Studies on the Reaction of 3,3,4,4-Tetraphenylthietan-2-one[1]

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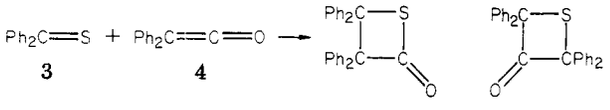
The chemical reactivity of 3,3,4,4-tetraphenylthietan-2-one (3,3,4,4-tetraphenyl-β-thiolactone, **5**) toward nucleophilic, reducing, and oxidizing reagents has been investigated. Compound **5** is relatively inert toward nucleophiles (1-butanethiol, sodium hydroxide, sodium methoxide). The only product obtained from these reactions which cannot be readily attributed to initial thermal fragmentation of the ring is tetraphenylethylene (**10**). Treatment of **5** with the strong reducing reagent $LiAlH_4$ gave four products upon workup: 2,2,3,3-tetraphenyl-1-propanol (**19**), 2,2,3,3-tetraphenylpropyl acetate (**20**), 1,1,3,3-tetraphenyl-2-propanone (**7**), and 1,1,3-triphenyl-2-indanone (**21**). The substituted acetone **7** was also obtained when DIBAL was added to **5**. Desulfurization experiments with Raney nickel and cobalt catalysts consistently gave **10** in varying amounts. In addition to the alkene **10**, compounds **7**, **21**, and 2,2,3-triphenyl-4,5,6,7-tetrahydro-1-indanone (**26**) were also isolated with W-2 Raney nickel. Finally, oxidation of **5** with *m*-chloroperbenzoic acid gave the novel mixed carboxylic–sulfinic acid anhydride (**32**). This molecule is of particular interest in light of the previous difficulty encountered in the preparation of this class of compounds. Many of the products obtained in these reactions are not those expected based upon previous studies of β-thiolactones. Potential pathways for the origin of the compounds obtained are suggested.

β-Thiolactones **1** like their oxygen counterparts (**2**) generally react with nucleophilic and reducing agents to give acyl bond cleaved products. The former systems (**1**), however, are considerably less reactive toward these reagents.[4]

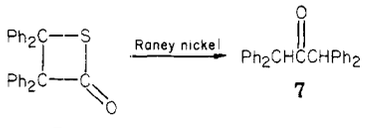
1, X = S
2, X = O

Recently we reinvestigated the reaction of thiobenzophenone (**3**) with diphenylketene (**4**).[5] The crystalline adduct obtained from this reaction was reassigned by us as 3,3,4,4-tetraphenyl-β-thiolactone (**5**) as opposed to the originally assigned 3-thietanone structure (**6**).[6]



3 **4** **5** **6**

Significantly, β-thiolactone **5** upon treatment with Raney nickel was reported to give 1,1,3,3-tetraphenyl-2-propanone (**7**) in 92% yield.[6b] In light of our findings, this result necessitated that extensive bond reorganization must have preceded product formation.



5 **7**

We now describe our results concerning the chemical reactivity of the highly substituted thiolactone **5** toward nucleophilic, reducing, and oxidizing agents. Unanticipated products have been isolated which suggest that pathways other than *S*-acyl bond cleavage may have occurred.

Results and Discussion

Reactions with Nucleophiles. The ease with which β-thiolactones react with nucleophiles decreases with increasing substitution on the ring.[4] It was not surprising, therefore, that 1-butanethiol, sodium hydroxide, and sodium methoxide did not readily react with **5**. Treatment of 3,3,4,4-tetraphenyl-β-thiolactone (**5**) in DME with 1-butanethiol (85 °C) gave a complex mixture (≥6 compounds by TLC). Separation of the products by preparative thick-layer chromatography gave butyl diphenylthioacetate (**8**, 88%) and benzophenone[7] (**9**, 69%). A

$$\mathbf{5} \xrightarrow[\text{DME, }\Delta]{n\text{-BuSH}} \underset{\mathbf{8}}{Ph_2CHC(O)SBu} + \underset{\mathbf{9}}{Ph_2CO}$$

DME solution of **5** containing aqueous NaOH (3 equiv, 85 °C, 15 h) gave tetraphenylethylene[8] (**10**), bis(diphenylmethyl) disulfide[9] (**11**), benzophenone (**9**), diphenylacetic acid[10] (**12**), and diphenylthioacetic acid[11] (**13**) along with recovered starting material (**5**, 15%). Finally, treatment

$$\mathbf{5} \xrightarrow[\Delta]{\text{NaOH}} \underset{\mathbf{10}\ (12\%)}{Ph_2C{=}CPh_2} + \underset{\mathbf{11}\ (23\%)}{Ph_2CHSSCHPh_2} + \underset{\mathbf{9}\ (43\%)}{Ph_2CO} + \underset{\mathbf{12}\ (20\%)}{Ph_2CHCO_2H} + \underset{\mathbf{13}\ (20\%)}{Ph_2CHC(O)SH}$$

of **5** with a large excess of NaOMe (10.2 equiv) at room temperature (72 h), followed by an anhydrous workup (MeI), led to the isolation of only 12% of the alkene **10** along with 50% recovered starting material (**5**).

$$\mathbf{5} \xrightarrow{\text{NaOMe}} \underset{\mathbf{10}\ (12\%)}{Ph_2C{=}CPh_2}$$

(1) Presented, in part, at the 178th National Meeting of the American Chemical Society, Washington DC, Sept 1979, Abstract ORGN 158.

(2) Abstracted from the Ph.D. dissertation of this author. Additional structure proof, discussion, and experimental and spectral data may be found in this reference.

(3) Alfred P. Sloan Fellow, 1977–1981; Camille and Henry Dreyfus Teacher-Scholar Grant Recipient, 1977–1982.

(4) Review: Lin'kova, M. G.; Kuleshova, N. D.; Knunyants, I. L. *Russ. Chem. Rev.* **1964**, *33*, 493 and pertinent references cited therein.

(5) Kohn, H.; Charumilind, P.; Gopichand, Y. *J. Org. Chem.* **1978**, *43*, 4961.

(6) For earlier reports concerning this reaction, see: (a) Staudinger, H. *Helv. Chim. Acta* **1920**, *3*, 862. See this reference also for a brief discussion concerning the chemical reactivity of **5**. (b) Rioult, P.; Vialle, J. *Bull. Soc. Chim. Fr.* **1967**, 2883.

(7) The experimentally obtained material proved to be identical with an authentic sample with respect to physical and spectral properties.

(8) Buckles, R. E.; Matlack, G. M. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 914.

(9) The spectral and analytical properties obtained for **11** have not ruled out the possibility that the compound exists as the thiol (Anal. Calcd for $C_{13}H_{12}S$: C, 77.95; H, 6.04; S, 16.01). For an earlier report on the preparation of **11**, see: Minoura, Y.; Tsuboi, S. *J. Org. Chem.* **1972**, *37*, 2064.

(10) Marvel, C. S.; Hager, F. D.; Caudle, E. C. "Organic Syntheses"; Wiley: New York, 1941; Collect. Vol. I, p 224.

(11) Tchoubar, B.; Dupré, L. *Bull. Soc. Chim. Fr.* **1947**, 792.

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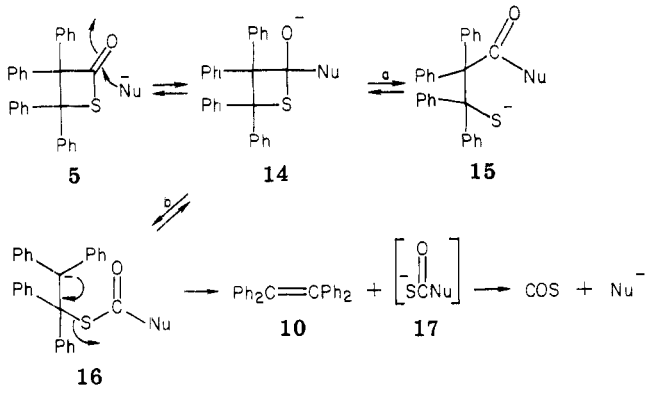
Scheme I



These results confirm the stability of the β-thiolactone ring toward nucleophilic reagents. In agreement with this observation, significant amounts of starting material (5) were recovered in both the NaOH and NaOMe experiments. Moreover, a majority of the products can be explained by reaction of the nucleophile with either diphenylketene (4) or thiobenzophenone (3). Thiolactone 5 thermally reverts back to these materials at elevated temperatures.[6] No significant amount of tetraphenylethylene (10) is observed during pyrolysis.[6] In light of this, 8, 12, and 13 could result from trapping ketene 4 with 1-butanethiol, NaOH, and NaSH (potentially generated from hydrolysis of 3), respectively. Correspondingly, the benzophenone (9) isolated in the 1-butanethiol and NaOH experiments may have been formed from thiobenzophenone (3) during the reaction (traces of water) or the workup. We have observed that dissolving 3 in undistilled DME (2 h) gave 82% 9.[12] The formation of 10 cannot be readily explained in terms of thermolysis of the starting material 5.[14] A mechanism consistent with the formation of this compound, in at least the NaOMe reaction, is shown in Scheme I. Nucleophilic attack (Nu = OMe^-) is envisioned to occur at the sterically hindered carbonyl group. Subsequent cleavage of this species by route a would give the product 15 normally observed for β-thiolactones with nucleophiles.[4] This product, however, can recyclize to 14. Alternatively, the tetrahedral intermediate 14 can collapse by route b to give the stabilized diphenyl carbanion 16. This anion can then fragment to give 10 and 17. Attempts to trap 17 as the thiocarbonate with MeI in the NaOMe experiment proved unsuccessful.

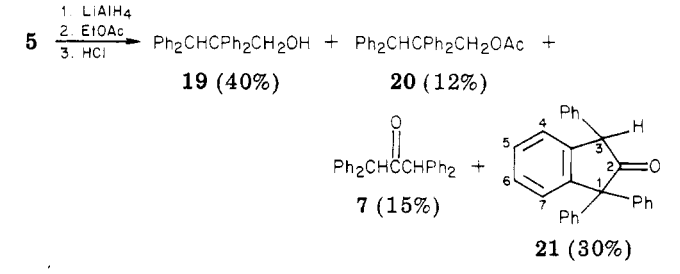
The previous reactions prompted us to treat β-thiolactone 5 with the strong base, lithium *n*-butylamide. Addition of this base to 5 in DME at room temperature gave an immediate reaction as evidenced by the appearance of a blue color which slowly faded away. After 15 h the reaction was quenched with MeI and then purified by chromatography to yield 90% tetraphenylethylene (10). The formation of 10 can be explained by a variety of pathways. One rationalization envisages a route similar to that depicted in Scheme I in which the nucleophilic species is $CH_3CH_2CH_2CH_2NH^-$. Attempts to detect the formation of the corresponding thiocarbamate ($BuNHC(O)SCH_3$) in the product mixture after methylation were unsuccessful. Alternatively, Wittig[15] and Benkeser[16] have demonstrated that substituted alkylamide salts readily donate hydride ion to carbonyl-containing compounds. This observation suggests that 10 could have resulted from initial attack of the thiolactone (5) by the smaller hydride ion (Scheme I, Nu = H^-). Finally, Scott and co-workers[17] have shown that electron-transfer processes cannot be discounted as viable pathways in reactions involving amide anion bases. The substituent pattern present in 5 should facilitate this type of transfer.

$$5 \xrightarrow{LiNHCH_2CH_2CH_2CH_3} \underset{10}{Ph_2C{=}CPh_2}$$

Reactions with Reducing Agents. In light of the lithium *n*-butylamide experiment, thiolactone 5 was treated with authentic hydride reagents ($NaBH_4$, $LiBH_4$, $LiAlH_4$, and DIBAL), as well as other reducing agents (Raney nickel and cobalt catalysts). Compound 5 did not readily react (45 °C, 72 h) with $NaBH_4$ provided the temperature of the solution was maintained below the point at which thermal reversion of the starting material became visually apparent. Only 10 was isolated in low yields (24%). $LiBH_4$, on the other hand, gave 18[18] (75%) and 11 (16%) under identical reaction conditions. These products are those compounds expected if fragmentation had occurred prior to reduction. Furthermore, these two experiments suggested that the lithium counterion facilitated the fragmentation of the ring. We were unable to confirm this hypothesis. Heating 5 with $NaBF_4$ and $LiBF_4$, respectively, in DME in the presence of 1-butanethiol (45 °C, 72 h) did not lead to the formation of 8.

$$5 \xrightarrow[DME]{LiBH_4} \underset{18}{Ph_2CHCH_2OH} + \underset{11}{(Ph_2HCS)_2}$$

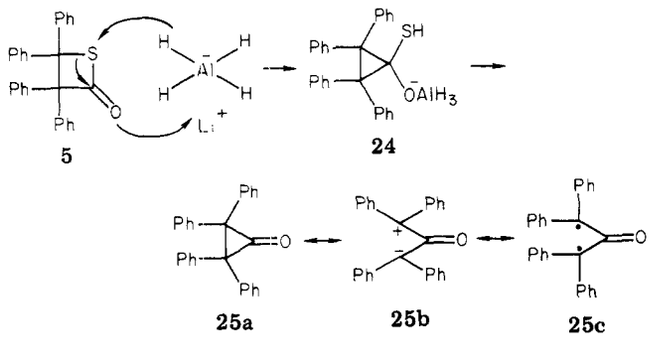
Chemical reduction of 5 with $LiAlH_4$ (7 equiv) followed by addition of ethyl acetate and acidification gave four compounds (TLC analysis). Partial purification of the product mixture by chromatography gave 2,2,3,3-tetraphenyl-1-propanol (19), 2,2,3,3-tetraphenylpropyl acetate (20), and a mixture of 1,1,3,3-tetraphenyl-2-propanone (7) and 1,1,3-triphenyl-2-indanone (21) which was subsequently separated by recrystallization.[19]



The structural assignment for 21 was based on examination of its spectral properties. The infrared spectrum showed a strong carbonyl absorption at 1760 cm^{-1}.[20] The ^1H NMR spectrum revealed a singlet at δ 4.68 and a multiplet at δ 6.70–7.25 in the ratio of 1:19. The proton-decoupled ^{13}C NMR spectrum exhibited resonance lines at 58.1, 68.8, 143.0, 144.8, and 213.8 ppm. The corresponding proton-coupled ^{13}C NMR spectrum revealed a doublet pattern centered at 58.1 ppm while the other previously mentioned signals remained unchanged. The

(12) Charumilind, P.; Kohn, H., unpublished results. For related studies see ref 13.
(13) Kondo, K.; Ojima, I. *J. Chem. Soc., Chem. Commun.* **1972**, 62.
(14) The origin of 11 in the NaOH reaction is not known.
(15) Wittig, G.; Schmidt, H. J.; Renner, H. *Chem. Ber.* **1962**, *95*, 2377. Wittig, G.; Frommeld, H. D. *Ibid.* **1964**, 97, 3541.
(16) Benkeser, R. A.; DeBoer, C. E. *J. Org. Chem.* **1956**, *21*, 281.
(17) Scott, L. T.; Carlin, K. J.; Schultz, T. H. *Tetrahedron Lett.* **1978**, 4637.
(18) Aldrich Chemical Co.
(19) Comparable results were obtained with a prefiltered $LiAlH_4$ solution: 19 (9%), 20 (48%), 7 (5%), 21 (37%).
(20) Nakanishi, K.; Solomon, P. H. "Infrared Absorption Spectroscopy", 2nd ed.; Holden-Day: San Francisco, 1977.

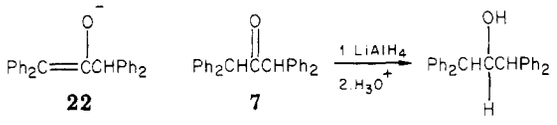
Scheme II



two bridgehead carbon absorptions (143.0 and 144.8 ppm) appeared at values similar to those observed for the corresponding carbons of indan (143.9 ppm).[21] These facts have led to a tentative ^{13}C NMR assignment for compound **21** in which the resonances previously mentioned have been assigned to the C-3, C-1, C-3a and C-7a, and C-2 carbons, respectively. The mass spectrum of **21** exhibited a molecular ion peak at m/e 360 and a major fragmentation peak at m/e 332 for the P – CO ion.

2,2,3,3-Tetraphenyl-1-propanol (**19**) and 2,2,3,3-tetraphenylpropyl acetate (**20**) were obtained as clear, viscous oils. Compound **20** could be independently prepared by the addition of acetyl chloride and pyridine to a methylene chloride solution of **19**. The product from this reaction proved to be identical in all respects (infrared and ^1H NMR spectra) with that obtained from the $LiAlH_4$ reaction.

The isolation of both **7** and **21** suggested the intermediate formation of the enolate anion of tetraphenylacetone (**22**). This rationalization was supported by the observation that tetraphenylacetone (**7**) was rapidly reduced by $LiAlH_4$ to the alcohol **23**.[22] One pathway leading to **22**



envisages the formation of cyclopropyl–aluminate species **24** (Scheme II). This complex can then break down to tetraphenylcyclopropanone (**25a**) or one of its zwitterionic (**25b**) or diradical (**25c**) resonance structures.[23] Reduction of the open-chain resonance form gives the enolate anion **22**, while cyclization of this species through a five-membered transition state leads to the 2-indanone ring skeleton. Finally, reduction of the cyclopropanone **25a** itself could give **19** and **20** after workup.

Interestingly, reduction of **5** with excess DIBAL (room temperature, 18 h) in DME gave the substituted acetone **7** (37%) along with benzophenone (**9**) (39%).

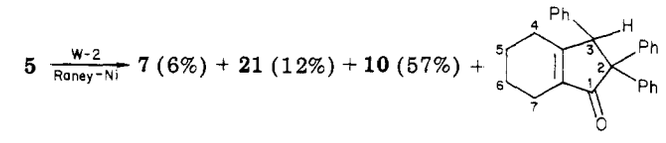
$$5 \xrightarrow{\text{DIBAL}} 7 + 9$$

Reductive experiments on **5** were also conducted with Raney nickel and cobalt catalysts[24] (Table I). These reactions were of particular interest in light of the earlier report on the high-yield formation of 1,1,3,3-tetraphenyl-2-propanone (**7**) from treatment of **5** with an unspecified type of Raney nickel.[6b] We were unable to duplicate these findings. The 2-propanone derivative **7**, however, was formed in low yield in one experiment (Table I, entry 1). This reaction also provided the greatest number of products. In addition to **7**, compounds **10**, **21**, and **26** were also obtained. Preparative thick-layer chromatography of the product mixture afforded a clean separation of compounds **10** and **26** but was unable to resolve compounds **7** and **21**. The binary mixture (**7** and **21**) was not further purified in this experiment, but rather the yields reported are based on ^1H NMR analysis.

Table I. Treatment of Thiolactone 5 with Raney Nickel and Raney Cobalt Catalysts

	conditions[a]		products[b]			
rxn	catalyst	time, h	10	7	21	26
1	W-2 Raney nickel[c]	18	57	6	12	22
2	W-2 Raney nickel,[c] deact (2 h)[d]	18	73		26	
3	W-2 Raney nickel,[c] deact (2 h),[d] EtOH (3 mL)	18	53		33	
4	W-2 Raney nickel,[c] deact (4 h),[d] EtOH (3 mL)	18	47		49	
5	W-4 Raney nickel[c]	18	91			
6	Raney cobalt[c]	18	92			
7	W-8 Raney nickel[c]	72	12[e]			

[a] All reactions were heated to reflux in benzene. [b] Purified percent yields. [c] See ref 24 for preparation of catalyst. [d] Deactivation of catalyst was accomplished by heating the designated Raney nickel in acetone for the stated period of time prior to use.[24] [e] Tetraphenylethane[25] (**27**, 31%) and ethyl 2,2-diphenylacetate[26] (**28**, 71%) were also recovered.



26 (22%)

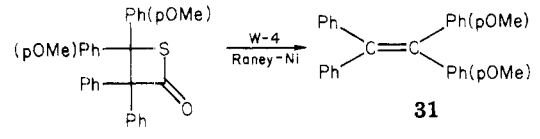
The structure of compound **26** has been tentatively assigned on the basis of the infrared, UV, ^1H and ^{13}C NMR, and mass spectral properties. The infrared spectrum showed a strong absorption at 1700 cm^{-1}, consistent with a 2-cyclopentenone ring.[20] The ^1H NMR spectrum exhibited complex multiplets at δ 1.20–2.67, 3.00–3.70, and 7.10–7.55 in the ratio of 7:2:15. Characteristic peaks in the proton-decoupled ^{13}C NMR spectrum were observed at 52.6, 64.0, 175.7, and 205.6 ppm.[27] The corresponding coupled spectrum exhibited a doublet pattern centered at 52.6 ppm while the peaks at 64.0, 175.7, and 205.6 ppm remained unchanged. These facts have led to the ^{13}C NMR assignment for the resonance lines previously mentioned as carbons 3, 2, 3a, and 1, respectively. The ultraviolet spectrum of **26** exhibited maxima at 220 (log

(21) Johnson, L. F.; Jankowski, W. C. "Carbon-13 NMR Spectra"; Wiley-Interscience: New York, 1972.
(22) Dean, D. O.; Dickinson, W. D.; Hoey, G. B.; Lester, C. T. *J. Am. Chem. Soc.* **1954**, *76*, 4988.
(23) For a detailed review on the reactivity of cyclopropanones, see: Turro, N. J. *Acc. Chem. Res.* **1969**, *2*, 25.
(24) For a discussion of Raney nickel and Raney cobalt catalysts, see: Augustine, R. L. "Catalytic Hydrogenation"; Marcel Dekker: New York, 1965; p 26–32, 131–133.
(25) Nauta, W. T.; Mulder, D. *Recl. Trav. Chim. Pays-Bas* **1939**, *58*, 1062.
(26) Brault, A. *C. R. Held. Seances Acad. Sci.* **1965**, *261*, 4443. Scarpati, R.; Sica, D. *Gazz. Chim. Ital.* **1962**, 1073; *Chem. Abstr.* **1963**, *59*, 1519.
(27) For the ^{13}C NMR chemical shift value of the olefinic carbons in α,β-unsaturated ketones, see: Levy, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, 1972. p 67.

ϵ_{max} 4.40) and 258 nm (3.97). These absorption values are in good agreement for the predicted maxima for conjugated ketones with similar substitution.[28]

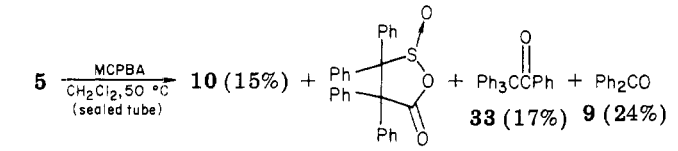
Catalytic reduction of **5** using more activated catalysts[24] (W-4 Raney nickel and Raney cobalt) led to the isolation of only tetraphenylethylene (**10**). Conversely, use of a less active catalyst (W-2 Raney nickel treated with acetone[24]) led to a higher proportion of the 2-indanone **21** as compared to the alkene **10**. The yield of the 2-propanone **7** could not be increased by the addition of EtOH (reactions 3 and 4). Finally, the most deactivated catalyst, W-8 Raney nickel, gave largely products (tetraphenylethane[25] (**27**) and ethyl 2,2-diphenylacetate[26] (**28**)) which could be attributed to fragmentation of the thiolactone **5** to **3** and **4**, followed by further reaction with the catalyst or the EtOH present in the reaction medium, respectively.

One rationalization consistent with the products observed with W-2 Raney nickel is presented in Scheme III. Desulfurization of thiolactone **5** with Raney nickel should give the key diradical **29**. This species (**29**) can undergo a number of different reactions. Decarbonylation of **29** would yield tetraphenylethylene (**10**). Alternatively, the diradical **29b** can cyclize to give tetraphenylcyclopropanone (**25a**) or one of its resonance forms (**25b** or **25c**).[23] This species (**25**) could then undergo further reduction to yield 1,1,3,3-tetraphenyl-2-propanone (**7**) or undergo cyclization followed by bond migration to give the 2-indanone **21**. Finally, the initially generated diradical species (**29a**) could undergo cyclization through a five-membered-ring transition state, followed by further reduction and isomerization, to yield the corresponding tetrahydro-1-indanone **26**. Attempts to trap intermediates along the reaction pathway with 2,5-dimethylfuran and anthracene were unsuccessful. Consistent with this mechanism, W-4 Raney nickel treatment of thiolactone **30**[6a] gave **31**[29] (68% yield). No symmetrical alkenes were isolated.



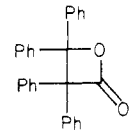
30 31

Reaction with Oxidizing Agents. Treatment of **5** with 2.3 equiv of *m*-chloroperbenzoic acid yielded 3,3,4,4-tetraphenyl-1,2-oxathiolan-5-one 2-oxide (**32**), tetraphenylethylene (**10**), benzopinacolone[30] (**33**), and benzophenone (**9**) along with unreacted starting material (**5**).[31]



32 (18%)

By use of 1 equiv of peracid, the formation of **32** was not prevented. Separation of this product mixture by conventional thick-layer chromatography led to decreased yields of **32** and increased yields of **10**, as well as the formation of 3,3,4,4-tetraphenyl-β-lactone (**34**).[32] In an effort to minimize the decomposition of mixed anhydride **32** during isolation, medium-pressure liquid chromatography was employed.



34

The product of primary interest in this reaction was **32**. Considerable effort has been directed toward the preparation of stable mixed carboxylic–sulfinic acid anhydrides.[34-39] To date these attempts have been mostly unsuccessful.[34-37,39] A brief discussion concerning the proof of structure **32** and its mode of formation, as well as its selected chemistry, has appeared.[41]

Experimental Section

General. Melting points were determined with a Thomas-Hoover melting-point apparatus and are uncorrected. Infrared spectra (IR) were run on Perkin-Elmer Models 700 and 237B spectrometers and calibrated against the 1601-cm^{-1} band of polystyrene. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Varian Associates Model T-60 instrument. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were determined on a Varian Associates Model XL-100-15 spectrometer. The XL-100 was equipped with a Nicolet Technology Corp. TT-100 data system. Chemical shifts are in parts per million relative to Me_4Si, and coupling constants (J values) are in hertz. Mass spectral data were obtained at an ionizing voltage of 70 eV on a Hewlett-Packard 5930 gas chromatograph–mass spectrometer. High-resolution (EI mode) mass spectra were performed by Dr. Ronald Grigsby at the Department of Biochemistry and Biophysics, Texas A & M University, on a CEC21-110B double-focusing magnetic-sector spectrometer at 70 eV. Exact masses were determined by peak matching. Precise mass measurement by chemical ionization was performed by Dr. G. Hansen at the Department of Chemistry, University of Delaware. Sample introduction was done by using an in-beam insertion technique. Elemental analyses were obtained at Spang

(28) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 3rd ed.; Wiley: New York, 1974; p 245.

(29) Bergmann, E.; Fujise, S. J. *Justus Liebigs Ann. Chem.* **1930**, *483*, 65.

(30) Normant, H.; Cuvigny, T.; Normant, J.; Angelo, B. *Bull. Soc. Chim. Fr.* **1965**, 3441.

(31) Yields obtained under nonsealed-tube conditions were nearly comparable to those obtained with sealed tubes.

(32) The β-lactone **34** could not be purified to homogeneity. All attempts (chromatography, recrystallization) gave a binary mixture of **10** and **34** in an approximately 1:1 ratio. Support for the proposed structure of **34** came from the infrared, ^{13}C NMR, and mass spectral properties of the binary mixture. In particular, a strong carbonyl absorption occurred in the infrared spectrum (KBr pellet) at 1820 cm^{-1}. The ^{13}C NMR spectrum of **34** exhibited a carbonyl resonance at 171.8 ppm. Both these signals are in good agreement with values obtained for β-lactones.[20,33] Mass spectral analysis (EI mode, 70 eV) of the mixture gave only a parent peak for tetraphenylethylene (**10**) at m/e 332. No molecular ion peak corresponding to the β-lactone (m/e 376) was observed, although a signal at m/e 194 was detected. This latter peak can be attributed to the Ph_2CCO fragment and was not noted in the spectrum of tetraphenylethylene (**10**). The inability to observe a parent peak for the β-lactone **34** under EI conditions prompted us to examine the mass spectrum of this compound in the CI mode. Fortunately, a peak corresponding to the P + 1 ion could be detected under both low- and high-resolution conditions.[2] Finally, it was demonstrated that addition of SiO_2 to a CH_2Cl_2 solution of **32** gave a low yield of **34**. No comparable reaction was observed by the addition of *p*-toluenesulfonic acid to a benzene solution of **32**.

(33) Krabbenhoft, H. O. *J. Org. Chem.* **1978**, *43*, 1305.

(34) Kobayashi, M. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 967.

(35) Schank, K. *Justus Liebigs Ann. Chem.* **1967**, *702*, 75.

(36) Panizzi, L.; Nicolaus, R. A. *Gazz. Chim. Ital.* **1950**, *80*, 431.

(37) Böhme, H.; Meyer-Dulheuer, K. H. *Justus Liebigs Ann. Chem.* **1965**, *688*, 78.

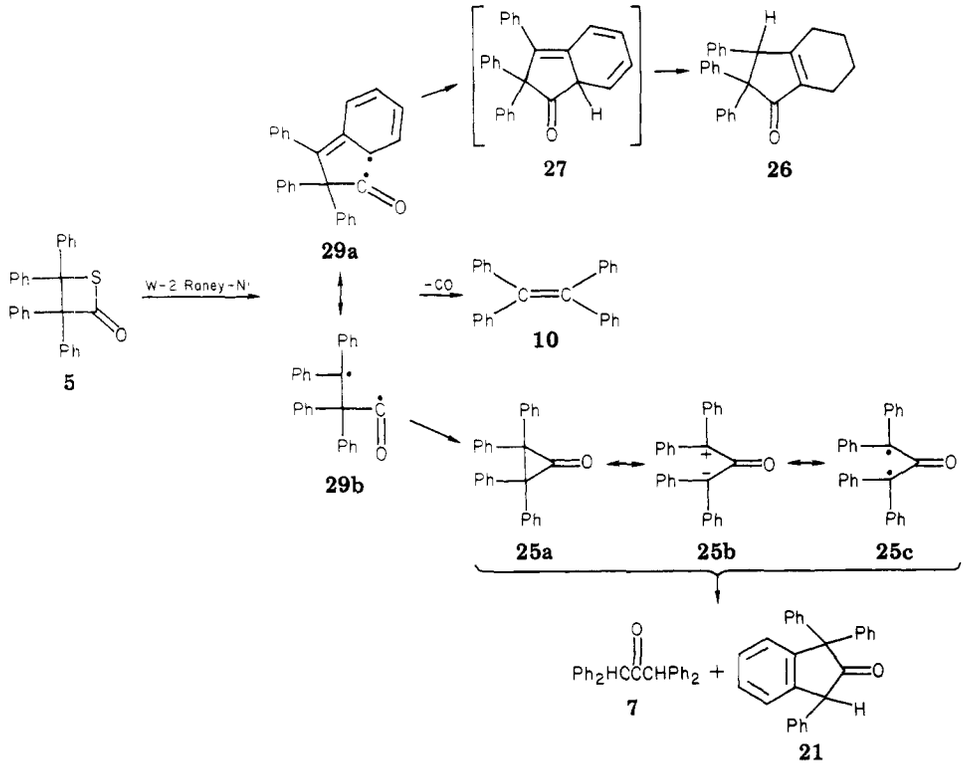
(38) Walter, W.; Krische, B.; Adiwidjaja, G.; Voss, J. *Chem. Ber.* **1978**, *111*, 1685.

(39) Chiang, Y. H.; Luloff, J. S.; Schipper, E. *J. Org. Chem.* **1969**, *34*, 2397.[40]

(40) For a correction of the structure of the originally proposed carboxylic–sulfinic acid anhydride, see: Kasperek, J. G.; Kasperek, G. J. *J. Org. Chem.* **1978**, *43*, 3393.

(41) Kohn, H.; Charumilind, P.; Simonsen, S. H. *J. Am. Chem. Soc.* **1979**, *101*, 5431.

Scheme III



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The solvents and reactants were of the best commercial grade available and were used without further purification unless noted. When dry solvents were required, methylene chloride was distilled from P_2O_5, benzene was distilled and then stored over sodium, anhydrous ether was distilled and stored over sodium metal, 1,2-dimethoxyethane (DME) was distilled from $LiAlH_4$, and methanol was dried by the addition of sodium and then distilled.

All reactions were run under nitrogen and all glassware was dried before use unless otherwise noted. Thick-layer preparative chromatographies were run on premade plates, using Merck silica gel 60 PF-254+366 and Merck silica gel 60 (70–230 mesh) was used for all column chromatography. Medium-pressure liquid chromatography was conducted by using two prepacked silica gel columns (Merck silica gel 60, size A and size B) in series with one another. The flow rate was adjusted to 5 mL/min and fractions were collected each minute with a Brinkmann Linear II fractionator.

Treatment of Thiolactone 5 with Sodium Hydroxide. A DME solution (100 mL) containing **5** (0.65 g, 1.66 mmol) was added to an aqueous 1 N solution (5 mL) of NaOH (3 equiv, 0.20 g, 5.00 mmol). Upon addition of the thiolactone a nearly clear solution was obtained which was heated to reflux (15 h). The dark blue solution which formed overnight was acidified (pH ~4) with 1 N HCl, the solvent was evaporated, and the residue was redissolved in CH_2Cl_2 (50 mL). The CH_2Cl_2 solution was extracted with an aqueous 1 N NaOH solution (20 mL). The aqueous layer was separated and acidified (pH ~4) with 6 N HCl. The aqueous solution was then extracted with CH_2Cl_2 (50 mL), the CH_2Cl_2 solution was dried (Na_2SO_4), and the solvent was evaporated in vacuo. The solid residue was reprecipitated with benzene–hexanes to give 0.07 g (20%) of **12**: mp 142–145 °C; mmp 145–147 °C (lit.[10] mp 144–145 °C); IR (KBr) 3080, 1710 cm^{-1}; NMR ($CDCl_3$) δ 5.03 (s, 1 H), 7.30 (s, 10 H), 10.30 (br, 1 H).

The benzene–hexanes filtrate was concentrated and then recrystallized from hexanes to yield 0.076 g (20%) of **13**: mp 58–59 °C (lit.[11] mp 55 °C); IR (neat, NaCl) 2540, 1690 cm^{-1}; NMR ($CDCl_3$) δ 5.00 (br, 1 H), 5.17 (s, 1 H), 7.30 (s, 10 H); mass spectrum, m/e (relative intensity) 229 (0.3), 228 (2), 168 (16), 167 (100), 166 (15), 165 (40).

The initial CH_2Cl_2 solution was evaporated in vacuo and the residue chromatographed on thick-layer silica gel plates, using methylene chloride–hexanes (50:50) as an eluant. The first zone (R_f 0.82) collected gave 0.068 g (12%) of **10**: mp 221–223 °C (lit.[8] mp 223–224 °C); IR (KBr) 1600, 1495, 1445 cm^{-1}; NMR ($CDCl_3$) δ 7.02.

The second zone (R_f 0.73) yielded 0.076 g (23%) of **11** after recrystallization from hexanes: mp 152–153 °C (lit.[9] mp 152–153 °C); IR (KBr) 3020, 1600, 1495, 1450 cm^{-1}; NMR ($CDCl_3$) δ 4.81 (s, 1 H), 7.30 (s, 10 H); mass spectrum, m/e (relative intensity) 199 (1), 167 (100), 166 (16), 165 (37), 152 (17).

Anal. Calcd for $C_{13}H_{11}S$: C, 78.35; H, 5.56; S, 16.09. Found: C, 77.94; H, 5.92; S, 15.96.

The third zone (R_f 0.55) collected gave 0.096 g (15%) of the starting material (**5**): mp 182–185 °C; mmp 182–185 °C.

The last zone (R_f 0.36) collected from the plates yielded 0.129 g (43%) of **9**: bp 50 °C (external temperature, 0.01 mm) (lit.[42] bp 187–190 °C (15 mm)); IR (neat, NaCl) 1660, 1600 cm^{-1}; NMR ($CDCl_3$) δ 7.20–7.93 (m).

Treatment of Thiolactone 5 with Sodium Methoxide. A methanolic solution of sodium methoxide (10.2 equiv) was prepared by adding sodium metal (0.30 g, 13.00 mmol) to distilled MeOH (15 mL) in a drybox. A DME solution (100 mL) of thiolactone **5** (0.50 g, 1.27 mmol) was then transferred to the solution of the alkoxide with the aid of a double-ended stainless steel needle (18G) under nitrogen pressure. The reaction solution was stirred at room temperature (3 days) during which time the color of the solution turned from clear to dark brown, and then the reaction was neutralized by the addition of excess MeI. The solution was concentrated in vacuo, and the precipitate was suspended in CH_2Cl_2 (100 mL). The organic layer was evaporated in vacuo and the resulting residue recrystallized from hexanes to give 0.18 g (36%) of recovered starting material **5**, mp 182–185 °C.

The hexanes filtrate was concentrated in vacuo and then chromatographed on a thick-layer silica plate, using methylene chloride–hexanes (50:50) as the eluant. The first fraction (R_f 0.81) was recrystallized from hexanes and identified as **10**: yield 0.05 g (12%); mp 221–223 °C.

The second fraction (R_f 0.62) yielded 0.07 g (14%) of **5**, mp 182–185 °C. The total amount of starting material recovered was 0.25 g (50%).

Treatment of Thiolactone 5 with 1-Butanethiol. 1-Butanethiol (0.16 mL, 1.53 mmol) was syringed into a DME solution (100 mL) containing **5** (0.50 g, 1.28 mmol). The reaction was

(42) Marvel, C. S.; Sperry, W. M. "Organic Syntheses"; Wiley: New York, 1941; Collect. Vol. I, p 95.

stirred at 65 °C (3 days). TLC analysis of the resulting blue solution still showed an appreciable amount of starting material. The reaction was then heated at reflux (85 °C) for an additional 24 h. The solvent was evaporated in vacuo and the residue (≥6 compounds by TLC) was chromatographed on a silica gel column (50 g), using methylene chloride–hexanes (50:50) as an eluant. The first major fraction isolated yielded 0.32 g (88%) of **8** after distillation at 100 °C (external temperature, 0.2 mm): IR (neat, NaCl) 2870, 1690 cm^{-1}; NMR ($CDCl_3$) δ 0.60–1.70 (m, 7 H), 2.84 (t, J = 7 Hz, 2 H), 5.15 (s, 1 H), 7.28 (s, 10 H); mass spectrum, m/e (relative intensity) 284 (2), 256 (3), 168 (15), 167 (100), 166 (10), 165 (29); mol wt 284.1227 (calcd for $C_{18}H_{20}OS$ 284.1235).

The second major fraction collected gave 0.16 g (69%) of **9**: IR (neat, NaCl) 1660, 1600 cm^{-1}; NMR ($CDCl_3$) δ 7.20–7.93 (m).

Treatment of Thiolactone 5 with Lithium *n*-Butylamide. The lithium salt of 1-butylamine was prepared immediately before use. To a serum-capped 25-mL pressure-equalizing dropping funnel attached to a three-neck flask were added freshly distilled 1-butylamine (0.15 mL, 1.52 mmol) and DME (15 mL). Butyllithium (0.95 mL of an ca. 1.6 M solution in hexane, 1.52 mmol) was then carefully syringed into the dropping funnel at a rate slow enough to ensure that the solution did not warm above 60 °C.

The amide was then added to a rapidly stirred solution of **5** (0.50 g, 1.275 mmol) in DME (100 mL). Upon addition of each drop of base a blue color appeared which slowly faded away. During the course of the addition, the solution turned to green and finally pale yellow (15 h). The reaction was quenched by addition of MeI (1.6 mL; pH ~7). The volatiles were then removed in vacuo, and the residue was redissolved in CH_2Cl_2 (50 mL) and then washed with H_2O (2 × 50 mL). The organic layer was dried (Na_2SO_4), concentrated in vacuo, and chromatographed on thick-layer silica gel plates, using methylene chloride–hexanes (60:40) as an eluant. The first zone (R_f 0.64) isolated gave 0.38 g (90%) of **10** after recrystallization from hexanes, mp 221–223 °C (lit.[8] mp 223–224 °C).

Reaction of Thiolactone 5 with $NaBH_4$. A DME solution (100 mL) containing **5** (0.50 g, 1.28 mmol) was added to a suspension of $NaBH_4$ (0.50 g, 13.16 mmol) in DME (50 mL). Upon addition of the thiolactone, a clear solution was obtained which was then stirred at 45–50 °C (72 h). The reaction was worked up by slowly pouring the mixture into cold water (50 mL), followed by acidification (pH ~4) with 6 N HCl. The organic layer was extracted with Et_2O (3 × 100 mL) and the Et_2O layers were combined and evaporated to dryness. The residue was chromatographed on thick-layer silica gel plates, using CH_2Cl_2 as the eluant. The first zone (R_f 0.80) collected gave 0.10 g (24%) of **10** by NMR.

Treatment of Thiolactone 5 with $LiBH_4$. A DME solution (100 mL) of **5** (0.50 g, 1.27 mmol) was added to a flask containing powdered $LiBH_4$ (0.50 g, 22.7 mmol). The mixture was heated at 40 °C (48 h), then poured into a beaker containing ice–water (100 mL), and acidified (pH ~3) with 6 N HCl. The clear solution was extracted with Et_2O (3 × 100 mL) and the combined Et_2O layers were dried (Na_2SO_4) and then evaporated in vacuo. The remaining residue was then purified by preparative thick-layer chromatography using hexanes–methylene chloride (60:40) as the eluant. The first fraction (R_f 0.82) was recrystallized from hexanes to give 0.04 g of **11** (16%), mp 152–153 °C (lit.[9] mp 152–153 °C).

The second fraction (R_f 0.18) isolated was identified as 2,2-diphenylethanol[18] (18, 75%).

Reaction of 5 with $LiAlH_4$. $LiAlH_4$ (1.80 g, 47.37 mmol) was added to anhydrous Et_2O (60 mL) and heated until most of the $LiAlH_4$ dissolved. An Et_2O solution (200 mL) containing **5** (2.64 g, 6.73 mmol) was then slowly added to the reducing agent at room temperature with vigorous stirring, and the mixture was heated at reflux (12 h). The reaction was worked up by slowly adding ethyl acetate and then acidifying the mixture with 6 N aqueous HCl. The Et_2O layer was separated, and the aqueous layer was washed with Et_2O (2 × 100 mL). The combined Et_2O layers were dried (Na_2SO_4) and concentrated in vacuo, and the residue was chromatographed on silica gel (100 g), using methylene chloride–hexanes (60:40) as the eluant. The first fraction obtained from the column (1.53 g) was tentatively identified as a 1:2 mixture of **7** and **21**. Distillation of this material at 150 °C (external temperature, 0.01 mm) did not separate the mixture. Trituration of the distillate with cold MeOH led to a solid. Successive recrystallizations of this material from MeOH and EtOH gave 0.36 g (15%) of **7**: mp 132–133 °C (lit.[43] mp 132–133 °C); IR (KBr) 1715 cm^{-1}; NMR (acetone-d_6) δ 5.40 (s, 1 H), 7.20 (s, 10 H); ^{13}C NMR ($CDCl_3$) 64.3, 128.0, 129.4, 129.8, 138.8, 206.1 ppm; mass spectrum, (CI mode) m/e 363 (P + 1); mass spectrum, m/e (relative intensity) 362 (2), 196 (1), 195 (4), 194 (9), 168 (14), 167 (100), 166 (13), 165 (37).

Concentration of the original MeOH layer from the trituration yielded 0.72 g (30%) of **21**: mp 108–110 °C; IR (KBr) 1760 cm^{-1}; NMR ($CDCl_3$) δ 4.68 (s, 1 H), 6.70–7.25 (m, 19 H); ^{13}C NMR ($CDCl_3$) 58.1, 68.8, 125.8, 127.0, 127.3, 127.8, 128.2, 128.3, 128.4, 128.6, 128.9, 129.2, 137.6, 141.4, 143.0, 144.8, 213.8 ppm. A proton-coupled ^{13}C NMR spectrum revealed a doublet pattern (J = 127.5 Hz) centered at 58.1 ppm; mass spectrum, m/e (relative intensity) 360 (100), 332 (34), 255 (41), 254 (100), 253 (47), 78 (78), 77 (46).

Anal. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59. Found: C, 89.73; H, 5.97.

The second eluted fraction yielded 0.34 g (12%) of **20** as an oil. This material remained an oil after further purification by thick-layer chromatography (2 ×): IR (neat, NaCl) 1745 cm^{-1}; NMR ($CDCl_3$) δ 1.70 (s, 3 H), 4.46 (s, 2 H), 5.20 (s, 1 H), 6.96 (s, 10 H), 7.06 (s, 10 H); mass spectrum, m/e (relative intensity) 347 (0.4), 249 (8), 239 (41), 198 (7), 197 (48), 180 (15), 179 (46), 168 (14), 167 (96), 166 (30), 165 (100), 152 (50), 105 (15).

Anal. Calcd for $C_{29}H_{26}O_2$: C, 85.68; H, 6.45. Found: C, 85.72; H, 6.50.

The last fraction yielded 0.98 g (40%) of **19** as an oil. This material remained as an oil after subsequent column chromatography, distillation (150 °C (external temperature, 0.01 mm)), and preparative thick-layer chromatography: IR (neat, NaCl) 3575, 1600, 1500 cm^{-1}; NMR ($CDCl_3$) δ 1.26 (m, 1 H), 3.93 (d, J = 6 Hz, 2 H), 5.26 (s, 1 H), 7.07 (s, 10 H), 7.18 (s, 10 H); ^{13}C NMR (acetone-d_6) 56.8, 58.2, 70.0, 126.8, 127.0, 127.7, 128.2, 131.8, 131.9, 143.2, 144.0 ppm. A proton-coupled ^{13}C spectrum revealed a doublet pattern (J = 120.9 Hz) centered at 56.8 ppm and a triplet pattern (J = 142.7 Hz) located at 70.0 ppm: mass spectrum, m/e (relative intensity) 349 (0.2), 348 (2), 347 (4), 333 (2), 198 (10), 197 (71), 196 (25), 168 (18), 167 (100); mol wt of fragments 333.1656 (calcd for $C_{26}H_{21}$ 333.1643), 197.0975 (calcd for $C_{14}H_{13}O$ 197.0966), 167.0855 (calcd for $C_{13}H_{11}$ 167.0861).

Preparation of 1,1,3,3-Tetraphenyl-2-propanol (23). Treatment of 0.10 g (0.28 mmol) of **7** in Et_2O (20 mL) with 0.12 g (3.16 mmol) of $LiAlH_4$ in Et_2O (15 mL) according to the preceeding procedure gave an oil upon workup. Purification of the product mixture by preparative thick-layer chromatography using methylene chloride–hexanes (60:40) as the eluant gave the corresponding alcohol (R_f 0.56): yield 0.06 g (60%); IR (neat, NaCl) 3580, 1600 cm^{-1}; NMR ($CDCl_3$) δ 1.70 (d, J = 4 Hz, 1 H), 3.90 (d, J = 6 Hz, 2 H), 5.03 (m, 1 H), 7.20 (s, 20 H); mass spectrum, m/e (relative intensity) 197 (15), 168 (100), 167 (54), 165 (31), 152 (23); mol wt of fragment 197.0960 (calcd for $C_{14}H_{13}O$ 197.0966).

Treatment of a Mixture of 7 and 5 with $LiAlH_4$. By use of the above method, a mixture of **7** (0.1770 g, 0.49 mmol) and **5** (0.1966 g, 0.50 mmol) in Et_2O (100 mL) was added to 0.46 g (12.05 mmol) of $LiAlH_4$ in Et_2O (10 mL). The residue upon workup was purified by preparative thick-layer chromatography using methylene chloride–hexanes (60:40) as the eluant. The first zone (R_f 0.68) collected gave 0.1158 g of material. NMR analysis of this binary mixture indicated the presence of compounds **7** and **21** in approximately 20 and 40% yield, respectively (based on **5**).

The second fraction (R_f 0.56) was identified by NMR as 1,1,3,3-tetraphenyl-2-propanol (**23**); yield 0.1713 g (96% based on **7**).

The third zone (R_f 0.24) collected was determined by NMR to be **19**; yield 0.0458 g (25% based on **5**).

Preparation of 2,2,3,3-Tetraphenylpropyl Acetate (20). To a CH_2Cl_2 solution (2 mL) containing 0.27 g (0.74 mmol) of **19** were added acetyl chloride (0.06 mL, 0.89 mmol) and pyridine (0.07 mL, 0.89 mmol). The solution was stirred at room temperature (18 h), diluted with CH_2Cl_2 (10 mL), and then washed with H_2O (2 × 30 mL). The organic layer was dried (Na_2SO_4), concentrated in vacuo, and then chromatographed on thick-layer silica gel plates,

(43) Dean, D. O.; Dickinson, W. B.; Quayle, O. R.; Lester, C. T. *J. Am. Chem. Soc.* **1950**, *72*, 1740.

using methylene chloride–hexanes (60:40) as the eluant. The desired compound (**20**, R_f 0.38) was obtained as an oil: yield 0.17 g (55%); IR (neat, NaCl) 1745 cm^{-1}; NMR ($CDCl_3$) δ 1.70 (s, 3 H), 4.46 (s, 2 H), 5.20 (s, 1 H), 6.96 (s, 10 H), 7.06 (s, 10 H).

Treatment of Thiolactone 5 with Diisobutylaluminum Hydride. A hexane solution of 1.25 M DIBAL (10 mL, 12.5 mmol) was syringed into a distilled DME solution (100 mL) of **5**. Addition of the reducing agent caused a rapid color change from clear to deep purple (15 min). The reaction was allowed to stir at room temperature (18 h) and then was quenched with MeOH (10 mL), causing the color of the solution to revert back to light purple. The reaction was acidified (pH ~3) with 2 N aqueous HCl, saturated aqueous NaCl solution (10 mL) was added, and then the mixture was extracted with Et_2O (2 × 100 mL). The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue was accomplished by preparative thick-layer silica gel chromatography using hexanes–methylene chloride (60:40) as the eluant. The first zone (R_f 0.49) identified was recrystallized from EtOH to give 0.17 g (37%) of **7**, mp 131–133 °C.

The second zone (R_f 0.35) collected gave 0.09 g (39%) of **9** after bulb-to-bulb distillation: bp 50 °C (external temperature, 0.01 mm) lit.[42] bp 187–190 °C (15 mm)); IR (neat, NaCl) 1660, 1600 cm^{-1}; NMR ($CDCl_3$) δ 7.20–7.93 (m).

Treatment of Thiolactone 5 with Raney Nickel and Raney Cobalt Catalysts. The following procedure utilized with W-2 Raney nickel catalyst[24] was used for the other desulfurization experiments listed in Table I. The approximate ratio (by weight) of compound to catalyst[24] used in reactions 2–7 is 1:20, 1:25, 1:25, 1:6, 1:6, and 1:15, respectively.

To a suspension of freshly prepared W-2 Raney nickel (3.00 g)[24] in benzene (10 mL) was added thiolactone **5** (0.50 g, 1.28 mmol) in benzene (50 mL). The mixture was refluxed (6 h), then the organic layer was decanted, and the remaining solid was triturated with benzene (3 × 30 mL). The benzene layers were combined and concentrated in vacuo, and then the resulting residue was triturated with MeOH (20 mL). The MeOH layer was concentrated in vacuo and chromatographed on thick-layer silica gel plates, using methylene chloride–hexanes (50:50) as the eluant. The first zone (R_f 0.68) collected gave 0.0303 g (7%) of **10** after reprecipitation from methylene chloride–hexanes, mp 221–223 °C (lit.[8] mp 223–224 °C).

The second fraction (R_f 0.38) isolated (0.0903 g) was tentatively identified by NMR and IR as an approximate 1:2 mixture of **7** and **21**: IR ($CHCl_3$) 1760, 1730 cm^{-1}; NMR ($CDCl_3$) δ 4.68 (s), 5.40 (s), 6.70–7.25 (m).

The last fraction (R_f 0.24) obtained from the thick-layer plates was determined to be **26**. Recrystallization from hexanes gave 0.1008 g (22%) of purified compound: mp 123–124 °C; IR (KBr) 1700 cm^{-1}; UV (EtOH) 220 nm (ϵ 25400), 258 (9500); NMR ($CDCl_3$) δ 1.20–2.67 (m, 7 H), 3.00–3.70 (m, 2 H), 7.10–7.55 (m, 15 H); ^{13}C NMR ($CDCl_3$) 25.8, 27.2, 29.6, 33.6, 52.6, 64.1, 126.2, 126.7, 127.6, 128.1, 128.3, 129.2, 129.8, 131.4, 135.0, 142.3, 142.6, 175.7, 205.6 ppm; mass spectrum, (CI mode) m/e 365 (P + 1); mass spectrum, m/e (relative intensity) 364 (100), 336 (12), 335 (32), 293 (8), 288 (11), 287 (47); mol wt 364.1812 (calcd for $C_{27}H_{24}O$ 364.1827).

The material remaining after the intitial MeOH trituration was identified as **10**. Purification by recrystallization from hexanes gave 0.21 g (50%) of the alkene, mp 221–223 °C (lit.[8] mp 223–224 °C).

Treatment of Thiolactone 30 with W-4 Raney Nickel. To a stirred mixture of W-4 Raney nickel[24] (1.20 g) in benzene (20 mL) was added a benzene solution (50 mL) of **30** (0.20 g, 0.44 mmol). The suspension was stirred at room temperature (18 h) and filtered, and the filtrate was evaporated in vacuo. The TLC of the crude product showed traces of decomposed starting material along with a major spot (R_f 0.62). The product mixture was purified by preparative thick-layer chromatography (silica gel) using CH_2Cl_2 as the eluant. The major zone was collected and recrystallized from hexanes to yield 0.12 g (68%) of **31**: mp 153–155 °C (lit.[29] mp 154–155 °C); IR (KBr) 1610, 1512, 1250, 1180 cm^{-1}; NMR ($CDCl_3$) δ 3.66 (s, 6 H), 6.40–6.96 (m, 18 H).

Oxidation of Thiolactone 5 with *m*-Chloroperbenzoic Acid. Thiolactone **5** (1.00 g, 2.55 mmol), *m*-chloroperbenzoic acid[18] (85%, 1.20 g, 6.90 mmol), and CH_2Cl_2 (25 mL) were added to a thick-wall cylindrical glass vessel (260 × 40 mm) which was sealed with a torch and then placed in an oil bath maintained at 50 ± 2 °C for 18 h. The vessel was opened, and the solution was successively washed with a saturated aqueous solution of $NaHCO_3$ (2 × 30 mL), a 5% aqueous solution of $Na_2S_2O_3$ (2 × 30 mL), and a saturated aqueous solution of NaCl (2 × 30 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was chromatographed by using medium-pressure liquid chromatography with methylene chloride–hexanes (40:60) as the eluant. The total time for the chromatogram was approximately 45 min (5-mL/min flow rate, 5-mL fraction size). The initial compound eluted (fractions 21–23) was identified as tetraphenylethylene (**10**). Further purification of this product by recrystallization from hexanes yielded 0.129 g (15%) of **10**: mp 221–223 °C (lit.[8] mp 223–224 °C).

The second material obtained from the column (fractions 25–28, 0.292 g) was identified as a mixture of unreacted starting material **5** and benzopinacolone (**33**). Fractional recrystallization from hexanes gave 0.120 g (12%) of **5**. Concentration of the mother liquor yielded 0.150 g (17%) of **33**: mp 179–180 °C (lit.[30] mp 179 °C); IR (KBr) 1675 cm^{-1}; NMR ($CDCl_3$) δ 7.33 (s, 18 H), 7.63–7.93 (m, 2 H); mass spectrum (CI mode), m/e 349 (P + 1); mass spectrum, m/e (relative intensity) 244 (2), 243 (100), 166 (13), 165 (92), 164 (8), 105 (31).

The next compound eluted (fractions 29–33) was the mixed anhydride **32**. Subsequent purification of this material by recrystallization from hexanes yielded 0.196 g (18%) of **32**: mp 233–235 °C dec; IR (KBr) 1795, 1100 cm^{-1}; UV (CH_3CN) 190 nm (ϵ 112170); NMR ($CDCl_3$) δ 6.70–7.46 (m); ^{13}C NMR ($CDCl_3$) 67.8, 87.4, 127.6, 128.0, 128.1, 128.3, 128.4, 128.7, 129.3, 129.6, 131.1, 131.7, 132.2, 132.3, 133.7, 135.6, 139.4, 140.1, 173.2 ppm; mass spectrum (CI mode), m/e 425 (P + 1); mass spectrum, m/e (relative intensity) 362 (0.1), 360 (0.1), 333 (28), 332 (100), 289 (6), 255 (13), 254 (20), 250 (8), 241 (11), 178 (10), 176 (10), 166 (12), 165 (33), 126 (11), 77 (14).

Anal. Calcd for $C_{27}H_{20}O_3S$: C, 76.39; H, 4.75; S, 7.55. Found: C, 76.43; H, 4.84; S, 7.45.

The last compound isolated (fractions 34–43) was identified as benzophenone (**9**). Bulb-to-bulb distillation of this material at 50 °C (external temperature, 0.01 mm) (lit.[42] bp 187–190 °C (15 mm)) gave 0.111 g (24%) of **9**.

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Registry No. 5, 67069-87-8; **7**, 7476-11-1; **8**, 74725-08-9; **9**, 119-61-9; **10**, 632-51-9; **11**, 1726-02-9; **12**, 117-34-0; **13**, 37673-57-7; **18**, 1883-32-5; **19**, 74725-09-0; **20**, 74725-10-3; **21**, 40112-66-1; **23**, 74725-11-4; **26**, 74725-12-5; **30**, 67951-98-8; **31**, 68161-05-7; **32**, 71816-86-9; **33**, 466-37-5; 1-butanethiol, 109-79-5.