Registry No.—**1,** 75-97-8; **2,** 564-04-5; **3,** 5405-79-8; **4,** 19078-97-8; **5,** 5340-64-7; **6,** 22921-92-2; **7,** 14705-50-7; **8,** 17535-47-6; **9,** 17535-48-7; **10,** 17535-49-8; **11,** 18295-58-4; **12,** 31938-27-9; $CH_3COCH_2COCH_3$, 123-54-6; $CH_3COCH(CH_3)COCH_3$, 815-57-6; $CH_3COCH(Et)COCH_3$, 1540-34-7; $CH_3COCH(n\text{-}Pr)COCH_3$, 1540-35-8; $CH_3COCH(i\text{-}Pr)COCH_3$, 1540-3-81.

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Photodimerization of 4-Thiapyrone

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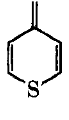
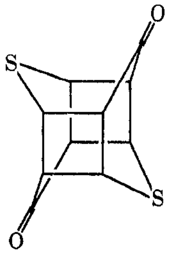
The photodimerization of unsaturated six-membered ring ketones which bear a heteroatom has been studied extensively. The structure of these photodimers depends upon the fragments of a polyene system which participate in a photoreaction. [2 + 2] cycloaddition products are obtained from 2-coumarins,[1] 2,3-dihydro-2,6-dimethyl-4-pyrone,[2] 2-pyrone,[3] and 2,6-diphenyl-4-thiapyrone;[4] [4 + 4] cycloaddition products from 4,6-dimethyl-2-pyrone[3] and 2-pyridones;[5] [2 + 2 + 2 + 2] cycloaddition products from 2,6-dimethyl-4-pyrone[6] and 2,6-dimethyl-4-thiapyrone.[7]

The present study is an attempt to extend these observations to 4-thiapyrone (I). The result on the photodimerization of I is reported here.

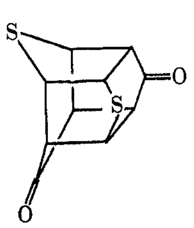
The irradiation of a 1% acetonitrile solution of I under nitrogen in a quartz tube with a medium-pressure lamp gave a photodimer, 3,9-dithiapentacyclo$[6.4.0.0^{2,7}.0^{4,11}.0^{5,10}]$dodecane-6,12-dione (II). The structure of II was determined from the following spectral data. An examination of its nmr spectrum showed a multiplet at δ 3.45–3.70 assigned to the four α-carbonyl protons and a second multiplet at δ 4.55–4.80 ascribed to the four α-sulfide protons. There was no absorption attributable to an olefinic proton. The photoproduct no longer showed uv absorption characteristic of an unsaturated ketone. The infrared spectrum of the photoproduct has a strong carbonyl absorption at 1710 cm^{-1} and lacks other significant absorption in the 1650–1750-cm^{-1} region. The mass spectrum of the photoproduct displays a parent peak at *m/e* 224, which suggests that the photoproduct is a dimer of I. Moreover, the molecular weight determined by vapor pressure osmometry was 212, which was consistent with a dimeric species. From these results the alternative structures III and IV, in addition to II, could be written for this photodimer.



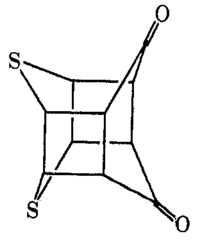
I



II



III



IV

Of these, III can be eliminated since there was no ir absorption of the carbonyl group in the five-membered ring (1745 cm^{-1}).[8] In the mass spectrum of the photodimer, the presence of a peak at *m/e* 112 corresponding to the ion of 4-thiapyrone, $(C_5H_4SO)^+$, and the absence of peaks at *m/e* 116 and 108 corresponding to the ions of 1,4-dithiacyclohexadiene, $(C_4H_4S_2)^+$, and 1,4-benzoquinone, $(C_6H_4O_2)^+$, respectively, suggest that the photodimer is assigned to the "head-to-tail" structure (II). Moreover, this assignment is confirmed from the fact that in addition to the peak of monomer I, an intense peak at *m/e* 86 was observed which may arise from I by expulsion of acetylene,[9] while the fragments at *m/e* 82, 80, and 54 were not observed, which could be expected from 1,4-benzoquinone ion.[10] These results indicate that the photoproduct has the structure II.

While the irradiation of I in dioxane (2% solution) gave II in 2% yield, II was obtained in very low yield (<1%) from the irradiation of a 2% methanol solution of I. The 10% acetonitrile solution of I did not increase the yield of II. The photoreaction of I sensitized by benzophenone resulted in formation of II in 2% yield. This result suggests that the photodimerization of I proceeds *via* the excited triplet state of I.

The photodimerization of I leads exclusively to the head-to-tail [2 + 2 + 2 + 2] cycloadduct in striking contrast to 2,6-diphenyl-4-thiapyrone[4] and in close analogy with 2,6-dimethyl- and 2,6-diethyl-4-pyrone[6,11] and 2,6-dimethyl-4-thiapyrone.[7] The presence of the phenyl group in the thiapyrone could increase the steric barrier to [2 + 2 + 2 + 2] cycloaddition. At the same time this could affect the nature of the excitation

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(1) C. H. Krauch, S. Faird, and G. O. Schenck, *Chem. Ber.*, **91**, 625 (1966); G. S. Hammond, C. A. Stout, and A. A. Lamola, *J. Amer. Chem. Soc.*, **86**, 3103 (1964).

(2) P. Yates and D. J. McGeor, *Tetrahedron Lett.*, 455 (1969).

(3) P. de Mayo and R. W. Yip, *Proc. Chem. Soc.*, 84 (1964); W. H. Pirkle and L. H. Mckendry, *J. Amer. Chem. Soc.*, **91**, 1179 (1969); C. T. Bedford, J. M. Forrester, and T. Money, *Can. J. Chem.*, **48**, 2645 (1970); J. P. Guthrie, C. L. McIntosh, and P. de Mayo, *ibid.*, **48**, 237 (1970).

(4) N. Sugiyama, Y. Sato, H. Kataoka, C. Kashima, and K. Yamada, *Bull. Chem. Soc. Jap.*, **42**, 3005 (1969).

(5) E. C. Taylor and R. O. Kan, *J. Amer. Chem. Soc.*, **85**, 776 (1963); L. A. Paquette and G. Slomp, *ibid.*, **85**, 765 (1963).

(6) P. Yates and M. J. Jorenson, *ibid.*, **80**, 6150 (1958); *ibid.*, **85**, 2956 (1963).

(7) N. Sugiyama Y. Sato, N. Kashima, and K. Yamada, *Bull. Chem. Soc. Jap.*, **43**, 3205 (1970).

(8) K. Nakanishi, "IR Absorption Spectroscopy," Nankodo, Tokyo, 1960, p 48.

(9) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco Calif., 1967, p 208.

(10) Reference 13, p 527.

(11) P. Yates and E. S. Hand, *J. Amer. Chem. Soc.*, **91**, 4749 (1969), and the previous papers.

step and/or the reaction of the excited state with a ground-state molecule.

Experimental Section

Melting points are uncorrected. The infrared spectra were recorded on a JASCO DS-402G spectrophotometer; the ultraviolet spectra were obtained with a Hitachi 124 spectrophotometer; the nmr spectra were measured with a JEOLCO C-60HL spectrometer using tetramethylsilane as an internal standard; the mass spectrum was recorded on a Hitachi RMU-6E spectrometer; the molecular weight was determined by a Hitachi 115 molecular weight measuring apparatus.

4-Thiapyrone (I).—4-Thiapyrone was prepared by the method of Arndt and Bekir,[12] which gave a colorless needle after recrystallization from carbon tetrachloride, mp 110° (lit.[12] 110°). The uv and nmr spectra are consistent with the reported spectra.[13,14]

Direct Irradiation of I.—A solution of 2 g of I in 200 ml of acetonitrile was irradiated for 50 hr with a 100-W medium pressure mercury arc through a quartz filter. Purified nitrogen was passed through the solution during irradiation. After removal of solvent under vacuum the residual solid was chromatographed on a silica gel with benzene–chloroform eluent to yield 40 mg of II. After isolation of II 95% of I was recovered. II, a colorless solid, was recrystallized from acetone: mp 248° dec; uv $\lambda_{max}^{CH_3CN}$ 307 nm (ϵ *ca.* 100); ir (KBr) 1710 cm^{-1} ($\nu_{C=O}$); nmr (DMSO-d_6) δ 3.45–3.70 (m, 4 H) and 4.55–4.80 (m, 4 H); the principal peaks of mass spectrum at *m/e* (rel intensity) 224 (48.5), 149 (23.5), 137 (16.0), 113 (60.0), 112 (100.0), 86 (44.0), 84 (61.7), 58 (37.8), and 57 (22.7).

Anal. Calcd for $C_{10}H_8O_2S_2$: C, 53.55; H, 3.59; O, 14.27; S, 28.59. Found: C, 53.45; H, 3.71; O, 14.40; S, 28.38.

Photosensitized Reaction of I.—A 200-ml benzene solution of 2 g of I and 1 g of benzophenone was irradiated for 50 hr with a 100-W medium-pressure mercury lamp filtered by a Pyrex glass. After similar work-up described above, 42 mg of II was isolated.

Registry No.—I, 1003-41-4; II, 32538-05-9.

Acknowledgments.—The authors are grateful to Professor K. Teramura for his interest in this work.

[12] F. Arndt and N. Bekir, *Chem. Ber.*, **63**, 2393 (1930).

[13] J. Jones, W. Derbyshire, and H. S. Gutowsky, *J. Phys. Chem.*, **69**, 1 (1965).

[14] R. Mayer, W. Brey, and R. Zahradnik, *Advan. Heterocycl. Chem.*, **8**, 249 (1967).

Rearrangement of the Grignard Reagent from 5-Chloro-1-pentene-*5,5-d*$_2$[1]

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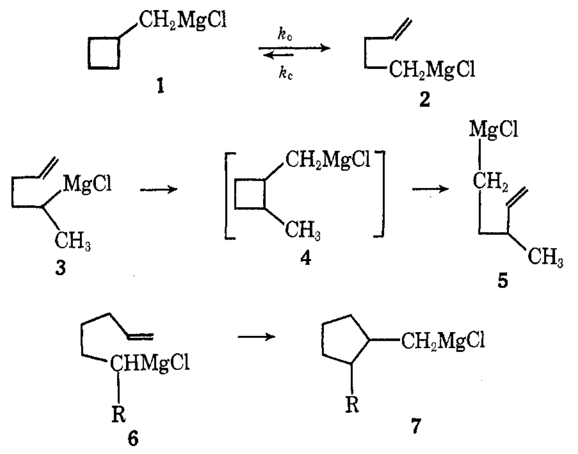
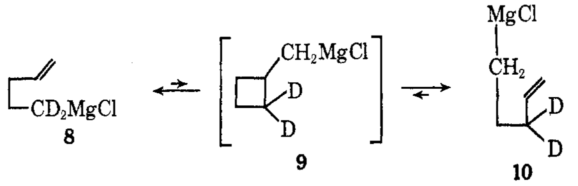
In previous work, it has been shown that the Grignard reagent **1** from cyclobutylmethyl chloride undergoes a ring-cleavage rearrangement to **2**.[2] In addition, rearrangement of Grignard reagent **3** to **5** was observed, the cyclized reagent **4** being proposed as an intermediate.[2a] In the latter case, the reaction most probably has as its driving force the conversion of a secondary Grignard reagent into a more stable primary one. Ring closure to a five-membered ring has also been observed[3] (eq 3). It thus appeared desirable to demonstrate directly the reversibility implied in eq 1.



A Grignard reagent was prepared from 5-chloro-1-pentene-*5,5-d*$_2$ in tetrahydrofuran. The original solution lacked the high-field nmr signal of hydrogens α to a magnesium. However, after heating for several hours at 140°, a high-field triplet from **10** appeared. From the rate of appearance of the α-proton signal, the rate of approach to equilibrium was determined.



After correction for Grignard reagent destroyed by reaction with the solvent (see Experimental Section), approximate rate constants of 3×10^{-6} sec^{-1} at 140° and 3.5×10^{-5} sec^{-1} at 160° were determined. If possible secondary isotope effects on the rates and equilibria are ignored, the rate of ring closure equals the rate of approach to equilibrium: each act of ring closure would produce a molecule of **9**, which on cleavage, has an equal probability of yielding isomer **8** or **10**.

1-Pentene, isolated from hydrolysis of a solution heated for several half-lives, was examined by nmr. Integration showed that about 40% of the 1-pentene had the deuterium distribution corresponding to **10**.

Extrapolation of rate constants for the *cleavage* of the cyclobutylmethyl Grignard reagent (see Experimental Section) yields a value of 7.5×10^{-3} sec^{-1} at 140°. With the ring closure rate, an equilibrium constant of 2.5×10^3 is derived for eq 1. In principle, it should be possible to derive ΔH for eq 1 from the temperature dependence of this equilibrium constant, and hence an estimate of the strain energy of the cyclobutane ring. Because of the competing reaction with solvent, the present kinetics are insufficiently precise to allow this approach. However, by an alternative approach, ΔG and an estimate of ΔS[4] for eq 1 may be combined to yield $\Delta H = -2.1$ kcal/mol.

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[1] This research was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

[2] (a) E. A. Hill, H. G. Richey, Jr., and T. C. Rees, *J. Org. Chem.*, **28**, 2161 (1963); (b) E. A. Hill and J. A. Davidson, *J. Amer. Chem. Soc.*, **86**, 4663 (1964).

[3] H. G. Richey, Jr., and T. C. Rees, *Tetrahedron Lett.*, 4297 (1966); E. A. Hill, R. J. Theissen, R. A. Doughty, and R. Miller, *J. Org. Chem.*, **34**, 3681 (1969).

[4] This estimate, 10.6 eu at 140°, uses the gas-phase entropy change of the model reaction methylcyclobutane $\leftrightarrows$ 1-pentene. The entropy of methylcyclobutane was obtained by adjustments from the published value for cyclobutane: G. W. Rathjens, Jr., N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, *J. Amer. Chem. Soc.*, **75**, 5634 (1953). The authors may be consulted for further details.