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A Theoretical Study of Photoenolization and Related Reactions

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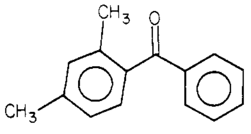
The ground-state and triplet-state reaction paths for the photoenolization of crotonaldehyde were studied with use of INDO semiempirical as well as the STO-3G and 4-31G ab initio MO methods. Extensive geometrical optimization was carried out for each geometry along these paths by using INDO. The energies corresponding to geometries of critical importance were recalculated for comparison by using the STO-3G and 4-31G ab initio methods. Three minima were found on the ground-state surface corresponding to crotonaldehyde and (*E*)- and (*Z*)-1-butadienol. Three minima were also found on the triplet surface that correspond to a planar structure intermediate between the aldehyde and the *Z* dienol, a dienol with a twisted 1,2 bond and an *E* dienol with a twisted 3,4 bond. The known chemistry of *o*-methyl aromatic ketones is discussed in terms of the model system. INDO calculations of some partially optimized species on the *o*-methylbenzophenone triplet surface illustrate some of the arguments.

Chemists have shown considerable interest on the photoenolization and subsequent reactions of ortho-methylated aromatic ketones and aldehydes since Yang and Rivas[2a] showed that the suppression of the photoreduction of benzophenone upon methylation in the ortho position is due to internal hydrogen abstraction rather than to a decrease in the reactivity of the triplet states. Porter and Tchir[2b,c] have detected five transient species in the flash photolyses of each of several ortho-methylated benzophenones. Four of these transients have been identified by indirect means. They correspond (in the case of 2,4-dimethylbenzophenone, **1**) to the triplet state of the ketone **2**, the *Z* and *E* enols **3**, and a dihydroanthrone, **4**, resulting from a secondary photolysis of the enols. The fifth transient corresponds to an unknown intermediate, **5**, which seems to be the primary product of a unimolecular reaction of the triplet **2**. It seems likely that both enols (*Z*)- and (*E*)-**3** may arise directly from **5**. Huffman et al. had earlier suggested that **5** might be a triplet of the enol(s). Since **5** is unreactive toward oxygen, Porter and Tchir seem less certain of this. However, they do not exclude this possibility, particularly if the enol triplet is twisted and/or insufficiently energetic to react with oxygen. More recently, other groups have observed *Z* and sometimes *E* enols in the study of other systems capable of photoenolization, particularly *o*-methylacetophenone (**6**). Scaiano has discussed the mechanism of these processes and their thermal reverse reactions in terms of biradical intermediates, while Wirz et al.[2j] have suggested a detailed reaction sequence for the photoenolization of *o*-methylacetophenone (**6**) that involves two equilibrating planar triplet states of the *Z* and *E* enols. They have also reassigned the structures of some of the transient species previously reported.[2j]



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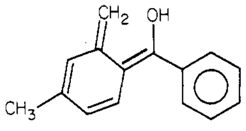

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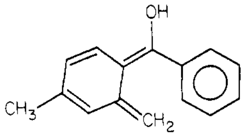

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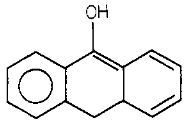

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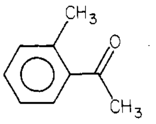

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The purpose of this paper is to provide a theoretical model of the reaction paths involved in photoenolization and the reverse reactions in the hope of stimulating further experimentation. A general rationale for this type of theoretical approach to mechanistic studies has previously appeared.[3] The reader is also referred to a comprehensive review of photoenolization for further discussion of these reactions.[4] Other theoretical treatments of this problem have previously been reported,[5] but none have applied large-scale geometrical optimization to this system.

Methods

In order to make the photoenolization reaction more tractable to a study of the reaction using MO methods with extensive geometrical optimization, we chose to consider the reaction of the more simple system, *cis*-crotonaldehyde, **7**. Since **7**, unlike aromatic ketones, can potentially undergo internal rotation about the 2,3 double bond (at least in its excited states), we chose to keep the four carbons and two vinyl hydrogens of **7** coplanar throughout. The hydrogen attached to the carbonyl was kept coplanar with the oxygen and carbons 1 and 2. The remaining 23 degrees of internal freedom were considered explicitly. One was chosen as a reaction coordinate and changed stepwise, while the other 22 were optimized for each value of the first. This is analogous to the procedures we have used in previous studies of reaction paths.[6]

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Table I. Calculated Energies for Stable and Metastable Species

species	rel energies, kcal/mol INDO	STO-3G	corrected STO-3G[a]	4-31G	total energies, hartrees 4-31G	STO-3G	STO-3G/CI[b]
7	0.0	0.0	0.0	0.0	−229.446 748	−226.869 178	−226.907 678
8	18.1	18.7		16.9	−229.426 237	−226.847 835	−226.864 605
9	21.1	13.4		12.9	−229.419 830	−226.839 306	−226.879 632
10	30.0	14.8	35.8	42.3	−229.379 306	−226.845 607	−226.763 385[c]
11	98.5	38.4	59.4	45.1	−229.374 935	−226.807 942	−226.780 058
12	99.5	36.1	57.1	42.6	−229.378 971	−226.811 603	−226.780 371
9^{T_1}[d]						−226.754 736	−226.764 260

[a] The triplet states were increased by 21.0 kcal/mol relative to the singlet states as explained in the text. [b] Energies are for STO-3G with 100 × 100 CI on assumed, unoptimized geometries, from ref 5b. [c] The assumed geometry for this intermediated differs markedly from the optimized geometry used in this work. [d] Vertical triplet state ($\pi \leftarrow \pi^*$).

Table II. Important Geometric Parameters for the Optimized Stable and Metastable Species[a]

species	$r_{C_1\text{-}O}$	$r_{C_1\text{-}C_2}$	$r_{C_2\text{-}C_3}$	$r_{C_3\text{-}C_4}$	$r_{O\text{-}H_a}$	$r_{C_4\text{-}H_a}$	dihedral $OC_1C_2C_3$
7	1.267	1.430	1.338	1.450	2.146	1.122	0
8	1.359	1.336	1.439	1.327	1.042	2.270	0
9	1.361	1.335	1.441	1.327	1.037	4.904	180.0
10	1.344	1.377	1.377	1.444	1.493	1.137	0
11	1.352	1.421	1.383	1.362	1.037	3.658	90.0
12	1.355	1.381	1.375	1.412	1.035	4.567	180.0

[a] Bond lengths are in angstroms, angles in degrees.

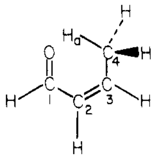
Despite the fact that crotonaldehyde is thought to be photoenolized by a singlet mechanism,[7] only the triplet mechanism is considered here as this is presumably the dominant mechanism in aromatic cases.

The INDO[8] level of approximation of MO theory was chosen for the first part of this study as it is relatively inexpensive, preserves the basic physical model of the molecule reasonably well, and has been used with sufficient frequency so that many of the cases where it is likely to err are already documented. This method has generally been successful in predicting the geometries that correspond to minima on potential surfaces (several serious errors attributed to its companion method, CNDO/2, have been shown to be due to lack of geometrical optimization),[9] although the relative energies of these minima are much more doubtful. For this reason, the energies of the critical points (minima and cols) on the optimized INDO reaction paths have been recalculated by using the STO-3G and 4-31G ab initio methods.

The geometrical optimizations were performed by using a Newton–Raphson procedure in uncoupled internal coordinates. The criteria for optimization (minimum energy with respect to geometrical change) was that (a) the preceding two iterations differed by no more than 0.06 kcal in energy, (b) all the diagonal second derivatives are positive (the off-diagonal second derivatives are zero in these independent coordinates), and (c) the first derivatives are small in comparison to the appropriate second derivatives. This method will be described more completely elsewhere.[11]

Results

The optimized planar *cis*-crotonaldehyde (**7**) and *Z*- and *E*-dienols **8** and **9** were initially obtained. The vertical triplet states (corresponding to the optimized ground-state geometries) were calculated as was an optimized triplet state, **10**. Second and third minima on the triplet surface, **11** and **12**, were later found while the areas of the triplet surface corresponding to the **8**–**9** interconversion and the variation of the C_1–C_2 torsional angles were investigated.



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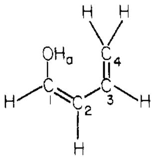

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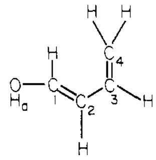

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The energy of these species are tabulated in Table I, while the most important geometrical features of each is tabulated in Table II.

The ground-state path between **7** and **8** was obtained, starting with the equilibrated *Z*-dienol **8**, by using the distance between the hydroxyl hydrogen and carbon 4 as the stepped reaction coordinate. This reaction path produced transition-state **13**. In similar fashion, the transition-state **14** between **9** and **8** was obtained by using the torsional angle about the C_1–C_2 bond as the reaction coordinate.

A second minimum on the triplet surface **11** was obtained by using the torsional angle about the C_1–C_2 bond starting the vertical triplet of **9**. Continuation along the same reaction coordinate eventually leads to **10** via the transition-state **15**. A third minimum on the triplet surface **12** was obtained by twisting the C_3–C_4 torsional angle,

Table III. Energies of Transition States

species	rel energy, kcal/mol INDO	STO-3G	corrected STO-3G[a]	4-31G
13	32.3	62.2		60.3
14	94.1	138.3	80[b]	115.1
15	106.8	45.0	66[c]	50.7

[a] Relative to **7**. [b] Twisted singlet energies were reduced by 59 kcal/mol to correct for CI (see text). [c] Triplet states were increased by 21 kcal/mol to correct for CI (see text).

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Table IV. Important Geometric Parameters for the Optimized Transition States[a,b]

species	$r_{C_1\text{-}O}$	$r_{C_1\text{-}C_2}$	$r_{C_2\text{-}C_3}$	$r_{C_3\text{-}C_4}$	$r_{O\text{-}H_a}$	$r_{C_4\text{-}H_a}$	dihedral $OC_1C_2C_3$
13	1.340	1.356	1.414	1.364	1.136	$\underline{1.38}$	1
14	1.361	1.345	1.399	1.334	1.037	4.675	$\underline{70}$
15	1.347	1.436	1.363	1.384	1.043	2.271	$\underline{140}$

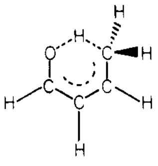
[a] The value of the reaction coordinate is underlined. [b] Bond lengths in angstroms, angles in degrees.

Table V. Relative Energy and Important Geometric Parameters for the Partially Optimized Triplet Species on the *o*-Methylbenzephenone Surface

species	$r_{C\text{-}O}$	$r_{C\text{-}C}$ (carbonyl-substituted ring)	$r_{C\text{-}C}$ (carbonyl-unsubstituted ring)	$r_{C\text{-}C}$ (methyl/methylene ring)	$r_{O\text{-}H_a}$	$r_{C\text{-}H_a}$	rel energy, kcal/mol
10a	1.334	1.582	1.590	1.464	1.594	1.138	44.3
11a	1.362	1.457	1.429	1.406	1.037	3.433	0

starting from the vertical triplet of **9**. An analogous calculation starting from the vertical triplet of **8** regenerated **10** rather than another minimum. Data related to the energies and geometries of these transition states appear in Tables III and IV. One should note that the transition states that are obtained by the methods used here can be prejudiced by the choice of reaction coordinate. Even using the same coordinate but stepping in two different directions (i.e., incrementing and decrementing) often leads to different predicted transition states. This phenomenon is due to the fact that stepping along a reaction coordinate will proceed along the least steep incline. Such a path may lead to a channel that is separated from that leading to a lower col. For this reason each reaction coordinate was stepped in both directions. In some cases other reaction coordinates were considered. The data reported here refer to the lowest col obtained for each reaction. The only rigorous means of ascertaining that no col of lower energy exists for these reactions would be to examine the entire surface.

Since the lowest triplet minimum **10** is necessarily central to any discussion of the mechanism of photoenolization, it was of interest to calculate the singlet energy that corresponds to the optimized geometry of **10**. This energy was calculated to be 33.4, 37.9, and 35.2 kcal/mol by the INDO, STO-3G, and 4-31G methods, respectively, very close to that of the triplet **10**, 30.0, 35.5 (corrected, see below), and 42.3 kcal/mol, by the same methods, indicating that the singlet and triplet surfaces are very close in this region.



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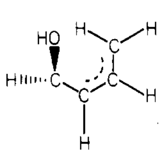

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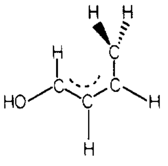

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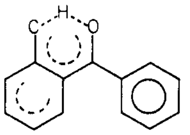
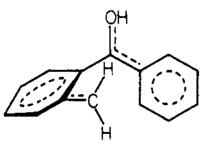


10a



11a

The energies of all the critical points for the system (minima and cols) were calculated *in their INDO optimized geometries* by using the STO-3G and 4-31G ab initio methods. These values are included in the appropriate tables and compared with the energies calculated by Sevin et al., who used STO-3G with 100 × 100 CI on unoptimized, assumed geometries.[5b] We can note that the effect of CI on the two geometries, **7** and **9**, most likely to be correct in their calculations is to lower the energies by about 28 kcal in the ground states and 7 kcal in the triplet state with respect to our STO-3G calculations. Further comparisons of the twisted singlet suggests 87 kcal to be the correction for the twisted ground states. These values when applied to our calculations suggest corrections raising the triplet states by 21 kcal and lowering the twisted singlet transition states by 59 kcal in comparison with the stable ground singlets. The corrections are applied in the appropriate tables.

Finally, two points on the triplet surface of *o*-methylbenzophenone were calculated for comparison. These are (a) the planar structure **10a** that is analogous to **10** on the crotonaldehyde surface and (b) the twisted **11a** that corresponds to **11** on the crotonaldehyde surface. To reduce the cost, the optimization was limited to 10 independent degrees of freedom, including the lengths of three C–C bonds that are not part of the rings, the C–O, C–H, or O–H bond, for the labile H, the H–O–C valence angles, and the dihedral angles of the three H's not bonded to the rings. For **10a**, the valence angles of the other two H's were varied systematically, while for **11a** the torsional angle between the substituted ring and the carbonyl was varied. All other bond lengths and angles were fixed at 1.39 Å (C–H) and 120°. No STO-3G calculations were performed on **10a** and **11a**. The data pertaining to these species are listed in Table V.

Discussion

The triplet-state photoenolization of crotonaldehyde can be visualized as excitation of **7**, intersystem crossing to the triplet, and geometrical relaxation to the optimized triplet **10**. We have not observed a barrier between the vertical triplet of **7** and **10**. The possibility exists that the initial excited singlet of **7** geometrically relaxes somewhat before intersystem crossing to a point on the triplet surface different from the vertical triplet of **7** and that a barrier might exist between this point and **10**. We cannot rule out this possibility despite our inability to find a fourth minimum (other than **10**–**12**) on the triplet surface. The geometry of **10** is such that it should be able to decay easily to the ground state as either **7** or **8**. The fact that the ground-state energy corresponding to the geometry of **10** is similar to that of the triplet for all methods except uncorrected STO-3G suggests that **10** lies at or near crossing between the triplet ground-state surfaces. For uncorrected STO-3G calculations the triplet lies well below the singlet, probably an artifactual result due to either the tendency of STO-3G to overestimate the stability of triplets or the inadequacy of the INDO optimized geometry for a STO-3G calculation. The corrected STO-3G and the 4-31G values agree well

Table VI. Activation Energies for Several Reactions

	activation energy, kcal/mol			
rctn	INDO	STO-3G	corrected STO-3G	4-31G
8 → **7**	14.2	49.7	*a*	43.4
9 → **8**	73.1	123.1	64[b]	102.2
11 → **10**	8.5	10.4		5.6

[a] The correction of 59 kcal/mol applied to twisted singlet transition states could not be applied here because it is larger than the activation energy and the transition state is not twisted. [b] Corrected by lowering the energy by 59 kcal/mol (see text).

with INDO results. Despite the tendency for INDO, for example, to predict longer (~1.11 Å) C–H bonds than does the STO-3G (1.09 Å), the fact that the relative energies for the stable singlet species **7**–**9** are similar to each other for all methods used (although the relative energies of **8** and **9** are reversed in INDO) argues in favor of the first reason, as does the "corrected" STO-3G values.

There is a disagreement among the methods with respect to whether **8** or **9** is the more stable enol. INDO calculations, which predict **8** to be more stable, are known to sometimes incorrectly predict the relative energies of potential minima; on the other hand, the ab initio calculations reported here have not been directly optimized. Since both ab initio methods agree in predicting **9** to be more stable, we shall use that prediction. Here the unoptimized STO-3G/CI results are clearly in error.[5b] The prediction that the *E* enol is 9.4 kcal more stable than the *Z* isomer **8** is surely due to inadequate optimization of **8** as the relative effect of CI in **7**–**9** should be small.

Some of the discrepancies between the relative energies calculated by STO-3G and the other methods for the transition states (Table III) become less troublesome when the corrected STO-3G values are used. They are restated as activation energies in Table VI. The activation energies are predicted in the same qualitative order by each method. Although without the CI corrections near-quantitative agreement is only evident for **9** → **10**, the corrected values agree much more closely.

Instead of relaxing to either **7** or **8**, **10** might rearrange to **11** (see Figure 1), which we feel might correspond to the elusive intermediate observed by Porter and Tchir,[2b] the biradical by Scaiano,[2n] or the enol triplets.[2j] The energy of **11** is calculated to be 68.5, 19.8, and 2.8 kcal/mol greater than that of **10** by INDO, STO-3G (corrected), and 4-31G, respectively. Here, the INDO value is almost certainly incorrect as INDO predicts a negative (−40 kcal) activation energy for the abstraction of a hydrogen from methane by methyl radical.[12] All three methods clearly predict **11** to be less stable than **10** (although by significantly different amounts) for the crotonaldehyde model system. For aromatic compounds such as the *o*-methylbenzophenone series, this situation may be reversed since twisting into an intermediate such as **11a** allows each phenyl ring to retain its aromaticity while separating the two unpaired electrons into what resembles substituted benzyl radicals. The intermediate that corresponds to **10**, **10a**, must maintain the C–O bond approximately coplanar with the ring whose methyl is undergoing abstraction, thus interfering with the aromaticity of the ring and assuring the destabilization interaction between the unpaired electrons. It is not unreasonable, therefore, to expect that the relative energies of **10a** and **11a** might be the reverse of **10** and **11**. The results of Table V support this contention. One should note that the calculations on **10a** and **11a** were performed with very limited geometrical optimization.

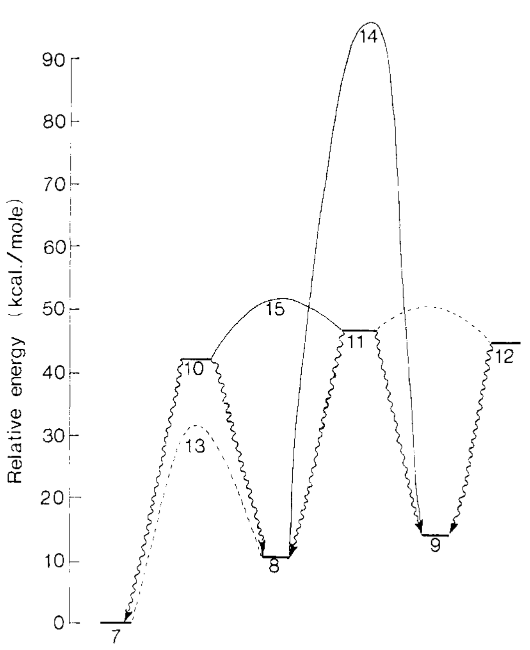
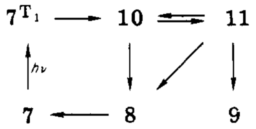


Figure 1. Reaction coordinate diagrams for the S_0 and T_1 surfaces of crotonaldehyde. All energies are from 4-31G calculations except for the INDO value for ΔE(**13**–**8**).

Scheme I



The second triplet minimum, **11**, can be expected to decay to either the *Z*- or *E*-enol **8** or **9** but not very readily to **7**, unless it returned to **10**. The third triplet minimum **12** can be reasonably expected to either decay to the *E*-dienol **9** or to rearrange to **11** via a simultaneous twisting of the C_1–C_2 and C_3–C_4 torsional angles. Species analogous to **12** are not likely to play an important role, in the reactions of the aromatic precursors since, unlike the case of **11a**, there is no apparent reason why the phenyl rings should stabilize them. For this reason, the reaction path between **9** and **12** was not studied in detail.

The mechanistic implications of this study depend very much upon the intermediacy of triplet states such as **10** and **10a** in the reaction sequences. It is important to establish that **10** is not an artifact of the INDO calculations. This is perhaps best shown by the comparison of the STO-3G energy of **10** with STO-3G/CI T_1 states previously reported.[5b] The energy of **10** is 35.0 kcal/mol (1.5157 eV) lower than the *lowest* triplet state among all the intermediates, including crotonaldehyde, both the enols, and four twisted species, proposed by Sevin et al.[5b] The existence of **10** or something very much like **10** is clearly supported since it is predicted to be the lowest energy triplet species by all three methods.

If one accepts **10** as an intermediate, in particular as the relaxed triplet of **7**, one expects the reactions shown in Scheme I. Quenching of **10** can lead to either **7** or **8** while quenching **11** would would lead to **8** or **9**. Assuming an equilibrium is established between **10** and **11** and that **7** (T_1) decays immediately to **10**, triplet quenching will always give rise to *Z*-enol **8** as well as **7** when the equilibrium concentration of **10** is significant and *E*- and *Z*-enols **8** and **9** when **11** is dominant. Wirz et al. report that high pi-

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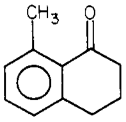
[12] Rayez-Meaume, M. T.; Dannenberg, J. J.; and Whitten, J. L. *J. Am Chem. Soc.* **1978**, *100*, 747–749.

perylene concentrations suppress the formation of the *E* enols of **6** and **16** but not all of the *Z* enols,[2j] presumably by quenching a precursor. They interpret this result as indicating that about 30% of the *Z* enols are formed via excited singlet-state pathways. In the case of **1**, however, the *Z*- and *E*-enols **3** are thought to occur via a pure triplet mechanism.[2j] To the extent that an intermediate analogous to **10** is important in the photolyses of **6** and **16**, one should expect quenching of the *E*-enol but not the *Z*-enol. This casts some doubt upon the singlet mechanism for **6** and **16**.



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The rapid equilibration of the *E*- and *Z*-enol triplets proposed by Wirz[2j] is replaced by a single twisted enol triplet, **11**, which can decay to either enol isomer. Wirz et al.[2j] have calculated a barrier of 16 kcal for the conversion of the *Z* and *E* enols of **6**, but experimental results require equilibration of the isomeric triplets within 100 ns, in disagreement with their calculations.[2j,l] They suggest that the triplet states of the enols of **6** and **16** must be planar since the absorption spectrum of triplet **6** is similar to that of triplet **16** and the saturated ring forces the enol of **16** to be planar. We are less convinced by this argument since the saturated ring in the enol triplet of **16** can presumably take a partial chair conformation. Doing this would reduce the interaction of the unpaired electrons, which generally should lower its energy. In addition, no direct (i.e., spectral) evidence exists for two enol triplets.[2] Furthermore, Scaiano has reported an activation energy for the dissapearance of the enol triplet of **6**.[2n] This observation is understandable if the triplet of enol **6** were twisted and of lower energy than the S_0 energy for the same geometry. In such a case one might expect that moving up along the triplet surface might bring the system to a point of degeneracy or near degeneracy of the T_1 and S_0 surfaces, where intersystem crossing might be facilitated. It is difficult to rationalize such an activation energy for planar triplet enols where the S_0 surface is surely below the T_1 surface. Scaiano has also shown that only one twisted enol triplet occurs in the photoenolization of *o*-methylbenzophenone.[2m] This intermediate is very likely **11a**.

Wirz et al. also put a lower limit of 18 kcal/mol on the barrier between the ground-state *E* and *Z* enols of **1**,[2j] well below our calculated barrier for **9** → **8** (which is certainly too high).

The barrier to ground-state reketonization for the *Z* enol of **6** has been determined to be 8 kcal/mol.[2n] As resonance stabilization of the ketone ought to make the reketonization of the *Z* enol of **6** more exergonic than that for **8**, one might expect the **8** → **9** barrier to be slightly higher by virtue of the Hammond postulate.[13] Thus the INDO value of 14.2 kcal/mol seems reasonable. The uncorrected STO-3G and 4-31G values of 49.7 and 43.4 kcal are surely too high. One would expect CI to lower **13** more than **7** or **8** as the electron correlation error is known to relatively destabilize transition states for H transfer in ab initio calculations.[14] Since Sevin and Bigot did not calculate a structure similar to **13**, it is difficult to assign a CI correction to that of **13**. The 59-kcal correction estimated for **14** can be used as an upper limit to the correction, but it is greater than the barrier height.

The report by Wagner and others that two ketone triplets exist for conformationally variable substrates have not been treated here. Triplet minima may exist for aromatic ketones that are absent for crotonaldehyde. The importance of geometrical optimization in this study is quite apparent from a comparison of our results with those of Sevin et al.[5b] Despite the use of moderate CI, they failed to give reasonable descriptions of the important intermediates, notably **10**. As our STO-3G total energy for **10** is lower than any triplet they report by at least 34 kcal[4b] and our twisted triplets **11** and **12** are also much lower in energy than the CI counterparts, it becomes clear that the completely optimized INDO surface, which predicted the structures, probably gives a more useful qualitative description of the problem than either set of STO-3G calculations taken separately. Only when the more elaborate 4-31G basis set is used or our STO-3G results are corrected by interpreting the probable effects of CI on our calculations by comparison with ref 5b does the ab initio surface become clearly preferable to the INDO surface. The STO-3G energy of **10** is lower than that of the two enols **8** and **9**, before CI corrections. The importance of geometrical optimization of reaction paths involving uncharacterized intermediates and transition state must be continually emphasized.

Conclusion

In summary, our calculations predict two triplet-state intermediates, formation of cis and trans enols, and more facile reversion of the cis than trans enol to the keto form. These results correlate reasonably well with the observation of several experimental groups and predict a specific model for a triplet-state intermediate that has not been previously proposed. Since the argument for the relative stabilities of intermediates such as **10** and **11** depend upon the various substituents to stabilize the twisted structures, a logical experimental corroboration of this study might include studies comparable to those already performed on systems containing gradations of stabilizing elements, such as substituted o-methylbenzophenones and benzaldehydes where the substituents are chosen to provide a range of twisted biradical stabilities. Presumably the relative yield of the *E* enol and the steady-state concentration of twisted enol triplet should decrease as the substituents become less radical stabilizing. A comprehensive set of MO calculations on a large number of model compounds might be useful here.

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Registry No. **6**, 577-16-2; **7**, 15798-64-8; **8**, 70415-58-6; **9**, 70411-98-2; **16**, 51015-28-2.

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[13] Hammond, G. S. *J. Am Chem. Soc.* **1955**, *77*, 334–339.

[14] Schaefer, H. F., III, *Acc Chem. Res.* **1979**, *12*, 288.