

## Effect of Additives and Solvents on the Fate of the Primary Photoproduct of 1,3-Dicarbonyl Compounds<sup>1</sup>

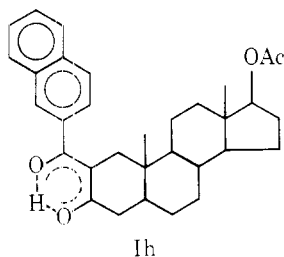
D. Veierov,\*<sup>2</sup> T. Bercovici, Y. Mazur, and E. Fischer

Departments of Organic and Structural Chemistry, The Weizmann Institute of Science, Rehovot, Israel

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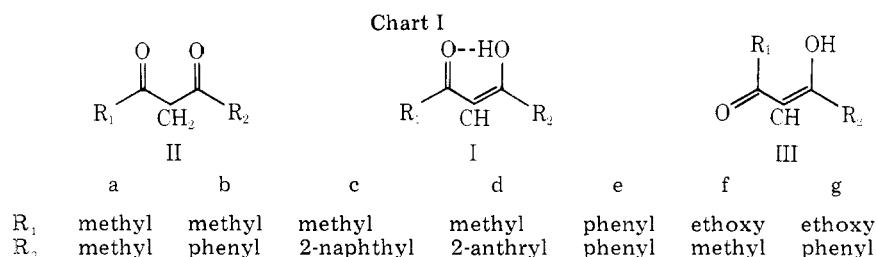
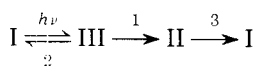
The primary photoproduct of the chelated enol tautomer of the title compounds is a nonchelated enol. Primary and tertiary amines added at up to equimolar concentrations greatly enhance the rate of the secondary thermal reactions, i.e., re-formation of the chelated enol, and tautomerization to the diketone. Triethylamine enhances the quantum yield of photoketonization. Ethanol added at up to 0.5 M concentrations also enhances the rate of the thermal re-formation of the starting compound. Differences between the solvents hexane, cyclohexane, benzene, and acetonitrile are marginal. It is suggested that the unchelated enol transient undergoes efficient formation of a complex with the amines and, to a much smaller extent, with ethanol. The rates of the spontaneous reactions of these complexes differ greatly from those of the free transient.

In our previous paper<sup>1</sup> we showed that the primary photoproduct of solutions of the (stable) chelated enols I in aliphatic hydrocarbons is a short-lived nonchelated enol III which then either reverts thermally to I or tautomerizes to the corresponding diketone II. (Both II and III may exist in several conformeric forms, Chart I). In steady irradiation experiments one observes only the so-called photoketonization I → II. Since in most cases I is thermodynamically more stable, II eventually reverts to I, but at rates much smaller than III → II. If the mechanism of photoketonization is indeed as indicated in Scheme I, the overall quantum yield of I → II will depend on the ratio of the rates of the thermal steps 1 and 2. Since these reactions involve either formation of an H bond (III → I) or a proton transfer (III → II), one may expect them to be sensitive to additives such as amines, alcohols, or acetonitrile and to be affected by the nature of the solvent used.



The results may in turn extend our knowledge of the postulated nonchelated enol III. Compounds a–h described earlier<sup>1</sup> were investigated in this context, but only b and c were studied in greater detail. As will be shown, the rates of all three thermal reactions, III → II, III → I, and II → I, are enhanced by amines and ethanol, while acetonitrile has little effect. The absorption spectra of I are in no case affected by the additives.

Scheme I



### Experimental Section

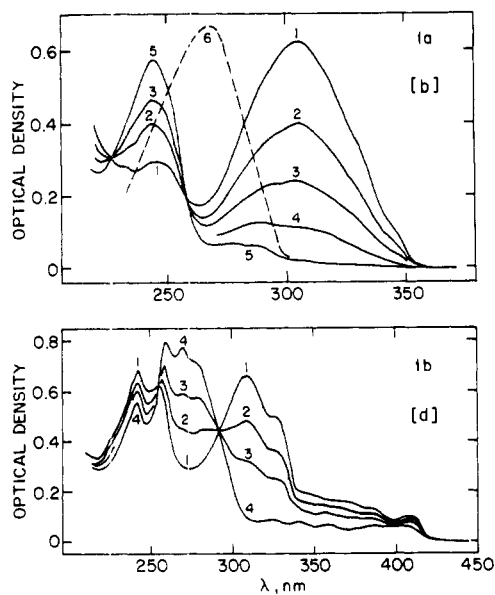
**Photochemical and Spectrophotometric Methods.** These were essentially as described.<sup>1</sup> The light intensity during irradiations was varied by using wire mesh screens of known transmission. After each experiment, the cell was rinsed with hydrochloric acid, followed by water, acetone, and finally benzene, before drying.

**Compounds, Solvents.** The compounds have been described.<sup>1</sup> *n*-Heptane, cyclohexane, and benzene were dried by passing them through columns filled with Woelm basic alumina and kept over Molecular Sieves. Absolute ethanol, triethylamine, and *n*-hexylamine were purified by standard methods.<sup>3a</sup>

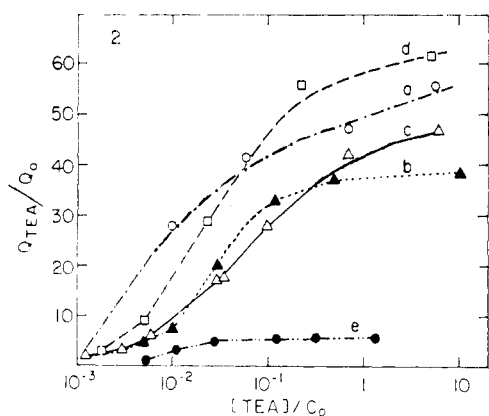
### Results

**Steady Irradiation Experiments. Photoketonization.** The relative rates of photoketonization I → II were studied spectrophotometrically in the presence of varying concentrations of additives.

(a) **Triethylamine, TEA.** Freshly prepared concentrated solutions of TEA in the respective hydrocarbon solvent were added to 10<sup>-4</sup> to 10<sup>-5</sup> M solutions of the compounds to give final TEA concentrations of up to 10<sup>-4</sup> M. Under these conditions the absorption spectrum above 200 nm is not affected by TEA (Figure 1). The solutions were irradiated in 10-mm cells at a wavelength determined by the absorption of the respective compound: 254 nm with compounds a and f, 295–410 nm with b–e, and 313 nm with g and h. As shown in Figure 1, almost complete conversion into the ketone can be obtained. The relative rates of photoconversion were measured in a range of TEA concentrations. In these experiments, Figure 2, the extent of photoconversion never exceeded 20%. The spectral changes in the absence and presence of TEA were identical. Isosbestic points were observed up to high extents of photoketonization and also during the subsequent slow thermal reversion to the enol I. Threefold to tenfold variations in the light intensity affected neither the nature nor the quantum yield of the reaction in any of the eight compounds. The quantum yield of I → II was enhanced by TEA, the extent varying widely with the compound (Figure 2). In those compounds in which the quantum yield is very small in the absence of TEA, addition of the latter caused a maximal 40–



**Figure 1.** Photoketonization: (a) Spectral changes induced by irradiation of a cyclohexane solution of b ( $3.70 \times 10^{-5}$  M) and TEA ( $4.0 \times 10^{-6}$  M): (curve 1) before irradiation, (curves 2–5) after 0.75, 1.5, 3, and 6 min of irradiation, respectively, (curve 6) absorption spectrum of IIIb, from flash measurements. (b) Spectral changes induced by irradiation of a cyclohexane solution of [d] ( $1.9 \times 10^{-5}$  M) and TEA ( $1.9 \times 10^{-6}$  M): (curve 1) before irradiation, (curves 2–4) following 0.5, 1.5, and 4.5 min of irradiation.



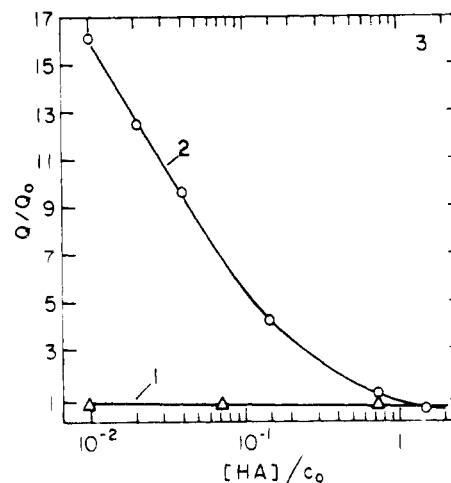
**Figure 2.** The ratio of the quantum yields in the presence ( $Q_{\text{TEA}}$ ) and absence ( $Q_0$ ) of TEA as a function of the ratio of concentrations of TEA and of the compound,  $C_0$ . Compounds as indicated for each curve.

60-fold increase (compounds a–d, where  $Q_{\text{I} \rightarrow \text{II}} \approx 10^{-3}$ ) or a sixfold increase (compound e,  $Q_{\text{I} \rightarrow \text{II}} \approx 5 \times 10^{-4}$ ). In fact, the spectra shown in Figure 1 could only be taken in the presence of TEA. In contrast, the rate of photoketonization in the two ketoesters f and g ( $Q_{\text{I} \rightarrow \text{II}} = 0.10\text{--}0.15$ ) and in the steroid diketone h ( $Q_{\text{I} \rightarrow \text{II}} = 4 \times 10^{-5}$ ) is hardly affected by TEA. Some results are summarized in Table I. The relative rate of photoketonization was found to be independent of the actual concentrations of either the enol or TEA in the approximate range  $10^{-6}$  to  $10^{-4}$  M, and to vary only with the ratio of the concentrations,  $[\text{TEA}]/[\text{compound}]$  (Figure 2). This point was checked by measuring the rates in cells of 100, 10, and 1 mm light path, using such concentrations of the compound and of TEA that the absorption spectra were the same in all three cells.

**(b) 1-n-Hexylamine, HA.** Addition of this primary amine, whose  $\text{p}K_b$  is similar to that of TEA, caused only a slight decrease in the rates of photoketonization, at concentrations up to equimolar with the two compounds investigated, b and c

**Table I. Quantum Yields of the Photoketonization I  $\rightarrow$  II in the Absence ( $Q_0$ ) and Presence of TEA ( $Q_{\text{TEA}}$ ) (Approximate Maximal Values, cf. Figure 2)**

Compd	$10^3 \times Q_0$	$10^2 \times Q_{\text{TEA}}$
a	1.3	8
b	1.2	5
c	1.9	9
d	0.66	5
e	0.46	0.3



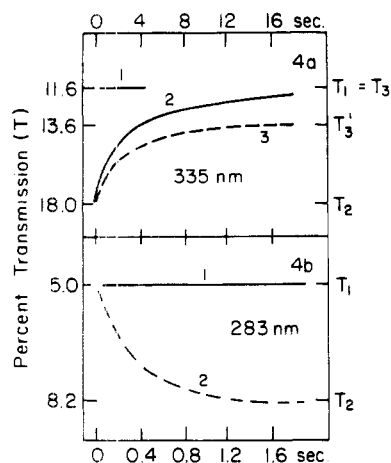
**Figure 3.** The effect of hexylamine, HA, on the relative quantum yield of photoketonization,  $Q/Q_0$ , of compound c in cyclohexane ( $C_0 = 3.8 \times 10^{-5}$  M) in the absence (curve 1) or presence (curve 2) of TEA ( $1.4 \times 10^{-6}$  M). Abscissa: the ratio of the concentrations of hexylamine and the compound.

( $4\text{--}5 \times 10^{-5}$  M in cyclohexane). However, when added together with TEA in cases where the latter sharply enhances the rates, HA reduces these rates and at sufficiently high concentrations may completely cancel the enhancement caused by TEA (Figure 3). The actual rate of photoketonization is determined only by the ratio  $[\text{HA}]/[\text{TEA}]$ , irrespective of the order in which the amines were added or any previous irradiation in the presence of TEA only.

**(c) Acetonitrile,  $\text{CH}_3\text{CN}$ ,**<sup>4</sup> did not affect the rates of photoketonization of b and c in cyclohexane even at 1 M.

**(d) Ethanol.** Ethanol attenuates the photoketonization rate of Ia–Ic both in the absence and in the presence of TEA. Thus, with a  $5 \times 10^{-5}$  M solution of b in cyclohexane, a tenfold decrease of the rate  $\text{Ib} \rightarrow \text{IIb}$  was achieved by adding ethanol to a final concentration of 0.5 M. In the presence of  $5 \times 10^{-6}$  M TEA a similar decrease is achieved by 0.15 M ethanol. Clearly the ethanol concentrations required to affect the photoketonization rates are four to five orders of magnitude higher than those of TEA. The ketoesters f and g show a completely different behavior; even when dissolved in ethanol their rates of photoketonization are similar to those observed in cyclohexane.

**Flash Experiments. Formation and Decay of the Nonchelated Enol, III.** Flash photolysis of solutions of enols I results in the transient formation of nonchelated enols, III, which decay in parallel paths to I and II.<sup>1</sup> In analogy with the steady irradiation experiments described in the previous paragraph we studied the effect of the same additives on the extent of the photoformation of III and, as far as possible, on the rates of its decay along both paths. The concentration of the III isomer was estimated<sup>1</sup> from the attenuation of the absorbance due to the depletion of I 1 ms after the flash (duration  $< 0.05$  ms). Solutions of b (ca.  $10^{-5}$  M) and c (ca.  $4 \times 10^{-6}$  M) were measured at 335 and 350 nm, respectively.



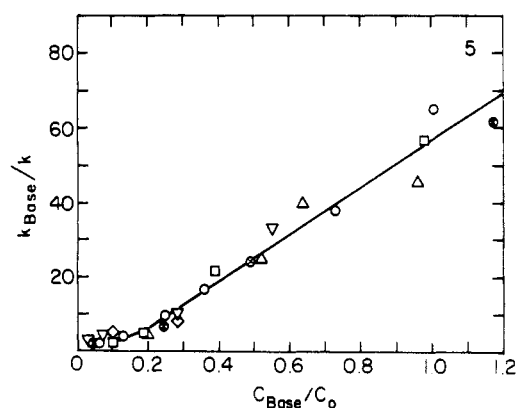
**Figure 4.** Flash photolysis of a *n*-heptane solution of **b** ( $1.2 \times 10^{-5}$  M) in the absence and presence of TEA ( $4.5 \times 10^{-6}$  M). (a) Time dependence of the optical transmission  $T$  at 335 nm, where only **Ib** absorbs: (curve 1) transmission before the flash, (curve 2) following a flash in the absence of TEA (top time scale), (curve 3) the same as curve 2 in the presence of TEA (bottom time scale!). (b) Time dependence of the transmission at 283 nm, following the flash: (curve 1) without TEA, (curve 2) with TEA (bottom time scale!). Cf. also Figure 1a.

Neither the two amines at up to  $10^{-5}$  M nor ethanol had any appreciable effect on the extent of **I** depletion in cyclohexane solutions, nor was there any marked difference between solutions in *n*-heptane, absolute ethanol, or acetonitrile. In both **b** and **c** the equilibrium enol-ketone is practically completely in favor of the enol **I** in all solvents used here. The time-resolved decay curves at various wavelengths help to understand the nature of the changes following the initial photoformation of **III**. At a wavelength where only **I** absorbs, one observed the re-formation of **I** from **III**, while at the isosbestic wavelength of the system  $\text{I} \rightleftharpoons \text{III}$ , at which **II** absorbs much less, it is possible to follow the reaction  $\text{III} \rightarrow \text{II}$  independently of any interconversion  $\text{III} \rightarrow \text{I}$ . In compounds **a**–**e** dissolved in either heptane, benzene, acetonitrile, 5% ethanol in heptane, or  $5 \times 10^{-6}$  M hexylamine in heptane, the only process observable in the flash apparatus is the regeneration of **I**, in accordance with the very low quantum yield (about  $10^{-3}$ ) of ketonization to **II** observed in steady irradiation experiments. However, addition of TEA to solutions of **a** ( $1.4 \times 10^{-5}$  M), **b** ( $1.2 \times 10^{-5}$  M), or **c** ( $8 \times 10^{-6}$  M) in heptane caused a different behavior. The absorbance of **I** was not recovered completely, and solutions measured in the Cary 14 a few minutes after flashing still showed partial conversion into the corresponding **II** form. (Complete reversion to **I** took place only after an hour or so.) Figure 4 furnishes a characteristic example, observed in a heptane solution of **b**, before and after addition of TEA (cf. also Figure 1a). The absorption at 335 nm, where only **I** absorbs, is seen to be reduced immediately after the flash to a similar extent both with and without TEA. However, in the absence of TEA the original absorption  $T_1$  recovers completely within about 20 s ( $T_3 = T_1$ ) while in its presence recovery is much faster but only partial, to  $T'_3$  (Figure 4a). The difference  $T'_3 - T_3$  increases with the concentration of TEA. At the isosbestic wavelength of the  $\text{I} \rightleftharpoons \text{III}$  system, 283 nm (Figure 4b), one observes in the presence of TEA a gradual decay of the absorption, starting immediately after the flash, while in the absence of TEA a horizontal line is of course obtained. From these and similar results we conclude that TEA enhances the otherwise very inefficient spontaneous conversion  $\text{III} \rightarrow \text{II}$ . Hexylamine, added on top of TEA, attenuated the difference  $T'_3 - T_3$  in Figure 4a and  $T_2 - T_1$  in Figure 4b. The correlation between the results of the steady and flash irradiation experiments is thus satisfactory.

**Table II.** Rate Constants of the Spontaneous Reaction  $\text{III} \rightarrow \text{I}$  at Room Temperature in Various Solvents<sup>a</sup>

Compd	Solvent	$k$ , s <sup>-1</sup>
a	H	0.27
	AN	0.92
	H + E	690
b	CH	0.33
	B	0.17
	AN	0.87
	H + E	290
c	CH	0.34
	B	0.14
	AN	0.99
	H + E	340
d	CH	0.49
	B	0.34
	AN	1.1
	H + E	350
e	CH	70
	B	9
	0.5% E in CH	110
	1.5% E in CH	700
h	CH	0.83
	B	0.10
	AN	0.69
	H + E	140
g	H	0.11
	H + E	2.8

<sup>a</sup>Concentrations were  $2.5$ – $8 \times 10^{-6}$  M. Solvents: H = *n*-heptane, CH = cyclohexane, B = benzene, AN = acetonitrile, H + E = 5% ethanol in heptane.



**Figure 5.** The base-induced enhancement of the rate of the thermal conversion  $\text{III} \rightarrow \text{I}$  in *n*-heptane solutions of compounds **a**,  $8.3 \times 10^{-6}$  M (triangles), **b** (circles), and **c**,  $3.5 \times 10^{-6}$  M (squares). Regular symbols denote solutions with hexylamine, twisted or X-ed symbols denote solutions with triethylamine. Abscissa: ratio of concentrations of base and compound; ordinate: ratio of reaction rate constants in the presence and absence of the respective base.

The solvent dependence of the rate of spontaneous isomerisation  $\text{III} \rightarrow \text{I}$  was studied in a series of solvents by looking at the kinetics of regeneration of **I** after a short light flash. Table II summarizes the results in heptane, benzene, acetonitrile, and 0.5–5% ethanol in *n*-heptane. Differences between the three solvents studied are seen to be small, but 5% ethanol in *n*-heptane enhances the rate up to 1000-fold as do 5 equiv of hexylamine or TEA. Figures 5 and 6 show the detailed variation of the rate of re-formation of **I**, after the flash, with the concentration of added base.

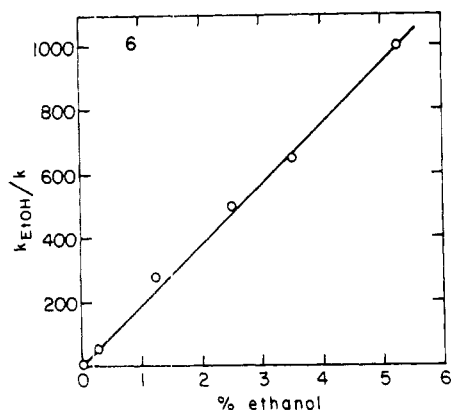


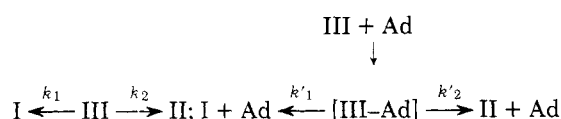
Figure 6. The effect of ethanol on the rate of the reaction IIIb  $\rightarrow$  Ib in a  $3.5 \times 10^{-5}$  M solution of b in *n*-heptane.  $k$  and  $k_{\text{ethanol}}$  denote the rate constants in the absence and presence of ethanol, respectively.

### Discussion

If we assume the correctness of the mechanism proposed earlier,<sup>1</sup> i.e., Scheme I, the results lead to the following conclusions: (a) the primary photoreaction I  $\rightarrow$  III is not affected by the additives nor by the solvents investigated, indicating that no "productive" interaction between the additives and I takes place in the ground or excited states; (b) the secondary thermal reactions I  $\leftarrow$  III  $\rightarrow$  II are strongly enhanced by hydrogen donors or acceptors (the two amines and ethanol) but not by using a medium of high dielectric constant per se (acetonitrile); (c) TEA specifically enhances III  $\rightarrow$  II in those cases where the photoketonization yield is small in the absence of additives, thereby increasing this yield dramatically, while ethanol preferentially enhances III  $\rightarrow$  I, causing a decrease in photoketonization yield; (d) to a lesser extent II  $\rightarrow$  I is also enhanced by all three additives. As a working hypothesis we may assume that III interacts strongly with the additives Ad by means of its free CO and OH groups, while I, in which these groups are neutralized by the chelate bond between them, does not interact. The complexes [III-Ad] thus formed from III undergo isomerization to I and tautomerization to II just like III but at much higher rates,  $k'_1 \gg k_1$ ,  $k'_2 \gg k_2$ , so that already at rather low extents of complexation the reactions of the complex will predominate and the extent of photoketonization will be determined by  $k'_2/k'_1$  for each additive. In fact, the possibility cannot be excluded that, at least in compounds b and c, the observed very inefficient photoketonization in the absence of additives is actually due to spurious impurities, at concentrations as low as  $10^{-7}$ – $10^{-8}$  M, acting as additives in the above sense.

The question thus arises by which mechanism complexes of III with amines and alcohols can undergo conversion into I and II much more efficiently than III itself and why TEA preferentially enhances III  $\rightarrow$  II. With regard to the hydrogen transfer from oxygen to carbon involved in ketonization, we assume that in III the conjugation effect of the adjacent keto group on the hydroxy group makes the latter a better proton donor. This assumption is supported by the observation<sup>5,6</sup> that the so-called "fixed trans enols" which contain a keto group

#### Scheme II

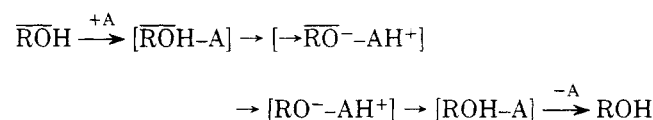


where Ad may be HA, TEA, or ethanol

conjugated to a hydroxy group, but unable to form an H bond with it, are much stronger acids than the chelated enolic forms of  $\beta$ -diketones. Thus a  $\text{p}K_{\text{a}} = 5.2$  was reported for dimedon and 2.8 for methylketene dimer,<sup>5</sup> as against 8.09 for Ia and 8.13 for If.<sup>6</sup> One may therefore expect that partial or even complete proton transfer takes place from the enolic OH groups to the amine,<sup>7</sup> which may then act as a transfer agent. This role of the nitrogen may be similar to that suggested by us<sup>1</sup> for the etheric oxygen in the 3-keto esters. Indeed in these compounds, g and f, the photoketonization yield is high from the start and not affected by TEA, meaning that the ratio  $k'_2/k'_1$  is barely influenced by the additive, while it is enhanced about 50-fold in compounds a–d. The fact that in compound e this ratio is affected much less, and in compound h not at all, indicates that in these two compounds additional factors are involved. In e the rate of IIIe  $\rightarrow$  Ie is particularly high, and it appears that the second aromatic group preferentially enhances  $k_1$ . In h the large steroid group may invoke steric factors<sup>8</sup> which enhance the energy of the transition state responsible for the reaction IIIh  $\rightarrow$  IIh. As to the isomerization III  $\rightarrow$  I, if it involves rotation about a quasisingle bond,<sup>1</sup> the rates observed ( $k = 0.1$ – $1 \text{ s}^{-1}$ , Table II) are rather slow for such a process and indicate that either the bond order is appreciably above unity because of contributing bipolar mesomeric forms or some other factor is involved.

The reaction III  $\rightarrow$  I involves a decrease in the number of degrees of freedom, and its rate may be determined largely by the activation entropy.<sup>9</sup> In the complex with an amine, in which the molecule probably exists as a negative ion, rotation is more facile, be it because of the lower bond order or because in the strongly polar complex the tendency is to minimize the extent of charge separation as achieved in the U form characteristic for the salts of 1,3-diketones.<sup>10</sup>

Schematically, if we denote the chelated enol ROH, the nonchelated (unstable) enol  $\overline{\text{ROH}}$ , and the amine A, the situation may be described by the following



The short but barred direct route is thus replaced by the multistep route in which smaller barriers have to be overcome. The difference between the primary and the tertiary amine may be due to steric factors. However, another reason may be that the primary amine can act either as a proton acceptor (from OH) or donor to form a hydrogen bond with the keto group. As such it may promote proton transfer from one oxygen to the other, in competition with the transfer from oxygen to carbon. A somewhat similar mechanism has been suggested for the proton transfer reactions in acetyl-acetone dissolved in secondary amines.<sup>11</sup>

The enhancement of the rate of III  $\rightarrow$  I by ethanol is probably due to  $k'_1 \gg k_1$  in a similar complex between III and ethanol. However, in this case much larger concentrations of additive are required, indicating that the complexes with ethanol are much weaker than those with amines. A possible role of ethanol as an acid catalyst cannot be ruled out but appears improbable in view of the fact<sup>1</sup> that the nonchelated enols III are themselves rather strong acids, certainly much stronger than ethanol.

It is interesting to note that  $k_1$  in benzene solutions is considerably smaller than in heptane or cyclohexane (Table II). This attenuation of rotation about the quasisingle bond may be due to formation of complexes, in which "the positive end of the molecular dipole (of the solute) is situated above the plane of the aromatic ring" (of the solvent).<sup>12</sup>

Finally<sup>13</sup> a word about the possible role of water. Obviously

the usual procedures of drying solvents and cells cannot prevent the presence of water in the solutions at concentrations at least as high as those of the compounds and the amines, i.e.,  $10^{-3}$ – $10^{-5}$  M. In the absence of experiments under "superdry" conditions it is not possible to assess the effect of such water traces. However, the very pronounced effect of amines on the kinetics observed in solutions containing such water traces remains an experimental fact. In nonpolar solvents it is reasonable that the compounds studied, as well as the amines, form associates with these traces of water.

**Registry No.**—Ia, 1522-20-9; Ib, 1704-14-9; Ic, 65311-55-9; Id, 65311-56-0; Ie, 1704-15-0; Ig, 1522-33-4; Ih, 65311-57-1; IIa, 123-54-6; IIb, 93-91-4; IIc, 13298-50-5; IID, 50593-99-2; IIe, 120-46-7.

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- (13) We are grateful to one of the referees for pointing out a possible role of water traces.

## Photochemistry of Epoxides. 4. Photoreduction of a Monoepoxide of *endo*-Dicyclopentadiene<sup>1a</sup>

Donald R. Paulson,\* A. Spencer Murray,<sup>1b</sup> and Eric J. Fornoret<sup>1c</sup>

Department of Chemistry, California State University, Los Angeles, Los Angeles, California 90032

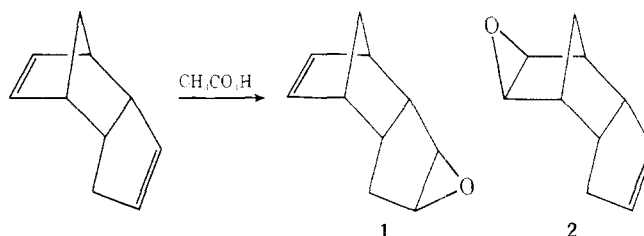
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Two monoepoxides of *endo*-dicyclopentadiene have been prepared by peracetic acid oxidation. Acetone sensitized photolysis of *endo*-4-oxatetracyclo[6.2.1.0<sup>2,7</sup>.0<sup>3,5</sup>]undec-9-ene (1) results in efficient photoreduction of the double bond via a free-radical mechanism. Photolysis of model compounds indicates that there is no interaction between the triplet state excited olefin and the epoxy moiety.

Photochemical  $2\pi + 2\pi$  intramolecular cyclizations have been used extensively in the synthesis of polycyclic molecules.<sup>2</sup> Recently,  $2\pi + 2\sigma$  photochemical cyclizations have been reported by Prinzbach and others.<sup>3</sup> As a continuation of our studies into the photochemical interaction of olefinic and epoxide moieties,<sup>4</sup> we have investigated the acetone sensitized photolysis of the monoepoxides of dicyclopentadiene. These molecules were chosen for study because the close proximity of the olefinic  $\pi$  bond and the carbon-carbon  $\sigma$  bond of the epoxy group might make them amenable to  $2\pi + 2\sigma$  intramolecular photocyclization.

Peracetic acid oxidation of *endo*-dicyclopentadiene gave two monoepoxides in a 1:1.5 ratio. The major product is assigned as *endo*-9-oxatetracyclo[5.3.1.0<sup>2,6</sup>.0<sup>8,10</sup>]undec-3-ene (2) while the minor product is assigned as *endo*-4-oxatetracyclo[6.2.1.0<sup>2,7</sup>.0<sup>3,5</sup>]undec-9-ene (1). The structures of these two epoxides were first correctly assigned by Alder and Stein.<sup>5</sup> However, they did not obtain a pure sample of epoxide 1. The assigned structures are readily confirmed by infrared and NMR analysis. Epoxide 1 shows strong absorption at  $835\text{ cm}^{-1}$  which is characteristic of the epoxy-cyclopentane system<sup>6</sup> while epoxide 2 shows strong absorption at  $850\text{ cm}^{-1}$  which is characteristic of the 2,3-epoxybicyclo[2.2.1]heptane system.<sup>6</sup> The NMR spectrum of epoxide 2 has an AB pattern centered at  $\delta$  1.1 for the protons at C<sub>11</sub>. This clearly indicates an *exo*-normornyl epoxy group.<sup>7</sup> The remainder of the spectral data is consistent with the assigned structures (see Experimental Section).

The photochemistry of 1 and 2 was then investigated. Epoxide 2 was found to be essentially inert in both polar and



nonpolar solvents using a wide variety of sensitizers and exciting wavelengths. In marked contrast, however, photolysis of 1 in degassed acetone solutions with a 450 W Hanovia medium pressure lamp equipped with a Pyrex filter resulted in formation of 3<sup>6</sup> in 18–36% yield, 4 (and 4') in 14–33% yield, and 2,5-hexandione in 2–10% yield. Low concentrations of 1 (0.01 M) favored 3 while higher concentrations of 1 (0.5 M) favored 4 (4').

The infrared spectrum of 3 has a strong band at  $838\text{ cm}^{-1}$  as expected for an epoxy-cyclopentane system. We were unable to completely separate 4 and 4'. However, the infrared spectrum displays a carbonyl band at  $1710\text{ cm}^{-1}$  and a strong epoxy cyclopentane band at  $837\text{ cm}^{-1}$ . The NMR shows the methyl ketone at  $\delta$  2.10.

In order to determine the effect, if any, of the epoxide functional group upon the photoreactivity of 1 and 2, the photolysis of 5<sup>6</sup> and 6<sup>8</sup> was investigated.

In analogy to epoxide 2, compound 5 was found to be essentially inert to a wide variety of photochemical conditions. However, photolysis of 6 in acetone solution resulted in the formation of 7<sup>9</sup> (14–28%), 8 (30–48%), and 2,5-hexandione