(0.9 mm) at 50° to give 38.5 g of crude 3-(*p*-chlorophenyl)-1,1-dideuteriopropionyl acetate.

The crude acetate was pyrolyzed at 600°. Distillation of the pyrolysate yielded 18.7 g (0.121 mol, 61% based on ethyl *p*-chlorophenylpropionate) of 3-(*p*-chlorophenyl)-1,1-dideuterio-1-propene, bp 46–50° (1.4 mm). Gas chromatography[21] showed the material to be 90% pure: nmr δ 2.73 (d, 6 H, $J = 7$ Hz), 5.15–5.50 (2 H, olefinic H), and 6.25–6.80 (4.5 H, aromatic H).

***p*-(γ,γ-Dideuterioallyl)cumyl *p*-Nitrobenzoate.**[15]—The Grignard reagent prepared from 5.0 g (0.038 mol) of 3-(*p*-chlorophenyl)-1,1-dideuterio-1-propene and 1.2 g (0.049 g-atom) of magnesium in 9 g of anhydrous tetrahydrofuran was allowed to react with excess acetone to give 3.2 g of material, bp 105–115° (1.5 mm). Gas chromatography[22] of the material showed *ca.* 85% one peak which had retention time identical with that observed upon chromatography of the nondeuterated analog. Ir spectra of distilled material showed strong OH absorption. Ir spectra of material collected by gas chromatography showed no OH absorption; *i.e.*, dehydration had occurred upon gas chromatography. Mass spectral analysis of the deuterated and nondeuterated olefins obtained by gas chromatography of the deuterated and nondeuterated alcohols showed the following composition for the deuterated anlog: 0.9% d_0, 4.9% d_1, 92% d_2, 0.7% d_3, 1.3% d_4.

Reaction of 3.2 g (0.018 mol) of the alcohol with 5.0 g (0.027 mol) of *p*-nitrobenzoyl chloride in 15 ml of pyridine yielded after normal work-up and recrystallization from pentane 2.66 g (0.0081 mol, 45%) of material, mp 38–39°. Two recrystallizations from pentane and drying under vacuum yielded material having mp 43.5–44° (cor) which was used for the kinetic measurements; nmr δ 3.30 (d, 2 H, $J = 7$ Hz), 5.7–6.0 (1 H, olefinic H), 7.0–7.34 (4 H, aromatic H), and 8.15 (4 H, aromatic H). No absorption was observed at 5 ppm where the nondeuterated derivative shows 2 H absorption.

Kinetic Procedure.—The desired amount of ester was dissolved in a preweighed quantity of acetone in a 100-ml volumetric flask, and the required weight of distilled, carbonate-free water was then added with shaking. The flask was placed in a thermostated bath and allowed to equilibrate for 15 min. In those cases where the half-life was less than 30 min, the solvents were preequilibrated at the bath temperature before mixing. At appropriate time intervals, 9-ml samples were removed and quenched with 10 ml of acetone at 0°, and the free *p*-nitrobenzoic acid was titrated with approximately 0.02 *N* sodium hydroxide using bromthymol blue as indicator. Infinity titers were taken after at least ten times the estimated half-life. Temperatures in all cases were controlled to at least ±0.03°.

Product Studies.—A solution of 0.307 g of *p*-allylcumyl *p*-nitrobenzoate in 100 ml of 50% w/w aqueous acetone was allowed to stand for 2 weeks at room temperature. After removing the acetone under reduced pressure, the aqueous residue was made basic with sodium bicarbonate, and the resultant solution was extracted with three 20-ml portions of ether. The extracts were combined, washed once with water, dried, and concentrated. The small quantity of residual oil which remained (*ca.* 50 μl) was distilled in a Hickman still. Capillary nmr spectra (Varian HA-100 spectrometer) of the distillate proved to be identical with that of *p*-allylcumyl alcohol. The infrared spectrum and retention times of the material upon vapor phase chromatography using GE SE-30 and FFAP liquid phases were identical with that of *p*-allylcumyl alcohol. No other components were detectable in the distillate. The pot residue had a melting point of 235–240°, undepressed on mixture with an authentic sample of *p*-nitrobenzoic acid.

In similar experiments, *p*-γ,γ-dimethylallyl-, *m*-allyl-, *p*-3-butenyl-, *p*-α,α-dimethylallyl-, and *p*-γ,γ-dideuterioallylcumyl *p*-nitrobenzoates were solvolyzed in an identical manner. Isolation of the product alcohols again proved rearrangement had not occurred by virtue of nmr, infrared, and gas chromatographic comparisons with authentic samples.

Registry No.—1-(*p*-Chlorophenyl)-3-methyl-2-butene, 23853-76-1; *p*-bromoallylbenzene, 2294-43-1; 3-(*p*-chlorophenyl)-1-butene, 23853-78-3; *m*-allylchlorobenzene, 3840-17-3; 3-(*p*-chlorophenyl)-3,3-dimethyl-1-butene, 1-(*p*-chlorophenyl)-1,1-dimethyl-2-propanone, 16703-39-2; 1-(*p*-chlorophenyl)-1,1-dimethyl-2-propanol (acetate), 23890-37-1; 3-(*p*-chlorophenyl)-1,1-dideuterio-1-propene, 23852-83-7; *p*-(γ,γ-dideuterioallyl)-cumyl *p*-nitrobenzoate, 23852-84-8.

Acknowledgment.—This work was supported in part by the Petroleum Research Fund, administered by the American Chemical Society. The authors are indebted to Dr. V. K. Jones for assistance with several aspects of this work.

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[21] A column packed with DC 710 on Gas-Chrom Q was employed.

[22] A column packed with Carbowax 20M on base-washed Chromosorb P was employed.

Photochemical Transformations of Small-Ring Carbonyl Compounds. XXVI. Ground-State and Photochemical Reactions in the Thiacyclobutane Series[1,2]

ALBERT PADWA[3] AND ROBERT GRUBER

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

Received December 8, 1969

Reaction of α-bromomethylchalcone with sodium hydrosulfide gives 3-phenyl-4-benzoyl-1 2-dithiolane (**3**), 2,4-diphenyl-5-benzoyl-1,3-dithiane (**4**), and 2-phenyl-3,5-dibenzoylthiane (**5**). Oxidation of dithiolane **3** with peracid affords 3-phenyl-4-benzoyl-1,2-dithiolane 2,2-dioxide (**7**), which was thermolyzed in dilute solution to give *trans*-2-phenyl-3-benzoylthietane (**2**). When thiosulfonate **7** was pyrolyzed in the neat, a mixture of *trans*-α-methylchalcone and 3-phenyl-4-benzoyl-1,2-dithiolane (**3**) was obtained. Irradiation of either dithiolane **3**, thiosulfonate **7**, or thiacyclobutane **2** afforded a mixture of *cis*- and *trans*-benzalacetophenone. The low bond dissociation energy of the C–S bond appears to be the major factor responsible for the photolytic cleavage of these sulfur heterocycles.

Phenomena regarding excited states of small-ring nitrogen ketones have received considerable attention during the past few years.[4] Interest in these compounds has been aroused in part by theoretical studies and in part by the unusual rearrangements that occur upon irradiation.[5,6] The general types of phototrans-

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[1] Part XXV: A. Padwa and W. Eisenberg, *J. Amer. Chem. Soc.*, **92**, 2590 (1970).

[2] For a preliminary report of this work, see A. Padwa and R. Gruber, *Chem. Commun.*, 5 (1969). This work was presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

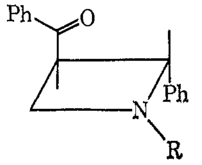
[3] Alfred P. Sloan Foundation Research Fellow, 1968–1970.

[4] For a review, see A. Padwa in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 92.

[5] A. Padwa and L. Hamilton, *J. Amer. Chem. Soc.*, **89**, 102 (1967).

[6] A. Padwa and W. Eisenhardt, *ibid.*, **90**, 2442 (1968).

formations which have been observed with four-membered nitrogen ketones have been summarized in recent papers from this laboratory.[7–9] Evidence has been advanced in favor of a mechanism involving transfer of an electron from nitrogen to the triplet n → π^* excited state. An intriguing question concerned the photochemical behavior of molecules of similar structure but possessing a different heteroatom as part of the ring. One such molecule is 2-phenyl-3-benzoylthietane (**2**), which is an analog of the much-studied arylaroylazetidine system (**1**). Not only is this system of interest because of its relationship to azetidine photochemistry, but also the possibility of electron transfer from sulfur was of intrinsic concern. The present paper reports on the photochemistry of several thiacyclobutane derivatives, as well as some of the interesting ground-state chemistry encountered with these systems.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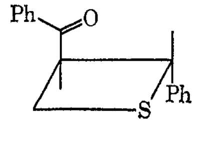
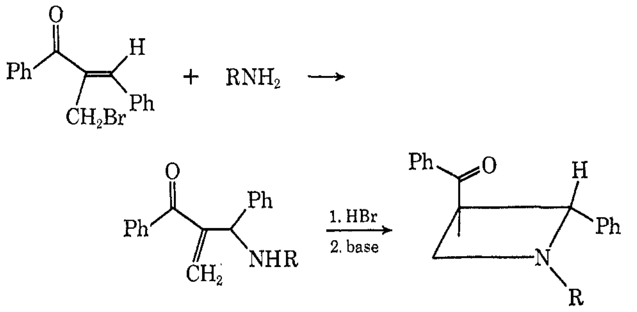
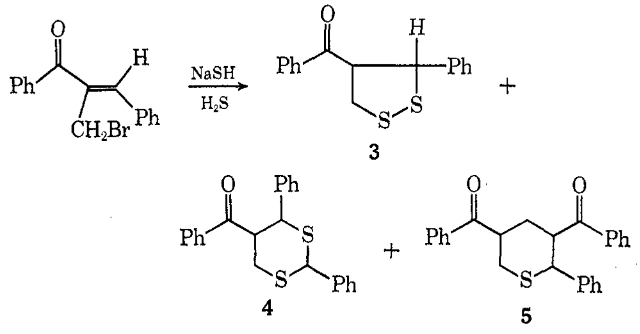
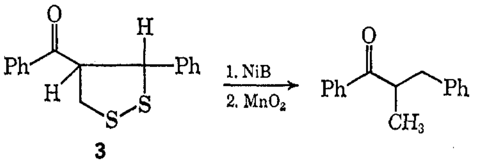

2

Synthetic Aspects.—A synthesis of *trans*-2-phenyl-3-benzoylthietane (**2**) was required. Earlier reports in the literature have shown that 2-[α-(N-*t*-butylamino)benzyl]acrylophenone reacts with hydrogen bromide to give a β-aroyl-γ-bromoallylamine hydrobromide, which on treatment with base affords a substituted aroylazetidine in high yield.[10,11] In an attempt to prepare the related four-membered sulfur heterocycle by an analogous route, we treated α-bromomethylchalcone with sodium hydrosulfide. Our initial expectations for preparing the desired thietane ring were not realized, and instead the reaction proceeded to give three new products. These products were separated by chromatography on silica gel and were purified by recrystallization. The compounds are designated as **3**, **4**, and **5** and were formed in relative proportions of 36, 40, and 20%, respectively.



Compound **3** was shown to have the molecular formula $C_{16}H_{14}S_2O$, mp 81–82°. It showed bands in its infrared spectrum at 6.01, 6.95, 7.78, 9.95, and 13.05 μ. The nmr spectrum ($CDCl_3$) showed an ABXY pattern: the AB part is centered at τ 6.50 and 6.25 (J_{AB} = 11.5 Hz, J_{AX} = J_{BX} = 7.5 Hz), the X proton appeared as a quartet at τ 5.53 (J_{XY} = 7.5 Hz), and the Y proton appeared as a doublet at τ 4.80 (J_{XY} = 7.5 Hz). A multiplet centered at τ 2.77 for ten aromatic protons was also evident. Simplification of the nmr spectrum could be readily achieved by heating compound **3** with sodium methoxide in CH_3OD. When this was done the nmr spectrum showed an AB pattern at τ 6.48 and a singlet at τ 4.80. This ready exchange implies that one proton is on a carbon atom adjacent to a carbonyl group. On the basis of these data and its origin, compound **3** is considered to be 3-phenyl-4-benzoyl-1,2-dithiolane. The assignment of structure **3** was confirmed in the following fashion. Desulfurization with nickel boride[12] followed by oxidation with activated manganese dioxide afforded 1,3-diphenyl-2-methylpropanone in high yield. The more stable *trans* structure is assigned to **3** in view of failure to detect any appreciable isomerism of **3** with sodium methoxide under conditions which exchanged the hydrogen atom α to the benzoyl group.





3

The formation of dithiolane **3** may be rationalized by assuming that sodium hydrosulfide first undergoes an S_N2' reaction with starting bromide and is then followed by further hydrogen sulfide addition across the conjugated double bond.[13,14] The intermediate dimercaptan undergoes subsequent oxidation to give the dithiolane ring. The oxidation of a dithiol to a disulfide has been previously described in the literature and can be accomplished by several methods.[15–17] Air oxidation in the presence of a trace of ferric ion was found to be among the best.[16,17] Other oxidizing agents that have been used to effect this conversion consist of iodine in alcohol, hydriodic acid in the presence of oxygen, and strong alkaline reagents in the presence

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(7) A. Padwa, R. Gruber and L. Hamilton, *J. Amer. Chem. Soc.*, **89**, 3077 (1967).

(8) A. Padwa and R. Gruber, *ibid.*, **90**, 4456 (1969).

(9) A. Padwa and R. Gruber, *ibid.*, **92**, 107 (1970).

(10) R. P. Rebman and N. H. Cromwell, *Tetrahedron Lett.*, No. 52, 4833 (1965).

(11) J. L. Imbach, E. Doomes, R. P. Rebman, and N. H. Cromwell, *J. Org. Chem.*, **32**, 78 (1967).

(12) W. E. Truce and F. M. Perry, *ibid.*, **30**, 1316 (1964).

(13) B. Lindberg and G. Bergson, *Ark. Kemi*, **23**, 319 (1965).

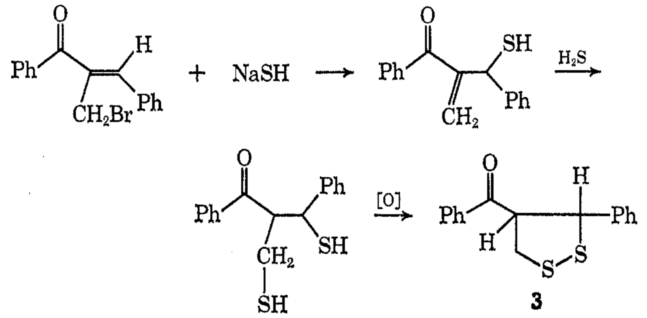
(14) B. H. Nicolet, *J. Amer. Chem. Soc.*, **57**, 1098 (1935).

(15) J. A. Barltrop, P. M. Hayes, and M. Calvin, *ibid.*, **76**, 4348 (1954).

(16) M. W. Bullock, J. J. Hand, and E. L. R. Stokslad, *ibid.*, **79**, 1975 (1957).

(17) M. W. Bullock, British Patent 796,894 (1958); *Chem. Abstr.*, **53**, 227 (1959).

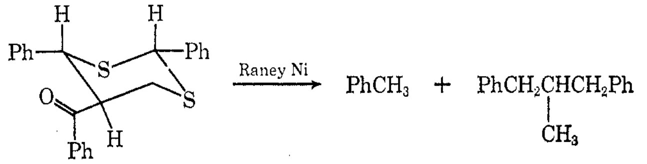
of oxygen. The nature of the oxidizing reagent responsible for the formation of **3** is presently uncertain, although a reasonable possibility would be either ferric ion (present in the sodium hydrosulfide) or simply the aerated alkaline solution.



3

Compound **4**, mp 192–193°, which is the major product from the above reaction, is assigned the structure of 2,4-diphenyl-5-benzoyl-1,3-dithiane. This compound has the correct elemental analysis and molecular weight for $C_{23}H_{20}S_2O$, and has uv absorption similar to propiophenone. The nmr spectrum (100 MHz, CCl_4, see Figure 1) showed the expected magnetic nonequivalence of the methylene protons adjacent to the sulfur atom, there being the predicted eight-line multiplet (AB part of an ABXY system) centered at τ 6.72 and 6.88 with J_{AB} = 14 Hz, J_{AX} = 9 Hz, and J_{BX} = 4 Hz. The X proton consisted of a triplet of doublets centered at τ 5.73 with J_{XY} = 10 Hz. The remaining portion of the spectrum consisted of a doublet at τ 5.40 (J_{XY} = 10 Hz), a singlet at τ 4.60, and a multiplet for the aromatic hydrogens centered at τ 2.52. With values of the coupling constants available it was possible to determine the theoretical nmr spectrum using a variation of the frequint IV program of Bothner-By.[18] The calculated spectrum is given in Figure 1 along with the experimental 100-MHz spectrum. It is seen that the fit is excellent both in line position and intensity.

The fact that protons X and Y are coupled with J = 10 Hz, while the coupling constant for protons B and X is 4 Hz, suggests that the 4-phenyl and 5-benzoyl groups are in the equatorial position. This situation is similar to that found with other substituted dithiane systems.[19] Confirmation of the assignment of structure **4** was obtained by desulfurization of **4** with Raney nickel to give toluene and 1,3-diphenyl-2-methylpropane.



Determination of the elemental analysis and the molecular weight of compound **5** established its molecular formula as $C_{25}H_{22}SO_2$. The nmr spectrum (100 MHz) showed multiplets centered at τ 8.03 (2 H), 7.10 (2 H), and 2.75 (15 H), a triplet of triplets centered at τ 6.20 (1 H, J = 12 and 4.0 Hz), a triplet of doublets centered at τ 5.85 (1 H, J = 10 and 4.0 Hz), and a doublet at τ 5.65 (1 H, J = 10 Hz). Simplification of the nmr spectrum could be achieved by refluxing **5** with sodium methoxide in CH_3OD. The nmr spectrum of the exchanged thiane showed two AB patterns at τ 7.90 (J = 14.0 Hz) and 7.07 (J = 14.0 Hz), a singlet at τ 5.60 (1 H), and a multiplet at τ 2.42. The sum of the available evidence requires that compound **5** have the structure of 2-phenyl-3,5-dibenzoylthiane (**5**). The location of all three substituents on the equatorial positions of the thiane ring is most consistent with the nmr data.

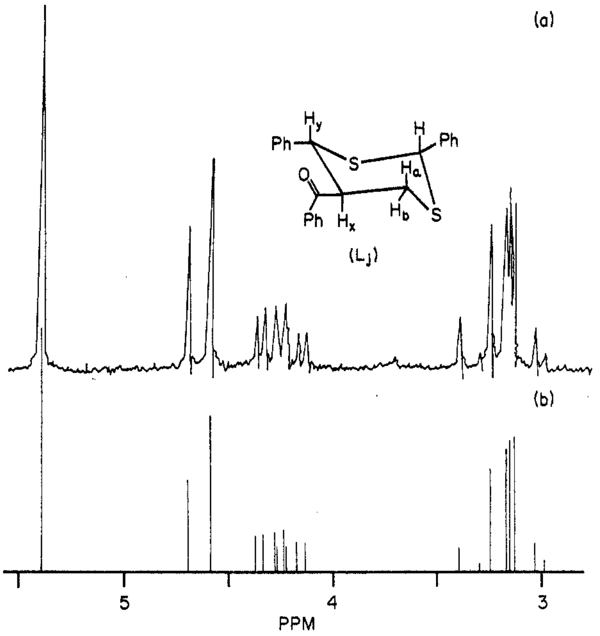


Figure 1.—Experimental (a) and calculated (b) 100-MHz spectrum of the ring protons of **4** in CCl_4.

We return now to the consideration of the origin of products **4** and **5** from the reaction of α-bromomethylchalcone with sodium hydrosulfide. A reaction sequence that accounts for their formation is presented in Scheme I. In this scheme, the reaction proceeds to afford the dimercaptan as previously described for the formation of **3**. At this stage the dimercaptan can be oxidized to give **3** or else fragment to give thiobenzaldehyde and phenyl vinyl ketone. Further reaction of either of these two extremely reactive species with the unsaturated mercaptan would readily account for the formation of both **4** and **5**.

In view of the unexpected reactions encountered with the above system, our attention was further directed to the peracid oxidation of **3**, since the expected thiosulfonate **7** would possess a structure that could be desulfonated to the desired thiacyclobutane. Compound **3** was oxidized with sodium metaperiodate to **6**, mp 150–151°, in 86% yield. The infrared spectrum of dithiolane 2-oxide (**6**) exhibited a characteristic sulfoxide stretching frequency at 1070 cm^{-1}. The nmr of **6b** (R = D) showed a multiplet centered at τ 2.5 (10 H), a singlet at τ 4.40 (1 H, benzylic methine), and an unsymmetric quartet centered at τ 6.38 (2 H, methylene). Oxidation of **6b** (R = D) with *m*-chloroperbenzoic acid afforded thiosulfonate **7b** (R = D), mp 169–170°, in excellent yield. Typical sulfonyl stretching absorptions at 1300 and 1125 cm^{-1} were observed in the in-

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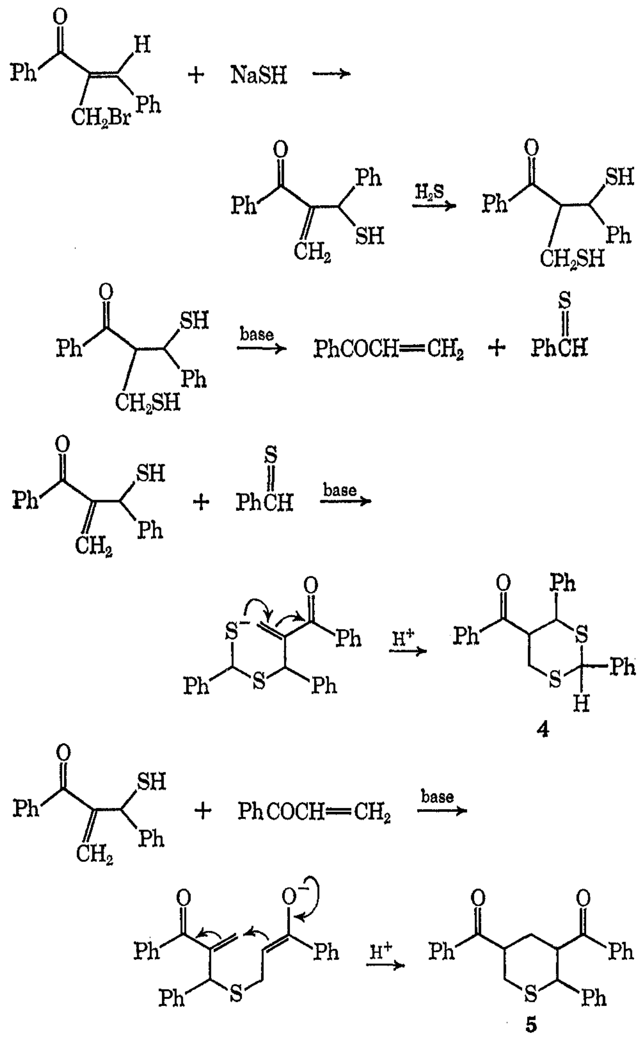
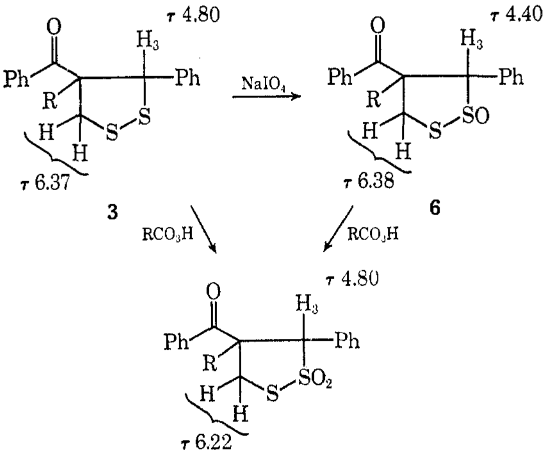
[18] A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, **83**, 231 (1961).

[19] A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *ibid.*, **91**, 5038 (1969).

SCHEME I



frared spectrum of compound **7b**. Its nmr spectrum showed absorptions at τ 2.45 (multiplet, 10 H, aromatic), 4.80 (singlet, 1 H, benzylic methine), and 6.22 (AB quartet, 2 H, methylene).



7

a, R = H
b, R = D

The stereochemical structure assignments for **6** and **7** rest on the following information. (A) Peracid oxidation of thiosulfinate **6** gave the same thiosulfonate as was obtained from **3**. This result demands that the same sulfur atom is always oxidized. It is interesting to note that this behavior contrasts with compounds of type $RS(CH_2)_nSOR$, where the sulfide sulfur atom is preferentially oxidized.[20-23] (B) The magnetic anisotropic effects of the sulfinyl function are such that protons *syn* to the S-O bond are deshielded and protons *anti* to the S-O linkage are shielded.[24,25] Thus proton H_3 in structure **6** must be *syn* to the S-O bond. (C) A comparison of the chemical shift of the methylene hydrogens of compounds **3**, **6**, and **7** reveals that the most deshielded methylene hydrogens are those of compound **7**. This observation is in agreement with the assumption that the sulfonyl moiety has a stronger electron-withdrawing inductive effect than the sulfinyl group.[26] It appears that the sulfinyl group has little effect on the chemical shift at the center of the AB quartet in **6** when compared with the equivalent quartet in the spectrum of disulfide **3**. (D) When a methanol solution of **3** was refluxed over anhydrous potassium carbonate for 2 days, conditions under which complete exchange of the acidic C-4 hydrogen occurred, only starting material was recovered. Therefore, **3**, **6**, and **7** must have the thermodynamically more stable *trans* arrangement of the benzoyl and phenyl moieties.

Recently, Fava and Koch reported that aryl arenethiosulfinates readily undergo thermal racemization *via* pyramidal inversion at sulfinyl sulfur.[27] It seemed to us that compound **6** should also racemize at elevated temperatures and that this racemization could be followed by variable-temperature nmr spectroscopy. When the nmr spectrum of **6** was recorded at a range of temperatures from 166 to −50°, the singlet at τ 4.40 did not change in chemical shift or intensity. Also, no new peaks appeared in the spectrum as the temperature was varied. There was no noticeable decomposition at the elevated temperatures employed. The nmr spectrum showed a slight modification of the AB quartet with decreasing temperature—it broadened slightly and became symmetrical. This change is tentatively ascribed to a retardation of conformer interconversions. Inversion of configuration of the sulfinyl sulfur, whether retarded by cooling or accelerated by heating, should have caused a decrease in intensity of the τ 4.40 singlet and the appearance of a new singlet at *ca.* 0.4–1 ppm upfield. The absence of such a shift leads us to conclude that, although asymmetric open-chain aryl arenethiosulfinates may undergo thermal racemization *via* pyramidal inversion at 50°, the cyclic thiolsulfinate **6** is configurationally stable up to 166°. At this time we cannot fully explain why open-chain asymmetric thiolsulfinates should be configurationally labile and the five-membered counterpart should not. Perhaps configurational stability is a function of ring size in sulfur heterocycles, as is the case with nitrogen heterocycles.[28,29]

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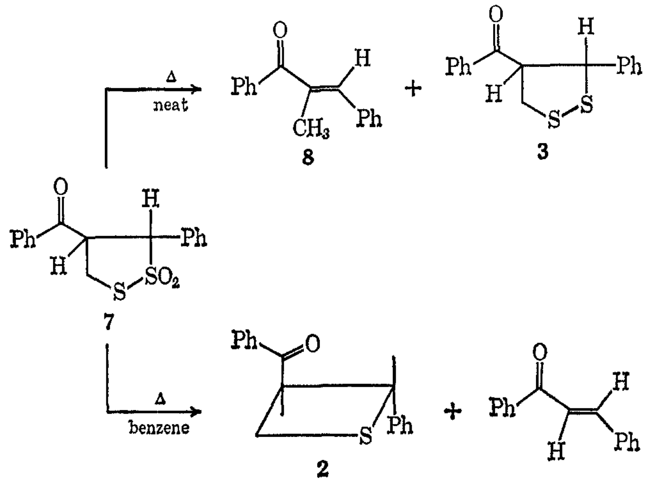
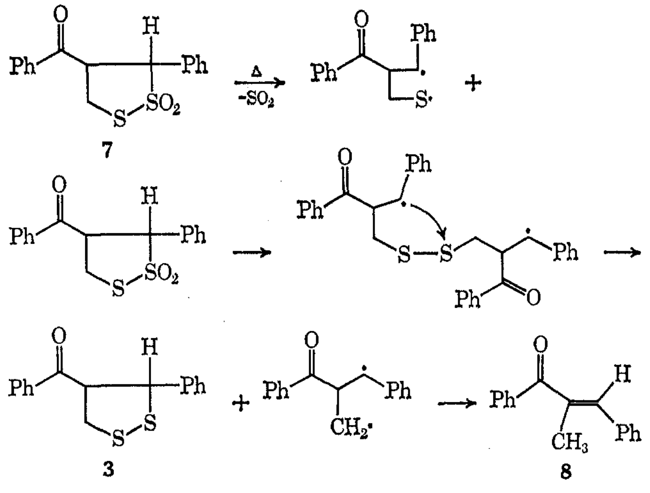
[20] D. Barnard and E. J. Percy, *Chem. Ind.* (London), 1332 (1960).
[21] P. Allen, P. J. Berner, and E. R. Malinowski, *ibid.*, 1164 (1961).
[22] J. Cymerman and J. B. Willis, *J. Chem. Soc.*, 1332 (1951).
[23] C. Frisell and G. Bergson, *Ark. Kemi*, **25**, 263 (1965).
[24] J. A. Deyrup and C. L. Mayer, *J. Org. Chem.*, **34**, 175 (1969).
[25] A. B. Foster, J. M. Duxbury, T. D. Inch, and J. M. Webber, *Chem. Commun.*, 881 (1967).
[26] C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962.
[27] A. Fava and P. Koch, *J. Amer. Chem. Soc.*, **90**, 3867 (1968).
[28] S. J. Brois, *ibid.*, **90**, 506 (1968).
[29] J. M. Lehn and J. Wagner, *Chem. Commun.*, 148 (1968).

Thermal extrusion of sulfur dioxide from thiosulfonate **7** was readily achieved in a sealed tube at 225°. The pyrolysis afforded two major products, which were subsequently identified as *trans*-α-methylchalcone (**8**, 22%) and 3-phenyl-4-benzoyl-1,2-dithiolane (**3**, 29%). Under these conditions a significant amount of polymerization occurred. The failure to observe a product derived from loss of SO_2 on heating **7** at 225° led to an investigation of its behavior under slightly different pyrolytic conditions. When the thermolysis was carried out in a dilute benzene solution, two new products were isolated. The minor product was identified as *trans*-benzalacetophenone (38%). The major product (55%) was a colorless solid, mp 79–80°, having the composition $C_{16}H_{14}SO$. Chemical and spectral evidence (see Experimental Section) shows that this new compound is *trans*-2-phenyl-3-benzoylthietane (**2**).

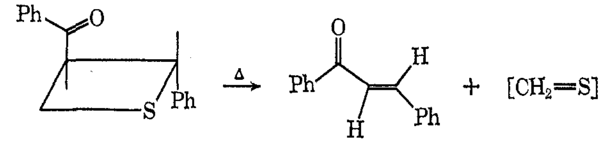


The formation of **3** from the thermolysis of **7** can be envisaged as occurring *via* homolytic cleavage of the sulfur–sulfur bond followed by loss of sulfur dioxide. At high concentrations of starting material the resulting diradical may attack another molecule of thiosulfonate by an S_H2 mechanism[30] as shown in Scheme II.

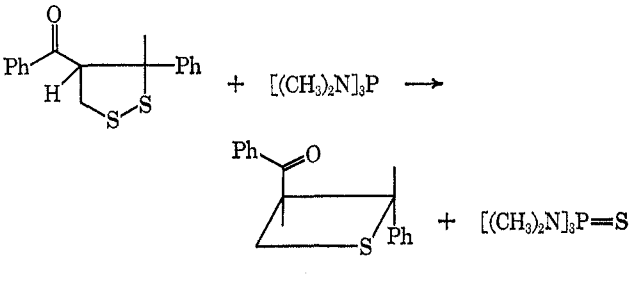
SCHEME II



The sequence of steps outlined above is not without precedent, as related S_H2 reactions of disulfides have been reported with similar systems.[31–33] In addition, the isolation of *trans*-α-methylchalcone from the above reaction mixture lends considerable strength to the reaction sequence postulated in Scheme II. When the thermolysis was carried out in a dilute benzene solution the diradical prefers to undergo ring closure, thus accounting for the formation of thiacyclobutane **2**. Further fragmentation of **2** on heating has been shown to result in the formation of *trans*-benzalacetophenone and thioformaldehyde.



Preparation of the thietane ring by this route is subject to a number of variables, all of which must be carefully controlled in order to obtain even a moderate amount of product. In order to increase the yield of thiacyclobutane **2**, several alternate methods were tried. Truce recently reported that nickel boride would convert a disulfide into the corresponding sulfide.[12] It was further noted that nickel boride was inert toward sulfones. It seemed reasonable to attempt this reaction with dithiolane **3**. However, treatment of either **3** or **7** with nickel boride gave only 1,3-diphenyl-2-methylpropanol. An alternate procedure which involved the reaction of triphenyl phosphine with **3** in refluxing toluene resulted in ill-defined tars. By using a procedure recently described by Harpp and Snyder for the conversion of disulfides into sulfides, the desired thietane could be prepared in good yield.[34] Thus treatment of **3** with tris(dimethylamino) phosphine led to *trans*-2-phenyl-3-benzoylthietane (**2**) in 60% overall yield.



Photochemical Studies.—Although the ground-state chemistry of substituted thietanes has received considerable attention,[35] the photochemical transformations of this ring system have been virtually unexplored. It was of particular interest to ascertain the photochemical routes available to the thietane ring in order to make a comparison with the photochemistry of the azetidine system, which is known to give diarylpyrroles upon irradiation.[9] In particular, the influence of the heteroatom in the photochemistry of these four-membered rings needed to be assessed.

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[30] W. A. Pryor, "Mechanism of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 51.

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[33] W. H. Stockmayer, R. O. Howard, and J. T. Clarke, *ibid.*, **75**, 1756 (1953).

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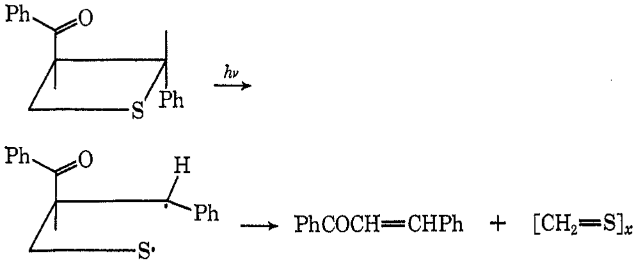
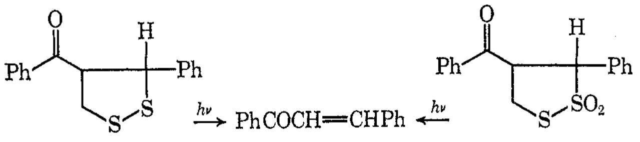
Exposure of a dilute solution of *trans*-2-phenyl-3-benzoylthietane (2) in 95% ethanol to a Hanovia 450-W mercury arc lamp for 3 hr resulted in the complete disappearance of 2 and clean conversion into a mixture of *cis*- and *trans*-benzalacetophenone. The anticipated 2,3- and 2,4-diphenylthiophene were not detected in the reaction mixture. This result indicates that the photochemistry of the thietane system proceeds by an entirely different path from that encountered in the azetidine series. The formation of *cis*- and *trans*-benzalacetophenone may be envisaged as proceeding by way of a homolytic cleavage of the benzylic carbon–sulfur bond. The resulting diradical undergoes subsequent fragmentation to thioformaldehyde and benzalacetophenone.



The low bond dissociation energy of the C–S bond may be the major factor responsible for the difference in photochemistry of the two heterocyclic systems. It is interesting to note that the reaction does not involve the extrusion of atomic sulfur as had been observed in the related episulfide system.[36]

The photoconversion of 2 into *cis*- and *trans*-benzalacetophenone could not be quenched by piperylene or naphthalene. Addition of acetophenone or irradiation in dilute acetone solution unequivocally demonstrates that photosensitization is observed. These data indicate that the triplet state of 2 is capable of undergoing fragmentation to benzalacetophenone. The lack of quenching by piperylene or naphthalene denotes either that the singlet state can also lead to product or that a triplet intermediate is formed but is rapidly consumed by reaction prior to diffusion.

It was also found that irradiation of 3 or 7 in cyclohexane afforded a mixture of *cis*- and *trans*-benzalacetophenone. It seems reasonable to assume that these



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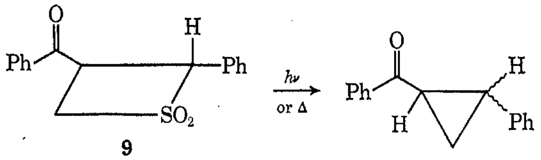
reactions proceed *via* homolytic cleavage of the S–S bond, followed by loss of sulfur (or sulfur dioxide) to give the same diradical as was proposed earlier.

As an extension of our investigations on the photochemistry of the thiacyclobutane ring, the irradiation of *trans*-2-phenyl-3-benzoylthietane 1,1-dioxide (9) was investigated next. The photochemical decomposition of cyclic sulfones has been frequently reported in the literature.[37,38] Cava has adequately demonstrated the ease with which sulfur dioxide can be eliminated from sulfones upon irradiation.[37] Photolysis of a dilute solution of 9, synthesized by the peracid oxidation of 2, in cyclohexane gave a mixture of *cis*- and *trans*-1-phenyl-2-benzoylcyclopropane. Similar results were



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obtained when 2 was pyrolyzed at 230°. An analogous case has been reported by Dodson and Klose,[39] who found that the pyrolysis of *cis*- and *trans*-diphenylthietane dioxide resulted in the formation of *cis*- and *trans*-diphenylcyclopropane. The better leaving ability of SO_2 compared with sulfur may account for the difference in the thermal and photochemical behavior of 2 *vs.* 9.

Experimental Section

General.—Nmr spectra were recorded on a Varian A-60 spectrometer using carbon tetrachloride as solvent. Infrared spectra were obtained on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark. Gas–liquid partition chromatographic analyses and preparative separations were carried out using an F & M Model 5720 instrument equipped with a 6 ft × 0.25 in. 20% Apiezon M on 60–80 mesh Chromosorb W column. Irradiations were carried out using Hanovia 450- and 550-W, medium-pressure mercury lamps with water-cooled quartz immersion wells.

Reaction of *trans*-α-Bromomethylchalcone with Sodium Hydrosulfide.—A solution of 250 g (3.35 mol) of sodium hydrosulfide, dissolved in a sufficient amount of water to give a total volume of 340 ml, was rapidly added to a solution containing 40 g (0.133 mol) of *trans*-α-bromomethylchalcone in 3 l. of methyl alcohol. The resultant solution was heated to reflux for 10 min and hydrogen sulfide was introduced into the refluxing mixture for an additional 30 min. The yellow solution was diluted with 5 l. of cold water and carefully acidified with concentrated hydrochloric acid to pH 5. Extraction with carbon tetrachloride, followed by removal of the solvent under reduced pressure, gave 60 g of a yellow oil. Chromatography of 6.0 g of this material on a silica gel column (1.5 × 32 in.) resulted in the separation of the crude oil into three components. The first component eluted from the column with benzene amounted to 1.4 g of a yellow solid which was recrystallized from benzene to give 3-phenyl-4-benzoyl-1,2-dithiolane (3) as a yellow, crystalline solid, mp 81.5–82.5°, yield 36%.

Anal. Calcd for $C_{16}H_{14}S_2O$: C, 67.09; H, 4.93; S, 22.39. Found: C, 66.93; H, 4.89; S, 22.60.

The infrared spectrum was characterized by bands at 6.01, 6.95, 7.78, 9.95, and 13.05 μ. The nmr spectrum ($CDCl_3$) showed a ABXY pattern with the AB part centered at τ 6.50 and 6.25 (J_{AB} = 11.5 Hz, J_{AX} = J_{BX} = 7.5 Hz), the X proton at τ 5.53 (q, J_{XY} = 7.5 Hz), and the Y proton at τ 4.80 (d, J_{XY} = 7.5 Hz). A multiplet centered at τ 2.77 for ten aromatic protons was also evident. The molecular weight (ebullioscopic) in chloroform had a value of 273 (calcd, 286) in agreement with the proposed structure.

Simplification of the nmr spectrum could be readily achieved by replacement of the acidic α hydrogen with deuterium. A solution of 0.5 g of 3-phenyl-4-benzoyl-1,2-dithiolane and 0.5 g of anhydrous potassium carbonate in 18 ml of methanol-O-*d* was heated to reflux for 2 days. At the end of this time the reaction mixture was evaporated and the oily residue was purified by preparative thick layer chromatography to afford 0.24 g of a yellow solid, mp 80–81°. The nmr spectrum ($CDCl_3$) showed an AB pattern centered at τ 6.48 and a singlet at τ 4.88. The

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[36] A. Padwa, D. Crumrine, and A. Shubber, *J. Amer. Chem. Soc.*, **88**, 3064 (1966).

[37] M. P. Cava, R. H. Schlessinger, and J. P. van Meter, *ibid.*, **86**, 3173 (1964).

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[39] R. M. Dodson and G. Klose, *Chem. Ind.* (London), 450 (1963).

quartet normally associated with the α hydrogen was completely absent. A similar experiment employing methanol gave only recovered starting material, thereby indicating that the thermodynamically more stable *trans* isomer was formed in the original reaction.

The second component eluted from the column (2% ethyl acetate–benzene) was recrystallized from benzene–heptane to give 2,4-diphenyl-5-benzoyl-1,3-dithiane (4) as a white, crystalline solid, mp 192–193°, yield 2.1 g (45%).

Anal. Calcd for $C_{23}H_{20}S_2O$: C, 73.36; H, 5.35; S, 17.03. Found: C, 73.12; H, 5.55; S, 16.66.

The infrared spectrum of this compound is characterized by bands at 6.00, 7.78, 8.40, 9.88, 12.95, 13.55, and 14.53 μ. The molecular weight (ebullioscopic) in chloroform had a value of 364 (calcd, 376). The 100-MHz nmr spectrum showed the expected magnetic nonequivalence of the methylene protons adjacent to the sulfur atom, there being the predicted eight-line multiplet (AB part of an ABXY system) centered at τ 6.72 and 6.88 with J_{AB} = 14 Hz, J_{AX} = 9 Hz, and J_{BX} = 4 Hz. The X proton of the ABXY system consisted of a triplet of doublets centered at τ 5.73 with J_{XY} = 10 Hz. The remaining portion of the spectrum consisted of a doublet at τ 5.40 (J_{XY} = 10 Hz), a singlet at τ 4.60, and a multiplet for the aromatic hydrogens centered at τ 2.52.

The third material isolated from the chromatography column with 3% ethyl acetate–benzene was crystallized from ethyl acetate to give 2-phenyl-3,5-dibenzoylthiane (5) as a white, crystalline solid, mp 180–181°, yield 1.1 g (20%).

Anal. Calcd for $C_{25}H_{22}SO_2$: C, 77.68; H, 5.73; S, 8.27. Found: C, 77.68; H, 5.75; S, 8.31.

The infrared spectrum was characterized by bands at 5.95, 6.02 (split), 6.95, 7.88, 12.85, and 14.54 μ. The molecular weight (ebullioscopic) in chloroform had a value of 378 (calcd, 386). The 100-MHz nmr spectrum ($CDCl_3$) showed multiplets centered at τ 8.03 (2 H), 7.10 (2 H), and 2.75 (12 H), a triplet of triplets centered at τ 6.20 (1 H, J = 12 and 4.0 Hz), a triplet of doublets centered at τ 5.85 (1 H, J = 10 and 4.0 Hz), a doublet at τ 5.65 (1 H, J = 10 Hz), and a doublet of split doublets at τ 2.10 (2 H, J = 1.0 Hz) and 2.32 (2 H, J = 1.0 Hz). The latter two signals are assigned to the *ortho* hydrogens on the benzoyl ring.

Simplification of the nmr spectrum could be achieved by replacement of the acidic α hydrogens with deuterium. A solution of 1.0 g of 5 and 0.1 g of sodium metal in 25 ml of methanol-O-*d* was heated to reflux for 2 days. At the end of this time the reaction mixture was evaporated and the residue was subjected to the exchange conditions for an additional three cycles. After the third cycle the residue was crystallized from ethyl acetate to afford a white solid, mp 180–181°, yield 0.3 g. The nmr spectrum of the exchanged thiane showed two AB patterns centered at τ 7.90 (J = 14.0 Hz) and 7.07 (J = 14.0 Hz), a singlet at τ 5.60, and a multiplet centered at τ 2.42.

Nickel Boride Desulfurization of 3-Phenyl-4-benzoyl-1,2-dithiolane (3).—The desulfurization of **3** was carried out according to the procedure of Truce and Perry.[12] A solution of 1.88 g (0.049 mol) of sodium boride in 20 ml of water was added dropwise to an ice-cooled solution of 3.9 g (0.0165 mol) of nickel(II) chloride hexahydrate and 0.44 g (1.65 mmol) of **3** in 100 ml of 95% ethanol. After the addition was complete the reaction was heated to reflux for 7 hr, cooled to 25°, and filtered. The filtrate was concentrated under reduced pressure to give a colorless oil. The infrared spectrum showed the presence of a strong hydroxyl group and a weak carbonyl band. This crude oil was dissolved in 200 ml of pentane and stirred at 25° with 5 g of activated manganese dioxide. After 36 hr the solution was filtered and the filtrate was concentrated to give a colorless oil. A short-path distillation at a pot temperature of 150° (0.12 mm) gave 0.30 g (88%) of a colorless oil which was identical in all respects with an authentic sample of 1,3-diphenyl-2-methylpropanone.

An attempt was also made to carry out the desulfurization of **3** with Raney nickel. *Ca.* 10 g of Raney nickel (W. R. Grace and Co., No. 28) was added to 150 ml of ethanol containing 0.50 g of **3**. After the solution had been refluxed for 25 hr, the nickel was removed by filtration and the solvent was evaporated under reduced pressure. The residue was distilled and the fraction boiling at 94° (1.1 mm) was collected. This material (0.22 g) was identified as 1,3-diphenyl-2-methylpropane by comparison of its nmr and infrared spectra with those of an authentic sample.

Raney Nickel Desulfurization of 2,4-Diphenyl-5-benzoyl-1,3-dithiane (4).—Desulfurization of compound **4** was accomplished by refluxing a solution containing 0.55 g of **4** and 5.0 g of Raney nickel in 50 ml of methanol for 2 days. The excess Raney nickel was removed by filtration and the solvent was removed by a careful distillation. The distillate was diluted with 300 ml of water and then extracted with 10 ml of carbon disulfide. Gas chromatographic analysis of the carbon disulfide extracts showed the presence of two components that corresponded to solvent and toluene. The material with the same retention time as toluene was collected (10 ft × 0.25 in., 5% SE-30 column on Diatoport S at 100°) and comparison of its infrared spectrum with that of toluene established its identity. Distillation of the remaining residue gave a colorless oil which was identical in all respects with an authentic sample of 1,3-diphenyl-2-methylpropane.

3-Phenyl-4-benzoyl-1,2-dithiolane 2-Oxide (6).—To a solution of 2.0 g (0.007 mol) of 3-phenyl-4-benzoyl-1,2-dithiolane (**3**) in 175 ml of dioxane was added a solution of 1.5 g (0.007 mol) of sodium metaperiodate in 50 ml of water. After the solution had been allowed to stand at room temperature for 2 hr, a solid material precipitated which was subsequently filtered and discarded. The filtrate was evaporated under reduced pressure to give 1.92 g of a yellow solid. Recrystallization from benzene–heptane gave 3-phenyl-4-benzoyl-1,2-dithiolane 2-oxide (**6**) as a white, crystalline solid, mp 150–151°, yield 1.86 g (86%).

Anal. Calcd for $C_{16}H_{14}S_2O_2$: C, 63.54; H, 4.66; S, 21.20. Found: C, 63.40; H, 4.66; S, 20.89.

The infrared spectrum was characterized by bands at 5.95, 7.73, 7.89, 8.18, 9.35, 13.02, and 14.23 μ. The 100-MHz nmr spectrum ($CDCl_3$) showed multiplets centered at τ 6.38 (2 H) and 4.57 (1 H) and a doublet at τ 4.40 (1 H, J = 4.5 Hz).

3-Phenyl-4-benzoyl-1,2-dithiolane 2,2-Dioxide (7).—A solution of 5.0 g of 3-phenyl-4-benzoyl-1,2-dithiolane (**3**) and 7.6 g of 90% *m*-chloroperbenzoic acid in 300 ml of methylene chloride was allowed to stand at room temperature for 4 hr. At the end of this time the precipitated *m*-chlorobenzoic acid was removed by filtration and the solution was washed with 10% sodium carbonate and dried over magnesium sulfate. The solvent was removed under reduced pressure to leave a white solid. Recrystallization from benzene–heptane gave 3-phenyl-4-benzoyl-1,2-dithiolane 2,2-dioxide as a white, crystalline solid, mp 169–170°, yield 4.3 g.

Anal. Calcd for $C_{16}H_{14}S_2O_3$: C, 60.15; H, 4.41; S, 20.15. Found: C, 60.04; H, 4.40; S, 20.05.

The infrared spectrum was characterized by bands at 5.98, 7.70, 8.89, 10.01, 14.42, and 14.70 μ. The 100-MHz nmr spectrum ($CDCl_3$) showed multiplets centered at τ 6.22 (2 H), 5.12 (1 H), and 2.45 (10 H) and a doublet at τ 4.83 (1, H, J = 5.5 Hz).

Nickel boride desulfurization of dioxide **7** was carried out in a manner similar to that described for dithiolane **3**. The product obtained (95% yield) was identified as 1,3-diphenyl-2-methylpropanone by comparison with an authentic sample.

Peracid Oxidation of Dithiolane 2-Oxide (6) to Dithiolane 2,2-Dioxide (7).—A mixture of 0.48 g of 3-phenyl-4-benzoyl-1,2-dithiolane 2-oxide (**6**) and 0.34 g of 80% *m*-chloroperbenzoic acid in 130 ml of methylene chloride was allowed to stand at room temperature for 4 hr. At the end of this time, the precipitated *m*-chlorobenzoic acid was removed by filtration and the solution was extracted with 10% sodium carbonate and then dried over magnesium sulfate. The solvent was removed under reduced pressure, leaving a white solid. The infrared spectrum of the solid showed it to be a mixture of **6** and **7**. The crude solid was subjected to preparative thick layer chromatography. Chloroform extraction of the upper band followed by recrystallization of the solid from benzene–heptane afforded a crystalline solid, mp 168–170°, yield 0.30 g. The infrared spectrum of this component was identical with that of dioxide **7** prepared from the peracid oxidation of **3**. The mixture melting point of these two materials was undepressed at 169–170°. Evaporation of the chloroform extracts of the lower band gave a white solid which was identical in all respects with starting dithiolane 2-oxide (**6**).

Thermolysis of 3-Phenyl-4-benzoyl-1,2-dithiolane 2,2-Dioxide (7). A. Neat.—In a sealed Carius tube a 1.0-g sample of **7** was heated to 225° for 75 min. The dark oil obtained was dissolved in benzene and chromatographed on a Florisil column (1 × 20 in). Elution with 500 ml of benzene gave 0.20 g (29%) of 3-phenyl-4-benzoyl-1,2-dithiolane (**3**) as yellow needles, mp 80–81°. Further elution of the column with an additional 800 ml of benzene gave 0.15 g (22%) of a yellow oil, whose nmr and infrared spectra were identical with those of an authentic sample of *trans*-α-methylchalcone. Further elution with 25% ethyl acetate–benzene afforded only ill-defined tars.

B. In Benzene.—A solution of 0.30 g of **7** in 30 ml of benzene was heated in a stainless steel tubular bomb at 230 ± 5° for exactly 75 min and then quickly cooled to room temperature. The solvent was removed under reduced pressure, leaving a light brown viscous oil. Preparative thick layer chromatography resulted in the separation of two distinct bands, which were taken up in chloroform. A yellow solid was isolated from the upper band, which, after recrystallization from 95% alcohol, afforded a white, crystalline solid, mp 79–80°, yield 0.13 g (55%). This material was assigned as *trans*-2-phenyl-3-benzoylthietane (**2**) on the basis of the following data.

Anal. Calcd for $C_{16}H_{14}SO$: C, 75.55; H, 5.54; S, 12.60. Found: C, 75.67; H, 5.59; S, 12.54.

The infrared spectrum was characterized by bands at 6.02, 7.01, 8.28, 8.95, 11.85, and 14.65 μ. The nmr spectrum (CCl_4) showed a multiplet centered at τ 2.57 (10 H), a sextet centered at τ 6.68 (2 H, J = 9.0 Hz), a quartet centered at τ 5.25 (1 H, J = 9.0 Hz), and a doublet centered at τ 4.75 (1 H, J = 8.5 Hz).

Removal of the solvent from the lower band of the thick layer plate gave 0.09 g (38%) of a yellow solid, which was subsequently identified as *trans*-benzalacetophenone by comparison with an authentic sample.

Formation of 2-Phenyl-3-benzoylthietane (2) by Selective Desulfurization of 3 with Tris(dimethylamino)phosphine.—In 25 ml of benzene was dissolved 2.86 g (0.01 mol) of 3-phenyl-4-benzoyl-1,2-dithiolane (**3**) and 1.7 g (0.011 mol) of tris(dimethylamino) phosphine. The solution was allowed to stand for 3 days at room temperature and was then evaporated to dryness under reduced pressure. The resulting residue was placed on a porous plate to remove the residual oil. Recrystallization of the solid from 95% alcohol afforded 1.5 g (60%) of 2-phenyl-3-benzoylthietane (**2**), mp 79–80°. The infrared spectrum of this material was identical in all respects with that of the product obtained from the pyrolysis of dioxide **7**. A mixture melting point was undepressed at 79–80°.

***trans*-2-Phenyl-3-benzoylthietane 1,1-Dioxide (9).**—A solution of 100 mg (0.394 mmol) of *trans*-2-phenyl-3-benzoylthietane (**2**) and 176 mg (0.804 mmol) of 80% *m*-chloroperbenzoic acid in 80 ml of methylene chloride was stirred at room temperature for 26 hr. The precipitated *m*-chlorobenzoic acid was removed by extraction with 10% sodium carbonate and then dried over magnesium sulfate. The solvent was concentrated to give a white solid, which was assigned as *trans*-2-phenyl-3-benzoylthietane 1,1-dioxide, mp 123–124°.

Anal. Calcd for $C_{16}H_{14}SO_3$: C, 67.10; H, 4.92; S, 11.19. Found: C, 66.94; H, 5.12; S, 10.92.

Pyrolysis of *trans*-2-Phenyl-3-benzoylthietane (2).—A 3-mg sample of **2** in 0.1 ml of benzene was heated to 230° in a sealed tube. After 1 hr the solution was concentrated to 0.05 ml and the residue was analyzed on a 10% FS-1265 Diatoport S column, 4 ft × 0.25 in, at 210°. The only product obtained was identified as *trans*-benzalacetophenone by comparison of retention time and infrared spectrum with those of an authentic sample.

Pyrolysis of *trans*-2-Phenyl-3-benzoylthietane 1,1-Dioxide (9).—A solid injector apparatus containing 5 mg of **9** was fitted into the injector port of an F & M gas chromatograph at 230°. After 1.5 hr the glass tube was crushed and the reaction mixture was allowed to enter a 6 ft × 0.25 in. Apeizon column at 230°. The glpc trace showed the presence of starting material (60%) and *trans*-1-phenyl-2-benzoylcyclopropane (30%). These assignments were made by comparison of retention times and infrared spectra with those of authentic samples.

Irradiation of *trans*-2-Phenyl-3-benzoylthietane 1,1-Dioxide (9).—A solution of 37 mg of 2-phenyl-3-benzoylthietane in 150 ml of cyclohexane was irradiated with an internal water-cooled mercury arc lamp (550 W) using a Pyrex filter. After 3 hr the solution was concentrated to give 29 mg of a yellow oil, which was chromatographed on a preparative thick layer plate. Elution with 5% ethyl acetate–benzene afforded only one band, which was subsequently taken up with chloroform. The chloroform extracts were distilled at 85° (0.04 mm) to give 27 mg (93%) of a mixture of *cis*- and *trans*-1-phenyl-2-benzoylcyclopropane. Gas chromatographic analysis (10% FS 1265 on Diatoport S column, 10 ft × 0.25 in., at 250°) of the oil indicated the presence of two peaks with retention times that corresponded to *cis*- (12 min) and *trans*- 1-phenyl-2-benzoylcyclopropane (14 min). Comparison of these components with authentic samples unequivocably established their identity.

Irradiation of 3-Phenyl-4-benzoyl-1,2-dithiolane (3).—2-Phenyl-3-benzoyl-1,2-dithiolane (0.200 g) in 500 ml of cyclohexane was irradiated for 5 hr using a Pyrex filter. Positive nitrogen pressure was maintained throughout the irradiation. Concentration of the solution left a yellow oil, which was chromatographed on a Florisil column. Elution of the column with 120 ml of benzene afforded 0.12 g (83%) of a pale yellow oil, whose infrared and nmr spectra indicated that it was comprised of a mixture of *cis*- and *trans*-benzalacetophenone (4:1).

Irradiation of 3-Phenyl-4-benzoyl-1,2-dithiolane 2,2-Dioxide (7).—A solution of 1.0 g of 3-phenyl-4-benzoyl-1,2-dithiolane 2,2-dioxide (**7**) in 1 l. of cyclohexane was irradiated with a 450-W Hanovia lamp using a Pyrex filter. After 3 hr the infrared spectrum showed only a trace of starting material. Concentration of the solution under reduced pressure left a pale yellow oil, which was subjected to preparative thick layer chromatography. Elution with an 8% ethyl acetate–benzene mixture afforded two bands, which were taken up in chloroform. Removal of the solvent from the lower band afforded 0.25 g (34%) of *trans*-benzalacetophenone, mp 54–56°. The upper band contained 0.22 g (30%) of a pale yellow oil, whose nmr and infrared spectra indicated it to be a mixture of *cis*- and *trans*-benzalacetophenone.

Irradiation of 2-Phenyl-3-benzoylthietane (2).—A solution of 39 mg of 2-phenyl-3-benzoylthietane in 100 ml of 95% ethanol was irradiated with a 450-W Hanovia lamp using a Pyrex filter. Aliquots were removed and analyzed by thin layer chromatography. After 3 hr the spot on a thin layer plate which was due to starting material had almost completely disappeared and a single new spot appeared in its place. Concentration of the solution left an oil which was chromatographed on a preparative thick layer plate. Elution with a 5% ethyl acetate–benzene mixture afforded a single band that was subsequently taken up in chloroform. Removal of the solvent left 27 mg (96%) of a light yellow solid, whose infrared and nmr spectra indicated it to be a mixture of *cis*- and *trans*-benzalacetophenone (4:1). Similar results were encountered when the irradiation of **2** was carried out in acetone using a Vycor filter.

Registry No.—**2**, 23852-85-9; **3**, 21551-57-5; **4**, 21551-58-6; **5**, 21551-59-7; **6**, 23853-92-1; **7**, 23877-34-1; **9**, 23852-86-0.

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