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The Photoreaction of 2,6-Diphenyl-4*H*-thiopyran-4-one and Its Related Compounds

Noboru SUGIYAMA, Yoshiaki SATO and Choji KASHIMA

Department of Chemistry, Tokyo Kyoiku University, Otsuka, Tokyo

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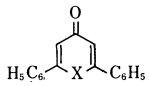
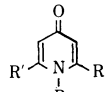
The irradiation of 2,6-diphenyl-4*H*-thiopyran-4-one (**1**) or 2,6-diphenyl-4*H*-pyran-4-one (**2**) in an alcohol in the presence of oxygen gave benzoic acid and a benzoylacetic acid ester, while that of **2** in benzene or 2,6-dimethyl-4*H*-thiopyran-4-one (**5**) in various solvents gave the corresponding cage dimer, (**9**) or (**10**). No photoreaction could be observed in case of the irradiation of 1,2,6-trimethyl-4-pyridone (**3**) and 6-methyl-1,2-diphenyl-4-pyridone (**4**). A reaction mechanism *via* the triplet state of the substrate was also proposed.

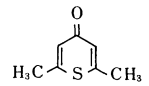
Previously we have reported that the irradiation of 2,6-diphenyl-4*H*-thiopyran-4-one (**1**) in non-polar solvents gave a head-to-tail, antidimer (**8**),[1] while that of 6-methyl-1,2-diphenyl-2,3-dihydro-4-pyridone (**6**) gave 6-methyl-2,5-diphenyl-2,3-dihydro-4(1*H*)-4-pyridone, 5-methyl-2,6-diphenyl-2,3-dihydro-4(1*H*)-4-pyridone and 2-anilino-6-phenyl-2,5-hexadiene-4-one.[2] Now we have found that the irradiation of **1** in polar solvents gave photooxidized products. For comparison, the photoreactions of **1** and its related compounds have been examined.



1 X=S
2 X=O



3 R=R'=CH$_3$
4 R=C$_6$H$_5$, R'=CH$_3$



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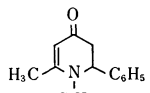

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Results and Discussion

The irradiation of **1** in methanol or ethanol by means of a high-pressure mercury lamp with a Pyrex filter gave benzoic acid and methyl or ethyl benzoylacetate (**7a** or **b**), but in the reaction mixture **8** was not detected. The results of irradiation reactions of **1** under various conditions are summarized in Table 1.

In order to ascertain whether or not this reaction is characteristic of thiopyrones, we studied the photoreaction of 2,6-diphenyl-4*H*-pyran-4-one (**2**),[3] 1,2,6-trimethyl-4-pyridone (**3**)[4] and 6-methyl-1,2-diphenyl-4-pyridone (**4**),[5] in which the sulfur atom in the thiopyrone ring is replaced by an oxygen or nitrogen atom. When **2** in methanol was irradiated under the same conditions as **1**, similar

1) N. Sugiyama, Y. Sato, H. Kataoka, C. Kashima and K. Yamada, This Bulletin, **42**, 3005 (1969); anti-type structure is also supported by the fact that the the further irradiation of this dimer does not give a cage dimer.

2) C. Kashima, M. Yamamoto, Y. Sato and N. Sugiyama, *ibid.*, **42**, 3596 (1969).

3) R. J. Light and C. R. Hauser, *J. Org. Chem.*, **25**, 538 (1960).

4) S. Garratt, *ibid.*, **28**, 1886 (1963).

5) S. Boatman, R. E. Smith, G. E. Morris, W. G. Kofron and C. R. Hauser, *ibid.*, **32**, 3817 (1967).

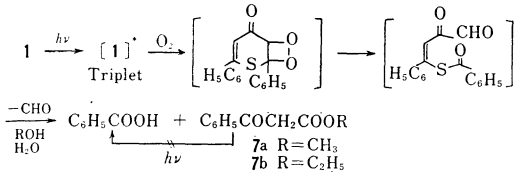
TABLE 1. PHOTOOXIDATION OF **1** AND **2**

Substrate	Solvent (0.01 mol/*l*)	Conditions	Time (hr)	Yield (%) Benzoic Acid	**7a** or **b**	Unreacted **1** or **2**
1	Benzene	P[a]	48	—	—	90
1	Ethanol	P	48	33	8(b)	51
1	Ethanol		26	49	14(b)	—
1	Methanol	P	48	48	8(a)	8
1	Methanol	P N_2 bubbling[b]	48	33	13(a)	21
1	Methanol	P O_2 bubbling	48	32	9(a)	12
1	Methanol	P N_2 sealed[c]	48	—	—	93
1	Methanol (Piperylene 0.02 mol/*l*)	P	48	18	4(a)	65
1	Methanol		26	48	9(a)	—
1	Methanol	O_2 bubbling	24	50	10(a)	—
2	Methanol	P N_2 sealed	168	—	—	98
2	Methanol	P	48	34	8(a)	24

a) Pyrex filter was used. The atmosphere was air.
b) Nitrogen gas was passed through the reaction vessel.
c) Nitrogen gas was passed for an hour before the irradiation and the reaction vessel was sealed with a rubber stopper.

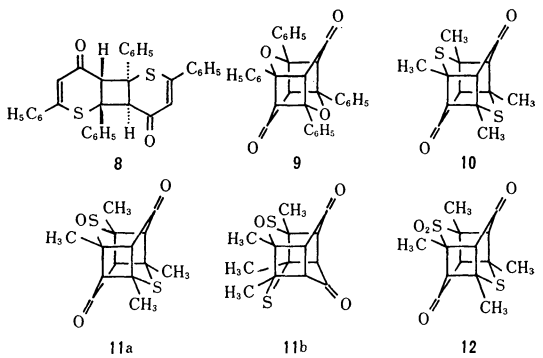
results of photooxidation were obtained, as is shown in Table 1. However, **3** or **4** under various conditions did not show any change, in contrast to the photolysis of **6**.[2]

The mechanism of these photooxidation was examined in detail. It was found that this reaction did not take place when an alcoholic solution of **1** or **2** was sealed in a nitrogen atmosphere before irradiation. Also, the photooxidation was not observed when the **1** in an alcohol was irradiated with a tungsten lamp, using methylene blue or rose bengal as a sensitizer. When **1** was treated with sodium hypochlorite and hydrogen peroxide,[6] no reaction occurred. This fact excluded the possible participation of O_2 in the above photooxidation. When oxygen or nitrogen gas was passed through an alcoholic solution of **1**, the UV absorption of **1** did not show any change; this suggests no participation of the charge-transfer complex at the ground state in this reaction.[7,8] Considering that oxygen seems to quench the excited state



Scheme 1

of **1**, as can be seen by comparing the disappearance rate of **1** under nitrogen with that under oxygen (Table 1), it can be speculated that the triplet state of **1** is an reactive species. This is also supported by the quenching effect with piperylene. The irradiation of **7** under the same conditions as in case of **1** or **2** did not give benzoic acid. All the above facts are in accord with the mechanism shown in Scheme 1, except that there is no clear evidence for the presence of dioxetane or keto-aldehyde intermediates.



On the other hand, when a benzene solution of **2** was irradiated under a nitrogen atmosphere for a week, a dimer (**9**) was obtained in a 37% yield. The structure of **9** seems to be a head-to-tail cage dimer, judging from the following data. The results of elemental analysis and the mass spectrum [*m/e* 391 ($M^+-C_6H_5-C{\equiv}O^+$)] confirm that **9** is a dimeric compound. The UV, IR, and NMR spectra indicate a saturated carbonyl compound. The ther-

6) E. Mckeown and W. A. Waters, *J. Chem. Soc., B*, **1966**, 1040.
7) K. Wei, J.-C. Mani and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **89**, 4225 (1967).
8) K. S. Wei and A. H. Adelman, *Tetrahedron Lett.*, **1969**, 3297.

mal decomposition of **9** afforded only **2**.[9,10] The mass spectrum of **9** shows a strong monomeric peak (*m/e* 248, 36%).

Furthermore, we studied the photoreaction of 2,6-dimethyl-4*H*-thiopyran-4-one (**5**)[11,12] in a benzene, ether, or methanol solution. The irradiation of **5** under a nitrogen atmosphere for 72 hr gave a dimer (**10**) in about a 1% yield in each case. The structure of **10** was determined to be a head-to-tail cage dimer on the basis of the following data.

The results of elemental analysis, the mass (*m/e* 280), UV, IR, and NMR spectra, and the thermal decomposition support the idea that **10** is a cage dimer. The head-to-tail form of **10** is unequivocally confirmed by the NMR spectrum of **11a** as follows. The oxidation of **10** by hydrogen peroxide at room temperature gave monosulfoxide **11a** and monosulfone (**12**). The structures of **11a** and **12** are supported by the results of elemental analysis and and the UV, IR, NMR, and mass spectra. In the NMR spectrum of **12** methine protones show a singlet signal at τ 6.73, while in that of **11a** they show two singlet signals at τ 7.00 and 6.94, indicating that **11a** has a head-to-tail form, for the head-to-head form (**11b**) may be expected to show an AB quartet pattern.

Since the photodimerization of **2** or **5** is strongly inhibited in the presence of oxygen, it seems reasonable to deduce that the triplet state of **2** or **5** is responsible for the photodimerization. Moreover, the photoreaction of **2** or **5** gives a head-to-tail cage dimer, and that of **1** or **2** in the presence of oxygen gives oxidation products, *via* the triplet state.

The theory that the photoreaction depends on the electron density in this pyrone ring has been proposed with regard to the photoreaction of **1** in various solvents.[1] The UV spectra of **2** and **5** in benzene, ether, ethanol, and methanol show little difference compared with that of **1** as will be shown in the Experimental Section. Therefore, it is expected that the photoreaction of **2** or **5** in those solvents would show the similar reaction. Indeed, the same photodimer was isolated in the photoreaction of **5** in benzene, ether, and methanol, but the photolysis of **2** in benzene gave a dimeric product, while that of **2** in methanol gave no product.

Moreover, we found interesting facts in the UV spectra of **9** and **10** and the mass spectra of **10**, **11a**, and **12**. The UV absorption of the 2,6-dimethyl-4*H*-pyran-4-one cage dimer shows a strong charge-transfer absorption at 233 nm (ε 2410).[13] That of **9** shows an absorption at 220 nm (ε 26000, sh), and that of **10** shows an absorption at 240 nm (ε 345). These are very similar to that of 9-thiabicyclo[3.3.1]-non-6-en-2-one (240 nm, ε 290)[14] and that of tetrahydro-4*H*-thiopyran-4-one (233 nm, ε 507).[15] The mass spectrum of **10** does not show any fragments of *p*-benzoquinone (*m/e* 108) or tetramethyl-1,4-dithiahexadiene (*m/e* 172), but it does show that of the correspondine monomer, **5** (*m/e* 140, 80%), as well as those of 2,5-dimethylthiophene (*m/e* 112, base peak), *m/e* 97 (25%) and *m/e* 59 (17%).[16] In addition to the fragment of the monomer **5**, the mass spectra of **11a** and **12** show a desulfoxide or desulfone fragment at *m/e* 148 (3 or 23% respectively), accompanied by decarbonylation, demethylation, decarbonylation and fission to the 1,2-dimethylcyclobutadiene cation radical[16] (Fig. 1, Scheme 2).

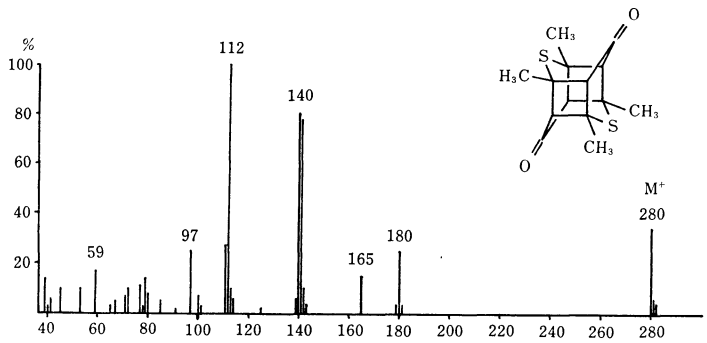


Fig. 1-a. The mass spectrum of **10**.

9) W. Flaig, J.-C. Salfeld and A. Llanos, *Angew. Chem.*, **72**, 110 (1960).

10) R. C. Cookson, D. A. Cox and J. Hudec, *J. Chem. Soc.*, **1961**, 4499.

11) M. Rolla, G. Traverso and M. Sanesi, *Ann. Chim.* (Rome), **42**, 515 and 673 (1952); *Chem. Abstr.*, **42**, 4178i (1948).

12) Ishibe, Kotani and Teramura reported the photoreaction of 4*H*-thiopyran-4-one which gave small amount of a cage dimer at the 22th Annual Meeting of the Chemical Society of Japan, April, 1969, Proceedings III, p. 1363.

13) P. Yates and M. J. Jorgenson, *J. Amer. Chem. Soc.*, **85**, 2956 (1963).

14) A. Padwa, A. Battisti and E. Shefter, *ibid.*, **91**, 4000 (1969).

15) N. J. Leonard, T. L. Brown and T. W. Milligan, *ibid.*, **81**, 504 (1959).

16) H. Budzikiewicz, C. Djerassi and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, p. 527, 625 (1967).

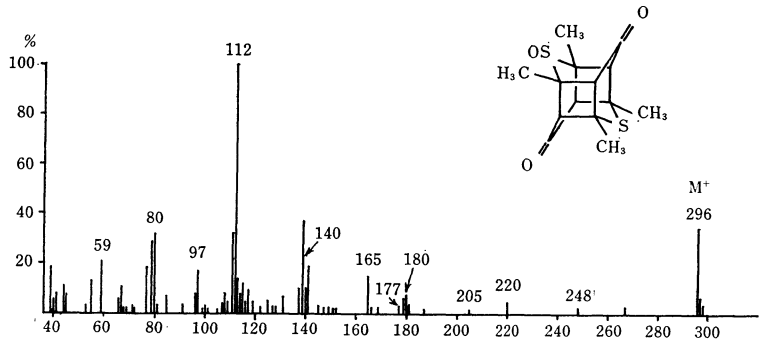


Fig. 1-b. The mass spectrum of **11a**.

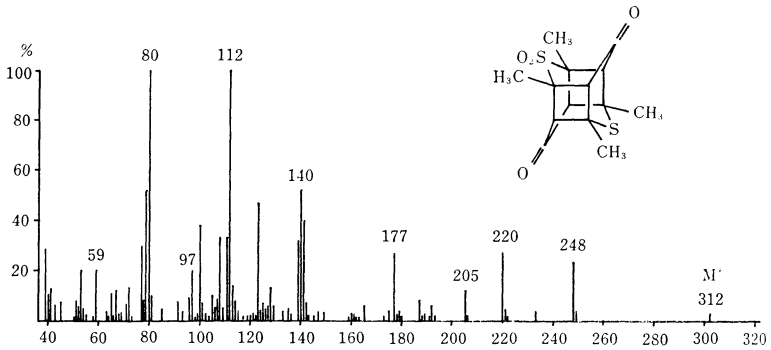
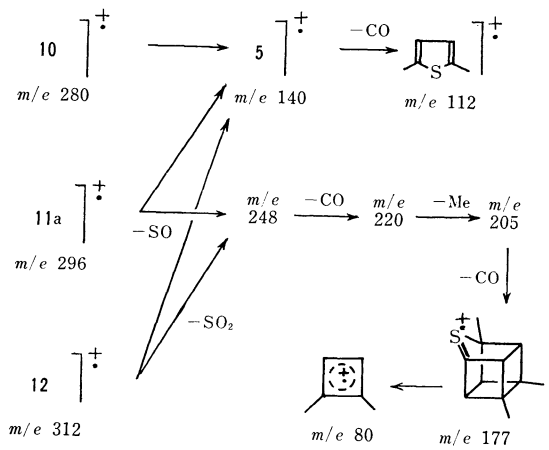


Fig. 1-c. The mass spectrum of **12**.



Scheme 2

Experimental

All the melting points are uncorrected. A Taika H-type 125 W high-pressure mercury lamp and a Toshiba 110 V, 200 W tungsten lamp were used as light sources. The UV, IR, NMR, and mass spectra were measured by means of a Hitachi EPS-3T-type spectrophotometer, a Hitachi EPI-S2-type spectrometer, a Hitachi H-60-type spectrometer, and a Hitachi RMU-6E-type spectrometer, respectively.

Photooxidation of 2,6-Diphenyl-4*H*-thiopyran-4-one (1). After a methanol solution (240 m*l*) of **1** (620 mg) has been irradiated by means of a high-pressure mercury lamp with a Pyrex filter while being stirred at room temperature for 48 hr, the methanol was removed and the residue was chromatographed on silica gel. From the benzene, benzene - ethyl acetate (1 : 1, v/v), and an ethyl acetate eluate, methyl benzoylacetate (**7a**) (33 mg, 8%), unreacted **1** (48 mg, 8%) and benzoic acid (270 mg, 48%) were obtained respectively. Each product was identified with the corresponding authentic sample by comparing the UV, IR, and NMR spectra as well as the R_f value on thin-layer chromatography on silica gel. The results of the photoreaction of **1** under various conditions are summarized in Table 1.

All the starting material was recovered when a methanol solution (30 m*l*) of **1** (100 mg) was treated with sodium hypochlorite (7 m*l*, containing 10—14% chlorine) and hydrogen peroxide (11 m*l*, 3%) by a previously-reported procedure,[6] or when a methanol solution (70 m*l*) of **1** (100 mg) containing methylene blue (5 mg) or rose bengale (5 mg) was irradiated with a tungsten lamp for 30 hr.

Preparation and Photolysis of Methyl Benzoylacetate 7a. By Hauser's method,[17] **7a** was prepared, as copper salt; mp 197—200°C (lit, mp 200—201°C). When a methanol solution (50 m*l*) of **7a** (200 mg) in a Pyrex tube was irradiated under the same conditions as have been described above, the formation of benzoic acid could not be observed.

Preparation of 2,6-Diphenyl-4*H*-pyran-4-one (2).

17) R. Leving and C. R. Hauser, *J. Amer. Chem. Soc.*, **66**, 1768 (1944).

By Hauser's method[3] **2** was prepared; mp 140—141.5°C (lit, mp 138.5—141.5°C). UV: $\lambda_{max}^{Benzene}$ nm (ε) 278 (24500), λ_{max}^{Ether} nm (ε) 257 (23600), 279 (26900), $\lambda_{max}^{Ethanol}$ nm (ε) 257 (22900), 283 (25800), $\lambda_{max}^{Methanol}$ nm (ε) 257 (22100), 285 (24000). IR: (KBr, cm^{-1}) 1645, 1600, 1380. NMR: (τ in $CDCl_3$) 3.19 (s, 2H), 2.53—2.3 (m, 6H), 2.3—2.04 (m, 4H).

Photooxidation and Photodimerization of 2. A methanol solution (240 m*l*) of **2** (600 mg) was irradiated; the photoproducts listed in Table 1 were obtained. After a benzene solution (2 m*l*) of **2** (300 mg) in a Pyrex tube had been irradiated at room temperature under a nitrogen atmosphere for a week, the solvent was removed and the reaction mixture was treated in chloroform to give undissolved white precipitates (**9**) (110 mg (37%)). Reprecipitation from chloroform afforded white powders; mp 268—274°C.

Found: C, 67.54; H, 4.37%. Cacld for $C_{34}H_{24}O_4$–$CHCl_3$: C, 68.35; H, 4.10%.

Recrystallization from methanol afforded colorless cubes; mp 271—278°C.

Found: C, 78.53; H, 5.49%. Calcd for $C_{34}H_{24}O_4$–CH_3OH: C, 79.52; H, 5.34%.

MS: *m/e* 391 (7%), 348 (4%), 248 (36%), 220 (100%), 149 (100%), 105 (40%), 102 (39%). UV: $\lambda_{max}^{Ethanol}$ nm (ε) 220 (26000) sh., 254 (2400) sh., 260 (1950) sh., 266 (1370), sh., 295 (186) sh. IR: (KBr, cm^{-1}) 1700, 1110, 1070. NMR: (τ in Pyridine-d_5) 5.61 (s, 4H), 3.0—2.7 (m, 12H), 2.6—2.2 (m, 8H).

The irradiation of **2** (300 mg) in a methanol solution (30 m*l*) for a week gave no product. When **9** was heated in a test tube, **9** turned quantitatively to **2** at 200°C, with a half life of 5 min, while it turned immediately at the melting point. Below 180°C, even at 10^{-4} mmHg **9** did not sublime at all. The 2,4-dinitrophenylhydrazone of **9** was an orange powder; mp 261—263°C (decomp.).

Found: C, 64.73; H, 3.98; N, 12.67%. Calcd for $C_{46}H_{32}O_{10}N_8$: C, 64.48; H, 3.76; N, 13.08%. UV: $\lambda_{max}^{Ethanol}$ nm (ε) 222 (44100), 256 (27200) sh., 366 (52800). IR: (KBr, cm^{-1}) 1615, 1593, 1510, 1335.

Preparation and Irradiation of 1,2,6-Trimethyl-4-pyridone (3) and 6-Methyl-1,2-diphenyl-4-pyridone (4). By Garratt's method[4] **3** was prepared; mp 245—247°C (lit, 247—248°C). By Hauser's method[5] **4** was prepared; mp 240—243°C (lit, 242—243°C). The irradiation of **3** or **4** in methanol, benzene, or aqueous hydrogen chloride (10%) in a Pyrex tube gave no product.

Preparation of 2,6-Dimethyl-4*H*-thiopyran-4-one (5). To a cold acetic acid solution (236 m*l*) of 2,6-dimethyl-4*H*-thiopyran-4-thione[18] (12 g), hydrogen peroxide (30%, 143 m*l*) and sodium acetate (23.6 g) were added. After the reaction mixture had then been stirred at room temperature for an hour, it turned dark blue; it was then poured into water (500 m*l*), extracted with chloroform, washed with water, and dried. The removal of the solvent gave a crude precipitate, which was recrystallized from water to afford colorless needles; 7.8 g (72%); mp 103—105°C (lit,[11] 104°C). UV: $\lambda_{max}^{Benzene}$ nm (ε) 288 (17700), 296 (13200) sh., λ_{max}^{Ether} nm (ε) 288 (15500), 296 (17700), $\lambda_{max}^{Ethanol}$ nm (ε) 288 (18200), 297 (18200), $\lambda_{max}^{Methanol}$ nm (ε) 288 (17800), 297 (17800). IR: (KBr, cm^{-1}) 1610, 1535. NMR: (τ in $CDCl_3$) 7.63 (s, 6H), 3.28 (s, 2H).

Irradiation of 5. After the irradiation of **5** in benzene (0.5 mol/*l*), ether (0.5 mol/*l*) or methanol (1 mol/*l*) in a Pyrex tube under a nitrogen atmosphere for 72 hr, the solvent was removed and the residue was chromatographed on silica gel with chloroform. The concentration of the eluted fraction gave crude products as pale yellow crystals; the crystals were collected, washed with methanol to afford colorless cubes (**10**) in a 1.3—0.9% yield in each case; mp 340—341°C (decomp.).

Found: C, 59.99; H, 5.75%. Calcd for $C_{14}H_{16}O_2S_2$: C, 60.23; H, 5.82%.

MS: *m/e* 280 (M^+). UV: $\lambda_{max}^{CH_3CN}$ nm (ε) 240 (345), 281 (319). IR: (KBr, cm^{-1}) 1693. NMR: (τ in $CDCl_3$) 8.35 (s, 12H), 6.83 (s, 4H).

In each case, most of the unreacted material (about 96%) was recovered. In the irradiation in the presence of oxygen, all of the starting material was recovered. When the photodimer **10** was heated above 220°C in a pressure tube under an atmosphere of nitrogen, the **10** was sublimed. When the **10** was heated at the melting point, the monomer **5** was obtained (R_f 0.25 on silica-gel thin-layer chromatography with ethyl acetate). Refluxing the photodimer **10** (5 mg) in ethanol (4 m*l*) and aqueous hydrogen chloride (10%, 2.5 m*l*) for an hour gave no other product.

Oxidation of the Photodimer 10 to the Monosulfoxide Dimer (11a) and the Monosulfone Dimer (12). To a cold acetic acid solution (10 m*l*) of **10** (48 mg), we added hydrogen peroxide (30%, 600 m*l*). After the reaction mixture had then been stirred at room temperature for an hour, the mixture was poured into water (50 m*l*) and extracted with chloroform. A procedure similar to that used for the isolation of **10** gave colorless cubes, (**11a**, 22 mg) and (**12**, 20 mg). **11a**; mp 335—340°C (decomp.).

Found: C, 56.47; H, 5.58%. Calcd for $C_{14}H_{16}O_3S_2$: C, 56.75; H, 5.44%.

MS: *m/e* 296 (M^+). UV: $\lambda_{max}^{CH_3CN}$ nm (ε) 223 (2840), 280 (170) sh. IR: (KBr, cm^{-1}) 1695, 1055. NMR: (τ in $CDCl_3$) 8.25 (s, 6H), 8.19 (s, 6H), 7.00 (s, 2H), 6.94 (s, 2H). **12**: mp 354—356°C (decomp.).

Found: C, 53.93; H, 5.22%. Calcd for $C_{14}H_{16}O_4S_2$: C, 53.84; H, 5.16%.

MS: *m/e* 312 (M^+). UV: $\lambda_{max}^{CH_3CN}$ nm (ε) 264 (367), 310 (42) sh. IR: (KBr, cm^{-1}) 1704, 1310, 1106. NMR: (τ in $CDCl_3$) 8.23 (s, 6H), 8.20 (s, 6H), 6.73 (s, 4H).

18) H. Kato, T. Ogawa and M. Ohta, This Bulletin, **33**, 1467 (1960).