

## A NEW LIQUID PHASE ACTINOMETER: QUANTUM YIELD AND PHOTO-CIDNP STUDY OF PHENYLGLYOXYLIC ACID IN AQUEOUS SOLUTION<sup>†</sup>

A. DEFOIN<sup>‡</sup>, R. DEFOIN-STRAATMANN, K. HILDENBRAND, E. BITTERS-MANN, D. KREFT and H. J. KUHN

*Max-Planck-Institut für Strahlenchemie, Stiftstrasse 34 - 36, D-4330 Mülheim an der Ruhr (F.R.G.)*

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### Summary

Phenylglyoxylic acid (1) in aqueous solution is recommended as a convenient chemical actinometer ( $\phi \approx 0.6 - 0.8$ ) for the region 250 - 400 nm. UV spectroscopy, nuclear magnetic resonance spectroscopy, gas chromatography, high performance liquid chromatography and titrimetry are suitable analytical methods for monitoring the photodecarboxylation of 1 and the formation of benzaldehyde (2). Quantum yield  $\phi$  determinations and <sup>1</sup>H photochemically induced dynamic nuclear polarization (photo-CIDNP) experiments in different media reveal that the photochemistry of 1 is strongly dependent on the nature, water content and pH value of the solvent. Photodecarboxylation of 1 requires the presence of water, and  $\phi$  is drastically enhanced by increasing the water concentration in acidic solution. On the basis of photo-CIDNP results it is suggested that the photoreduction of 1 in 2-propanol, yielding a 1:1 mixture of *meso*- and D,L-2,3-diphenyl-tartaric acid, proceeds via a radical-pair mechanism. Two pathways are discussed for the formation of 2 by photodecarboxylation of 1. The main reaction is proposed to occur without polarization under photo-CIDNP conditions while side reactions give rise to polarized benzoin and benzaldehyde proton nuclear magnetic resonance spectra.

### 1. Introduction

The necessity to calibrate and periodically check an advanced electronically integrating actinometer [1] led us to search for a chemical actinometer in the important region 250 - 400 nm that could be handled

<sup>†</sup>Dedicated to Professor D. Schulte-Frohlinde on the occasion of his 60th birthday.

<sup>‡</sup>New address: École Nationale Supérieure de Chimie, Université de Haute Alsace, 3 rue Alfred Werner, F-68093 Mulhouse Cédex, France.



We describe here the results of a comparative quantitative and photochemically induced dynamic nuclear polarization (photo-CIDNP) study of the course of the photodecarboxylation of **1** in different aqueous media and of the photoreduction of **1** in 2-propanol in order to judge the applicability of these two reactions for the purpose of actinometry.

## 2. Experimental details

### 2.1. Materials

**1** (EGA, purity, 97%) was recrystallized from benzene and then from  $\text{CCl}_4$  under argon to give colourless needles of melting point 65 - 66 °C on a preheated Kofler hot stage. The solid acid is stable in the dark for at least a year and in solution at room temperature for at least a day as judged by gas chromatography (GC) analysis for **2**.

The solvent compositions refer to volume ratios. All solvents were saturated with argon.  $\text{CH}_3\text{CN}$  (Merck, spectroscopic grade) was purified by passage through a column of basic  $\text{Al}_2\text{O}_3$  and by distillation. Water was triply distilled. All other solvents were Merck analytical quality. Merck Titrisols NaOH and HCl were used.  $\text{CH}_2\text{N}_2$ -ether-methanol solution was prepared from Diazald (Aldrich).

#### 2.1.1. *meso*- and *D,L*-2,3-diphenyltartaric acid and dimethyl esters

Irradiation (1 h, Philips HP 125 W, Solidex glass immersion well) of 8 g **1** in 100 ml 2-propanol under argon until the decrease in absorption between 350 and 390 nm came to an end gave an oily residue that was treated with 50 ml  $\text{CH}_2\text{Cl}_2$ . The precipitate (3.4 g) was recrystallized from acetone-toluene to give pure *D,L*-acid (melting point, 195 - 198 °C (*cf.* ref. 21: melting point, 152 °C)). Addition of 20 ml toluene to the residue, the filtrates left after evaporation, gave 2 g crude *meso*-acid (melting point, 80 - 90 °C (*cf.* ref. 27: melting point, 217 - 219 °C)). Esterification by  $\text{CH}_2\text{N}_2$  and recrystallization from 2-propanol gave the pure dimethyl esters: *D,L*-ester melting point, 122 - 124 °C (*cf.* ref. 27: melting point, 119 - 121 °C; note that the assignment of melting points to the acids given in ref. 27 is erroneous); *meso*-ester melting point, 158 - 159 °C (*cf.* ref. 27: melting point, 151.5 - 153 °C). Thin-layer chromatography ( $\text{SiO}_2$  (Merck),  $\text{CH}_2\text{Cl}_2$ ): *D,L*-ester,  $R_F = 0.25$ ; *meso*-ester,  $R_F = 0.55$ . GC at 240 °C: isomerization to 1:1 mixture. IR (KBr) *D,L*-ester: 3440s, 3090, 3050, 3022, 2950, 2850, 1735s, 1705s, 1600, 1490, 1445/1442, 1350, 1325 and 1260s  $\text{cm}^{-1}$ ; *meso*-ester: 3480s, 3410, 3072, 3030, 2992, 2950, 2845, 1710s, 1600, 1493, 1450s, 1438s, 1352 and 1265s  $\text{cm}^{-1}$ . Proton nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR) ( $\delta$  in ppm,  $\text{CDCl}_3$ ), *D,L*-ester:  $\text{OCH}_3$ , 3.79, s, 6H; OH, 4.27, s, 2H; H aromatic, 7.30, m, 10H;  $^1\text{H}$  NMR *meso*-ester:  $\text{OCH}_3$ , 3.78, s, 6H; OH, 5.03, s, 2H; H aromatic, 7.08, s, 10H. Mass spectra for *D,L*-ester and *meso*-ester:  $m/e$  51, 77, 105, 166, 221, 253 and 271.

## 2.2. Methods

$^1\text{H}$  NMR spectra were recorded using Bruker WP 80 WG or Varian HX 60E instruments.  $^1\text{H}$  photo-CIDNP spectra were obtained using a Bruker WH 90 spectrometer with an  $^1\text{H}$  probe modified for irradiation with a lens-pipe arrangement [28] and equipped with a 1000 W Xe-Hg lamp. 30 transients were accumulated with a pulse sequence of 1 s and a pulse angle of  $30^\circ$  after pre-irradiation for 10 s. The chemical shifts were measured relative to the solvent ( $\delta_{\text{CD}_2\text{HCN}} = 1.93$ ). The IR spectra were recorded using a Perkin-Elmer 580 spectrometer. The GC analyses were performed using a Varian 1400 equipped with a 25 m OV 101 capillary column at 50 - 200  $^\circ\text{C}$  and a Spectra Physics SP 1400 computer integrator. A Zeiss PMQ 3 was used for the UV measurements. Metrohm potentiographs E 436 with Dosimat 436 D and an H 65 Schott glass electrode and E 536 with Dosimat E 535 and an EA 126 electrode, and a Radiometer TT 61 Digital Titrator, were used for the titrations. The latter was also employed for pH determinations.

The irradiations were carried out under argon (although oxygen or air had no significant effect on the quantum yields (see below)) at room temperature in quartz cells of optical path length 1 cm (3 ml) or 2 cm, each with a septum, with continuous stirring by magnetic bars in an electronically integrating actinometer similar to that first described by Amrein *et al.* [1]. The apparatus had the following components: an Hg-Xe lamp (1000 Watt Hanovia) mounted in a Schoeffel LH 151 NZ 1000 housing equipped with an LHC 151/1 quartz focusing condenser lens (35 mm in diameter), water and 0.0226 M  $\text{CuSO}_4$  IR filters (optical path lengths 150 mm and 30 mm respectively, liquids circulated by convection), an electronically controlled Compur shutter and a Schoeffel GM 200 double monochromator, all mounted on an optical bench. The power supply was an NTN 1000 XQ (F und G Elektronik). An identical system without the  $\text{CuSO}_4$  filter was used for quantum yield determinations at 254 nm. Both systems had been calibrated by potassium ferrioxalate actinometry [2 - 6]. Quantum yields calculated from the absorbance at 350 nm, 360 nm and 370 nm were corrected for the presence of **2** by multiplying by a factor  $\epsilon_1/(\epsilon_1 - \epsilon_2)$ .

For titrimetry with NaOH, 3 ml irradiated solution were diluted with 20 ml water and during analysis argon was bubbled through in order to remove  $\text{CO}_2$  and to avoid the formation of benzoic acid from **2**. The result was subtracted from that for a non-irradiated reference. The best results were obtained when the experiment was performed in an argon-filled glove-box.

For NMR analysis, 6 ml photolysed solution were extracted three times with  $\text{CH}_2\text{Cl}_2$  (10 ml, 5 ml and 5 ml) in an argon-flushed double-bulb separating funnel, the extract was dried over  $\text{MgSO}_4$ , the solvent was removed and the residue was dissolved in  $\text{CDCl}_3$ . The chemical conversion was calculated from the integrated ortho protons of the phenyl rings of **1** at  $\delta = 8.1$  and of **2** at  $\delta = 7.9$  with reference to the meta and para ring protons at  $\delta = 7.6$ .

For GC analysis, samples of volume 2 ml were mixed with a standard naphthalene solution and  $\text{MgSO}_4$ ; after 15 min,  $\text{CH}_2\text{N}_2$  solution was added

(this is unnecessary for the analysis of 2). The reproducibility was better than  $\pm 8\%$  error for 2.

### 2.3. Use of 1 as a chemical actinometer

A known volume  $V$  (l) of a 0.4% solution of 1 ( $c_1 = 0.025$  M) in  $\text{CH}_3\text{CN}$ -water (3:1 by volume), having an absorbance  $A \approx 1.75$  at 350 nm, is irradiated with constant stirring. An optical path length of 2 cm is recommended at irradiation wavelengths of 330 nm or longer. Absorption is then complete except at 405 nm. The decrease in  $A$  at wavelengths in the range 360 - 390 nm against irradiation time  $t$  is measured with reference to the non-irradiated sample or an identical blank kept in the dark at the same temperature. Readings at 370 nm and below must be corrected for the content of 2. The conversion should not exceed 30%.  $E_{\lambda,t}$  (einstein) is the number of moles of quanta absorbed during  $t$ , and  $\phi_\lambda$  is the quantum yield (see Tables 2, 4 and 5 below) for the experimental conditions employed (*i.e.* solvent mixture and irradiation wavelength  $\lambda$ ). The value of  $\epsilon_1 - \epsilon_2$  for  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  (3:1) is 59 at 350 nm, 56 at 360 nm, 44.5 at 370 nm, 29 at 380 nm, 16 at 390 nm and 8 at 400 nm.

$$E_{\lambda,t} = \frac{\Delta c_1 V}{\phi_\lambda} = \frac{\Delta A V}{\phi_\lambda (\epsilon_1 - \epsilon_2)}$$

## 3. Results

### 3.1. UV and IR spectra of phenylglyoxylic acid

Water interacts with 1 and is obviously intimately involved in the mechanism of photodecarboxylation [8, 19]; it also stabilizes the photo-product 2 against secondary photoreactions [29]. The UV absorption of 1 changes markedly on going from non-polar to polar solvents (Table 1) owing to the breakage of intramolecular hydrogen bonds and the formation of solvates [30 - 32]. The long wavelength edge of the absorption of 1 in acetonitrile solution is shifted to shorter wavelengths by water. In dilute NaOH there is a distinct sinusoidal maximum at 344 nm while in dilute acid, owing to the formation of the protonated form of 1, only a shoulder is left near 350 nm (inset, Fig. 1). The presence of acetonitrile at pH 13 causes a blue shift of the short wavelength maximum and a red shift of the long wavelength maximum as compared with a 0.1 N NaOH solution.

Also, the IR spectra show that the structure of 1 in solution is strongly influenced by the concentration, the solvent polarity and the amount of water present. In  $\text{CCl}_4$  (0.025 M 1) we observed two pairs of sharp bands at 1697/1727 and 1673/1782  $\text{cm}^{-1}$ . The first pair is weakened by the addition of 0.1 - 1 vol.% water; in more dilute  $\text{CCl}_4$  solution (0.002 M) a very weak band at 1760  $\text{cm}^{-1}$  appears instead of that at 1727  $\text{cm}^{-1}$  and the 1697  $\text{cm}^{-1}$  band becomes very weak while the 1673/1782  $\text{cm}^{-1}$  pair remains stable. The four bands in dilute  $\text{CCl}_4$  solution have been assigned [33] to free and intramolecularly bonded  $\alpha$ -carbonyl and carboxyl groups and it was

TABLE 1  
UV maxima of 1 in solution at room temperature

Solvent	$\lambda_{\max}$ (nm) ( $\epsilon$ (l mol <sup>-1</sup> cm <sup>-1</sup> ))	
	<sup>1</sup> ( $\pi \rightarrow \pi^*$ ) band	<sup>1</sup> (n $\rightarrow \pi^*$ ) band
C <sub>6</sub> H <sub>6</sub>		376(88)
CH <sub>2</sub> Cl <sub>2</sub>	274(8600)	sh 358(86)
	278.9(8850) <sup>a</sup>	372(106)
CH <sub>3</sub> OH	252(9200)	345(54)
<i>t</i> -(CH <sub>3</sub> ) <sub>3</sub> COH	250(11600)	343(70)
CH <sub>3</sub> COCH <sub>3</sub>		347(73)
CH <sub>3</sub> COCH <sub>3</sub> -25vol.%H <sub>2</sub> O		347(74)
CH <sub>3</sub> CN	254(10930)	347(69)
	252.8(10300) <sup>a</sup>	sh 360(34)
CH <sub>3</sub> CN-0.1 vol.%H <sub>2</sub> O	254(11090)	347(69)
CH <sub>3</sub> CN-5vol.%H <sub>2</sub> O	251(11600)	345(74)
CH <sub>3</sub> CN-50vol.%H <sub>2</sub> O	249(12070)	343(73)
CH <sub>3</sub> CN-25vol.%H <sub>2</sub> O (pH about 1)	252(11250)	343(72)
CH <sub>3</sub> CN-25vol.%H <sub>2</sub> O (pH about 13)	247(13090)	353(74)
H <sub>2</sub> O	251(13170), sh 290(1356)	343(74)
0.1 N HCl	254(12130)	sh 350(68)
0.1 N NaOH	252.5(13010)	344(76)

<sup>a</sup>From ref. 30.

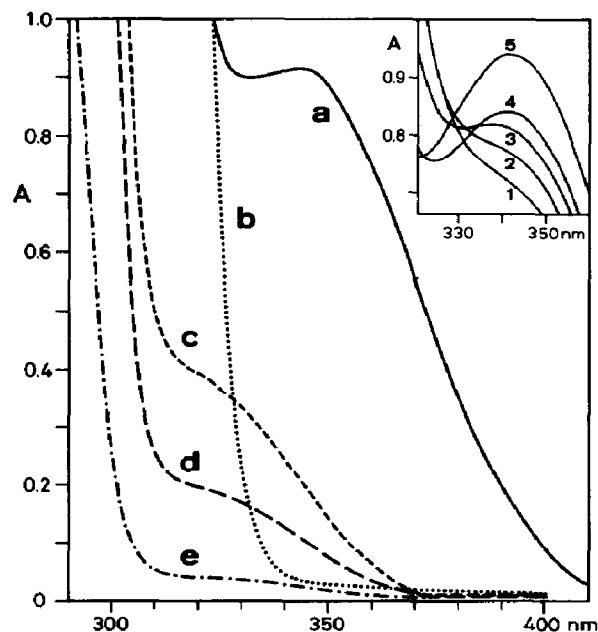


Fig. 1. UV spectra (optical pathlength, 1 cm) of 1 (0.0125 M, curve a) and 2 (0.0125 M, curve c; 0.00625 M, curve d; 0.00125 M, curve e) in CH<sub>3</sub>CN-H<sub>2</sub>O (3:1). Curve b: pure solvent acetone-H<sub>2</sub>O (3:1). Inset, 1 (0.0125 M) in different mixtures of 0.1 N HCl-0.1 N NaOH (1:0, curve 1; 1:0.2, curve 2; 1:0.6, curve 3; 1:1, curve 4; 0:1, curve 5).

concluded that in dilute inert solution the intramolecularly chelated form of **1** predominates. In dry  $\text{CH}_3\text{CN}$  or with up to 1 vol.%  $\text{H}_2\text{O}$  the four bands collapse into two at  $1690\text{ cm}^{-1}$  (CO) and  $1743\text{ cm}^{-1}$  (COOH) and a shoulder at  $1760\text{ cm}^{-1}$  which disappears in the presence of 1 vol.%  $\text{H}_2\text{O}$ . In 5 vol.%  $\text{H}_2\text{O}$  solution the carboxyl band is slightly broadened and shifted to  $1733\text{ cm}^{-1}$  while the  $\alpha$ -carbonyl band remains sharp and stable. It is known from a UV study [30] that acetonitrile destroys the intramolecular hydrogen bonds and forms 1:1 solvent complexes with **1**. Thus, in acetonitrile–water mixtures solvates exist with both water and acetonitrile. In benzene (0.025 M) we found a pattern ( $1695/1755$  and  $1678/1781\text{ cm}^{-1}$ ) similar to that displayed in dilute  $\text{CCl}_4$  except for there being a much stronger band at  $1695\text{ cm}^{-1}$  (free  $\alpha$ -carbonyl). At higher concentration (0.124 M, benzene) five bands can be seen ( $1678, 1697, 1727, 1760$  and  $1782\text{ cm}^{-1}$ ); the additional band at  $1727\text{ cm}^{-1}$  is at the same position as in  $\text{CCl}_4$  (see above) and may be assigned to dimers. Dimeric association of **1** has been proved to predominate in benzene [34] and is assumed to occur in aqueous solution, to an unknown extent [35]. No evidence for “activated ester”-type [36] dimerization of **1** has been found.

### 3.2. Quantum yields of photodecarboxylation

#### 3.2.1. UV analysis

The presence of water is necessary to bring about the selective photodecarboxylation of **1** (*cf.* Section 3.2.4). Mixtures of acetonitrile or acetone with water were found to be suitable solvents. Photoreduction as a competing reaction is strongly suppressed: at 25 vol.% water only 1% of each of the diphenyltartaric acids are formed at 95% conversion [18].

The  $^1(n \rightarrow \pi^*)$  band of **1** (Fig. 1) is extended over the range 300 - 400 nm. The range 350 - 400 nm can be used for measuring the absorbance of the acid. At conversions below 50%, side products are formed in amounts of about 1% and do not cause any problems. Graphs of [**1**] *versus* absorbance were straight lines for the range 0.001 - 0.5 M (in  $\text{H}_2\text{O}$  or  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  (3:1) or  $\text{CH}_3\text{COCH}_3-\text{H}_2\text{O}$  (3:1)). The existence of a hydrate of **1** [37] can be disregarded because it does not absorb above 300 nm. Also, plots of the decrease in absorbance at wavelengths of 350 - 400 nm *versus* quanta absorbed form perfectly straight lines up to at least 36% conversion. The steeper slopes in the range 350 - 370 nm are more suitable than the rather flat slopes at 380 - 400 nm for the evaluation of  $\phi$  (*cf.* Table 2).

Figure 1 illustrates the contribution of the product **2** to the absorbance of photolysed solutions of **1**. Quantum yields calculated from absorbances at or below 370 nm have to be corrected for the **2** content of the photolysed solutions in order to be less dependent on the monitoring wavelengths (*cf.* Table 2). The quantum yields at 365 nm are about the same in aqueous  $\text{CH}_3\text{CN}$  as in  $\text{CH}_3\text{COCH}_3$  while they are somewhat higher in aqueous  $\text{CH}_3\text{COCH}_3$  at 334 nm where absorption (Fig. 1) and triplet sensitization by acetone come into play.

TABLE 2

Quantum yields<sup>a</sup> of decomposition of 1 (0.025 M) measured at different wavelengths in acetonitrile–water (3:1) (pH about 1.9) and acetone–water (3:1) (pH about 2.4, values in parentheses) at 24 °C

Observation wavelength (nm)	Irradiation wavelength (nm)					
	254	300	313	334	365	405
350	0.61	0.75	0.80	0.662 (0.78)	0.701 (0.685)	0.804 (0.74)
360	0.63	0.78	0.81	0.697 (0.81)	0.719 (0.715)	0.829 (0.77)
370	0.62	0.80	0.82	0.71 (0.83)	0.724 (0.72)	0.83 (0.82)
380	0.63	0.79	0.82	0.717 (0.79)	0.735 (0.70)	0.83 (0.81)
390	0.62	0.81	0.80	0.728 (0.76)	0.728 (0.68)	0.80 (0.74)
400	0.61	0.72	0.78	0.77 (0.71)	0.730 (0.65)	0.75 (0.63)

<sup>a</sup>Values corrected for absorption of 2; reproducibility about  $\pm 0.005$  where the numeral is given to three decimal points, and better than  $\pm 0.05$  where numerals are given to two decimal points.

1 is also photolysed to 2 by irradiation into the  $^1(\pi \rightarrow \pi^*)$  band at 254 nm (Table 2). Although the absorption coefficients of 1 (11 230) and 2 (8875) at 254 nm in  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  (3:1) are of the same order of magnitude, the plots of the absorbance decay of 1 (at 350 - 400 nm) *versus* quanta absorbed form satisfactorily straight lines (for conversions up to at least 22%).

At a standard concentration (0.025 M) and an optical path length of 2 cm the absorbance of 1 in  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  (3:1) is 6 at 313 nm, 3.6 at 334 nm, 2.8 at 365 nm and only 0.22 at 405 nm. For direct UV spectrometry the use of cells of both 2 cm (irradiation) and 1 cm (measuring) path length proved advantageous. The total absorption is not a constraint when using an integrating electronic actinometer [1] which automatically compensates for light passing through the sample. The relatively low absorbance of 1 is therefore advantageous: it allows direct spectrophotometric measurements to be made without dilution procedures as well as actinometric calibration of thick-layer vessels and long-time light averaging. There is no significant concentration effect of 1 on  $\phi$  in the range 0.0025 - 1.0 M.

Performing measurements with only 10% or 50% of the normally applied light intensity showed that the incident light intensity has practically no effect on  $\phi$ . Measurements at 15 and 27 °C instead of the normal 22 - 24 °C resulted in a rather small positive temperature dependence of  $\phi$  ( $\lambda_{\text{irr}} = 365$  nm, 0.025 M 1 in  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  (3:1),  $\Delta\phi/\Delta T = 0.0029 \pm 0.0007$  °C<sup>-1</sup> at the



monitoring wavelengths 350 - 400 nm). Thermal decomposition of 1 need not be considered since the absorbance remained constant in the dark at 42 °C for several hours. There is no significant influence of oxygen on  $\phi$ . The values determined at 365 nm in CH<sub>3</sub>CN-H<sub>2</sub>O (3:1) saturated with argon, air or even oxygen were identical to within  $\pm 0.008$ .

### 3.2.2. NMR analysis

The decrease in 1 and the increase in 2 on irradiation of 1 in aqueous acetonitrile or acetone can be monitored by NMR. A plot of conversion *versus* irradiation time showed that the rate of formation of 2 correlates very well with the rate of decomposition of 1. Calibration measurements resulted in less than 5% error at 40% conversion. Quantum yields of about 0.7 for CH<sub>3</sub>CN-H<sub>2</sub>O (3:1) and 1 for CH<sub>3</sub>COCH<sub>3</sub>-H<sub>2</sub>O (3:1) were obtained. The rather high value for the latter and the appearance of benzoic acid in some of the spectra indicate that decomposition of both 1 and 2 occurs during the necessary work-up procedure.

### 3.2.3. Other methods of analysis

By means of an automatic titrator, fast and elegant acid determinations using even rather concentrated solutions of 1 are possible (Table 3). Problems arising from the appearance of benzoic acid and carbon dioxide can be avoided by bubbling an inert gas through the solution.

TABLE 3

Quantum yields<sup>a</sup> of decomposition of 1 as measured by titration

Solvent	c (M)	Irradiation wavelength (nm)		
		334	365	405
CH <sub>3</sub> CN-H <sub>2</sub> O (3:1)	1.0	0.83	0.83	0.70
CH <sub>3</sub> COCH <sub>3</sub> -H <sub>2</sub> O (3:1)	0.05	0.71	0.78	0.71

<sup>a</sup> $\pm 6\%$  error.

After esterification by diazomethane, methyl phenylglyoxylate can be determined by GC besides 2. Quantum yields of formation of 2 ( $\pm 8\%$  error) were found to be 0.71 (334 nm, 1.0 M 1, CH<sub>3</sub>CN-H<sub>2</sub>O (3:1)) and 0.66 (365 nm, 0.05 M 1, CH<sub>3</sub>COCH<sub>3</sub>-H<sub>2</sub>O (3:1)). Quantum yields around 1 calculated from the ester concentration were not satisfactorily reproducible. Reverse phase high performance liquid chromatography (HPLC) allows analysis of 1 and 2 in a single run.

### 3.2.4. Effects of solvent

The influence of water concentration and of pH value on  $\phi$  is presented in Tables 4 and 5. The photoreactivity of 1 in aprotic solvents is drastically different from that in water. In acetonitrile, either dry or with 1 vol.% H<sub>2</sub>O,

TABLE 4

Quantum yields<sup>a</sup> of decomposition of 1 (0.025 M) at 365 nm measured by UV spectrometry in acetonitrile with different water contents

Observation wavelength (nm)	Water in acetonitrile (vol.%)							
	≈ 0 <sup>b</sup>	1 <sup>b</sup>	2.5 <sup>b</sup>	5	15	25	50	100 <sup>c</sup>
350	≈ 0.04	≈ 0.05	0.18	0.402	0.622	0.573	0.463	0.136
370	≈ 0.07	≈ 0.05	0.22	0.511	0.795	0.705	0.563	0.157
390	≈ 0.07	≈ 0.03	0.20	0.501	0.838	0.728	0.569	0.180

<sup>a</sup>Not corrected for the content of 2 (see Section 2.2); for error see Table 2.

<sup>b</sup>Values increase with irradiation time; the results given are for  $6.5 \times 10^{-5}$  einsteins absorbed.

<sup>c</sup>pH 1.8.

TABLE 5

Quantum yields<sup>a</sup> of decomposition of 1 (0.025 M) at 365 nm measured by UV spectrometry at different pH values<sup>b</sup>

Observation wavelength (nm)	pH of acetonitrile–water (3:1)						
	≈ 0.3 <sup>c</sup>	≈ 0.8 <sup>c</sup>	≈ 1.9	≈ 2.4 <sup>d</sup>	≈ 3.2 <sup>d</sup>	≈ 4.1 <sup>d</sup>	≈ 9.7 <sup>d</sup>
350	0.60	0.57	0.573	0.42	0.15	≈ 0.04	≈ 0.01
370	0.75	0.71	0.705	0.45	0.14	≈ 0.05	≈ 0.02
390	0.77	0.72	0.728	0.43	0.14	≈ 0.01	≈ 0.02

Observation wavelength (nm)	pH of water						
	0.4 <sup>e</sup>	0.8 <sup>c</sup>	1.3 <sup>f</sup>	2.3 <sup>d</sup>	2.9 <sup>d</sup>	5.0 <sup>d</sup>	12.3 <sup>g</sup>
350	≈ 0.3	0.32	0.31	0.043	0.024	0.027	0.023
370	≈ 0.4	0.35	0.35	0.049	0.022	0.029	0.026
390	≈ 0.3	0.25	0.29	0.045	0.008	0.023	0.018

<sup>a</sup>Not corrected for the content of 2 (see Section 2.2); for the error see Table 2.

<sup>b</sup>For results for pH 1.8 see Table 4, 100% water.

<sup>c</sup>Addition of HCl.

<sup>d</sup>Addition of NaOH.

<sup>e</sup>1 N HCl, initial value, decomposition.

<sup>f</sup>0.1 N HCl.

<sup>g</sup>0.1 N NaOH; values slightly increasing with irradiation time.

decomposition of 1 started only very sluggishly after an induction period without a distinct change in absorbance. The quantum yields obtained are about 0.05 and are poorly reproducible. In dry acetonitrile with 0.05 M *p*-toluenesulphonic acid, a slight initial increase in absorption ( $\phi_{365} \approx 0.1$ ) was followed by a decrease and a yellowish colouring. In benzene, slow decomposition followed by the development of a yellowish colouring was observed. Photolysis in benzene in the presence of pyridine (0.05 M) also gave an

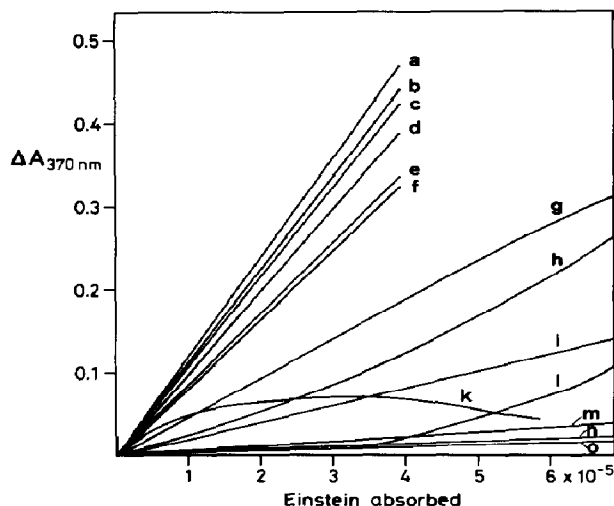


Fig. 2. Decrease in absorbance at 370 nm *vs.* number of quanta absorbed at 365 nm by **1** (0.025 M) in different media (percentages refer to acetonitrile solutions unless otherwise indicated): curve a, 15 vol.% H<sub>2</sub>O; curve b, 25 vol.% 1 N HCl, pH about 0.3; curve c, 25 vol.% H<sub>2</sub>O, pH about 1.9; curve d, 25 vol.% H<sub>2</sub>O-acetone; curve e, 50 vol.% H<sub>2</sub>O; curve f, 5 vol.% H<sub>2</sub>O; curve g, 0.1 N HCl, pH 1.3; curve h, 2.5 vol.% H<sub>2</sub>O; curve i, H<sub>2</sub>O, pH 1.8; curve k, 1 N HCl, pH 0.4; curve l, acetonitrile; curve m, 25 vol.% H<sub>2</sub>O, pH about 4; curve n, 25 vol.% H<sub>2</sub>O, pH about 9.7; curve o, 0.1 N NaOH, pH 12.3.

increase in absorption and a yellow colour. In pure benzene and in acetonitrile-*p*-toluenesulphonic acid no trace of **2** was detected by HPLC. The onset of an effective photodecarboxylation in acetonitrile solution was found between 1 and 2.5 vol.% H<sub>2</sub>O where  $\phi$  is about 0.2 (increasing with irradiation time). A 5 vol.% water content is sufficient to accelerate the photolysis by a factor of about 10, to achieve a perfectly linear plot of  $\Delta A$  *versus* absorbed quanta (Fig. 2), and the quantum yields are reproducible to within  $\pm 0.005$ .  $\phi$  increases with water concentration up to a maximum at near 15 vol.% water but decreases again beyond this value, in pure water reaching a value of less than one fourth (Fig. 3). A water content of 15 - 25 vol.% which effects optimum quantum yields corresponds to 330 - 560 molecules H<sub>2</sub>O per molecule of **1**. The effect of water cannot be satisfactorily mimicked by an alcohol; photolysis at 365 nm in acetonitrile-*tert*-butanol (3:1) caused a non-linear decrease in absorbance with an initial  $\phi$  of about 0.05. In contrast to other authors [19] we could not observe any significant solvent isotope effect on the decomposition of **1** ( $\phi_{\text{H}_2\text{O}}/\phi_{\text{D}_2\text{O}} = 0.98 \pm 2\%$ , from UV spectroscopy) and the formation of **2** ( $\phi_{\text{PhCHO}}/\phi_{\text{PhCDO}} = 1.08 \pm 2\%$ , from NMR analysis) in CH<sub>3</sub>CN-H<sub>2</sub>O or CH<sub>3</sub>CN-D<sub>2</sub>O (3:1).

A very similar dependence of  $\phi$  on water content has been observed for the photodeuteration of **2** by steady state irradiation [29] and laser flash photolysis [38]. The structure of acetonitrile-water mixtures [39], the breakage and formation of intramolecular and intermolecular hydrogen bonds [33, 34], the dependence of solvation and dissociation of **1** in the ground and excited state on solvent composition, and the action of water on the primary photolysis products of **1** may contribute to these effects.

Addition of NaOH to 1 in acetonitrile–water or pure water reduces  $\phi$  (Fig. 2, Table 5) but 2 is still formed. Similar results have been reported for 1 [19] and before that for pyruvic acid [8]. This means that the anion of 1 is unsuitable for photodecarboxylation, as is undissociated 1 in anhydrous benzene or acetonitrile. However,  $\phi$  can be enhanced by addition of mineral acid (Fig. 2, Table 5), *i.e.*  $\phi$  increases with decreasing pH and decreasing degree of dissociation of 1. The pronounced enhancing effect of acetonitrile is retained. As estimated from the pK value (1.39 [40]) 1 is about 60% dissociated at pH 1.9 and only 8% dissociated at pH 0.3. Figure 4 shows that the pH of maximum increase in  $\phi$  corresponds to the pK value of 1. In the presence of acetonitrile, which is a very weak base [41], this point is shifted to a higher pH value.

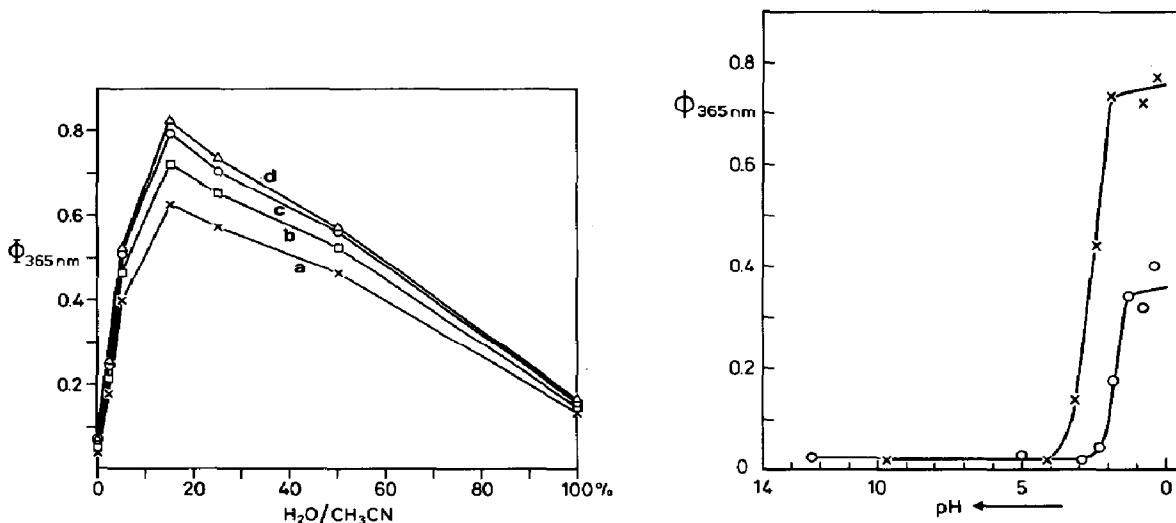


Fig. 3. Effect of water content in solvent acetonitrile on quantum yields of decomposition (not corrected for content of 2) of 1 (0.025 M) at 365 nm as measured at different wavelengths of observation: curve a, 350 nm; curve b, 360 nm; curve c, 370 nm; curve d, 380 nm.

Fig. 4. Dependence of quantum yields of decomposition of 1 (0.025 M) at 365 nm on the pH (observation wavelength, 380 nm):  $\times \times \times$ , in  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  (3:1);  $\circ \circ \circ$ , in  $\text{H}_2\text{O}$ .

### 3.3. Photopinacolization

The photopinacolization of 1 in 2-propanol is a clean and efficient reaction, as is the photodecarboxylation of 1 in water. The mechanism of formation of 3 by dimerization of two ketyl radicals of 1 [22, 23] suggested that the reaction should proceed with a high quantum yield and could also be useful as a chemical actinometer. However, UV spectrometry gave quantum yields of decomposition of 1 that were virtually irreproducible, the values being scattered between about 1.5 and 2.5. Toluene also proved to be impracticable as a solvent. In our irradiation experiments with 1 (0.5 M) in 2-propanol we found that not only the D,L isomer of 3 [20, 21] but also

the meso form is produced, in about equal amounts (total yield 67%; analysis as the methyl esters).

### 3.4. Photo-CIDNP experiments

No CIDNP signals were detected when **1** was irradiated in dry CD<sub>3</sub>CN, whereas, in the presence of 2.5 vol.% water, polarized signals of **2** and benzoin (**4**) were observed (Fig. 5 and Table 6). The pattern is reminiscent of the CIDNP effects reported for **2** in C<sub>6</sub>D<sub>6</sub> [42, 43] and in water [29]. Figure 6 shows the low field region of the <sup>1</sup>H NMR spectra of a solution of **1** in CD<sub>3</sub>CN–2-propanol (97.5:2.5) before, during and after irradiation. The strong emission signals at  $\delta = 5.1$  and  $\delta = 7.4$  in Fig. 6(b) are assigned to mandelic acid (**5**) which is a minor side product. Besides **5**, the main photoproducts acetone and the 2,3-diphenyltartaric acids (**3a** and **3b**) as well as the proton donor 2-propanol give rise to polarized proton signals (*cf.* Table 6). Upon addition of water to the CD<sub>3</sub>CN–2-propanol mixture the photo-CIDNP spectra look like a superposition of Figs. 5(b) and 6(b) owing to the competition between photoreduction and photodecarboxylation.

TABLE 6

<sup>1</sup>H NMR spectral assignments and polarization phases for photo-CIDNP experiments with **1**

Spectral assignment	$\delta_{\text{TMS}}$	Polarization phase	
		Observed	Predicted <sup>a</sup>
<i>In acetonitrile–water (97.5:2.5)</i>			
PhCHO ( <b>2</b> )	10.0	A	A(10)
PhCH(OH)COPh ( <b>4</b> )	6.1	E	E(8)
<u>Ph</u> CH(OH)COPh ( <b>4</b> )	7.2	A	—
b	7.3	E	—
b	7.6	E	—
b	7.8	A	—
<i>In acetonitrile–2-propanol (95:5)</i>			
<u>CH</u> <sub>3</sub> CH(OH) <u>CH</u> <sub>3</sub>	1.1	E	E(13)
CH <sub>3</sub> <u>CH</u> (OH)CH <sub>3</sub>	3.8	A	A(13)
PhCH(OH)COOH ( <b>5</b> )	5.1	E	E(14)
<u>Ph</u> CH(OH)COOH ( <b>5</b> )	7.4	E	—
(PhC(OH)(COOH)) <sub>2</sub> ( <b>3a</b> and <b>3b</b> )	7.2 - 7.5	A and E	—
( <u>Ph</u> C(OH)(COOH)) <sub>2</sub> ( <b>3b</b> )	7.1	E	—
<u>CH</u> <sub>3</sub> CO <u>CH</u> <sub>3</sub>	2.1	A	E(14) A(17)

<sup>a</sup>Net polarization phases were predicted by Kaptein's rules from the reaction steps (in parentheses) in Figs. 7 and 8 as indicated in the table; *g* values and signs of hyperfine constants were taken from Table 7. In general, predictions of aromatic proton polarization phases are not possible because of difficulties with the spectral assignments and a lack of information on signs of hyperfine constants.

<sup>b</sup>Spectral assignment not possible because of the overlap of aromatic resonances of **1**, **2** and **4**.

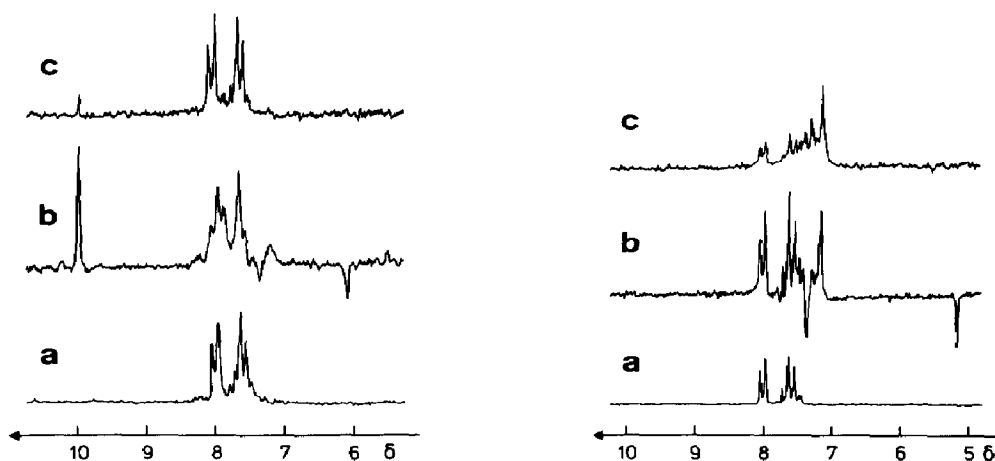


Fig. 5.  $^1\text{H}$  NMR spectra of **1** (0.1 M) in  $\text{CD}_3\text{CN}-\text{H}_2\text{O}$  (97.5:2.5): spectrum a, before irradiation; spectrum b, photo-CIDNP spectrum; spectrum c, after 30 s irradiation. (Figure 5 is to the left.)

Fig. 6.  $^1\text{H}$  NMR spectra of **1** (0.1 M) in  $\text{CD}_3\text{CN}-2\text{-propanol}$  (95:5): spectrum a, before irradiation; spectrum b, photo-CIDNP spectrum; spectrum c, after 30 s irradiation. (Figure 6 is to the right.)

#### 4. Discussion

Photodecarboxylation of **1** takes place in the presence of water at acidic pH values only and yields **2** almost exclusively. The reacting species appears to be undissociated **1** solvated by water. The main mechanistic issues are the estimation of the contribution of radical intermediates to the overall reaction and the explanation of the specific effect of water. It is obvious that the reaction mechanism of photodecarboxylation of **1** is quite different from that of pyruvic acid which may serve as the prototype for photodecarboxylation of an  $\alpha$ -keto acid via radical mechanisms [44]. The reaction is initiated by the cleavage of the carbonyl-carboxy bond, followed by rapid reduction of ground state pyruvic acid by the carboxyl radicals. The main photo-product giving rise to CIDNP signals is 2-hydroxy-2-methylacetoacetic acid ( $\text{CH}_3\text{COC}(\text{CH}_3)(\text{OH})(\text{COOH})$ ) which after being formed is immediately hydrolysed to give acetoin. Polarized signals of acetaldehyde were detected only when acetaldehyde was added to the solutions [44].

In contrast to pyruvic acid, the main product during the photodecarboxylation of **1** is **2**. The polarizations of the aldehyde peak ( $\delta = 10.0$ ) and of **4** ( $\delta = 6.1$ ,  $\delta = 7.1$  and  $\delta = 7.3$ ) are of the same order of magnitude (Fig. 5(b)). We know, however, that the stationary concentration of photochemically formed **2** is higher than that of **4** by more than two orders of magnitude. Therefore, it is obvious that the main pathway to **2** does not give rise to polarization of the aldehyde peak and that side reactions only are responsible for the CIDNP effects. The possibility that **4** is formed photochemically from **2** is very unlikely since **2** absorbs much less light than **1** above 300 nm (Fig. 1), its concentration being small, and since its triplet state is about  $42 \text{ kJ mol}^{-1}$  higher in energy than that of **1** [8, 10, 24]. The experimental

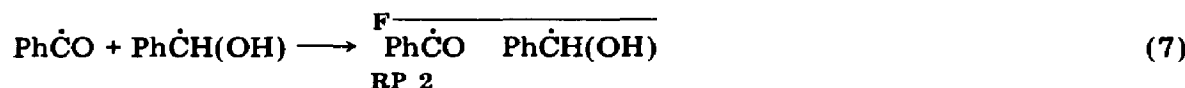


Fig. 7. Reactions in the presence of water.

observations are summarized in Fig. 7. According to this scheme the main route for formation of **2** could be either the concerted decarboxylation step (2) or the disproportionation of the radical pair **1** (RP 1) in step (4). Owing to the fact that the difference in *g* values of the radicals of RP 1 is very small (Table 7), the net polarization of photoproduct **2** obtained in step (4) should be close to zero; a similar situation has been described by Closs and Miller [44] for the formation of acetaldehyde from a triplet radical pair consisting of an acetyl and a carboxyl radical.

Thus, the reason for the difference between the decarboxylations of **1** and pyruvic acid [44] can be seen to be due to the fact that **2** is formed from **1** either via reaction (2) and/or (3)/(4) while the main photoproducts of pyruvic acid in the absence of hydrogen donors are formed by reactions of radicals escaping from the first radical pair. So far it has not been possible to decide whether step (2) or step (3)/(4) is the main reaction path.

The radical reactions (5) - (10) are side reactions. We assume that the ketyl radical  $\text{Ph}\dot{\text{C}}\text{H}(\text{OH})$  is formed by reduction of **2** according to reaction (6). A similar process has been proposed for the formation of the ketyl radical  $\text{CH}_3\dot{\text{C}}(\text{OH})(\text{COOH})$  by reduction of pyruvic acid [44] and, in principle, could also be expected to afford  $\text{Ph}\dot{\text{C}}(\text{OH})(\text{COOH})$  from **1**. However,

TABLE 7

Magnetic properties of the free radical intermediates involved in photodecarboxylation and photoreduction of 1

Radical	<i>g</i>	Reference	Sign $a_{\text{H}}^a$
Ph $\dot{\text{C}}\text{O}$	2.0006	[46]	
Ph $\dot{\text{C}}\text{H}(\text{OH})$	2.0032	[47]	$\text{H}_{\alpha} < 0$ $\text{H}_{\text{OH}} > 0$
$\dot{\text{C}}\text{OOH}$	2.0002	[44]	$< 0$
Ph $\dot{\text{C}}(\text{OH})\text{COOH}$	<sup>b</sup>		$\text{H}_{\text{OH}} > 0$
CH <sub>3</sub> $\dot{\text{C}}(\text{OH})\text{CH}_3$	2.0032	[48]	$\text{H}_{\text{CH}_3} > 0$ $\text{H}_{\text{OH}} > 0$

<sup>a</sup>For simple  $\sigma$  radicals it is reasonable to assume negative signs of the hyperfine constant for  $\text{H}_{\alpha}$  and positive ones for  $\text{H}_{\beta}$ .

<sup>b</sup>For the predictions of polarization phases we assumed  $g\{\text{Ph}\dot{\text{C}}(\text{OH})(\text{COOH})\} > g\{\text{CH}_3\dot{\text{C}}(\text{OH})(\text{COOH})\}$ . The value for  $g\{\text{CH}_3\dot{\text{C}}(\text{OH})(\text{COOH})\}$  is 2.0037 [49].

neither polarized nor stationary products due to the presence of this radical could be detected. 4 is thought to be produced from an F pair formed by random encounter of a free ketyl radical (Ph $\dot{\text{C}}\text{H}(\text{OH})$ ) and a free benzoyl radical (Ph $\dot{\text{C}}\text{O}$ ). The enhanced absorption of the benzaldehyde peak ( $\delta = 10.0$ ) can be predicted from the hydrogen transfer between an escaping Ph $\dot{\text{C}}\text{H}(\text{OH})$  radical and 2 in step (10) [42, 43].

The existence of a photodecarboxylation pathway not involving long-lived radicals is indicated by the insensitivity of the reaction to oxygen and by laser flash spectroscopy experiments [25]. Sensitization experiments with 9,10-dicyanoanthracene gave no indication that an electron transfer mechanism might be operative as has been advanced for the photolysis of pyruvic acid [45]. Water could influence a concerted decarboxylation reaction (step (2)) by breaking intramolecular hydrogen bonds of 1 [30]. However, it is difficult to account for the fact that radical steps (3) - (10) are possible in the presence of water only.

While there are substantial differences between the photodecarboxylation of 1 and of pyruvic acid, this is not the case for the photoreduction of the two  $\alpha$ -keto acids by 2-propanol. Irradiation of 1 as well as of pyruvic acid [44] leads to a primary radical pair formed by transfer of a hydrogen atom from 2-propanol to the excited triplet state of the acid. The escaping ketyl radical is involved in various combination reactions according to Fig. 8, which accounts for the polarization phases given in Table 6.

Reactions (16) and (17) lead to the observed quantum yield of about 2 for the disappearance of 1 owing to dimerization of the ketyl radical. The formation of diphenyltartaric acids according to Fig. 8 should be much more sensitive to impurities and oxygen than the photodecarboxylation (Fig. 7) which is in accordance with the observation of badly reproducible quantum yields in 2-propanol or toluene solution.



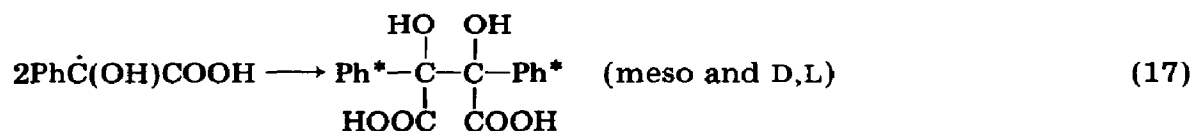
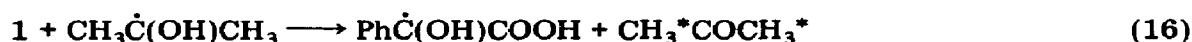
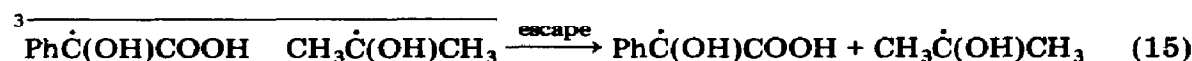
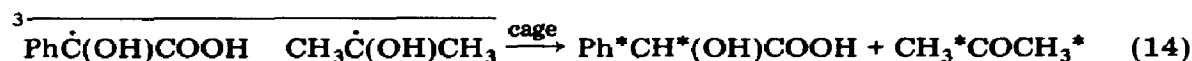
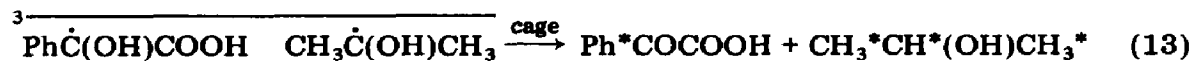


Fig. 8. Reactions in the presence of 2-propanol.

## 5. Conclusions

1 in aqueous acidic solution meets most of the demands made on a convenient chemical liquid phase actinometer. It is cheap, readily accessible in pure crystalline form, insensitive to oxygen, stable in solution even at elevated temperatures and decarboxylates readily upon irradiation by UV light (250 - 400 nm) with a high quantum yield in an irreversible reaction which is linear up to high conversions and can be easily monitored. Of the five analytical methods discussed above, direct UV spectrometry of the disappearance of 1 around 360 nm is shown to be the most precise and is recommended. Analysis by titration, GC or HPLC may be advantageous when rather concentrated actinometer solutions have to be used. The crucial role of water in the mechanism of photodecarboxylation of 1 must be studied further.

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