The liquid could not be converted to a solid salt with fluoroboric acid in methanol. All attempts to effect hydride abstraction with triphenylmethyl fluoroborate in methylene chloride were unsuccessful, although the expected blue color was observed.

7-(4-Dimethylaminophenyl)-1,3,5-cycloheptatriene (2b).—The lithium reagent[4] was prepared from 16 g. (0.080 mole) of 4-bromo-N,N-dimethylaniline, 1.2 g. (0.18 g.-atom) of lithium wire, and 300 ml. of ether, cooled in an ice bath, and stirred while a solution of 11.2 g. (0.092 mole) of 7-methoxy-1,3,5-cycloheptatriene in 50 ml. of ether was added to it. Cooling and stirring were continued for 1 hr. Excess water was added and the organic layer was separated, washed with cold water, dried, and concentrated below 20°. A solid was obtained when the residue was taken up in ethanol and cooled. It was recrystallized from ethanol at −10°. After three recrystallizations, 2.85 g. (17%) of amine **2b** was obtained which had m.p. 49–51° (lit.[6] m.p. 49°).

Anal. Calcd. for $C_{15}H_{17}N$: C, 85.3; H, 8.1; N, 6.6. Found: C, 85.3; H, 8.4; N, 6.9.

Thermal Isomerization of 7-(4-Dimethylaminophenyl)-1,3,5-cycloheptatriene (2b) to 3-(4-Dimethylaminophenyl)-1,3,5-cycloheptatriene (3b).—A solution of 1.5 g. of **2b** (m.p. 49–51°) in 15 ml. of toluene was heated at reflux. At intervals of 2, 4, and 21 hr., samples were removed and analyzed by n.m.r. spectroscopy. The spectrum of the 2-hr. sample showed allylic ring proton bands for the 3 isomer **3b** (τ 7.75, triplet) in addition to those for the 7 isomer **2b** (τ 7.26, triplet). The areas of these bands indicated approximately equal amounts of each isomer after 4 hr. The spectrum was identical with that of **3b** after 21 hr. Recrystallization of this material from methanol gave a solid melting at 64–65°.

7-(1-Dimethylamino-4-naphthyl)-1,3,5-cycloheptatriene (2a).—The procedure of Jutz and Voithenleitner[6] for the preparation of 7-(4-dimethylaminophenyl)-1,3,5-cycloheptatriene was used with 1-dimethylaminonaphthalene (0.040 mole) and gave 10.0 g. (96%) of the amine as an oil. It was dissolved in ether, and hydrogen chloride gas was passed into the solution for 10 min. The precipitate, 10.0 g. (84%), melted at 186–187° dec. and was not further purified by recrystallization from benzene. The amine, liberated with dilute base, was a viscous oil.

Anal. Calcd. for $C_{19}H_{19}N$: C, 87.4; H, 7.3; N, 5.3. Found: C, 87.8; H, 7.3; N, 5.5.

7-(3-Methyl-N,N-diethylaminophenyl)-1,3,5-cycloheptatriene (2c).—The procedure for the preparation of **2a** was used with N,N-diethyl-*m*-toluidine (0.040 mole) and gave 10.0 g. (99%) of oil which was converted to the hydrochloride salt, m.p. 199–200° dec. This solid dissolved in ether when excess hydrogen chloride gas was added. Amine **2c** was obtained as an oil from the hydrochloride salt upon treatment with base.

Anal. Calcd. for $C_{18}H_{23}N$: C, 85.3; H, 9.2; N, 5.5. Found: C, 85.5; H, 9.6; N, 5.3.

1-Dimethylamino-4-naphthyltropylium Fluoroborate (4a).—A 4.3-g. (0.0165-mole) sample of amine **1a** was taken up in 50 ml. of methylene chloride, and a solution of 9.6 g. (0.029 mole) of triphenylmethyl fluoroborate[14] in 100 ml. of methylene chloride was added in portions, with swirling. A dark blue oil separated and the methylene chloride solution was decanted. The oil crystallized when it was heated with 150 ml. of methanol and gave 1.6 g. of solid. An additional 1.0 g. was obtained by concentration of the methanol solution. The yield was 2.6 g. (46%) of solid which decomposed at 180°. An analytical sample was prepared by recrystallization from methanol.

Anal. Calcd. for $C_{19}H_{18}BF_4N$: C, 65.6; H, 5.2; N, 4.0. Found: C, 65.2; H, 5.1; N, 4.1.

Treatment of 1-Dimethylamino-4-naphthyltropylium Fluoroborate with Sodium Methoxide.—A solution of excess sodium methoxide in methanol was added to a suspension of 1.0 g. (0.0029 mole) of 1-dimethylamino-4-naphthyltropylium fluoroborate (**4a**) in 20 ml. of methanol. When the blue color disappeared, the mixture was filtered, concentrated, treated with water, extracted with ether, and dried. The solvent was removed, leaving a noncrystalline solid (0.72 g., 90%). The infrared spectrum showed the presence of a hydroxyl group (3500 cm.$^{-1}$).

When the solid (0.72 g.) was taken up in 15 ml. of 1,2-dimethoxyethane and treated with 1 ml. of 40% fluoroboric acid, a purple color developed. The solid that separated was collected, washed with ether, and air dried to give 0.76 g. (84%) of 1-dimethylamino-4-naphthyltropylium fluoroborate, which was identified by comparison of its infrared spectrum with that of authentic material.

4-Dimethylaminophenyltropylium Fluoroborate (4b).—A solution of 4.0 g. (0.019 mole) of amine **3b** in 25 ml. of methylene chloride was treated with a solution of 8.2 g. (0.025 mole) of triphenylmethyl fluoroborate[14] in 100 ml. of methylene chloride. A deep blue color developed and a blue oil separated. After the mixture had been swirled for 10 min., the solvent was decanted and the oil was dried to a dark powder (1.6 g., 35%), which did did not melt below 300°. An analytical sample was prepared by recrystallization from methanol.

Anal. Calcd. for $C_{15}H_{16}BF_4N$: C, 60.6; H, 5.4; N, 4.7. Found: C, 60.2; H, 5.0; N, 4.6.

Acknowledgments.—The author is grateful to Miss Thelma J. Davis for the infrared spectra and Drs. J. K. O'Loane and T. Regan for n.m.r. spectra.

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[14] H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

Reactions of Thiyl Radicals with 4-Vinylcyclohexene

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Thiyl radicals generated by photolysis of either diphenyl disulfide or dibenzyl disulfide in 4-vinylcyclohexene add to a vinylic double bond in preference to abstraction of α-hydrogen. The resulting carbon free radical then abstracts an α-hydrogen leading to an adduct and a new radical which is the source of dehydro dimers and substitution products, or it reacts further to yield a higher molecular weight material. The characterization of the products from these and related reactions is discussed.

This study of the reactions of thiyl radicals with 4-vinylcyclohexene is part of a continuing study of the reactions of free radicals with olefins.

Preceding papers in this series[2-4] dealt with the reactions of alkoxy and alkyl peroxy radicals with the same compound. This olefin provides a useful combination of a vinyl plus a *cis* internal double bond together with five α-hydrogens, and thus affords opportunity for both addition and abstraction by the free radical.

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[1] This work was supported by the Goodyear Tire and Rubber Co. and is taken from the Ph.D. Thesis of A. E. Champ.

[2] J. R. Shelton and J. N. Henderson, *J. Org. Chem.*, **26**, 2185 (1961).

[3] J. R. Shelton and A. E. Champ, *ibid.*, **28**, 1393 (1963).

[4] J. R. Shelton and H. G. Gilde, *ibid.*, **29**, 482 (1964).

Previous workers[5] have shown that disulfides in the presence of abstractable hydrogens will, upon irradiation, yield mercaptans. Hydrogen abstraction was the predominant reaction resulting from the photolysis of isobutyl disulfide in cumene.[6] Mercaptans have also reacted with olefins under free-radical condition, to yield addition products.[7-9] Disulfides, under appropriate conditions, have initiated vinyl polymerization.[10,11] Thus, it seemed interesting to treat a disulfide with 4-vinylcyclohexene under free-radical conditions.

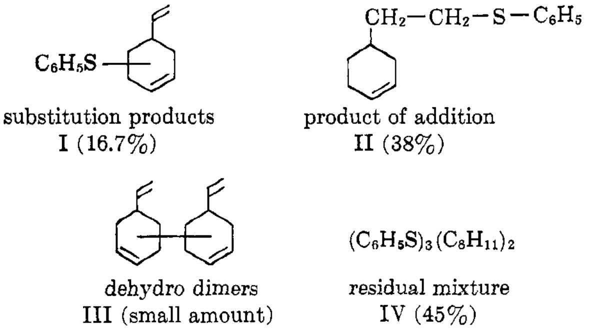
The temperature at which thermal homolysis of disulfides occurs is the subject of much confusion in the literature[12-14]; however, photolysis is generally agreed to produce thiyl free radicals.[15,16]

Results and Discussion

Photolysis of Diphenyl Disulfide in 4-Vinylcyclohexene.— The reaction of diphenyl disulfide in 4-vinylcyclohexene under ultraviolet radiation yields a mixture of products consistent with both hydrogen abstraction reactions and addition of free radicals to double bonds. However, it appears that thiyl radicals preferentially add to the vinyl double bond and that other products are formed by further reactions of the resulting adduct radicals. The major products of this reaction are shown in Chart I.

CHART I

PRODUCTS OF THE PHOTOLYSIS OF DIPHENYL DISULFIDE IN 4-VINYLCYCLOHEXENE



substitution products
I (16.7%)

product of addition
II (38%)

dehydro dimers
III (small amount)

residual mixture
IV (45%)

The substitution products represented by I are a mixture of position isomers, there being two major constituents. The infrared spectra of these two are quite similar in minor, as well as major, absorptions. Both show infrared absorptions indicating the presence of vinyl and internal unsaturation and also the presence of a monosubstituted aromatic ring. The ultraviolet absorption spectrum is consistent with the presence of a phenyl sulfide group. The elemental analyses also confirm that they are isomers, presumably substituted in the 3- and 6-positions in analogy with previous work.[2,4] The substitution products account for 16.7% of the diphenyl disulfide.

Product II shows the lack of vinyl absorption in the infrared spectrum; however, the presence of internal unsaturation and a monosubstituted aromatic ring is indicated. The ultraviolet absorption spectrum confirms the presence of a phenyl sulfide residue. The absence of any methyl absorption excludes the isomer with the thiyl group on the carbon next to the ring. The product obtained is identical in retention time on the gas chromatograph and in infrared spectrum with the product produced by the photolysis of benzenethiol in 4-vinylcyclohexene. The elemental analysis further confirms the assigned structure. This addition product accounts for 38% of the diphenyl disulfide.

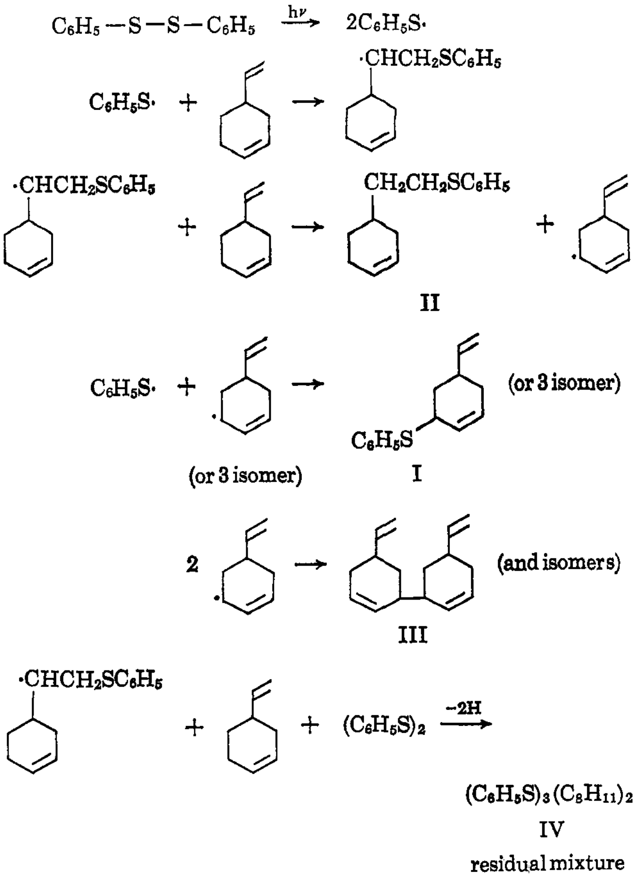
The small amount of dehydro dimers (III) formed have infrared spectra similar to that reported previously and are identical in retention time on the gas chromatograph and in infrared spectra to those dehydrodimers produced in the di-*t*-butyl peroxide work previously reported.[4]

The three sulfur-containing products, I, II, and IV, account for 99.7% of the diphenyl disulfide reacted, based on the compositions assigned in Chart I.

A reaction sequence consistent with the observed products is presented in Chart II. The initial step is, of course, cleavage of the disulfide by irradiation with ultraviolet light to produce free thiyl radicals. The addition of thiyl radical to the external double bond ap-

CHART II

REACTIONS RESULTING FROM THE PHOTOLYSIS OF DIPHENYL DISULFIDE IN 4-VINYLCYCLOHEXENE



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(5) M. Nakasaki, *Nippon Kagaku Zasshi*, **74**, 403, 405 (1953); *Chem. Abstr.*, **48**, 12018*a*,*h* (1954).

(6) C. Walling, and R. Rabinowitz, *J. Am. Chem. Soc.*, **81**, 1137 (1959).

(7) F. Ashworth and G. N. Burkhardt, *J. Chem. Soc.*, 1791 (1928).

(8) J. I. Cunneen, *ibid.*, 36 (1947).

(9) S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958).

(10) M. S. Kharasch, W. Nudenberg, and T. H. Meltzer, *J. Org. Chem.*, **18**, 1233 (1953).

(11) T. Otsu, *J. Polymer Sci.*, **21**, 559 (1956).

(12) H. P. Koch, *J. Chem. Soc.*, 401 (1949).

(13) A. Mustafa and M. Kamel, *Science*, **118**, 411 (1953).

(14) R. E. Davis and C. Perrin, *J. Am. Chem. Soc.*, **82**, 1590 (1960).

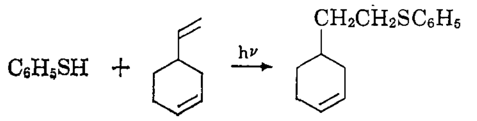
(15) T. E. Ferington and A. V. Tobolsky, *ibid.*, **80**, 3215 (1958).

(16) R. J. Kern, *ibid.*, **77**, 1382 (1955).

pears to be the predominant reaction, since all observed products can be accounted for through subsequent reactions of the carbon free radical formed in this step. Three alternatives are hydrogen abstraction, addition to a vinyl double bond, and termination by coupling. Hydrogen abstraction leads to product II and another carbon free radical which may couple with thiyl free radicals to give substitution products I, or dimerize to yield dehydro dimer III. Either of the other alternatives for the adduct radical would contribute to formation of nonvolatile residue IV.

Initial hydrogen abstraction by thiyl radicals is not included in the chart, since no benzenethiol was found in the reaction mixture, either by gas chromatography or by chemical tests. Heating the nonvolatile residue did produce benzenethiol as a product of decomposition.

If benzenethiol were produced it would photolyze to give the adduct, as shown by the formation of II when benzenethiol in 4-vinylcyclohexene was exposed to ultraviolet light.



It is unlikely that the thiyl radical would abstract hydrogen when the alternative of addition to a double bond is available, for the transfer constant of benzenethiol is quite high,[17,18] and the abstraction of hydrogen by thiyl radicals has been shown to be reversible.[19,20] Thus, the equilibrium would be quite unfavorable for the formation of mercaptan.

One can also visualize the formation of I by an induced decomposition mechanism. However, we do

$$R\cdot + C_6H_5SSC_6H_5 \longrightarrow RSC_6H_5 + C_6H_5S\cdot$$

not believe that this is occurring to a significant extent, since an attempt to initiate the reaction by decomposition of azobisisobutyronitrile resulted in quantitative recovery of the diphenyl disulfide.

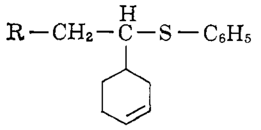
Seven hours proved to be an appropriate reaction time for the photolysis of diphenyl disulfide with 4-vinylcyclohexene at the temperature and concentration used for this study. Longer irradiation periods produced no increase in volatile products, and the ratio of volatile substitution to addition products was essentially the same after 2, 5, and 14 hr. Thus, prolonged irradiation does not alter the products of the reaction.

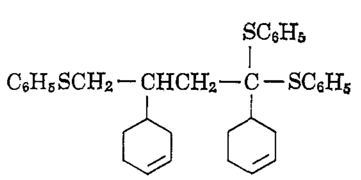
Attempted hydrogenation of the substitution product I using palladium-on-charcoal catalyst was unsuccessful despite previous success in hydrogenation of certain sulfides by this method.[21]

Nonvolatile Products.—The residual nonvolatile material was obtained after distillation of all other materials and, consequently, it could include products of distillation pyrolysis. However, evaporation of the volatile products at lower temperatures still yields essentially the same material. Pyrolysis of IV results in a mixture of products of which about half is benzenethiol. Thus, when a mixture containing this residue is subjected to gas chromatography at high block temperatures (*e.g.*, 300°), benzenethiol is observed in the resulting chromatogram. The infrared spectrum of product IV showed weak vinyl absorption along with strong internal unsaturation and monosubstituted aromatic absorptions. The ultraviolet absorption spectrum confirmed the presence of the phenyl sulfide grouping.

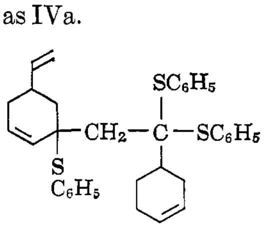
The elemental analysis and molecular weight of approximately 500 observed experimentally are consistent with two vinylcyclohexene units combined with three benzenethiyl groups in the nonvolatile residue as indicated for IV in Chart I. Estimation of the vinyl unsaturation from infrared spectra using 4-vinylcyclohexene as a standard indicates the presence of only one-half vinyl group for an average molecular weight of approximately 500. This indicates that at least half of the residual product contained no vinyl unsaturation, and that the remainder includes only one vinyl group for each two vinylcyclohexene units. Attempts to separate the mixture by extraction and by elution chromatography were unsuccessful.

One can deduce reasonable structures for the main components of the nonvolatile residue from consideration of these analytical, spectroscopic, and molecular weight data, along with the reaction sequence postulated in Chart II to account for the other observed products. The radical formed by addition of thiyl radical to the vinyl group can react with additional 4-vinylcyclohexene either by hydrogen abstraction, as indicated in Chart II, or by addition to the vinyl group to form a similar radical of higher molecular weight. Termination by combination with thiyl radicals is indicated by the high sulfur content of the product, which also suggests that additional substitution occurs to give an average of three thiyl groups for each two vinylcyclohexene units. Coupling with thiyl radicals would produce a tertiary C–H group in which the H is also α to sulfur. This hydrogen would be particularly susceptible to hydrogen abstraction, and subsequent combination with another thiyl radical derived from the disulfide would lead to products such as IVa.





IVa (mol. wt. 542)



IVb (mol. wt. 540)

Addition of a vinylcyclohexenyl radical to another 4-vinylcyclohexene molecule would account for the observation of vinyl unsaturation in the sulfur-containing residue. Farrissey[22] has shown that a tertiary allylic hydrogen is more reactive than secondary only when the tertiary C–H and the adjacent double bond are part of the same ring. Thus, the tertiary hydrogen

[17] R. A. Gregg, D. M. Alderman, and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 3740 (1948).

[18] J. L. O'Brien and F. Gornick, *ibid.*, **77**, 4757 (1955).

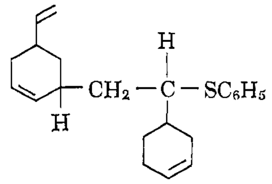
[19] W. A. Pryor, "Mechanisms of Organic Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[20] L. H. Slaugh and J. H. Raley, *J. Am. Chem. Soc.*, **82**, 1259 (1960).

[21] L. Bateman and F. W. Shipley, *J. Chem. Soc.*, 2888 (1958).

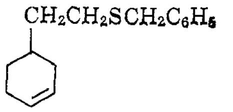
[22] W. J. Farrissey, Jr., *J. Org. Chem.*, **29**, 391 (1964).

in the 4-position of 4-vinylcyclohexene is relatively unreactive as compared to the methylene hydrogens in the 3- and 6-positions. However, the allylic tertiary hydrogen resulting from addition of a vinylcyclohexenyl radical to a vinyl double bond would be more reactive than the methylene hydrogens activated by the same double bond. Preferential abstraction of both activated tertiary hydrogens in such an intermediate and subsequent combination with thiyl groups would account for products of the type represented by IVb.



Structures IVa and b are thus representative of the principal types of compounds which appear to be present in the mixture of nonvolatile products formed in the photolysis of diphenyl disulfide in 4-vinylcyclohexene.

Photolysis of Dibenzyl Disulfide in 4-Vinylcyclohexene.—The reaction of dibenzyl disulfide with 4-vinylcyclohexene under photolytic conditions was also examined for comparison. The major volatile product was an adduct corresponding to



Smaller amounts of two products having infrared spectra consistent with substitution products were also observed. Dehydro dimer was identified and a nonvolatile residue remained after distillation. Thus, the products are analogous to those obtained from diphenyl disulfide.

All addition products obtained in these studies involved the external double bond. This is not surprising considering the excess of 4-vinylcyclohexene and the relative reactivity of the two types of unsaturation.[23]

Experimental Section

Reagents.—The 4-vinylcyclohexene used was Phillips Petroleum pure grade (99 mole % minimum purity) passed over a column of activated alumina immediately before use. The diphenyl disulfide was supplied by Aldrich Chemical Co., the dibenzyl disulfide was a product of Eastman Organic Chemicals, and the benzenethiol was obtained from K & K Laboratories, Inc.

Photolysis of Diphenyl Disulfide in 4-Vinylcyclohexene.—The apparatus consisted of a General Electric H85A3/UV lamp in a quartz test tube, 15 by 4.2 cm., which was inserted in a Pyrex test tube, 17 by 6 cm., and secured at the top by a layer of asbestos. A condenser was attached by a ground glass joint to a side arm 5 cm. from the top, and a nitrogen capillary bleed tube entered at the bottom. Thus, the material to be photolyzed was held in a thin layer around the quartz test tube. The entire apparatus was supported in a bath of flowing water for temperature control.

Diphenyl disulfide (5.9 g., 0.027 mole) was mixed with 40 g. (0.37 mole) of 4-vinylcyclohexene and photolyzed for 7 hr. at 37°. The resulting material was analyzed by gas chromatography on a 12-ft. Carbowax 20M column. The yield of substitution product I was 1.95 g. (0.009 mole, 16.7 %), and of addition product II was 4.5 g. (0.021 mole, 38%). A small amount of dehydro dimer was observed. Distillation of a portion of the photolysis mixture to remove both 4-vinylcyclohexene and volatile products indicated that 4.4 g. (0.008 mole, 45%) of residue IV was formed in the reaction. In this distillation the pot temperature did not exceed 150°.

Method of Analysis for Yield of the Products.—The material resulting from photolysis of diphenyl disulfide in 4-vinylcyclohexene was subjected to distillation on a 4-ft. spinning-band column. Fractions rich in the various products were collected and subjected to gas chromatography. The respective pure components were trapped in 4-mm. glass tubing inserted into the exit port of the F & M Model 500 gas chromatograph. Weighed amounts of each pure component were injected into the gas chromatograph onto a 12-ft. Carbowax column (20M) at 235° with the block and injection port temperatures at 200°. The flow rates of helium were 120 cc./min. on the detector and 15 cc./min. on the reference. The resulting area of the peak was then measured and graphs of area to weight were constructed. A weighed sample of material from the photolysis was injected into the gas chromatograph, and the area of the individual peaks was calibrated. Using the graphs previously constructed, the yield of each component could be determined.

In order to test the validity of this method in the presence of large excesses of 4-vinylcyclohexene, a weighed amount of addition product plus a large excess of 4-vinylcyclohexene was subjected to the above treatment. The excess had no observable effect on the results. This treatment was also verified with the presence of the other components.

Sampling for hydrogen gas was attempted by sweeping the reaction mixture during photolysis with nitrogen and trapping a representative gas sample. This was then analyzed by mass spectrometer. No hydrogen was found.

Identification of Products from Photolysis.—Pure materials trapped from the gas chromatograph were used for elemental analysis, infrared spectra, and ultraviolet spectra.

Addition Product.—The infrared spectra showed no vinyl absorption, but strong absorption at 3030 cm.$^{-1}$ indicated the presence of an internal double bond and aromatic absorption was observed at 3084, 2000–1650, 1500, 1450, 740, and 690 cm.$^{-1}$. This material exhibited an ultraviolet absorption maxima at 256 mμ which was consistent with the report of Fehnel and Carmack[24] that many phenyl sulfides have maxima at 254–258 mμ.

Anal. Calcd. for $C_{14}H_{18}S$: C, 76.99; H, 8.32; S, 14.69; mol. wt., 218.4. Found: C, 76.82; H, 8.48; S, 14.36; mol. wt., 217.

Substitution Products.—The over-all infrared spectra of both of the isomeric substitution products were quite similar. Vinyl unsaturation was indicated by the characteristic absorptions at 3090, 1640, 995, and 910 cm.$^{-1}$, and internal unsaturation was observed at 3030 cm.$^{-1}$. The presence of phenyl groups was indicated by absorptions at 1500 and 1450 cm.$^{-1}$ and by the monosubstituted aromatic absorptions at 740 and 690 cm.$^{-1}$. Ultraviolet absorption maximum at 256 mμ confirmed the presence of the phenyl sulfide group.

Anal. Calcd. for $C_{14}H_{16}S$: C, 77.75; H, 7.48; S, 14.83; mol. wt., 216.2. Found (A): C, 77.54; H, 7.71; S, 14.76; mol. wt., 214. Found (B): C, 77.68; H, 7.70; S, 14.60; mol. wt., 219.

Dehydro Dimers.—The dehydro dimers, being formed in only small amounts, were identified by retention time on the gas chromatograph and comparison of infrared spectra with that of previous work.[4]

Residual Mixture.—The infrared spectra of this material showed weak vinyl absorption, and very strong absorption characteristic of internal unsaturation at 3030 cm.$^{-1}$. The ultraviolet spectrum showed an absorption at 256 mμ characteristic of the phenyl sulfide group. Pyrolysis of 0.9 g. of this material yielded 0.7 g. of volatile material of which about half was characterized as benzenethiol.

In order to obtain a larger quantity of material for investigation, an apparatus of three times the capacity was constructed. Diphenyl disulfide (18 g., 0.08 mole) was photolyzed for 15 hr. in 120 g. of 4-vinylcyclohexene. The excess olefin was removed under aspirator vacuum on a steam bath and the remaining material was subjected to high vacuum distillation from an oil bath at 150° for 8 hr. to remove the addition and substitution prod-

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(23) M. S. Kharasch and M. Sage, *J. Org. Chem.*, **14**, 537 (1949).

(24) E. A. Fehnel and M. Carmack, *J. Am. Chem. Soc.*, **71**, 84 (1949).

ucts. The residual nonvolatile material amounted to 13.2 g. (0.024 mole, 45% yield calculated as IV).

The vinyl concentration in this material was measured in terms of vinyl groups per mole weight from the infrared spectrum. The extinction value (E/mole ml. cm.) of the vinyl group at 910 cm.$^{-1}$ was determined from a reference sample of 4-vinylcyclohexene. This calculated to be 14.6×10^4. From the vinyl absorption of the material observed at 910 cm.$^{-1}$ the concentration of vinyl groups was calculated to be 0.917 *M*. Assuming the density of the material to be 0.9, the vinyl concentration would be 0.917 mole/900 g. or 1 vinyl group/980 molecular weight. Since the observed molecular weight was 498, this indicates that approximately half of the material contained no vinyl unsaturation, and that the other half contained one vinyl group per mole, consistent with structures IVa and IVb, respectively.

Eight grams of the nonvolatile residue was extracted in a Soxhlet extractor for 80 hr. with isopropyl alcohol. The undissolved residue was 3.1 g. On cooling of the solvent, an oil separated (0.9 g.) and evaporation of the solvent yielded 3.5 g. of material. All fractions gave identical infrared spectra, and elemental analysis and molecular weight data were similar to the values obtained for the original material.

Anal. Calcd. for $C_{34}H_{37}S_3$: C, 75.4; H, 6.9; S, 17.7; mol. wt., 542. Found: C, 75.8; H, 6.68; S, 17.4; mol. wt., 498.

Elution chromatography was attempted by placing 0.7 g. of the residue on a column of 100 g. of silicic acid and eluting with chloroform. Collection of the first and main fraction contained most of the material (0.6 g.). The spectra and analytical data were unchanged by this treatment.

Attempted Hydrogenation of Unsaturated Sulfides.—Hydrogenation of both adduct and substitution product was attempted in separate experiments at atmospheric pressure. Two types of catalyst were employed: palladium chloride on carbon[21,25] and palladium on carbon (American Platinum Works). Both attempts were unsuccessful.

Chemical Analysis for Benzenethiol.—A mixture of diphenyl disulfide was photolyzed in 4-vinylclohexene for 2 hr. The resulting mixture was treated with alcoholic potassium hydroxide and extracted with water. The water layer was separated, washed with ether then acidified with hydrochloric acid and extracted with ether. No benzenethiol was observed on evaporation of the ether.

Attempted Induced Decomposition of Diphenyl Disulfide.—Into two 250-ml. iodine flasks, which had been blackened on the outside, 21.6 g. (0.2 mole) of 4-vinylcyclohexene was placed together with 4.4 g. (0.02 mole) of diphenyl disulfide. Into one of these flasks was also placed 1.6 g. (0.01 mole) of azobisisobutyronitrile. The flasks were then kept in a water bath at 45° for 30 days. At the end of this period the 4-vinylcyclohexene was removed from each sample. Diphenyl disulfide was recovered quantitatively from both flasks.

Determination of Effect of Photolysis Time.—In order to determine the required time of irradiation for this reaction and also to note the effect, if any, of prolonged photolysis, an experiment similar to the above photolysis was performed. The photolysis apparatus was fitted with a length of hypodermic tubing. Onto this at appropriate time intervals were placed evacuated serum vials to withdraw a sample. These samples were analyzed as previously described.

Photolysis of Benzenethiol in 4-Vinylcyclohexene.—Benzenethiol (4.40 g., 0.04 mole) and 4-vinylcyclohexene (32 g., 0.3 mole) were placed in the photolysis apparatus and irradiated for 21 hr. The major product as indicated by gas chromatography was the expected adduct.

This material was identical in retention time and infrared spectrum with the adduct II obtained from the disulfide reaction. Judging by the retention time on the gas chromatograph a small amount of substitution products was also obtained. Distillation at pot temperatures no greater than 160° yielded a small amount of residual material.

Photolysis of Dibenzyl Disulfide in 4-Vinylcyclohexene.—Dibenzyl disulfide in the amount of 6.0 g. (0.024 mole) and 32 g. (0.3 mole) of 4-vinylcyclohexene were placed in the photolysis apparatus and irradiated for 21 hr. The resulting solution was then examined by gas chromatography. Inspection of the chromatogram indicated that more dehydro dimer was found in this reaction than in the diphenyl disulfide case.

Identification of Products.—The above photolysis mixture was distilled on a 4-ft. spinning-band column. The fractions rich in the various products were then subjected to gas chromatography, and pure components were collected as described previously.

The dehydro dimers were recognized by retention time on the gas chromatogram and by their infrared spectra.

The infrared spectrum of the addition product was similar to that of the diphenyl disulfide adduct. There is no vinyl absorption, but internal unsaturation at 3030 cm.$^{-1}$ and an aromatic grouping at 3086, 1500, 1450, and 690 cm.$^{-1}$ are indicated.

Anal. Calcd. for $C_{15}H_{20}S$: (231): C, 78.0; H, 8.3; S, 13.9. Found: C, 78.5; H, 8.06; S, 13.75.

These data together with an analogy to the diphenyl disulfide reaction suggested a structure analogous to II.

Two peaks were observed on the gas chromatogram of this reaction mixture, whose retention time compared with the diphenyl disulfide substitution products. Their infrared spectra showed vinyl unsaturation at 3087, 1640, 995, and 916 cm.$^{-1}$, aromatic absorption at 1500, 1454, and 690 cm.$^{-1}$, plus internal unsaturation at 3030 cm.$^{-1}$. Thus, these peaks are probably due to substitution products analogous to I.

Distillation to remove the above products from the photolysis mixture yielded a residual material. The infrared spectra of this material showed the presence of internal unsaturation and aromatic grouping, with a very weak vinyl absorption.

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(25) R. Mozingo, *Org. Syn.*, **26**, 78 (1946).