b) in the triplet manifold, an intersystem crossing must take place before reaching **2d** since this point of the reaction coordinate corresponds to an energy maximum where the system cannot remain long enough to undergo spin inversion and then lead to ring formation.

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[6] Since Z_1 and $^1D_{\sigma\pi}$ are very close in energy we do not define the nature of the first singlet state; in this system they play a comparable role.

(It is also clearly established that cyclobutenols can easily open thermally [2a] [19], but we shall not examine this reaction here.)

Interconversion between 2b and 2c. - Another question arises: can **2b** and **2c** interconvert without passing through a planar form which would collapse into the stable dienols *Z*-**3** or *E*-**3**? Starting from **2b**, a synchronous rotation of both ends of the molecule yields **2c**, avoiding a planar intermediate. The lost conjugation on one end is compensated by the developing one on the other end of the system. In those conditions **2d** (no conjugation at all) is an upper limit of the corresponding barrier, and we can therefore reasonably estimate that this process does not involve a high energy barrier. In the absence of a careful analysis of the whole motion, we shall only consider this process as a potentially feasible and low energy path. It would be greatly facilitated in reality by the non-planarity of the system induced by the substituents, and thus would provide a possibility to interconvert the precursors of *Z*- and *E*-dienols *remaining on high energy triplet or, possibly, singlet PEC's.*

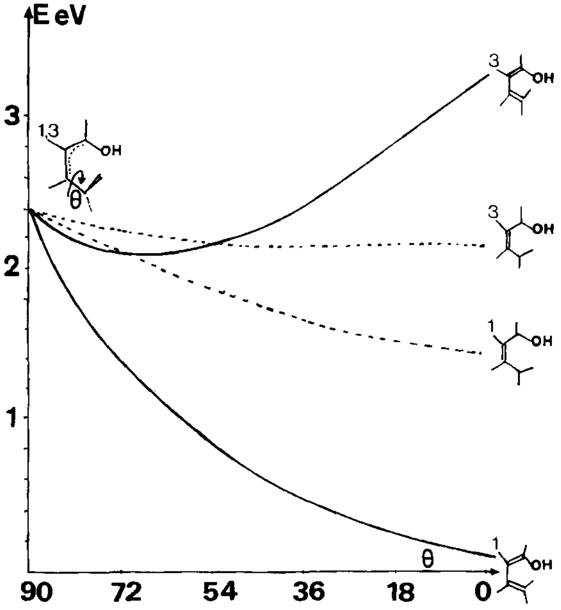

Figure 3

Dienol Formation. - Let us examine as a prototype the formation of the *Z*-dienol from **2b**. The low energy PEC's corresponding to this process are drawn in *Figure 3*.

In the first case the C(1), C(2)- and C(3), C(4)-bonds were progressively brought to their final standard values (solid lines) and in the other case, the CH_2 end was rotated without changing the bond lengths[7]) (dotted lines). Obviously, we thus

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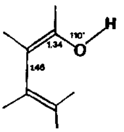
[7]) The geometries are:



All other angles = 120°.
All CH bonds = 1.09 Å.
Values identical for the *E*-isomer.

obtain only a very crude indication of the main trends observed during the real dienol formation.

As expected, the stable GS of the dienol is a closed shell molecule with classical double bonds. Upon elongation of the C(1), C(2)- and C(3), C(4)-bonds, C(2), C(3) being shortened at the same time, a net destabilization of the GS results (1.35 eV)[8]). This is not the case for the first triplet state which is more stable in the elongated geometry by 1.15 eV. From this dichotomy, as the CH_2-rotation proceeds, the stabilization is very important for the singlet state, the bonds rearranging notably to yield the *Z*-dienol in its GS geometry. At the same time the triplet biradical tends to retain its initial bond lengths even though in this case, its stabilization is much less than for the corresponding singlet, being only 0.25 eV.

Conversely, starting from the *Z*-dienol, the first triplet state leads spontaneously to an energy optimum by a significant rotation of the CH_2-end[9]). This minimum is very close to the **2b** geometry ($\theta = 18°$); a similar finding is obtained by rotation of the CHOH extremity (this time, $\theta = 24°$) which yields a species very close to **2c**. It should be noted that in these *gauche* forms, the bond elongation is well advanced since in our simulation (solid lines) the reactions coordinate is in fact the superposition of a rotation *and* a concomitant bond relaxation. These findings are in good agreement with the trends observed in the butadiene series [20]; such a behaviour has also been observed for acrolein derivatives [10] where the first triplet state is more stable in a twisted conformation, as is the case for an isolated double bond [20].

From *Scheme 2* we see that **2c** is also a potential precursor for *Z*-**3**. The formation of the *E*-dienol from **2c** is more exothermic than the formation of the *Z*-dienol, and the corresponding PEC's are similar to those in *Figure 3*.

Overall Description of the Photochemical Reactivity. - The above findings are summarized in *Figure 4*, where the energies of the various states of interest are collected, and in *Scheme 2*.

Upon excitation, the initial molecule yields intermediate **2a**, which is rather unstable and is likely to reform the initial system, especially if the singlet biradical is formed, or to yield exothermally a more stable conformer, **2b**, thus possessing in both singlet and triplet form a maximum energy excess of 0.5 eV. This extra energy will play a prominent role during the evolution of the system, since all the barriers now involved in the further transformation of **2b** are inferior to this energy value. Of course, only a part of this energy is available, but it is possible that it will nevertheless act as a driving force for any process requiring some activation energy.

Now, two possibilities must be considered, depending on the multiplicity of the biradical which is obtained.

Let us first examine the singlet reactivity:

Once intermediate **2b** is formed, the most exothermic pathway consists in generating directly the *Z*-dienol with a large excess of energy. Two competing but

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[8]) For this geometry, the corresponding eigenstate depicts a covalent biradical, *i.e.* with the two electrons localized at both extremities of the system.

[9]) We have in fact two distinct effects, a neat bond reorganization and a CH_2-rotation whose hierarchy remains unknown without optimization of the corresponding transformation.

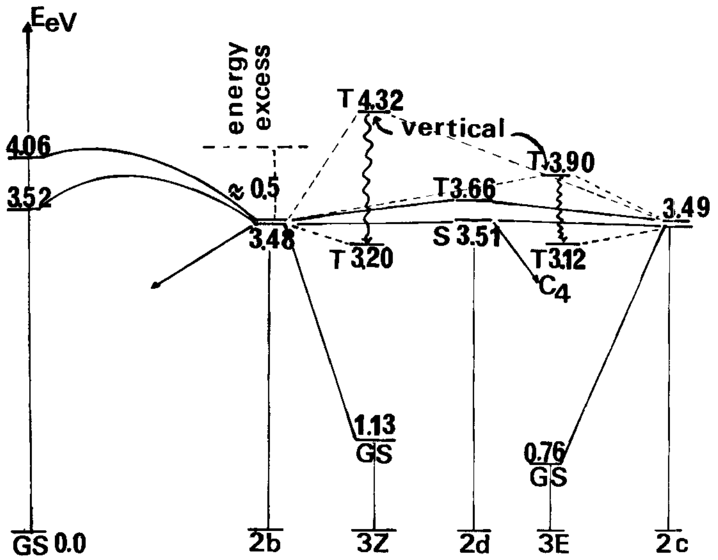

Figure 4

less probable reactive routes are available. The first consists in formation of **2d** which spontaneously leads to cyclobutenol. The second is provided by an equilibration of **2b** with **2c**, remaining on a high energy PEC, this process requiring only a weak energy variation. From **2c**, the *E*- or *Z*-dienol can be formed, the thermodynamic data (steepest descent) being in favour of *E*-**3**[10]), in our model compound. Under those conditions, dienol *Z*-**3** is preferentially formed, isomer *E*-**3** being generated by less probable reactive pathways. Along the **2b**→**2c** singlet surface, **2d** provides a leak for the formation of singlet cyclobutene (GS), through an overall exothermal process (collapse of the face-to-face cyclobutene biradical).

If the system remains in the triplet state, the situation is quite different. Starting from **2b**, rotation of the CH$_2$-extremity yields a stable species, which lies around 3,2 eV above the GS of the initial system. In fact, the equilibrium geometry of this biradical is intermediate between **2b** and the all-planar form coming from the bond rearrangement of the vertical *Z*-**3** triplet (which lies more than 1 eV above). The complete determination of the corresponding geometry is beyond the scope of this study, but even our crude calculation reveals the presence of a potential energy well located between the *Z*-**3** and the **2b** structure *(vide supra, Fig. 3)*. The situation is similar between *E*-**3** and **2c**, where a rotation of the CHOH-extremity also leads to an energy well for the triplet species. To make this point clear, the qualitative picture of *Figure 5* may be used.

When the triplet reaches its potential well, coming from **2b**, it possesses a neat energy excess, allowing the direct equilibration, through conformational changes, with its counterpart, near *E*-**3**. Along this surface, the **2d** geometry appears as an energy maximum. In this region, the triplet surface is in near touching with the singlet surface. A leak thus exists which allows the cyclobutene formation *via* an

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[10]) Obviously this can be reversed by suitable substitution.

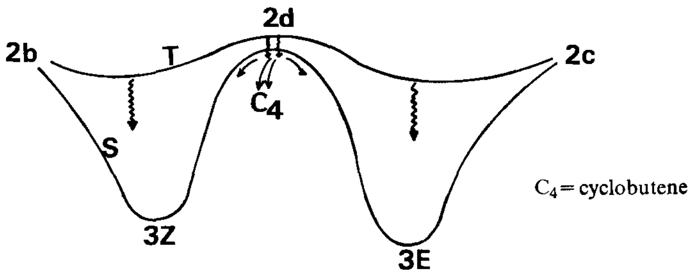

Figure 5

intersystem crossing. This intersystem crossing may lead with quite equal probabilities to Z-**3** or E-**3**, all processes being exothermal.

The decay from the triplet potential wells (phosphorescence), to the GS-dienols is not very likely to occur; it implies important structural rearrangements since the wells geometries widely differ from the dienols ones. Hence rather long lifetimes are predicted for the triplet biradicals.

We thus see that, in the triplet manifold, the dienols precursors interconvert through complex sequences of CH_2- and CHOH-rotations, without important bond length variations. The corresponding energy requirement is inferior to the initial energy excess of the **2b** species.

All these findings are in very good agreement with the recent study of 2-methylacetophenone by *Haag et al.* [2j], using ns flash photolysis, whose conclusion is that the Z- and E-isomers are formed in about equal amounts in the triplet state while the direct enolization from the singlet pathway yields predominantly the Z-isomer.

Our conclusions were obtained from a model structure and our semiqualitative results cannot pretend to depict thoroughly the real behaviour of the parent systems; nevertheless they provide a rationale for most of the experimental observations related to this type of reaction. Moreover, some words of caution must be added, regarding the limits of our model calculation. In parent aromatic systems, the formation of the dienols is expected to be less exothermic since in these compounds the overall aromaticity is destroyed. As a consequence, the energy separation between the GS-dienols and the biradicalar forms would be much lower than our calculated values[11]).

A word of caution must be added regarding the role of substitution in aromatic compounds. It is clear that introduction of alkyl or phenyl groups on the dienol skeleton forces the system to adopt severely twisted conformations whose determination is beyond the scope of this study. In those conditions, the relative stabilities of the Z- and E-isomers depend on each specific case of substitution and no simple rule can be proposed. These steric interactions, undoubtedly must be taken into account in *Diels-Alder* trapping reactions; they would play an important part in the frequent dichotomy observed between flash photolysis experiments [2i,j] [4e,h] and classical chemical analysis [2a,l,m].

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[11]) A kinetic determination has shown that from the Z-isomer, the hydrogen-atom reversion only necessitates a 0.3 eV activation energy [2j].

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