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PHOTOLYSIS OF 2,6-DIPHENYL-4H-PYRAN-4-THIONE AND 2,6-DIPHENYL-4H-THIOPYRAN-4-THIONE

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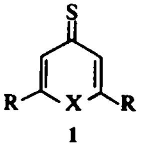
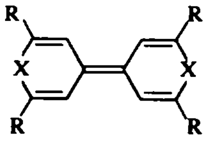
Abstract – Photolysis of 2,6-diphenyl-4H-pyran-4-thione and 2,6-diphenyl-4H-thiopyran-4-thione resulted in desulfurization and furnished 2,2′,6,6′-tetraphenyl-4,4′-di(pyranylidene) and 2,2′,6,6′-tetraphenyl-4,4′-di(thiopyranylidene) as the products. The mechanism was studied by quantum yield measurements. In dioxane, the quantum yield of di(pyranylidene) formation was concentration-dependent, while in benzene, it was independent of the concentration. The photoreaction proceeds *via* the triplet state of 2,6-diphenyl-4H-pyran-4-thione and 2,6-diphenyl-4H-thiopyran-4-thione and the H atom abstraction from solvents appears to be a key step in the formation of di(pyranylidene).

Compounds with a thioketone structure frequently dimerize with the elimination of surfur. In the 4H-pyran-4-thiones (**1**, X=O) and 4H-thiopyran-4-thiones (**1**, X=S) the thermochemical dimerization with the elimination of sulfur to yield di(pyranylidene) derivatives (**2**) is well documented.[1–4] The mechanism of the formation of **2** is still not clear.[†] There are also many reports on photodimerization of 4H-pyran-4-one and 4H-thiopyran-4-one derivatives,[6–8] which afford [2+2] or [2+2+2+2] cycloadducts. We recently found[9,‡] that the photolysis of 2,6-diphenyl-4H-pyran-4-thione (**1a**) gives 2,2′,6,6′-tetraphenyl-4,4′-di(pyranylidene) (**2a**) accompanied by elimination of sulfur, detected as hydrogen sulfide gas.[10] This paper describes the mechanism of the formation of **2a** and 2,2′,6,6′-tetraphenyl-4,4′-di(thiopyranylidene) (**2b**) from **1a** and 2,6-diphenyl-4H-thiopyran-4-thione (**1b**) by photolysis.



1

1a: X = O, R = Ph
1b: X = S, R = Ph
1c: X = O, R = H
1d: X = O, R = Me



2

2a: X = O, R = Ph
2b: X = S, R = Ph

RESULTS AND DISCUSSION

Irradiation of **1a** in dioxane using a medium-pressure mercury lamp with a Pyrex filter gave **2a**. Photolysis of **1b** under the same condition as above yielded **2b**. The structure of the photoproducts, **2a** and **2b** was established by comparison of their m.p., IR and UV spectra with those of the authentic samples[1,2] prepared from **1a** and **1b** by heating. In photolysis of **1a** and **1b** formation of hydrogen sulfide gas was detected by flushing the reaction with N_2 followed by passing the gas through iodine-potassium iodide solution,[10] but no sulfur, S_8, was isolated. This photodimerization with the elimination of sulfur as hydrogen sulfide gas did not occur to any great extent (0–3%) in the case of 4H-pyran-4-thione (**1c**) or 2,6-dimethyl-4H-pyran-4-thione (**1d**). Irradiation of **1c** in dioxane gave only polymeric compounds, while the photolysis of **1d** resulted in the recovery of the starting material. This dimerization with desulfurization was observed on heating **1a** and **1b**.[1–3] However, heating **1c** and **1d** did not give any dimer, **2**.[1–3] The nature of the substituent seems to be of importance in the formation of **2** both in photolysis and thermolysis of **1**. As a working rule it can be assumed that **2** are easily formed from **1** if the thioketone nature of the thione group is well-developed.

In order to understand the mechanism of the photochemical dimerization of **1** to **2** the quantum yield determination during the formation of **2a** and **2b** at 360 nm was carried out in various solvents. The quantum yield in the formation of **2a** were consistent with those of disappearance of **1a** within the experimental error. The results of quantum yield in the formation of **2a** and **2b** are summarized in Table 1. The effect of the initial concentration of **1a** on the quantum yield in the formation of **2a** was studied in benzene and dioxane, and the results are collected in Table 2.

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[†] While a mechanistic study of the formation of **2** by heating **1** was carried out Mayer,[5] the detail of work has not been published yet.

[‡] The conclusion on the nature of the excited state for photodimerization of **1a** to **2a** was not duly interpreted.

Table 1. Solvent effect upon quantum yield of the formation of **2a** and **2b**[a]

Substrate	Initial concentration of substrate (mole/l × 10^4)	Solvent	ϕ
1a	8·00	Benzene	0·02
1b	11·00	Benzene	0·04
1a	8·63	Acetonitrile	0·03
1b	12·40	Acetonitrile	0·04
1a	2·80[b]	2-Propanol	0·48
1a	7·60	Dioxane	0·41
1b	7·00	Dioxane	0·32
1a	6·48	Tetrahydrofuran	0·79
1b	8·80	Tetrahydrofuran	0·80

[a] All runs at 25°; irradiation conditions described in the Experimental section.

[b] Saturated soln because of the poor solubility of **1a** in 2-propanol.

Table 2. Dependency of quantum yield in the formation of **2a** on concentration of **1a**

Solvent	Initial concentration of **1a** (mole/l × 10^4)	ϕ
Benzene	33·1	0·018
Benzene	8·00	0·020
Benzene	3·79	0·018
Benzene	0·39	0·016
Dioxane	35·9	0·69
Dioxane	8·4	0·53
Dioxane	7·6	0·41
Dioxane	5·9	0·40
Dioxane	4·3	0·30
Dioxane	3·6	0·26
Dioxane	0·38	0·045

Two types of behavior of excited **1a** and **1b** come to attention from these data: (1) In some solvents (benzene and acetonitrile) the quantum yield is small (< 0·1) and is concentration-independent as in benzene; (2) in dioxane 2-propanol, and tetrahydrofuran, the quantum yield is very high and at least in dioxane is dependent on the concentration of **1a** and tends toward a limiting value of around 0·8. These results could be interpreted on the basis of R—H bond energy of solvent in which the excited **1** and/or the radical generated from the excited **1** abstract an H atom. The bond energy with respect to the H atom abstraction in benzene is relatively high (> 100 kcal/mole) and this high energy is enough to retard the hydrogen abstraction by the radical. On the other hand, the excited **1** and/or the radical derived from **1** can abstract an H atom from solvents such as dioxane, 2-propanol, and tetrahydrofuran quite readily, since the C—H bond energies of these solvents being about 75–80 kcal/mole. Similar tendency in the change of the quantum yield in various solvents was also noticed in the photoreduction of benzophenone to benzpinacol.[11, 12] To confirm the occurrence of H atom abstraction, the photolysis of **1a** in the presence of benzhydrol in benzene was carried out, which gave both **2a** and benzpinacol. This result suggests that excited **1a** abstracts the H atom from benzhydrol to give a ketyl radical, which then dimerizes to benzpinacol.

The electronic absorption spectra of **1a** and **1b** in dioxane showed intense bands at 258 (ϵ 3·8 × 10^4), 322 (3·1 × 10^4), 379 (2·2 × 10^4) and a weak band at 536 nm (ϵ 8), intense bands at 240 (ϵ 1·9 × 10^4), 323 (1·3 × 10^4), 408 (1·7 × 10^4) and a weak band at 560 nm (ϵ 13). From the magnitude of the molar extinction coefficients, the intense and weak bands in **1** can be assigned to the π,π^* and n,π^* transitions, respectively. Moreover, the weak band of **1a** showed a blue shift upon addition of methanol, as expected from the n,π^* type of transition.

To elucidate the multiplicity of the excited state of **1**, quantum yields for reactions quenched by dienes were determined in dioxane. The results in Table 3 show that the photoconversion of **1** to **2** was quenched by Z- and E-piperylene and cyclohexa-1,3-diene, good triplet quenchers[13] at the concentration used, although the quenching efficiency was low. A plot of the reciprocal of quantum yield for formation of **2a** *vs* Z-piperylene concentrations gave a good straight line with a slope of 30 M^{-1} and intercept 2·3. This results suggest the photodimerization of **1** to **2** proceeds *via* the triplet state of **1**. This deduction was supported by effective sensitization. The quantum yield in the photolysis of **1a** in dioxane (7·4 × 10^{-4} mole/l) sensitized by 4,4′-bis(dimethylamino)benzophenone (E_T = 61·0 kcal/mole[14]) was 0·80, in which this sensitizer shows a rapid decay rate and efficient intersystem crossing to the triplet state.[14] Both quenching of the excited **1** by dienes and the high quantum efficiency under triplet sensitization indicate that the photodimerization proceeds *via* the triplet state of **1**.

Table 3. Quantum yield of formation of **2a** in the presence of dienes[a]

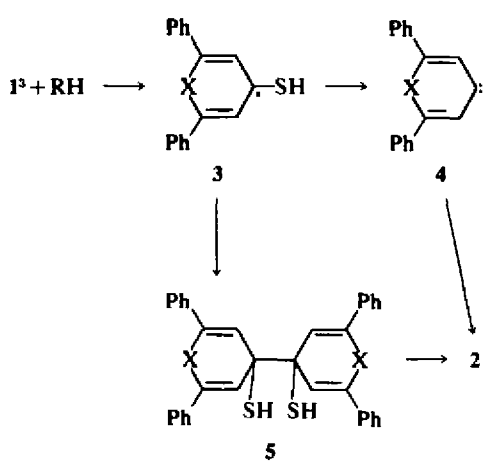
Dienes	Concentration of dienes (M × 10^2)	ϕ
Z-Piperylene	0·17	0·39
Z-Piperylene	1·7	0·35
Z-Piperylene	2·5	0·32
Z-Piperylene	3·2	0·30
E-Piperylene	2·5	0·34
Cyclohexa-1,3-diene	2·6	0·33

[a] Solvent, dioxane; initial concentration of **1a**, 7·6–7·8 × 10^{-4} mole/l.

Next problem is to determine whether the n,π^* or π,π^* triplet state is responsible for this photodimerization. As already described, the UV spectra of **1a** and **1b** showed the π,π^* and n,π^* bands. Direct photolysis of **1a** and **1b** at 360 nm light (π,π^* excitation of **1**) gave **2a** and **2b** in 83 and 86% yield, respectively. On the other hand, the photolysis of **1a** at 546 nm light[15] (n,π^* excitation of **1a**) gave **2a** in 3% yield only. These results, however, cannot be taken as an evidence to support the contention that the photodimerization of **1** to **2** proceeds *via* the π,π^* state of **1**, since the molar extinction coefficients of the n,π^* transition in **1** is much smaller than those of the π,π^* transition. The absorption spectra of **1** suggest that the energy of the n,π^* triplet state lie below 50 kcal/mole, which is lower than that of piperylene ($E_T = 56{\cdot}9$–$58{\cdot}8$ kcal/mole[16]). The quenching of the photodimerization of **1** to **2** by piperylene, however, could be due to energy transfer to a lower form of piperylene[17] or to the reaction of radical intermediate with dienes as in the case of ketyl radical.[18] Therefore, it is not conclusive from low quenching efficiency of the photodimerization by dienes whether the n,π^* or π,π^* triplet state is responsible for the photodimerization of **1**. As mentioned previously, the photolysis of **1** in hydrogen donating solvents produced hydrogen sulfide gas and gave the high quantum efficiency for the formation of **2**. Even in benzene, the formation of hydrogen sulfide gas was detected.[10] The hydrogen abstraction from benzene has recently been proved in photochemical reaction of phenanthrenquinone with benzene.[19] Alkanones, aralkyl ketones, ary ketones, and thiobenzophenones have been long known to be voracious hydrogen atom abstractors, of which the n,π^* excited state is the chemically active state.[11,12,20,21] Lacking additional evidence, the photoreaction of **1** to **2** might proceed mainly *via* the n,π^* triplet state of **1**.

In the photolysis of **1a** in dioxane, the quantitative analysis of hydrogen sulfide[10] indicated that two moles of hydrogen sulfide was formed to the formation of one mole of **2a** within experimental error. Since the hydrogen atom abstraction seems to be a key step for this photoreaction, it was anticipated that the radical formed by the photolysis of **1** can be detected by ESR spectroscopy. This was indeed the case in the photolysis of **1a** in tetrahydrofuran both at room temperature and $-50°$. Lack of hyperfine structure in the spectra, however, prevented the definite identification of the structure of radical.

The mechanism for the photodimerization of **1** to **2** is proposed as below.



Compound **1** in the excited singlet state undergoes intersystem crossing to the n,π^* triplet state which is the chemically reactive species. **1** in the n,π^* triplet state abstracts an H atom from solvent to give the radical, **3**, which might dimerize to **5**, and then oxidized to **2**; alternatively, **3** could get converted to the carbene, **4**, which then would dimerize to the product. An attempt to trap the carbene **4** was unsuccessful. Irradiation of **1b** in the presence of high concentration of Z-1,2-dichloroethylene or diphenylacetylene did not give any stable photoaddition product. **2b** and 2,6-diphenyl-4H-thiopyran-4-one were isolated. Both **1a** and **1b** did not form a "head-to-tail" cage dimer or a dimer involving the cyclobutan ring, as has been observed in the case of 4H-pyran-4-one and 4H-thiopyran-4-one derivatives.[6–8] This could be due to both the nature of the excited state of **1** and the fast hydrogen atom abstraction rate of the chemically reactive species.

EXPERIMENTAL

The m.p's were not corrected. The IR spectra were taken with a JASCO DS-402G spectrophotometer and the UV spectra with a Hitachi 124 spectrophotometer. The mass spectra were run with a Hitachi RMU-6 spectrometer. The ESR spectra were obtained with a JEOL JES-ME-3X spectrometer. 2,6-Diphenyl-4H-thiopyran-4-thione and 2,6-diphenyl-4*H*-thiopyran-4-thione were prepared by the replacement of the CO oxygen of the corresponding ketones with P_2S_5. Their m.p's and spectra (UV, IR and NMR) are consistent with the reported ones[1–3,22] 2,2′,6,6′-Tetraphenyl-4,4′-di(pyranylidene) and 2,2′,6,6′-tetraphenyl-4,4′-di(thiopyranylidene) were prepared according to the El-Kuschef's method.[2] All solvents and chemicals commercially available were purified by distillation or recrystallization.

Preparative photolysis of **1a**. A soln of **1a** (0·67 g) in dioxane (160 ml) was irradiated under N_2 with a 100-W medium-pressure mercury lamp through a Pyrex filter for 50 hr. After removal of solvent under vacuum, the residual reddish black solid was washed with EtOH and was recrystallized from xylene to yield red crystals of **2a** in 80% yield; m.p. 318–319°; UV (dioxane) λ_{max} 270 (ϵ 3·3 × 10^4, sh), 276 (3·4 × 10^4), 437 (3·7 × 10^4) and 458 nm (5·0 × 10^4); IR (KBr) 3045, 1655, 1596, 1494, 920, and 688 cm^{-1}; mass spectrum at *m/e* (relative intensity), 466 (7·2), 465 (37·4), 464 (100, M^+), 435 (3·6), 359 (11·4), 341 (3·6), 257 (6·8), 254 (6·2), 253 (6·2), 232 (26·0, M^{++}), 105 (44·2), 104 (17·7), 91 (22·4), and 77 (28·2). (Found: C, 87·41; H, 5·26; O, 6·75. Calcd. for $C_{34}H_{24}O_2$: C, 87·88; H, 5·21; O, 6·89%.)

Irradiation of **1a** in dioxane ($1{\cdot}3 \times 10^{-2}$ mole/l) with 360 nm light, obtained by filtration through a soln of $CuSO_4 \times 5H_2O-CoSO_4 . 7H_2O$ also gave **2a** in 83% yield.

Preparative photolysis of **1b**. A soln of **1b** (0·5 g) in dioxane (200 ml) was irradiated under the same condition as in the case of **1a**. Similar working-up of the mixture gave dark green crystals of **2b** in 85% yield; m.p. 317–318°; UV (dioxane) λ_{max} 258 (ϵ $4{\cdot}3 \times 10^4$), 265 ($2{\cdot}6 \times 10^4$), and 476 nm ($4{\cdot}3 \times 10^4$); IR (KBr) 3030, 1618, 1592, 1490, 840, 760, and 685 cm^{-1}; mass spectrum at *m/e* (relative intensity) 498 (10·3), 497 (35·9), 496 (100, M^+), 463 (12·8), 419 (51·4), 386 (15·4), 385 (15·4), 248 (37·2, M^{++}), 216 (25·3). 121 (15·4), and 91 (41·0). (Found: C, 82·10; H, 4·93; S, 12·87. Calcd. for $C_{34}H_{24}S_2$: C, 82·22; H, 4·87; S, 12·91%.)

Irradiation of **1a** *at* 546 *nm light*. A soln of **1a** (0·8 g) in dioxane (180 ml) was irradiated under N_2 for 50 hr with a 100-W medium-pressure mercury lamp equipped with the filter system for 546 nm light described by Calvert and Pitts, Jr.[15] The spectrophotometric determination of the concentration of **2a** at 458 nm indicated that **2a** was formed in 3% yield. After concentration of the mixture, only a trace of **2a** was detected by TLC (silica gel).

Irradiation of **1a** *in the presence of benzhydrol*. A mixture of **1a** (0·132 g, $5{\cdot}0 \times 10^{-4}$ M) and 1·58 g of benzhydrol ($8{\cdot}5 \times 10^{-3}$ M) in 180 ml benzene was irradiated under N_2 for 24 hr with a 100-W medium-pressure mercury lamp equipped with a filter system for 360 nm light. After removal of the solvent, the residual solid was chromatographed on silica gel with benzene as eluant to yield 30 mg of **2a** and 100 mg of benzpinacol.

Photolysis of **1b** *in the presence of* Z-1,2-*dichloroethylene*. A soln of **16** (0·5 g) in Z-1,2-dichloroethylene (20 g) was irradiated under N_2 for 50 hr with a 100-W medium pressure mercury lamp through a Pyrex filter. After evaporation of the solvent, column chromatography of the residual solid on silica gel with benzene as eluant yielded **2b** and 2,6-diphenyl-4H-thiopyran-4-one.

Quantum yield determinations. The quantum yield measurements were carried out on a rotating "merry-go-around" assembly using a 100-W medium-pressure mercury arc as the central light source. Samples sealed in ampoules were placed in holders on the assembly approximately 4 cm from the immersion well. The light source was filtered by circulation of a cooled soln containing 75 g of cobaltous sulfate heptahydrate and 100 g of copper sulfate pentahydrate in 1000 ml of water through the cooling jacket of the quartz immersion well. This soln permitted light of the following wavelength distribution to pass through: 15% 3130 Å, 90% 3341 Å, 95% 3650 Å, 20% 4358 Å. Quantum yield determinations were made at room temp. Samples placed in 15 × 200 mm Pyrex tubes were degassed to a pressure of 10^{-3} mmHg or less in three freeze-thaw cycles, and then sealed under vacuum. Potassium ferrioxalate actinometry[23] was used to determine the lamp intensity. An actinometer quantum yield of 1·21 was chosen. Reliably reproducible output rate of $1{\cdot}95 \times 10^{15}$ quanta/sec were recorded. After irradiation the concentration of photoproducts, **2a** and **2b**, was determined at 458 and 476 nm respectively by quantitative ultraviolet spectroscopy. The conversions in **1a** and **1b** were run to 20% or less.

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