chloric acid. A white inorganic solid, which did not burn, precipitated on cooling. Its ir spectrum showed the following absorptions: 3000 (m), 2640 (m), 2540 (m), 1675 (s), 1580 (m), 1550 (m), 1455 (m), 1425 (m, sh), 1410 (m), 1305 (m), 1280 (m), 1255 (s), 1200–1030 (s, broad), 900 (m), 810 (m), 740 (s), and 690 (m) cm^{-1}. The solid was refluxed for 24 hr in 50 ml of concentrated hydrochloric acid. A tan solid precipitated when the solution was cooled. The filtrate was washed with two 50-ml portions of chloroform which were combined and evaporated to dryness leaving an additional amount of the tan solid. Recrystallization from methanol-water afforded 0.287 g (8.98×10^{-4} mol, 79.9%) of pure tan solid, mp 302–303° (uncor). The ir spectrum showed the following absorptions: 3000–2800 (m), 2640 (w), 2540 (w), 1680 (s), 1580 (m), 1555 (m), 1455 (m), 1410 (m), 1305 (m), 1285 (m), 1255 (s), 1165 (w), 1145 (m), 1115 (w), 1055 (m), 1035 (m), 960 (w), 900 (m, broad), 810 (m), 740 (s), and 693 (m) cm^{-1}. Based on the ir spectrum and a mixture melting point, 301.5–302.5° (authentic sample from Aldrich Chemical Co., mp 304°), the compound was identified as 2,2′-dicarboxyphenyl disulfide.

The dioxane was removed by means of a rotating evaporator leaving 0.153 g (8.42×10^{-4} mol, 71.2%) of a clear oil. A comparison of the ir spectrum of the oil with an authentic sample of benzophenone indicated that the two compounds were identical. Treatment with an acidic solution of 2,4-dinitrophenylhydrazine gave a bright orange solid. This was dissolved in a minimum amount of chloroform and chromatographed on a Florisil (100–200 mesh) column. The column was eluted with chloroform. Two bands separated with the first being bright orange and the second a deep red. After evaporation of solvent and recrystallization from chloroform–ethanol the first band afforded benzophenone 2,4-dinitrophenylhydrazone, mp 237–238°, mmp 237–238°. An authentic sample of the 2,4-dinitrophenylhydrazone was prepared from benzophenone and its ir spectrum and melting point (238°) were identical with those of the hydrazone obtained from the product of hydrolysis of the 2,2-diphenyl-3,1-benzoxathian-4-one. The red band afforded 2,4-dinitrophenylhydrazine, mp 199°.

Registry No.—Thiobenzophenone, 1450-31-3; benzenediazonium-2-carboxylate, 18761-40-5; 1, 19185-81-0.

2,4,5-Triphenyl-2H-1,3-oxathiole from Desyl Thiocyanate[1]

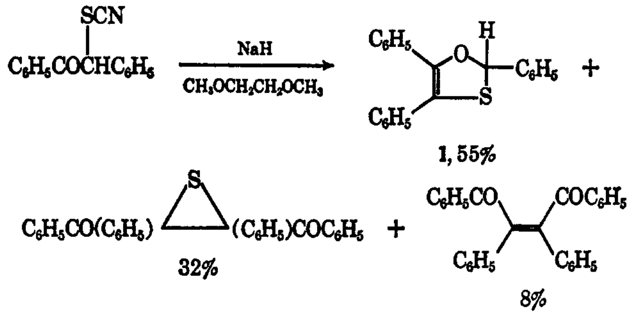
George E. Kuhlmann and Donald C. Dittmer

Department of Chemistry, Bowne Hall, Syracuse University, Syracuse, New York 13210

Received September 12, 1968

A pale yellow solid, $C_{21}H_{16}OS$ (55% yield, mp 77–78°), was obtained when desyl thiocyanate (2-thiocyanato-2-phenylacetophenone) was treated with excess sodium hydride in 1,2-dimethoxyethane. *cis*-Dibenzoylstilbene episulfide (2,3-dibenzoyl-2,3-diphenylthiirane, 32%) and *cis*-dibenzoylstilbene (8%) were isolated also from the reaction mixture. When the sodium hydride was not in excess, a 75–85% yield of yellow *cis*-dibenzoylstilbene episulfide was obtained, as had been reported previously.[2]

The data for compound $C_{21}H_{16}OS$ are consistent with the structure 2,4,5-triphenyl-2H-1,3-oxathiole (**1**). Few simple 1,3-oxathioles are known,[3] and this new method may be applicable generally to the synthesis of 2,4,5-triaryl-1,3-oxathioles. The structure of the oxathiole was deduced from an analysis for elements, a molecular weight determination, the infrared, ultraviolet, and proton nmr spectra, and the mass spectrum.



The infrared spectrum showed absorption at 3030 (aromatic protons), 2880 (benzylic proton), 1620 (carbon–carbon double bond), 1245 (asymmetric carbon–oxygen stretching), and 1060 cm^{-1} (symmetric carbon–oxygen stretching). Absorption in the infrared spectrum of 2-trichloromethyl-4,5-diphenyl-1,3-dioxole at 1667, 1250, and 1124 cm^{-1} has been ascribed to the carbon–carbon double bond and to the carbon–oxygen bonds, respectively.[4] In 1,3-dioxole itself there is absorption at 1631, 1176–1156, and 1087–1075 cm^{-1}.[5] The ultraviolet spectrum of the oxathiole in 95% ethanol shows maxima at 225 mμ (ϵ 18,600) and 342 mμ (ϵ 6760). The ultraviolet spectrum of 5,6-dihydro-1,4-oxathiin has an absorption maximum at 229 mμ (ϵ 3820)[6] and 2,3-diphenyl-5,6-dihydrooxathiin is reported to be pale yellow[7] but spectroscopic data were not given.

The proton nmr spectrum (60 MHz, $CDCl_3$) shows a complex multiplet at 433 Hz and a singlet at 418 Hz relative to tetramethylsilane. The ratio of the areas of the two absorptions was 14.4:1 which is close to the 15:1 ratio calculated for the oxathiole. The benzylic proton presumably causes the absorption at 418 Hz; it is at low field because it is adjacent to an oxygen atom, a sulfur atom, and a phenyl ring. Diamagnetic anisotropy effects of the carbon–carbon double bond, the sulfur atom, and the phenyl rings probably have a role in deshielding the benzylic proton. The absorption of the aliphatic proton in 2-trichloromethyl-4,5-diphenyl-1,3-dioxole appears at 373 Hz.[4]

Mass spectrometry (Scheme I) supports the molecular formula $C_{21}H_{16}OS$. The molecular ion (P) was also the base peak and prominent fragments occurred at *m/e* 284 (P − S), 283 (P − SH), 239 (P − C_6H_5), 211 (P − C_6H_5CO), 210 (P − C_6H_5CHO), 178 (P − C_6H_5CHO − S), 167 and 165. The fragments at *m/e* 165 and 167 may be fluorenyl-type ions whose formation would involve a migration of a phenyl group. Treatment of a small amount of the oxathiole with refluxing ethanolic hydrogen chloride gave hydrogen

---

[1] This work was aided by Grant GP-5513 of the National Science Foundation and by Grant CA 08250 of the National Cancer Institute, National Institutes of Health.

[2] D. C. Dittmer and G. C. Levy, *J. Org. Chem.*, **30**, 636 (1965); D. C. Dittmer, G. E. Kuhlmann, G. C. Levy, and R. Keene, paper in preparation.

[3] For a recent review of 1,3-oxathioles, see D. S. Breslow and H. Skolnik, "Heterocyclic Compounds, Multisulfur and Sulfur and Oxygen Five- and Six-Membered Heterocycles," Part One, A. Weissburger, Ed., Interscience Publishers, Inc., New York, N. Y., 1966, p 203 ff.

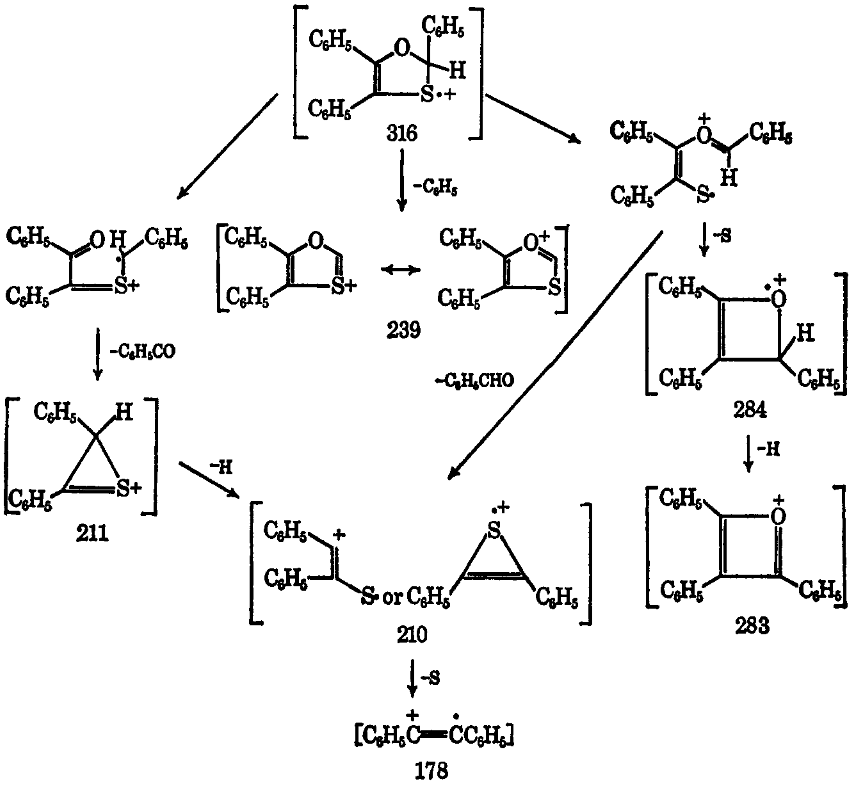
[4] H. J. Dietrich and J. V. Karabinos, *J. Org. Chem.*, **31**, 1127 (1966).

[5] N. D. Field, *J. Amer. Chem. Soc.*, **83**, 3504 (1961).

[6] W. E. Parham, I. Gordon, and J. D. Swalen, *ibid.*, **74**, 1824 (1952).

[7] J. R. Marshall and H. A. Stevenson, *J. Chem. Soc.*, 2360 (1959).

SCHEME I

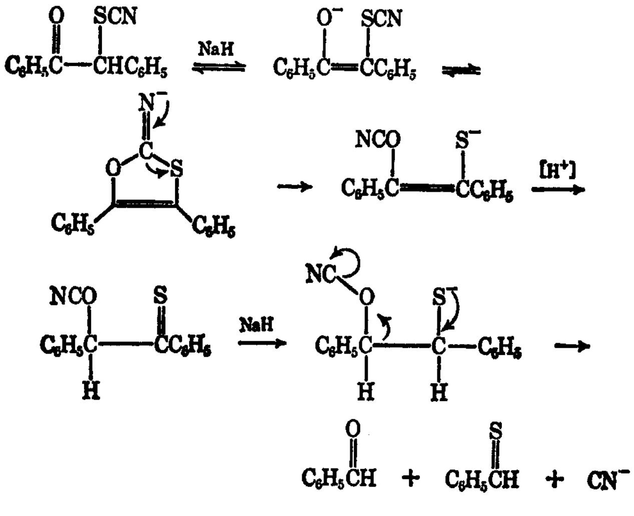


sulfide [a result consistent with hydrolysis of the oxathiole to monothiobenzoin (2-mercapto-2-phenylacetophenone) and loss of sulfur by hydrolysis] and benzaldehyde, which was identified as a 2,4-dinitrophenylhydrazone. Thin layer chromatography of the hydrolysis products indicated the presence of the benzaldehyde and benzoin. A third spot of unknown origin was observed.

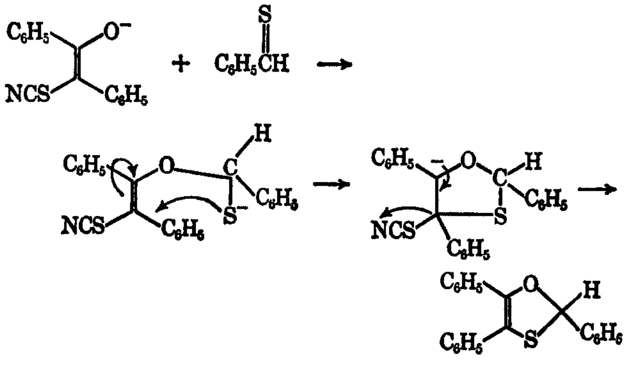
Alternate structures, 3,4,5-triphenyl-3H-1,2-oxathiole and 3,4,5-triphenyl-5H-1,2-oxathiole, are less in accord with the data. The ultraviolet spectra of these derivatives should be similar to the spectra of vinyl sulfides or vinyl ethers, none of which has absorption at as high a wavelength as the compound obtained from desyl thiocyanate in which both oxygen and sulfur are conjugated with the carbon–carbon double bond. The oxathiole does not give a test with acidified potassium iodide and starch paper as sulfenate esters (thioperoxides) are reported to do.[8] Formation of benzaldehyde on hydrolysis of the oxathiole is more difficult to rationalize on the basis of the 1,2-oxathiole structures.

Schemes II and II show the formation of the oxathiole under the reaction conditions used beginning with the enolization of desyl thiocyanate. This enol can give 1-mercapto-2-cyanato-1,2-diphenylethane[9] which may decompose to thiobenzaldehyde and benzaldehyde. The thiobenzaldehyde, presumably being more reactive than benzaldehyde,[10] may react with the enolate anion of desyl thiocyanate with formation of the oxathiole. Desyl thiocyanate may be the source of protons used in Scheme III.

SCHEME II



SCHEME III



---

[8] T. L. Moore and D. E. O'Connor, *J. Org. Chem.*, **31**, 3587 (1966).

[9] Compare the scheme for the formation of episulfides from epoxides by treatment with thiocyanate ions: E. E. van Tamelen, *J. Amer. Chem. Soc.*, **73**, 3444 (1951).

[10] J. C. Powers and F. H. Westheimer, *ibid.*, **82**, 5431 (1960).

Experimental Section

Infrared spectra were taken on a Perkin-Elmer Model 137 spectrophotometer and ultraviolet spectra were taken on a Perkin-Elmer Model 202 spectrophotometer. Nmr spectra were obtained on a Varian Associates A-60 spectrometer, and mass spectra on a Perkin-Elmer Hitachi RMU-6E spectrometer. Melting points were taken on a Fisher-Johns melting point apparatus. The analysis for elements was done by Galbraith Laboratories, Inc., Knoxville, Tenn., and by the Scandinavian Micro-Analytical Laboratory, Herlev, Denmark. Desyl thiocyanate was prepared from desyl chloride and potassium thiocyanate.[2]

2,4,5-Triphenyl-2H-1,3-oxathiole (1).—Sodium hydride (13.4 g, 0.312 mol, 56% dispersion in mineral oil) was added to 100 ml of dry dimethoxyethane. A solution of desyl thiocyanate (48.7 g, 0.192 mol) in 200 ml of dimethoxyethane was cooled to −10° and added in three portions over a 20-min period to the sodium hydride which also was cooled to −10°. The temperature quickly rose to room temperature. Stirring was continued for 90 min. Water (3 ml) was added to destroy any remaining sodium hydride, and the inorganic salts were removed by filtration and washed with two 30-ml portions of ether. The solvents were then removed on a rotary evaporator, the residue was dissolved in 350 ml of ether and washed with two 25-ml portions of water, and the ether solution was dried over anhydrous magnesium sulfate overnight. Evaporation of the solvent to about 200 ml precipitated *cis*-dibenzoylstilbene (3.10 g, 0.00795 mol, 8.3%) after several hours. Recrystallization from glacial acetic acid gave white crystals, mp 211-212° and mmp 209.5-211° (lit.[11] mp 210.0-210.8°). The olefin was further identified by thin layer chromatography (tlc) and its infrared and ultraviolet spectra which were the same as those reported.[11,12] The material remaining in the ether solution was chromatographed on a silicic acid column with benzene as eluent. A light yellow band, which preceded the band of *cis*-dibenzoylstilbene episulfide, was collected. A total of 11.1 g of crude 2,4,5-triphenyl-2H-1,3-oxathiole (0.0352 mol, 55%) and episulfide (13.1 g, 0.0311 mol, 32%) was collected. The oxathiole was recrystallized from petroleum ether (66–78°) several times and purified on a silicic acid column using a 4:1 pentane–benzene mixture as the eluent. Yellow crystals, mp 77–78°, were obtained which gave only one spot (R_f 0.67) on a tlc plate (Merck silica gel GF_{254}, benzene eluent). *Anal.* Calcd for $C_{21}H_{16}OS$: C, 79.71; H, 5.10; S, 10.13; mol wt, 316. Found: C, 79.57; H, 5.16; S, 10.19; mol wt, 328 (osmometry in acetone). The infrared spectrum of the oxathiole (KBr disk) exhibited bands at 3030 (w), 2880 (w), 1620 (m), 1600 (m), 1570 (m), 1495 (m), 1440 (m), 1350 (w), 1315 (w), 1245 (s), 1210 (m), 1175 (w), 1155 (w), 1080 (m), 1070 (m), 1060 (s), 1020 (m), 990 (m), 955 (m), 920 (w), 910 (w), 875 (m), 827 (w), 781 (w), 765 (m), 750 (s), 710 (s), and 691 (s) cm^{-1}. The ultraviolet spectrum was obtained in two solvents: $\lambda_{max}^{CH_3CN}$ 226, 342 mμ; $\lambda_{max}^{95\% C_2H_5OH}$ 225 mμ (ε 18,600), 342 mμ (ε 6760).

Mass spectrometry also was used to establish the empirical formula of the oxathiole using the isotope abundances of the molecular ion *m/e* 316 (P) at *m/e* 317 (P + 1) and *m/e* 318 (P + 2). *Anal.* Calcd[13] for $C_{21}H_{16}OS$: $100[(P+1)/P]$, 23.8; $100[(P+2)/P]$, 7.1. Found: $100[(P+1)/P]$, 22.6; $100[(P+2)/P]$, 7.3. The mass spectrum of the oxathiole was obtained at 110° using the direct inlet at 20-ev ionizing potential:[14] *m/e* 318 (7.62), 317 (26.3), 316 (100), 284 (15.5), 283 (5.50), 239 (5.47), 212 (6.58), 211 (38.8), 210 (20.4), 179 (6.66), 178 (28.4), 167 (23.4), 166 (5.28), 165 (26.0), 121 (7.86), 106 (7.95), 105 (9.54).

The proton nmr spectrum (60 MHz in $CDCl_3$) of the oxathiole had a complex multiplet centered at 433 Hz and a sharp resonance absorption at 418 Hz relative to tetramethylsilane. The ratio of the high-field absorbance to the low-field absorbance was 1:14.4 (calcd 1:15).

When the oxathiole (0.051 g, 0.00016 mol) was refluxed in 20 ml of 95% ethanol and 1 ml of concentrated hydrochloric acid, hydrogen sulfide was evolved as detected by lead acetate paper. Thin layer chromatography indicated also the presence of benzaldehyde, benzoin, and possibly monothiobenzoin. The solution from hydrolysis of the oxathiole was treated with an amount of 2,4-dinitrophenylhydrazine reagent[15] sufficient only to react with the benzaldehyde. The orange precipitate was filtered and recrystallized from a commercial mixture of xylenes to give benzaldehyde 2,4-dinitrophenylhydrazone, mp 240–241° (lit.[16] mp 239–240°). The infrared spectrum of the derivative was identical with that of authentic benzaldehyde 2,4-dinitrophenylhydrazone.[17]

Registry No.—1, 19206-52-1; desyl thiocyanate, 19203-00-0.

---

[11] N. M. Bikales and E. I. Becker, *J. Org. Chem.*, **21**, 1405 (1956).

[12] R. E. Lutz, W. J. Welstead, Jr., R. G. Bass, and J. I. Dale, *ibid.*, **27**, 1111 (1962).

[13] J. H. Beynon and A. E. Williams, "Mass Abundance Tables for Use in Mass Spectroscopy," Elsevier Publishing Co., New York, N. Y., 1963.

[14] Percentage of base peak is given in parenthesis. Only fragments which were 5% or greater of the base peak and above *m/e* 104 are tabulated.

[15] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1956, p 219.

[16] G. D. Johnson, *J. Amer. Chem. Soc.*, **75**, 2720 (1953).

[17] "Sadtler Standard Spectra," Midget ed, The Sadtler Research Laboratories, Philadelphia, Pa., 1962, No. 4156.

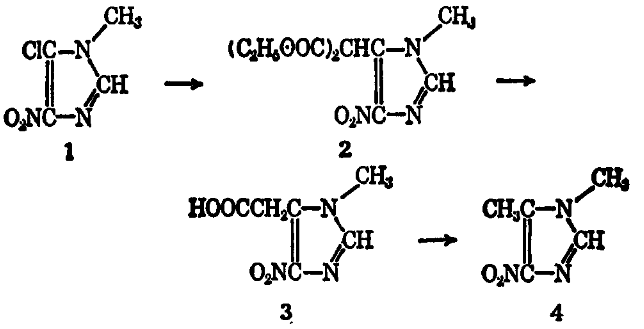
Hydrolysis and Decarboxylation of Diethyl 1-Methyl-4-nitro-5-imidazolylmalonate

H. C. GODT, JR., AND F. F. BLICKE[1]

Research Department, Organic Chemicals Division,
Monsanto Company, St. Louis, Missouri 63177,
and
Pharmaceutical Chemistry Department,
University of Michigan, Ann Arbor, Michigan

Received October 18, 1968

During a study of certain imidazole derivatives, 1-methyl-4-nitro-5-imidazolylacetic acid (3) was desired. A convenient route appeared to be the conversion of 5-chloro-1-methyl-4-nitroimidazole (1)[2] into its corresponding diethyl 5-imidazolylmalonate (2) followed by hydrolysis and decarboxylation. Starting compound 1 was prepared by nitration of 5-chloro-1-methylimidazole.[3–5]



1 2 3 4

The formation of the substituted malonic ester 2 was achieved in good yield by a malonic ester condensation reaction. However, when acid hydrolysis (1.2 *N* aqueous HCl) of 2 was attempted, 1,5-dimethyl-4-nitroimidazole (4)[6] was isolated as the sole product in high yield.[7]

---

[1] Deceased.

[2] J. Sarasin and E. Wegmann, *Helv. Chim. Acta*, **7**, 713 (1924).

[3] O. Wallach and A. Boehringer, *Ann.*, **184**, 50 (1877).

[4] O. Wallach, *ibid.*, **214**, 257 (1882).

[5] F. F. Blicke and H. C. Godt, Jr., *J. Amer. Chem. Soc.*, **76**, 3653 (1954).

[6] A. Windaus [*Ber.*, **42**, 758 (1909)] prepared this compound by nitrating 1,5-dimethylimidazole with fuming nitric acid.