255. The Photoenolization of 2-Methylacetophenone and Related Compounds

by **Roland Haag** and **Jakob Wirz**[1])

Physikalisch-chemisches Institut der Universität Basel,
Klingelbergstrasse 80, CH-4056 Basel, Switzerland

and **Peter J. Wagner**

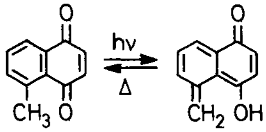
Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, U.S.A.

(30.VIII.77)

Summary

A reinvestigation of 2-methylacetophenone (**1**) by ns flash photolysis has provided detailed evidence for the reaction sequence of photoenolization. The triplet reaction proceeds adiabatically from the lowest excited triplet state of the ketone, ^{3}**K** (**1**), to the enol excited triplet state, ^{3}**E** (**1**), which decays both to enol and ketone ground state. The *Z*- and *E*-isomers of the photoenol, *Z*-**E** (**1**) and *E*-**E** (**1**) are formed in about equal yield by the triplet pathway, while direct enolization from the lowest excited singlet state of **1** yields (predominantly) the *Z*-isomer. Intramolecular reketonization from *Z*-**E** (**1**) to **1** proceeds at a rate of *ca.* $10^8 s^{-1}$ in cyclohexane, but can be retarded to *ca.* $10^4 s^{-1}$ in hydrogen-bond-acceptor solvents. The proposed mechanism is summarized in *Scheme 1* and rationalized on the basis of a state correlation diagram, *Scheme* 2. 3,3,6,8-Tetramethyl-1-tetralone (**2**) was used as a reference compound with fixed conformational position of the carbonyl group, and some results from a brief investigation of 2,4-dimethylbenzophenone (**3**) are also reported.

We have recently found [1] that the photoenolization of 5-methyl-1,4-naphthoquinone takes place with high efficiency and that the thermal reketonization to starting material is very fast at room temperature. The great retardation of the back reaction from a rate of *ca.* $10^5 s^{-1}$ in cyclohexane to *ca.* $10^1 s^{-1}$ in hexamethyl phosphoric acid triamide (HMPA) was striking but not surprising: The solvation of the enolic proton in hydrogen-bond-acceptor (HBA) solvents obviously provides an



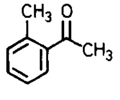
---

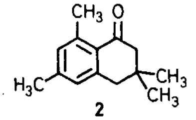
[1]) Author, to whom correspondence should be addressed.

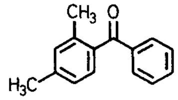
additional barrier to the intramolecular [1.5]-hydrogen shift by which the quinone is reformed.

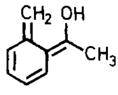
Assuming that such behaviour should be characteristic of thermally unstable (*Z*)-dienols in general, we proposed to use this solvent dependence as a criterion for the identification of the various transient intermediates observed by flash photolysis of *ortho*-alkyl substituted aromatic ketones, since the controversial question [2] about the configuration of their photoenols is both of theoretical and practical concern. We now report our results from a reinvestigation of 2-methylacetophenone (**1**), using 3,3,6,8-tetramethyl-1-tetralone (**2**) as a reference compound with fixed *syn*-conformation of the carbonyl group relative to the *ortho*-methyl group, as well as some preliminary data obtained with 2,4-dimethyl benzophenone (**3**). Our observations allow for a straightforward rationalization of a number of seemingly inconsistent findings of previous investigations [2–6].

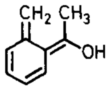
Results. - Three distinct transient species have been detected by flash photolysis of **1** using frequency tripled (353 nm) or quadrupled (265 nm) pulses of *ca.* 30 ns half-width from a Nd glass laser as an excitation source. These transients are assigned to the triplet state of the photoenols, ^{3}E (**1**), and to the *Z*- and *E*-isomers of the enol in the electronic ground state, *Z*-E (**1**) and *E*-E(**1**), respectively. Flash excitation of **2** gave rise to two transients corresponding to ^{3}E (**2**) and *Z*-E (**2**)[2]). Furthermore, in aqueous solution the triplet state of the ketone **2**, ^{3}**K** (**2**), was sufficiently long-lived to be identified as the precursor of ^{3}E (**2**). The short-lived transients observed by flash photolysis of **3** are attributed to ^{3}E (**3**) and *Z*-E (**3**). The assignments are based on the experimental data given in small print below and shall be justified in the discussion.

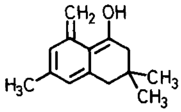

1

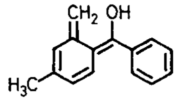

2

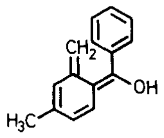

3


Z-E(1)


E-E(1)


Z-E(2)


Z-E(3)


E-E(3)

1. *2-Methylacetophenone* (**1**) *and 3,3,6,8-tetramethyl-1-tetralone* (**2**). - *Excited triplet state of the ketones,* ^{3}**K** (**1**) *and* ^{3}**K** (**2**). With a single exception, the lifetimes of ^{3}**K** (**1**) and ^{3}**K** (**2**) were too short to permit the detection of their triplet-triplet absorption after the exciting laser pulse of *ca.* 30 ns. Accordingly, the addition of $> 10^{-3}$M naphthalene (E_T 61 kcal/mol) to solutions of **1** or **2** was necessary in order to obtain appreciable sensitization of the characteristic naphthalene triplet absorption after excitation of **1** or **2** (E_T *ca.* 73 kcal/mol) at 353 nm. A plot of the inverse of the initial absorbance due to naphthalene triplet (monitored at 420 nm) *vs.* the inverse of the naphthalene concentration (10^{-3} to 10^{-1}M) in a 10^{-1}M solution of **1** in benzene yielded a slope/intercept ratio of 0.02 ± 0.01 indicating a

---

[2] The labels *Z* and *E* designate the configuration of the dienol moieties, irrespective of the residual molecule, to avoid label changes for structurally related systems.

lifetime of ^{3}**K** (**1**) of *ca.* 10 ns. The lifetime of ^{3}**K** (**2**) in water containing 2 percent alcohol was found to be considerably longer (100 ns in degassed and *ca.* 40 ns in oxygen-saturated solution) and was monitored directly by the decay of its absorption at 480 nm. The spectrum of ^{3}**K** (**2**) shown in *Figure 1a* was obtained point by point from the absorbance immediately after the laser flash and corrected in the range of 390±60 nm for some contribution due to Z-E (**2**) which is partly formed within the flash by the singlet pathway (see below). It is similar to the spectrum of triplet acetophenone in water which has been determined previously by *Lindqvist et al.* [7].

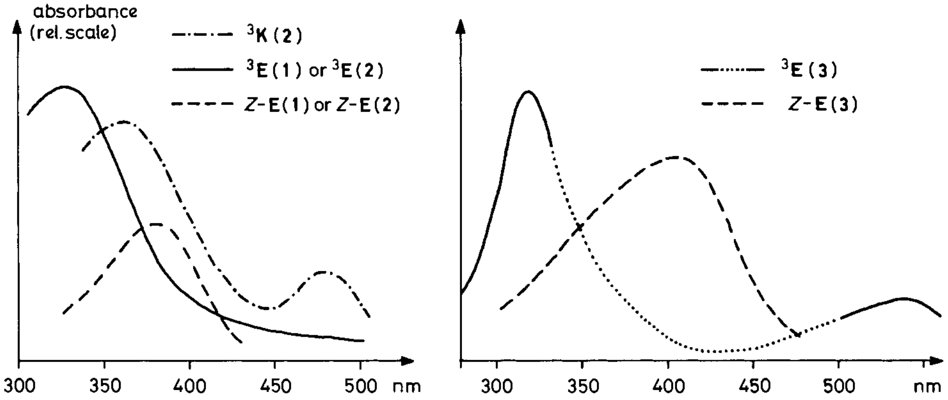


Fig. 1. *Absorption spectra of transient intermediates observed by flash photolysis of* **1** or **2**, **2** and **3**

Excited triplet state of the photoenols, ^{3}E (**1**) *and* ^{3}E (**2**). The absorption spectrum observed immediately after excitation of **1** *(Fig. 1a)*, again corrected for the absorption due to Z-E (**1**) in the range of 390±60 nm, is attributed to ^{3}E (**1**). The lifetime of this species was determined at 330 nm and was found to depend on the HBA basicity [8] of the solvent, ranging from 130 ns in degassed cyclohexane to 2.6 µs in degassed HMPA *(Table 1)*. It is quenched by oxygen with a rate very close to the diffusion-controlled limit, *i.e.* somewhat faster than the triplet state of aromatic hydrocarbons [9]. Lifetimes in air-saturated solutions are also given in *Table 1.* The initial absorption due to ^{3}E (**2**) and its decay observed after flash photolysis of **2** were quite similar to that of ^{3}E (**1**), the lifetimes of the former were somewhat higher both in aerated and degassed solution *(Table 1)*. The formation of ^{3}E (**2**) from ^{3}**K** (**2**) was directly observable in aqueous solution by a delayed enhancement of the absorbance at 330 nm, which grew in with the same rate of $1 \cdot 10^7$ s^{-1} after the flash, as was found for the decay of ^{3}**K** (**2**). In the other solvents this process occurs within the lifetime of the laser pulse, but it is manifested by the effect of adding *cis*-piperylene to these solutions: While the lifetime of neither ^{3}E (**1**) nor ^{3}E (**2**) was appreciably affected by the addition of *cis*-piperylene to cyclohexane solutions of **1** and **2**, respectively, the formation of these transients was suppressed, albeit with different efficiency. The dependencies of the initial absorbances due to ^{3}E (**1**) and ^{3}E (**2**) on the concentration of *cis*-piperylene are shown in *Figure 2.* The nonlinear curve obtained for **1** is indicative of two kinetically independent excited state precursors of ^{3}E (**1**), but its precision is insufficient for a detailed analysis. The lifetime of the single precursor of ^{3}E (**2**) is estimated as *ca.* 1 ns assuming a near diffusion controlled quenching rate by *cis*-piperylene of $5 \cdot 10^9$M^{-1}s^{-1}. Neither ^{3}E (**1**) nor ^{3}E (**2**) are capable of sensitizing naphthalene by triplet energy transfer.

The lifetime of ^{3}E (**2**) was little affected by temperature. In degassed EPA solution (5 parts ether, 5 parts isopentane, 2 parts ethanol) it increased from 4 µs at room temperature to 15 µs at *ca.* − 60° and did not change any further upon cooling down to *ca.* − 180°, until a rather sudden change was observed when the EPA solution froze to a rigid glass. The decay was then non-exponential but on the average faster than in the liquid solution (first half-life *ca.* 5 µs). It appears that EPA at − 196° is too rigid to allow for proper solvation of the hydroxyl group within a few µs after its formation.

Photoenols in the electronic ground state, Z-E (**1**), *E*-E (**1**), *and* Z-E (**2**). Two transients absorbing at 390±60 nm with similar absorption spectra *(Fig. 1a)* but widely different kinetic behaviour arose from

Table 1. *Lifetimes of photoenol triplets and Z-photoenols in various solvents at room temperature*

Solvent	^{3}E (**1**)		^{3}E (**2**)		*Z*-E (**1**)	*Z*-E (**2**)	*Z*-E (**3**)
	degassed	aerated	degassed	aerated			
Cyclohexane	130 ns	50 ns	230 ns	80 ns	< 20 ns	< 20 ns	~ 30 ns
Benzene	-	-	-	-	28 ns	30 ns	50 ns
Diethyl ether	570 ns	100 ns	2.5 μs	170 ns	110 ns	130 ns	430 ns
Acetonitrile	830 ns	90 ns	3.5 μs	160 ns	160 ns	270 ns	450 ns
Tetrahydrofuran	860 ns	110 ns	5 μs	190 ns	480 ns	500 ns	1.4 μs
2-Propanol	1.2 μs	100 ns	6 μs	150 ns	700 ns	760 ns	1.1 μs
Methanol	0.9 μs	100 ns	5 μs	100 ns	730 ns	1.0 μs	2.6 μs
Water	1.0 μs	520 ns	3.3 μs	750 ns	1.0 μs	1.6 μs	-
Dimethyl sulfoxide	1.4 μs	450 ns	6 μs	560 ns	15 μs	18 μs	35 μs
HMPA	2.6 μs	1.2 μs	9 μs	430 ns	160 μs	200 μs	300 μs

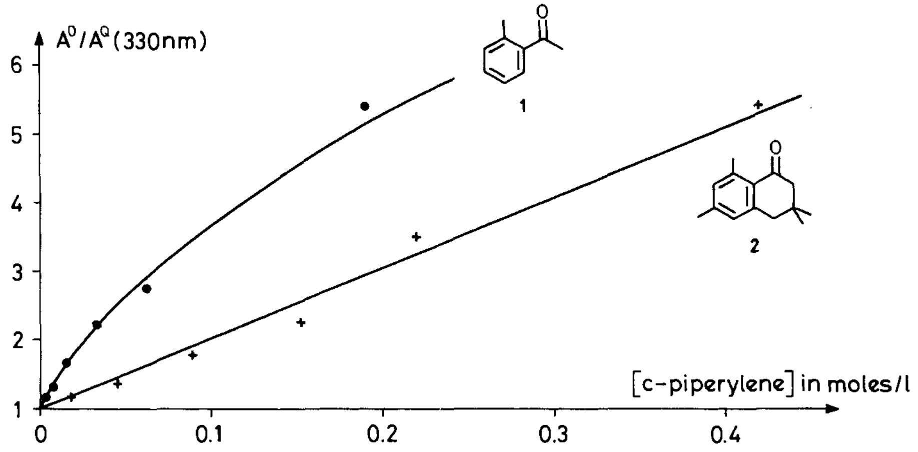


Fig. 2. *Initial absorbance A at 330 nm due to* ^{3}E *in the presence of* cis-*piperylene*

flash photolysis of **1**. The long-lived species, to which we assign the structure *E*-E (**1**), has been observed previously and will not receive much attention here. Its lifetime is longest in highly pure aprotic solvents (*ca.* 4 s in cyclohexane [4] [6]) and its reaction rates with oxygen and maleic anhydride are $2 \cdot 10^5$ and $2 \cdot 10^4$ M^{-1} s^{-1}, respectively [4]. The lifetime of *Z*-E (**1**) was extremely short, less than that of its precursor ^{3}E (**1**) in all but the strongest HBA solvents dimethyl sulfoxide (DMSO) and HMPA where it amounted to 15 and 160 μs, respectively. Assuming that the two dienol isomers have a comparable reactivity towards oxygen, we would not expect an appreciable shortening of the lifetime of *Z*-E (**1**) by saturating the solutions with oxygen (1 atm). This was indeed found to be the case for DMSO and HMPA solutions. The lifetime of *Z*-E (**1**) in the other solvents *(Table 1)* was thus measured in oxygen-saturated solutions. The decay of ^{3}E (**1**) was then considerably faster than that of *Z*-E (**1**) and the reaction sequence ^{3}E (**1**)$\rightarrow$*Z*-E (**1**)+*E*-E (**1**) was directly reflected by a delayed increase of the absorbance at 390 nm, growing in with the same rate as the decay of ^{3}E (**1**) monitored at 330 nm. In apolar solvents, the quenching of ^{3}E (**1**) by oxygen was accompanied by an increase in the photoenol yield to approach that in polar solvents in which the presence of oxygen had little effect. Upon the addition of *cis*-piperylene, the yield of *E*-E (**1**) was suppressed concomitantly with the yield of ^{3}E (**1**) *(Fig. 2)*, while that of *Z*-E (**1**) was only reduced to about one half of its original value by quencher concentrations up to 5 M.

The assignment of the two photoenol isomers of **1** is strongly supported by the observations with **2** which yielded only a single enol species, *Z*-E (**2**). Its spectrum and kinetics of formation and decay were virtually identical with those of *Z*-**E** (**1**). The yield of *Z*-**E** (**2**) from **2** under various conditions was approximately equal or slightly larger than the combined yields of *Z*- and *E*-**E** (**1**) from **1**, assuming equal extinction coefficients for all three enols at 390 nm. In an EPA glass at 77 K, *Z*-**E** (**2**) was stable for hours and its absorption spectrum is shown in *Figure 3*. We have not been able to detect any fluorescence or phosphorescence of *Z*-**E** (**2**). It was reconverted to **2** either by warming the glass up to *ca.* 90 K or by irradiation at 406 nm, though the photochemical reketonization was accompanied by a side reaction yielding unidentified products irreversibly.

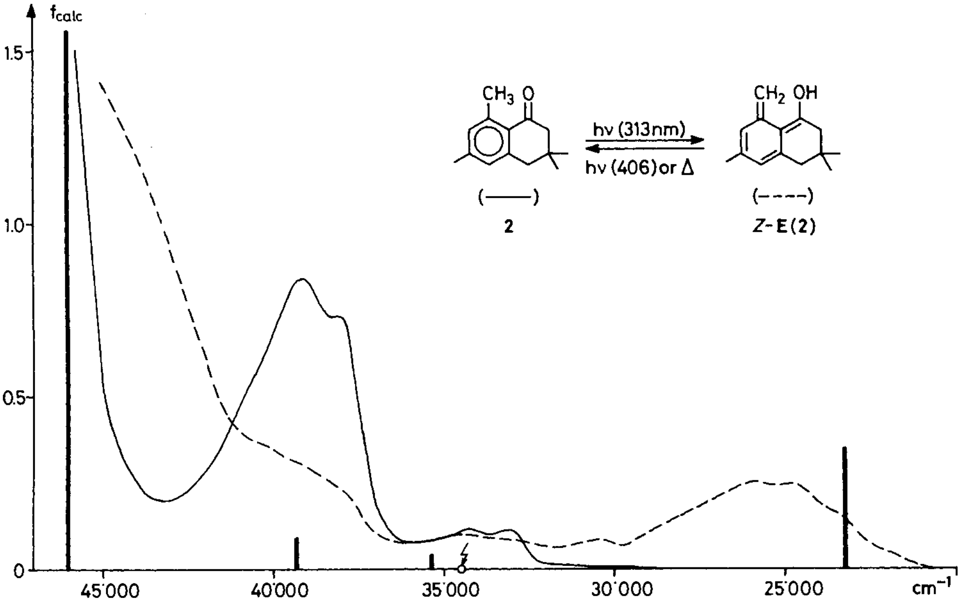
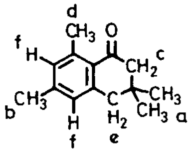


Fig. 3. *Photoenolization of* **2** *in EPA glass at 77 K.* Vertical bars indicate oscillator strengths f and transition energies calculated for *Z*-**E** (**1**)

Photoinduced deuteration of the 8-methyl group of **2**. The extent of deuteration of **2** during continuous irradiation in the presence of D_2O was monitored by NMR. The 100-MHz-^{1}H-NMR. spectrum of **2** in CCl_4 consists of five singlet peaks which were assigned as shown in *Table 2* on the basis of their integrated relative intensities and by comparison of the chemical shifts with suitable reference compounds. These assignments were corroborated by the effect of adding Eu $(fod)_3$ as a paramagnetic shift reagent [10]. The induced shift parameters S given in *Table 2* are in qualitative agreement with the

Table 2. *^{1}H-NMR. data of* **2** *in CCl_4 solution*

Group	δ_{TMS} [ppm]	Relative Intensity	$S = \frac{\Delta\delta}{\text{Eu equiv.}}$
a	1.07	6	0.65
b	2.30	3	0.53
c	2.35	2	3.68
d	2.57	3	2.70
e	2.76	2	1.04
f	6.79 (br.)	2	0.98, 0.65



expectations from the pseudocontact shift equation [11]. Saturation occurred at equimolar concentrations of **2** and Eu(fod)$_3$, indicating 1:1 complexation.

Irradiation of a $3 \cdot 10^{-2}$M solution of **2** in 0.5 ml DMSO-d$_6$, containing 30 percent CD$_3$OD, with 313 nm light filtered from a 200 W high-pressure mercury arc did not induce a significant deuteration of **2** within 1 h. We concluded that the short lifetime of *Z*-**E** (**2**) does not allow for efficient exchange of its hydroxyl proton with the solvent. The experiment was thus repeated with a 10^{-1}M solution of **2** in DMSO-d$_6$ containing 30% D$_2$O and a catalytic amount (*ca.* $2 \cdot 10^{-2}$ equiv.) of NaOD. In this solution complete exchange of the a-methylene protons of **2** (group c in *Table 2*) took place within minutes in the dark, but the intensity of the remaining signals kept unchanged for hours at room remperature. Irradiation for 30 min with 313 nm light resulted in a 70% intensity reduction of the signal due to the 8-methyl protons (group d in *Table 2*) without affecting the other signals. Mass spectral analysis of a sample of **2** isolated from this solution indicated 66% deuteration of the 8-methyl group.

2. *2,4-Dimethylbenzophenone* (**3**). - *Excited triplet state of the photoenol,* ^{3}**E** (**3**). The short-lived transient formed within the duration of the 343 or 265 nm laser pulse (λ_{max} 320 and 535 nm, *Fig. 1b*) is attributed to ^{3}**E** (**3**). It decays with a lifetime of *ca.* 30 ns in both apolar (cyclohexane) and polar (methanol) solvents, too fast to be affected by the presence of oxygen ($\leqslant 1$ atm). Addition of *cis*-piperylene does not reduce its lifetime, but its yield is approximately halved at a quencher concentration of 0.05M in cyclohexane, suggesting a lifetime of *ca.* 5 ns for its precursor, ^{3}**K** (**3**). Sensitization of naphthalene triplet after excitation of **3** at 353 nm occurs exclusively during excitation, *i.e.* ^{3}**E** (**3**) is not efficient as an energy donor.

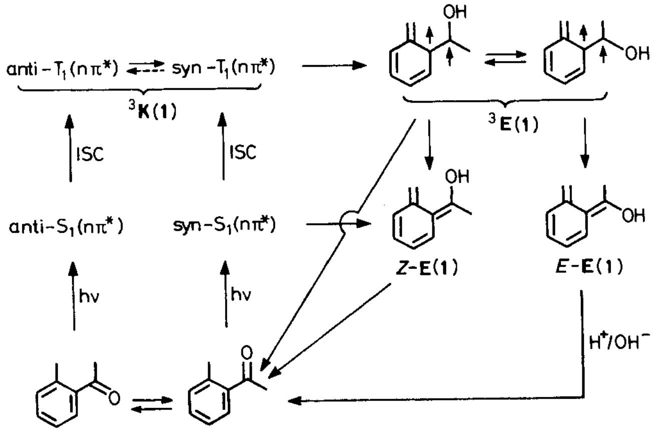
Photoenols in the electronic ground state, Z-**E** (**3**) *and E*-**E** (**3**). The major part of the transient absorbance observed 100 ns after the flash in the range of 420 ± 60 nm is due to the two isomeric enols *Z*-**E** (**3**) *(Fig. 1b)* and *E*-**E** (**3**). At 420 nm their absorbance increased from virtually zero at the end of the exciting pulse with a rate matching the decay of ^{3}**E** (**3**) at 320 or 535 nm. Again, the decay kinetics and its solvent dependence was characteristically different for the two enol isomers. The lifetime of *Z*-**E** (**3**) ranged from *ca.* 30 ns in cyclohexane to 300 µs in HMPA *(Table 1)*. The long-lived *E*-**E** (**3**) and the remaining weakly absorbing species [3] were not studied in detail.

3. *Semiempirical calculations.* - *Absorption spectra of the photoenols in the ground state.* The qualitative reliability of standard PPP/SCF/CI calculations in predicting the low-energy allowed transitions of quinonoid compounds is well-documented [1] [12]. The results of such a calculation for *Z*-**E** (**1**) with standard parameters [1] and inclusion of all singly excited configurations are shown in *Figure 3*. The first transition of *Z*-**E** (**3**) is predicted to lie at 495 nm (f = 0.69) followed by several weak bands at 340, 324, 296 nm, *etc.* The discrepancy with the experimental maximum of the first absorption band (420 nm, *Fig. 1b*) presumably indicates that the coplanar geometry of the two rings of *Z*-**E** (**3**) assumed for the calculation is unrealistic.

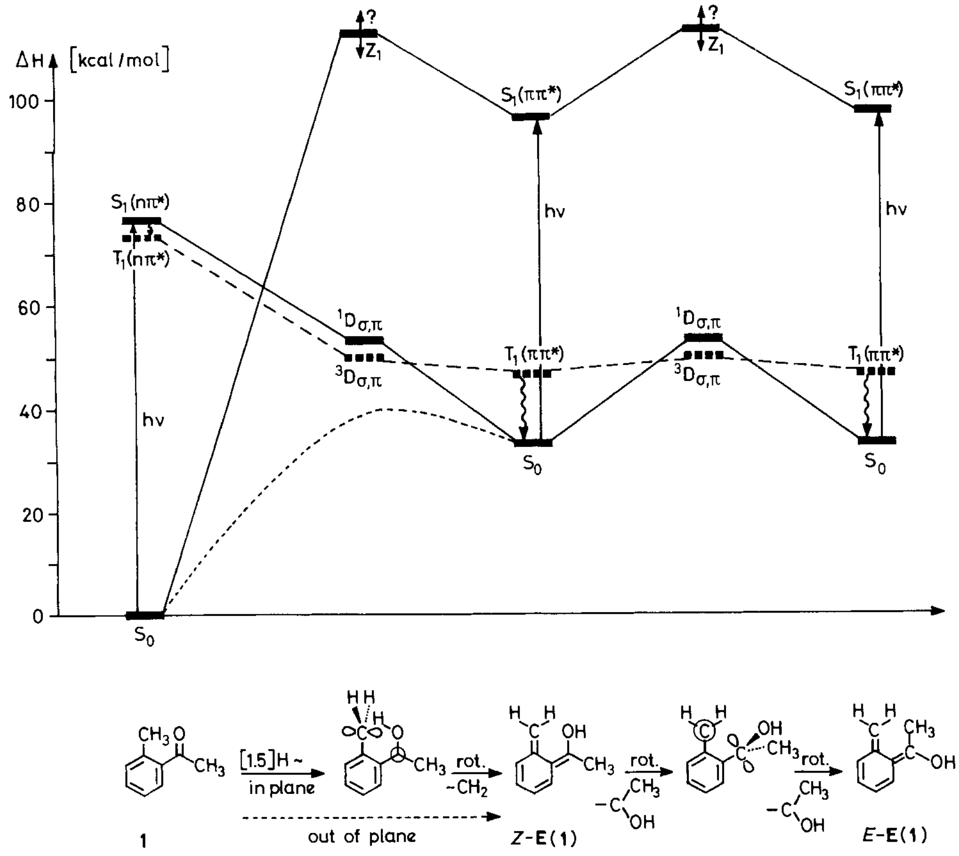
Absorption spectra and rotational barriers for the exocyclic methylidene groups of the triplet excited photoenols, ^{3}**E** (**1**) *and* ^{3}**E** (**3**). - The semiempirical PPP model which adopts the basic approximations of σ,π-separation and zero differential overlap has been applied to even open-shell systems (π,π-biradicals) as follows [13]. Starting from *Hückel* orbitals, a restricted open-shell SCF calculation (half-electron approximation [14]) is performed for the lowest configuration with two singly occupied frontier orbitals. The SCF-MO's are used to construct CI matrices for the singlet and triplet manifold, mixing in up to 49 wave-functions which arise from single excitations to or from the frontier orbitals. Rotations around exocyclic bonds are simulated by reduction of the corresponding resonance integrals β. The standard PPP parameter set for closed-shell calculations [1] is used throughout. These calculations have yielded promising results for the absorption spectra of π,π-biradicals such as trimethylenemethane [15] and 1,8-naphthoquinodimethane [16] as well as for the triplet absorption spectra and energies of benzenoid hydrocarbons. Details shall be given elsewhere.

The optical transitions predicted for the enol triplets with planar geometry are in satisfactory agreement with the experimental spectra *(Fig. 1)*. ^{3}**E** (**1**): 537 (oscillator strength $f < 0.01$), 446 (< 0.01), 336 (0.07), 309 nm (0.40), *etc.* ^{3}**E** (**3**): 530 (0.03), 483 (0.08), 415 (< 0.01), 405 (0.04) 355 (0.20), 333 nm (0.33), *etc.* The triplet energies of ^{3}**E** (**1**) and ^{3}**E** (**3**) are calculated as 10.5 and 9.8 kcal/mol, respectively. The π-electron energy contribution to the rotational barriers of the substituted exocyclic methylidene group, *i.e.* for the interconversion of *Z*- and *E*-enol isomers, in the singlet ground and first excited states and in the lowest triplet state have been computed as follows: For **E** (**1**): 26.9, 50.8, and 16.4 kcal/mol, and for **E** (**3**): 26.1, 39.3, and 16.4 kcal/mol, respectively.

Scheme 1. *Mechanism for the photoenolization of* **1**



Scheme 2. *State correlation diagram for the photoenolization of* **1**



Discussion. - The results of this investigation provide a fairly complete and consistent picture for the evolution of enolization after excitation of the *ortho*-methylphenyl ketones **1** to **3**. Both, 2-methylacetophenone (**1**) and 2,4-dimethylbenzophenone (**3**), have already been studied by the technique of flash photolysis [3] [4] [6] and, apart from a single observation stated below (see p. 2603 and Footnote 3 therein), our experimental results are in agreement with those of previous workers. However, we are convinced that our additional findings, as well as the comparison with the conformationally locked tetralone **2**, necessitate a reassignment of most transients observed previously. Some partly conflicting suggestions for such reassignments have been made in the recent literature: *Porter*'s attribution of transients C and D [3] to *E*-E (**3**) and *Z*-E (**3**), respectively, has been questioned by *Sammes* [2] on the basis of chemical trapping experiments, and two contradictory identifications of the transient B[3] were proposed [6] [17] of which we support the latter. Further, a redefinition of *Lindqvist*'s 320 nm transient arising from flash photolysis of **1** [4] was suggested by *Tchir* [6].

Scheme 1 presents the sequential interrelations of the metastable species which are considered to be involved in the photoenolization of **1**. We should note that this Scheme is not new in principle. It has been considered more or less explicitly in several previous investigations [2-6] [18] and is in accord with theoretical expectations [19], but we believe that the present study provides new evidence for most of the intermediate steps involved.

An attempt to sketch a cross section through the relevant portions of the three lowest potential surfaces (S_0, T_1, S_1) of **1** is made in the state correlation diagram, *Scheme 2*. The relative energies of the states or intermediates marked by a horizontal bar have been drawn from experimental data wherever possible, or else were taken from the semiempirical calculations described above. The reaction *Z*-E (**1**)→**1** is estimated to be 39 kcal/mol exothermic using *Benson*'s tables of group increments [20]. This value may be about five kcal/mol too high considering the most recent thermochemical estimate for acetone ⇄ 2-propenol [21], and allowing for a small amount of resonance energy in *Z*-E (**1**) [22]. Qualitatively, *Scheme 2* corresponds to a combination of the diagrams for hydrogen abstraction and olefin twist by *Salem et al.* [23]. It provides a convenient, self-explanatory basis to rationalize all the photophysical and photochemical properties of **1** and its photoenols which have been observed in this work. It is, however, inadequate for the description of the reketonization of *Z*-E (**1**) to **1** in the electronic ground state. The reaction is forbidden by state symmetry and should have an activation energy of some 30 kcal/mol according to *Scheme 2*. This is an artefact of the restraints imposed on the reaction coordinate. If this restriction is alleviated, the reaction, a [1.5]-sigmatropic hydrogen shift, becomes allowed both by state and orbital symmetry. Experimentally, the reaction rate amounts to *ca.* 10^8 s^{-1} in apolar solvents which corresponds to an activation energy of *ca.* 7 kcal/mol (dotted line connecting *Z*-E (**1**) and **1**).

We now proceed to summarize the main arguments for the assignments of the various transient species which have been observed. Previous product studies in quenching and sensitization experiments [5] have revealed the existence of two kinetically independent ketone triplet states of **1** which were associated with the *anti-* and *syn*-conformers of ^{3}**K** (**1**) *(Scheme 1).* The decay rates of $3 \cdot 10^7 s^{-1}$ for *anti*-^{3}**K** (**1**) and $5 \cdot 10^9 s^{-1}$ for *syn*-^{3}**K** (**1**) were attributed to the rates of *anti*→*syn* interconversion and enolization from *syn*-^{3}**K** (**1**), respectively. This hypothesis was strongly supported by the observation of only a single, short-lived ^{3}**K** in the case of the conformationally fixed 8-methyl-1-tetralone. The 30 ns duration of the exciting flash used in this study thus precluded the direct detection of *syn*-^{3}**K**'s, except for ^{3}**K** (**2**) in aqueous solution. In this case the rate of enolization is apparently reduced to $10^7 s^{-1}$ due to the combined effects of the alkyl substituents on the phenyl ring and of the hydrogen bonding solvent in lowering the energy of the nonreactive $\pi\pi^*$ triplet state of **2** [24] [25]. This is fortunate, since it provided direct evidence for the adiabatic process *syn*-^{3}**K**→^{3}**E** by the matching kinetics for the first-order decay of ^{3}**K** (**2**) and the formation of ^{3}**E** (**2**) monitored at different wavelengths in aqueous solution. Before turning to the question of the *anti*-^{3}**K**'s we need to discuss some evidence for the triplet enols, ^{3}**E** (**1** to **3**).

The strong transient absorptions due to ^{3}**E** (**1**) and ^{3}**E** (**3**) have been observed previously [4] [3], but were then attributed to ^{3}**K** (**1**) and ^{3}**K** (**3**), respectively. The latter assignments were difficult to reconcile with the complete absence of photopinakolization of **1** and **3** in 2-propanol [26] and especially with the low quantum yield of type II photoelimination of orthomethylvalerophenone [27], since from the known rates of these reactions in related compounds a more efficient competition with photoenolization might have been expected. Clear evidence against such an assignment comes from the following observations: (*i*) The absorption spectra *(Fig. 1),* decay kinetics *(Table 1),* and susceptibility to various quenchers of ^{3}**E** (**1**) and ^{3}**E** (**2**) are nearly identical. The latter cannot be attributed to *anti*-^{3}**K** (**2**) for stereochemical reasons and its lifetime is much too long for *syn*-^{3}**K** (**2**).(*ii*) None of the species ^{3}**E** (**1** to **3**) is quenched by piperylene³) or naphthalene with a rate approaching the diffusion-controlled limit, because their triplet energy is too low. Although some chemical quenching (*Schenck*-type [28]) of such biradicaloid species as ^{3}**E** by piperylene may be expected, it is apparently too slow to be detected.

We are thus forced to conclude that the absorptions due to the long-lived *anti*-conformers of ^{3}**K** (**1**) and ^{3}**K** (**3**), the lifetimes of which were determined as 10^{-8} to 10^{-7} s by steady-state analyses [5] [25], are buried under the strong ^{3}**E** absorptions. This is not too surprising considering the low yield of *anti*-^{3}**K**'s (20% in the case of **1** in benzene solution) and the spectral overlap of related ^{3}**K**'s with the ^{3}**E**'s. However, the following experiments have provided further indirect evidence for the intermediacy of a long-lived *anti*-^{3}**K** (**1**): Since piperylene does not affect the ^{3}**E** (**1** or **2**) it can be used to quench their ^{3}**K** precursors which results in suppressing the formation of ^{3}**E**. The corresponding *Stern-Volmer* plot for **1** was non-linear in contrast to that for **2** *(Fig. 2)* in qualitative agreement with previous product studies [5] [25]. Furthermore, sensitization studies of the characteristic triplet absorption of naphthalene by excitation of **1** yielded an estimate of 10 ns

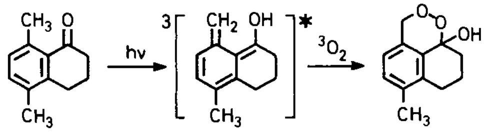
---

³) Diffusion-controlled quenching of the absorption which we attribute to ^{3}**E** (**1**) was quoted [4] as evidence for its assignment to ^{3}**K** (**1**). We are unable to provide an explanation for this discrepancy with our results.

for the lifetime of *anti*-^{3}K (**1**) in benzene. While the precision of these data is definitely inferior to those of the previous product studies, the findings do provide an independent check of the proposed mechanism at an earlier stage of the reaction.

The lifetime of ^{3}E (**2**) in EPA is essentially independent of temperature in the range of $-60°$ to $-180°$. This is a clear indication of its electronically excited nature. The photoenols, being derivatives of *ortho*-xylylene, may be expected to have very low triplet energies. Our open-shell PPP/SCF/CI calculations have given E_T *ca.* 10 kcal/mol and rotational barriers for the exocyclic $-C(R)OH$ groups of *ca.* 16 kcal/mol. The calculations are presumably correct in predicting a coplanar equilibrium conformation (ignoring steric hindrance in the case of ^{3}E (**3**)), since both the absorption spectra and decay kinetics of ^{3}E (**1**) and ^{3}E (**2**) are closely similar. The latter compound is forced by the saturated ring to assume an essentially coplanar conformation. The calculated barriers are, however, too high, because the relative yield of the two isomeric ground state enols (see below and *Scheme 1*) does not depend on the lifetime of ^{3}E (**1**). Hence, the equilibrium between the two coplanar conformers of ^{3}E (**1**) must be reached within 100 ns which corresponds to a barrier of less than 10 kcal/mol.

Molecular oxygen is a very efficient quencher of the triplet enols. The quenching process yields predominantly the enols in the electronic ground state (see below), but some chemical trapping by a spin-allowed triplet + triplet *Diels-Alder* addition also occurs, as indicated by the work of *Sammes* [18] and *Yates* [29] who have isolated the corresponding cyclic peroxides:



4 ^{3}E(**4**) **5**

The peroxide **5** must have been formed from ^{3}E (**4**), as suggested by *Sammes*, since the reaction rate of oxygen with ground state dienols (*ca.* $2 \cdot 10^5 \text{M}^{-1} \text{s}^{-1}$ [4]) is far too slow to compete with the intramolecular reketonization of *Z*-E (**4**). It is interesting to note that the rates for ^{3}E quenching by oxygen (deduced from the results in *Table 1*) are nearly twice as high as those of 3,4-benzpyrene triplet [9] in various solvents. The latter is considered a typical representative of a triplet donor of intermediate energy which is quenched by energy transfer producing ${}^1O_2$ at one out of nine encounters. If the excitation energies of the triplet enols are indeed lower than that of ${}^1O_2$ (22.5 kcal/mol), as predicted by our calculations, then oxygen must be a very effective catalyst for enhancing the intersystem crossing of ^{3}E. This may well proceed *via* a strongly associated peroxy-biradical species.

We are left to discuss the ground state photoproducts, the photoenols E. As expected from previous work [1], the *Z*-isomers are extremely short-lived (*ca.* 10^{-8}s) in apolar solvents, due to rapid intramolecular reketonization to starting material. The rate of this reaction is retarded by up to four orders of magnitude by solvation of the enols in HBA-solvents *(Table 1)*. *Lindqvist* [4] has not observed *Z*-E (**1**) in his flash photolytic investigation of **1**, because under the conditions of his experiments its lifetime is shorter than that of its precursor ^{3}E (**1**). *Porter & Tchir* [3] have observed the transient absorption due to *Z*-E (**3**), but its assignment (transient B in their terminology) was left open to question. Both *E*-E (**1**) and *E*-E (**3**) were detected previously and attributed to the corresponding photoenols, though the configuration of *E*-E (**1**) was not specified [4] and that of *E*-E (**3**) was thought to be *Z* (transient D [3]). Our assignments derive from the following observations: (*i*) The decay kinetics and its characteristic solvent dependence were closely similar for the *Z*-enol isomers of **1** to **3** *(Table 1)*. (*ii*) Flash photolysis of **2** gave *Z*-E (**2**) in high yield, but no long-lived species similar to *E*-E (**1**). (*iii*) *Z*-E (**2**) was formed as a stable photoproduct by 313 nm irradiation of **2** in EPA at 77 K *(Fig. 3)*. Reketonization from *Z*-E (**2**) to **2** took place either upon warming to *ca.* 90 K or upon irradiation at 400 nm. The feasibility of reketonization from the excited singlet state of *Z*-E (**2**) may be predicted from *Scheme 2*. (*iv*) Light-induced photodeuteration of the 8-methyl group of **2** was observed in D_2O/DMSO containing catalytic amounts of base. (*v*) Enol-quenching by oxygen or piperylene was well below the diffusion-controlled limit, too slow to affect the lifetimes of the *Z*-isomers. Further evidence for the assignment of *Z*-E (**3**) is given in [17]. The *E*-enols reketonize by intermolecular proton exchange and are thus highly susceptible to acid or base impurities in the solvent. Reketonization by the pathway *E*-**E** → *Z*-E → **K** does not appear to be competitive and a lower limit of 18 kcal/mol for the activation energy of *E* → *Z* isomerization can be deduced from the lifetime of *E*-E (**1** or **3**) of *ca.* 4s in deaerated cyclohexane at ambient temperature.

The enols of **3** are formed entirely by the triplet pathway *via* ^{3}E (**3**). This follows from the matching kinetics of the decay of ^{3}E (**3**) and the formation of *Z*- and *E*-E (**3**) and from the complete suppression of photoenolization at high concentrations of piperylene, and again agrees with the results of steady-state analyses of 2-methylbenzophenone [25]. It is not surprising that intramolecular hydrogen abstraction cannot compete with the extremely rapid rate of intersystem crossing from ^{1}**K** (**3**) to ^{3}**K** (**3**) [30]. Partial grow-in of the absorption due to the enols is also observed concomitantly with the decay of ^{3}E (**1**) and ^{3}E (**2**). However, when the formation of ^{3}E(**1** or **2**) is completely quenched by high concentrations (> 5 M) of piperylene, this is not accompanied by a complete suppression of the formation of *Z*-E (**1** or **2**). Hence a small amount (*ca.* 30% of the total yield) of the *Z*-dienols must be formed directly from the excited singlet states of **1** and **2**. Further work is needed to establish the efficiency of this pathway which is nicely accommodated by the state correlation diagram, *Scheme 2*. It is possible that the crossing of two singlet surfaces along the hydrogen-transfer-reaction coordinate causes some energy wasting by direct return to the ground state surface as the intersection is approached [23] [25]. We wish to note, however, that the inefficiency of deuterium incorporation by the singlet pathway [25] provides no evidence for this energy wasting, since the *Z*-dienols are too short-lived for efficient proton exchange with the solvent in the absence of base catalyst.

Tchir [6] has noted that the yield of *E*-E (**1**), formed by flash photolysis of **1** in cyclohexane, is increased in the presence of oxygen. This unusual effect was interpreted in terms of the formation of an oxygen quenchable enol triplet which can decay either to enol or ketone ground state. The present work has provided direct evidence to support this suggestion. In apolar solvents the predominant decay pathway of ^{3}**E**(**1**) and ^{3}**E** (**2**) (but not of ^{3}**E** (**3**)) is the spin-forbidden reketonization to **1** and **2**, respectively. This reaction is inhibited by HBA solvents which results in an increase both of the lifetime of ^{3}**E** *(Table 1)* and the yield of ground state enols. Thus the oxygen-induced acceleration of the decay of ^{3}**E** to ground state enols, which is observed in all solvents *(Table 1)*, affects the enol yield only in apolar solvents. The reaction ^{3}**E** (**1**)$\rightarrow$**1** cannot proceed *via* ^{3}**K** (**1**) for energetic reasons *(Scheme 2)*. We may conclude that the crossing of the S_0 and T_1 surfaces along this reaction coordinate provides an espace hatch from the T_1 surface. Indeed, the two states are coupled by spin-orbit interactions, because their leading electronic configurations differ in the population of an σ- and a π-orbital, allowing for a rapid intersystem crossing in that region [31].

In conclusion we wish to add a few remarks concerning the practical implications of the present work. We have shown that in the absence of stereochemical restraints the photoenolization of *ortho*-alkylphenyl ketones yields both geometrical dienol isomers in roughly equal amount. The elusiveness of the *Z*-isomers in chemical trapping experiments [2] is explained by their extremely rapid reketonization to starting material. Although the chances to use *Z*-dienols as reactive intermediates of synthetic interest are rather remote, they may be raised by using hydrogen-bond-acceptor solvents such as DMSO, pyridine, or HMPA and highly reactive dienophiles in high concentrations or directly attached to the potential diene component [32]. Further work is needed to explain the photochemical behaviour of 2,6-dialkylphenyl ketones [3] [25].

This work is part of project No. 2.531-0.76 of the *Swiss National Science Foundation*. Financial support by *Ciba-Geigy* SA, *F. Hoffmann-La Roche & Cie* SA, and *Sandoz* SA is gratefully acknowledged.

REFERENCES

[1] *E. Rommel & J. Wirz*, Helv. *60*, 38 (1977).
[2] *P. G. Sammes*, Tetrahedron *32*, 405 (1976).
[3] *G. Porter & M. F. Tchir*, J. chem. Soc. *A 1971*, 3772.
[4] *H. Lutz, E. Bréhéret & L. Lindqvist*, J. chem. Soc. Faraday Trans. I *60*, 2096 (1973).
[5] *P. J. Wagner & C.-P. Chen*, J. Amer. chem. Soc. *98*, 239 (1976).
[6] *D. M. Findlay & M. F. Tchir*, J. chem. Soc. Faraday Trans. I *72*, 1096 (1976).
[7] *H. Lutz, E. Bréhéret & L. Lindqvist*, J. physic. Chemistry *77*, 1758 (1973).
[8] *R. R. Minesinger, M. E. Jones, R. W. Taft & M. J. Kamlet*, J. org. Chemistry *42*, 1929 (1977) and previous papers of the series.
[9] *O. L. J. Gijzeman, F. Kaufman & G. Porter*, J. chem. Soc. Faraday Trans. II, *69*, 708 (1973).
[10] *R. E. Rondeau & R. E. Sievers*, J. Amer. chem. Soc. *93*, 1522 (1971).
[11] *H. M. McConnell & R. E. Robertson*, J. chem. Physics *29*, 1361 (1958).
[12] *L. Edwards, J. Kolc & R. S. Becker*, Photochem. Photobiol. *13*, 423 (1971); *P. Seiler & J. Wirz*, Helv. *55*, 2693 (1972); *J. Wirz*, Helv. *57*, 1283 (1974); *W. Rettig & J. Wirz*, Helv. *59*, 1054 (1976); *M. Gisin & J. Wirz*, Helv. *59*, 2273 (1976).
[13] *M. Gisin*, unpublished work.

[14] *M. J. S. Dewar, J. A. Hashmall & C. G. Venier,* J. Amer. chem. Soc. *90,* 1953 (1968).
[15] *J. H. Davies & W. A. Goddard III,* J. Amer. chem. Soc. *99,* 4242 (1977).
[16] *M. Gisin, J. Wirz, M. Burnett & R. M. Pagni,* work in progress.
[17] *K. Uji-ie, K. Kikuchi & H. Kokubun,* Chemistry Letters *1977,* 499.
[18] *B. J. Arnold, S. M. Mellows, P. G. Sammes & T. W. Wallace,* J. chem. Soc. Perkin I, *1974,* 401.
[19] *M. J. S. Dewar & R. C. Dougherty,* The PMO Theory of Organic Chemistry, Plenum Press, p. 458 (1975).
[20] *H. K. Eigenmann, D. M. Golden & S. W. Benson,* J. physic. Chemistry *77,* 1687 (1973).
[21] *S. K. Pollack & W. J. Hehre,* J. Amer. chem. Soc. *99,* 4845 (1977).
[22] *J. Aihara,* J. Amer. chem. Soc. *98,* 2750 (1976).
[23] *W. G. Dauben, L. Salem & N. J. Turro,* Accounts chem. Res. *8,* 41 (1975).
[24] *H. Lutz, M.-C. Duval, E. Bréhéret & L. Lindqvist,* J. physic. Chemistry *76,* 821 (1972); *P. J. Wagner, M. J. Thomas & E. Harris,* J. Amer. chem. Soc. *98,* 7675 (1976).
[25] *P. J. Wagner,* Pure appl. Chemistry *49,* 259 (1977).
[26] *N. C. Yang & C. Rivas,* J. Amer. chem. Soc. *83,* 2213 (1961).
[27] *W. R. Bergmark, B. Beckmann & W. Lindenberger,* Tetrahedron Letters *1971,* 2259.
[28] *G. O. Schenk & R. Steinmetz,* Bull. Soc. chim. Belgique *71,* 781 (1962).
[29] *P. Yates, A. C. Mackay & E. X. Garneau,* Tetrahedron Letters *1968,* 5389.
[30] *R. M. Hochstrasser, H. Lutz & G. W. Scott,* Chem. Physics Letters *24,* 162 (1974).
[31] *N. J. Turro & A. Devaquet,* J. Amer. chem. Soc. *97,* 3859 (1975).
[32] *W. Oppolzer,* Angew. Chem. *89,* 10 (1977).