PHOTOLYSIS OF METHYL 2-CHLORO-3-OXOBUTANOATE

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(Received September 11, 1986; in revised form November 25, 1986)

Summary

Irradiation of methyl 2-chloro-3-oxobutanoate (I) in 50% ethanol yielded methyl 3-oxobutanoate, 2-methyl-2-pentanol-4-one, 2,5-dioxo-hexane-3,4-dicarboxylic acid dimethyl ester, 4-hydroxy-4,5-dimethyltetra-hydrofuran-2-one, 2,4-dimethylfuran-3,5-dicarboxylic acid dimethyl ester, 2,4-dimethyl-3-acetyl-2,3-dihydrofuran-3,5-dicarboxylic acid dimethyl ester and 1,4-dimethyl-6-acetyl-3,5,6-trimethoxycarbonyl-2-oxabicyclo[3.1.0]hex-3-ene.

The photolysis of I involves homolytic cleavage of the C—Cl bond, α-cleavage and α-elimination of hydrogen chloride, the last step resulting in the intermediate formation of carbomethoxyacylcarbene.

A possible route for the formation of the reaction products is discussed.

1. Introduction

In an earlier communication [1] it was shown that the photolysis of ethyl 3-oxobutanoate in a polar solvent involves homolytic cleavage of the C_1—C_2 and C_2—C_3 bonds of the excited β-ketoester. In this paper we report the results of the photolysis of methyl 2-chloro-3-oxobutanoate (I). In view of the small bond dissociation energy of the C—Cl bond we can presume that in the case considered here the main primary photolysis step will be the cleavage of this bond. Although a relatively large number of studies are devoted to the photochemistry of α-halogenated carboxylic acids and their derivatives and of α-halogenated ketones, the photochemical behaviour of α-halogenated derivatives of β-keto acids is still unknown.

2. Experimental details

2.1. Apparatus and materials

[1]H nuclear magnetic resonance (NMR) spectra were obtained in deuterochloroform on a Brucker-250 apparatus. Chemical shifts (δ) are in parts per million relative to tetramethylsilane. Coupling constants (J values) are in hertz. Multiplicities are designated as singlet (s), doublet (d), triplet (t),

quartet (q) or multiplet (m). ^{13}C spectra were determined on a Brucker-60.3 apparatus. Mass spectra were obtained on a Jeol instrument (70 eV) and the chemical ionization was carried out with isobutane. IR spectra were obtained using a UR-20 spectrophotometer.

Melting points were determined with a Buchi-510 immersion melting point apparatus and are uncorrected. Analytical thin-layer chromatography (TLC) was performed on precoated silica-gel plates (Silicagel 60) containing a fluorescent indicator and supplied by Merck. Visualization was effected with UV light (254 nm). Preparative thin-layer chromatography (PTLC) was performed on precoated silica-gel plates. All solvents used were reagent grade.

2.2. Photolysis

A solution of I (3.5 g, 0.023 mol) in 50% ethanol (100 cm³) was irradiated with a 400 W mercury arc (medium pressure) lamp. The reaction was monitored by TLC. Irradiation was continued until almost all the starting ester was consumed (about 7 h). The reaction mixture was poured into water, neutralized with $NaHCO_3$ and extracted with ether. The ether solution was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to give an oil (2.15 g). This was chromatographed over silica gel (200 g) (Merck) with *n*-hexane—ether (4:1) as eluant.

3. Analytical results

3.1. Methyl-3-oxobutanoate (II)

Yield, 0.42 g. IR (neat): 3480, 3300, 1735 cm^{-1}. High resolution mass spectrometry—chemical ionization (HRMS–CI): $m/e = 117$ (M$^+$ + 1); calculated for $C_5H_8O_3$, 116. The product was identical with an authentic sample.

3.2. 2-Methyl-2-pentanol-4-one (III)

Yield, 0.182 g. IR (neat): 3470, 3290, 1730 cm^{-1}. HRMS–CI: $m/e = 117$ (M$^+$ + 1); calculated for $C_6H_{12}O_2$, 116. ^1H NMR: 1.28 (s, 6H), 2.21 (s, 3H), 2.66 (s, 2H), 3.94 (s, 1H).

3.3. 2,5-Dioxohexane-3,4-dicarboxylic acid dimethyl ester (IV)

Yield, 0.021 g. Colourless solid of melting point 137 - 138 °C. IR (KBr): 2980, 2930, 1740, 1710, 1290, 1250 cm^{-1}. HRMS–CI: $m/e = 231$ (M$^+$ + 1); calculated for $C_{10}H_{14}O_6$, 230. ^1H NMR: 2.43 (s, 6H), 3.72 (s, 6H), 4.51 (s, 2H).

3.4. 4-Hydroxy-4,5-dimethyltetrahydrofuran-2-one (V)

Yield, 0.32 g of a mixture (50:50) of two diastereoisomers. IR (neat): 3400, 1760 cm^{-1}. HRMS–CI: $m/e = 131$ (M$^+$ + 1); calculated for $C_6H_{10}O_3$, 130. ^1H NMR: 1.30, 1.38 (d, $J = 6.6$, 3H), 1.37, 1.40 (s, 3H), 2.61, 2.63 (broad, 2H), 4.37, 4.49 (q, $J = 6.6$, 1H).

3.5. 4-Acetoxy-4,5-dimethyltetrahydrofuran-2-one (VI)

Compound V (40 mg) was dissolved in acetic anhydride (0.5 cm^3). A catalytic amount of ZnCl$_2$ was added. The mixture was allowed to stand for about 30 min. The crude product (60 mg) was purified by PTLC to give VI as a mixture (50:50) of diastereoisomers VIa and VIb.

3.5.1. VIa

Yield, 20 mg. IR (neat): 1780, 1730 cm^{-1}. ^{1}H NMR: 1.37 (d, J = 6.6, 3H), 1.57 (s, 3H), 2.05 (s, 3H), 2.82 (d, J = 18, 1H), 2.91 (d, J = 18, 1H), 4.79 (q, J = 6.6, 1H).

3.5.2. VIb

Yield, 20 mg. IR (neat): 1780, 1730 cm^{-1}. ^{1}H NMR: 1.40 (d, J = 6.6, 3H), 1.60 (s, 3H), 2.05 (s, 3H), 2.70 (d, J = 18, 1H), 2.90 (d, J = 18, 1H), 4.83 (q, J = 6.6, 1H).

3.6. 2,4-Dimethylfuran-3,5-dicarboxylic acid dimethyl ester (VII)

Yield, 0.05 g of a colourless solid of melting point 81 - 82 °C. IR (KBr): 1720, 1680, 1650, 1580, 1550, 1476, 1450, 1242 cm^{-1}. HRMS–CI: m/e = 213 (M$^+$ + 1); calculated for C$_{10}$H$_{12}$O$_5$, 212. ^{1}H NMR: 2.56 (s, 3H), 2.62 (s, 3H), 3.68 (s, 3H), 3.96 (s, 3H). UV (ethanol): λ^{max} = 256 nm.

3.7. 2,4-Dimethyl-3-acetyl-2,3-dihydrofuran-3,5-dicarboxylic acid dimethyl ester (VIII)

Yield, 0.65 g of a mixture (50:50) of the diastereoisomers VIIIa and VIIIb. The diastereoisomers were separated and purified by PTLC.

3.7.1. VIIIa

Colourless solid of melting point 56 - 57 °C. IR (KBr): 1750, 1730, 1700, 1660, 1440, 1370 cm^{-1}. UV (ethanol): λ^{max} = 248 nm. ^{1}H NMR: 1.11 (d, J = 6.9, 3H), 2.31 (s, 3H), 3.73 (s, 3H), 3.80 (s, 3H), 3.96 (q, J = 3.9, 1H). ^{13}C NMR: 12.43, 15.23, 28.08, 43.23, 51.05, 53.46, 65.83, 96.04, 165.09, 169.45, 202.17. High resolution mass spectrometry–electron impact (HRMS–EI): m/e, 257 (M$^+$ + 1), 239, 225, 213, 197, 183, 169, 155; calculated for C$_{12}$H$_{16}$O$_6$, 256. Found: C, 53.90%; H, 6.24%. Calculated for C$_{12}$H$_{16}$O$_6$: C, 53.30%; H, 6.24%.

3.7.2. VIIIb

Colourless oil. IR (neat): 1753, 1730, 1700, 1660, 1450, 1380 cm^{-1}. UV (ethanol): λ^{max} = 251 nm. ^{1}H NMR: 1.14 (d, J = 6.9, 3H), 2.25 (s, 3H), 2.30 (s, 3H), 3.71 (s, 3H), 3.83 (s, 3H), 3.96 (q, J = 6.9, 1H). ^{13}C NMR: 12.50, 15.20, 28.00, 41.18, 51.10, 52.80, 65.80, 108.25, 166.85, 169.00, 202.00. HRMS–EI: m/e, 257 (M$^+$ + 1), 239, 225, 213, 197, 143; calculated for C$_{12}$H$_{16}$O$_6$, 256. Found: C, 53.36%; H, 6.30%. Calculated for C$_{12}$H$_{16}$O$_6$: C, 53.30%; H, 6.25%.

3.8. 2,4-Dimethyl-3(α-hydroxyethyl)-2,3-dihydrofuran-3,5-dicarboxylic acid dimethyl ester (IX)

Compound VIIIa (30 mg) was dissolved in methanol (0.5 ml) and NaBH$_4$ (0.003 mg) was added. The mixture was allowed to stand for about 10 min. The crude product was purified by PTLC to afford IXa (28 mg). The same procedure was applied to VIIIb.

3.8.1. IXa

IR (neat): 3500, 1740, 1728, 1654 cm^{-1}. ^{1}H NMR: 1.13 (d, J = 6.8, 3H), 1.22 (d, J = 6.9, 3H), 2.27 (s, 3H), 2.45 (1H, disappears with D$_2$O), 3.36 (q, J = 6.8, 1H), 3.71 (s, 3H), 3.83 (s, 3H), 3.91 (q, J = 6.9, 1H). HRMS–CI: m/e = 259 (M$^+$ + 1); calculated for C$_{12}$H$_{18}$O$_6$, 258.

3.8.2. IXb

IR (neat): 3500, 1735, 1728, 1660 cm^{-1}. ^{1}H NMR: 1.27 (d, J = 6.8, 3H), 1.32 (d, J = 6.9, 3H), 2.25 (s, 3H), 2.83 (d, J = 10.8, 1H, disappears with D$_2$O), 3.38 (m, 1H), 3.71 (s, 3H), 4.11 (q, 1H). HRMS–CI: m/e = 259 (M$^+$ + 1); calculated for C$_{12}$H$_{18}$O$_6$, 258.

3.9. 1,4-Dimethyl-6-acetyl-3,5,6-trimethoxycarbonyl-2-oxabicyclo[3.1.0]-hex-3-ene (X)

Yield, 0.021 g of a colourless solid of melting point 120 - 121 °C. IR (KBr): 1750, 1730, 1700, 1640, 1435, 1377, 1355, 1326 cm^{-1}. ^{1}H NMR: 1.69 (s, 3H), 2.32 (s, 3H), 2.34 (s, 3H), 3.70 (s, 3H), 3.72 (s, 3H), 3.81 (s, 3H). HRMS–CI: m/e = 327 (M$^+$ + 1), 295, 285, 267; calculated for C$_{15}$H$_{18}$O$_6$, 326.

Since the photolysis of I causes liberation of hydrogen chloride the reaction mixture became acidic. Therefore it was essential to carry out control experiments in order to check the possibility of secondary dark reactions. However, it was proved that the types of reaction products do not depend on the acidity of the reaction mixture or on the presence of atmospheric oxygen. Efforts to discriminate the diastereoisomers eventually formed from compounds IV and X failed because these compounds were present in trace amounts in the reaction mixture. The quantum efficiency of the disappearance of the starting ester I was found to be 0.45.

4. Results and discussion

Irradiation of I in 50% ethanol led to the formation of the products II - V, VII, VIII and X. The photolysis of I proceeded with an intensive liberation of hydrogen chloride.

A considerable amount of work has been done on the photochemical behaviour of halogen-containing esters. Matuszewski and coworkers [2 - 5] have shown that the homolytic cleavage of a C—X bond is the main primary photolysis step. The reaction, followed by hydrogen abstraction from the

Me—CO—CH—COOMe   Me—CO—CH$_2$—COOMe   Me—C(OH)—CH$_2$—CO—Me
      |
     Cl   Me

I   **II**   **III**

Me—CO—CH—COOMe
Me—CO—CH—COOMe

IV

Me—C(OH)——CH$_2$
Me—CH—O—C=O

V

Me—C═══C—COOMe
MeOOC—C—O—C—Me

VII

Me—C═══C(COOMe)(COMe)
MeOOC—C—O—CH—Me

VIII

Me—C═══C—C(COOMe)(COMe)(Me)
MeOOC—C—O—C—COOMe

X
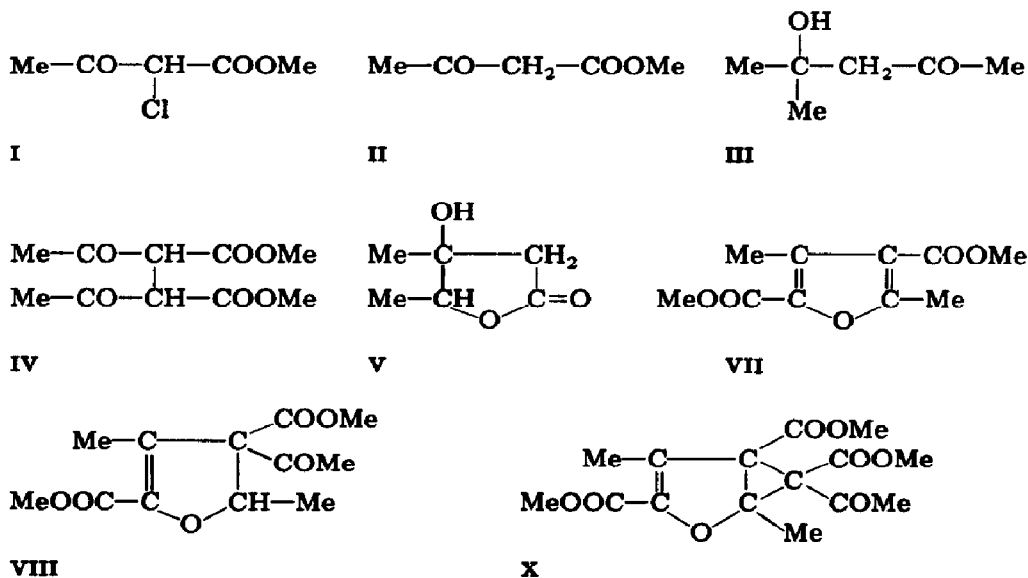
solvent molecule, gives the basic photolysis products. The formation of the corresponding dimers is related to the intermediate appearance of radical-type particles. According to Purohit and Sonawane [6], the photochemistry of the carbon—halogen bond is very much affected by the α-keto group which favours the expulsion of a halogen atom rather than that of a halide anion, making radical behaviour the predominant process.

At present not enough is known concerning the nature of the photochemical processes leading to the formation of products II - V, VII, VIII and X to permit a definite mechanistic proposal. There is no apparent way, as yet, of distinguishing between the radical mechanism outlined in ref. 3 and the transformations eventually arising as a result of the heterolytic cleavage of the C—X bond. However, it seems that in the case considered here, there is a great deal of indirect evidence for the following primary photolysis steps:

$$I \xrightarrow{h\nu} I^*$$

$$I^* \xrightarrow[k_d]{} I$$
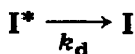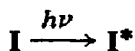
On absorption of 260 nm light, the molecules of I are promoted to an excited state having an energy content in excess of that required to effect homolytic cleavage of almost all the bonds in the ester molecule. The intermediate formation of radical-type particles owing to homolytic cleavage of the C—Cl bond in some halogenated esters has recently been reported by Garcia *et al.* [7]. Presumably II arises via hydrogen abstraction of the radical A from the solvent molecule. Such a process can compete with the intramolecular transformations [8]. Another possible reaction pathway leading to methyl acetoacetate is the interaction of methoxycarbonylacetylcarbene (B)

$$\text{I}^* \longrightarrow
\begin{array}{l}
\xrightarrow[\;k'_{\mathrm{r}}\;]{\text{homolysis of C—Cl bond}} \quad \overset{\overset{\displaystyle O}{\parallel}}{\text{Me—C}}\text{—}\overset{\displaystyle\cdot}{\text{C}}\text{H—COOMe + Cl}^{\bullet} \\[4pt]
\qquad\qquad\qquad\qquad\qquad\qquad \text{A} \\[8pt]
\xrightarrow[\;k''_{\mathrm{r}}\;]{\alpha\text{-elimination of HCl}} \quad \text{Me—CO—}\overset{\displaystyle\cdot\cdot}{\text{C}}\text{—COOMe + HCl} \\[4pt]
\qquad\qquad\qquad\qquad\qquad\qquad \text{B} \\[8pt]
\xrightarrow[\;k'''_{\mathrm{r}}\;]{\alpha\text{-cleavage}} \quad \text{MeCO}^{\bullet} + \overset{\displaystyle\cdot}{\text{C}}\text{H(Cl)COOMe}
\end{array}$$
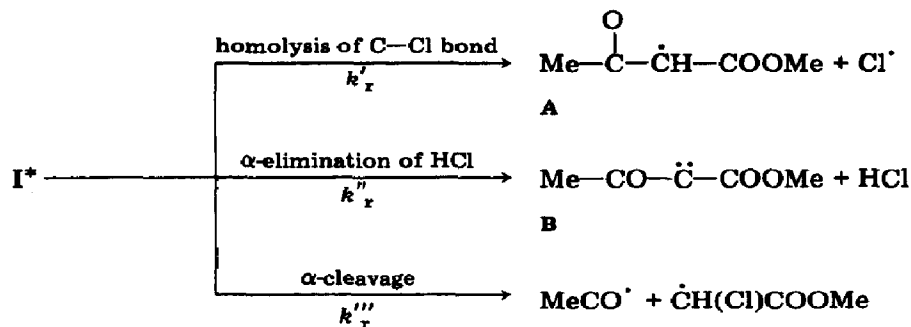
Scheme 1.

with the reaction medium. As shown by Weygand et al. [9], irradiation of trifluoroacetyldiazoacetic ester in alcohols produces ethyl trifluoroacetate with simultaneous dehydrogenation of the alcohol. The production of IV is especially interesting. This product may be formed according to the solvent-cage recombination mechanism [10]. Reactions of radical pairs in a solvent cage should be very fast, for example, the reaction

$$2\text{Me—CO—}\overset{\displaystyle\cdot}{\text{C}}\text{H—COOMe} \longrightarrow \text{IV}$$
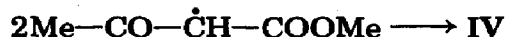
The formation of substituted furans from various acetylenes and carbethoxycarbene was first reported by Diakonov and Komendatov [11] and has been studied also by Breslow and Chipmen [12]. Furans appear when triplet bis(carbomethoxy)carbene is generated and added to alkyl acetylenes [13]. From this point of view the formation of VII can be regarded as a dipolar 1,3-addition of carbomethoxyacetylcarbene (B) to the ethylenic double bond of th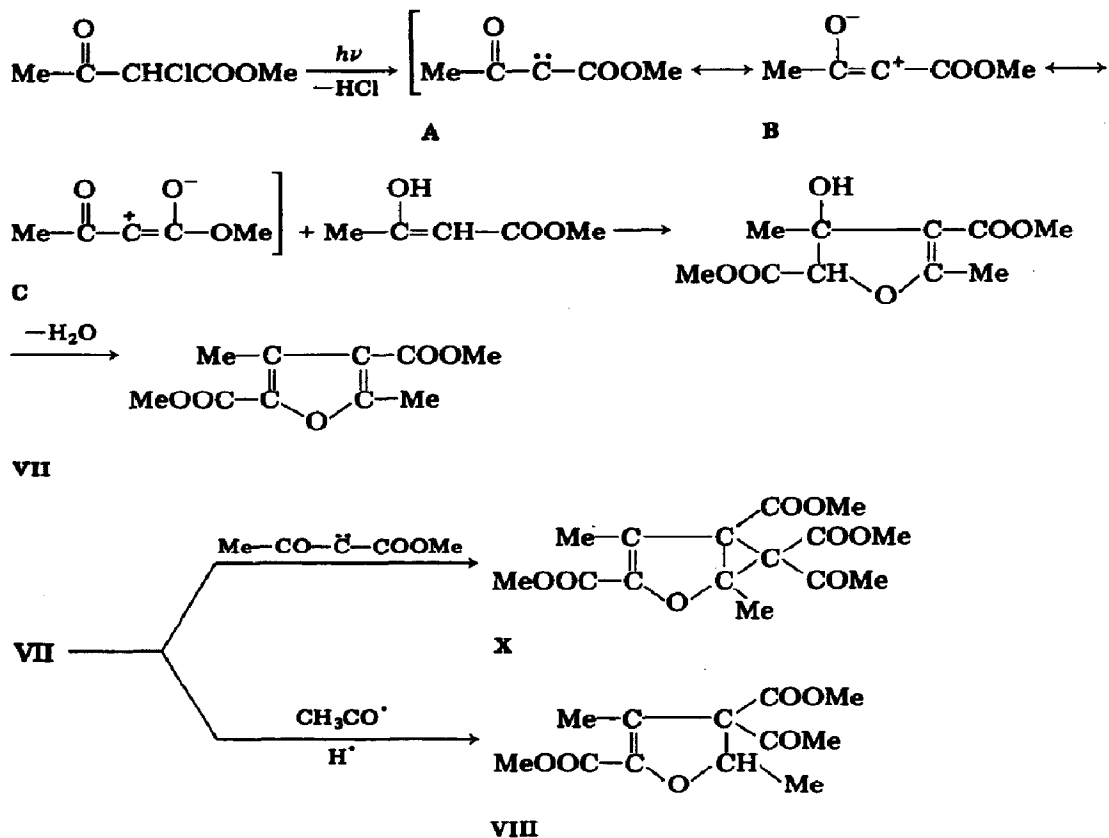e enol form of II. The detection of compound X supports the intermediacy of B. As shown by Schenck and Steinmetz [14], the irradiation of the methyl ester of diazoacetic acid in furan leads to 6-methoxycarbonyl-2-oxabicyclo[3.1.0]hex-3-ene. It also seems that the formation of compound VIII is a result of the addition of an acyl radical, arising from an α-cleavage of I, to the ethylenic double bond of VII and subsequent hydrogen abstraction from the solvent. It is noteworthy that VIII is formed as a mixture (50:50) of two diastereoisomers VIIIa and VIIIb. Their reduction with $NaBH_4$ gave the respective diastereoisomers IXa and IXb.

Two basic questions can be answered if Scheme 2 is operative. The first is the question of the origin of methoxycarbonylacetylcarbene. Little seems to have been done on the preparation of these kinds of particles. Methoxycarbonyltrifluoroacetylcarbene was first detected by Weygand et al. [9, 15] as a result of the photodecomposition of trifluoroacetyldiazoacetic ester. More recently, Dworschak and Weygand [16] have trapped methoxycarbonyltrifluoroacetylcarbene as a 1,3-dipole. As previously mentioned, in the case considered here, the methoxycarbonylacetylcarbene particles arise possibly owing to α-elimination of hydrogen chloride from I. The possibility of α-elimination occurring on irradiation of halogen-containing

$$\text{Me—C—CHClCOOMe} \xrightarrow[-\text{HCl}]{h\nu} \left[\text{Me—C—}\ddot{\text{C}}\text{—COOMe} \longleftrightarrow \text{Me—}\overset{O^-}{\text{C}}\text{=}\overset{+}{\text{C}}\text{—COOMe} \longleftrightarrow \right.$$

A   **B**

$$\left. \text{Me—}\overset{O}{\text{C}}\text{—}\overset{+}{\text{C}}\text{=}\overset{O^-}{\text{C}}\text{—OMe} \right] + \text{Me—}\overset{OH}{\text{C}}\text{=CH—COOMe} \longrightarrow$$

C

$$\begin{array}{c} \overset{OH}{\underset{|}{\text{Me—C}}}\text{———C—COOMe} \\ \text{MeOOC—CH}\diagdown\text{O}\diagup\text{C—Me} \end{array}$$

$$\xrightarrow{-\text{H}_2\text{O}} \quad \begin{array}{c} \text{Me—C———C—COOMe} \\ \text{MeOOC—C}\diagdown\text{O}\diagup\text{C—Me} \end{array}$$

VII

$$\text{VII} \Bigg\langle$$

$$\xrightarrow{\text{Me—CO—}\overset{\cdot\cdot}{\text{C}}\text{—COOMe}} \quad \begin{array}{c} \text{Me—C———C}\diagup\overset{\displaystyle\text{COOMe}}{\underset{\displaystyle\diagdown\text{COOMe}}{\text{C}}} \\ \text{MeOOC—C}\diagdown\text{O}\diagup\underset{\text{Me}}{\text{C}}\diagdown\text{COMe} \end{array}$$

X

$$\xrightarrow[\text{H}^\cdot]{\text{CH}_3\text{CO}^\cdot} \quad \begin{array}{c} \text{Me—C———C}\diagup\overset{\displaystyle\text{COOMe}}{\diagdown\text{COMe}} \\ \text{MeOOC—C}\diagdown\text{O}\diagup\text{CH}\diagdown\text{Me} \end{array}$$

VIII

Scheme 2.

organic compounds in polar solvents has been previously suggested but not established experimentally [17]. The photochemical α-elimination of hydrogen halides from α-halo esters is particularly interesting as a possible route to ketocarbalkoxycarbenes. This interest arises from the fact that attempts to achieve α-elimination of hydrogen halides from this type of compound by thermal processes resulted in condensation reactions of the intermediate carbanions rather than the elimination of halide ion.

However, special attention has to be given to the features of the addition of methoxycarbonylacetylcarbene to the enol form of II. In principle, the following mutual orientations of the interacting molecules have to be considered:

$$\overset{OH}{\underset{|}{\text{Me—C}}}\text{=CH—COOMe} \qquad \overset{OH}{\underset{|}{\text{Me—C}}}\text{=CH—COOMe} \qquad \overset{OH}{\underset{|}{\text{Me—C}}}\text{=CH—COOMe} \qquad \overset{OH}{\underset{|}{\text{Me—C}}}\text{=CH—COOMe}$$

$$\underset{\text{MeOOC Me}}{\overset{+}{\text{C}}\text{=C}\diagup\overset{O^-}{}} \qquad \underset{\text{OC OMe}}{\overset{+}{\text{C}}\text{=C}\diagup\overset{O^-}{}} \qquad \overset{-\text{O}}{\diagdown}\underset{\text{Me}}{\text{C}}\text{=}\overset{+}{\text{C}}\diagdown\text{COOMe} \qquad \overset{-\text{O}}{\diagdown}\underset{\text{MeO CO}}{\text{C}}\text{=}\overset{+}{\text{C}}$$

1   **2** Me   **3**   **4**   Me
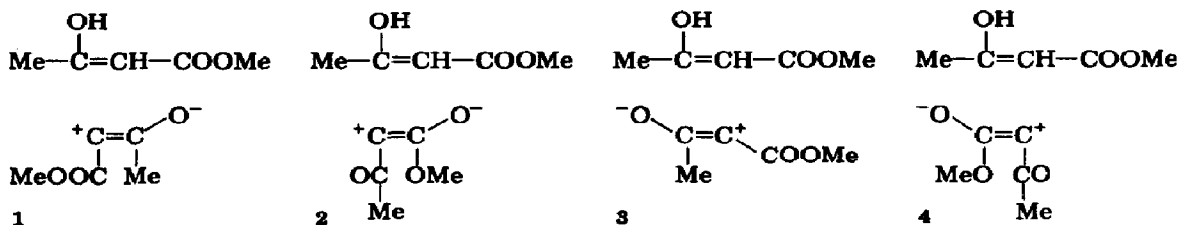
Since analysis of the reaction products shows only the formation of **VII** and its derivatives (compounds **VIII** and **X**), it may be concluded that the 1,3-dipolar addition of methoxycarbonylacylcarbene to the enol form of **II** may be explained in terms of a polar resonance structure **B** (Scheme 2).

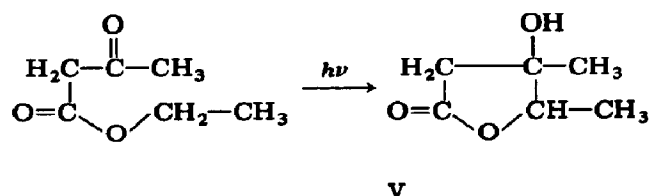The interaction shows strong discrimination, related to a specific mutual orientation of the reacting particles as presented by complex 1. Presumably the species add via a transition state with a substantial polarization of the olefin carbon atoms of **II**. As suggested by von Doering and Knox [18], the presence of the alkoxycarbonyl group in the carbene molecule decreases its reactivity because of resonance stabilization. The increase in the free energy of activation of the addition of the methoxycarbonylacetylcarbene to the C=C bond of the enol form of **II** permits the differences in the inherent reactivity of the substrate molecule to be observed. The steric effect should also be considered in order to correlate the observed discrimination with the possibility of relieving the conformational strain on forming the transition state. As is easily seen, the precursor state 3 leading to the formation of 2,5-dimethylfuran-3,4-dicarboxylic acid dimethyl ester is less probable than 1 because of the significant steric hindrance arising from the two closely positioned bulky methoxycarbonyl groups.

An alternative way of explaining the formation of **VII** is related to the possibility of a head-to-tail gemination of the radical **A** (scheme 1), followed by an $n \rightarrow \pi^*$ excitation of compound **XI** and γ-H abstraction:

$$
\underset{\underset{\text{COOMe}}{|}}{\overset{\overset{\text{O}}{\parallel}}{\text{Me}-\text{C}-\text{CH}^{\cdot}}} \;+\; {}^{\cdot}\text{O}-\overset{\overset{\text{CH}-\text{COOMe}}{\parallel}}{\text{C}}-\text{Me} \quad \xrightarrow{h\nu} \quad \underset{\underset{\text{COOMe}}{|}}{\overset{\overset{\text{O}}{\parallel}}{\text{Me}-\text{C}-\text{CH}-\text{O}}}-\overset{\overset{\text{HC}-\text{COOMe}}{\parallel}}{\text{C}}-\text{Me}
$$

$$\textbf{XI}$$

$$
\xrightarrow{h\nu} \left[\underset{\underset{\text{COOMe}}{|}}{\overset{\overset{\text{O}}{\parallel}}{\text{Me}-\text{C}-\text{CH}-\text{O}}}-\overset{\overset{\text{HC}-\text{COOMe}}{\parallel}}{\text{C}}-\text{Me} \right]^{n \rightarrow \pi^*} \xrightarrow{\gamma\text{-H abstraction}} \quad \underset{\text{MeOOC}-\overset{\diagdown\;\;/}{\underset{\text{O}}{}}\text{CH}}{\overset{\text{OH}}{\text{Me}-\text{C}}}\underset{}{\overset{\diagup}{}}\overset{}{\underset{\text{C}-\text{Me}}{\text{C}-\text{COOMe}}}
$$

$$\xrightarrow{-\text{H}_2\text{O}} \textbf{VII}$$
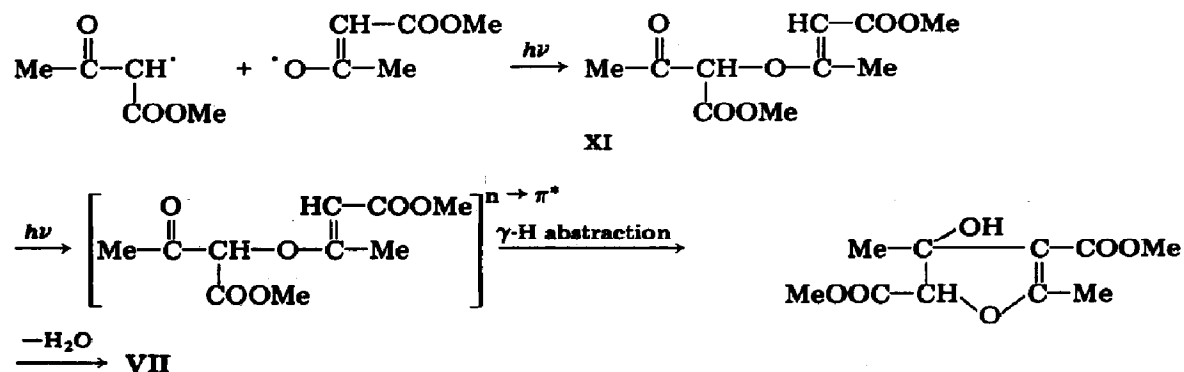
However, an attempt to prove the intermediate formation of **XI** was unsuccessful.

The compound **V** probably arises because of an ester exchange followed by intramolecular hydrogen abstraction and coupling:

$$
\underset{\text{O}=\underset{\diagdown\;\underset{\text{O}}{}\;\diagup}{\text{C}}\text{CH}_2-\text{CH}_3}{\overset{\overset{\text{O}}{\parallel}}{\text{H}_2\text{C}-\text{C}-\text{CH}_3}} \quad \xrightarrow{h\nu} \quad \underset{\text{O}=\underset{\diagdown\;\underset{\text{O}}{}\;\diagup}{\text{C}}\text{CH}-\text{CH}_3}{\overset{\overset{\text{OH}}{|}}{\text{H}_2\text{C}-\text{C}-\text{CH}_3}}
$$

$$\textbf{V}$$

It has been established by Coyle *et al.* [19] that such a process occurs during the photolysis of 4-methyl-4-methoxypentan-2-one. The reaction medium used (50% ethanol) and the liberation of hydrogen chloride during the photolysis provide the necessary conditions for an ester exchange of II to give ethyl-3-oxobutanoate.

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