(10) J. C. Sheehan, M. Goodman, and G. P. Hess, *J. Amer. Chem. Soc.*, **78,** 1367 (1956).
(11) P. B. Mendershausen and C. C. Sweeley, *Biochemistry*, **8,** 2633 (1969).
(12) (a) C. A. Grob and E. F. Jenny, *Helv. Chim. Acta*, **35,** 2106 (1952); (b) E. F. Jenny and C. A. Grob, *ibid.*, **36,** 1454 (1953).
(13) R. C. Gaver and C. C. Sweeley, *J. Amer. Chem. Soc.*, **88,** 3643 (1966).

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

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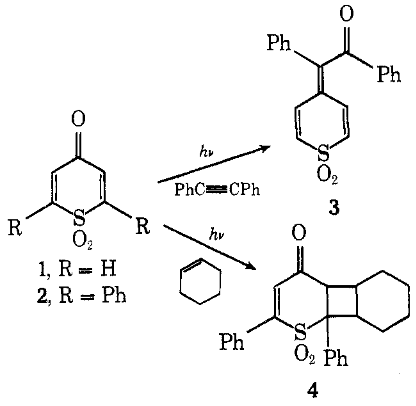
Photoaddition of *p*-quinones to olefins or acetylenes has attracted considerable attention.[2] Two major pathways are cycloaddition of the carbonyl function to the unsaturated carbon–carbon bond to give oxetanes[3] or their rearranged products[4,5] and cycloaddition of the ring double bond of *p*-quinone to a carbon–carbon double or triple bond to yield cyclobutane or cyclobutene derivatives.[6] Even though 4*H*-thiopyran-4-one 1,1-dioxides (1 and 2) are structurally similar to *p*-quinones,[7] only few photochemical studies have so far been reported on this project. Ultraviolet irradiation of 1 and diphenylacetylene yields 3,[8] similar to the photoreaction of *p*-benzoquinone and diphenylacetylene.[4] Also 2 adds photochemically to cyclohexene to form 4,[9] a reaction identical with the photoaddition of 2-methoxy-*p*-benzoquinone to acetylenes.[6]

The present research, photoaddition of 2,6-diphenyl-4*H*-thiopyran-4-one 1,1-dioxide (2) and arylacetylenes, is part of our continued studies on the photoreaction of *p*-quinones and unsaturated hydrocarbons.[5b,10]



A mixture of 2 and an arylacetylene (diphenylacetylene, methylphenylacetylene, or phenylacetylene) in benzene was irradiated with a medium-pressure mercury lamp using a Pyrex filter. Column chromatography of the reaction mixture in each case gave a single product in significant quantity. The infrared spectra of these photoproducts showed strong absorption bands at 1270–1285 and 1110–1125 cm^{-1}, characteristic of antisymmetric and symmetric stretch of the SO_2 group.[11] Absence of a carbonyl band in the infrared rules out structures similar to 3 or 4 as the structure of the photoproduct. The mass spectra obtained at 70 eV for the photoproducts from 2 and diphenylacetylene, methylphenylacetylene, or phenylacetylene displayed the base peak at the highest mass of *m/e* 382, 320, and 306, respectively, their magnitude corresponding to the expulsion of sulfur dioxide from their parent peaks ($M - SO_2$). Lowering the electron energy to 15 eV for the photoproduct of 2 and diphenylacetylene led to the appearance of a weak peak at *m/e* 446, indicative of its mass number. Molecular weights determined by osmometry were 450 and 370 for the products from 2 and diphenylacetylene and 2 and phenylacetylene. These results clearly indicate that the photoproducts are the decarbonylated compounds of the 1:1 adducts of 2 and arylacetylenes. The nmr spectra of the reaction products showed the olefinic and the aromatic protons at δ 6.8–8.0. The ultraviolet spectrum of the photoproduct from 2 and diphenylacetylene exhibited absorptions at 217 nm (ϵ 3.6 $\times 10^4$), 265 (2.6×10^4), and 315 (5.4×10^3). This spectrum appears to match that of tropone,[12] while the uv spectrum of the parent thiepin 1,1-dioxide[13] is similar to that of cycloheptatriene.[14] Naturally these spectral properties suggest that the photoproducts have the structure of thiepin 1,1-dioxide.[13,15,16]

Confirmation of the thiepin 1,1-dioxide structure was obtained by thermolysis and hydrogenation of the photoproduct from 2 and diphenylacetylene (Scheme I). Heat-

Scheme I

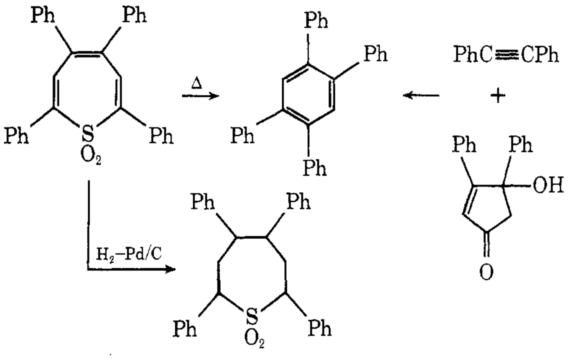
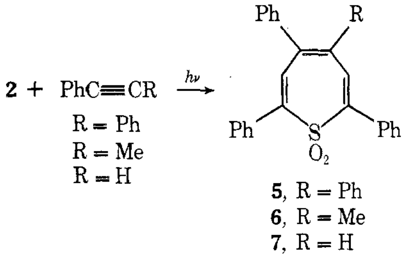


Table I
Spectral and Physical Data for the Photoproducts

Product	Yield, %	Mp, °C	Ir, cm^{-1} (KBr)	Uv (CH_2Cl_2) λ, nm	Uv (CH_2Cl_2) ε	Nmr, δ (acetone-d_6)	Mass spectra, *m/e* (rel intensity) (70 eV)	Mol wt	Anal. Calcd (found), % C	H	O	S
5	60[a]	224–225	1600, 1490, 1285, 1125, 755, 685	217 265 315	36,330 26,000 5,400	7.1–6.2 (m, 10 H) 7.3–7.6 (m, 10 H) 7.9–8.0 (m, 2 H)	496 (M^+, <1)[d], 383 (32), 382 (100), 381 (81), 367 (6), 305 (14), 304 (8), 291 (13), 290 (6), 289 (5)	450	80.54 (80.69)	4.85 (4.96)	7.01 (7.01)	7.07 (7.02)
6	26[b]	88–92	1490, 1445, 1285 1120, 760, 690			1.33 (s, 3 H) 6.87 (s, 1 H) 6.97 (s, 1 H) 7.0–7.8 (m, 15 H)	321 (28), 320 (100), 305 (33), 304 (22), 272 (21)		78.10 (77.92)	5.24 (5.01)		8.34 (8.35)
7	20[c]	172–174	1595, 1485, 1440 1120, 760, 690			7.0–7.3 (m, 11 H) 7.5–7.7 (m, 5 H) 7.9–8.0 (m, 2 H)	307 (25), 306 (100), 305 (20), 290 (20), 288 (21), 102 (33), 91 (20) 77 (29)	370	77.81 (78.07)	4.96 (5.01)		8.44 (8.44)

[a] Recovery of **2** was 11%. [b] Recovery of **2** was 35%. [c] Recovery of **2** was 27%. [d] At 15 eV.

ing of **5** in tetralin yielded 1,2,4,5-tetraphenylbenzene, which is identical (melting point, ir and nmr spectra) with the authentic sample prepared from 3,4-diphenyl-4-hydroxycyclopent-2-en-1-one with diphenylacetylene.[17] Hydrogenation of **5** over Pd/C resulted in the uptake of 3 molar equiv of hydrogen and gave 2,4,5,7-tetraphenylthiacycloheptane 1,1-dioxide. The thermal decomposition to the benzene derivative and sulfur dioxide and ready catalytic hydrogenation to hexahydrothiepin 1,1-dioxide are characteristic with thiepin 1,1-dioxide.[13] These results, in addition to the spectral properties, support the contention that the photoproducts of **2** with diphenylacetylene, methylphenylacetylene, and phenylacetylene are **5**, **6**, and **7**,[18] respectively.



5, R = Ph
6, R = Me
7, R = H

Irradiation of a mixture of **2** and dimethyl acetylenedicarboxylate in benzene resulted in the recovery of the starting materials, whereas photolysis of **2** and 2- or 3-hexyne in benzene gave a polymeric material. Irradiation of a mixture of 3,5-diphenyl-4*H*-thiopyran 1,1-dioxide and diphenylacetylene did not furnish thiepin 1,1-dioxide derivative. The nature of the substituents, both in 4*H*-thiopyran-4-one 1,1-dioxide and acetylenes, seems to be important in the formation of thiepin 1,1-dioxide. Careful study of the ultraviolet spectra of a mixture of **2** and diphenylacetylene in benzene or cyclohexane showed no specific interaction in the ground state, although **2** was expected to function as an electron acceptor in a charge-transfer complex, as has been observed in the case of *p*-quinones.[20]

Experimental Section

Melting points were not corrected. The infrared spectra were recorded on a JASCO DS-402G spectrophotometer. The ultraviolet spectra were obtained with a Hitachi 124 spectrophotometer and the nmr spectra were measured with a JEOL PS-100 spectrometer. The mass spectra were recorded on a Hitachi RMU-6L spectrometer. The molecular weights were determined by a Hitachi 115 molecular weight measuring apparatus.

2,6-Diphenyl-4*H*-thiopyran-4-one 1,1-dioxide[21] was prepared by the oxidation of 2,6-diphenyl-4*H*-thiopyran-4-one with hydrogen peroxide. Arylacetylenes commercially available were used, after purification by distillation or recrystallization.

Irradiation of 2 with Arylacetylenes. A mixture of **2** (0.3 g) and arylacetylene (1.2–3.0 g) in benzene (300 ml) was irradiated under nitrogen for 4 hr using a 300-W medium-pressure mercury lamp equipped with a Pyrex filter. After removal of the solvent, the residual solid was chromatographed on silica gel with cyclohexane–benzene to yield a colorless solid, which was recrystallized from *n*-hexane to give the thiepin 1,1-dioxides. The spectral and physical data of the photoproducts are summarized in Table I.

Thermolysis of 5 in Tetralin. A solution of **5** (0.1 g) in tetralin (3 ml) was refluxed for 3 hr. The reaction mixture was chromatographed on silica gel and eluted with cyclohexane–benzene to give a colorless solid. This solid was recrystallized from ligroin to furnish 1,2,4,5-tetraphenylbenzene in 63% yield: mp 274–275°; *mmp* 272–275°; nmr ($CDCl_3$) δ 7.25 (s, 20 H), 7.57 (s, 2 H).

Anal. Calcd for $C_{30}H_{22}$: C, 94.13; H, 5.89. Found: C, 94.20; H, 5.80.

Catalytic Hydrogenation of 5. Catalytic hydrogenation of **5** (0.06 g) in ethyl acetate (50 ml) with 10% Pd/C was carried out at room temperature under 15 atm for 50 hr. After removal of the solvent under reduced pressure, preparative thin layer chromatography of the residual solid afforded 2,4,5,7-tetraphenylthiacycloheptane 1,1-dioxide in 60% yield: mp 308–310°; ir (KBr) 1585, 1480, 1435, 1280, 1125, 755, 690 cm^{-1}; nmr ($CDCl_3$) δ 1.2–2.6 (m, 8 H), 7.0–8.0 (m, 20 H).

Anal. Calcd for $C_{30}H_{28}O_2S$: C, 79.61; H, 6.24. Found: C, 79.48; H, 6.28.

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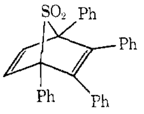
Registry No. 2, 41068-60-4; **5,** 42867-24-3; **6,** 42867-25-4; **7,** 42867-26-5; diphenylacetylene, 501-65-5; methylphenylacetylene, 673-32-5; phenylacetylene, 536-74-3; 2,6-diphenyl-4*H*-thiopyran-4-one, 1029-96-5; 1,2,4,5-tetraphenylbenzene, 3383-32-2; 2,4,5,7-tetraphenylthiacycloheptane 1,1-dioxide, 42867-28-7.

References and Notes

(1) Author to whom correspondence should be addressed at the Dow Chemical Co., Research and Development Laboratory, Freeport, Texas 77541.
(2) For recent reviews, see R. D. Arnold, *Advan. Photochem.*, **6**, 301 (1968); J. M. Bruce, *Quart. Rev., Chem. Soc.*, **21**, 405 (1968).
(3) J. A. Barltrop and H. A. Carless, *Chem. Soc. Rev.*, **1**, 465 (1972); *J. Amer. Chem. Soc.*, **94**, 8761 (1972), and references cited therein.
(4) H. E. Zimmerman and L. Craft, *Tetrahedron Lett.*, 2131 (1964); C. Bryce-Smith, G. I. Frey, and A. Gilber, *ibid.*, 2137 (1964).
(5) (a) H. Gotthardt, R. Steinmetz, and G. S. Hammond, *J. Org. Chem.*, **33**, 2774 (1968); (b) N. Ishibe and I. Taniguchi, *Tetrahedron*, **27**, 4883 (1971).
(6) S. P. Pappas, B. C. Pappas, and N. A. Portnoy, *J. Org. Chem.*, **34**, 520 (1969), and references cited therein.
(7) E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, **70**, 1813 (1948).
(8) L. A. Paquette and L. Wise, unpublished results, cited in E. Block, *Quart. Rep. Sulfur Chem.*, **4**, 324 (1969).
(9) N. Sugiyama, Y. Sato, T. Nishio, and H. Aoyama, 24th Annual Meeting of the Chemical Society of Japan, Osaka, 1971, Abstract 3, p 1370.
(10) N. Ishibe and Y. Yamaguchi, *J. Chem. Soc., Perkin Trans. 1*, in press; N. Ishibe, K. Hashimoto, and Y. Yamaguchi, manuscript in preparation.
(11) L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen, London, 1968, p 219.
(12) H. J. Dauben and H. J. Ringold, *J. Amer. Chem. Soc.*, **73**, 876 (1951); W. von E. Doering and F. L. Detert, *ibid.*, **73**, 876 (1951).
(13) W. L. Mock, *J. Amer. Chem. Soc.*, **89**, 1281 (1967).
(14) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **76**, 3203 (1954).
(15) L. A. Paquette and S. Maiorana, *J. Chem. Soc., Chem. Commun.*, 313 (1971).
(16) For a review, see L. A. Paquette, "Nonbenzenoid Aromatics," Vol. 1, J. P. Snyder, Ed., Academic Press, New York, N. Y., 1969, p 250.
(17) W. Dilthey and G. Hartig, *Chem. Ber.*, **67**, 2004 (1934).
(18) A referee pointed out the possibility **8** for the structure of **5**. It seems, however, unlikely that **8** is stable at room temperature, since the 7-thiabicyclo[2.2.1]hepta-2,5-diene derivative, never isolated, was proposed only as a reaction intermediate.[19] Moreover, cycloaddition of **5** with tetracyanoethylene or dimethyl acetylenedicarboxylate did not occur, while a homo-Diels–Alder reaction of *norbornadiene is well established*. We believe that the photoproduct has the structure of thiepin 1,1-dioxide, though the structure **8** cannot be ruled out conclusively.



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(19) T. J. Barton, M. D. Martz, and R. G. Zika, *J. Org. Chem.*, **37**, 552 (1972).
(20) R. Foster, D. L. Hammick, and P. J. Placito, *J. Chem. Soc.*, 3881 (1956).
(21) R. Arndt, P. Nachwey, and J. Pusch, *Chem. Ber.*, **58**, 1633 (1925).

The Synthesis of 2-Methylproline and 2-Methylornithine

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Interest in analogs of the natural amino acids has increased at a rapid rate since du Vigneaud, *et al.*,[1] first re-