significant even when compared to other thiane structures.[1] This flattening is not unexpected if the steric requirements of the nonbonded electrons on sulfur and the four bulky methyl groups at positions C(2) and C(6) are considered. On one side of the ring there are close intramolecular contacts between H(8b) and H(17a) (2.42 Å) and of S(1) with H(8b) (2.91 Å) and H(17c) (2.90 Å). Moreover, on the other side there are close contacts between S(1) with H(7b) (2.87 Å), H(7c) (2.86 Å), H(16a) (2.82 Å), H(16c) (2.86 Å), H(3a) (2.95 Å), and H(5a) (2.98 Å), all smaller than the expected van der Waals distance of 3.00 Å for a sulfur–hydrogen atom contact. The phenyl group is tilted out of the possible mirror plane through S(1), C(4), O(9), and C(10). The angle between this plane and the phenyl group is 16.6°, and the tilt is such that C(15) is closer to C(3) than to C(5), with the shortest contact between H(15) and H(3a) (2.16 Å). This distance cannot be increased without decreasing the already close contact between O(9) and H(11) (2.35 Å), the other phenyl ortho-hydrogen atom. The phenyl group is therefore locked in the conformation which is observed. Other close intramolecular contacts of O(9) are H(8a) (2.48 Å) and H(17a) (2.46 Å). The strain which exists in the molecule can also be seen by the significant increase of the bond angles at C(3) and C(5), when compared to the normal tetrahedral value and by an increase of the bond angle at S(1) compared to that in other thiane ring systems.[1]

The bond distances appear quite normal and are self-consistent within similar bond types. The average of the C–S bond distances (1.840 ± 0.001 Å) is slightly longer than that observed in thianol 14 (average 1.829 Å) and also longer that the 1.817 (5) Å given by Sutton[18] as the mean for a parafinnic C–S distance and the 1.816 Å observed for trithiane.[21] The *gem*-dimethyl substitution at C(2) and C(6) is probably the cause for this small elongation of the C–S bonds.

The hydroxyl group forms one hydrogen bond with S(1) $(x, {}^3/_2 - y, {}^1/_2 + z)$. The contact distance between the sulfur and hydrogen atom is 2.48 Å, about 0.5 Å smaller than the sum of van der Waals radii if 1.75 Å is accepted to be the radius of the sulfur atom.[22] The S(1)···O(9) distance is 3.346 Å and the S(1)···O(9) angle is 168 (2)°.

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Registry No. 1, 18456-46-7; 2, 68296-31-1; 3, 68296-37-7; 4, 68226-25-5; 5, 32428-23-2; 6, 68296-48-0; 7, 68296-49-1; 8, 72121-27-8; 9, 18456-47-8; 10, 18456-50-3; 11, 68226-14-2; 12, 68296-39-9; 13, 68226-23-3; 14, 68296-40-2; 15, 68226-24-4; 16, 29683-23-6; 17, 68600-05-5; 18, 20931-54-8; 19, 32510-65-9; 20, 32428-18-5; 21, 68226-69-7; 22, 68296-52-6; 23, 68226-70-0; 24, 68296-53-7; 25, 72121-28-9; 26, 20931-56-0; 2,2-dimethyl-4-thianone, 2323-13-9; 2,2,6,6-tetramethyl-4-thianone, 22842-41-7.

Supplementary Material Available: Anisotropic thermal parameters, hydrogen positional and thermal parameters, and a listing of observed and calculated structure factor amplitudes (for 14 and 26) (25 pages). Ordering information is given on any current masthead page.

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Halogenation of Pentaphenylethane[1]

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Recently we have attempted to prepare the reportedly "stable" pentaphenylethyl free radical by the method of Schlenk and Mark.[2] Since no useful yield of the radical has been achieved by their method, we turned to the more conventional method of radical generation by metal–halogen abstraction from the corresponding pentaphenylethyl halides. These we had hoped to generate by the photochemical halogenation of the ethane since they are unreported in the literature.

Bachmann[3] reported the treatment of pentaphenylethane with bromine in dibromoethane at 100 °C to give triphenylmethyl bromide (55%). The rational assumption was made that he was observing the bromination of thermal dissociation fragments of the ethane. We have observed by ESR spectroscopy that pentaphenylethane starts to dissociate above 80 °C. However, there is no perceptible dissociation with visible light at room temperature in carbon tetrachloride.

The bromination of pentaphenylethane in carbon tetrachloride was carried out at room temperature with visible light and 1 or 2 equiv of halogen. Since the triphenylmethyl halides and the diphenylmethyl dihalides are sensitive to both heat and moisture, the reaction products were analyzed by carbon-13 NMR. The chemical shifts of the appropriate model compounds are given in Table I. These parameters for pentaphenylethane and related hydrocarbons have been reported previously.[4]

When 2 equiv of bromine was used, only the carbon-13 absorptions of triphenylmethyl bromide and diphenylmethyl dibromide were found in the product. Peak intensities indicated these to be in equal amounts. Since the dibromide could arise from the prior formation and bromination of benzhydryl bromide, a similar experiment was carried out with 1 equiv of bromine. The results in this instance showed about one-half of the starting ethane remaining and only the two halides noted before as

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[1] Presented in part at the EUCHEM Conference on Organic Free Radicals, Cirencester, England, September, 1979.

[2] W. Schlenk and H. Mark, *Ber.* 55, 2285 (1922).

[3] W. E. Bachmann, *J. Am. Chem. Soc.*, 55, 3005 (1933).

[4] T. W. Proulx and W. B. Smith, *J. Magn. Reson.*, 23, 477 (1976).

Table I. Carbon-13 Chemical Shifts[a] of Phenyl-Substituted Alkyl Halides

compound	alkyl	C-1	ortho, meta	para
$(C_6H_5)_2CHCl$	64.13	140.93	127.61, 128.39	127.87
$(C_6H_5)_2CHBr$	55.23	140.99	128.39	127.93
$(C_6H_5)_2CCl_2$	91.87	143.91	127.28, 128.00	128.91
$(C_6H_5)_2CBr_2$	69.20	145.15	127.80, 128.39	128.78
$(C_6H_5)_3CCl$	81.28	145.21	127.67, 129.62	*b*
$(C_6H_5)_3CBr$	78.78	145.66	127.63, 130.64	127.79
$[(C_6H_5)_2CCl]_2$	83.17	143.00	125.98, 132.74	127.48

[a] Parts per million from Me_4Si. [b] Line probably hidden under the peak at 127.67 as judged by relative peak heights.

products. Thus, it appears that the course of the reaction is shown in eq 1–4. The radicals in step 4 complete the

$$Br_2 \xrightarrow{h\nu} 2Br\cdot \qquad (1)$$

$$(C_6H_5)_3C{-}CH(C_6H_5)_2 + Br\cdot \rightarrow (C_6H_5)_3C{-}\dot{C}(C_6H_5)_2 + HBr \qquad (2)$$

$$(C_6H_5)_3C{-}\dot{C}(C_6H_5)_2 + Br_2 \rightarrow (C_6H_5)_3C{-}CBr(C_6H_5)_2 + Br\cdot \qquad (3)$$

$$(C_6H_5)_3C{-}CBr(C_6H_5)_2 \rightleftarrows (C_6H_5)_3C\cdot + \cdot CBr(C_6H_5)_2 \qquad (4)$$

sequence by reacting with bromine.

The photobromination of pentaphenylethane in the presence of oxygen cleanly gives triphenylmethyl bromide and benzophenone. In related experiments it was observed that the photobromination of benzhydryl bromide with oxygen led to the ketone also. In fact, when diphenylmethyl dibromide is irradiated with oxygen in carbon tetrachloride solution, the dibromide is quantitatively converted to the ketone.

An alternative route to the scheme presented above would have the pentaphenylethyl radical dissociating to triphenylmethyl and diphenylcarbene. The reaction of the latter with bromine to form diphenylmethyl dibromide seems not to be a known reaction, though the reaction with oxygen to form benzophenone has been reported.[5] The data presented here do not allow a clear differentiation of these possibilities.

The chlorination reaction yields the chlorine analogues of the above bromination products. With 1 equiv of chlorine, about one-half of the ethane is consumed. It is clear from both the carbon and proton NMR that a small amount of nuclear chlorination occurs. With 2 equiv of chlorine the reaction product is quite complex, showing NMR bands for triphenylmethyl chloride, diphenylmethyl dichloride, and some starting materials, many extraneous peaks from nuclear chlorination, and no benzhydryl chloride.

Experimental Section

All reactions were run at room temperature using 0.410 g (1 mmol) of pentaphenylethane (kindley provided a Professor P. D. Bartlett) in 10 mL of analytical reagent grade carbon tetrachloride in a volumetric flask. The appropriate amount of halogen was added, and the flask and mixture were swept with nitrogen. Experiments conducted with oxygen were carried out in a 50-mL flask flushed with oxygen. Product analysis was carried out by evaporating off the solvent under reduced pressure and dissolving the residue in 1.5 mL of deuteriochloroform containing a small amount of tetramethylsilane. Carbon-13 NMR spectra were obtained on a JEOL FX-60 operating at 15.1 MHz. A 45° pulse width was used with 8K data points and a spectral width of 4 KHz. A 5-s pulse repetition time was used. A set of standard compounds (Table I) were run for comparison. Since each compound had two or more unique lines, identification was quite certain. Peak heights of ortho- or meta-protonated carbons were used in estimating relative yields where possible. Irradiation was carried out about 2 in. in front of a standard slide projector with a 300-W bulb.

The following reactions were carried out with results noted in the text: (a) 0.160 mg (1 mmol) of bromine under nitrogen; (b) 0.320 mg (2 mmol) of bromine under nitrogen; (c) 0.320 mg (2 mmol) of bromine under oxygen; (d) 0.071 mg (1 mmol) of chlorine under nitrogen; and (e) 0.0142 mg (2 mmol) of chlorine under nitrogen. In one experiment 1 mmol of diphenylmethyl dibromide in 10 mL of carbon tetrachloride was irradiated while dry oxygen was bubbled into the system for 2 h. The solution turned red, and presumed bromine vapor was noted at the exit tube. Benzophenone was the sole product. A similar result was obtained when 0.290 g (1.17 mmol) of benzhydryl bromide was photobrominated with 1 equiv of bromine in 10 mL of carbon tetrachloride under oxygen.

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Registry No. Pentaphenylethane, 19112-42-6; benzophenone, 119-61-9; $(C_6H_5)_2CHCl$, 90-99-3; $(C_6H_5)_2CHBr$, 776-74-9; $(C_6H_5)_2CCl_2$, 2051-90-3; $(C_6H_5)_2CBr_2$, 6425-27-0; $(C_6H_5)_3CCl$, 76-83-5; $(C_6H_5)_3CBr$, 596-43-0; $[(C_6H_5)_2CCl]_2$, 1600-30-2.

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[5] P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **84**, 3408 (1962).

On the Purported Photochemical Oxidation of Alcohols by Ag(I). A Reexamination

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It was recently reported[2] that when aqueous (or aqueous dimethyl sulfoxide) solutions of primary or secondary alcohols are irradiated at 350 nm in the presence of silver(I) ion, a nearly quantitative redox reaction takes place to give the derived aldehyde (or ketone) and metallic silver. In view of our studies on the (dark) oxidation of alkoxide ions by silver(I)[3] and our need for a mild oxidation technique for certain water-soluble polyols, these results caught our attention. Our suspicions were aroused, however, upon reading the experimental details. In a typical reaction a solution of 7.5 mmol of silver nitrate and 5 mmol of cyclohexanol in ca. 20 mL of Me_2SO–water (3/1, v/v) was degassed and irradiated (quartz vessel,[4] 350 nm) for 1.5 h. Cyclohexanone was reported to be isolated in 90% yield as its 2,4-DNP derivative; metallic silver precipitated quantitatively. In a similar experiment, irradiation of an aqueous solution of 5.6 mmol of 1,4-butanediol and 8 mmol of silver nitrate was reported to give the corresponding dialdehyde in 91% yield, together with metallic silver. It was further pointed out that these reactions did *not* proceed in the dark nor in the presence of oxygen.

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[1] (a) University of Cincinnati. (b) North Dakota State University.

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[3] R. S. Macomber, J. C. Ford, and J. H. Wenzel, *Synth. React. Inorg. Met.-Org. Chem.*, **7**, 111 (1977).

[4] Why quartz was employed at this wavelength was not specified.[2]

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