BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1007—1008 (1973)

The Photoreaction of 2,6-Diphenyl-4*H*-thiopyran-4-one 1,1-Dioxide

Hiromu Aoyama, Yoshiaki Sato, Takehiko Nishio, and Noboru Sugiyama
Department of Chemistry, Faculty of Science, Tokyo Kyoiku University, Otsuka, Tokyo

(Received July 19, 1972)

Previously, we have reported that the irradiation of 2,6-diphenyl-4*H*-thiopyran-4-one (Ia) in non-polar solvents gave a head-to-tail anti-dimer[1] and in polar solvents gave photooxidized products,[2] while that of 2,6-diphenyl-4*H*-pyran-4-one (Ib) gave the corresponding cage dimer.[2] This paper will be concerned with the photoreaction of 2,6-diphenyl-4*H*-thiopyran-4-one 1,1-dioxide (II).

The irradiation of II in a methanol solution (0.02 mol/l) with a high-pressure mercury lamp under a nitrogen atmosphere gave a methanol-adduct (III) (mp 208—210°C) in a 14% yield and a trace of benzoic acid. The structure of III was determined as follows. The NMR spectrum of III showed a singlet at δ 3.51 (3H) assignable to methoxy protons and a singlet at δ 4.86 (2H) assignable to methylene protons. The IR spectrum of II showed a carbonyl band at 1640 cm^{-1}, but that of III showed it at 1690 cm^{-1}. The mass spectrum of III showed a peak at *m*/*e* 328 (M^+, $C_{18}H_{16}O_4S$) and base peaks at *m*/*e* 134 ($M-C_9H_6O_3S$) and 264 ($M-SO_2$). The hydrogenation of III in a mixture of acetic acid and ethanol by means of palladium-charcoal gave IV. Its NMR spectrum exhibited a pair of doublets at δ 4.42 (1H) and 4.73 (1H) due to methylene protons at C-3. The irradiation of II in benzene gave an intractable mixture.

When a mixture of II and cyclohexene in benzene was irradiated under the same conditions for 4 hr, a 1 : 1-adduct (V) was obtained in a 93% yield. The NMR spectrum of V showed two doublets at δ 6.59 (0.75 H) and 6.52 (0.25 H) assignable to an olefinic proton. The product V was therefore considered to be a mixture of stereoisomers at the cyclobutane ring. Furthermore, the results of the elemental analysis confirmed that V was a 1 : 1-adduct, and the UV and IR spectra indicated the presence of an enone system.[3] Also, the hydrogenation of V afforded VII quantitatively. The NMR spectrum of VII exhibited a multiplet at δ 4.94 (1H) attributable to the methine proton at C-2. The IR spectrum also indicated a saturated carbonyl band at 1710 cm^{-1}.

When a mixture of II and cyclooctene in benzene was irradiated under the same conditions for 5 hr, a 1 : 1-adduct (VI) was also obtained in a 50% yield. The structure of VI was determined on the basis of its elemental analysis and spectral data. The product VI also seems to be a mixture of stereoisomers at the cyclobutane ring like V, for the NMR spectrum of VI exhibited two doublets at δ 6.57 (0.55 H) and 6.47 (0.45 H) assignable to an olefinic proton.

Experimental

Material. 2,6-Diphenyl-4*H*-thiopyran-4-one 1,1-dioxide (II)[4] was synthesized by Arndt's method,[5] mp 143—144.5°C (lit,[5] 144—145°C).

Irradiation of II. A solution of 600 mg of II in 100 ml of methanol was irradiated with a high-pressure mercury lamp through a Pyrex filter under nitrogen for 6 hr. After the removal of the solvent, the residue was chromatographed on a silica-gel column. Elution with benzene–ethyl acetate (19 : 1) yielded 86 mg of II and 91 mg of III. Recrystallizations of III from benzene afforded colorless prisms. Found: C, 65.69; H, 4.94%. Calcd for $C_{18}H_{16}O_4S$: C, 65.85; H, 4.91%. UV: $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε), 217 (21,700) and 292 (9,900). IR: $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}, 1690 (C=O). NMR: (δ in $CDCl_3$) 7.85—7.33 (m, 10H, phenyl), 6.54 (s, 1H, olefinic), 4.86 (s, 2H, methylene), 3.51 (s, 3H, methoxy).

Hydrogenation of III. When 40 mg of III was hydrogenated in 10 ml of acetic acid and 5 ml of ethanol with 30 mg of palladium-charcoal, IV was quantitatively obtained. Recrystallizations of IV from benzene afforded colorless prisms; mp 231—232°C. Found: C, 65.43; H, 5.61%. Calcd for $C_{18}H_{18}O_4S$: C, 65.44; H, 5.49%. IR: $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}, 1728 (C=O), 1312, 1113 (SO_2). NMR: (δ in $CDCl_3$) 7.40 (s, 10H, phenyl), 4.73 (d, 1H, $J=15$, methylene at C-3) and 4.42 (d, 1H, $J=15$, methylene at C-3), 4.43 (d, 1H, $J=3.5$, methine), 3.80 (d, 1H, $J=15$, methylene at C-5) and 3.02 (dd, 1H, $J=15$, $J=3.5$, methylene at C-5), 3.37 (s, 3H, methoxy).[6] When the signal of the methine proton at δ 4.43 was irradiated, the signal of the methylene protons at δ 3.80 and 3.02 changed into a pair of doublets (AB q.) at δ 3.12 and 2.89.

Irradiation of the Mixture of II and Cyclohexene. A solution of 500 mg of II and 2 ml of cyclohexene in 30 ml of benzene was irradiated under the same conditions as have been described above for 4 hr. After the solvent had been removed, the residue was chromatographed on a silica-gel column with benzene–*n*-hexane (9 : 1). The evaporation of the solvent from the eluted fraction gave a crude product as a pale yellow crystals, which were then collected, and washed with *n*-hexane to afford colorless prisms; 594 mg of V; mp 175.5—177°C. Found: C, 72.79; H, 5.97%. Calcd for $C_{23}H_{22}O_3S$: C, 73.00; H, 5.86%. UV: $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε), 220 (16,200) and 294.5 (10,600). IR: $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}, 1685 (C=O), 1308, 1135 (SO_2). NMR: (δ in $CDCl_3$) 7.50—7.25 (m, 10H, phenyl), 6.59 (d, 0.75H, olefinic

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[1] N. Sugiyama, Y. Sato, H. Kataoka, C. Kashima and K. Yamada, This Bulletin, **42**, 3005 (1969).

[2] N. Sugiyama, Y. Sato, and C. Kashima, *ibid.*, **43**, 3205 (1970).

[3] *E. g.*, H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962).

[4] UV: $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε), 226 (sh. 16,200), 314 (11,700) and 327 (sh. 11200). IR: $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}, 1640 (C=O), 1305, 1128 (SO_2). NMR: (δ in $CDCl_3$) 7.97—7.63 (m, 10H, phenyl), 6.63 (s, 2H, olefinic).

[5] F. Arndt, P. Nachtwey and J. Pusch, *Ber.*, **58**, 1633 (1925).

[6] This assignment was determined by comparing the NMR spectrum of IV with that of 2,6-diphenyl-2,3,5,6-tetrahydro-4*H*-thiopyran-4-one 1,1-dioxide. δ ($CDCl_3$) 7.39(s, 10H, phenyl), 4.52 (dd, 2H, $J=15$, $J=3.5$, methine), 3.67 (dd, 2H, $J=15$, $J=15$, methylene), 2.90 (br d, 2H, $J=15$, methylene).

and 6.52 (d, 0.25H, olefinic), 3.82—2.92 (m, 3H, methine), 2.80—0.88 (m, 8H, methylene).

Hydrogenation of V. When a 300-mg portion of V was hydrogenated in 25 ml of acetic acid and 40 ml of ethanol with 50 mg of palladium-charcoal, VII was quantitatively obtained. Recrystallizations of VII from benzene afforded colorless prisms; mp 178—179°C. Found: C, 72.88; H, 6.36%. Calcd for $C_{23}H_{24}O_3S$: C, 72.61; H, 6.36%. IR: ν_{max}^{KBr} cm^{-1}, 1710 (C=O), 1305, 1125 (SO_2). NMR: (δ in $CDCl_3$) 7.5—6.9 (m, 10H, phenyl), 4.94 (m, 1H, methine at C-2), 3.92—3.2 (m, 5H, methylene at C-3 and methine), 2.95—1.0 (m, 8H, methylene). When the signal of the methine proton at δ 4.94 was irradiated, the signal of the methylene protons at C-3 appeared as a broad singlet at δ 3.38.

Irradiation of the Mixture of II and Cyclooctene. A solution of 500 mg of II and 5.5 ml of cyclooctene in 30 ml of benzene was irradiated under the same conditions as have been described above for 5 hr. After the solvent had been removed, the residue was chromatographed on a silica-gel column. Elution with benzene-ethyl acetate (9 : 1) yielded 203 mg of VI. Recrystallizations of VI from *n*-hexane afforded colorless prisms; mp 209—211°C. Found: C, 73.53; H, 6.48%. Calcd for $C_{25}H_{26}O_3S$: C, 73.86; H, 6.45%. UV: λ_{max}^{EtOH} nm (ε), 220.5 (19,500) and 293.5 (11,000). IR: ν_{max}^{KBr} cm^{-1}, 1692 (C=O), 1300, 1125 (SO_2). NMR: (δ in $CDCl_3$) 7.48—7.05 (m, 10H, phenyl), 6.57 (d, 0.55H, olefinic) and 6.47 (d, 0.45H, olefinic) 3.8—3.0 (m, 3H, methine), 2.1—0.85 (m, 12H, methylene).