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

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Although numerous reports on the photoreaction of nonbenzenoid aromatic compounds have been published,[1] there has been only one report on the photochemistry of a γ-pyrone-type compound, *i. e.*, 2,6-dimethyl-4*H*-pyran-4-one.[2] This paper will be concerned with the photoreaction of 2,6-diphenyl-4*H*-thiopyran-4-one(I).

The irradiation of I in a benzene solution (0.3 mol/*l*) by a high-pressure mercury lamp gave pale yellow crystals (II), mp 160—161°C, in a 25% yield. When the benzene solution of I was irradiated by a high-pressure mercury lamp with a Pyrex filter or a low-pressure mercury lamp with a quartz filter, the yield of II decreased to 8 or 2% respectively. When a solution of I in ether, methylene chloride, or ethanol was irradiated, hardly any formation of II detected. By the irradiation of I in the solid state, only an oily substance was produced. It was observed that a conversion of II to I of several per cent took two weeks to proceed at room temperature, but it occurred quantiatively at the melting point of II in only five minutes. In the boiling benzene, this conversion occurred with a half-life of five hours.

The structure of II was determined as follows. The NMR spectrum of II showed a singlet signal at τ 5.50 whose intensity was equivalent to that of a vinyl proton at τ 3.41. The IR spectrum of I showed a carbonyl band at 1600 cm^{-1}, but that of II showed it at 1640 cm^{-1}. The thermal formation of I from II and the NMR and IR spectra of II suggested that the structure of II was a dimer of I containing a cyclobutane ring.

For this type of dimer, four isomers are possible. However, their NMR spectra would show their cyclobutane methine protons as singlets in each case, for the environments of both methine protons would be equivalent. In order to distinguish the two protons, II was converted to a monobromo-derivative (III) by treating with a half mole of bromine. In its IR spectrum III showed carbonyl bands at 1657 and 1640 cm^{-1}. This fact indicates that the substitution with bromine occurred at the α-position of one enone system. This was also supported by the UV spectrum of III, which showed at 339 nm(ε 11200) the absorption maximum which was observed at 335 nm(ε 13200) in II. In the NMR spectrum of III, two singlet signals, at τ 5.31 and 5.28, show that both methine protons are situated at 1,3-positions in the cyclobutane ring. If both the protons are situated at 1,2-positions, they should have the coupling constant of 2.7—11 Hz.[3] Thus, the structure of II was

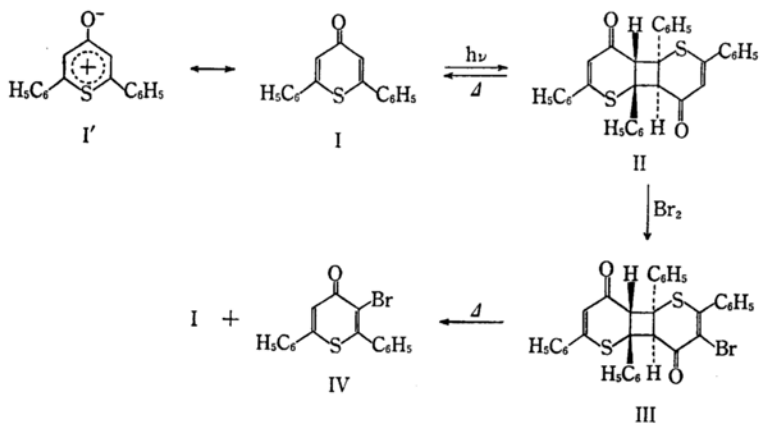

Fig. 1

1) *E. g.*, T. Tezuka, Y. Akasaki and T. Mukai, *Tetrahedron Letters*, **1967**, 5003.

2) P. Yates and M. J. Jorgenson, *J. Am. Chem. Soc.*, **85**, 2956 (1963); P. Yates and J. W. J. Still, *ibid.*, **85**, 1208 (1963).

3) I. Fleming and D. H. Williams, *Tetrahedron*, **23**, 2747 (1967).

determined to be a head-to-tail dimer.

Moreover, the chemical shift of the vinyl proton of III is exactly the same as that of II. This fact indicates that the vinyl proton of III is not affected by the substitution with the bromine atom, though the chemical shifts of two methine protons of III are moved to a lower field. Therefore, the anti type is the preferable structure.

When III was heated at the melting point, both I and IV were quantitatively obtained. IV was identified with the authentic sample, which was synthesized from 2,6-diphenyl-tetrahydro-4*H*-thiopyran-4-one (V).

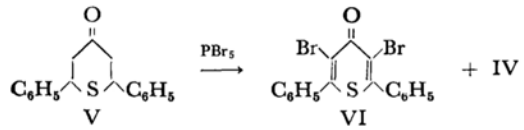

Fig. 2

In conclusion, it was proved that an anti, head-to-tail dimer was produced by the irradiation of I. This result indicates that the behavior of I in the excited state is similar to that of the enone system[4] in spite of its aromaticity. In the case of the irradiation of I in polar solvents, there was no product of II. This result seems to be attributable to the readier π-electron decrease (I') in its ring in the polar solvent, which gives rise to its aromaticity. This theory may be supported by the UV and NMR spectra of I in various solvents, shown in the Experimental section.

Experimental

Preparation of 2,6-Diphenyl-4*H*-thiopyran-4-one (I). I was synthesized by Arndt's method.[5] Mp 131—132°C (lit 132—133°C).

UV: $\lambda_{max}^{Benzene}$ nm(ε), 278(22500)
λ_{max}^{Ether} nm(ε), 276(22600)
$\lambda_{max}^{CH_2Cl_2}$ nm(ε), 266(26800), 300(15700)
λ_{max}^{EtOH} nm(ε), 265(19000), 304(21400)

IR: ν_{max}^{KBr} cm^{-1}, 1600

NMR: (τ in CCl_4), 2.2—2.7(m. 10H), 3.01(s.2H)
(τ in Ether), 2.2—2.7(m.10H), 2.97(s. 2H)
(τ in CH_2Cl_2), 2.2—2.7(m.10H), 2.85(s. 2H)
(τ in $CDCl_3$), 2.2—2.6(m.10H), 2.80(s. 2H)

Irradiation of I. On the irradiation of a benzene solution of I (0.3 mol/*l*) with a high-pressure mercury lamp under a nitrogen atmosphere for a week, pale yellow crystals (II) were produced on the wall of the reaction vessel in a 25% yield. These crystals were collected, chromatographed on silica gel with chloroform, and recrystallized from benzene or a chloroform-*n*-hexane mixture.

UV: $\lambda_{max}^{CHCl_3}$ nm(ε), 283(23700), 335(13200)

IR: ν_{max}^{KBr} cm^{-1}, 1640, 1560

a) Recrystallization from Benzene. Upon recrystallization from benzene, II gave pale yellow prisms. Mp 160—161°C. Found: C, 79.78; H, 5.29%. Calcd for $C_{34}H_{24}O_2S_2 \cdot C_6H_6$: C, 79.19; H, 4.98%.

NMR: (τ in $CDCl_3$) 2.4—2.8(m.26H), 3.41(s.2H), 5.50(s.2H).

b) Recrystallization from Chloroform-n-Hexane. This recrystallization of II gave pale yellow leaflets; mp 159—160°C. Found: C, 70.38; H, 4.17%. Calcd for $C_{34}H_{24}O_2S_2 \cdot 1/2CHCl_3$: C, 70.35; H, 4.32%.

NMR: (τ in $CDCl_3$) 2.4—2.8(m.20H), 3.41(s.2H), 5.50(s.2H). From these data of elemental analyses and NMR spectra, it can be said that II, which was recrystallized from benzene or chloroform - *n*-hexane, contains the solvents of crystallization. These solvents were not removed by heating under reduced pressure because of the instability of II described above.

When a high-pressure mercury lamp with a Pyrex filter or a low-pressure mercury lamp with a quartz filter was used under the same conditions, the yield of II was decreased to 8 or 3% respectively. By the irradiation of I in ether (0.1 mol/*l*) or in benzene (0.03 mol/*l*), only a trace of II was detected. However, on the irradiation of I in methylene chloride (0.3 mol/*l*) or in ethanol (0.1 mol/*l*), II was not detected at all. From the irradiated solutions, I was mainly recovered.

Irradiation in the solid state with a high-pressure mercury lamp produced an oily substance.

Preparation of the Monobromo-substituted Dimer (III). To an ice-cooled chloroform (5 m*l*) solution of II (80 mg) there was added a chloroform (2 m*l*) solution of bromine (24 mg). After the solution had been stirred for half an hour, the solvent was evaporated. The residue was chromatographed on silica gel with chloroform. As the main product, III (40 mg) was obtained; it was recrystallized from chloroform-*n*-hexane to afford colorless crystals; mp 170—171°C.

Found: C, 66.47; H, 3.95%. Calcd for $C_{34}H_{23}O_2S_2Br$ C, 67.21; H, 3.79%.

UV: $\lambda_{max}^{CHCl_3}$ nm(ε), 281 (21900), 339(11200).

IR: ν_{max}^{KBr} cm^{-1}, 1657, 1640, 1555.

NMR: (τ in $CDCl_3$) 2.3—2.8(m.20H), 3.41(s.1H), 5.28(s.1H), 5.31(s.1H).

Preparation of 3-Bromo-2,6-diphenyl-4*H*-thiopyran-4-one(IV) and 3,5-Dibromo-2,6-diphenyl-4*H*-thiopyran-4-one(VI). A benzene solution (10 m*l*) of 2,6-diphenyl-tetrahydro-4*H*-thiopyran-4-one (V) (530 mg) was refluxed with phosphorus pentabromide (3 g) for 5 hr. To the reaction mixture a saturated aqueous sodium thiosulfate solution (50 m*l*) was then added, and the mixture was extracted with benzene. The benzene solution was washed with water and dried over sodium sulfate. After the removal of the solvent, the residue was chromatographed on silica gel with benzene and benzene - ethyl acetate (19 : 1). VI (60 mg) and IV (30 mg) were obtained from the former and the latter respectively. The structure of VI was supported by its IR, UV and NMR spectra. The recrystallization of IV from carbon tetrachloride gave colorless needles; mp 121—123°C.

Found: C, 59.37; H, 3.27%. Calcd for $C_{17}H_{11}OSBr$: C, 59.42; H, 3.21%.

UV: $\lambda_{max}^{CHCl_3}$ nm(ε), 273(23300), 308(16800).

IR: ν_{max}^{KBr} cm^{-1}, 1603.

NMR: (τ in CCl_4) 2.60 (s. 10H), 2.94(s. 1H).

4) *E. g.*, P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 (1962).

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

Recrystallization of VI from methanol afforded yellow needles; mp 163.5—164.5°C.
Found: C, 48.32; H, 3.13%. Calcd for $C_{17}H_{10}SOBr_2$: C, 48.34; H, 2.37%.

UV: $\lambda_{max}^{CHCl_3}$ nm(ε), 273 (21800), 317(14600).
IR: ν_{max}^{KBr} cm^{-1}, 161.
NMR: (τ in CCl_4) 2.60(s.).