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(7) Previous work has shown that attempts to prepare nitrones from aldehydes containing an α-hydrogen atom often lead to isoxazolidines effectively through self-condensation of the nitrone: A. D. Baker, J. E. Baldwin, D. P. Kelly, and J. DeBernardis, *Chem. Commun.*, 344 (1969).
(8) The addition of chlorine to benzylideneaniline was reported in the early literature, but the products were not characterized; see T. C. James and C. W. Rudd, *J. Chem. Soc.*, 105 (1914).
(9) Subsequent treatment of the filtrate with hydrogen chloride caused precipitation of the remainder of imines in solution as their hydrochlorides. These were shown to be, again, an approximately equal mixture of benzylideneaniline hydrochloride and benzylidene-*p*-chloroaniline hydrochloride.
(10) Whether intermediate II exists in the form shown or as PhCH(Cl)N(Cl)Ph is irrelevant. The same chlorinated imine hydrochloride should be formed as α-chloroamines readily isomerize to imine hydrochlorides.
(11) (a) P. Haberfield and D. Paul, *J. Amer. Chem. Soc.*, **87**, 5502 (1965); (b) another example is given by R. S. Neale, R. G. Schepers, and M. R. Walsh, *J. Org. Chem.*, **29**, 3390 (1964).
(12) The small amount of para isomer observed in some cases can be accounted for by an S_N2' type process to which intermediate II might be subject.
(13) The reaction procedure was based on the method described by A. C. Cope and E. Ciganek, "Organic Synthesis," Collect. Vol. IV, Wiley, New York, N. Y., 1963, pp 339, 612.
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(15) For comparison purposes, iodobenzene dichloride was prepared by the accepted procedure: H. J. Lucas and E. R. Kennedy, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 482.
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1,3-Oxathiole 3,3-Dioxides and Benzoyl-Substituted Thiirane 1,1-Dioxides

Ulla Jacobsson, Tomas Kempe, and Torbjörn Norin*

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden

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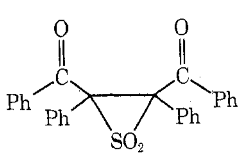
Bis(phenacyl) sulfone on bromination to bis(α-bromophenacyl) sulfone (**2**) and then treatment with base yielded 2-benzoyl-4-bromo-5-phenyl-1,3-oxathiole 3,3-dioxide (**5**). Reduction of **5** with triphenylphosphine in methanol gave 2-benzoyl-5-phenyl-1,3-oxathiole 3,3-dioxide (**10**), which can be degraded with base to the known 5-phenyl-1,3-oxathiole 3,3-dioxide (**7**). The structural assignments for the compounds previously ascribed to be 2,3-dibenzoyl-2,3-diphenylthiirane (**15**) and the corresponding thiirane 1-oxides and 1,1-dioxide are revised. It is suggested that the compounds are 2-benzoyl-2,4,5-triphenyl-1,3-oxathiole (**14**), and the corresponding 3-oxides **18a** and **18b** and 3,3-dioxide **12**, respectively. The reactions and properties of these compounds will be discussed in terms of the new structural assignments. 2-Benzoyl-5-phenyl-1,3-oxathiole 3,3-dioxide (**10**) can be specifically deuterated in the 2 and 4 positions. There is no deuterium exchange between the two positions at room temperature, or at the melting point (150°). Rearrangement between 1,3-oxathiole 3,3-dioxides and 2,3-dibenzoylthiirane 1,1-dioxides is therefore negligible under these conditions.

Thiirane 1,1-dioxides easily undergo thermal decomposition to yield alkenes and sulfur dioxide. 2,3-Dibenzoyl-2,3-diphenylthiirane 1,1-dioxide (**1**) is, however, reported to be unusually thermostable.[1]

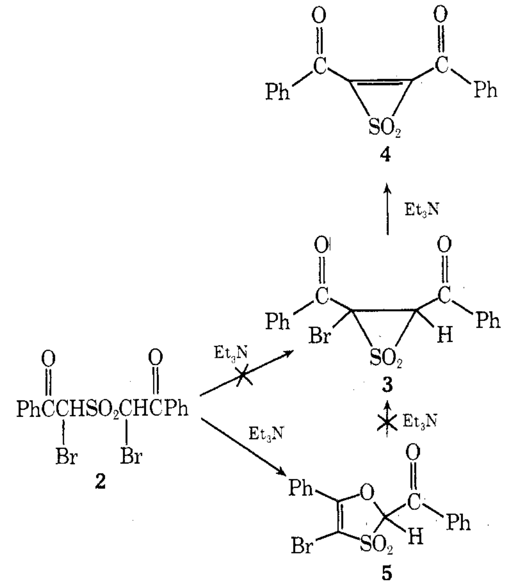


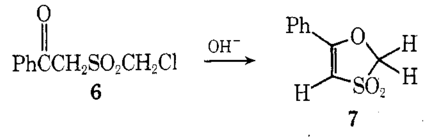
1

It was therefore of interest to investigate the possible synthesis of this and related compounds from the corresponding α-halo sulfones, thus for the first time being able to trap an intermediate thiirane 1,1-dioxide in a Ramberg–Bäcklund rearrangement.[2] However, efforts to prepare 2-bromo-2,3-dibenzoylthiirane 1,1-dioxide (**3**) or the corresponding thiirene 1,1-dioxide **4** from bis(α-bromophenacyl) sulfone (**2**) failed. Instead 2-benzoyl-4-bromo-5-phenyl-1,3-oxathiole 3,3-dioxide (**5**) was formed in a high yield, which is in agreement with a previous synthesis of 5-phenyl-1,3-oxathiole 3,3-dioxide (**7**) from the α-halo keto sulfone **6**.[3]

The present paper describes the synthesis and properties of some 1,3-oxathiole 3,3-dioxides. Furthermore, the structure of the compound previously assigned to be 2,3-dibenzoyl-2,3-diphenylthiirane 1,1-dioxide (**1**) will be questioned, and evidence for the 1,3-oxathiole 3,3-dioxide structure **12** will be presented. In view of this new structural assignment the previously reported reactions of this[1] and related compounds[4,5] will be discussed.

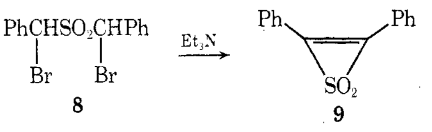
Bis(phenacyl) sulfone was prepared from bis(phenacyl) sulfide[6] by oxidation with 3-chloroperbenzoic acid in chloroform. The sulfone was brominated with 2 equiv of bromine in chloroform to yield bis(α-bromophenacyl) sulfone[7] (**2**), which precipitated from the reaction mixture. The compound was almost insoluble in most solvents and was therefore difficult to obtain chromatographically pure (tlc). Treatment of the crude compound with triethylamine in methylene chloride at room temperature gave 2-benzoyl-4-



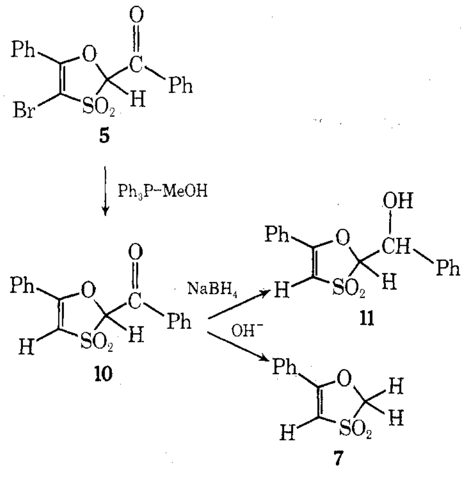


bromo-5-phenyl-1,3-oxathiole 3,3-dioxide (**5**). 2-Benzoyl-5-phenyl-1,3-oxathiole 3,3-dioxide (**10**) was also detected (tlc) in the reaction mixture. It appears to be formed from traces of a monobrominated product in the starting material.

Thiirene 1,1-dioxides are known to be formed from α,α'-dibromo sulfones on treatment with base.[8] Thus bis(α-bromobenzyl) sulfone (**8**) yields the 2,3-diphenylthiirene 1,1-dioxide (**9**). However, there were no indications of the presence of the thiirene 1,1-dioxide **4** in the reaction mixture from the triethylamine treatment of bis(α-bromophenacyl) sulfone (**2**). The 1,3-oxathiole 3,3-dioxide **5** was stable when treated with excess triethylamine in refluxing benzene for 1 hr and thus does not rearrange to an intermediate bromothiirane 1,1-dioxide **3** which would be expected to give the thiirene 1,1-dioxide **4**.



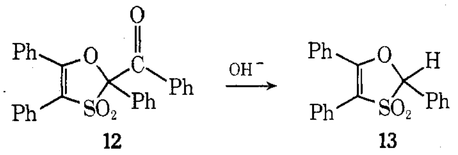
Treatment of 2-benzoyl-4-bromo-5-phenyl-1,3-oxathiole 3,3-dioxide (**5**) with triphenylphosphine[9] in refluxing methanol for 1 hr gave a product which after recrystallization from ethanol was characterized as 2-benzoyl-5-phenyl-1,3-oxathiole 3,3-dioxide (**10**). Reduction of 2-benzoyl-5-phenyl-1,3-oxathiole 3,3-dioxide (**10**) with sodium borohydride in ethanol gave a diastereomeric mixture of 2-(α-hydroxybenzyl)-5-phenyl-1,3-oxathiole 3,3-dioxides (**11**) which were not separated.



It has recently been reported[10] that γ-benzoyl-γ-chloro-γ-methylsulfonylbutyronitrile under alkaline conditions splits off the benzoyl group to give γ-chloro-γ-methylsulfonylbutyronitrile. When 2-benzoyl-5-phenyl-1,3-oxathiole 3,3-dioxide (**10**) is treated with base under similar conditions the known 5-phenyl-1,3-oxathiole 3,3-dioxide (**7**)[3,11] is formed. The structural assignments of compounds **5, 10,** and **7** follow from their mode of preparation and from spectral properties (see Experimental Section), which are all consistent with 1,3-oxathiole 3,3-dioxide structures.

Hoffmann, *et al.*,[12] have presented some theoretical aspects of the bonding in some three-membered rings containing sulfur. They discussed the long C–C bond of thiirane 1,1-dioxides and conclude that π-acceptor substituents will weaken still more this long C–C bond. It is, therefore, not surprising to find that the 1,3-oxathiole 3,3-dioxide **5** is formed instead of the benzoyl-substituted thiirane 1,1-dioxide **3** when the bromo sulfone **2** is treated with base. Furthermore, the structure of the stable compound previously assigned[1] to be 2,3-dibenzoyl-2,3-diphenylthiirane 1,1-dioxide (**1**) must be questioned. According to the predictions, this thiirane 1,1-dioxide **1** should be less stable than the corresponding tetraphenylthiirane 1,1-dioxide. However, the tetraphenylthiirane 1,1-dioxide is reported[13] to undergo a facile thermal rearrangement *via* C–C bond fission.

The compound ascribed the structure **1** was prepared by the method described in the original paper and was found to have spectral properties similar to those of the 1,3-oxathiole 3,3-dioxides **5, 10,** and **7.** Moreover, the compound could be degraded under alkaline conditions in a reaction similar to the formation of **7** from **10.** Consequently, there seems to be no doubt that the compound is 2-benzoyl-2,4,5-triphenyl-1,3-oxathiole 3,3-dioxide (**12**), and that the product formed in the alkaline degradation is 2,4,5-triphenyl-1,3-oxathiole 3,3-dioxide (**13**). A borohydride reduction of **12** also yielded this product, presumably by a reduction to the secondary alcohol followed by a cleavage analogous to a retro-aldol condensation.



Main ms fragmentations of the 1,3-oxathiole 3,3-dioxides are shown in Scheme I. The mass spectra of all compounds exhibit peaks corresponding to acetylenic fragments, *e.g.*, bromophenylacetylene (*m/e* 180), phenylacetylene (*m/e* 102), and diphenylacetylene (*m/e* 178). A metastable ion peak at *m/e* 130 occurs in the mass spectra of compounds **12** and **13** due to the breakdown of the ion *m/e* 242 giving the ion *m/e* 178 as indicated in Scheme I. The base peaks in the mass spectra of compounds possessing benzoyl or hydroxybenzyl groups in the 2 position arise from splitting off of these substituents.

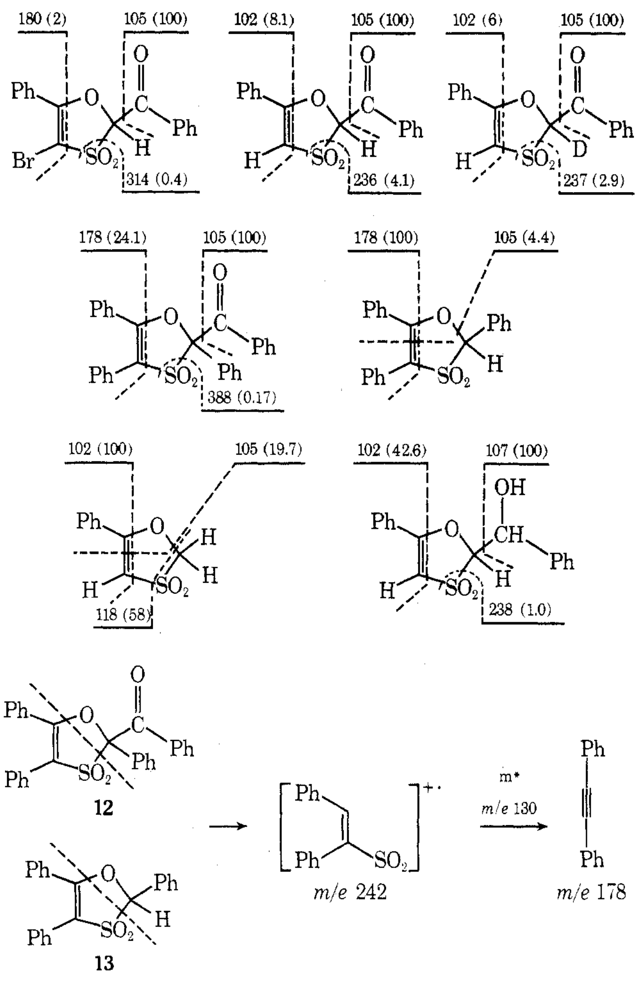
Since it has originally been suggested that the 2-benzoyl-2,4,5-triphenyl-1,3-oxathiole 3,3-dioxide (**12**) was the thiirane 1,1-dioxide **1,** it was of interest to investigate whether the starting material for the synthesis of compound **12** was the 2-benzoyl-2,4,5-triphenyl-1,3-oxathiole (**14**), and not the thiirane **15.** Compound **14** was prepared according to the original method.[1] The ir of this compound exhibits characteristic bands at 1680 and 1625 cm^{-1} due to the car-

Table I
^{13}C Nmr Data of Some 1,3-Oxathiole Derivatives[a]

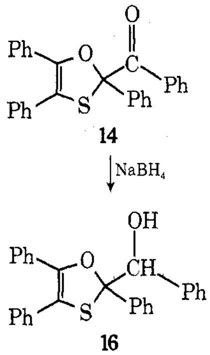
Compd (registry no.)	Ring carbons[b]			Substituent carbons				
	C—2	C—4	C—5	C aromatic				>C=O
5-Phenyl-1,3-oxathiole 3,3-dioxide (**7**) (21120-03-6)	82.3	99.1	164.7	126.6	127.8	128.9	132.4	
2-Benzoyl-5-phenyl-1,3-oxathiole 3,3-dioxide (**10**) (51911-51-4)	90.4	97.6	164.9	126.9	127.4	128.6	129.0	184.6
				129.2	132.7	134.4	135.0	
2-Benzoyl-2,4,5-triphenyl-1,3-oxathiole 3,3-dioxide (**12**) (51911-52-5)	98.6	114.7	154.9	124.5	125.1	128.2	128.3	191.0
				128.5	129.0	129.1	129.4	
				129.6	129.7	130.3	130.4	
				131.1	131.9	133.3	135.7	
2-Benzoyl-2,4,5-triphenyl-1,3-oxathiole (**14**) (51911-53-6)	100.9	111.1	142.1	126.0	126.9	127.9	128.2	194.1
				128.4	128.6	128.8	129.1	
				129.3	129.4	129.8	130.4	
				131.8	133.0	133.8	138.9	

[a] ^{13}C nmr spectra (22.63 MHz, chemical shifts in parts per million from TMS, internal standard) were recorded on a Brucker pulsed nmr spectrometer B-KR 322S equipped with an external field stabilizer. [b] Numbering of carbon atoms according to the *Chemical Abstracts* nomenclature rules.

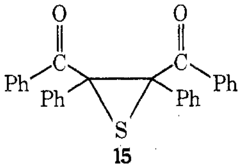
Scheme I



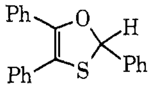
bonyl and the carbon–carbon double bond. Compound **14** was reduced with sodium borohydride to yield a mixture of diastereomeric alcohols **16.** The ir of this crude mixture did not exhibit any carbonyl band. The nmr spectrum (CDCl$_3$) of the diastereomeric mixture shows two singlets at δ 5.1 and δ 5.2, together equivalent to one proton, which are due to the methine protons of the two isomeric alcohols. The alcohols were formed in the proportions 1:4. A thiirane structure would have given rise to a more complex mixture possessing two protons of this type.



14 **16**



15



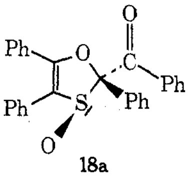
17

The 2,4,5-triphenyl-1,3-oxathiole (**17**) previously described by Kuhlmann and Dittmer[14] exhibits some very characteristic spectroscopic properties [ir (KBr) 1620 and 1245 cm^{-1}; uv max (EtOH) 342 nm (ϵ 6760)] which are also shown by compound **14** [ir (KBr) 1625 and 1230 cm^{-1}; uv max (EtOH) 330 nm (ϵ 7000)] and the diastereomeric alcohols **16** [ir (KBr) 1625 and 1230 cm^{-1}; uv max (EtOH) 339 nm (ϵ 6330)].

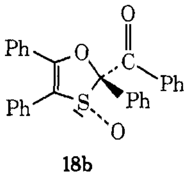
The collected evidence presented above leaves little doubt that the compound previously reported to be the thiirane **15** must be the 2-benzoyl-2,4,5-triphenyl-1,3-oxathiole (**14**).[15]

The structural assignment of compound **14** is also confirmed by its ^{13}C nmr spectrum (Table I). Most significant is the presence of only one signal due to a carbonyl carbon which together with the 20 signals of aromatic carbons (four nonequivalent phenyl groups) rules out the thiirane structure **15.**

Accordingly, the sulfoxides previously prepared[1a,4] from this oxathiole must be the epimeric mixture of the 2-benzoyl-2,4,5-triphenyl-1,3-oxathiole 3-oxides (**18a** and **18b**). The spectroscopic data reported for this compound are consistent with a 1,3-oxathiole 3-oxide structure.



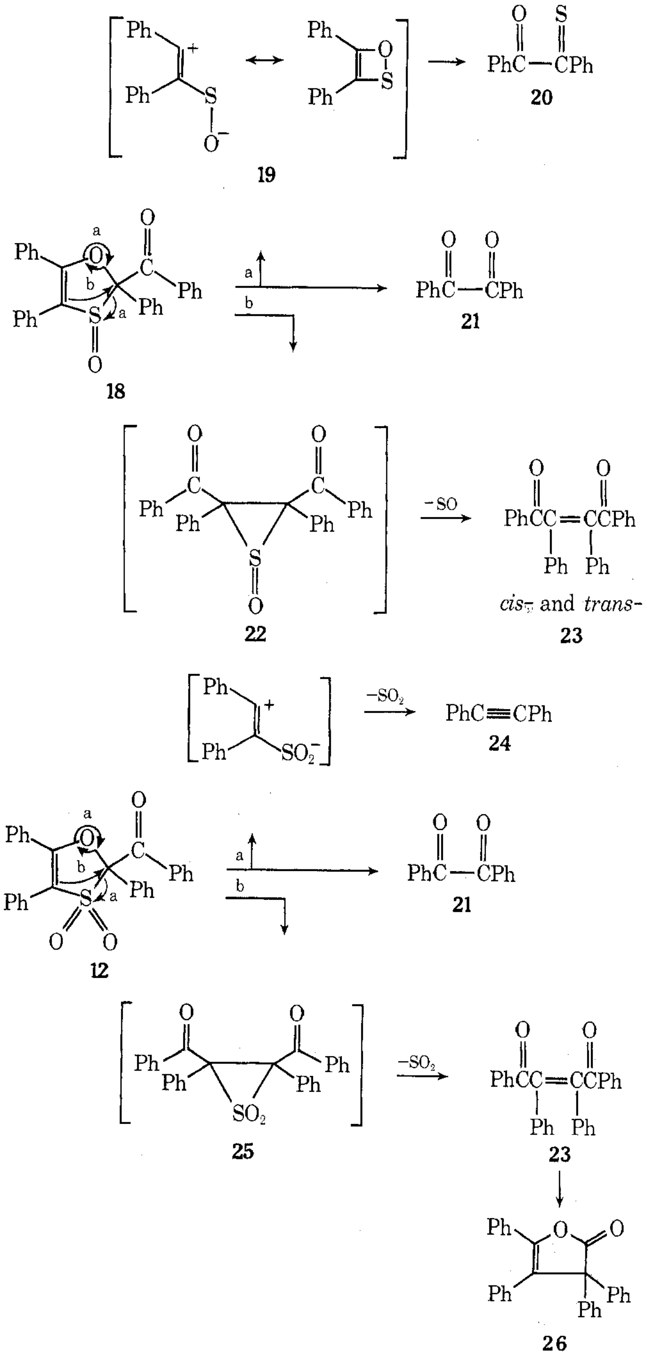
18a



18b

The 1,3-oxathiole structures of compounds **12** and **18** make it of interest to examine the previously reported[1b,4a] results on the thermal decomposition of these two compounds. Pyrolysis of the 1,3-oxathiole 3-oxides **18a** and **18b** at 200–210° yields monothiobenzil (**20**), benzil (**21**), and *cis*- and *trans*-dibenzoylstilbene (**23**). Pyrolysis (300°) of the 1,3-oxathiole 3,3-dioxide **12** gives benzil (**21**), diphenylacetylene (**24**), and the lactone **26** of 4-hydroxy-2,2,3,4-tetraphenyl-3-butenoic acid. The lactone **26** could have been formed from an intermediate dibenzoylstilbene (**23**) according to a known[16] reaction. The product patterns of the two pyrolysis reactions can be explained by assuming two reaction paths (Scheme II, a and b). Path a in the pyrolysis of the 1,3-oxathiole 3-oxide **18** gives benzil (**21**) and monothiobenzil (**20**), the latter *via* a rearrangement of a 1,2-oxathiete intermediate **19** (*cf.* the α-dithione–1,2-dithiete equilibrium).[17]

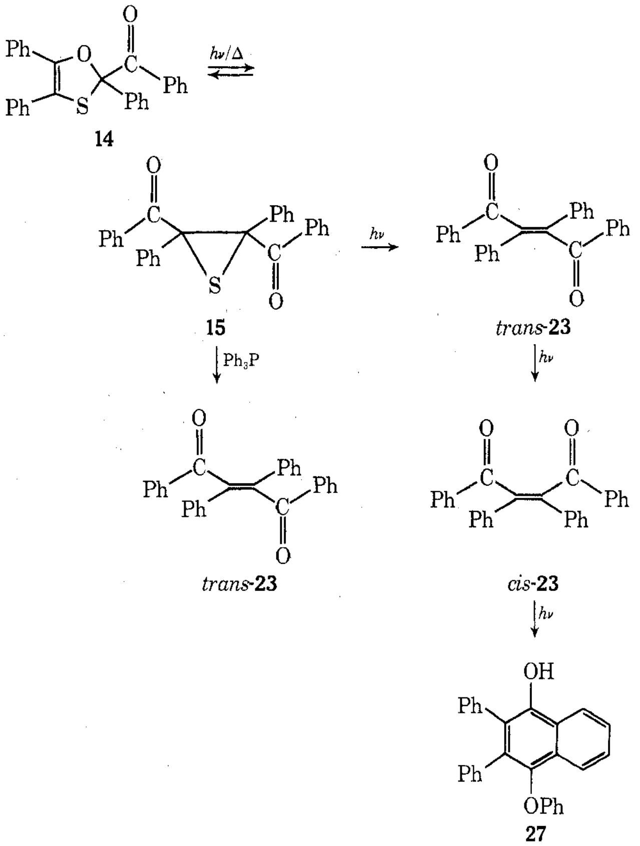
Scheme II



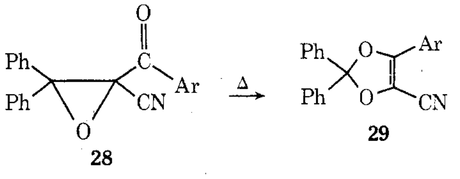
The formation of dibenzoylstilbene (**23**) can be rationalized assuming an intermediate thiirane 1-oxide **22** with elimination of sulfur oxide according to path b.

The pyrolysis of the 1,3-oxathiole 3,3-dioxide **12** *via* path a gives benzil (**21**) and diphenylacetylene (**24**) after elimination of sulfur dioxide. Path b gives the lactone **26** and it can be rationalized from an intermediate thiirane 1,1-dioxide **25** which decomposes to dibenzoylstilbene (**23**) and cyclizes at the pyrolysis temperature (300°).

Padwa, *et al.*,[5] have investigated the photochemical transformation of the compound previously ascribed to be the 2,3-dibenzoyl-2,3-diphenylthiirane (**15**). The photolysis afforded the *cis*- and *trans*-dibenzoylstilbenes (**23**) together with minor amounts of 1-hydroxy-2,3-diphenyl-4-phenoxynaphthalene (**27**) and a 2,3-dibenzoyl-2,3-diphenylthiirane (**15**), the configuration of which was assigned to be cis. Padwa also reported that this thiirane upon heating in refluxing xylene for 30 min was transformed to the thermodynamically more stable starting material of the photolysis reaction. The naphthol **27** was found to be a secondary product derived from the dibenzoylstilbenes.



Padwa's results may well be rationalized using the new structural assignment **14** of the starting material. The photolytic transformation of the 1,3-oxathiole **14** to the dibenzoylstilbene **23** is proposed to proceed *via* the thiirane **15**, which is in equilibrium with the thermodynamically more stable 1,3-oxathiole **14**. The transformation of the thiirane **15** to the 1,3-oxathiole **14** upon heating in xylene is analogous to the known[18] conversion of α-aroyloxiranes **28** to 1,3-dioxoles **29**.

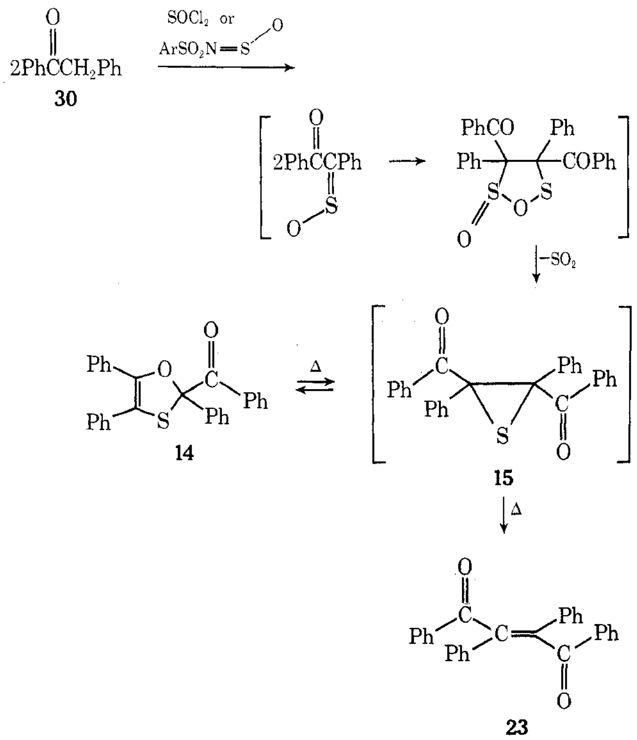


An equilibrium between the 1,3-oxathiole **14** and the thiirane **15** also explains the reactions of the two compounds with triphenylphosphine in refluxing xylene to yield *trans*-dibenzoylstilbene (*trans*-**23**). The desulfurization step is known to be stereospecific,[19] which suggests that the thiirane **15** possesses a trans configuration.

A comparison of the spectral data reported for the trans thiirane **15** (Padwa's *cis*-dibenzoyldiphenylthiirane)[5] with those of the 1,3-oxathiole **14** gives some further support for the proposed structures of the two compounds. The ir of the 1,3-oxathiole **14** exhibits a strong band at 1625 cm^{-1}, which is assigned to the carbon–carbon double bond of the oxathiole ring. This band is not reported to be present in the thiirane **15**. The 1,3-oxathiole **14** shows strong uv absorption at 330 nm (ϵ 7000) which is assigned to the enethiole ether chromophore of the oxathiole ring. The thiirane **15** exhibits only weak absorption in this region (345 nm, ϵ 900).

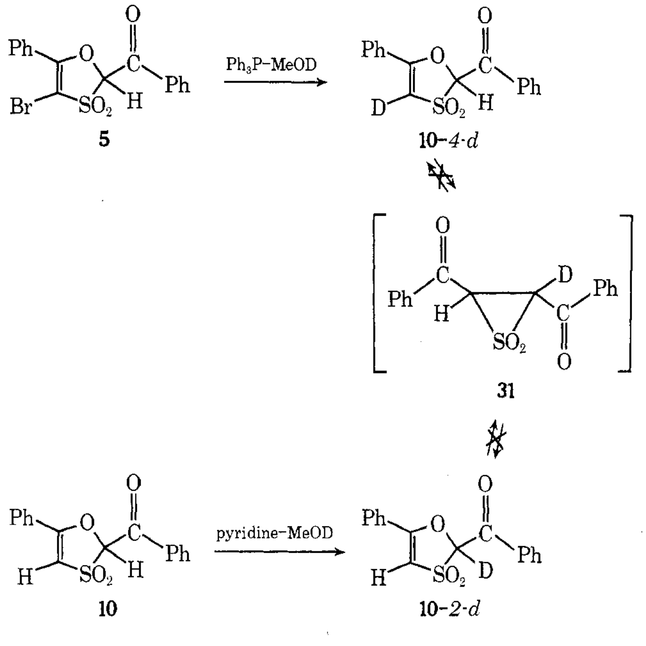
Recently, Ireland and Pizey[20] studied the reaction of deoxybenzoin (**30**) with thionyl chloride (Scheme III). They reported the isolation of a product which upon heating yielded dibenzoylstilbene (**23**). The same product was also prepared by Kresze and Wucherpfennig[21] by treatment of deoxybenzoin (**30**) with *N*-sulfinyl-*p*-toluenesulfonamide. The product was supposed to be 2,3-dibenzoyl-2,3-diphenylthiirane (**15**).[20,21] Its melting point and spectral data were similar to those reported by Dittmer, *et al.*[1] However, the intermediate ought to be2-benzoyl-2,4,5-triphenyl-1,3-oxathiole (**14**). In order to confirm this prediction, we have repeated the experiments by Ireland[20] and Kresze.[21] From the reaction mixtures a compound was isolated which was shown to be identical in all respects with the 1,3-oxathiole **14**. The formation of this product may initially proceed, according to the reaction scheme III proposed by Kresze and Wucherpfennig,[21] to an intermediate thiirane **15** which rearranges to the 1,3-oxathiole **14**.

Scheme III



The possible rearrangement of 1,3-oxathiole 3,3-dioxides to thiirane 1,1-dioxides has been investigated (Scheme IV). When 2-benzoyl-5-phenyl-1,3-oxathiole 3,3-dioxide (**10**) was treated with acetone-d_6 and methanol-*O*-*d* in the presence of triethylamine, deuterium exchange occurred in both 2 and 4 positions. Exchange in the 2 position (followed by nmr) was almost instantaneous at room temperature. The exchange at the 4 position was much slower but was nearly complete after 1 hr at 40° ($t_{1/2}$ 10.5 min). If the deuterium exchange was carried out in a mixture of chloroform-d_1 and methanol-*O*-*d* in the presence of pyridine there was an exchange in the 2 position (**10**-*2-d*) but no exchange was observed in the 4 position after 6 hr at 25°. A specific deuteration of the 4 position (**10**-*4-d*) was obtained by reduction of the bromo compound **5** with triphenylphosphine in methanol-*O*-*d*. There was no deuterium scrambling in the specifically deuterated compounds **10**-*4-d* and **10**-*2-d* under the conditions of preparation. Nor was there any scrambling when compound **10**-*2-d* was heated above its melting points (150°) for 25 min. Thus, there was no observable equilibrium between the 1,3-oxathiole 3,3-dioxide (**10**-*2-d*) and the thiirane 1,1-dioxide **31**

Scheme IV



Experimental Section

All melting points are uncorrected. Uv spectra were recorded in ethanol (95%) on a Beckman DK-2 spectrophotometer and ir spectra on a Perkin-Elmer Model 421 infrared spectrophotometer. Nmr spectra (60 MHz, TMS internal standard) were run on a Varian Model A-60A instrument. Mass spectra were obtained (direct inlet) using an LKB Model 9000 mass spectrometer.

Thin layer chromatograms were run on fluorescent silica gel (Merck HF-254) with light petroleum, bp 40–60°, unless otherwise stated.

Bis(phenacyl) Sulfone.—A solution of bis(phenacyl) sulfide[6] (18.9 g, 0.07 mol) in chloroform (250 ml) was cooled to 5° and solid 3-chloroperbenzoic acid (80%, 30 g, 0.14 mol) was added in small portions. The temperature was not allowed to rise above 20°. After the addition, the solution was stirred at room temperature for 24 hr. The white precipitate of 3-chlorobenzoic acid was filtered off. The filtrate was washed with saturated sodium bicarbonate solution and dried and the solvent was evaporated *in vacuo*. The residue was recrystallized from ethanol to yield bis(phenacyl) sulfone as white crystals: mp 124–126° (lit.[22] mp 124°); yield 17 g (80%); ir (KBr) 1680 (C=O), 1330, 1140 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 4.95 (s, 4, CH_2), 7.5–7.9 (m, 10, aromatic).

Anal. Calcd for $C_{16}H_{14}O_4S$: C, 63.56; H, 4.67; S, 10.61. Found: C, 63.49; H, 4.56; S 10.60.

Bis(α-bromophenacyl) Sulfone (2). A solution of bis(phenacyl) sulfone (6 g, 0.02 mol) in chloroform (100 ml) was treated with bromine (6.4 g, 0.04 mol) in chloroform (50 ml) at room temperature. After stirring for about 2 hr all the bromine had been consumed and the product had precipitated. The solvent was evaporated *in vacuo* and the residue was washed with cold methanol. To obtain an analytically pure sample of bis(α-bromophenacyl) sulfone (**2**), the product was recrystallized from ethanol: mp 185–186°

(lit.[7] mp 186°); yield 9 g (89%); ir (KBr) 1670 (C=O), 1300, 1150 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 7.6–8.1 (m, aromatic and CH).

Anal. Calcd for $C_{16}H_{12}Br_2O_4S$: C, 41.76; H, 2.63; Br, 34.73; S, 6.97. Found: C, 42.22; H, 2.59; Br, 34.39; S, 6.94.

2-Benzoyl-4-bromo-5-phenyl-1,3-oxathiole 3,3-Dioxide (5). To a mixture of crude bis(α-bromophenacyl) sulfone (**2**, 4.6 g, 0.01 mol) in methylene chloride (75 ml) was added triethylamine (1.5 g, 0.015 mol). The clear solution was stirred at room temperature for 1 hr. The solution was then extracted with dilute hydrochloric acid to remove excess triethylamine, washed with water, and dried.

The crude mixture (3.8 g) which remained after evaporation *in vacuo* was chromatographed on silica gel. Benzene eluted a product which after recrystallization from ethanol yielded the 1,3-oxathiole 3,3-dioxide **5**: mp 160–161°; yield 2.4 g (63%); R_f (benzene) 0.25; uv max 254 nm (ε 21,900), 260 (21,900); ir (KBr) 1690 (C=O), 1610 (C=C), 1320, 1150 (SO_2), 1250 cm^{-1} (C=C–O); nmr ($CDCl_3$) δ 6.50 (s, 1, CH), 7.50–7.95 (m, 10, aromatic); nmr (acetone-d_6) δ 7.20 (s, 1, CH), 7.6–8.05 (m, 10, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 380 (1.54), 378 (1.50), 316 (0.42), 314 (0.42), 182 (2.04), 180 (2.08), 106 (7.92), 105 (100), 102 (4.13), 101 (4.04), 89 (2.13), 78 (1.96), 77 (26.3).

Anal. Calcd for $C_{16}H_{11}BrO_4S$: C, 50.67; H, 2.92; Br, 21.07; S, 8.46. Found: C, 50.45; H, 2.85; Br, 21.51; S, 8.22.

2-Benzoyl-5-phenyl-1,3-oxathiole 3,3-Dioxide (10). To the crude 2-benzoyl-4-bromo-5-phenyl-1,3-oxathiole 3,3-dioxide (**5**, 3.8 g) in methanol (50 ml) was added triphenylphosphine (3.2 g, 0.012 mol). The mixture was refluxed during 1 hr. Evaporation of the solvent *in vacuo* gave a solid residue. Recrystallization from ethanol yielded 2-benzoyl-5-phenyl-1,3-oxathiole 3,3-dioxide (**10**): mp 139–140°; yield 1.5 g (50%); R_f (benzene) 0.14; uv max 255 nm (ε 24,000), 259 (24,000); ir (KBr) 1700 (C=O), 1610 (C=C), 1310, 1140 (SO_2), 1250 cm^{-1} (C=C–O); nmr ($CDCl_3$) δ 6.45 (s, 2, CH and =CH), 7.5–8.0 (m, 10, aromatic); nmr (acetone-d_6) δ 7.00 (s, 1, CH), 7.17 (s, 1, =CH), 7.5–8.0 (m, 10, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 301 (0.09), 300 (0.43), 237 (0.74), 236 (4.14), 208 (0.07), 207 (0.09), 179 (0.07), 178 (0.16), 135 (0.07), 134 (0.17), 133 (0.10), 131 (0.09), 118 (0.22), 107 (0.48), 106 (7.93), 105 (100), 103 (1.55), 102 (8.10), 101 (0.22), 91 (0.40), 90 (0.76), 89 (1.34), 78 (2.14), 77 (29.3).

Anal. Calcd for $C_{16}H_{12}O_4S$: C, 63.99; H, 4.03; S, 10.68. Found: C, 64.03; H, 3.96; S, 10.67.

5-Phenyl-1,3-oxathiole 3,3-Dioxide (7). A solution of 2-benzoyl-5-phenyl-1,3-oxathiole 3,3-dioxide (**10**, 1.5 g, 0.005 mol) in methanol (40 ml) was mixed with anhydrous potassium carbonate (0.3 g) in water (10 ml). The solution was refluxed during 4.5 hr and then diluted with water (200 ml) and extracted with chloroform. The chloroform phase was washed with water, dried, and evaporated *in vacuo*. Recrystallization of the residue (1.45 g) from methanol yielded 5-phenyl-1,3-oxathiole 3,3-dioxide (**7**): mp 168–170° (lit.[3] mp 165–168°); yield 0.4 g (27%); R_f (benzene), 0.08; uv max 264 nm (ε 14,300); ir (KBr) 1610 (C=C), 1300, 1285, 1130 (SO_2), 1270 cm^{-1} (C=C–O); nmr ($CDCl_3$) δ 5.05 (s, 2, CH_2), 6.52 (s, 1, =CH), 7.5 (m, 5, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 198 (3.06), 197 (6.39), 196 (58.3), 167 (0.83), 149 (0.56), 148 (1.94), 138 (5.00), 137 (3.33), 121 (3.33), 119 (5.56), 118 (58.3), 110 (3.33), 105 (19.7), 103 (10.0), 102 (100), 94 (8.61), 91 (2.22), 90 (8.06), 89 (4.17), 78 (1.39), 77 (16.4). Spectral data were identical with those reported by Nozaki, *et al.*[11]

Anal. Calcd for $C_9H_8O_3S$: C, 55.09; H, 4.11; S, 16.34. Found: C, 55.20; H, 4.17; S, 16.20.

Diastereomeric 2-(α-Hydroxybenzyl)-5-phenyl-1,3-oxathiole 3,3-Dioxides (11). To a solution of 2-benzoyl-5-phenyl-1,3-oxathiole 3,3-dioxide (**10**, 702 mg, 2.3 mmol) in absolute ethanol (75 ml) was added a solution of sodium borohydride (87.4 mg, 2.3 mmol) in absolute ethanol (25 ml). The reaction mixture was stirred for 1 hr, poured into water (300 ml), acidified with aqueous hydrochloric acid (1 *M*), and extracted with chloroform. The chloroform solution was washed with water, dried, and evaporated *in vacuo*. The oily residue was dissolved in a limited amount of ethyl ether. On addition of light petroleum (bp 40–60°) the diastereomeric alcohols **11** precipitated as white crystals: mp 134–136°; yield 240 mg (35%); uv max 267 nm (ε 10,600); ir (KBr) 3440 (OH), 1615 (C=C), 1290 (broad), 1140 cm^{-1} (SO_2); nmr (acetone-d_6) overlapping signals at δ 5.12 and 5.17 (integrated area 1.3 H) assigned to the two vicinal CH in one of the epimers and at δ 5.32 and 5.37 (0.7 H) assigned to the corresponding CH groups of the other epimer, 7.05 (s, 1, =CH), 7.4 (m, 10, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 304 (0.80), 303 (2.13), 302 (11.9), 278 (0.53), 238 (0.96), 220 (0.96), 198 (2.66), 197 (5.21), 196 (47.9), 150 (1.06), 136 (0.74), 135 (0.64), 134 (0.53), 120 (1.81), 119 (0.74), 118 (1.06), 115 (0.74), 108 (7.77), 107 (100), 106 (2.13), 105 (17.0), 104 (3.72), 103 (40.4), 102 (42.6), 101 (0.96), 92 (0.85), 91 (8.62), 90 (2.23), 89 (3.30), 86 (2.87), 80 (2.45), 79 (37.2), 78 (4.79), 77 (34.0).

Anal. Calcd for $C_{16}H_{14}O_4S$: C, 63.56; H, 4.67; S, 10.61. Found: C, 63.48; H, 4.67; S, 10.49.

2-Benzoyl-2,4,5-triphenyl-1,3-oxathiole (14). This compound, originally suggested[1] to be 2,3-dibenzoyl-2,3-diphenylthiirane (**15**), was prepared according to the previous method by Dittmer, *et al.*[1] The compound was chromatographed on silica. Benzene eluted the product, which after recrystallization from methanol exhibited similar properties to those reported by Dittmer, *et al.*:[1] mp 104–106° (lit.[1] mp 106–122°); R_f (benzene) 0.63; uv max 229 nm (ε 25,000), 250 shoulder (21,500), 330 (7000); ir (KBr) 1680 (C=O), 1625 (C=C), 1230 cm^{-1} (C=C–O); mass spectrum (70 eV) *m/e* (rel intensity) 421 (0.15), 420 (0.45), 389 (0.13), 388 (0.38), 373 (0.05), 372 (0.18), 318 (1.28), 317 (7.00), 316 (21.5), 315 (100), 299 (0.15), 255 (0.33), 210 (0.33), 179 (0.15), 178 (0.80), 106 (1.03), 105 (12.5), 78 (0.10), 77 (0.08).

2-(α-Hydroxybenzyl)-2,4,5-triphenyl-1,3-oxathiole (16). A solution of 2-benzoyl-2,4,5-triphenyl-1,3-oxathiole (**14**, 420 mg, 0.001 mol) in absolute ethanol (40 ml) was mixed with sodium borohydride (76 mg, 0.002 mol) in absolute ethanol (15 ml) and the solution was stirred for 15 min. The reaction mixture was then poured into water (200 ml) and extracted with ethyl ether. The organic phase was washed with water, dried, and evaporated *in vacuo* to a semicrystalline residue: yield 400 mg (95%); R_f (benzene) 0.26; uv max 339 nm (ε 6330); ir (KBr) 3440 (broad, OH), 1625 (C=C), 1230 cm^{-1} (C=C–O); nmr ($CDCl_3$) δ 5.1 and 5.2 (two signals with integrated areas corresponding to 0.2 and 0.8 H, respectively, assigned to the methine proton, CH), 7.1 (m, 15, aromatic); mass spectrum (20 eV) *m/e* (rel intensity) 404 (0.23), 373 (0.39), 372 (1.02), 318 (1.56), 317 (8.36), 316 (26.2), 315 (100), 300 (0.86), 255 (0.55), 228 (0.39), 227 (0.70), 226 (1.02), 212 (0.39), 211 (0.94), 210 (1.02), 196 (1.88), 179 (0.78), 178 (3.40), 167 (0.78), 122 (0.86), 121 (3.83), 107 (0.78), 106 (6.33), 105 (53.1), 91 (0.31), 78 (0.78), 77 (1.56).

2-Benzoyl-2,4,5-triphenyl-1,3-oxathiole 3,3-Dioxide (12). The crude compound (**14**, 11.6 g) was dissolved in hot acetic acid (100 ml) and hydrogen peroxide (30%, 15 ml) was added. The reaction mixture was heated at 90–95° for 3 hr and then allowed to stand at room temperature overnight. White crystals (5 g) precipitated. The crystalline material was dissolved in chloroform and the solution was washed with water and dried. Evaporation of the solvent *in vacuo* gave a product which after recrystallization from benzene–light petroleum yielded crystals of **12**: mp 92–96° (lit.[1] mp 90–93°); R_f (ethyl ether–light petroleum, 40:60) 0.23; uv max 233 nm shoulder (ε 25,300), 253 (21,200), 285 shoulder (11,000); [lit.[1] uv 233 nm shoulder (ε 21,500), 254 max (19,500)]; ir (CS_2) *cf.* lit.[1] 1690 (C=O), 1650 (C=C), 1330, 1155 (SO_2), 1265 cm^{-1} (C=C–O); mass spectrum (70 eV) *m/e* (rel intensity) *cf.* also lit.[1] 454 (0.11), 453 (0.31), 452 (1.01), 389 (0.05), 388 (0.17), 372 (0.07), 347 (0.23), 283 (0.10), 255 (0.06), 254 (0.04), 253 (0.08), 252 (0.12), 242 (0.14), 226 (0.23), 210 (0.10), 180 (0.28), 179 (2.77), 178 (24.1), 177 (1.34), 176 (2.17), 175 (0.31), 166 (0.23), 165 (1.13), 164 (0.20), 163 (0.29), 153 (0.25), 152 (1.69), 151 (1.19), 150 (0.42), 140 (0.07), 139 (0.60), 138 (0.13), 128 (0.20), 127 (0.18), 126 (0.69), 121 (0.41), 115 (0.29), 107 (0.48), 106 (7.23), 105 (100), 102 (0.30), 89 (0.40), 77 (18.1).

2,4,5-Triphenyl-1,3-oxathiole 3,3-Dioxide (13). A solution of 2-benzoyl-2,4,5-triphenyl-1,3-oxathiole 3,3-dioxide (**12**, 0.55 g, 1.2 mmol) in methanol (40 ml) and dimethoxyethane (10 ml) was mixed with anhydrous potassium carbonate (0.2 g) in water (3 ml). The solution was refluxed during 40 min. The mixture was cooled and concentrated *in vacuo*. Ethyl ether was added and the organic phase was washed with water and dried. The residue (0.4 g) after evaporation of the solvents was recrystallized from ethanol to yield 2,4,5-triphenyl-1,3-oxathiole 3,3-dioxide (**13**): mp 167–168°; yield 0.35 g (84%); R_f (ethyl ether–light petroleum, 40:60) 0.29; uv max 279 nm (ε 11,900); ir (KBr) 1640 (C=C), 1310, 1140 (SO_2), 1240 cm^{-} (C=C–O); nmr ($CDCl_3$) δ 6.05 (s, 1, CH), 7.40 (m, 15, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 350 (0.15), 349 (0.37), 348 (1.56), 300 (0.41), 244 (0.37), 243 (0.96), 242 (5.56), 180 (1.07), 179 (13.7), 178 (100), 177 (3.26), 176 (5.56), 165 (1.00), 163 (0.52), 153 (0.52), 152 (3.96), 151 (2.81), 150 (1.07), 139 (1.19), 126 (1.52), 121 (1.04), 105 (4.44), 102 (0.70), 77 (4.44).

Anal. Calcd for $C_{21}H_{16}O_3S$: C, 72.39; H, 4.63; S, 9.20. Found: C, 72.28; H, 4.56; S, 9.22.

Treatment of 2-benzoyl-2,4,5-triphenyl-1,3-oxathiole 3,3-dioxide (**12**) in ethanol with sodium borohydride at room temperature for 2 hr also yielded 2,4,5-triphenyl-1,3-oxathiole 3,3-dioxide (**13**).

2-Benzoyl-2-deuterio-5-phenyl-1,3-oxathiole 3,3-Dioxide (10-2-*d*). A mixture of 2-benzoyl-5-phenyl-1,3-oxathiole 3,3-dioxide (**10**, 0.5 g) in chloroform-d_1 (3 ml), methanol-*O-d* (1 ml) and pyridine (0.1 g) was stirred at room temperature for 20 min. On addition of light petroleum the deuterated product **10**-2-*d* crystallized: mp 139–140°; yield 0.4 g; R_f (benzene) 0.14; nmr (acetone-d_6) δ 7.17 (s, 1, =CH), 7.5–8.0 (m, 10, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 301 (0.40), 300 (0.10), 238 (0.50), 237 (2.90), 236 (0.90), 107 (0.45), 106 (7.00), 105 (100), 104 (0.65), 103 (1.25), 102 (6.00), 92 (0.25), 91 (0.30), 90 (0.70), 89 (0.75), 78 (2.20), 77 (23.5).

2-Benzoyl-4-deuterio-5-phenyl-1,3-oxathiole 3,3-Dioxide (10-4-*d*). 2-Benzoyl-4-bromo-5-phenyl-1,3-oxathiole 3,3-dioxide (**5**, 70.9 mg) was added to a solution of acetone-d_6 (0.4 ml) and methanol-*O-d* (0.1 ml). The nmr of the mixture showed peaks at δ 7.20 (s, 1, CH), and 7.6–8.05 (m, 10, aromatic). Triphenylphosphine (70 mg) was added and the reduction reaction was followed by nmr at about 40°. The peak at δ 7.2 (CH in **5**) disappeared almost instantly and a peak developed at δ 7.0 (CH in **11**-4-*d*) reaching a maximum in about 20 min. No deuterium scrambling, *e.g.*, the formation of compound **11**-2-*d* (δ 7.17, =CH), was detected under the conditions used.

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Registry No.—**2**, 51911-54-7; **5**, 51911-55-8; **10**-2-*d*, 51911-56-9; **11**, 51911-57-0; **13**, 51911-58-1; **16**, 51911-59-2; bis(phenacyl) sulfone, 3708-08-5; bis(phenacyl) sulfide, 2461-80-5.

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Sulfonylation of Alkylidene- and Arylidenephosphoranes. An Unexpected Rearrangement

B. A. Reith, J. Strating, and A. M. van Leusen*

Department of Organic Chemistry, The University, Zernikelaan, Groningen, The Netherlands

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Sulfonyl-stabilized alkylidene- and arylidenetriphenylphosphoranes have been synthesized from alkyl- and aralkylsulfonyl fluorides and phosphoranes. A number of these reactions have been interpreted by [2 + 2] cycloadditions of sulfenes and phosphoranes to form four-membered ring intermediates, which will ring open in one or two possible directions, depending on the size of the substituents. This frequently leads to phosphonium ylides of rearranged structure. Relatively large substituents at the ylide carbon are sterically unfavorable.

In a previous paper[1] we have reported a useful method for the synthesis of sulfonyl-stabilized methylenetriphenylphosphoranes. These ylides (**3**, R^2 = H) were obtained in yields of 60–80% according to eq 1 for R^1 = aryl or alkyl.

$$\underset{\mathbf{1}}{R^1SO_2F} + \underset{\mathbf{2}}{2R^2CH{=}PPh_3} \xrightarrow[20^\circ]{\text{THF}} \underset{\mathbf{3}}{R^1SO_2CR^2{=}PPh_3} + R^2CH_2\overset{+}{P}Ph_3\overset{-}{F} \qquad (1)$$

For other studies we needed derivatives of the sulfonylmethylenephosphoranes **3** with R^2 = alkyl or aryl, insted of H. However, the results of reaction 1 were unsatisfactory when the less reactive benzylidenetriphenylphosphorane (**2**, R^2 = phenyl) was used. Even under more severe reaction conditions compounds **3** (R^1 = aryl; R^2 = phenyl) were obtained only in 12–15% yields.[1]

In an attempt to improve these results, we investigated the utility of more reactive sulfonylating agents (*i.e.*, sulfonic anhydrides and alkanesulfonyl fluorides) in the reaction with arylidenetriphenylphosphoranes. During these investigations an unexpected and intriguing rearrangement was discovered, the scope of which is evaluated in the present paper.

Two separate examples of compounds of type **3** with R^2 = phenyl[2a] and benzyl[2b] have been reported previously by other groups.

α-Sulfonylarylidenetriphenylphosphoranes.

The sulfonylation of benzylidenetriphenylphosphorane (**2**, R^2 = phenyl, prepared in the usual way from benzyltriphenylphosphonium bromide and butyllithium) was not improved by using, in reaction 1, *p*-toluenesulfonic anhy-