Additions of 1,1-Diethoxyethene to 1,2-Diketones†

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The ketene acetal **2** undergoes thermally noncatalyzed additions to various 1,2-diketones under formation of [1:1]- and [1:2]-adducts. Only with biacetyl **1a** could an oxetane, **3**, be isolated whereas mainly substituted 6-oxo-2,4-hexadienoic acid ethyl esters **6** and **7** are formed with aromatic 1,2-diketones. The regioselectivities and the product ratios are discussed in terms of a mechanism via zwitterionic intermediates.

Thermal cycloadditions between ketene acetals and carbonyl compounds have been extensively studied by Scheeren and coworkers.[1] In most cases these reactions only proceed in the presence of $ZnCl_2$ as a catalyst unless the carbonyl compounds are activated by sufficiently electrophilic substituents. Recently we have shown that biacetyl **1a** and 1,1-diethoxyethene **2** form the oxetane **3** in a noncatalyzed reaction via a dipolar intermediate.[2] Our results contrast with those of Scheeren insofar as he believed that 1,1-dialkoxyethenes do not react with aldehydes and ketones.[3] In extension of those studies we have investigated the thermally noncatalyzed reactions of various, 1,2-diketones **1a–c** with **2**.

Results

For preparation of the products (see Scheme I) [1:1] mixtures of the corresponding 1,2-diketone **1** and the ketene acetal **2** were kept at room temperatures in the dark for 3 days.[4] All procedures were carried out in acid-free glass apparatuses in order to prevent both polymerization of **2**[5] and acid-catalyzed cleavage of the products—especially of **3**.[2] Only with biacetyl **1a** could an oxetane, **3**, be isolated by carefully performed distillation at low temperature. The other products were isolated by means of HPLC.

The yields and the product ratios are summarized in Table I and they leave the following conclusions: (a) the reactivity of the 1,2-diketones decreases from **1a** to **1c** (see conversion); (b) the formation of [1:2] adducts **6** and **7** is favored with increasing aromatic substitution of **1**; (c) most of the [1:2] adducts of **1b** result from addition of **2** onto the aromatic carbonyl group; (d) the formation of *E,E* isomers is favored in the [1:2]-adduct series. These effects are also reflected in the concentration dependences of the product ratios. Whereas benzil **1c** only yields [1:2] adducts independently of the ratios of the educts, both **1a** and **1b** preferentially give these types of products with increasing concentration of **2** (Table II). Moreover the strongest effect is observed with **1a**, which corresponds to the above cited statement (b).

The structures of the products are assigned primarily according to NMR measurements. In particular the following arguments lead to the structures of the isomers **6** and**7**: The *E,E* isomers **7** exhibit a ca. 10 ppm downfield shift of the C4 carbons in the ^{13}C NMR spectra compared to those values of the *E,Z* isomer **6** (δ 130.14–131.70 for **7** and δ 118.10–121.25 for **6** respectively, see Experimental Section). A similar but somewhat weaker effect is observed for C2. Moreover the EtO–C3 protons (vinyl ether group) of **6b** (δ 0.76 and 3.50), **6d** (δ 0.80 and 3.60), **7c** (δ 0.68 and 3.53), and **7d** (δ 0.78 and 3.60) are shifted upfield in the ^1H NMR spectra with regard to the normal values of δ ~1.3 and 3.9 (see Experimental Section). These striking effects can only be explained if there is a phenyl group close to this ethoxy group.

Table I. Chemical Yields and Ratios of the Products[a]

1,2-diketone	yield, %[b]	product ratio[c]
1a	70	**3**[d]:**4a**:**5a**:**6a**:**7a** = 0.85:0.20:0.08:1:0.38
1b	65	**4b**:**4c**:**6b**:**7b**:**6c**:**7c** = 0.05:0.28:0.24:0.12:1:0.41
1c	79	**6d**:**7d** = 1:0.90

[a] Whereas the formation of unidentified side products is low in reactions with **1b** and **1c** (ca. 10%), **1a** gives at least three unidentified products in ca. 25% yield. [b] Referring to conversion of the 1,2-diketones (**1a** 66%, **1b** 38%, **1c** 30% conversion after 3 days at room temperature; see experimental section). [c] Ratios correspond to the sum of identified products = 100% and were determined by HPLC in combination with NMR. [d] Before the chromatographic separation **3** was distilled from the reaction mixture.

Table II. Dependence of the Ratio of [1:2] and [1:1] Addition on the Educt Concentration[a]

1,2-diketone	1/2	[1:2]/[1:1]
1a	5	1.2
	1	1.8
	0.2	4.6[b]
1b	5	1.9
	1	3.0
	0.2	3.6[b]

[a] *c* (**1**) 5 mmol L^{-1} in acetonitrile was kept constant in each experiment. Product ratios were determined by means of HPLC. [b] Besides the adducts **3–7** the HPLC analyses indicate the formation of other products, which may be assigned [1:*n*] adducts with $n > 2$ due to their higher retention times.

Discussion

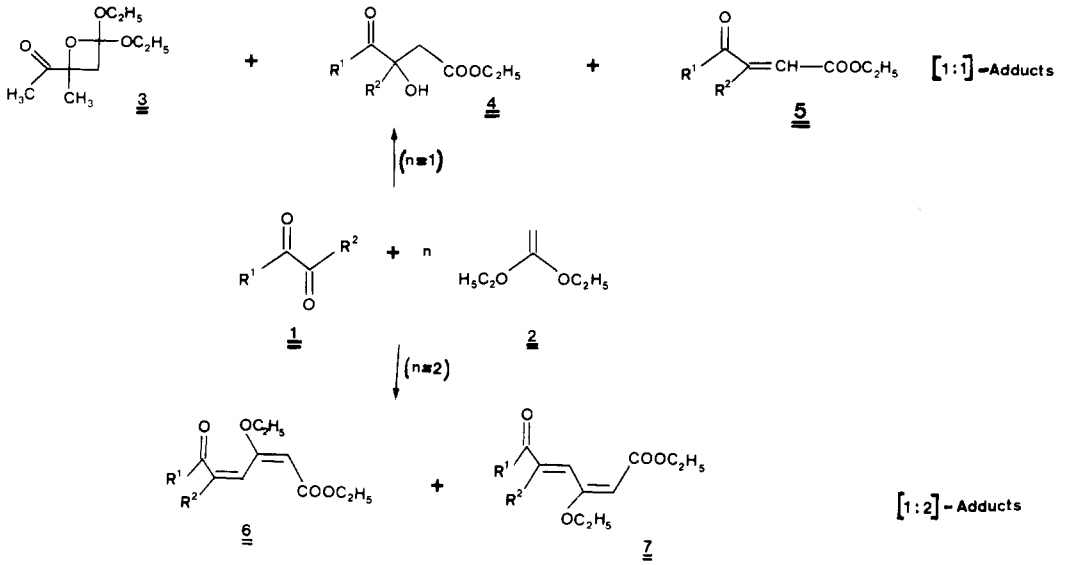
Most remarkable is the fact that these reactions only proceed in polar solvents. Dilute mixtures[6] of **1** and **2** in nonpolar solvents like cyclohexane or benzene do not show significant reactivities toward adduct formation. Moreover the rate of addition accelerates with increasing solvent polarity.[2] On the basis of these results and according to a frontier MO treatment of cycloadditions by Houk[7] the

† Part 2 of "Thermal Reactions of Donor–Acceptor Systems". For part 1, see ref 2.

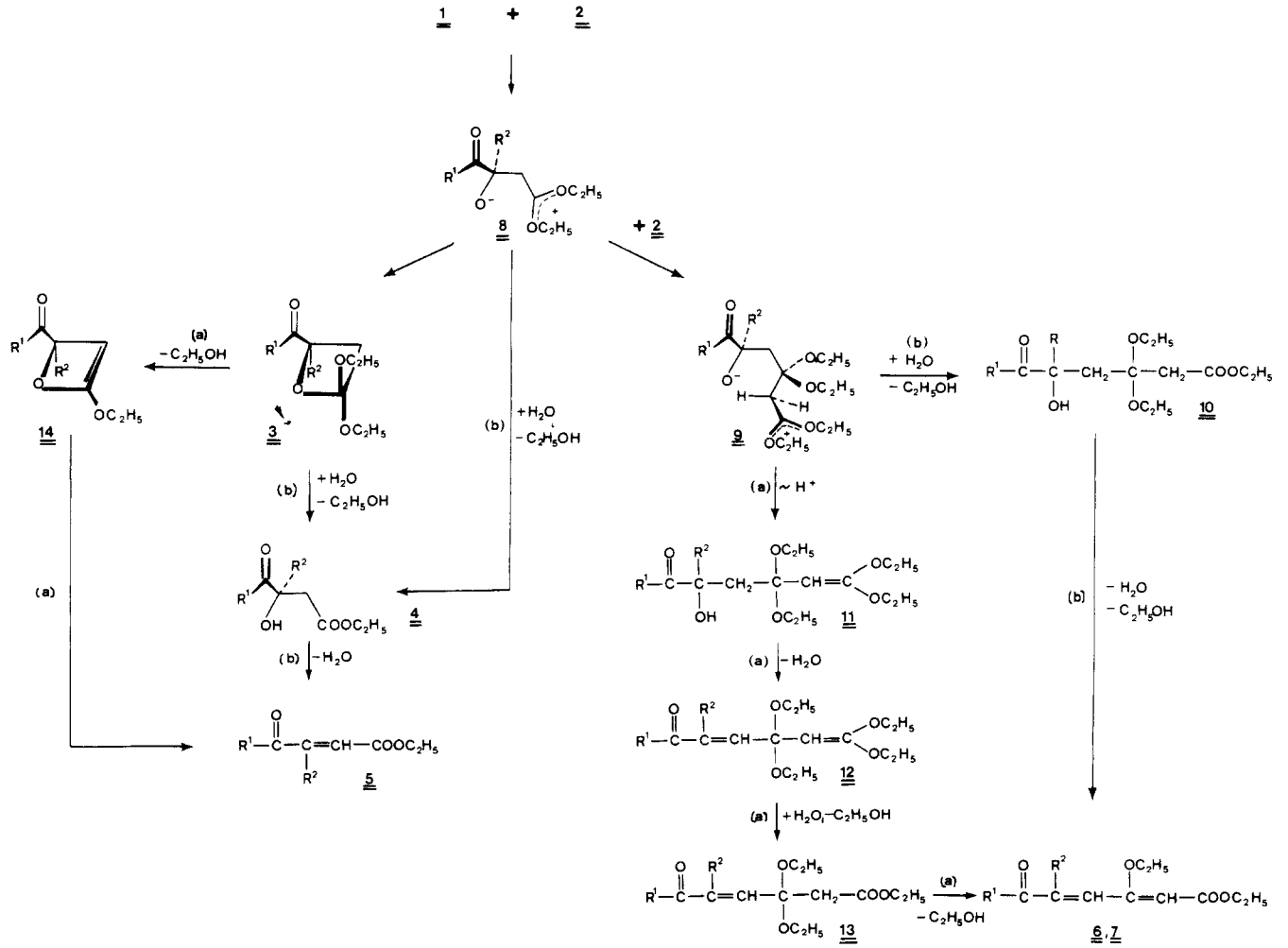
(1) Bakker, C. G.; Scheeren, H. W.; Nivard, R. J. F. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 96.
(2) Mattay, J.; Gersdorf, J.; Freudenberg, U. *Tetrahedron Lett.* **1984**, 817.
(3) Scheeren, H. W.; Aben, R. W. M.; Ooms, P. H. J.; Nivard, R. J. F. *J. Org. Chem.* **1977**, *42*, 3128.
(4) Light should be excluded in order to prevent the ketone/olefin systems from photochemically induced reactions which might be possible due to the long-wavelength absorption of the 1,2-diketones (e.g., see ref 2).
(5) Borrmann, D. In "Methoden der organischen Chemie (Houben-Weyl)"; Thieme, Stuttgart, 1968; Vol. 714, p 340.
(6) Whereas **1** and **2** do undergo addition at *c* 5 mmol L^{-1} in acetonitrile (see Table II) no significant reaction is observed in benzene or cyclohexane under the same conditions.
(7) Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361.

0022-3263/85/1950-2815$01.50/0

Scheme I. Products of Thermal Reactions of 1,2-Diketones with 1,1-Diethoxyethene[a]



Scheme II. Proposed Mechanism of Formation of the [1:1] and [1:2] Adducts (for an Alternative, see discussion)



[a] 1: a, $R^1 = R^2 = CH_3$; b, $R^1 = C_6H_5$, $R^2 = CH_3$; c, $R^1 = R^2 = C_6H_5$. 4–7: a, $R^1 = R^2 = CH_3$; b, $R^1 = C_6H_5$, $R^2 = CH_3$; c, $R^1 = CH_3$, $R^2 = C_6H_5$; d, $R^1 = R^2 = C_6H_5$.

HOMO (2)–LUMO (1) interaction ($1s^D + 1s^A$) should first lead to a dipolar intermediate 8 (see Scheme II). Both the regioselectivity of the additions and the formation of [1:1] and [1:2] adducts may be best rationalized on the basis of this key intermediate:

(1) The intramolecular ring closure forms the oxetane 3 and competes with the bimolecular addition of a second olefin molecule 2 under formation of the zwitterion 9. This competition is influenced by the concentration of 2 (see Table II) or by steric repulsion of substituents. Conse-

quently benzil **1c** only forms [1:2] adducts. It should be noted that no [1:2] adducts are attainable from **3a** in the presence of **2** under these conditions. This result indicates that the oxetane **3a** and the zwitterion **8** do not equilibrate at room temperature.

(2) Formally ethanol is eliminated during the formation of the acyclic [1:2] and [1:1] adducts **6** and **7** and **5**, respectively. These reactions may rationalized by various mechanisms. (a) An intramolecular proton shift via a six-membered transitation state may lead from the zwitterion **9** to **11**. This intermediate may eliminate water which then directly hydrolizes **12** under formation of **13**. Elimination of ethanol should lead to the 6-oxo-2,4-hexadienoic acids **6** and **7**. The formation of **5** may also be possible by elimination of ethanol from **3** and electrocyclic ring opening of **14**.[8] (b) An additional possibility should be considered since water could be formed according to mechanism a (water may either scavange the zwitterionic intermediates **8** and **9** under formation of **4** and **10** or it could hydrolize the oxetane **3**). This latter possibility has been proved by a separately performed hydrolysis of **3a**. However, this mechanism may only count for a minor part of the formation of the acyclic adducts, since water should also be scavanged by **2**. (c) The formation of **4–7** could also be rationalized by an alternative mechanism.[10] According to this mechanism the glass wall OH groups act as catalysts as outlined below for **4**. Here no water is involved as a reactant.

$$R^1COC(O^-)R^2CH_2C^+(OEt)_2 + \text{wall-OH} \rightarrow \underset{8}{}$$

$$R^1COC(OH)R^2CH_2C^+(OEt)_2 + \text{wall-O}^- \rightarrow$$

$$R^1COC(OH)R^2CH_2COOEt + \text{wall-OEt} \underset{4}{}$$

Despite the higher reactivity of aliphatic ketones in nucleophilic additions[11] most of both [1:1] and [1:2] products arise from addition onto the aromatic carbonyl group. This may be due to higher lifetimes of intermediates of type **8** and **9** with R^2 = phenyl which form the products rather than cleave back to the educts. An analogous preference for the product formation resulting from an attack onto the benzoyl group is observed in the Paterno–Büchi reaction between **1b** and olefins.[14,15]

Experimental Section

The 1,2-diketones **1a** and **1c** are commercially available and the other starting compounds were prepared according to methods described in literature: **1b**[16] and **2**.[17] Acetonitrile (from Fluka, spectrophotometric grade) was further purified by adsorptive filtration over basic aluminum oxide (Woelm) which had been activated by heating to 250 °C at 0.01 torr before use. All glass apparatuses were immersed over night in an aqueous sodium hydroxide solution to prevent acid-catalyzed side reactions.

Infrared spectra were recorded on a Perkin-Elmer 377 spectrometer. ^1H and ^{13}C NMR spectra were measured using a Varian EM 390 (90 MHz) and a Varian CFT 20 (20 MHz) spectrometer, respectively. Gas chromatographic analyses were performed on a Carlo Erba Fractovap 2101 using a 5% OV 101 glass column. A Perkin-Elmer series 3-LC-65 T and a Gilson 303 Chromatograph were used for analytic and preparative chromatographic separations, respectively. In both cases of Chromosorb Si60 columns and mixtures of a maximum 5% ethyl acetate in hexane as eluates were used. After a maximum threefold chromatographic purification all isolated products were at least 95% pure and satisfactory microanalytical data were obtained: ±0.25% for C, H.

General Procedure for the Preparation and Isolation of the Products. 1,1-Diethoxyethene (**2**) (30 mmol) was added to a solution of **1** (30 mmol) in 50 mL of purified acetonitrile under cooling with ice/wate r. Then the mixture was stoned at room temperature in the dark for 3 days. The mixture were separated into the components by liquid chromatography after acetonitrile and **2** (and eventually **1a**) had been removed by distillation under reduced pressure at room temperature. Only for the isolation of **3** a high-vacuum distillation was performed before the above operations.

2,2-Diethoxy-4-acetyl-4-methyloxetane (3): yield 34%; bp 58 °C (2.5 mmHg); IR (neat) 2980, 2935, 2899 (CH), 1720 (C=O), 1273, 1213, 1095, 1050 (COC) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 and 1.24 (2 t, J = 7 Hz, 6 H, OEt), 1.53 (s, 3 H, CH_3), 1.97 (s, 3 H, Ac), 2.50 and 2.80 (AB, J = 12 Hz, 2 H, CH_2), 3.39 and 3.44 (2 q, 4 H, OEt); ^{13}C NMR (C_6D_6) δ 15.23 and 15.33 (CH_3 of OEt), 23.42 (CH_3), 24.25 (CH_3 of Ac), 57.42 and 57.49 (CH_2 of OEt), 41.62 (C3), 78.31 (C4), 113.22 (C2), 210.00 (C=O).

The 3-hydroxy-3-methyllevulinic acid ethyl ester (**4a**) was isolated in 60% yield after hydrolysis of **3** in acetone/water at room temperature according to a method described by Schroeter:[18] bp 100 °C (12 mmHg) (Kugelrohr).

Liquid Chromatographic Separations. A prepurification was performed by liquid chromatography under normal pressure on silica gel (Woelm 32–100 mesh) using 5% ethyl acetate/hexane as eluate. Then the mixture was separated into the components by HPLC on a Si-60 column using the same eluate with 5% ethyl acetate (for products from **1a** and **1c**) or with 2% ethyl acetate (for products of **1b**).

Products from 1a. 3-Hydroxy-3-methyllevulinic acid ethyl ester (4a): oil, IR (neat) 3470 (OH), 1735 and 1715 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (s, 3 H, CH_3), 1.26 (t, J = 7 Hz, 3 H, CH_3 of OET), 2.31 (s, 3 H, Ac), 2.56 and 3.05 (AB, J = 17 Hz, 2H, CH_2), 4.16 (q, J = 7 Hz, 2 H, CH_2 of Et).

3-Methyl-4-oxo-2-pentenoic acid ethyl ester (5a): oil; IR ($CDCl_3$) 1710 (C=O), 1630 cm^{-1} (C=C); ^1H NMR ($CDCL_3$) δ 1.32 (t, J = 7 Hz, 3 H, OEt), 2.20 (d, J = 1.5 Hz, 3 H, R^2), 2.38 (s, 3 H, R^1), 4.26 (q, J = 7 Hz, 2 H, OEt), 6.57 (q, J = 1.5 Hz, 1 H, =CH); ^{13}C NMR ($CDCl_3$) δ 13.08 (R^2), 14.23 (CH_3 of OEt), 26.17 (R^1), 60.82 (CH_2 of OEt), 126.53 (C-2), 166.23 (C-1).

3-Ethoxy-5-acetyl-5-methyl-2(*E*),4(*Z*)-pentadienoic acid ethyl ester (6a): oil; IR ($CDCl_3$) 1700 (br, C=O), 1620 and 1640 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (t, J = 7.1 Hz, 3 H, EtO–C1), 1.30 (t, J = 7.0 Hz, 3 H, EtO–C3), 19.8 (d, J = 1.5 Hz, 3 H, R^2), 2.26 (s, 3 H, R^1), 3.87 (q, J = 7.0 Hz, 2 H, EtO–C3), 4.15 (q, J = 7.1 Hz, 2 H, EtO–C1), 5.05 (s, 1 H, H–C2), 7.15 (q, J = 1.5 Hz, 1 H H–C4); ^{13}C NMR ($CDCl_3$) δ 13.45 (R^2 and CH_3 of OEt–C1), 14.39 (CH_3 of OEt–C3), 29.23 (R^1), 59.64 (CH_2 of OEt–C1), 64.52 (CH_2 of OEt–C3), 92.97 (C2), 119.25 (C4), 146.58 (C5), 164.67 (C3), 166.98 (C1), 206.08 (C6).

3-Ethoxy-5-acetyl-5-methyl-2(*E*),4(*E*)-pentadienoic acid ethyl ester (7a): mp 72–73 °C; IR ($CDCl_3$) 1715 (br, C=O), 1620 and 1660 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (t, J = 7.1 Hz, 3 H, EtO–C1), 1.42 (t, J = 6.7 Hz, 3 H, EtO–C3), 2.02 (d, J = 1.3 Hz, 3 H, R^2), 2.46 (s, 3 H, R^1), 3.96 (q, J = 6.7 Hz, 2 H, EtO–C3), 4.18 (q, J. = 7.1 Hz, 2 H, EtO–C1), 5.24 (s, 1 H, H–C2), 8.05 (q, J = 1.3 Hz, 1 H, H–C4), ^{13}C NMR ($CDCl_3$) δ 13.25 (R^2), 14.18 (CH_3 of OEt–C1), 14.40 (CH_3 of OEt–C3), 26.06 (R^1), 59.93 (CH_2 of OEt–C1), 64.49 (CH_2 of OEt–C3), 96.17 (C2), 131.14 (C4) 142.26 (C5), 166.56 (C3), 166.94 (C1), 200.82 (C6).

(8) Elimination of alcohol from 2,2-dialkoxyoxetanes under formation of oxetenes has already been proposed by Mc Elvain[9] and Scheeren.[3]
(9) Mc Elvain, S. M.; Degginger, E. R.; Bekun, J. D. *J. Am. Chem. Soc.* **1954**, *76*, 5736.
(10) We gratefully acknowledge this suggestion, which has been made by one reviewer.
(11) Due to the CO/CO dihedral angle of ca. 70–110° in the ground state[12,13] the carbonyl groups of 1-phenyl-1,2-propanedione **1b** should be distinguishable in their reactivities. Therefore the observed preference in product formation cannot be rationalized on the basis of the different rates of attack onto the benzoyl or acetyl group.
(12) Arnett, J. F.; Newkome, G.; Mattice, W.L.; Mc Glynn, S. P. *J. Am. Chem. Soc.* **1974**, *96*, 4385.
(13) Sarphatie, L. A.; Verheijdt, P. L.; Cerfontain, H. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 9.
(14) Shima, K.; Shigeki, T.; Yokoyama, K.; Yamaguchi, H. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 761.
(15) Mattay, J.; Gersdorf, J.; Görner, H., unpublished results.
(16) Hartman, W. W.; Roll, L. J. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. 3, p 20.
(17) McElvain, S. M.; Kundiger, D. "Organic Syntheses"; Wiley: New York 1955; Collect. Vol. 3, p 506.
(18) Schroeter, S. H.; Orlando, C. M. *J. Org. Chem.* **1969**, *34*, 1181, 1188.

Products from 1b. 3-Benzoyl-3-hydroxybutyric acid ethyl ester (4b): oil; IR ($CDCl_3$) 3450 (OH), 1705 (ester), 1670 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (t, J = 7.2 Hz, 3 H, CH_3 of OEt), 1.60 (s, 3 H, R^2), 2.63 (d, J = 16.7 Hz, 1 H, H_a of C2), 3.27 (d, J = 16.7 Hz, 1 H, H_b of C2), 4.16 (q, J = 7.2 Hz, 2 H, CH_2 of OEt), 4.8 (s, 1 H, OH), 7.4–7.5 (m, 3 H, meta and para H of R^1), 8.22 (m, 2 H, ortho H of R^1); ^{13}C NMR ($CDCl_3$) δ 14.06 (CH_3 of OEt), 26.63 (R^2), 44.42 (C2), 61.05 (CH_2 of OEt), 78.67 (C3), 134.61, 130.16, 128.25, 132.79 (R^1 C1′, ortho, meta, para C), 173.14 (C1), 203.22 (C4).

3-Phenyl-3-hydroxy-4-oxovaleric acid ethyl ester (4c): oil; IR ($CDCl_3$) 3440 (OH), 1700 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (t, J = 7.2 Hz, 3 H, CH_3 of OEt), 2.16 (s, 3 H, R^1), 2.80 (d, J = 16.5 Hz, 1 H, H_a of C2), 3.40 (d, J = 16.5 Hz, 1 H, H_b of C2), 4.17 (q, J = 7.2 Hz, 2 H, CH_2 of OEt), 5.2 (s, 1 H, OH), 7.3–7.5 (m, 5 H, R^2); ^{13}C NMR ($CDCl_3$) δ 14.00 (CH_3 of OEt), 23.99 (R^1), 42.77 (C2), 61.23 (CH_2 of OEt), 81.34 (C3), 139.36, 125.03, 128.69, 128.12 (R^2 C1′, ortho, meta, para C), 173.08 (C1), 209.06 (C4).

3-Ethoxy-5-benzoyl-5-methyl-2(*E*),4(*Z*)-pentadienoic acid ethyl ester (6b): oil; IR ($CDCl_3$) 1710 (br, C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.76 (t, J = 7.0 Hz, 3 H, EtO–C3), 1.30 (t, J = 7.1 Hz, 3 H, EtO–C1), 2.13 (d, J = 1.5 Hz, 3 H, R^2), 3.50 (q, J = 7.0 Hz, 2 H, EtO–C3), 4.17 (q, J =7.1 Hz, 2 H, EtO–C1), 4.94 (s, 1 H, H–C2), 7.3–7.5 (m, 3 H, H_m and H_p of R^1), 7.95 (m, 2 H, H_0 of R^1), H–C4 is covered by aromatic proton signals; ^{13}C NMR ($CDCl_3$) δ 12.80 (CH_3 of OEt–C1), 14.38 (CH_3 of OEt–C3), 22.31 (R^2), 59.66 (CH_2 of OEt–C1), 64.16 (CH_2 of OEt–C3), 92.86 (C2), 121.25 (C4), 128.77, 128.56, 133.04 (R^1, ortho, meta, para C, C1′ is not observable because of its low intensity), 144.00 (C5). 164.68 (C3), 167.04 (C1), 199.70 (C6).

3-Ethoxy-5-benzoyl-5-methyl-2(*E*),4(*E*)-pentadienoic acid ethyl ester (7b) was only obtained in a mixture with **6b**.

3-Ethoxy-5-acetyl-5-phenyl-2(*E*),4(*Z*)-pentadienoic acid ethyl ester (6c): oil, IR ($CDCl_3$) 1680–1730 (C=O), 1625 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (t, J = 7.1 Hz, 3 H, EtO–C1), 1.36 (t, J = 7.0 Hz, 3 H, EtO–C3), 2.34 (s, 3 H, R^1), 3.92 (q, J = 7.0 Hz, 2 H, EtO–C3), 4.16 (q, J = 7.1 Hz, 2 H, EtO–C1), 5.14 (s, 1 H, H–C2), 7.3–7.5 (m, 5 H, R^2), 7.72 (s, 1 H, H–C4); ^{13}C NMR ($CDCl_3$) δ 13.44 (CH_3 of OEt–C1), 14.40 (CH_3 of OEt–C3), 31.07 (R^1), 60.00 (CH_2 of OEt–C1), 64.64 (CH_2 of OEt–C3), 94.68 (C2), 118.10 (C4), 126.78, 128.94, 129.25, 134.93 (R^2, ortho, meta, para C, C1′), 148.66 (C5), 164.64 (C3), 167.06 (C1), 204.71 (C6).

3-Ethoxy-5-acetyl-5-phenyl-2(*E*),4(*E*)-pentadienoic acid ethyl ester (7c): oil; IR ($CDCl_3$) 1665–1720 (C=O), 1620 (C=C) cm^{-1}; ^1H-NMR ($CDCl_3$) δ 0.68 (t, J = 6.9 Hz, EtO–C3), 1.31 (t, J = 7.1 Hz, 3 H, EtO–C1), 2.44 (s, 3 H, R^1), 3.53 (q, J = 6.9 Hz, 2 H, EtO–C3), 4.21 (q, J = 7.1 Hz, 2 H EtO–C1), 5.16 (s, 1 H, H–C2), 7.1–7.6 (m, 5 H, R^2), 8.12 (s, 1 H, H–C4); ^{13}C NMR ($CDCl_3$) δ 13.18 (CH_3 of OEt–C1), 14.39 (CH_3 of OEt–C3), 28.79 (R^1), 60.00 (CH_2 of OEt–C1), 64.10 (CH_2 of OEt–C3), 96.94 (C_2), 127.56, 128.79, 127.41 (R^2, ortho, meta, para C, C1′ is not observable because of its low intensity), 131.70 (C4), 145.38 (C5), 165.68 (C3), 167.00 (C1), 199.44 (C6).

Products from 1c. 3-Ethoxy-5-benzoyl-5-phenyl-2(*E*),4-(*Z*)-pentadienoic acid ethyl ester (6d): oil; IR ($CDCl_3$) 1720 (br, C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80 (t, J = 7.0 Hz, 3 H, EtO–C3), 1.29 (t, J = 7.0 Hz, 3 H, EtO–C1), 3.60 (q, J = 7.0 Hz, 2 H, EtO–C3), 4.20 (q, J = 7.0 Hz, 2 H, EtO–C1), 5.07 (s, 1 H, H–C2), 7.3–7.4 (m, 5 H, R^2), 7.4–7.5 (m, 3 H, H_m and H_p of R^1), 7.98 (m, 2 H, H_0 of R^1), 8.15 (s, 1 H, H–C4); ^{13}C NMR ($CDCl_3$) δ 12.81 (CH_3 of OEt–C1), 14.39 (CH_3 of OEt–C3), 59.79 (CH_2 of OEt–C1), 64.38 (CH_2 of OEt–C3), 94.52 (C2), 120.35 (C4), 126.93, 128.53, 120.34 (R^2, ortho, meta, and para C, C1′ is not observable because of its low intensity), 129.17, 128.86, 133.09 (R^1, ortho, meta, and para C, too low intensity of C1″), 145.64 (C5), 164.72 (C3), 167.19 (C1), 196.93) (C6).

3-Ethoxy-5-benzoyl-5-phenyl-2(*E*),4(*E*)-pentadienoic acid ethyl ester (7d): oil; IR ($CDCl_3$) 1700 (br, C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.78 (t, J = 7.0 Hz, 3 H, EtO–C3), 1.22 (t, J = 7.1 Hz, 3 H, EtO–C1), 3.60 (q, J = 7.0 Hz, 2 H, EtO–C3), 4.14 (q, J = 7.1 Hz, 2 H, EtO–C1), 5.16 (s, 1 H, H-C2), 7.3 (m, 5 H, R^2), 7.4–7.5 (m, 3 H, H_m and H_p of R^1), 8.00 (m, 2 H, H_0 of R^1), H–C4 is covered by aromatic proton signals; ^{13}C NMR ($CDCl_3$) δ 13.32 (CH_3 of OEt–C1), 14.32 (CH_3 of OEt–C3), 59.80 (CH_2 of OEt–C1), 64.21 (CH_2 of OEt–C3), 96.17 (C2), 127.71, 128.38, 127.70 136.93 (R^2, ortho, meta, and para C, C1′), 130.25, 128.63, 132.84, 136.93 (R^1, ortho, meta, and para C, C1″), 130.14 (C4), 145.22 (C5), 165.70 (C3), 166.84 (C1), 196.75 (C6).

Dependence of the [1:1]-/[1:2]-Addition Ratio on the Concentration of 2. Mixtures of 1 (c 5 mmol L^{-1}) and 2 (c 1–25 mmol L^{-1}) in purified acetonitrile were analyzed by HPLC after a 24-h reaction at room temperature. The product ratios were determined by means of a differential refractometer.

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Photochemistry of Aromatic α,β-Epoxy Ketones. Substituent Effects on Oxirane Ring-Opening and Related Ylide Behavior[1]

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Upon 337.1-nm laser excitation, chalcone epoxides containing donor/acceptor substituents at para positions of phenyl and benzoyl groups undergo triplet-mediated ring opening to carbonyl ylides observable by broad absorption spectra (λ_{max}^{Y} = 520–600 nm, ϵ_{max}^{Y} (13–27) × 10^3 M^{-1} cm^{-1} in benzene) on a microsecond time scale (τ_Y = 0.4–24 μs in benzene). The short-lived, carbonyl-type triplets (τ_T = 0.8–100 ns) giving rise to ylides are monitored in some cases by direct transient absorption on a nanosecond time scale and, for all systems, are probed by quenching studies with 1-methylnaphthalene and 2,5-dimethyl-2,4-hexadiene. Substituent effects on ylide absorption maxima, ylide decay kinetics, reactivity toward dipolarophiles and methanol, and precursor triplet lifetimes are discussed in the light of charge delocalization in dipolar structures, variation in HOMO/LUMO energies, complexity of thermal processes contributing to ylide decay, and energy gap between an ylide triplet and its triplet carbonyl precursor (ring closed).

In the early studies[3-8] of α,β-epoxy ketones based on steady-state irradiation, the phototransformation that has received maximum attention is the photocleavage of C–O bonds of the oxirane ring producing diradical intermediates

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