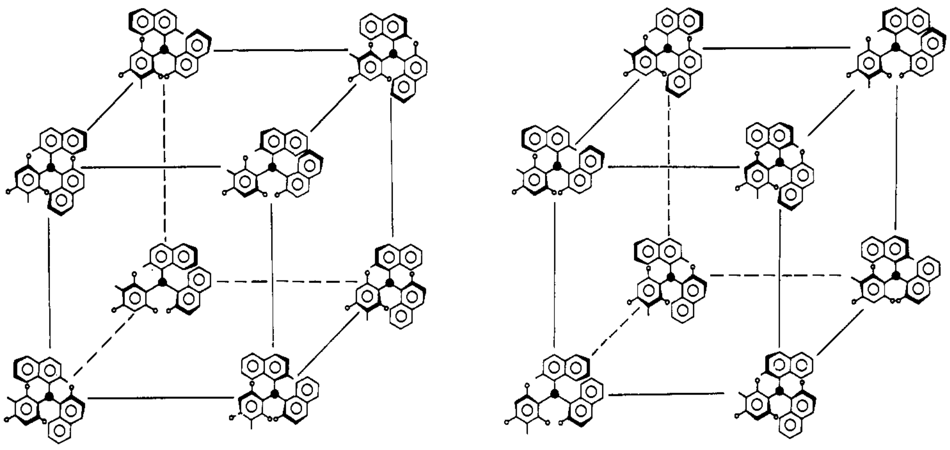

Figure 1. The 16 structures depict one-half of the 32 possible stereoisomers of **1** (the ones having the *R* configuration at the chiral center). The 16 isomers are grouped into two sets of eight each, shown at the corners of the two cubes. The edges connecting the structures represent stereoisomerization pathways by the two-ring flip mechanism. The heavy dot in the center of each structure stands for C–H, the small circles denote methoxy groups, and the short lines denote methyl groups.

terial from benzene gave an analytical sample[3] of **1a**, more than 95% diastereomerically enriched, mp 210–213°. From the mother liquors a fraction,[3] mp 158–163°, was obtained, consisting of **1a** and **1b** in a ratio of *ca.* 30:70. The rate of interconversion of the diastereomers was determined by conventional means and gave $\Delta G^{\ddagger}_{122} = 30.6$ kcal/mol for **1a** → **1b** and $\Delta G^{\ddagger}_{122} = 30.4$ kcal/mol for the reverse process.[4]

It has been shown[5] that the two-ring flip is the stereoisomerization mechanism of lowest energy (threshold mechanism) in all systems of the type Ar_3Z and Ar_3ZX thus far examined where such isomerization occurs by correlated rotation of the aryl groups. In addition, for systems where two-ring flip pathways for stereoisomerizations requiring higher energies are available, these pathways are evidently followed preferentially.[5] This conclusion applies with equal force to the present case, where all stereoisomerizations by this mechanism occur rapidly on the nmr time scale at ambient temperatures. However, given the substitution pattern of **1**, rapid stereoisomerization by two-ring flips is incapable of interconverting all diastereomeric conformations.[2] Consequently, a novel type of stereoisomerism arises.

The various interconversion pathways by the two-ring flip mechanism are shown in Figure 1. The cube on the left might be taken to represent one of the diastereomers, arbitrarily **1a**, whereas the other represents the second diastereomer, arbitrarily **1b**.

The key features to be noted are the following. First, each of the three aryl rings in **1a** or **1b** may rotate by multiples of π radians in the course of the two-ring flips without achieving interconversion of **1a** and **1b**. Thus, there is no restriction on the torsional angle of any of the individual aryl groups, the only constraint being a mechanistic one. Another way of putting it is that the restriction lies in the relationship of the torsional angles of the three groups, rather than in the absolute value of each. In consequence, conventional definitions of "conformer" which are couched in terms of torsional angles around a single bond appear to be inadequate to deal with the present case, without modification, since it is difficult to see how any such definition is capable of differentiating **1a** and **1b**, which are, after all, diastereomeric *conformers*. By the same token, any one of the eight rapidly interconverting forms depicted at the vertices of either cube in Figure 1 may be taken as a representative conformation for **1a** or **1b**.

Second, it must be emphasized that the existence of separable diastereomers **1a** and **1b** (*residual stereoisomerism*) depends primarily on the structural and mechanistic constraints described above, and only secondarily on steric congestion about the central atom. A system with bulkier blocking substituents (*e.g.*, methyl in place of some of the methoxy groups) would presumably exhibit a barrier to diastereomerization substantially higher than 31 kcal/mol.

It remains to consider the mechanism for the interconversion of **1a** and **1b**. As previously indicated[2] such interconversion could in principle occur by either a one- or a three-ring flip. On the basis of empirical force field calculations,[5] we conclude that the mechanism in question is the one-ring flip.

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[3] All compounds exhibited analytical and spectral properties consistent with the given structural assignments.

[4] The same value for the equilibrium constant ($K = 0.7$ for **1a** ⇄ **1b** at 122°) was obtained starting either with **1a** or with material enriched in **1b**.

[5] P. Finocchiaro, D. Gust, and K. Mislow, *J. Amer. Chem. Soc.*, in press; J. D. Andose and K. Mislow, *ibid.*, in press.

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Received September 26, 1973

Photoisomerization of β-Diketones and β-Keto Esters

Sir:

While studying the photo-Fries rearrangement[1] of enol esters, we have observed that the β-diketones formed were affected by light, resulting in a shift of their enol–keto equilibrium ratio. Recently a similar change in the enol content of ethyl acetoacetate under the influence of ultraviolet (uv) irradiation was de-

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[1] Part of a Ph.D. Thesis to be submitted by D. Veierov to the Feinberg Graduate School of the Weizmann Institute of Science. For previous publications on this subject see: M. Gorodetsky and Y. Mazur, *Tetrahedron*, **22**, 3607 (1966), and references cited therein.

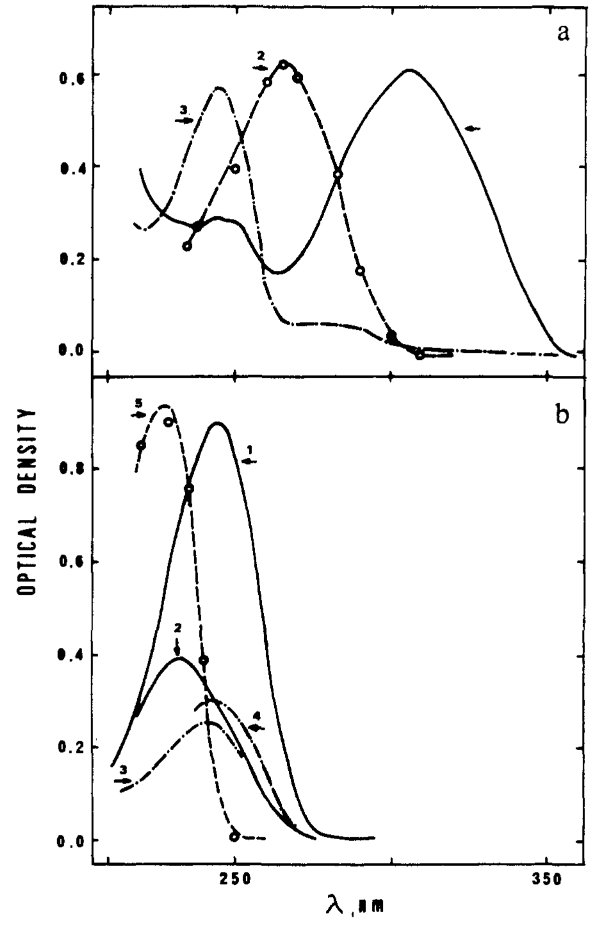


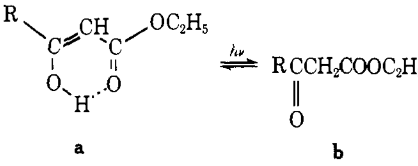
Figure 1. (a) Uv absorption spectrum of benzoylacetone (**4**) in cyclohexane (*ca.* 4×10^{-5} *M*): curve 1, before irradiation; curve 2, immediately after a 10-μsec flash; curve 3, after steady irradiation at 313 nm, in the presence of triethylamine (= diketo form **b**). (b) Uv absorption spectrum of ethyl acetoacetate (**1**) in *n*-heptane (*ca.* 10^{-4} *M*): curve 1, before irradiation; curve 2, after 2-min steady irradiation at 254 nm; curves 3 and 4, same, after 15 and 30 min, respectively, in the dark; curve 5, taken within 1 msec after a 10-μsec flash.

scribed.[2] We wish to report on related photo and dark processes of aliphatic and aromatic β-keto esters and β-diketones.

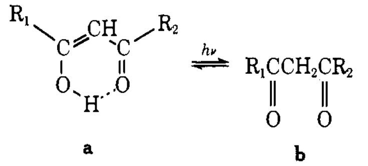
Solutions of β-keto esters **1** and **2** and β-diketones **3–7** in aliphatic hydrocarbon solvents were irradiated in quartz cells at 254 (**1** and **3**) and 313 nm (**2**, **4–7**). The resulting changes in the uv absorption spectra were measured in a Cary 14 spectrophotometer. The disappearance of the characteristic *cis*-enol peak (curve 1 in Figures 1a and 1b) was observed in all compounds, but the relative quantum yield of this disappearance was 50–100 times higher in the β-keto esters (**1** and **2**) than in the β-diketones (**3–7**). However, in the latter the rates could be enhanced at least 20-fold by the addition of equimolar quantities of triethylamine, which did not affect the absorption spectra.

In all cases the thermodynamic enol–keto equilibrium was eventually reestablished, in the dark, at rates which varied widely with the compound, solvent, temperature, and the presence of catalysts.

Deeper insight into the mechanism of the photoinduced tautomerization was gained by flash photolytic



1, R = CH_3
2, R = C_6H_5



	R_1	R_2
3	CH_3	CH_3
4	CH_3	C_6H_5
5	CH_3	$2\text{-}C_{10}H_5$
6	CH_3	2-anthryl
7	C_6H_5	C_6H_5

experiments with all the above compounds. Within the first millisecond following a 10-μsec light flash, a new absorption peak appeared at a wavelength shorter than that of the starting enol, but longer than that of the final keto product (*cf.* Table I, curve 2 in Figure 1a and curve 5 in Figure 1b). Furthermore, it was observed that the new peaks, assigned to a transient, decay in the dark in hydrocarbon solvents, with first-order rate constants of 0.1–1 sec^{-1} in compounds **1–6** and of 20 sec^{-1} in dibenzoylmethane (**7**). The addition of polar solvent or triethylamine enhanced these rates considerably. In the β-diketones **3–7** this decay results in the reappearance of the enol form. On the other hand in the β-diketo esters **1** and **2** the decay is much slower, and leads to the formation of both the keto and the enol forms. Only in ethyl acetoacetate **1** is the transient sufficiently stable to be observable in the spectrophotometer. Figure 1b describes a relevant experiment; when a solution (curve 1) was irradiated at 254 nm for 2 min, curve 2 resulted. Curves 3 and 4 are the spectra taken subsequently, in the dark, at 15-min intervals. Curve 5 describes the absorption of the same solution 1 immediately following a 10-μsec light flash. The primary phototransformation is thus described by curve 1 → 5 while curves 2–4 result from the gradual disappearance of the transient **a** (curve 5), and appearance of the keto form **b**, which is the main product of the thermal decay of the transient. A subsequent, very slow, enolization re-forms curve 1 within a day or two. The corresponding transient of **2** decays to give both

Table I. Uv Absorption Spectra of Enol and Keto Forms of β-Diketones and β-Keto Esters

	λ_{nm} ($\epsilon \times 10^{-4}$)		
Compd	*cis*-Enol	Transient	Keto form
1	244 (0.81)	228[a]	
2	288 (1.0)	250[a]	241 (1.1)
3	271 (1.0)	250[b]	
4	306 (1.7)	265[b]	245 (1.6)
5	318 (2.0)	258, 270, 287[b]	250 (5.1), 284 (0.94)
6	310 (3.6); 328 (1.7)	285[b]	260 (4.2), 270 (4.2), 279 (4.0)
7	336 (2.2)	260, 280[b]	251 (2.6)

[a] $\epsilon > 10^4$. [b] $10^4 > \epsilon > 10^3$.

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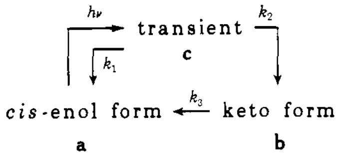
(2) P. Markov, L. Shishkova, and Z. Zdravkova, *Tetrahedron Lett.*, 4017 (1972).

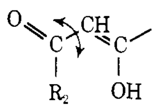
the enol **a** and the ketone **b** while the transients of the β-diketones **3**–**7** convert only to the corresponding *cis*-enol forms **a**.

These results may be rationalized by Scheme I, in

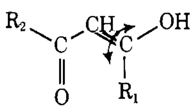
Scheme I



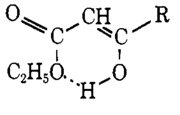
which k_1–k_3 denote the rate constants for the dark reactions. Two structures, A and B, in which the hydrogen bond of the *cis*-enol **a** is opened, may be proposed for these transients: structure A, having an s-trans arrangement of the α,β-unsaturated keto chromophore and derived from the enol form **a** by rotation around the CO—C single bond, and structure B, having an s-cis arrangement and derived by rotation around the C=C double bond.[3] We prefer structure A since it



A



B



C

explains the facile reconversion of the transient into the starting *cis*-enol by rotation around the "single" bond. If B were the correct structure, this enol–enol interconversion would involve rotation around the C=C double bond, and one might expect[5] an activation energy of at least 25 kcal, and therefore a decay predominantly to the keto form.

In the β-diketones the enol–enol interconversion (k_1) is faster than the alternative ketonization (k_2) which latter involves an intermolecular hydrogen transfer from oxygen to carbon. However, triethylamine greatly enhances this hydrogen transfer process.

In the β-keto esters the corresponding transient enol C is probably stabilized by hydrogen bonding involving the ether oxygen. This may be expected to enhance the energy barrier of rotation around the single bond and decrease k_1, thereby favoring the alternative ketonization process k_2.

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(3) The photoisomerization of diaroyl acetates described recently[4] may be explained by a similar mechanism.

(4) P. Courtot and S. Y. Le Saint, *Tetrahedron Lett.*, 33 (1973).

(5) Y. Shvo, E. C. Taylor, and Y. Bartuliu, *Tetrahedron Lett.*, 3259 (1967).

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Received August 27, 1973

Electron Spin Resonance Study of Allylic Monomer Radical Formation from Tetramethylethylene Dimer Radical Cation Due to Intramolecular Proton Transfer in γ-Irradiated 3-Methylpentane Glasses

Sir:

It has been shown by means of esr that γ-irradiated 3-methylpentane (3-MP) glasses containing small

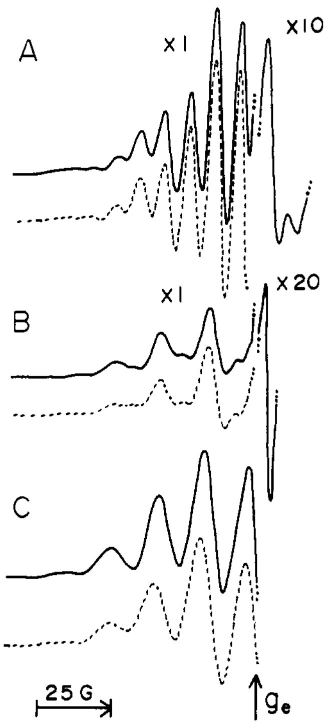

Figure 1. Low field sides of esr spectra (solid line) of 3-MP glasses containing 10 mol % TME: (A) 0.2 mol % CO$_2$ present, measured 20 min after irradiation; (B) same as A but 40 days after irradiation; (C) without CO$_2$, 40 days after irradiation. The fields near g_e in the spectrum A and B were recorded at reduced sensitivities. Dotted lines show the computed spectra consisting of the lines from the paramagnetic species: (A) (TME)$_2^+$ (55%) and 3-MP radical (45%); (B) (TME)$_2^+$ (10%), R$_a$ (80%), and 3-MP radical (10%); (C) R$_a$ (90%) and 3-MP radical (10%).

amounts of tetramethylethylene (TME) produce the solute radical cations at 77°K.[1] At high solute concentrations the dimer radical cation (TME)$_2^+$ has been found to be formed. In the present work, we wish to report that the dimer cation produced changes into the allylic monomer radical $\dot{C}H_2(CH_3)C{=}C(CH_3)_2$ at 77°K in the dark, which suggests allyl radical formation through intramolecular proton transfer of the dimer cation.

Samples prepared from purified materials were cooled to 77°K and subjected to ^{60}Co γ-irradiation at a dose rate of 5 × 10^{17} eV g^{-1} min^{-1}. Esr measurements were carried out with a conventional X-band spectrometer at 77°K.

Shown in Figure 1A, by the solid line, is the low field side of the esr spectrum of 3-MP glass containing 10 mol % TME and 0.2 mol % CO$_2$ measured 20 min after irradiation. The spectrum was interpreted as a superposition of lines from three paramagnetic species,[1] *i.e.*, CO$_2^-$ anions (a strong asymmetric line), 3-MP radical (broad six lines with an average spacing of 22.2 G), and (TME)$_2^+$ cations (a set of 25 lines with an average spacing of 7.8 G). The observed spectrum may be compared with the composite spectrum (dotted line) which consists of a computed 3-MP radical spectrum (45%) with intensity ratios of 1:5:10:10:5:1 and a computed (TME)$_2^+$ spectrum (55%) with a binominal distribution of intensity ratios; the aforementioned spacings and a Gaussian line shape were used for the

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(1) T. Ichikawa and P. K. Ludwig, *J. Amer. Chem. Soc.*, **91**, 1023 (1969).