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Organic Photochemical Reactions. XXV. The Photoaddition of 1-Phenyl-1,2-propanedione to Olefins[1]

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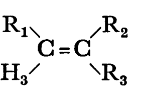
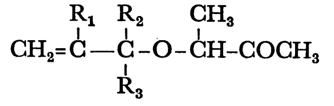
Synopsis. The irradiation of 1-phenyl-1,2-propanedione and olefins, such as 2,3-dimethyl-2-butene and α-methylstyrene, in benzene gives mainly oxetanes, in sharp contrast to the results obtained from the photoaddition of biacetyl to these olefins. The differences between these results are discussed in terms of the reactivity of the 1,4-biradical intermediates.

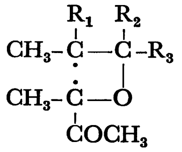
In a previous publication,[2] it was suggested that biacetyl adds to methyl-substituted olefins, such as 2,3-dimethyl-2-butene, 2-methyl-2-butene, α-methylstyrene and 2-ethoxypropene, to give unsaturated ethers (I),[3] which are the products expected from the disproportionation of 1,4-biradical intermediates (II). In order to investigate the scope and limitations of these photoaddition reactions, the photoaddition of 1-phenyl-1,2-propanedione (IIIa) and 1-(*p*-tolyl)-1,2-propanedione (IIIb) to 2,3-dimethyl-2-butene and α-methylstyrene was studied.



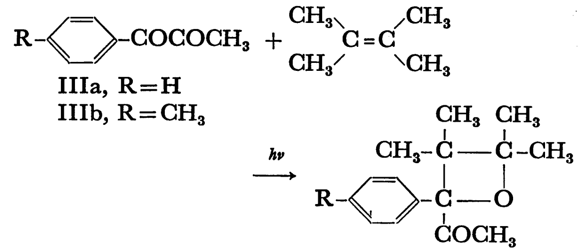
a, $R_1=R_2=R_3=CH_3$
b, $R_1=R_2=CH_3$, $R_3=H$
c, $R_1=C_6H_5$, $R_2=R_3=H$
d, $R_1=OC_2H_5$, $R_2=R_3=H$



I



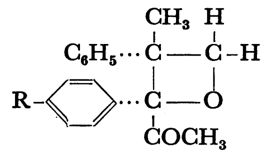
II



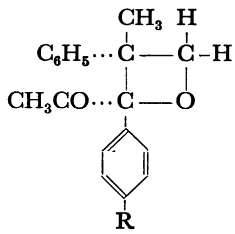
IIIa, R=H
IIIb, R=CH_3

IVa, R=H, 75%
IVb, R=CH_3, 89%

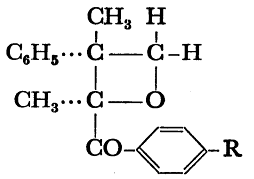
The irradiation of a benzene solution of IIIa and 2,3-dimethyl-2-butene using a 300-W high-pressure mercury lamp through a filter solution of naphthalene in hexane gave an oxetane (IVa) as the main product (75%).[4] IVa was isolated by column chromatography on silica gel and characterized by spectroscopic methods. The IR spectra of IVa showed absorption by an acetyl carbonyl at 1715 cm^{-1} and its NMR spectra showed an acetyl proton at δ 2.09. From these results, the structure of the oxetane was assigned to 1,1,2,2-tetramethyl-3-acetyl-3-phenyloxetane (IVa). Similarly, the addition of IIIb to 2,3-dimethyl-2-butene gave 1,1,2,2-tetramethyl-3-acetyl-3-(*p*-tolyl)oxetane (IVb) in an 89% yield. On the other hand, the photoaddition of IIIa (or IIIb) to α-methylstyrene gave three isolated products: Va, Vb, and Vc (or VIa, VIb, and VIc).[5] In these cases, addition products for acetyl carbonyl to α-methylstyrene were also observed. The stereochemistry of Vb and Vc can be deduced from a comparison of the NMR spectra of their methyl protons: the *trans* isomer (Vc) shows methyl absorption at a field higher than that of the *cis* isomer (Vb) due to the ring current of the phenyl group. The stereochemistry of Va was deduced using the same reasoning.



Vb (R=H), 40%
VIb (R=CH_3), 55.3%

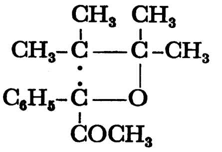


Vc (R=H), 36%
VIc (R=CH_3), 11.1%

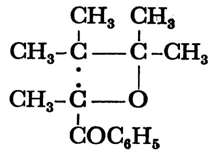


Va (R=H), 24%
VIa (R=CH_3), 33.4%

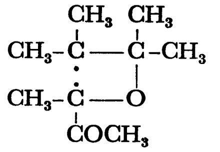
In the present experiment, unsaturated ethers, whose formation was a predominant process in the case of biacetyl and 2,3-dimethyl-2-butene, could not be detected. This sharp contrast can be explained by the smaller hydrogen abstraction ability of 1,4-biradical VIIa compared with VIII. In addition, the absence of product IX could be a reflection of a difference in



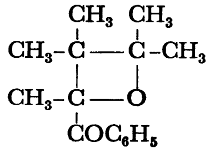
VIIa



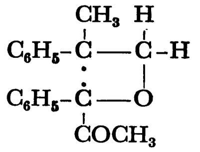
VIIb



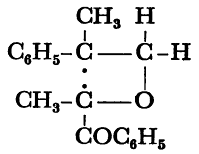
VIII



IX



Xa



Xb

the stability of 1,4-biradicals VIIa and VIIb. In the case of the reaction of IIIa with α-methylstyrene, the product expected from the addition of an acetyl carbonyl in IIIa to α-methylstyrene was obtained, though as a minor product. Probably the difference in the stability of 1,4-biradicals Xa and Xb is not as large as that of VIIa and VIIb. Finally, the absence of the stereoisomer of Va (or VIa) may be a reflection of a steric requirement in 1,4-biradicals: bulkier phenyl and aroyl groups may be far apart.

Experimental

General. NMR spectra were obtained with a JEOL JNM-MH 100 instrument for solutions in CCl_4 containing tetramethylsilane as the internal standard, IR spectra with a JASCO IRA-1 spectrophotometer, mass spectra with a Hitachi Perkin-Elmer RMU-60 spectrometer, and VPC with a Shimadzu GC-3BF apparatus using a column of Ucon Oil LB-550X (20% on Celite 545, 2 m) at 200 °C.

The following materials were prepared by previously reported procedures: 1-phenyl-1,2-propanedione (IIIa),⁶,⁷⁾ 1-(*p*-tolyl)-1,2-propanedione (IIIb),⁶⁻⁸⁾ and 2,3-dimethyl-2-butene.⁹⁾

Irradiation of 1-Phenyl-1,2-propanedione (IIIa) and 2,3-Dimethyl-2-butene. A solution of IIIa (22.2 g, 0 .15 mol) and 2,3-dimethyl-2-butene (17.7 g, 0.21 mol) in benzene (60 ml) was irradiated for 5 days using a 300-W high-pressure mercury arc filtered through a hexane solution of naphthalene in nitrogen at room temperature. After the removal of the low-boiling materials, the remaining liquid was distilled under reduced pressure to give a liquid (11 g, bp 82—107 °C/3 mmHg), leaving a viscous liquid (1 g). VPC of the distillate showed an oxetane (IVa, 75%), benzoic acid (14%), and a small amount of an unidentified product (11%). IVa was isolated by chromatography on silica gel: bp 59 °C/5.5 mmHg;¹⁰⁾ *m*/*e* 189(M^+-COCH_3), 105(base, $C_6H_5CO^+$), and 77($C_6H_5^+$); IR 1715 and 970 cm^{-1}; NMR δ 0.80(3H, s), 1.25 (3H, s), 1.26(3H, s), 1.37(3H, s), 2.09(3H, s), 7.27(3H, m), and 7.53(2H, m). Found: C, 77.43; H, 8.59%. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%.

*Irradiation of 1-(*p*-Tolyl)-1,2-propanedione (IIIb) and 2,3-Dimethyl-2-butene.* A mixture of IIIb (8.1 g, 0.05 mol) and 2,3-dimethyl-2-butene (5.9 g, 0.07 mol) in benzene (20 ml) was irradiated for 5 days. After the removal of the unreacted materials, a fraction boiling at 92—119 °C/5 mmHg (4.7 g) was collected; residues, 1 g. VPC analysis showed three products with a relative ratio of peak areas of 89: 9.7: 1.3. The major product (IVb) was isolated by chromatography on silica gel: bp 94 °C/2 mmHg;¹¹⁾ *m*/*e* 203, 119(base), and 91; IR 1715 and 980 cm^{-1}; NMR δ 0.78(3H, s), 1.23(3H, s), 1.26(3H, s), 1.37(3H, s), 2.07(3H, s), 2.35(3H, s), 7.12(2H, m), and 7.41(2H, m). Found: C, 78.26; H, 9.02%. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00%.

Irradiation of 1-Phenyl-1,2-propanedione (IIIa) and α-Methylstyrene. A solution of IIIa (10.4 g, 0.07 mol) and α-methylstyrene (11.8 g, 0.1 mol) in benzene (60 ml) was irradiated for 10 days. After the removal of the unreacted materials, a fraction boiling at 80—140 °C/3 mmHg(3.9 g)¹²⁾ was collected; residues, 4.8 g. The distillate was chromatographed on silica gel in hexane using 4% acetone as the eluent, giving three isolated products. The first eluted product was 1,*t*-2-dimethyl-1-benzoyl-2-phenyloxetane (Va, 24%): mp 85 °C; *m*/*e* 266(M^+), 118(base), 105, and 77; IR 1680 and 995 cm^{-1}; NMR δ 1.41(3H, s), 1.52(3H, s), 4.09(1H, d, *J*=5.7 Hz), 4.94(1H, d, *J*=5.7 Hz), 7.09(8H, m), and 7.95(2H, M). Found: C, 81.12; H, 6.67%. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%. The second eluted product was 1,*c*-2-diphenyl-1-acetyl-2-methyloxetane (Vb, 40%): bp 145 °C/5 mmHg; *m*/*e* 266, 118, 105, and 77; IR 1715 and 990 cm^{-1}; NMR δ 1.77 (3H, s), 2.12(3H, s), 4.19(1H, d, *J*=5.7 Hz), 5.10(1H, d, *J*= 5.7 Hz), 6.99(8H, m), and 7.23(2H, m). Found: C, 81.42; H, 6.84%. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%. The third eluted product was 1,*t*-2-diphenyl-1-acetyl-2-methyloxetane (Vc, 36%): mp 71 °C; *m*/*e* 266, 118, 105, and 77; IR 1720 and 990 cm^{-1}; NMR δ 1.21(3H, s), 1.90(3H, s), 4.30(1H, d, *J*=5.7 Hz), 4.92(1H, d, *J*=5.7 Hz), 7.13(8H, m), and 7.47 (2H, m). Found: C, 81.21; H, 6.77%. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%.

*Irradiation of 1-(*p*-Tolyl)-1,2-propanedione (IIIb) and α-Methylstyrene.* After 10 days of irradiation of a mixture of IIIb (8.1 g, 0.05 mol) and α-methylstyrene (8.4 g, 0.07 mol) in benzene (20 ml), a fraction boiling at 105—130 °C/4 mmHg (1.8 g)¹³⁾ was obtained; residues, 2 g. The distillate was chromatographed on silica gel. The first eluted product was VIa (33.4%): *m*/*e* 280(M^+), 119(base), 118, 91, and 43; IR 1675 and 990 cm^{-1}; NMR δ 1.42(3H, s), 1.53(3H, s), 2.41(3H, s), 4.16(1H, d, *J*=5.7 Hz), 5.06(1H, d, *J*=5.7 Hz), 7.24(7H, m), and 8.01(2H, m). The second eluted product was VIb(55.5%): *m*/*e* 280, 119(base), 118, and 91; IR 1715 and 990 cm^{-1}; NMR δ 1.74(3H, s), 2.07(3H, s), 2.12(3H, s), 4.14(1H, d, *J*=5.7 Hz), 5.07(1H, d, *J*=5.7 Hz), and 6.95(9H, m). The third eluted product was VIc(11.1%): *m*/*e* 119, 118, and 91; IR 1720 and 995 cm^{-1}; NMR δ 1.23(3H, s), 1.95(3H, s), 2.35(3H, s), 4.44 (1H, d, *J*=5.7 Hz), 5.05(1H, d, *J*=5.7 Hz), and 7.40(9H, m).

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References

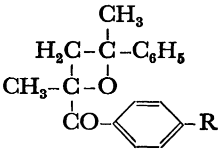
1) Part XXIV, K. Shima, T. Kubota, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **49**, 2567 (1967).

2) H.-S. Ryang, K. Shima, and H. Sakurai, *Tetrahedron Lett.*, **1970**, 1094; *J. Am. Chem. Soc.*, **93**, 5270 (1971); *J. Org. Chem.*, **38**, 2860 (1973).

3) In the photoaddition of biacetyl to α-methylstyrene and 2-ethoxypropene, the major products are oxetanes. The ratio of oxetanes to unsaturated ethers are *ca.* 2.²⁾

4) Unsaturated ethers were not detected in this photoreaction.

5) No other by-products are produced in this photoreaction. Also, no oxetanes such as XI were detected in these reactions.



XI

6) W. H. Hartung and F. Crossley, *Org. Synth.*, Coll. Vol. II, 363 (1943).

7) W. W. Hartman and L. J. Roll, *Org. Synth.*, Coll. Vol. III, 20 (1955).

8) R. Adams, *J. Am. Chem. Soc.*, **46**, 1889 (1924).

9) I. Shurman and C. E. Boord, *J. Am. Chem. Soc.*, **55**, 4930 (1933).

10) Yield of IVa based on the IIIa used: 23.7 mol%.

11) Yield of IVb based on the IIIb used: 34 mol%.

12) Yield of products based on the IIIa used: total 20.9 mol%; Va, 5.0 mol%; Vb, 8.4 mol%; Vc, 7.5 mol%.

13) Yield of products based on the IIIb used: total 12.9 mol%; VIa, 4.3 mol%; VIb, 7.2 mol%; VIc, 1.4 mol%.