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Organic Photochemical Reactions. XXII.[1] The Photoaddition of Methyl Pyruvate to Methyl-substituted Olefins

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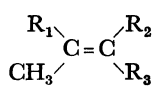
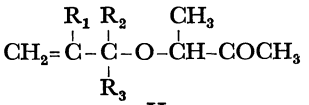
Synopsis. The irradiation of methyl pyruvate (III) and several methyl-substituted olefins (I) in acetonitrile gives allylic ethers (IV) as well as oxetanes (V) and alcohols (VI). Quenching studies suggest that IV and V are formed from the triplet state of methyl pyruvate, while VI is produced from the excited singlet state.

We have recently described a novel photoreaction in which biacetyl adds to methyl-substituted olefins, such as 2,3-dimethyl-2-butene (Ia), 2-methyl-2-butene (Ib), α-methylstyrene (Ic), and 2-ethoxypropene (Id), to afford allylic ethers (II).[2] We now find that the formation of allylic ethers is not confined to biacetyl, but is also applicable to methyl pyruvate (III), the simplest α-ketoester.[3]



I



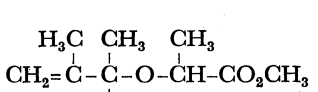
II

$CH_3COCO_2CH_3$

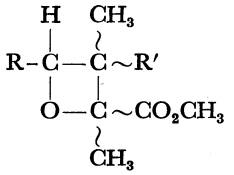
III

a, $R_1=R_2=R_3=CH_3$
b, $R_1=R_2=CH_3$, $R_3=H$
c, $R_1=C_6H_5$, $R_2=R_3=H$
d, $R_1=OC_2H_5$, $R_2=R_3=H$

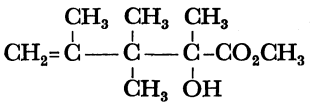
The irradiation of a solution of methyl pyruvate and 2,3-dimethyl-2-butene using a 300 W high-pressure mercury arc filtered through an *n*-hexane solution of naphthalene yielded IVa, VIa-1, and VIa-2. No detectable amounts of oxetanes were isolated in this photoreaction, as was the case with biacetyl and Ia. Furthermore, large amounts of alcohols (VIa-1 and VIa-2), the products expected from the hydrogen abstraction of Ia by excited III, were obtained. Similarly, the irradiation of methyl pyruvate and 2-methyl-2-butene gave IVb, Vb, and VIb. The major products from the irradiation of methyl pyruvate with α-methylstyrene and 2-ethoxypropene were the Vc and Vd oxetanes respectively. No detectable amounts of allylic ethers and alcohols were isolated in these reactions. These 1:1 adducts were isolated by preparative vpc and by distillation.



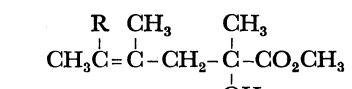
IVa, R=CH_3
IVb, R=H



Vb, R=R′=CH_3
Vc, R=H, R′=C_6H_5
Vd, R=H, R′=OC_2H_5



VIa-1



VIa-2, R=CH_3;
VIb, R=H

Table 1 shows the yields and ratios of oxetanes to allylic ethers for these reactions. The formation of IV and V is quenched by the presence of 1,3-cyclohexadiene or 2,3-dimethyl-1,3-butadiene. The Stern-Volmer plots are linear in benzene and acetonitrile.[4] On the other hand, the formation of VI is not quenched at all by large amounts of these triplet quenchers. From this observation, it is evident that VI is formed from an excited singlet state of methyl pyruvate. These results are very interesting because it has been reported that the rate of the hydrogen abstraction from an excited singlet carbonyl compound is slow.[5]

Table 1. Product yields in the photoreaction of III with Ia—Id

Olefin	Product yield, %			Ratio of V/IV
	IV	V	VI	
Ia	21	—	74	0 (0)
Ib	24	15	25	0.61 (0.41)
Ic	—	50, 27	—	(1.8)
Id	—	54, 46	—	(2.1)

Experimental

General. The NMR spectra were recorded on a Hitachi Perkin-Elmer R-20 or on a JEOL JNM-100 spectrometer in CCl_4. The infrared spectra were obtained on a JASCO IRA-1 infrared spectrophotometer. The mass spectra were obtained on a Hitachi Perkin-Elmer RMU-60 mass spectrometer. The vapor-phase chromatographic analyses were run on a Shimadzu gas chromatograph, GC-3BF or GC-2C.

The following materials were prepared by the previously-reported procedures: 2,3-dimethyl-2-butene (Ia),[6] 2-methyl-2-butene (Ib),[7] 2-ethoxypropene (Id),[8] methyl pyruvate (III),[9] 2,3-dimethyl-1,3-butadiene,[10] and 1,3-cyclohexadiene.[11]

Irradiation of Methyl Pyruvate (III) with 2,3-Dimethyl-2-butene (Ia). A solution of III (10.2 g) and Ia (8.4 g) in acetonitrile was irradiated for 120 hr using a 300 W high-pressure mercury arc filtered through an *n*-hexane solution of naphthalene under nitrogen at room temperature. Vpc (PEG 6000, 150 °C) showed the starting materials plus four products with a relative ratio of the peak areas of 21: 5: 29: 45. After the evaporation of the low-boiling fractions, a fraction boiling at 105—125 °C/30 mmHg (5.0 g) was collected; residues, 1.1 g. These products were separated by preparative vpc on a 3 m PEG 6000 column (140 °C).

The first component was identified as 1,1,2-trimethyl-2-propenyl 1′-carbomethoxyethyl ether (IVa): bp 82 °C/25

mmHg; *m/e* 186 (M^+), 171, 127, and 87 (base); IR 1755, 1640, and 1125 cm^{-1}; NMR δ 1.22 (3H, s), 1.25 (3H, d, J=7 Hz), 1.27 (3H, s), 1.73 (3H, s), 3.63 (3H, s), 3.80 (1H, q, J=7 Hz), and 4.89 (2H, m). Found: C, 64.19; H, 10.04%. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74%.

Due to its instability, the second component was neither isolated nor identified.

The third component was identified as methyl 2-hydroxy-2,3,3,4-tetramethyl-4-pentenoate (VIa—l): bp 101 °C/25 mmHg; *m/e* 186 (M^+), 168, 127, 104, and 43 (base); IR 3590, 1740, and 1640 cm^{-1}; NMR δ 1.14 (6H, s), 1.29 (3H, s), 1.76 (3H, s), 3.10 (1H, s, OH), 3.70 (3H, s), and 4.70—4.92 (2H, m). Found: C, 64.26; H, 9.58%. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74%.

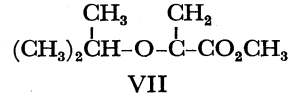
The fourth component was identified as methyl 2-hydroxy-2,4,5-trimethyl-4-hexenoate (VIa-2): bp 107 °C/22 mmHg; *m/e* 186 (M^+), 168, 127, 104, and 83 (base); IR 3530 and 1735 cm^{-1}; NMR δ 1.33 (3H, s), 1.64 (9H, s), 2.44 (2H, s), 2.99 (1H, s, OH), and 3.70 (3H, s). Found: C, 64.56; H, 9.72%. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74%.

Irradiation of Methyl Pyruvate (III) with 2-Methyl-2-butene (Ib). A mixture of III (10.2 g) and Ib (7.0 g) in acetonitrile was irradiated for 250 hr. After the removal of the unreacted materials, a fraction boiling at 83—99 °C/30 mmHg (7.6 g) was collected; residues, 4.0 g. Vpc analysis (PEG 6000, 120 °C) showed five products with a relative ratio of peak areas of 24: 27: 15: 25: 9. These products were separated by preparative vpc on a 3 m PEG 6000 column at 125 °C.

The first component was identified as 1,2-dimethyl-2-propenyl 1'-carbomethoxyethyl ether (IVb): bp 75 °C/19 mmHg; *m/e* 172; IR 1755, 1650, and 1120 cm^{-1}; NMR δ 1.20 (3H, d, J=7 Hz), 1.29 (3H, d, J=7 Hz), 1.70 (3H, s), 3.62 (3H, s), 3.85 (2H, q, J=7 Hz), and 4.60—4.88 (2H, m). Found: C, 62.67; H, 9.31%. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36%.

The second component proved to be an inseparable mixture of two products (areas, *ca.* 40: 60). The minor product was assumed to be VII from the NMR data of the hydrogenation product of this component. The structure of the major one has not yet been determined.

The third component was identified as 2,3,3,4-tetramethyl-2-carbomethoxyoxetane (Vb); bp 89 °C/23 mmHg; *m/e* 172; IR 1745 and 980 cm^{-1}; NMR δ 0.99 (3H, s), 1.12 (3H, s),



VII

1.16 (3H, d, J=7 Hz), 1.44 (3H, s), 3.67 (3H, s), and 4.34 (1H, q, J=7 Hz). Found: C, 62.60; H, 9.23%. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36%.

The fourth component was identified as VIb: bp 93 °C/20 mmHg; *m/e* 172; IR 3500 and 1735 cm^{-1}; NMR δ 1.32 (3H, s), 1.55—1.82 (6H, m), 2.16—2.46 (2H, m), 2.93 (1H, s, OH), 3.72 (3H, s), and 4.85—5.40 (1H, m). Found: C, 62.51; H, 9.34%. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36%.

The fifth component is an alcohol, but its exact structure remains undetermined.

Irradiation of Methyl Pyruvate (III) with α-Methylstyrene (Ic). After a 120 hr irradiation of a mixture of III (10.2 g) and Ic (23.6 g) in acetonitrile, a fraction boiling at 112—115 °C/4 mmHg (1.9 g) was obtained; residues, 0.9 g. The products were analyzed and separated by vpc using a 3 m Silicone DC 550 column at 190 °C. The relative ratio of the peak areas of the two major peaks was 27: 50.

The first component was identified as 2,*t*-3-dimethyl-2-carbomethoxy-3-phenyloxetane (Vc-1): bp 104 °C/4 mmHg; *m/e* 220; IR 1745 and 990 cm^{-1}; NMR δ 1.61 (3H, s), 1.64 (3H, s), 3.15 (3H, s), 4.20 (1H, d, J=5 Hz), 5.23 (1H, d, J=5 Hz), and 6.90—7.40 (5H, m). Found: C, 70.61; H, 7.50%. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%.

The second component was identified as 2,*c*-3-dimethyl-2-carbomethoxy-3-phenyloxetane (Vc-2): mp 68.5—69 °C; IR 1750 and 982 cm^{-1}; NMR δ 1.27 (3H, s), 1.57 (3H, s), 3.83 (3H, s), 4.20 (1H, d, J=5 Hz), 4.96 (1H, d, J=5 Hz), and 7.05—7.35 (5H, m). Found: C, 70.65; H, 7.35%. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%.

Irradiation of Methyl Pyruvate (III) with 2-Ethoxypropene (Id). A solution of III (10.2 g) and Id (8.6 g) in acetonitrile was irradiated for 300 hr. After the removal of the unreacted materials, a fraction boiling at 98—123 °C/15 mmHg (3.1 g) was collected; residue, 1.8 g. The vpc analysis (DNP, 3 m, 150 °C) of the distillate showed one major peak. The product, isolated by preparative vpc, was identified as a mixture of 2,*t*-3- and 2,*c*-3-dimethyl-2-carbomethoxy-3-ethoxyoxetane (Vd-1 and Vd-2) from the NMR spectra (ratios, *ca.* 6: 5): bp 103 °C/18 mmHg; NMR, Vd-1 δ 1.22 (3H, t, J=7 Hz), 1.41 (3H, s), 1.50 (3H, s), 3.46 (2H, q, J=7 Hz), 3.68 (3H, s), 4.07 (1H, d, J=6 Hz), and 4.36 (1H, d, J=6 Hz); Vd-2 δ 1.10 (3H, t, J=7 Hz), 1.46 (3H, s), 1.58 (3H, s), 3.37 (2H, q, J=7 Hz), 3.68 (3H, s), 4.07 (1H, d, J=6 Hz), and 4.62 (1H, d, J=6 Hz). Found: C, 57.19; H, 8.66%. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57%.

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3) It was also found that dimethyl oxomalonate photochemically adds to isobutene and 2-butenes to give such allylic ethers. This result will be reported elsewhere. Recently, Carless has reported that such allylic ethers are also produced by the photoreaction of acetone with Ia; H. A. J. Carless, *J. Chem. Soc., Chem. Commun.*, **1973**, 316.

4) $\Phi_0/\Phi=1+k_q\tau[Q]$; $k_q\tau$ in benzene 91 for IVa; 189 for IVb (quencher: 1,3-cyclohexadiene). $k_q\tau$ in benzene 28.5 for IVa; 51.6 for IVb; 46 for Vb (quencher: 2,3-dimethyl-1,3-butadiene).

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