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$$x^2 - \frac{p_2}{p_1}x + \frac{p_3}{p_1} = 0$$

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# Photoisomerization of the Enol Form of 1,3-Dicarbonyl Compounds[1]

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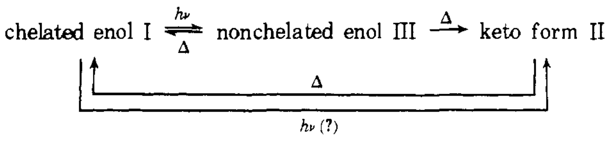
**Abstract:** 1,3-Dicarbonyl compounds II, which exist in hydrocarbon solvents predominantly in the chelated enol form I, are shown by flash photolysis to undergo facile photoisomerization to the corresponding nonchelated and short-lived enol form III (Scheme I), whose existence and UV absorption spectra are reported here for the first time. The III isomers are thermally unstable and revert spontaneously to either I (diketones), II (ethyl acetoacetate), or both (ethyl benzoylacetate). A UV-induced low-yield photoconversion I → II and the reverse thermal reaction are observed with stationary spectrophotometric methods.

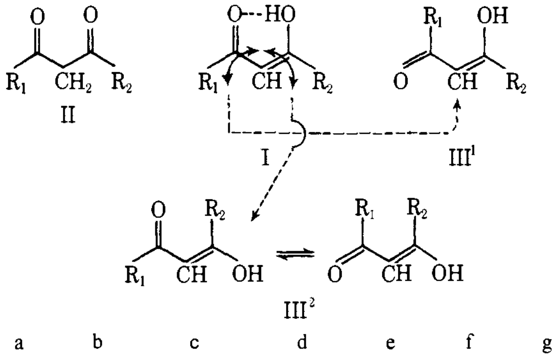
Open-chain β-dicarbonyl compounds can in principle exist in three forms: a chelated enol I, a keto form II, and several nonchelated enols III. However, in hydrocarbon solvents they usually exist as an equilibrium mixture of I and II (Scheme II). (For $R_1 \neq R_2$ either of the two acylic groups may undergo enolization, giving rise to a second set of enols derived from $R_1C(OH){:}CHCOR_2$.) An exception are several 2-formyl esters which exist[3] in solution as III. The chelated enolic form I with its "pseudoaromatic" ring was considered to be photochemically stable,[4] except compounds a and f which undergo photoketonization[5] I → II.

We now report[1] a photoisomerization I → III observed with eight compounds, $I_a$–$I_h$, with quantum yields of 5–20%. III reverts spontaneously to I and II.

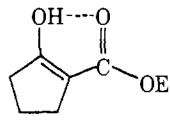
Scheme I



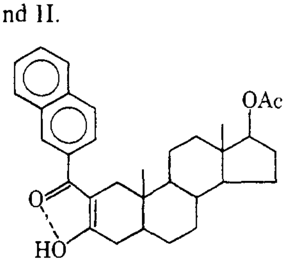
Scheme II



| | a | b | c | d | e | f | g |
|---|---|---|---|---|---|---|---|
| $R_1$ | methyl | methyl | methyl | methyl | phenyl | ethoxy | ethoxy |
| $R_2$ | methyl | phenyl | 2-naphthyl | 2-anthryl | phenyl | methyl | phenyl |



$I_i$



$I_h$

## Experimental Section

**Photochemical Methods.** Ultraviolet (UV) irradiations and spectrophotometry were carried out in a Cary 14 recording spectrophotometer. Analysis was based on the changes in the UV absorption spectrum, as determined separately. Irradiations were at wavelengths where $I_{a-i}$ absorb 50–100 times more than the corresponding $II_{a-i}$. In solutions of these compounds in aliphatic hydrocarbons, the thermal equilibrium is largely in favor of the I form. Light sources used for steady irradiations were: at 254 nm, a low-pressure mercury arc, combined with a chlorine filter (30-mm light path, at 1 atm) and a Co/Ni filter ($CoSO_4{\cdot}7H_2O$ (145 g) + $NiSO_4{\cdot}6H_2O$ (450 g) in 1 L of $H_2O$, placed in a 30-mm cell); a HBO-200 Osram mercury arc, combined with a Schott interference filter for 313 nm, or a Corning Glass filter combination 7-54 + 0-54 for 295–410 nm. Irradiations were carried out in regular 10-mm square cells in the Cary 14 cell compartment, unless stated otherwise. The light flux under these conditions was determined by ferrioxalate actinometry.[6] Representative values were $4.4 \times 10^{-8}$ einsteins/min at 254 nm and $5.0 \times 10^{-9}$ einsteins/min at 313 nm. Relative light intensities were determined

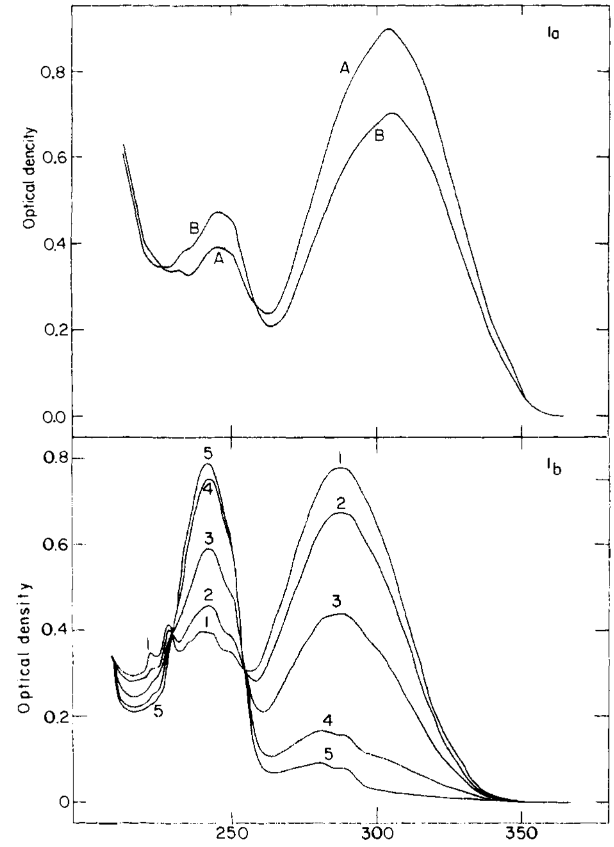


Figure 1. (a) Absorption spectra of compound b in cyclohexane ($5.5 \times 10^{-5}$ M): A, before irradiation; B, following irradiation in the range 295-420 nm. (b) Absorption spectra of compound g in hexane ($7.8 \times 10^{-5}$ M): 1, before irradiation; 2-5, following irradiation at 313 nm for 0.16, 1, 3, and 5 min, respectively.

with a similar cell filled with Rhodamine B solution,[6] serving as quantum converter, and a fluorescence meter. Optical densities at the wavelength used for irradiation with monochromatic light never exceeded 0.6. In determinations of quantum yields, the extent of the photoconversion was kept below 15%. The flash photolysis experiments were carried out in 15-mm i.d. tubular cells of 50- or 100-mm light path.[7] The transient spectra are all based on absorbance measurements before and 1 ms after the flash (flash half-width about 5 μs). The range of wavelengths used for flash irradiation was limited upward by Corning Code 9863 filters not transmitting above 410 nm and, in some cases, downward by UV cut-off filters not transmitting below 255 nm (compounds c and h) or 295 nm (d). Concentrations in the range $10^{-5}$-$10^{-6}$ M were employed in cells of 5- or 10-cm light path. Measurements were made pointwise, at wavelength intervals of 5 nm. In order to avoid effects due to minor irreversible side reactions and, in particular, to eliminate the possibility of irradiating the keto photoproducts, fresh solutions of f and g were employed for each flash. With a-e and h, fresh solutions were used following three-four flashes.

The ratio [I]/[II] between the tautomers was determined by means of UV absorption spectra (cf. Results). **H NMR spectra** were taken with a Varian A-60 instrument. **Infrared spectra** were measured with a Perkin-Elmer 237 instrument. Solutions were flushed with either argon, nitrogen, or oxygen.

**Solvents.** Spectrograde *n*-hexane, *n*-heptane, cyclohexane, and benzene were dried by chromatography over Woelm alumina columns. Absolute ethanol was prepared using common procedures. All solvents were kept over "molecular sieves".

**Compounds. Acetylacetone (a)** was purified by preparative VPC (Carbowax 5%, 80 °C). Its UV absorption maxima and extinction coefficients were: hexane, 271 nm (10 000); ethanol, 274 nm (8500); 0.1 N HCl, 274 nm (1500).

**Benzoylacetone (b)** was recrystallized from ethanol and then from petroleum ether. UV absorptions were: hexane; 306 (17 000); ethanol, 308 (16 800).

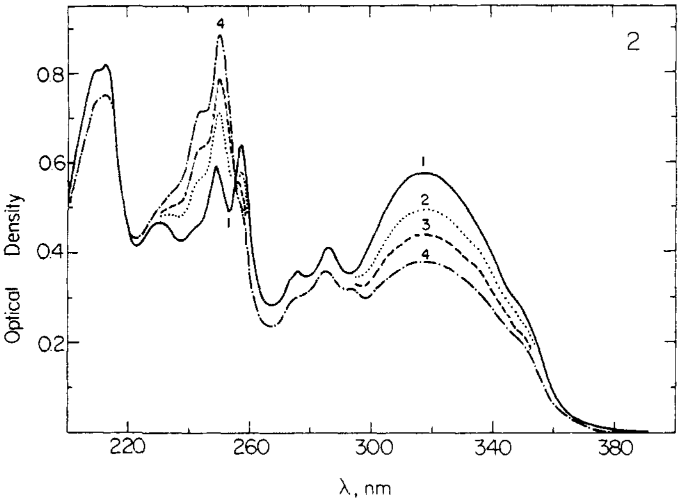


Figure 2. Absorption spectra of compound c in cyclohexane ($2.7 \times 10^{-5}$ M): 1, before irradiation; 2-4, following irradiation at 313 nm for 10, 20, and 30 min, respectively.

Table I. Wavelengths λ (in nm) and Molar Absorption Coefficients ε of UV Absorption Peaks of the Chelated Enol and the Keto Forms of β-Diketones and β-Keto Esters

| Compd | Chelated enol<br>λ ($10^{-4}\epsilon$) | Keto<br>λ ($10^{-4}\epsilon$) |
|---|---|---|
| a | 271 (1.0) | |
| b | 306 (1.7) | 245 (1.6) |
| c | 318 (2.0) | 250 (5.1), 284 (0.94) |
| d | 310 (3.6), 328 (1.7) | 260 (4.2), 270 (4.2), 279 (4.0) |
| e | 366 (2.2) | 251 (2.6) |
| f | 244 (0.81) | |
| g | 288 (1.0) | 241 (1.1) |
| h | 318 (1.36) | 233 (2.4), 239 (3.1), 249 (2.0) |

**2-Naphthoylacetone (c)** was synthesized as described.[8] The crude product (1 g) was absorbed on a silica column (30 g), eluted with a 6:94 (by volume) mixture of chloroform and hexane, and recrystallized from ethanol, mp, 79-80 °C. Its main absorption peak in the infrared (IR) was at 6.25 μ ($CS_2$ solution). UV absorption peaks were, in cyclohexane: 213 (31 000), 230 (16 000), 250 (20 600), 258 (22 200), 275 (12 200), 286 (14 100), 318 (20 200). NMR signals (ppm, in $CDCl_3$) and assignments were: 2.20 (methyl), 6.30 (vinylic proton), 7.5-8.5 (naphthyl protons), 16.35 (hydroxyl).

**2-Anthroylacetone (d)** was synthesized as follows: 10 g of anthroyl chloride and 14 g of acetylacetone-copper complex were dissolved in 50 mL of chloroform and kept at 60 °C for 48 h. The solution was first washed with dilute sulfuric acid (10%), then with a saturated solution of sodium bicarbonate in water, and finally with a saturated aqueous solution of sodium chloride. The solution was then dried over sodium sulfate, the chloroform evaporated, and the residue boiled with 3 N ammonia for 15 min. Acidification with 3 N HCl resulted in an oily precipitate, which was washed with water, dried, and dissolved in hexane, deposited on a 30-g silica column, and eluted with a 2:8 benzene-hexane mixture. Recrystallization from ethyl acetate yielded 0.1 g of the desired product (mp 180 °C). The main IR peak (in $CS_2$) was at 6.25 μ. The UV absorption peaks were, in cyclohexane: 243 (37 600), 256 (34 800), 310 (35 800), 328 (27 100), 348 (10 800), 367 (8700), 388 (6800), 405 (5600). NMR signals (ppm, in $CDCl_3$) and assignments were: 2.27 (methyl), 6.32 (vinylic proton), 7.1-8.6 (anthryl protons). Anal. Calcd for $C_{18}H_{14}O_2$: C, 80.19; H, 5.26. Found: C, 82.24; H, 5.38.

**Dibenzoylmethane (e).** A commercial product was recrystallized from ethanol and then from cyclohexane.

**Ethyl Acetoacetate (f).** A commercial product was shaken with aqueous sodium bicarbonate and then with water, distilled from calcium chloride, and then fractionally distilled under reduced pressure.

**Table II.** Rate Constants $k$ of the Reaction Keto → Chelated Enol (II → I) of Several Diketones, at Room Temperature, in Benzene (B) or Cyclohexane (CH)

| | Compound (solvent) | | | | | | |
|---|---|---|---|---|---|---|---|
| | a (CH) | b (CH) | b (B) | c (CH) | c (B) | e (CH) | e (B) |
| $10^3k$, $s^{-1}$ | 23 | 14 | 7.7 | 17 | 3.8 | 68 | 22 |

**Table III.** Rate Constants $k$ of the Reaction X → I in Cyclohexane (CH) or Heptane (H) at Room Temperature

| | Compound (solvent) | | | | | | |
|---|---|---|---|---|---|---|---|
| | a (H) | b (CH) | c (CH) | d (CH) | e (CH) | g (H) | h (CH) |
| $k$, $s^{-1}$ | 0.27 | 0.33 | 0.34 | 0.49 | 70 | 0.11 | 0.83 |

**Ethyl Benzoylacetate (g).** A commercial product was distilled three times at reduced pressure, taking the middle fraction in each case.

**Compound h** was prepared by a photo-Fries rearrangement of $\Delta^2$-androstene-3,17$\beta$-diol 3-(2-naphthoate) 17-acetate, and recrystallized from methylene chloride/hexane. It had mp 176 °C and proved to be pure on TLC (silica, benzene–chloroform 1:3): IR peaks (in $CCl_4$) 5.85, 6.3, 8.0 $\mu$; UV peaks (in hexane) 215 nm (58 000), 233 (17 800), 240 (17 000), 350 (18 300), 261 (14 500), 281 (10 000), 291 (11 400), 318 (13 600). NMR signals (ppm, in $CDCl_3$) and assignments were: 0.72 (18- and 19-methyl), 2.00 (acetyl), 2.35 and 2.37 (allylic protons), 4.62 ($C_{14}$-H), 7.5–8.2 (naphthyl), 16.97 (hydroxyl).

**Ethyl Ester of Cyclopentanone-2-carboxylic Acid (i).** A Fluka product (purum) was used without purification.

## Results

**Keto–Enol Equilibrium in Solution.** Compounds which exist in aliphatic hydrocarbon solution predominantly (95%) as the chelated enol I are $I_a$,[9] $I_b$,[10] $I_c$ and $I_d$ (estimated by comparing NMR signals of the vinylic and hydroxylic protons), $I_e$,[11] $I_h$ (NMR signals of OH and 17-acetyl protons, absence of signal at 3.5–4.5 ppm where $\alpha$-diketonic protons absorb).[12] Lower enol contents were reported for f (51%),[13] g (72%),[14] and i (25%).[15]

**Photoinduced Conversion: Chelated Enol I → Diketone II.** UV irradiation of solutions in hexane, heptane, or cyclohexane of $I_a$, $I_f$, $I_i$ at 254 nm and of $I_b$, $I_c$, $I_d$, $I_e$, $I_g$, $I_h$ at 313 nm or in the range 295–420 nm resulted in changes in the absorption spectra. At room temperature the latter slowly revert to the starting spectra (Figures 1 and 2). Isosbestic points[16] are maintained during both the photoconversion and the thermal reversion. The light-induced spectral changes are clearly due to a conversion I → II. In those compounds containing aromatic groups, both the disappearance of the absorption bands of I and the appearance of those of II can be observed (Figures 1 and 2). In a, f, i the extinction coefficients of II are too small at $\lambda$ >210 nm, and therefore only the changes in concentration of I can be followed spectrophotometrically. The "keto" UV absorption bands characterizing the postulated II tautomers were identified as follows (cf. also Table I): The irradiation products of compounds $I_{a\text{-}d}$ and $I_h$ have absorption spectra closely similar to those of the products of the photo-Fries rearrangement of the corresponding enol esters,[17] and the spectra of the irradiation products of $I_b$ and $I_g$ are in accordance with those calculated by various authors[14,15b] for the respective keto forms. In general, the absorption spectra of the irradiation products fit those assigned to the corresponding acylic groups: acetyl and benzoyl,[18] 2-naphthoyl,[19] and 2-anthroyl.[20] The longest main absorption bands in $CH_3COC_6H_5$ are at 278 (1000) and 239 nm (13 200), while those for $C_6H_5COCH_2COC_6H_5$ are at 275 (2500) and 251 nm (26 000), i.e., the main band is shifted bathochromically in the diketone.

**Thermal reversion** II → I, i.e., the reestablishment of the thermal equilibrium I $\rightleftharpoons$ II, is a pseudo-first-order reaction. The rate constants observed spectrophotometrically for four compounds in cyclohexane and in benzene are given in Table II. They are similar in both solvents and increase in the order $I_e < I_b = I_c < I_a$, which is also the order of the corresponding proton dissociation constants.[21,22] $II_h$ in aliphatic hydrocarbons is practically stable at room temperature. Addition of absolute ethanol (about one-fifth of the volume) causes practically immediate conversion into $I_h$.

**Detailed Mechanism of the Photoreaction of the Chelated Enols I: The Phototransient.** A flash-photolytic investigation of compounds a–h in solutions similar to those used in the static experiments described above showed that the major or sole primary photoproduct is a short-lived transient "X" which undergoes fast thermal conversion into I, into the corresponding diketone II, or into a mixture of the two. The changes in absorbance following the light flash are negative at longer wavelengths and positive at shorter ones, with one or more invariant wavelengths, $\lambda_i$, at which no flash-induced change in absorbance takes place. If we assume that the phototransient X does not absorb at the long wavelength side of the spectrum of I in all cases, we can estimate the extent of photoconversion soon after the flash by means of the attenuation at these longer wavelengths and therefrom extrapolate the spectrum of the pure transient. In this way the spectra of the transients in Figures 3–6 were calculated for all compounds. (The spectrum of X in Figure 5c at $\lambda$ <235 was calculated by combining flash data at longer wavelengths and data taken on the Cary 14 at shorter wavelengths.)

**Thermal Reactions Following Formation of the Phototransient.** In compounds a–e and h, the original spectrum is restored within a short time after the flash. This reaction was observed at wavelengths at which only I absorbs and found to follow first-order kinetics. At the invariant $\lambda_i$'s the absorbance did not change during the thermal reversion, indicating that no substantial conversion into the keto form II takes place neither during the flash, nor as a secondary thermal reaction: $I_{a\text{-}e}$, $I_h \rightleftharpoons (h\nu, \Delta)$ transient $X_{a\text{-}e}$, $X_h$. The rate constants of re-formation of I are in the range 0.1–0.8 $s^{-1}$ with all compounds investigated, except with $I_e$, where it reaches 70 $s^{-1}$ (Table III). There is no evidence for the photoformation of II, as described in the static experiments, probably because of quantum yields much below those of the formation of the phototransient. II may thus be formed via X or in a parallel photoreaction. Compounds $I_f$ and $I_g$ exhibit special phenomena: In solutions of $I_f$ the phototransient was found to decay much more slowly, with a half-life of the order of 10 min and could be observed spectrophotometrically. Typical kinetic

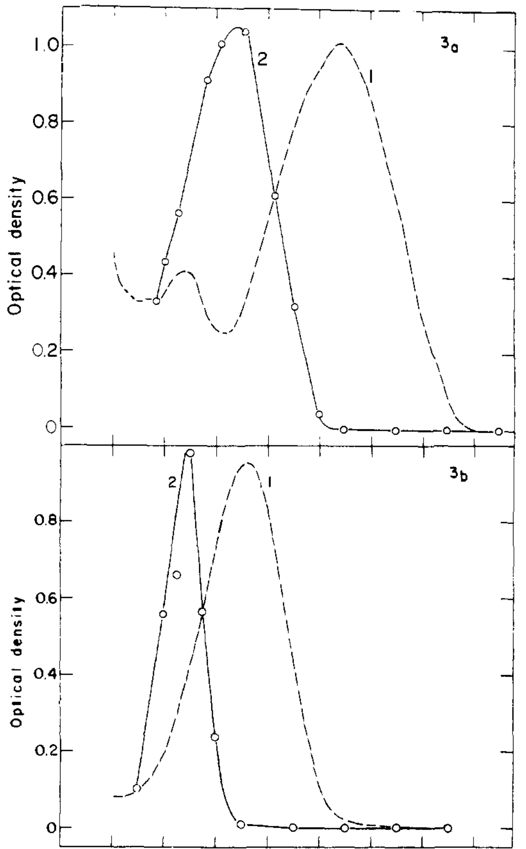


**Figure 3.** (a) Absorption spectra of compound b in cyclohexane (6 × 10$^{-6}$ M) in a 100-mm cell: 1, before irradiation; 2, extrapolated absorption spectrum of the initial photoproduct III$_b$ observed in flash photolysis experiments. (b) As in 3a, but with a 9.5 × 10$^{-6}$ M solution of compound a in hexane, yielding photoproduct III$_a$.

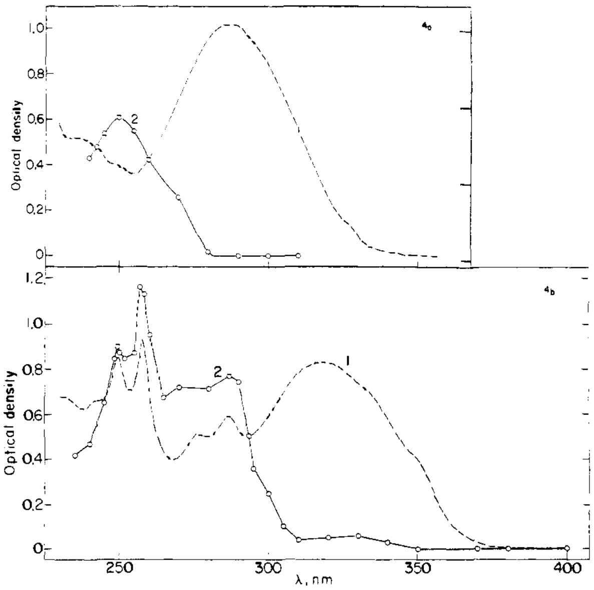


**Figure 4.** Absorption spectra of compounds g, ca. 10$^{-5}$ M (Figure 4a) and c, 3.8 mult 10$^{-6}$ M (Figure 4b), in cyclohexane, 100-mm cell: curves 1, before irradiation, curves 2, extrapolated absorption spectra of the short-lived photoproducts III and III$_c$ observed in flash photolysis experiments.

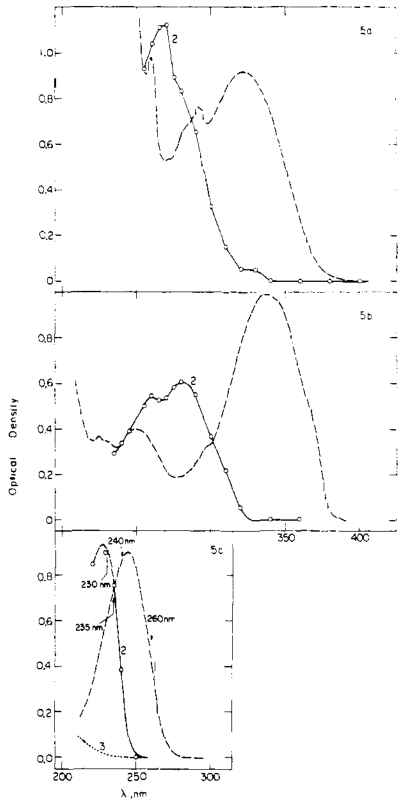


**Figure 5.** (a) Absorption spectra of compound h in cyclohexane (6.7 × 10$^{-6}$ M), 100-mm cell: 1, before irradiation; 2, extrapolated spectrum of III$_h$ observed in flash photolysis. (b) As in 5a, but with a 4.5 × 10$^{-6}$ M solution of e yielding photoproduct III$_e$. (c) Absorption spectra of compound f in *n*-heptane, ca. 10$^{-4}$ M: 1, before irradiation; 2, calculated for III$_f$; 3, diketo form II$_f$. Cf. Figure 7 for the variation with time of the absorbance at the four wavelengths indicated by arrows.

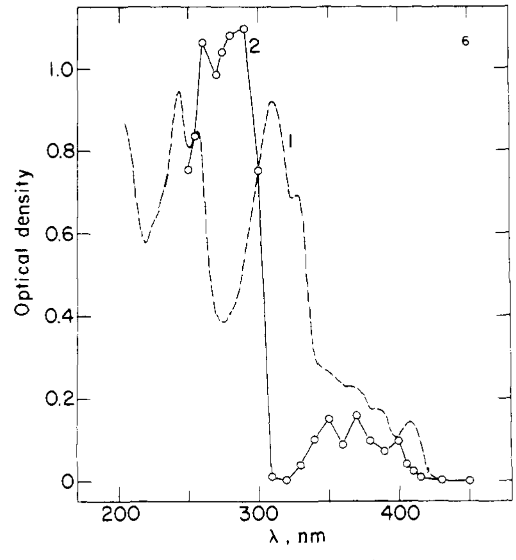


**Figure 6.** Absorption spectra of compound d in cyclohexane, ca. 2.5 × 10$^{-6}$ M, 100-mm cell: 1, before irradiation; 2, extrapolated absorption spectrum of the short-lived form III, observed in flash photolysis.

curves at four wavelengths are given in Figure 7. In this context one should recall that the thermal reversion II → I described earlier is much slower still, with a half-life of the order of several hours. The kinetic curves in Figure 7 should be seen in conjunction with the absorption spectra of I$_f$, II$_f$, and X$_f$ in Figure 5c. We interpret these curves as follows: At 260 nm, where I is the only absorbing species, there is no thermal change within the first 16 min. Later a very slow increase, due to formation of I$_f$, takes place. At 240 and 230 nm, where the transient X$_f$ absorbs, a decay within the first 16 min is observed. This holds also at the invariant λ$_i$ 235 nm, where the decay is a first-order reaction. We conclude that X$_f$ decays to

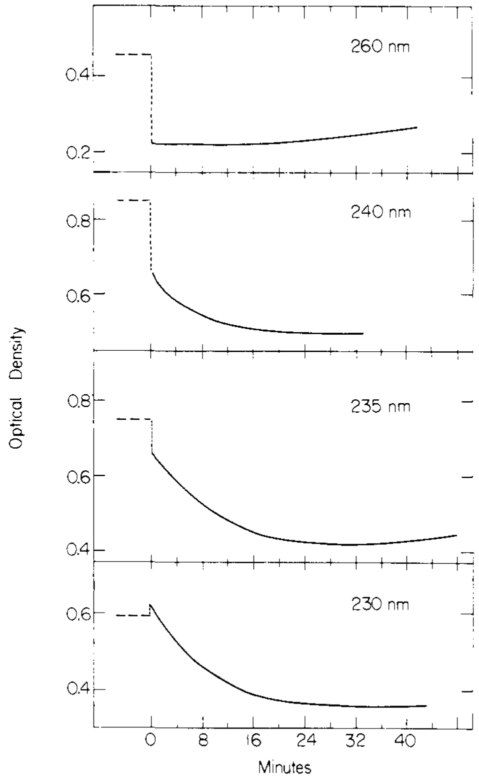


Figure 7. Variation with time of optical density of the solution described in Figure 5c, at the wavelengths indicated, following UV irradiation. The flat initial portions of the curves indicate the absorbance before irradiation, the vertical ones denote the change resulting from irradiation. Cf. Figure 5c, according to which at 260 nm, only $I_f$ absorbs, and one observes its slow formation via $II_f$; at 240 nm, $III_f$ absorbs, but less than $I_f$, thus the large initial drop following irradiation, and the subsequent fast disappearance of $III_f$, to give $II_f$; at 235 nm, the invariant point of curves 1 and 2 in Figure 5c, the drop "during the irradiation" is actually due to the conversion of $III_f$, formed primarily, into $II_f$ during the irradiation and the time elapsed until the photometric measurement was started; this conversion continued during the initial part of the curve: at 230 nm, $III_f$ absorbs more strongly than $I_f$ and $II_f$, and one observes a light-induced increase, followed again by the decay of $III_f$ to $II_f$. (In this experiment, irradiation and transfer of the cell to the cell compartment of the spectrophotometer took several minutes.)

$II_f$, which then slowly reverts to $I_f$. In solutions of $I_g$ the situation is even more complex. In Figure 8 we show kinetic curves at 260 nm, an invariant $\lambda_i$ according to the spectra in Figure 4a, and at 320 nm, where only $I_g$ absorbs (Figures 1b and 4a). Again we recall that the reaction $II_g \rightarrow I_g$ takes hours, so that it can be ignored in kinetic curves in the "seconds" range. At 260 nm $D_I = D_X$, $D_{II} < D_I$, and the observed decrease within the first 4 s may be ascribed to a conversion X → II. At 320 nm the initial partial increase should be due to a process X → I. We thus conclude that with this compound the phototransient X decays in parallel reactions to I and II:

$$I \xleftarrow{k_I} X \xrightarrow{k_{II}} II$$

The ratio $k_{II}/k_I$ may be estimated in two ways: directly, by means of the initial kinetics at 320 and 260 nm, and indirectly, by comparing the quantity of I formed in the fast stage with that eventually formed during the slow second stage ($D_3$-$D_2$ and $D_1$-$D_3$ in Figure 8). The first method yields a value of 5.3, the second 4.1, in good agreement with each other, as expected for two simultaneous first-order reactions. The results may be summarized as follows:

$$I_g \underset{k_I}{\overset{h\nu}{\rightleftharpoons}} X_g \xrightarrow{k_{II}} II_g \xrightarrow{k} I_g \qquad k_{II} > k_I \gg k$$

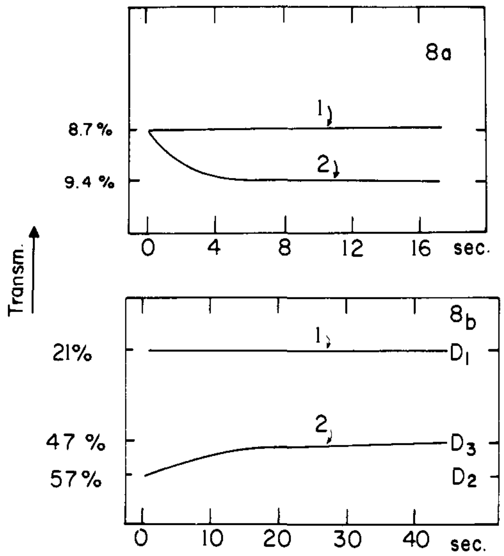


Figure 8. Kinetics of the light transmission of a cyclohexane solution of g, ca. 3 × $10^{-5}$ M, 100-mm cell, at 260 nm (8a) and 320 nm (8b): 1, before flashing; 2, following a short light flash. Cf. Figures 1b and 4a; at 260 nm, the invariant point in Figure 4a, the transmission immediately after the flash does not change, the subsequent decrease is due to $III_g \rightarrow II_g$. At 320 nm, where only $I_g$ absorbs, the immediate drop in absorption (≡100% transmission) is due to $I_g \rightarrow III_g$, the subsequent increase is caused by partial thermal reversal $III_g \rightarrow I_g$.

Table IV. Quantum Yields of the Photoketonization I → II ($Q_k$) and of the Formation of the Phototransient I → X ($Q_x$)

| Compd | $10^3 Q_k$ | Fraction of X converted into II | Estimated $Q_x$ |
|---|---|---|---|
| f | 120 | 1 | 0.12 |
| g | 150 | 0.8 | 0.19 |
| a | 1.3 | <0.02 | >0.06 |
| b | 1.2 | <0.01 | >0.12 |
| c | 1.9 | <0.02 | >0.09 |
| d | 0.66 | <0.02 | >0.03 |

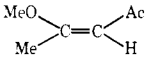
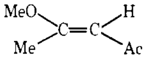
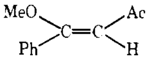
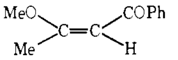
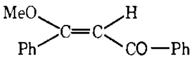
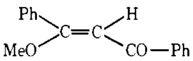
**Effect of Oxygen on the Formation of the Phototransient X.** No effect on either the extent of formation or rate of thermal disappearance of X was observed with $I_{a,b,e,h}$. With $I_c$, oxygen reduces the extent of photoconversion to half its value in nitrogen- or argon-flushed solutions. It is noteworthy that, in the photoketonizations described above, $I_c$ is again the only one in which the quantum yield is affected by oxygen, being *enhanced* to twice its value in nitrogen-flushed solutions.

**Quantum Yields of Photoketonization I → II and of Transient Formation I → X.** Photoketonization yields were determined directly. Those of X formation were estimated from the photoketonization yields and the percentage of X being thermally converted into ketone II in each case. Since this percentage is known in most cases only as an upper limit, only lower limits can be estimated for the quantum yields of X formation in these compounds. Table IV summarizes the results.

## Discussion

The major question arising from the results reported here concerns the nature of the photoisomer X. In trying to answer, the following facts should be kept in mind: (1) X is a photoproduct of compounds $I_{a-h}$ dissolved in aliphatic hydrocarbons (and also in benzene, in those cases examined). (2) No other simultaneous photoproducts were detected. (3) The UV absorption spectrum of X is blue-shifted relative to I. (4) X reverts spontaneously and quantitatively to I, II, or both, without

Table V. Wavelengths λ and Absorption Coefficients ε of the Phototransient X and of Several Model Compounds (cf. references in the last column)

| Compd | λ, nm | $10^{-3}\,\epsilon$ | Model compd | λ, nm | $10^{-3}\,\epsilon$ |
|---|---|---|---|---|---|
| $X_a$ | 250 | 11.5 |  | 245 | 12.2[a] |
| | | |  | 247 | 11.9[a] |
| $X_b$ | 265 | 17.8 |  | 272 | 16[b] |
| | | |  | 278<br>248 | 13.4[b]<br>9.8 |
| $X_e$ | 280<br>260 | 14.4<br>13 |  | 306<br>242 | 16.5[c]<br>10.7 |
| | | |  | 284<br>249 | 10[c]<br>10 |
| $X_f$ | 230 | 15.7 | MeC(OEt)=CHCOOEt | 230 | 15.7[d] |
| | | | cis Ph-CH=CH-COOH | 266 | 9.5[e] |
| $X_g$ | 250 | 7.8 | trans Ph-CH=CH-COOH | 273 | 20.5 |
| | | | cis Ph-CH=CH-COOEt | 266 | 9.7[f] |
| | | | trans Ph-CH=CH-COOEt | 275 | 20 |
| | | | cis Ph-C($CH_3$)=CH-COOH | 246 | 9[g] |
| | | | trans Ph-C($CH_3$)=CH-COOH | 266 | 14.8 |
| | | | cis Ph-C(Cl)=CH-COOEt | 256 | 8.1[h] |
| | | | trans Ph-C(Cl)=CH-COOEt | 254 | 14.1 |
| $X_c$ | 287<br>270<br>258 | 18.8<br>17.6<br>28.3 | | | |
| $X_d$ | 285 | 43.7 | | | |

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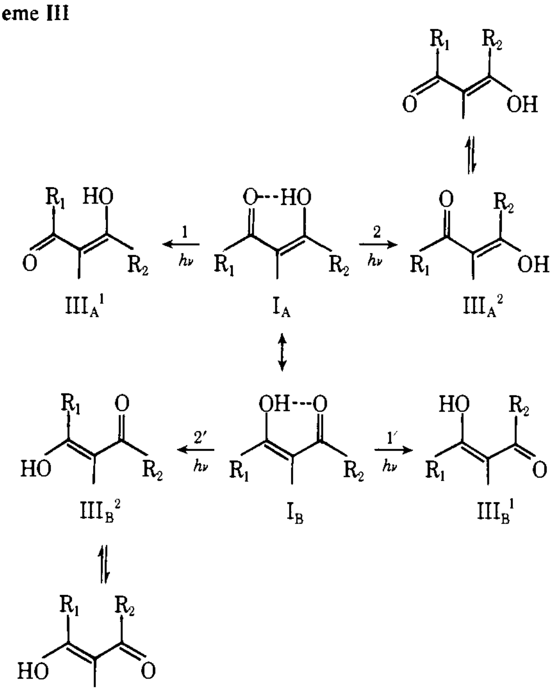
other reactions. We suggest[1] that X is actually the nonchelated enol III, formed from the photoexcited chelated enol I by rotation around either the C=C "double bond", or the OC-CH "single bond", whereby the H bond is broken (Scheme III). In each of the two tautomers, $I_A$ and $I_B$ (if one can distinguish between the two), the H bond can be broken either by rotation around the quasi-double bond, paths 2 and 2′, or around the quasi-single bond, paths 1 and 1′. The photoformation of III from I could thus be considered as a sort of trans-cis isomerization. Whether III exists as $III^1$ or $III^2$ is an open question. In compounds h, i, of course, only a path analogous to 1 is possible. The high rate of thermal reversion III → I seems to favor a reaction $III^1$ → I and thus, by implication, forms $III^1$. However, extensive delocalization of the π electrons of the double bond[23] could enhance isomerization rates, as would paths involving proton movements.

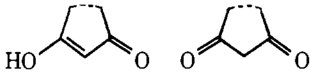
A somewhat similar photoisomerization has been reported for the chelated enol forms of ethyl diaroylacetates.[24] A geometrical photoisomerization in certain chelated enols has been suggested as an intermediate stage,[25] but only as a photosensitized reaction.

Scheme III

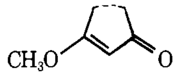


$\xleftarrow{1}$, rotation around the OC—CH single bond
$\xrightarrow{2}$, rotation around the C=C double bond

The cycloalkane-1,3-diones IV tautomerize to "fixed" enols which are unable to form intramolecular H bonds. Their UV absorption spectra are closely similar to those of the corresponding ethers V.[26] Comparably, we observed that the spectra of the transient X in a number of compounds are rather similar to those of the corresponding methyl enol esters, as shown in Table V. This supports the assumption of structures III. In this context one should recall that the effect of substituents on the spectra of enones is well known,[27] and little difference between OH and $OCH_3$ has been reported.



IV

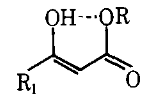


V

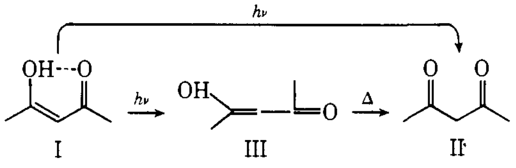
UV spectra do not allow us to distinguish between the A and B tautomers. Furthermore, α,β-unsaturated carbonyl compounds undergo efficient "geometrical" photoisomerization as a major reaction.[28] Formally, our chelated enols I are derived from these carbonyl compounds by introducing an OH group at the β position. Of course, the pseudoaromatic chelate ring in I causes considerable stabilization of the molecule.

Hitherto, no nonchelated enol tautomer has been detected in 1,3-diketones or 3-keto esters capable of forming an intramolecular hydrogen bond;[3,29] the existence of such tautomers in very dilute solutions has been suggested.[3] Nonchelated enolic forms have been described in some β-aldo esters,[3,29] HCO-C-COOR, but no UV absorption spectra have been reported.

In the 3-keto esters, $III_f$ and $III_g$, a hydrogen bond between the hydroxyl group and the etheric oxygen is feasible. It would be expected to enhance the energy barrier to rotation around the quasi-single bond and attenuate the barrier to proton transfer from oxygen to carbon, by way of stabilizing enolate-like transition forms.



The photoketonization of the chelated enols $I_{a-e}$, $I_h$ takes place with such low yields ($\approx 10^{-3}$) that the formation of the diketones $II_{a-e}$, $II_h$ could not be followed by means of the flash technique. We therefore could not distinguish between the two possible modes of formation of II, i.e., directly or via III. The effect of oxygen favors the direct path: In oxygen-flushed solutions the relative quantum yield of photoketonization I → II is double that in nitrogen-flushed solutions, while the reverse holds for the photoisomerization I → III. One possibility is that photoketonization takes place in the singlet state, while photoisomerization involves intersystem crossing, which may be expected to be very efficient. In this respect photoketonization would resemble the well-known 1,3 migration which characterizes enolic systems.[4] Another possible explanation would be that both II and III arise from a common intermediate by competitive decays, one of which is enhanced by oxygen at the expense of the other.



Finally, the present results indicate the usefulness of photo-induced relaxation methods in studies of the three processes III → I, II → I, III → II, including proton-transfer reactions in nonpolar solvents.[3]

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# Prostanoid Endoperoxide Model Compounds: 1-Oxatrimethylene Diradicals in the Thermolysis and Photolysis of 1,2-Dioxolanes[1]

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*Received July 19, 1976*

**Abstract:** Thermo- and photodeketonization of a series of methyl and phenyl substituted 1,2-dioxolanes, considered as prostanoid endoperoxide model compounds, affords fragmentation and rearrangement ketones and epoxides as the major volatile products. The product data show that the relative leaving group abilities for deketonization are in the order $Ph_2C{=}O > MePhC{=}O > Me_2C{=}O$. Furthermore, with increasing leaving group ability, or with increasing phenylation of the dioxolane, the efficiency for the rearrangement increases, but the efficiency for cyclization decreases. In the rearrangement methyl outweighs phenyl migration and the ratio of methyl to phenyl shift increases with increasing leaving group ability. Kinetics of the thermolysis of the tetramethyl- and tetraphenyl-1,2-dioxolanes gave $\Delta H^{\ddagger} = 27.0 \pm 0.3$ and $21.7 \pm 1.0$ kcal/mol and $\Delta S^{\ddagger} = -24.8 \pm 2.0$ and $-30.8 \pm 2.2$ gibbs/mol, respectively, revealing that these activation parameters are a function of leaving group structure. Finally, a stereolabeling experiment on (*S*)-(−)-3,3,4-trimethyl-1,2-dioxaspiro[4.4]nonane shows that the rearrangement ketone (*S*)-(−)-2-methylcyclohexanone is formed with 8.4 ± 2.0% net retention of configuration, under conditions where the rearrangement ketone is optically stable. On the basis of these product, kinetic, and stereolabeling results the thermo- and photodeketonization of 1,2-dioxolanes is postulated to proceed via a 1-oxatrimethylene diradical.

The involvement of endoperoxides **1** as precursors to prostaglandins and the recent demonstration[3] that such prostanoid endoperoxides show even greater physiological activity than the prostaglandins themselves have served as main impetus in the elucidation of these novel cyclic peroxides. Although the syntheses of authentic endoperoxides **1** have not been reported,[4] the simpler 1,2-dioxolanes **2**, which can be considered as model compounds, have been known for several decades.[5] Recently several new synthetic methods for 1,2-dioxolanes have been described, e.g., perhydrolysis of 1,3-disulfonates,[6]