ture used. This tends to confirm the previous interpretation of two compensating factors, both having the same isokinetic temperature, by eliminating the possibility that the reactions had been studied at the isokinetic temperature. The 2-fluoro compound shows no deviation that might be attributed to some proximity effect such as an intramolecularly hydrogen-bonded intermediate[9] or a steric effect. The slow cyclization of both the 2- and 4-fluoro ketones has been interpreted[8,9] as being due to a strong resonance interaction at the reaction center. Even the 2-chloro ketone is only slightly off the straight line although the steric crowding at the reaction center must be quite severe in the transition state. It would be interesting to determine the location of the 2-methyl and 2-bromo compounds on this plot.

Registry No.—I (X = H), 4919-84-0; I (X = 4-Cl), 18793-94-7; I (X = 3-CF$_3$), 394-75-2; I (X = 2-F), 740-35-2; I (X = 2-Cl), 18793-96-9; I (X = 2-Br), 18793-97-0.

Acknowledgments.—This work was supported by the Research Corp. with supplementary support from the National Science Foundation and from the American Association for the Advancement of Science, administered by the Tennessee Academy of Science.

Sulfur-Bridged Carbocycles. III. Photocyclization of β,β'-Diphenyldivinyl Sulfide[1]

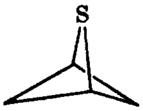
Eric Block and E. J. Corey

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Received September 6, 1968

β,β'-Diphenyldivinyl sulfide (**2a**) has been found to undergo facile cyclization on irradiation to *trans*-2,3-diphenyl-5-thiabicyclo[2.1.0]pentane (**3a**), the first known example of a cyclobutene episulfide. Bicyclic sulfide **3a** undergoes desulfurization with trivalent organophosphorus compounds giving *trans,trans*-1,4-diphenylbutadiene, presumably by way of thermally unstable *trans*-3,4-diphenylcyclobutene (**9**). A second product of the irradiation of sulfide **2a** has been identified as 2,3-dihydro-3,4-diphenylthiophene (**10**).

With the objective of synthesizing 2-thiabicyclo[1.1.1]pentane (**1**), the simplest symmetrical sulfur-bridged carbocycle,[2] we have investigated the photochemistry of divinyl sulfides. It was anticipated that photocyclization of the type observed by Srinivasan in the acyclic diene series[3] would occur affording bicyclic sulfides. In contrast to the nonconjugated dienes (such as 1,4-pentadiene) which are transparent in the ultraviolet region above 180 mμ, vinyl sulfides absorb strongly at 230 mμ (see Table I). Furthermore, a bathochromic shift is observed on going from vinyl sulfides to divinyl sulfides. This shift is thought to indicate through-conjugation of the double bonds.[4]

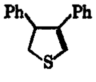


1

Although irradiation of divinyl sulfide[5] itself under various conditions was unproductive,[6] brief irradiation of the isomers of β,β'-diphenyldivinyl sulfide[7] (**2a**, preparation outlined in eq 1) afforded a new compound, characterized as *trans*-2,3-diphenyl-5-thiabicyclo[2.1.0]-

Table I

Ultraviolet Spectra of Vinyl Sulfides

Compound	λ_{max}, mμ	ε	Ref
$CH_2{=}CHSCH(CH_3)_2$	230	6000	4a
$CH_2{=}CHSCH{=}CH_2$	240, 255	8350,.7600	4a
 Ph Ph S **10**	226, 306	16,200, 15,200	This work
$C_6H_5CH{=}CHSCH_3$	286	15,500	4b
$C_6H_5CH{=}CHSCH{=}CHC_6H_5$ (**2a**)	229, 320	24,000, 36,000	This work

---

[1] Paper II: E. J. Corey and E. Block, *J. Org. Chem.*, in press.

[2] For the synthesis and reactions of the second and third members of the class of symmetrical sulfur-bridged carbocycles, see the preceding paper and E. J. Corey and E. Block, *J. Org. Chem.*, **31**, 1663 (1966); also see E. Block, Ph.D. Thesis, Harvard University, 1967 [*Dissertation Abstr.*, **28**, 1849B (1967)].

[3] (a) R. Srinivasan and K. H. Carlough, *J. Am. Chem. Soc.*, **89**, 4932 (1967); (b) also see J. Meinwald and G. W. Smith, *ibid.*, **89**, 4923 (1967).

[4] (a) C. E. Scott and C. C. Price, *ibid.*, **90**, 2202 (1968); (b) M. C. Caserio, R. E. Pratt, and R. J. Holland, *ibid.*, **88**, 5747 (1966).

[5] For the preparation of divinyl sulfide, see K. K. Georgieff and A. Dupré, *Can. J. Chem.*, **37**, 1104 (1959).

[6] Wynberg and coworkers have similarly reported that irradiation of bis(1-propenyl) sulfide gives no detectable amounts of cyclization products: S. H. Groen, R. M. Kellogg, J. Buter, and H. Wynberg, *J. Org. Chem.*, **33**, 2218 (1968).

[7] (a) Reaction i: O. Scherer and G. Stähler, German Patent 1,080,101 (1960); *Chem. Abstr.*, **55**, 16422*i* (1961). (b) Reactions ii and iii: K. Dimroth, H. Follmann, and G. Pohl, *Chem. Ber.*, **99**, 642 (1966).

pentane (**3a**), in 30–34% yield. Bicyclic sulfide **3a** is the first example of a cyclobutene episulfide.[8]

(i) $CH_2{=}O + HCl + H_2S \rightarrow ClCH_2SCH_2Cl$

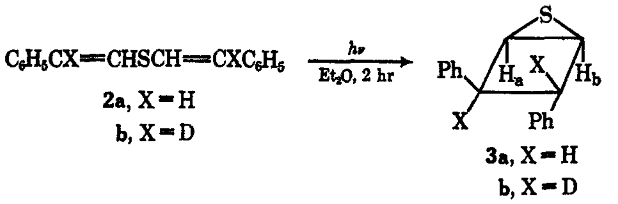
(ii) $ClCH_2SCH_2Cl + 2(C_6H_5)_3P \rightarrow$

$$(C_6H_5)_3P^{+}CH_2SCH_2P^{+}(C_6H_5)_3 + 2Cl^{-} \quad (1)$$

(iii) $[(C_6H_5)_3P^{+}CH_2{-}]_2S + 2C_6H_5CHO \xrightarrow[MeOH]{NaOMe}$

$$C_6H_5CH{=}CHSCH{=}CHC_6H_5$$

2a

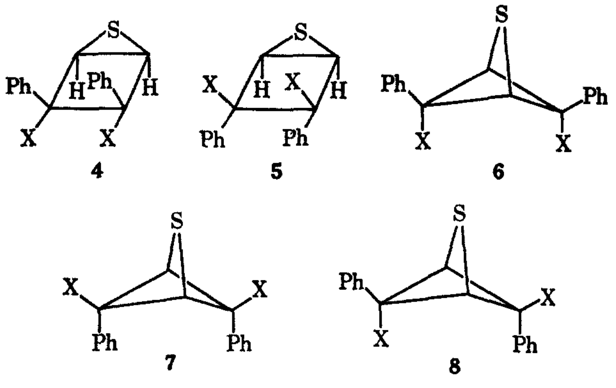


2a, X = H
b, X = D

3a, X = H
b, X = D

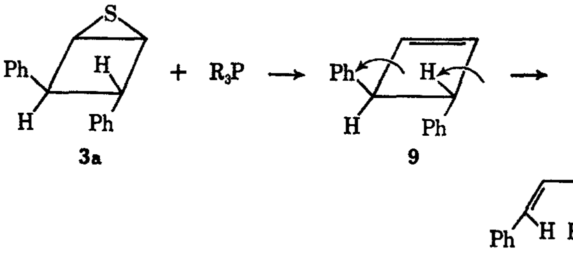
Alternate structures for the photoproduct, such as the *cis*-diphenyl compounds **4** and **5** (Chart I) as well as **6–8** which possess the 2-thiabicyclo[1.1.1]pentane skeleton, were eliminated by nmr studies of the photoproduct from *cis,trans*-β,β′-dideuterio-β,β′-diphenyldivinyl sulfide (**2b**). The isotopically labeled sulfide **2b** was prepared as in eq 1 using benzaldehyde-1-*d*.[9] The complex multiplet present in the nmr spectrum of the undeuterated photoproduct at δ 3.3–3.9, and assigned to the protons on the saturated ring carbons, was reduced to an AB quartet with J_{AB} = 4 cps in the deuterated photoproduct. Of the six possible structures **3–8** (deuterated α to the aromatic ring), all but structure **3** are symmetric through the plane bisecting the C–S–C bond angle and would be expected to show a singlet in the upfield region of their nmr spectra. The observed difference in chemical shift between protons H_a and H_b of 0.25 ppm undoubtedly reflects the shielding of proton H_b by the adjacent *cis*-phenyl group.[10] The observed coupling constant J_{AB} = 4 cps may be compared with the coupling constant for *cis* protons in episulfides of 6 cps.[11] Analysis of the nmr spectrum of the undeuterated photoproduct **3a** at 100 Mc, utilizing double-resonance techniques, lends additional weight to the structural assignment. A full explanation of the nmr data is given in the Experimental Section.

CHART I



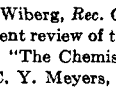
a, X = H; **b**, X = D

Additional evidence supporting structure **3a** is the formation of *trans,trans*-1,4-diphenylbutadiene on warming the photoproduct with trimethyl phosphite or tributylphosphine, reagents known to desulfurize episulfides.[12] It is likely that the butadiene is the product of conrotatory[13] opening of the intermediate *trans*-3,4-diphenylcyclobutene (**9**), predicted to be thermally unstable.[14] Several unsuccessful attempts were made to isolate cyclobutene **9**.

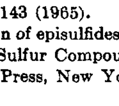


Further studies on the photocyclization of β,β′-diphenyldivinyl sulfides indicated that the all-*trans* and the all-*cis* isomers cyclized to the same product **3a** formed from the *cis,trans* isomer **2a**. Furthermore, triplet-sensitized irradiation of *cis,trans* isomer **2a** with camphorquinone as sensitizer, or irradiation of *cis,trans*-**2a** at low temperatures led principally to the formation of *cis,cis*-β,β′-diphenyldivinyl sulfide.

In two isolated cases during the photocyclization studies, a second major photoproduct was isolated. This product was characterized as 2,3-dihydro-3,4-diphenylthiophene (**10**) by physical methods and by dehydrogenation to 3,4-diphenylthiophene. Isomer **10** was not formed from the photochemical or thermal decomposition of photoproduct **3a** nor was isomer **10** formed when 1% of methanol was present in the ethereal solvent during the photolysis of **2a**. Dihydrothiophene **10** may be derived from diradical intermediate **11** or



10



11

possibly from radical attack on divinyl sulfide **2a**.[15]

---

[8] For syntheses of cyclobutene epoxides, see A. C. Cope, P. T. Moore, and W. R. Moore, *J. Amer. Chem. Soc.*, **80**, 5505 (1958); R. Criegee and K. Noll, *Ann.*, **627**, 1 (1959); W. R. Moore and C. H. Beede, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963, p 11M; J. L. Ripoll and J. M. Conia, *Tetrahedron Lett.*, 979 (1965); A. Padwa, *J. Amer. Chem. Soc.*, **87**, 4205 (1965).

[9] D. Seebach, B. W. Erickson, and G. Singh, *J. Org. Chem.*, **31**, 4303 (1966).

[10] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p 125.

[11] J. I. Musher and R. G. Gordon, *J. Chem. Phys.*, **36**, 3097 (1962). The coupling constant between the bridgehead protons in bicyclo[1.1.1]pentane is 18 cps: K. B. Wiberg, *Rec. Chem. Prog.*, **26**, 143 (1965).

[12] For a recent review of the desulfurization of episulfides, see L. Goodman and E. J. Reist, "The Chemistry of Organic Sulfur Compounds," Vol II, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, New York, N. Y., 1966, p 105.

[13] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

[14] M. A. Battiste and M. E. Burns, *Tetrahedron Lett.*, 523 (1966).

[15] It is of interest that cyclopentene is one of the minor products isolated from the photolysis of 1,4-pentadiene.[3b]

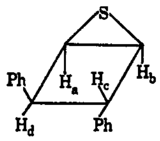
Experimental Section[16]

Photolysis of Divinyl Sulfide.—Divinyl sulfide was prepared in poor yield from β,β′-dihydroxyethyl sulfide (thiodiglycol) by distillation from potassium hydroxide at 200°.[5] A 0.1 *M* solution in *n*-pentane was irradiated for 26 hr with unfiltered light from a low-pressure mercury lamp (output principally at 2537 Å). Quantitative ultraviolet and vpc analysis indicated only a very slow disappearance of starting material. A brown polymeric coating formed on the wall of the photolysis well. No improvement was realized on sensitizing the photolysis either with acetophenone (irradiating with a medium-pressure mercury lamp through a Pyrex filter) or cuprous chloride.

***trans*-2,3-Diphenyl-5-thiabicyclo[2.1.0]pentane (3a).**—A solution of 0.50 g of recrystallized *cis,trans*-β,β′-diphenyldivinyl sulfide[7] (**2a**) (2.1 mmol) in 150 ml of anhydrous ether in a nitrogen atmosphere was irradiated with a 450-W medium-pressure Hanovia mercury lamp (Model L: 679A) using a Pyrex filter. Irradiation was continued for 2 hr while the ether refluxed gently. The progress of the photolysis was followed by quantitative ultraviolet spectroscopy. At the end of the irradiation period a small amount of polymeric material appeared as a precipitate. The colorless solution was concentrated *in vacuo* and the residue was extracted with several portions of boiling *n*-hexane. There remained as residue 0.17 g of a colorless, polymeric solid, soluble in methylene chloride but insoluble in pentane and hexane, showing a very broad, uninformative nmr spectrum. Concentration of the hexane solution *in vacuo* followed by distillation of the residual light yellow liquid at 75° (0.04 mm) afforded 0.17 g of **3a** as a colorless solid, mp 66–71.5° (34% yield). Recrystallization of the crude solid from boiling methanol raised the melting point to 73.1–73.6°. The infrared spectrum ($CHCl_3$) differed from that of diphenyldivinyl sulfide (**2a**) in particular by the absence of intense absorption in the 10–12-μ region (*trans*-disubstituted double bond); the nmr spectrum ($CDCl_3$) at 60 and 100 Mc[17] showed peaks at δ 3.46 (multiplet, one proton), 3.96 (multiplet, two protons), 7.25 (singlet, five protons), and 7.37 (singlet, five protons); the assignment of nmr peaks and coupling constants is given in Table II. The ultraviolet spectrum had $\lambda_{\max}^{\text{pentane}}$ 228, 260, 265, 271, and 300 mμ (ε 9700, 1040, 1015, 813, 32, respectively); the molecular weight determined mass spectrometrically was 238.0819 (calcd for $C_{16}H_{14}S$, 238.0816).

Table II

Assignment of Nmr Peaks and Coupling Constants in Photoproduct **3a**



3a

Proton	Chemical shift, δ	Coupling constants, cps
H_a	3.96	$J_{ab} = 4$
H_b	3.69	$J_{bc} = 1.9$
H_c	3.96	
H_d	3.46	$J_{ad} + J_{cd} = 5.8$

***cis,trans*-β,β′-Dideuterio-β,β′-diphenyldivinyl Sulfide (2b).**—The conditions for the reaction of benzaldehyde with dimethyl sulfide–α,α′-triphenylphosphonium bromide[7] were followed, substituting benzaldehyde-1-*d*[9] for benzaldehyde. The recrystallized dideuteriodiene **2b** had mp 94–96° (the undeuterated *cis,trans* diene **2a** had mp 95.2–96.0°) and ultraviolet $\lambda_{\max}^{\text{EtOH}}$ 234 and 320 mμ (ε 14,200 and 30,600), in good agreement with the properties of the undeuterated *cis,trans* diene. The infrared spectrum ($CHCl_3$) of **2b** differed from that of the undeuterated *cis,trans* diene **2a**, showing, in particular, a weak band at 4.47 μ (assigned to C–D); the nmr spectrum ($CDCl_3$) had peaks at δ 6.40 (broad singlet, one proton), 6.75 (triplet, J = 1.9 cps, one proton), and 7.2–7.6 (a multiplet with a major peak at 7.26, ten aromatic protons). The molecular weight determined mass spectrometrically was 240.0936 (calcd for $C_{16}H_{12}D_2S$, 240.0942).

***trans*-2,3-Dideuterio-2,3-diphenyl-5-thiabicyclo[2.1.0]pentane (3b).**—A solution of 0.750 g of recrystallized **2b** (3.12 mmol) in 225 ml of anhydrous ether was irradiated as described in the preparation of **3a**. Isolation of products as described above afforded 0.335 g of polymer and 0.227 g (30% yield) of **3b**, mp 73–74° (after recrystallization from methanol), having $\lambda_{\max}^{\text{pentane}}$ 228, 255 (sh), 260, 264, 271, 300, and 340 mμ (ε 22,000, 570, 840, 960, 510, 15, and 7, respectively). The infrared spectrum ($CHCl_3$) of **3b** differed from that of **3a** showing, in particular, a band at 4.6 μ (C–D). The nmr spectrum ($CDCl_3$) showed an AB quartet with doublets centered at δ 3.64 (J = 4 cps, one proton) and 3.88 (J = 4 cps, one proton) in addition to two aromatic singlets at δ 7.22 and 7.32 (ten protons). The molecular weight determined mass spectrometrically was 240.0939 (calcd for $C_{16}H_{12}D_2S$, 240.0942).

Stereochemistry of Photoproduct 3b as Determined by Spin Decoupling and Deuterium Labeling.—The nmr spectrum of photoproduct **3a** in deuteriochloroform at 60 Mc showed three closely spaced multiplets at δ 3.46, 3.69, and 3.96 (integrating for one, one, and two protons, respectively) in addition to two aromatic singlets at δ 7.25 and 7.37 (five protons each). The high-field multiplets were better separated but not significantly simplified at 100 Mc.[17] Substitution of protons H_c and H_d (see **3a** above) by deuterium resulted in a considerably simpler spectrum showing two doublets (each having J = 4 cps) centered at δ 3.68 and 3.92 and integrating for a single proton each in addition to the ten-proton aromatic doublet. Considering the known ability of an aromatic ring to shield a sterically adjacent proton[10,18] the peak at δ 3.68 can be assigned to proton H_b and therefore the peak at δ 3.92 can be assigned to proton H_a (which is in a 1,3 position relative to the phenyl group). It is now apparent that the two-proton multiplet at δ 3.96 is due to the fortuitous overlap of the H_a peak with either the H_c or H_d peak. Field sweep double resonance at 100 Mc allowed an unequivocal assignment to be made for protons H_c and H_d. Saturation of the multiplet at δ 3.69 (H_b) resulted in the collapse of the δ 3.96 multiplet (H_a and H_c or H_d) to a doublet (J = 2.9 cps) but did not alter the δ 3.46 multiplet. Similarly, saturation of the multiplet at δ 3.46 simplified the δ 3.96 multiplet to a doublet (J = 2.9 cps) without affecting the signal at δ 3.69. Saturation of the multiplet at δ 3.96 led to the simplification of both the δ 3.69 and 3.46 multiplets to *singlets*.

It therefore follows that the proton at δ 3.46 which is not coupled to proton H_b must be proton H_d. It is known that the value of the diagonal coupling constant (*i.e.*, J_{bd} and J_{ac}) in cyclobutyl derivatives is less than 1 cps.[18,19] For the system $H_aH_bH_c$, the observed coupling constant $J_{a,c/b}$ = 2.9 cps can be represented as an average of the coupling constants J_{ab} and J_{bc}.[20] Since J_{ab} = 4 cps, it follows that J_{bc} = 1.9 cps. These coupling constants are in good agreement with the respective *cis* and *trans* coupling constants of 4.9 and 1.9 cps reported for 1,3-diphenylcyclobutene by Masamune.[18]

Desulfurization of Photoproduct 3a.—In an nmr tube was placed 101 mg (0.4 mmol) of crude photoproduct **3a** together with 284 mg of distilled tributylphosphine (1.4 mmol). The homogeneous solution was examined by nmr spectroscopy while warming the sample at 100° in a temperature probe. After several minutes at 100° the high-field proton signals at δ 3–4.0 disappeared and were replaced by a complex multiplet at δ 6–7.3. After 5 min at 100°, fine crystals appeared in the nmr tube. The mixture was kept at 100° for 30 min and then cooled to room

---

[16] Exact molecular weights and mass spectra were determined on an Associated Electrical Industries, Ltd., Model MS-9 double-focusing mass spectrometer. All melting points were obtained on a Büchi melting point apparatus and are corrected. Nuclear magnetic resonance (nmr) spectra were obtained on a Varian Associates Model A-60 nmr spectrometer (60 Mc) and a Japan Electron Optics Laboratory Co. JNM-4H-100 (100 Mc; built-in spin decoupler) with tetramethylsilane as internal standard. Spin decoupling at 60 Mc was accomplished using a Varian Associates Model V-6058 spin decoupler in conjunction with the Varian A-60 nmr spectrometer. Infrared spectra were obtained on a Perkin-Elmer Model 137 sodium chloride spectrometer and a Perkin-Elmer Model 237 grating infrared spectrometer using polystyrene as a calibration standard. Ultraviolet data were obtained using a Perkin-Elmer Model 202 spectrophotometer and Cary Models 11M and 14 spectrophotometer with ethanol as solvent unless otherwise indicated. Vapor phase chromatography (vpc) was performed on F & M Models 300, 609, and 810 chromatographs.

[17] We are grateful to Japan Electron Optics Laboratory Co., Ltd., Medford, Mass., for determining the 100-Mc spectrum and performing double-resonance experiments.

[18] S. Masamune, *Tetrahedron Lett.*, 945 (1965).

[19] H. Ziffer, N. E. Sharpless, and R. O. Kan, *Tetrahedron*, **22**, 3011 (1966).

[20] See footnote 10, p 92.

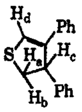
temperature and diluted with methanol. A colorless solid (44 mg, 51% yield) having mp 141–153° was isolated. Recrystallization of the crude product from boiling methanol afforded 28 mg of strongly fluorescent plates having mp 151.4–152.5° (*trans,trans*-1,4-diphenylbutadiene is reported to form strongly fluorescent crystals with mp 152.5°[21]) and $\lambda_{max}^{pentane}$ at 230 (sh), 314, 328, 344 mμ (ε 13,100, 30,400, 37,000, 22,700, respectively) in excellent agreement with the literature values for *trans,trans*-1,4-diphenylbutadiene; the mass spectrum indicated a molecular weight of 206 confirming the empirical formula $C_{16}H_{14}$.

Very similar results were obtained on warming photoproduct **3a** with trimethyl phosphite to 100° for 60 min. Attempts to extrude sulfur from **3a** by irradiation of a trimethyl phosphite solution of **3a** with Vycor-filtered light from a medium-pressure Hanovia mercury lamp or by warming **3a** with the powerful phosphorus nucleophile 2-phenyl-1,3-dimethyl-1,3-diazaphospholidine[22] were unsuccessful. During the course of all the above experiments, there was no evidence for the formation of 3,4-diphenylcyclobutene (**9**).

2,3-Dihydro-3,4-diphenylthiophene (**10**).—On two isolated occasions, irradiation of *cis,trans*-β,β'-diphenyldivinyl sulfide (**2a**) led to the formation of photoproduct **10** in addition to, or instead of, photoproduct **3a**. Both of these reactions were carried out on a slightly larger scale than that previously described for the preparation of **3a**. Thus, when a solution of 3.0 g of recrystallized *cis,trans*-β,β'-diphenyldivinyl sulfide (**2a**) in 50 ml of anhydrous methylene chloride was added during 17 hr to 700 ml of anhydrous ether in an argon atmosphere during irradiation (as described previously for the preparation of **3a**), a colorless solid could be isolated in 16% yield. The product, after sublimation and recrystallization from methanol, had mp 111.5–112.5°; infrared $\lambda_{max}^{CHCl_3}$ 3.4, 6.43, and 12.1–12.3 μ (the latter two bands were absent in the infrared spectrum of **3a**); ultraviolet, $\lambda_{max}^{pentane}$ 226 and 306 mμ (ε 16,200 and 15,200, respectively); the molecular weight determined mass spectrometrically was 238 indicating that the photoproduct was isomeric with photoproduct **3a**. The nmr spectrum ($CDCl_3$) was very informative, showing peaks at δ 3.12 (doublet of doublets, J_1 = 3.7 cps, J_2 = 11.4 cps, one proton), 3.87 (doublet of doublets, J_3 = 11.3 cps, J_4 = 9.5 cps, one proton), 4.56 (set of doublets of doublets, J_5 = 1.0 cps, J_6 = 9.5 cps, J_7 = 3.5 cps, one proton), and 6.81 (doublet, J_8 = *ca.* 1 cps, one proton) in addition to an aromatic multiplet at 7.16 and 7.28 (twelve protons). The assignment of nmr peaks and coupling constants is given in Table III. Assuming that the proton appearing at highest field is the methylene proton shielded by the *cis*-phenyl group (proton H_b),[10] the assignment of chemical shifts and coupling constants can be readily and unambiguously made.[23]

TABLE III

ASSIGNMENT OF NMR PEAKS AND COUPLING CONSTANTS IN PHOTOPRODUCT 10



10

Proton	Chemical shift, δ	Coupling constants, cps
H_a	3.87	J_{ab} = 11.4
H_b	3.12	J_{bc} = 3.6
H_c	4.56	J_{ca} = 9.6
H_d	6.81	J_{dc} = 1

Additional support for the structural assignment of **10** as a dihydrothiophene is found in the facile dehydrogenation of **10** to 3,4-diphenylthiophene by elemental sulfur. Thus, 52.4 mg of recrystallized photoproduct **10** (0.22 mmol) and 7 mg of sulfur (0.22 mmol) were heated for 4 hr at 200° in a small sublimation apparatus.[24] Hydrogen sulfide evolution occurred. Recrystallization of the crude sublimate from methanol gave 40.1 mg (77% yield) of slightly yellow needles (contaminated by traces of sulfur), mp 110–111°; nmr ($CDCl_3$) showed singlets at δ 7.19 (five protons) and 7.21 (one proton). Repeatedly purified material had ultraviolet $\lambda_{max}^{pentane}$ at 234 and 254 mμ (ε 22,900 and 12,300, respectively), and the infrared spectrum ($CHCl_3$) was quite different from that of **10**, showing in particular no C–H bands above 3.40 μ; the molecular weight determined mass spectrometrically was 236 indicating the molecular formula $C_{16}H_{12}S$. The physical constants found are in good agreement with those reported for 3,4-diphenylthiophene.[25]

Other Photochemical Studies of the β,β'-Diphenyldivinyl Sulfides.—Irradiation of an ethereal solution of *trans,trans*-β,β'-diphenyldivinyl sulfide[7b] under the same conditions employed in the photolysis of the *cis,trans* isomer (see above) led to the isolation in 28% yield (after sublimation) of a colorless solid spectrally indistinguishable from *trans*-2,3-diphenyl-5-thiabicyclo[2.1.0]pentane (**3a**).

Irradiation of an ethereal solution of *cis,trans*-β,β'-diphenyldivinyl sulfide (**2a**) at −78° for 6 hr led to the formation of a new difficultly purified isomer whose nmr spectrum ($CDCl_3$) had no peaks at higher field than δ 6.0 and whose nmr spectrum at lower field was distinctly different from those of the all-*trans*- or *cis,trans*-β,β'-diphenyldivinyl sulfide. This same product was formed from the photosensitized irradiation of the *cis,trans* isomer using D-camphorquinone ($\lambda_{max}^{Et_2O}$ at 472 mμ with ε 40) as sensitizer and a filter cutting off light of wavelength less than 400 mμ. Attempted purification by chromatography on alumina led to the isomerization of the product to the *cis,trans* isomer. The infrared spectrum of the product distilled at 90° (0.1 mm) was different from the spectra of the all-*trans* or *cis,trans* isomers. The product is tentatively assigned the structure *cis,cis*-β,β'-diphenyldivinyl sulfide (**2a**). Irradiation of an ethereal solution of this isomer at 18° for 2 hr using the experimental procedure previously described led to the isolation of a photoproduct whose nmr spectrum was identical with that of *trans*-2,3-diphenyl-5-thiabicyclo[2.1.0]pentane (**3a**).

Registry No.—**2a**, 4973-48-2; **2b**, 18963-95-6; **3a**, 18963-96-7; **3b**, 18963-97-8; **10**, 18962-99-7.

Acknowledgment.—We are indebted to the National Institutes of Health and the National Science Foundation for Predoctoral Fellowships to Eric Block, 1962–1967.

---

[21] J. H. Pinckard, B. Wille, and L. Zechmeister, *J. Amer. Chem. Soc.*, **70**, 1938 (1948).

[22] E. J. Corey and C. C. Cumbo, unpublished findings.

[23] For tabulations of coupling constants in five-membered rings, see A. A. Bothner-By, *Advan. Magn. Resonance*, **1**, 195 (1965).

[24] See H. Wynberg, A. Logothetis, and D. VerPloeg, *J. Amer. Chem. Soc.*, **79**, 1972 (1957).

[25] J. Degani, A. Tundo, and C. Zauli, *Boll. Sci. Fac. Chim. Ind. Bologna*, **19**, 50 (1961).