(t, 2 H, J = 7 Hz), 4.05 (t, 2 H, J = 7 Hz).

Comparison of these authentic materials with the cleavage products of the dioxetane decomposition reaction showed identical spectra and physical data.

Addition of Methanol to 1,2-Dioxetanes. Samples of 1,2-dioxetanes **2**, **8**, **14**, **21**, and **27** were dissolved in $CDCl_3$, precooled to about −20 °C, and an equimolar amount of methanol, precooled to this temperature, was added. The mixture was slowly warmed up to room temperature; after several hours, the dioxetanes had disappeared (^1H NMR spectra).

With **2**, **8**, and **14** as starting dioxetanes, the ^1H NMR spectra of the product mixtures exhibited signals of dioxetane cleavage products **5**, **11**, and **18**, respectively, in addition to those attributed to methanol addition products **36**, **37**, and **38**, respectively, obtained by RB-photosensitized oxygenation of 2,3-dihydrofurans **1**, **7**, and **13** in methanol (for numerical values, see Results). Attempts to isolate methanol addition products by distillation at reduced pressure or by chromatography failed.

From dioxetanes **21** and **27**, only cleavage products **24** and **31**, respectively, were observed.

H_2O_2 Elimination Products from Allylic Hydroperoxides. The furans were identified by their ^1H NMR spectra.

Furan (6):[54] δ 6.30 (m, 2 H), 7.38 (m, 2, H).

2-Methylfuran (12):[55] δ 2.24 (s, br, 3 H), 5.88 (m, 1 H), 6.18 (m, 1 H), 7.18 (m, 1 H).

2,3-Dimethylfuran (19):[56] δ 1.90 (s, 3 H), 2.15 (s, 3 H), 6.08 (d, 1 H, J = 2 Hz), 7.10 (d, 1 H, J = 2 Hz).

3-Carbomethoxy-2-methylfuran (25):[56] δ 2.53 (s, 3 H), 3.78 (s, 3 H), 6.54 (d, 1 H, J = 2 Hz), 7.14 (d, 1 H, J = 2 Hz).

Supplementary Material Available: ^1H NMR spectra of **2**, **3**, **8**, **9**, **14**, **16**, **21**, **22** + **23**, **27**, **28**, and **33** + **34** and ^{13}C NMR spectra of **2**, **8**, **14**, **16**, **21**, **22** + **23**, **27**, and **28** (16 pages). Ordering information is given on any current masthead page.

(54) Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der organischen Chemie*; Thieme: Stuttgart, West Germany, 1979; p 110.
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Dye-Sensitized Photooxygenation of 2,3-Dihydrothiophenes: Formation of Stable 1,2-Dioxetanes from 4,5-Dialkyl-Substituted Derivatives

Klaus Gollnick* and Karen Knutzen-Mies

Institut für Organische Chemie der Universität München, Karlstr. 23, D-8000 München 2, West Germany

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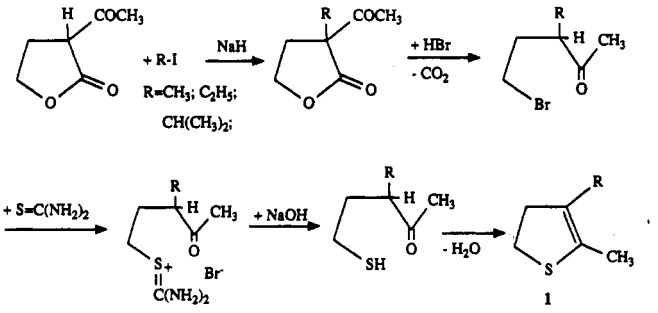
Singlet oxygen reacts with 4,5-dimethyl- (**1a**), 4-ethyl-5-methyl- (**1b**), and 4-isopropyl-5-methyl-2,3-dihydrothiophene (**1c**) to give 1,2-dioxetanes **2a–c** in high yields (>90%). **2a–c** represent the first examples of sulfur-substituted dioxetanes that could be isolated. Less than 5% of allylic hydroperoxides **3a**, **4a**, and **3b**, identified by their ^1H NMR spectra, and less than 5% of *S*-oxides **5a–c** were formed in competing ene reactions and sulfoxide-producing steps, respectively. Due to its decreased rigidity, dioxetane **2a** is less stable than its oxygen counterpart. Increased flexibility of dioxetanes derived from dihydrothiophenes and dihydrothiopyrans, as compared to those derived from dihydrofurans and dihydropyrans, causes dioxetanes **9** and **16**, obtained from 4-carbomethoxy-5-methyl-2,3-dihydrothiophene (**8**) and 5,6-dimethyl-3,4-dihydro-2*H*-thiopyran (**14**), to cleave into dicarbonyl compounds readily at low temperatures. Sulfur-substituted allylic hydroperoxides are also less stable than their oxygen counterparts. Formation of the expected endocyclic allylic hydroperoxides **3a**, **3b**, and **10** is inferred from the appearance of their H_2O_2 elimination products, thiophenes **7a**, **7b** and **13**, respectively.

Introduction

A considerable number of alkyl- and/or aryl-substituted 1,2-dioxetanes and 1,2-dioxetanes derived from enol ethers have been prepared, isolated, and characterized.[1,2a] Although many thioenol ethers were subjected to dye-sensitized photooxygenation, only a few sulfur-substituted 1,2-dioxetanes have been obtained and characterized by spectroscopic means at low temperatures in solution.[2b-4] Due to the rather labile nature of sulfur-substituted 1,2-dioxetanes, none of these compounds was isolated in substance, and, in fact, formation of most hetero (O, S, and N) substituted 1,2-dioxetanes was postulated on the basis of the observed characteristic cleavage products.[5-8]

Scheme I. Synthesis of 4-Alkyl-5-methyl-2,3-dihydrothiophenes



In the preceding paper,[9] we showed that singlet oxygen ($^1O_2$) reacts with 2,3-dihydrofurans to form 1,2-dioxetanes in high yields. Alkyl substitution at the C–C double bond of 2,3-dihydrofuran increases the reaction rate and stabilizes the resulting bicyclic dioxetane. Compared with a series of other dioxetanes,[2a] that derived from 4,5-dimethyl-2,3-dihydrofuran is more stable by 2 to 3 kcal/mol,

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(2) (a) Adam, W. In *The Chemistry of Peroxides*; Patai, S., Ed.; John Wiley and Sons: New York, 1983; p 829. (b) Adam, W.; Arias, L. A.; Scheutzow, D. *Tetrahedron Lett.* **1982**, *23*, 2835.
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(4) Handley, R. S.; Stern, A. J.; Schaap, A. P. *Tetrahedron Lett.* **1985**, *26*, 3183.
(5) (a) Ando, W. *Sulfur Rep.* **1981**, *1*, 147. (b) Ando, W.; Nagashima, T.; Saito, K.; Kohmoto, S. *J. Chem. Soc., Chem. Commun.* **1979**, 154. (c) Ando, W.; Watanabe, K.; Migita, T. *J. Chem. Soc., Chem. Commun.* **1975**, 961. (d) Ando, W.; Suzuki, J.; Arai, T.; Migita, T. *Tetrahedron* **1973**, *29*, 1507.
(6) Bartlett, P. D.; Landis, M. E. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; p 243.
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(9) Gollnick, K.; Knutzen-Mies, K. *J. Org. Chem.*, preceding paper in this issue.

0022-3263/91/1956-4027$02.50/0

proposed to be due to the rigidity of this compound.[10]

Assuming that 2,3-dihydrothiophenes, especially when methylated at the C–C double bond, may also afford 1,2-dioxetanes at apreciable yields and that these products may be sufficiently stable to permit their isolation, we subjected a series of 2,3-dihydrothiophenes to dye-sensitized photooxygenation at −78 °C in various solvents. Some of our results were published in a previous communication, which dealt mainly with the activation parameters and excitation properties of the 1,2-dioxetanes prepared from the 4,5-dimethyl derivatives of 2,3-dihydrofuran and 2,3-dihydrothiophene.[10] In the present paper, we report on the photooxygenation of 2,3-dihydrothiophenes and of 5,6-dimethyl-3,4-dihydro-2*H*-thiopyran in some detail.

Results

Synthesis of Starting Thioenol Ethers. 4,5-Dimethyl- (**1a**), 4-ethyl-5-methyl- (**1b**), and 4-isopropyl-5-methyl-2,3-dihydrothiophene (**1c**), to the best of our knowledge not yet described in the literature, were prepared according to Scheme I.

α-Acetyl-γ-butyrolactone was transformed via α-alkyl-substituted α-acetyl-γ-butyrolactones into 3-alkyl-1-bromo-4-pentanones. Reaction of the latter with thiourea to form isothiuronium salts followed by hydrolysis proved to be the best method for preparation of the 2,3-dihydrothiophenes **1a–c**.

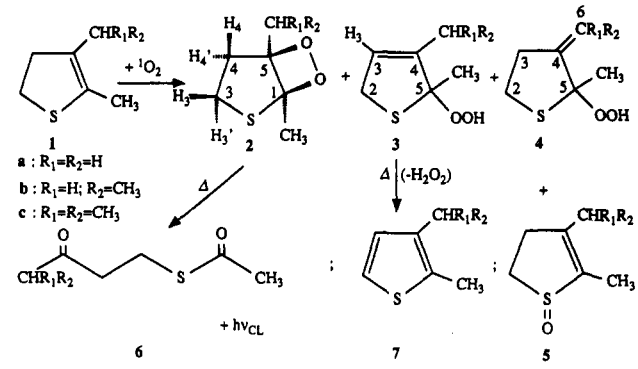
Photooxygenation of 2,3-Dihydrothiophenes and 5,6-Dimethyl-3,4-dihydro-2*H*-thiopyran in Aprotic Solvents at Low Temperatures. General Results. 2,3-Dihydrothiophenes **1a–c**, irradiated at −78 °C in oxygen-saturated solutions of $CDCl_3/CFCl_3$ in the presence of tetraphenylporphin (TPP) as a sensitizer, each consumed 1 molar equiv of O_2. Dioxetanes **2a–c** were isolated. However, attempts to isolate the other primary products, allylic hydroperoxides **3** and **4**, failed. Allylic hydroperoxides **3a** and **4a** were observed in the reaction mixture by ^1H NMR analysis, but allylic hydroperoxides **3b** and **3c** as well as **4b** and **4c** were not, obviously because they were formed in yields lower than about 5%. However, the appearance of **3b** is inferred from the observation of thiophene **7b** after removal of dioxetane **2b** from the reaction mixture.

In the case of 4-carbomethoxy-5-methyl-2,3-dihydrothiophene (**8**), dioxetane **9** could not be separated from the other reaction products but could be unambiguously identified by its ^1H NMR spectrum. Again, the production of the allylic hydroperoxide **10** is too low for identification, but its H_2O_2 elimination product, thiophene derivative **13**, was observed beyond doubt. Furthermore, all the reaction mixtures contained some 2,3-dihydrothiophene *S*-oxides (**5a–c**, **11**), about or less than 5% in each case according to ^1H NMR analysis.[11]

With 5,6-dimethyl-3,4-dihydro-2*H*-thiopyran (**14**), irradiation at −78 °C in a series of solvents yielded 5-(acetylthio)-2-pentanone (**15**) exclusively.

Preliminary studies had shown that 2,3-dihydrothiophene and 5-methyl-2,3-dihydrothiophene gave rise to mixtures of decomposition products. From these mixtures, only the *S*-oxides were identified beyond doubt by their ^1H NMR spectra.

Scheme II. Singlet Oxygen Reactions with 4-Alkyl-5-methyl-2,3-dihydrothiophenes 1a–c



Detailed Results. 4,5-Dimethyl-2,3-dihydrothiophene (1a). At room temperature, dioxetane **2a** (1,5-dimethyl-2-thia-6,7-dioxabicyclo[3.2.0]heptane) yields slowly 4-(acetylthio)-2-butanone (**6a**). At elevated temperature, the cleavage reaction is fast and accompanied by a very weak chemiluminescence that can be observed, however, only in the presence of 9,10-dibromoanthracene[10] (Scheme II).

The ^{13}C NMR spectrum of **2a** shows two singlets at δ 106.8 and 98.8, two triplets at 43.1 and 30.4, and two quartets at 21.2 and 19.8 attributed unambiguously to carbon atoms C-1, C-5, C-3, and C-4 and those of the CH_3 groups at C-1 and C-5, respectively. In its ^1H NMR spectrum, **2a** exhibits two singlets at δ 1.61 and 1.79 due to the CH_3 groups at C-5 and C-1, respectively; furthermore, it shows four multiplets at 1.98 (H-4′), 2.45 (H-4), 2.98 (H-3′), and 3.71 (H-3). From spread ^1H NMR spectra (5 Hz/cm, 80 MHz), the chemical shifts of the latter protons were determined, whereas the six coupling constants $^2J_{4,4'}$ = 14.5 Hz, $^2J_{3,3'}$ = 12.0 Hz, $^3J_{3,4}$ = 5.0 Hz, $^3J_{3',4}$ = 6.0 Hz, $^3J_{3,4'}$ = 11.5 Hz, and $^3J_{3',4'}$ = 6.5 Hz were derived in analogy to those obtained from the corresponding 1,5-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane.[9]

Analysis of the ^1H NMR spectrum of the original product mixture shows that, in addition to dioxetane **2a**, two rather than three allylic hydroperoxides were formed in a ratio of about 1:1. In the ^1H NMR spectrum, the singlets at δ 1.48 (3 H) and 1.40 (3 H) are attributed to the CH_3 groups at C-5 of 4,5-dimethyl-5-hydroperoxy-2,5-dihydrothiophene (**3a**) and 5-hydroperoxy-5-methyl-4-methylenetetrahydrothiophene (**4a**), respectively. The doublet at δ 2.25 (3 H, J = 1.5 Hz) is due to the CH_3 group at C-4 of **3a**, whereas the multiplet at 6.03 (1 H) and the two broad singlets at 4.90 (1 H) and 5.15 (1 H) represent the olefinic protons at C-3 of **3a** and at C-6 of **4a**, respectively. The multiplet at 2.9 (6 H) is due to the protons at C-2 of **3a** as well as to those at C-2 and C-3 of **4a**. Finally, there is a broad singlet at 8.78 (2 H), which is due to the protons of the OOH groups of **3a** and **4a**. The "missing" allylic hydroperoxide, 4-hydroperoxy-4-methyl-5-methylenetetrahydrothiophene, is formed at yields lower than 5%, if at all. By comparison with authentic material, the remaining signals could be attributed to sulfoxide **5a**.

At elevated temperatures, the product mixture yielded 4-(acetylthio)-2-butanone (**6a**), 2,3-dimethylthiophene (**7a**), and sulfoxide **5a**, as was established by comparison with authentic samples.

By using the signals of H-3 and H-3′ of **2a**, of the olefinic H at C-3 of **3a**, and of the two methylene protons at C-6 of **4a**, the relative amounts of **2a**:**3a**:**4a** were determined to be 90:5:5, as was obtained for photooxygenations at −78 °C in CCl_4, $CHCl_3$, $CDCl_3/CFCl_3$ (1:1), CH_2Cl_2, CH_3CN,

(10) Adam, W.; Griesbeck, A. G.; Gollnick, K.; Knutzen-Mies, K. *J. Org. Chem.* **1988**, *53*, 1492.

(11) Singlet oxygen may oxidize sulfides to sulfoxides.[12] However, whether the dihydrothiophenes are oxidized by $^1O_2$ or, e.g., by the peroxidic products, dioxetanes and allylic hydroperoxides, was not examined.

(12) Liang, J. J.; Gu, C. L.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4717.

and methanol. Only in acetone was the ratio found to be slightly different (82:6:12).

In contrast to the 1,2-dioxetane derived from 4,5-dimethyl-2,3-dihydrofuran, dioxetane **2a** does not add methanol to give a methoxy hydroperoxide. The kinetic analysis of the rose bengal photosensitized oxygenation of **1a** in methanol, excecuted as described in the preceding paper,[9] yields $k_r = 7.3 \times 10^7$ M^{-1} s^{-1} for the reaction of singlet oxygen with **1a**. This rate constant is only insignificantly lower than that of the reaction of 4,5-dimethyl-2,3-dihydrofuran with $^1O_2$ in methanol ($k_r = 1.09 \times 10^8$ M^{-1} s^{-1}).

4-Ethyl-5-methyl-2,3-dihydrothiophene (1b) and 4-Isopropyl-5-methyl-2,3-dihydrothiophene (1c). At room temperature, 1,2-dioxetanes **2b** (5-ethyl-1-methyl-2-thia-6,7-dioxabicyclo[3.2.0]heptane) and **2c** (5-isopropyl-1-methyl-2-thia-6,7-dioxabicyclo[3.2.0]heptane) yield 1-(acetylthio)-3-pentanone (**6b**) and 1-(acetylthio)-4-methyl-3-pentanone (**6c**), respectively.

The ^{13}C NMR spectrum of **2b** exhibits signals at δ 107.0 (s, C-1), 101.0 (s, C-5), 39.9 (t, C-3), 30.6 (t, C-4), 20.9 (q, CH_3 at C-1), 26.6 (t), and 7.5 (q) of the CH_2CH_3 group at C-5. Similarly, the ^{13}C NMR spectrum of **2c** shows signals at δ 106.6 (s, C-1), 103.2 (s, C-5), 34.7 (t, C-3), 31.1 (t, C-4), 21.0 (q, CH_3 at C-1), 30.1 (d), and 17.3 (q) of the $CH(CH_3)_2$ group at C-5.

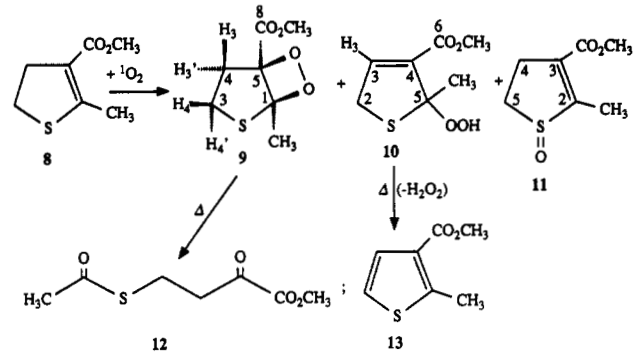
The ^1H NMR spectra of the dioxetanes are also in accord with structures **2b** and **2c**. Thus, **2b** shows signals at δ 1.00 (t, 3 H, J = 7 Hz) and 1.81 (q, 2 H, J = 7 Hz) for the CH_2CH_3 group, at 1.83 (s, 3 H, CH_3 at C-1), 2.13 (m, $H_{4'}$), 2.49 (m, H_4), 3.05 (m, $H_{3'}$), and 3.70 (m, H_3). Similarly, the signals of **2c** appear at δ 0.95 (d, 6 H, J = 7 Hz) and 2.75 (m) for the $CH(CH_3)_2$ group, at 1.88 (s, 3 H, CH_3 at C-1), 2.05 (m, $H_{4'}$), 2.25 (m, H_4), 3.09 (m, $H_{3'}$), and 3.68 (m, H_3).

As mentioned above, allylic hydroperoxides **3b**, **3c**, **4b**, and **4c** were not observed. However, after removal of dioxetane **2b** from the mixture obtained from **1b**, 3-ethyl-2-methylthiophene (**7b**) was identified by its ^1H NMR spectrum and comparison with authentic material. **7b** should be the H_2O_2 elimination product of **3b**, and we therefore assume that allylic hydroperoxides are formed during the photooxygenation of **1b** and **1c**, though in smaller relative amounts than in the case of **1a**. Furthermore, sulfoxides **5b** and **5c** were formed along with the other photooxygenation products, as was shown by NMR spectroscopic analysis by comparison with authentic samples.

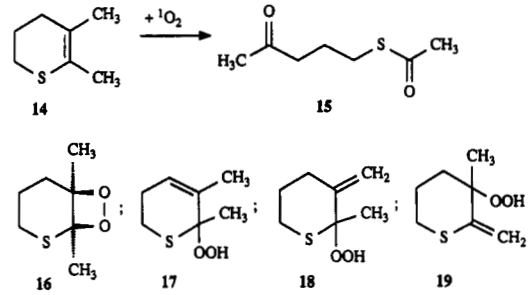
4-Carbomethoxy-5-methyl-2,3-dihydrothiophene (8). Photooxygenation of **8** yielded a product mixture, which could not be resolved by distillation or chromatography. According to its ^1H NMR spectrum, the mixture contained dioxetane **9** as the major component, with signals at δ 1.88 (s), 2.50 (m), 3.18 (m), and 3.90 (s) due to the CH_3 group at C-1, the methylene protons H_4, $H_{4'}$ and H_3, $H_{3'}$, and the protons of the CO_2CH_3 group, respectively. At least two other products were formed in minor amounts, as is inferred from the occurrence of two more singlets at δ 3.80 and 3.65 due to the protons of two further CO_2CH_3 groups. In analogy to the product mixtures obtained from dihydrothiophenes **1a–c**, we assume that these products represent the allylic hydroperoxide **10** and the sulfoxide **11**. At room temperature, the original mixture slowly changed into a mixture of sulfoxide **11**, cleavage product **12**, and thiophene derivative **13** (Scheme III).

5,6-Dimethyl-3,4-dihydro-2*H*-thiopyran (14). At −78 °C, photooxygenation of **14** in various solvents yielded in each case 1-(acetylthio)-4-pentanone (**15**) as the only observable product. None of the expected primary products, **16** through **19**, was obtained (Scheme IV).

Scheme III. Singlet Oxygen Reaction with 4-Carbomethoxy-5-methyl-2,3-dihydrothiophene (8)



Scheme IV. Singlet Oxygen Reaction with 5,6-Dimethyl-3,4-dihydro-2*H*-thiopyran (14)



Discussion

In analogy to the study of 2,3-dihydrofurans and 5,6-dimethyl-3,4-dihydro-2*H*-pyran[9], the correspondingly substituted 2,3-dihydrothiophenes and dihydrothiopyran derivative **14** were subjected to singlet oxygen reactions. As expected, the cyclic thioenol ethers yield 1,2-dioxetanes and allylic hydroperoxides; in addition, *S*-oxides are formed to less than about 5% of the total amounts of products. However, the dioxetanes and allylic hydroperoxides are less stable than those derived from the corresponding cyclic enol ethers. Preliminary studies have shown that, apart from some *S*-oxides, only decomposition products were obtained with 2,3-dihydrothiophene and its 5-methyl derivative. 5,6-Dimethyl-3,4-dihydro-2*H*-thiopyran (**14**) yielded 1-(acetylthio)-4-pentanone (**15**) exclusively. This compound should represent the cleavage product of dioxetane **16** as well as the Hock cleavage product of the allylic hydroperoxides **17** to **19**, the expected primary photooxygenation products of **14**. Interestingly enough, the α,β-unsaturated ester **8** yielded dioxetane **9** (^1H NMR analysis), but attempts to isolate **9** produced only a product mixture whose ^1H NMR spectrum is compatible with that expected to contain **12**, the cleavage product of **9**, *S*-oxide **11**, and thiophene derivative **13**. The latter should be the H_2O_2 elimination product of the allylic hydroperoxide **10**.

As with the dihydrofuran derivatives, the 4,5-dimethyl derivative **1a** turned out to yield the most stable products. Apart from some *S*-oxide **5a**, the $^1O_2$ reaction with **1a** yielded dioxetane **2a** and allylic hydroperoxides **3a** and **4a** in a 90:5:5 ratio in nonpolar and polar aprotic solvents and in methanol. If at all, a third allylic hydroperoxide, 4-hydroperoxy-4-methyl-5-methylenetetrahydrothiophene, is formed at too low a yield (<5%) to be detected by NMR spectroscopic means. These results are in perfect agreement with those obtained with 4,5-dimethyl-2,3-dihydrofuran.[9] Furthermore, in methanol, the rates of $^1O_2$ reac-

tions with **1a** and its oxygen analogue are almost the same, suggesting that the mechanism proposed for singlet oxygen reactions with 2,3-dihydrofurans should also apply to those with 2,3-dihydrothiophenes.

Dioxetane **2a** was isolated; its cleavage to 4-(acetylthio)-2-butanone (**6a**) was shown to occur with a free energy of activation, $\Delta G^{\ddagger}$, and an activation enthalpy, $\Delta H^{\ddagger}$, of 22.7 ± 1.2 kcal/mol at 343 K and 19.4 ± 0.8 kcal/mol, respectively.[10] The activation enthalpy is thus about 9 kcal/mol smaller than that of the dioxetane derived from 4,5-dimethyl-2,3-dihydrofuran. Therefore, it is not very surprising that the dioxetanes expected from the other dihydrothiophenes and from the dihydrothiopyran derivative **14** decompose readily at low temperatures.

In contrast to its oxygen counterpart, dioxetane **2a** does not add methanol to afford 2,3-dimethyl-3-hydroperoxy-2-methoxytetrahydrothiophene. The latter compound was expected to be formed regiospecifically by heterolytic opening of the dioxetane ring by proton addition to give the more effectively stabilized cationic site at C-2. Interestingly enough, the endoperoxides derived from 2,5-dimethylfuran[13] and 2,5-dimethylthiophene[14] show a similar behavior toward methanol: whereas the former adds readily methanol to yield *cis*-2,5-dimethyl-2-hydroperoxy-5-methoxy-2,5-dihydrofuran, the latter does not react at all with methanol. Two effects are thought to be responsible for the different behavior of the two endoperoxides: enhanced O–O bond cleavage of the sulfur compound and decreased capability of sulfur to stabilize an adjacent cationic site.[14,15] These assumptions may also explain the fact that **2a** does not add methanol.

Results obtained with 4-ethyl- (**1b**) and 4-isopropyl-5-methyl-2,3-dihydrothiophene (**1c**) are similar to those obtained with **1a**. To the best of our knowledge, dioxetanes **2a–c** represent the only sulfur-substituted dioxetanes that could be isolated to date.

The decreased thermal stability of the dioxetanes obtained from 2,3-dihydrothiophenes and 3,4-dihydro-2*H*-thiopyrans compared with those obtained from 2,3-dihydrofurans and 3,4-dihydro-2*H*-pyrans should be due to the decreased rigidity of the sulfur heterocycles as a consequence of the larger atomic radius of sulfur compared to that of oxygen.[10]

Experimental Section

Caution! Preparations and reactions of 1,2-dioxetanes and hydroperpoxides were carried out behind safety shields. Neat samples of dioxetanes can be very hazardous and should be handled only in amounts less than about 100 mg.

For solvent purification and instrumentation, see ref 9.

The purity of 1,2-dioxetanes **2a-c** was judged to be ≥90% by ^{1}H and/or ^{13}C NMR spectral determinations. The spectra are published as supplementary material.

Preparation of Oxygen Acceptors. 4,5-Dimethyl-2,3-dihydrothiophene (1a). To a solution of 33.8 g (200 mmol) of 1-bromo-3-methylpentan-4-one (bp 65–67 °C/12 Torr), prepared in analogy to 1-bromo-3-ethylpentan-4-one,[17] in 20 mL water was added 15.2 g (200 mmol) of thiourea, and the mixture was refluxed for 15 h. The solution was hydrolyzed with 15 mL of 5% sodium hydroxide under nitrogen and refluxed for another 15 h. After cooling under nitrogen, the solution was neutralized with 2 N HCl and extracted three times with 30 mL of ether. The organic layer was dried over $MgSO_4$ and the solvent removed by distillation up to 200 Torr. Subsequent distillation at 12 Torr into a dry ice cooled trap gave a mixture of product and water. For further purification the product was distilled twice through a 15-cm Vigreux column, yielding 4.49 g (20%) of a colorless liquid, bp 42 °C at 12 Torr (purity 99% GC). The product was stored under nitrogen in a refrigerator. ^{1}H NMR δ 1.63 (s, br, 3 H), 1.79 (s, br, 3 H), 2.70 (m, 2 H), 3.06 (m, 2 H); ^{13}C NMR δ 13.7 (q), 14.4 (q), 29.7 (t), 41.8 (t), 124.6 (s), 126.9 (s); IR 1650 cm^{-1} (C=C); UV (MeCN) λ_{max} = 235 nm.

Anal. Calcd for $C_6H_{10}S$ (114.21): C, 63.10; H, 8.83; S, 28.07. Found: C, 63.36; H, 8.71; S, 27.81

4-Ethyl-5-methyl-2,3-dihydrothiophene (1b). 1-Bromo-3-ethyl-4-pentanone[17] (36.2 g, 200 mmol), treated with 15.2 g (200 mmol) of thiourea as described above, yielded 14.6 g (57%) of a colorless liquid, bp 64–65 °C at 12 Torr; ^{1}H NMR δ 0.98 (t, 3 H, J = 12 Hz), 1.80 (s, 3 H), 2.16 (t, 3 H, J = 6 Hz), 2.77 (m, 2 H), 3.03 (m, 2 H); ^{13}C NMR δ 13.0 (q), 13.5 (q), 22.2 (t), 30.0 (t), 39.1 (t), 126.6 (s), 130.7 (s); IR 1645 cm^{-1} (C=C); UV (MeCN) λ_{max} = 237 nm.

Anal. Calcd for $C_7H_{12}S$ (128.24): C, 65.56; H, 9.43; S, 25.00. Found: C, 65.45; H, 9.32; S, 24.78.

4-Isopropyl-5-methyl-2,3-dihydrothiophene (1c). 1-Bromo-3-isopropyl-4-pentanone (39.0 g, 200 mmol), prepared in analogy to 1-bromo-3-ethyl-4-pentanone[17] and treated with 15.2 g (200 mmol) of thiourea as described above, afforded 7.54 g (30%) of a colorless liquid, bp 64 °C at 12 Torr; ^{1}H NMR δ 1.00 (d, 6 H, J = 7 Hz), 1.81 (s, 3 H), 2.70 (m, 2 H + CH(CH$_3$)$_2$), 3.05 (m, 2 H); ^{13}C NMR δ 13.4 (q), 21.4 (q), 27.9 (d), 30.3 (t), 34.9 (t), 125.7 (s), 134.6 (s); IR 1655 cm^{-1} (C=C); UV (MeCN) λ_{max} = 238 nm.

Anal. Calcd for $C_8H_{14}S$ (142.26): C, 67.54; H, 9.92; S, 22.54. Found: C, 67.39; H, 9.98; S, 22.63.

4-Carbomethoxy-5-methyl-2,3-dihydrothiophene (8). 8 (12.9 g) (74%), bp 54–56 °C at 0.5 Torr, was obtained from 18.1 g (110 mmol) of α-acetyl-γ-thiabutyrolactone according to the procedure described by Duus and Lawesson:[18] ^{1}H NMR δ 2.28 (s, 3 H), 3.11 (m, 4 H), 3.68 (m, 3 H); ^{13}C NMR δ 16.4 (q), 30.7 (t), 36.9 (t), 50.9 (q), 119.8 (s), 157.3 (s), 164.4 (s).

5,6-Dimethyl-3,4-dihydro-2*H*-thiopyran (14). 14 (6.6 g) (50%), bp 73–75 °C at 12 Torr, was obtained from 14.8 g (100 mmol) of 2-mercapto-5-methyl-6-heptanone according to the procedure described by Bateman and Glazebrook:[19] ^{1}H NMR δ 1.68 (s, br, 3 H), 1.78 (s, br, 3 H), 1.98 (m, 4 H), 2.78 (m, 2 H); ^{13}C NMR δ 19.5 (q), 20.5 (q), 24.0 (t), 27.8 (t), 30.8 (t), 118.6 (s), 121.7 (s).

General Procedure for Photooxygenations. For a description, see ref 9.

1,2-Dioxetanes. Samples of 3 to 7 mmol of 2,3-dihydrothiophenes (**1a–c**, **8**) and 5,6-dimethyl-3,4-dihydro-2*H*-thiopyran (**14**) were dissolved in a 1:1 mixture of $CDCl_3$ and $CFCl_3$, containing 8 × 10^{-4} M of TPP, and cooled to −78 °C while being purged with a gentle stream of oxygen gas. (Other sensitizer/solvent systems used were TPP in CCl_4, $CHCl_3$, and CH_2Cl_2 and RB in acetone, CH_3CN, and methanol.) The solution was irradiated with a constant oxygen flow for 3 to 6 h. The solvent was removed at −50 to −30 °C at 10^{-4} Torr. The 1,2-dioxetane was distilled at −20 to 0 °C at 10^{-4} Torr in a cold trap kept at liquid nitrogen temperature. The dioxetanes are yellow oils that can be stored in solution on dry ice for several months. The NMR spectroscopic data of the 1,2-dioxetanes are reported in the Results as are those of the allylic hydroperoxides **3a** and **4a** produced along with dioxetane **2a**.

The NMR signals of the allylic hydroperoxides were extracted from the NMR spectra of the original product mixtures, published as supplementary material.

Cleavage Products of the 1,2-Dioxetanes. 4-(Acetylthio)-2-butanone (6a)[20] [bp 101–103 °C at 12 Torr; ^{1}H NMR δ 2.13 (s, 3 H), 2.28 (s, 3 H), 2.73 (m, 2 H), 2.97 (m, 2 H)], **1-(acetylthio)-3-pentanone (6b)**[21] [bp 108–111 °C at 12 Torr;

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^{1}H NMR δ 1.05 (t, 3 H, J = 7 Hz), 2.26 (s, 3 H), 2.41 (q, 2 H, J = 7 Hz), 2.70 (m, 2 H), 3.05 (m, 2 H)], **1-(acetylthio)-4-methyl-3-pentanone (6c)** [^{1}H NMR δ 1.11 (d, 6 H, J = 7 Hz), 2.26 (s, 3 H), 2.40 (q, 1 H, J = 7 Hz), 2.73 (m, 2 H), 2.98 (m, 2 H)], and **5-(acetylthio)-2-pentanone (15)**[19] [bp 120–122 °C at 12 Torr; ^{1}H NMR δ 1.83 (t, 2 H, J = 7 Hz), 2.20 (s, 3 H), 2.38 (s, 3 H), 2.56 (t, 2 H, J = 7 Hz), 2.86 (t, 2 H, J = 7 Hz)] were synthesized independently, following literature procedures. Comparison of these authentic materials with the cleavage products of the dioxetane decomposition reaction showed identical spectral and physical data.

H_2O_2 Elimination Products from Allylic Hydroperoxides. 2,3-Dimethylthiophene (7a)[22] [^{1}H NMR δ 2.08 (s, 3 H), 2.26 (s, 3 H), 6.70 (d, 1 H, J = 5 Hz), 6.90 (d, 1 H, J = 5 Hz)] and **3-ethyl-3-methylthiophene (7b)**[23] [^{1}H NMR δ 1.08 (t, 3 H, J = 6 Hz), 2.25 (s, 3 H), 2.36 (q, 2 H, J = 6 Hz), 6.65 (d, 1 H, J = 5 Hz), 6.82 (d, 1 H, J = 5 Hz)] were identified by their literature ^{1}H NMR spectra.

Sulfoxides. The sulfoxides were prepared in analogy to a procedure described by Krug and Boswell.[24] Samples of 100 mmol of the thioenol ethers were dissolved in 40 to 50 mL of acetone and cooled to 0 °C. An equimolar amount of H_2O_2 (30%) was slowly added to the solution so that the temperature never exceeded 8 °C. After 50 h at 0 °C, the solvent was removed on a rotor-evaporator. The residue was extracted with chloroform and the organic layer was dried over $MgSO_4$. Chloroform was removed on a rotor-evaporator and subsequently in vacuo at room temperature. Distillation of the sulfoxides at low pressure (10^{-4} Torr) yielded decomposition products only.

4,5-Dimethyl-2,3-dihydrothiophene 1-oxide (5a): ^{1}H NMR δ 1.86 (s, br, 3 H), 2.03 (s, br, 3 H), 2.73 (m, 2 H), 3.36 (m, 2 H); IR 1650 (C=C), 1030 cm^{-1} (S=O); UV (MeCN) λ_{max} = 260 nm.

4-Ethyl-5-methyl-2,3-dihydrothiophene 1-oxide (5b): ^{1}H NMR δ 1.08 (t, 3 H, J = 8 Hz), 2.01 (m, 3 H), 2.27 (q, 2 H, J = 8 Hz), 2.70 (m, 2 H), 3.34 (m, 2 H); IR 1645 (C=C), 1020 cm^{-1} (S=O); UV (MeCN) λ_{max} = 262 nm.

4-Isopropyl-5-methyl-2,3-dihydrothiophene 1-oxide (5c): ^{1}H NMR δ 1.06 (d, 6 H, J = 7 Hz), 1.84 (m, 3 H), 2.79 (m, 2 H + C*H*(CH$_3$)$_2$), 3.10 (m, 2 H); IR 1640 (C=C), 1025 cm^{-1} (S=O); UV (MeCN) λ_{max} = 265 nm.

5,6-Dimethyl-3,4-dihydro-2*H*-thiopyran 1-oxide (20): ^{1}H NMR δ 1.68 (s, br, 3 H), 1.81 (s, br, 3 H), 2.11 (m, 4 H), 2.84 (m, 2 H); IR 1640 (C=C), 1020 cm^{-1} (S=O); UV (MeCN) λ_{max} = 263 nm.

Supplementary Material Available: ^{1}H NMR spectra of **2a–c**, **3a**, **4a**, **9**, and **15** and ^{13}C NMR spectra of **2a–c** (9 pages). Ordering information is given on any current masthead page.

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Reaction of Phosphole Sulfides with Diazoalkanes as a New Route to Phosphinines

Serge Holand, Louis Ricard, and François Mathey*

Laboratoire de Chimie du Phosphore et des Métaux de Transition, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France

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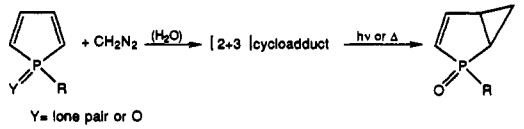
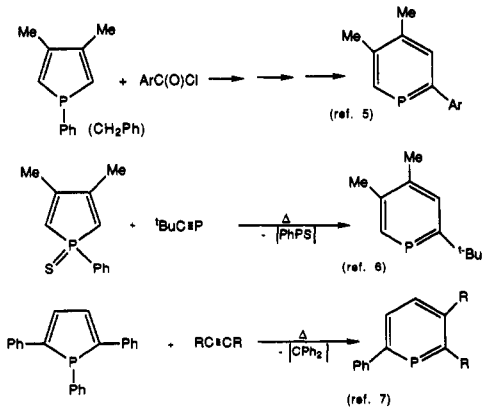
The reaction of ethyl diazoacetate with 1-(methylthio)-3,4-dimethylphosphole 1-sulfide (**6**) in refluxing xylene leads to the corresponding diene–carbene [2 + 1] cycloadduct **7**. The stereochemistry of **7** was established by X-ray crystal structure analysis. Compound **7** is converted into 2-(ethoxycarbonyl)-4,5-dimethylphosphinine (**4**) upon reaction with triphenyl phosphite at 160 °C. On the basis of the X-ray data, the proposed mechanism includes the opening of the cyclopropane ring of **7** with selective phosphorus-assisted migration of the ethoxycarbonyl group. This kind of chemistry can be transposed to a 2,2′-biphosphole to prepare a 2,2′-biphosphinine.

Surprisingly, the reaction of phospholes with diazoalkanes has been the subject of only a few studies.[1-3] In all cases, the reaction led to the corresponding homophospholes. In one instance, the thermal or photochemical



cleavage of the bicyclic system gave para-bridged six-membered ring dimers.[4] On the other hand, three methods for the conversion of phospholes into phosphinines have been described in the literature. When applied



to reasonably accessible 2,2′-biphospholes,[8,9] none of these

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