Cyclic Sulfonium Ylids. I. Reaction of 2-Methyl-1,3-dihydroisothianaphthenylium Iodide with Phenyllithium[1,2]

Joseph Bornstein, Joan E. Shields, and Jerome H. Supple

Department of Chemistry, Boston College, Chestnut Hill, Massachusetts 02167

Received November 9, 1966

The expectation that treatment of 2-methyl-1,3-dihydroisothianaphthenylium iodide (4) with phenyllithium would yield isothianaphthene (2) *via* sulfonium ylid 3 was not realized. Instead, methyl phenyl sulfide, spiro-[5.5]-1-methylthio-2,3-benz-6-methylthiomethyleneundeca-7,9-diene (11) and 3,4-bis(methylthio)-1,2,5,6-dibenz-1,5-cyclooctadiene (5a) were formed. The characterization and possible origin of these unexpected compounds are discussed.

Wittig and his co-workers[3] have described the conversion of N,N-dimethylisoindolinium bromide to N-methylisoindole and methane by phenyllithium. This remarkable reaction which proceeds through the ylid intermediate (1) is apparently inapplicable to the synthesis of the parent compound, isoindole.[4] It occurred to us that isothianaphthene[5] (2), the sulfur analog of isoindole, might yield to synthesis if the sulfonium ylid (3) could be formed from 2-methyl-1,3-dihydroisothianaphthenylium iodide (4).[6] The present paper describes the results which have been obtained from a study of the reaction of phenyllithium with sulfonium salt 4.
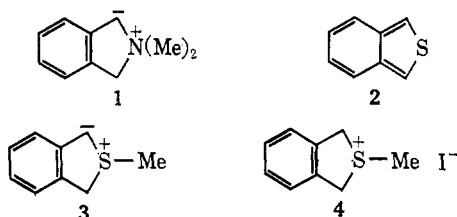
When an ethereal suspension of 2-methyl-1,3-dihydroisothianaphthenylium iodide (4) was treated with excess phenyllithium in diethyl ether at room temperature a vigorous reaction occurred. Examination of the reaction product with special care failed to reveal the presence of isothianaphthene (2). Several attempts to trap 2 with maleic anhydride[7] were fruitless. The following substances were found in the reaction mixture: (1) a somewhat unstable, white, crystalline solid melting at 106.5–107.4°, molecular formula $C_{18}H_{20}S_2$, separable by filtration in 16% yield; (2) a distillable, colorless oil (30–45% yield) identified as methyl phenyl sulfide[8] by spectral data and by its oxidation to the corresponding sulfone; (3) a nonvolatile, polymeric,

orange gum, from which was isolated by chromatography on alumina a new compound (1.4–2.2% yield), mp 123.5–124.0°, shown by means of its elemental analysis and molecular weight to be an isomer of the unstable substance of mp 106.5–107.4°.

The compound of mp 123.5–124.0° was identified by spectral and chemical means as 3,4-bis(methylthio)-1,2,5,6-dibenz-1,5-cyclooctadiene (5a). Thus, desulfurization of the compound with Raney nickel in ethanol afforded 1,2,5,6-dibenz-1,5-cyclooctadiene (6, 69% yield), identical in all respects with an authentic sample.[9] Dehydrothiomethylation of 5a with ethanolic potassium hydroxide proceeded smoothly and afforded in 71% yield a new compound, 3-methylthio-1,2,5,6-dibenz-1,3,5-cyclooctatriene (7). The vinylic thioether (7) was characterized by spectral data (see the Experimental Section) and by its conversion on acidolysis to the known ketone, 1,2,5,6-dibenz-1,5-cyclooctadien-3-one (8),[10] in 72% yield (see Scheme I).

Scheme I
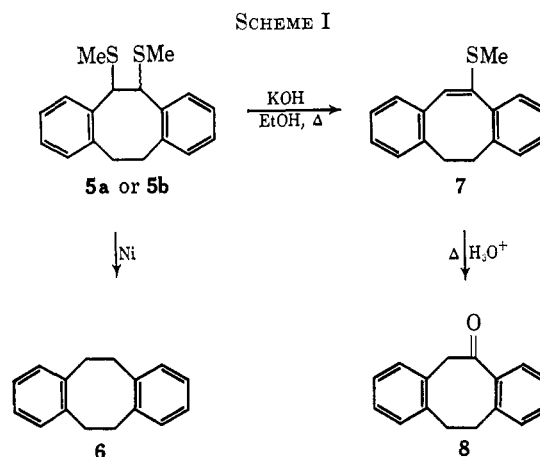
In connection with the foregoing proof of structure, it is worth noting that at one time 3,7-bis(methylthio)-1,2,5,6-dibenz-1,5-cyclooctadiene (9) had been considered as an alternative structure for the substance of mp 123.5–124.0°. It appeared that the preparation of one of the possible geometrical isomers of diene 9 could be carried out readily since the required starting compounds were known and easily accessible. Accordingly, the synthesis of 3,7-bis(methylthio)-1,2,5,6-dibenz-1,5-cyclooctadiene (9) was carried out for the purpose of comparison. Treatment of 3,7-dibromo-1,2,5,6-dibenz-1,5-cyclooctadiene (10)[9] with sodium methyl mercaptide in boiling ethanol afforded the de-

(1) This research has been supported by the National Institutes of Health, Grant No. GM-10222.

(2) For a preliminary report of some of these results, see J. Bornstein and J. H. Supple, *Chem. Ind.* (London), 1333 (1960).

(3) G. Wittig, H. Tenhaeff, W. Schoch, and G. Koenig, *Ann.*, 572, 1 (1951).

(4) Recently prepared in solution and isolated as the Diels-Alder adduct of both maleic anhydride and N-phenylmaleimide by R. Kreher and J. Seubert, *Z. Naturforsch.*, 20b, 75 (1965).

(5) This compound, unknown at the time this investigation was initiated,[2] has been prepared by catalytic dehydrogenation of 1,3-dihydroisothianaphthene [R. Mayer, H. Kleinert, S. Richter, and K. Gewald, *J. Prakt. Chem.*, [4] 20, 244 (1963)]. See also B. D. Tilak, H. S. Desai, and S. S. Gupte, *Tetrahedron Letters*, 1953 (1966). A most unusual preparation of isothianaphthene has been described recently by M. P. Cava and N. M. Pollack, *J. Am. Chem. Soc.*, 88, 4112 (1966).

(6) J. von Braun, *Ber.*, 58, 2165 (1925).

(7) The maleic anhydride adduct of 2 is a known compound.[5]

(8) D. A. Shirley, "Preparation of Organic Intermediates," John Wiley and Sons, Inc., New York, N. Y., 1951, p 277. The methyl phenyl sulfide could also be isolated by column chromatography (see the Experimental Section).

(9) A. C. Cope and S. W. Fenton, *J. Am. Chem. Soc.*, 73, 1668 (1951).

(10) N. J. Leonard, A. J. Kresge, and M. Oki, *ibid.*, 77, 5078 (1955). An authentic comparison sample was kindly furnished by Professor Leonard.
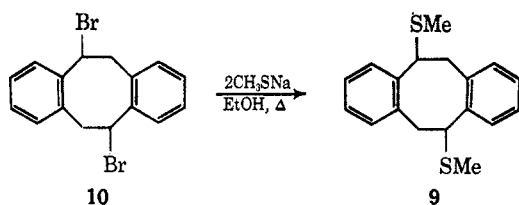
sired compound in 50% yield. Evidence that no re-arrangement had occurred in the course of preparation of **9** was obtained from desulfurization with Raney nickel; 1,2,5,6-dibenz-1,5-cyclooctadiene (**6**) was isolated in 69% yield. Compound **9** differed in melting point (94.5–95.0°) and in infrared and nmr spectral properties from isomer **5a**. Furthermore, compound **9** was completely resistant to boiling ethanolic potassium hydroxide under conditions that led to the formation of triene **7** from diene **5a**. This difference in reactivity is readily understandable since the hydrogen atoms at the 4 and 8 positions of compound **9** are doubtless less acidic than those at the 3 and 4 positions of compound **5a**.

The elucidation of the structure of the compound of mp 106.5–107.4° was hampered by its instability, which severely limited the types of reactions that could be brought to bear on the problem. Solutions of the substance were extensively decomposed in a matter of hours at room temperature. When heated in solution the compound rapidly underwent skeletal rearrangement (described below). The solid itself could be stored in the cold (0° or below) for several weeks with only slight decomposition. Ultimately, a series of reactions of the unknown compound was uncovered which, together with the compound's spectral properties, permitted structure **11** to be assigned. It will be noted that the proof of structure of spiro[5.5]-1-methylthio-2,3-benz-6-methylthiomethyleneundeca-7,9-diene (**11**) rests in part on the chemical and physical properties of the unstable parent compound, spirodi-o-xylylene (spiro[5.5]-2,3-benz-6-methyleneundeca-7,9-diene, **12**).[11]
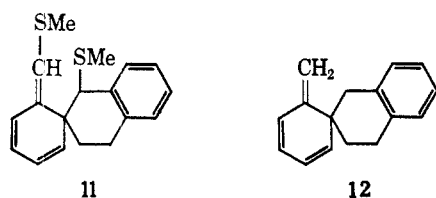
The presence of a conjugated exo-methylthiomethylene group in **11** was inferred from a comparison of its ultraviolet absorption spectrum with that of the spiro hydrocarbon (**12**). Thus, the spectrum of the former compound shows λ_{max} 345 mμ (ϵ 6761), whereas spirodi-o-xylylene (**12**) exhibits maximum absorption at 304 mμ (ϵ 2558).[11] These differences in wavelength and intensity of absorption are fully consistent with the effects to be expected of an S-methyl group directly bonded to an unsaturated carbon atom.[12] Additional evidence for the polyene structure of **11** was obtained from its nmr spectrum.[13] The methyl protons appeared as two singlets at τ 7.69 (S-methyl group on

unsaturated exo-carbon atom) and 8.00 (S-methyl group on saturated carbon atom), and the integration curve showed that three of the four methylene protons appeared at 6.95 and 7.30; the fourth methylene proton was spread out over the region τ 7.90 to 8.40. The spectrum also showed a doublet at τ 6.25 possibly indicative of the presence of two isomeric forms of the benzylic proton geminal to the S-methyl group, a multiplet centered at τ 4.1 for five olefinic protons, and a singlet at τ 3.02 for four aromatic protons.

Spiran **11** failed to give an adduct with either maleic anhydride or dimethyl acetylenedicarboxylate; only polymeric material was formed in these attempts. On the other hand, treatment of spiro compound **11** with N-phenylmaleimide in tetrahydrofuran at room temperature led to the formation of a stable Diels–Alder adduct (**13**), mp 212–213° dec, in 15% yield. The assignment of structure **13** to the adduct is based on its ultraviolet and nmr spectra (see the Experimental Section).
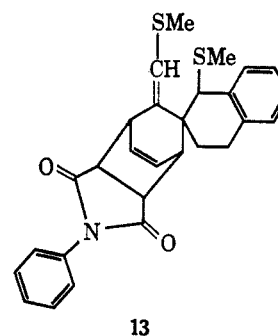
When spiro compound **11** was heated either in solution or neat it isomerized to a mixture of two compounds. Best results were obtained when this thermal rearrangement was effected in the absence of solvents at 150°. The mixture could not be resolved by chromatography, but was separable by fractional crystallization from methanol. The compound formed in smaller amount (15% yield) was found by spectral means and melting point (123.0–124.0°) to be identical with 3,4-bis(methylthio)-1,2,5,6-dibenz-1,5-cyclooctadiene (**5a**) isolated earlier from the reaction of phenyllithium with sulfonium iodide **4**. The main product (55% yield) had mp 102–103° and its elemental analysis and infrared, ultraviolet, and nmr spectra suggested that it was a geometrical isomer (**5b**) of compound **5a**. This possibility was confirmed[14] by desulfurization of compound **5b** with Raney nickel which afforded 1,2,5,6-dibenz-1,5-cyclooctadiene (**6**, 41% yield) and by dehydrothiomethylation with potassium hydroxide in ethanol which yielded 3-methylthio-1,2,5,6-dibenz-1,3,5-cyclooctatriene (**7**, 71% yield).

Interestingly, spirodi-o-xylylene (**12**) does not undergo thermal isomerization of the type observed with spiro compound **11**. It has been reported[11] that **12** polymerizes when it is warmed either in solution or in bulk. Clearly, the different behavior displayed by compound **11** is caused by the presence of the S-methyl groups. It is conceivable that the sulfur atoms of compound **11** participate in both electron-

(11) L. A. Errede, J. Am. Chem. Soc., **83**, 949 (1961).

(12) For a study of the effect of various auxochromes, including the S-alkyl group, on the ultraviolet absorption of unsaturated systems, see K. Bowden, E. A. Braude, and E. R. H. Jones, J. Chem. Soc., 948 (1946).

(13) Kindly interpreted by Drs. L. A. Errede and G. V. D. Tiers.

(14) The lower melting compound (**5b**) cannot be a dimorphic modification of **5a** because their solutions in carbon tetrachloride do not show identical infrared spectra. Several attempts, all unsuccessful, were made to interconvert the two compounds by seeding the melt or solutions of one with crystals of the other.

releasing and -attracting conjugation, thereby not only enhancing the intrinsic tendency of the spiro structure to undergo aromatization,[15] but also stabilizing the intermediate resulting from such a transformation. A reaction path based on this view is shown in the following equation. However, the fact that the


11
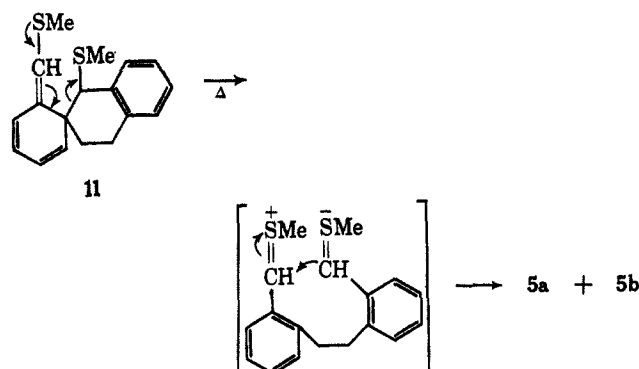
rearrangement of 11 is thermally induced suggests that a free-radical rather than a polar mechanism may be involved in the transformation. A reaction path based on this possibility and involving initial rupture of one of the spiro-bridgehead bonds to give the highly stabilized diradical intermediate 19 is described in a later section of this paper (Scheme II).
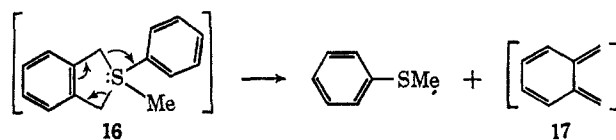
SCHEME II
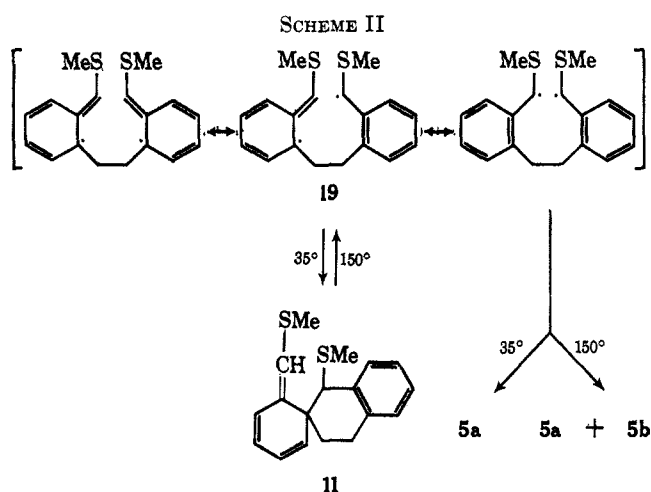
A second instance in which spiro compound 11 underwent aromatization was encountered during an attempt to desulfurize it to the parent substance, spirodi-o-xylylene (12). When 11 was allowed to react with sodium in liquid ammonia at −78° for 2 hr none of the desired compound 12 was formed; instead, 1,2-di-o-tolylethane (14) was produced in 69% yield. The behavior of 11 under these conditions is not unique since it was found subsequently that spirodi-o-xylylene (12) when subjected to the same treatment also affords ethane 14 (53% yield). A number of other attempts to desulfurize 11 to 12 were made. Thus, treatment of 11 with aluminum amalgam in moist tetrahydrofuran, nickel boride,[16] degassed Raney nickel, and deactivated Raney nickel[17] failed to bring about the desired transformation. In general, complex mixtures con-

taining some polymeric material were formed in these experiments.

On the other hand, treatment of spiro compound 11 with a large excess of activated Raney nickel[18] in ethanol at room temperature for 18 hr afforded an oily product from which was isolated by preparative thin layer chromatography on silica gel the known compound, spiro[5.5]-2,3-benz-6-methylundecane[11] (15, 87% yield). The identity of 15 was established by means of its elemental analysis and spectral data, and by comparison with an authentic specimen, prepared from spirodi-o-xylylene (12) by reduction with activated Raney nickel under the same experimental conditions used with compound 11.[19] Actually, some minor differences in the infrared and nmr spectra of both specimens of compound 15 were observed in spite of the fact that they had identical refractive indices and ultraviolet spectra and were chromatographically indistinguishable.[20] Thus, the infrared spectra of both samples (determined neat) were completely superimposable except for the presence of three additional very weak bands in the fingerprint region of the spectrum of the reduction product from spirodi-o-xylylene (12). Although these bands may be caused by the presence of impurities it appears more likely that this reduction product is a mixture of two stereoisomers. Some support for this possibility is provided by the nmr spectra of the two samples (determined in carbon tetrachloride). Comparison of the spectra reveals a distinct difference in the methyl region of the otherwise essentially identical spectra. Whereas the methyl protons in the spectrum of 15 prepared from 11 appear as a broad singlet at τ 9.1, the corresponding protons in the authentic material formed from 12 appear in the same region as a well-defined doublet of almost equal intensity.

14   15
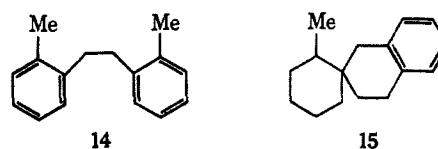
Reaction Pathway.—Methyl phenyl sulfide can be visualized as arising from an unusual extrusion of sulfur[2] brought about by nucleophilic attack by phenyl anion on the sulfur atom of sulfonium salt 4. Support for this view is provided by the observations of Franzen and Mertz[21] who showed that exchange of organic anions occurred when triphenylsulfonium bromide was treated with organolithium compounds. It is conceivable that because of the ability of sulfur to utilize its 3d orbitals, the neutral intermediate (16) is formed first and that this subsequently collapses to methyl phenyl sulfide and o-quinodimethane (17).
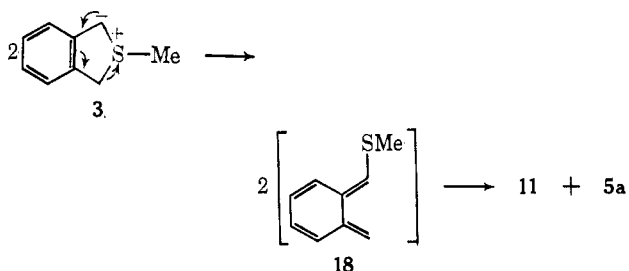

16   17

(15) Some interesting examples of aromatization accompanying the addition of various reagents to spirodi-o-xylylene are described in ref 11.

(16) W. E. Truce and F. M. Perry, J. Org. Chem., 30, 1316 (1965).

(17) A. V. McIntosh, A. M. Searcy, E. M. Meinzer, and R. H. Levin, J. Am. Chem. Soc., 71, 3317 (1949).

(18) The Raney nickel was activated by the procedure of R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 181.

(19) L. A. Errede[11] originally prepared 15 by hydrogenating 12 in heptane at 67 atm for 3.5 days in the presence of Raney nickel.

(20) Thin layer chromatography on silica gel and programmed gas chromatography (silicone gum rubber) were used.

(21) V. Franzen and C. Mertz, Angew. Chem., 72, 416 (1960).

The failure to observe o-quinodimethane or its possible cyclization products, benzocyclobutene and 1,2,5,6-dibenz-1,5-cyclooctadiene (6), in the reaction product does not preclude the postulated mechanism. Mann and Stewart[22] have shown that reactions which would be expected to generate o-quinodimethane often yield polymers.

It is believed that both spiro compound 11 and 3,4-bis(methylthio)-1,2,5,6-dibenz-1,5-cyclooctadiene (5a) arise from dimerization of α-methylthio-o-quinodimethane (18), the o-quinoid form of ylid 3. Any mech-

anism for such a cycloaddition process must not only explain why compound 11 is the sole spiro compound produced, but must also account for the absence of the isomers of 5a, namely, 5b and 3,7-bis(methylthio)-1,2,5,6-dibenz-1,5-cyclooctadiene (9). It is possible to propose a mechanism which fulfills these requirements if the reasonable assumption is made that two molecules of 18 undergo head-to-head coupling initially at the methylenic carbon atoms to form the diradical intermediate (19).[23] Of the three possible diradicals (19, 20, and 21) which could be formed by coupling of
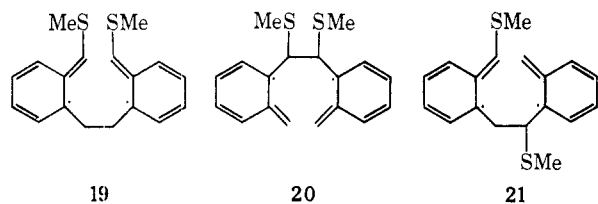
species 18, 19 would be the most stable since its odd electrons are not only involved as benzyl-type radicals, but also because both electrons are capable of being further delocalized by interaction with the sulfur atoms of the S-methyl groups.[24] Formation of carbon-carbon bonds between the appropriate sites in the common diradical intermediate (19) would then complete the cycloaddition process affording both 11 and 5a as outlined in Scheme II. The fact that the reaction of sulfonium salt 4 with phenyllithium affords none of compound 5b, which in marked contrast is the major component of the mixture produced when spiro compound 11 is thermally isomerized, suggests that the direction of ring closure of diradical intermediate 19 is highly sensitive to temperature. It appears almost certain that the relatively small amount of 5a accompanying 11 is not formed by isomerization of the latter by the organometallic reagent. Thus, treatment of spiro compound 11 with an ethereal solution of

phenyllithium, under the same conditions used in carrying out the reaction of sulfonium salt 4, failed to furnish any of compound 5a; only the starting spiran, contaminated by a small quantity of polymeric material, was recovered.

Experimental Section[25]

Reaction of 2-Methyl-1,3-dihydroisothianaphthenylium Iodide (4) with Phenyllithium. A. Spiro[5.5]-1-methylthio-2,3-benz-6-methylthiomethyleneundeca-7,9-diene (11).—This reaction was carried out in an atmosphere of dry nitrogen. To a stirred slurry of 20.0 g (0.072 mole) of 2-methyl-1,3-dihydroisothianaphthenylium iodide (4)[6] in 40 ml of ether at room temperature was added over a period of 30 min a solution of 100 ml of 1.5 N phenyllithium in ether. The addition of the organometallic reagent was accompanied by a vigorous reaction causing the solvent to reflux; the reaction mixture assumed first a yellow and then a light brown color. The reaction mixture was stirred at room temperature for an additional 45 min and was then decomposed in the cold by the cautious addition of 60 ml of a cold, saturated solution of ammonium chloride in water. The deep yellow ether layer was separated, washed twice with water, and dried for only 1 hr.[26] Removal of the solvent under reduced pressure at 20–25° gave a light orange, viscous oil permeated with solid. This residue was treated with 25 ml of dry ether and, after the resulting suspension had been allowed to stand at 0° for 30 min, the white needles were collected by filtration and washed with dry ether. The yield of spiro[5.5]-1-methylthio-2,3-benz-6-methylthiomethyleneundeca-7,9-diene (11), which was stored at 0° or below to minimize decomposition, was 1.75 g (16%), mp 105–106° dec. An analytical sample, having an unpleasant odor reminiscent of methyl sulfide, was prepared by recrystallization from ligroin (bp 60–90°) and had mp 106.5–107.4° dec; $\lambda_{max}^{CS_2}$ 3.29, 3.43, 7.63, 8.24, 11.10, 11.33, 12.08, 12.48, 13.25, 13.45, 13.70, 14.26, and 14.53 μ; λ_{max} 345 mμ (ε 6761).

Anal. Calcd for $C_{18}H_{20}S_2$: C, 71.96; H, 6.71; S, 21.34; mol wt, 300.5. Found: C, 71.53; H, 6.88; S, 21.48; mol wt, 317.

Treatment with maleic anhydride under a variety of conditions of the dried ether solution of the reaction product or the ethereal mother liquor from which compound 11 had been separated failed to furnish an adduct of isothianaphthene.[7]

B. Methyl Phenyl Sulfide.—Concentration under reduced pressure of the ethereal solution from which spiran 11 was obtained, as described above, gave a light orange, foul-smelling oil. Distillation of the residual oil through a semimicro column gave 3.16 g (35%) of a colorless oil [bp 76–77° (22 mm), n^{25}D 1.5827] shown to be identical with an authentic sample of methyl phenyl sulfide[8] by infrared and ultraviolet spectral comparison. The derived sulfone had mp 86–87° (lit.[27] mp 86.5–86.8°) and was found to be identical in all respects with an authentic specimen.[27]

C. 3,4-Bis(methylthio)-1,2,5,6-dibenz-1,5-cyclooctadiene (5a).—The viscous, orange distillation residue (5.1 g) resulting from the removal of the methyl phenyl sulfide as described above was chromatographed three times on a column of basic alumina using in succession hexane and hexane–benzene and benzene–ether mixtures as eluents. The 3,4-bis(methylthio)-1,2,5,6-dibenz-1,5-cyclooctadiene (5a) thus obtained as colorless, odorless prisms (231 mg, 2.1%, mp 118–122°) was recrystallized twice from methanol to furnish an analytical sample, mp 123.5–124.0°. The infrared spectrum showed bands in the region 5.13–5.95 μ characteristic of an *ortho*-disubstituted benzene and a band at

(22) F. G. Mann and F. H. C. Stewart, *J. Chem. Soc.*, 2826 (1954). See also W. E. Parham and M. T. Kneller, *J. Org. Chem.*, **23**, 1702 (1958).

(23) Several reactions of o-quinodimethane and its derivatives have been interpreted as proceeding by a free-radical mechanism; see, for example, M. P. Cava and A. A. Deana, *J. Am. Chem. Soc.*, **81**, 4266 (1959). However, see also D. T. Longone and F. P. Boettcher, *ibid.*, **85**, 3436 (1963).

(24) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962, p 27.

14.55 μ, indicative of an S-methyl group. The ultraviolet spectrum showed maximum absorption at λ_{max} 276 mμ (ϵ 484). The nmr spectrum had a broad singlet at τ 3.1 for eight aromatic protons, a multiplet centered at 5.6 for two benzylic protons geminal to the S-methyl groups, a second multiplet centered at 6.8 for four benzylic protons, and a broad singlet at 8.05 for six protons of the two S-methyl groups.

Anal. Calcd for $C_{18}H_{20}S_2$: C, 71.96; H, 6.71; S, 21.34; mol wt, 300.5. Found: C, 71.7; H, 6.9; S, 21.0; mol wt, 303.

On several occasions a second and more direct method of isolating both **5a** and methyl phenyl sulfide was used. This consisted of concentrating under reduced pressure the ethereal solution from which spiro compound **11** had been separated and then chromatographing the resulting viscous residue on a column of basic alumina using the same eluents described above. The early fractions thus obtained contained methyl phenyl sulfide and these were followed by those containing compound **5a**. The yields of both products isolated by this alternative procedure were practically the same as those obtained by the procedure involving a combination of distillation and chromatography as used above.

Desulfurization of 5a. Formation of 1,2,5,6-Dibenz-1,5-cyclooctadiene (6).—A solution of 50 mg (0.167 mmole) of **5a** in 20 ml of absolute ethanol was heated under reflux for 2 hr with about 1 g (one-third teaspoon) of activated Raney nickel.[18] Concentration under reduced pressure of the filtered ethanolic solution afforded colorless crystals which were recrystallized once from methanol to give 24.3 mg (69%) of 1,2,5,6-dibenz-1,5-cyclooctadiene (**6**): mp 109–110°; λ_{max} 263 mμ (ϵ 488), 272 mμ (ϵ 465). The hydrocarbon was characterized by comparison of its ultraviolet and infrared spectra with those of an authentic sample;[9] the melting point was not depressed when mixed with a genuine specimen.

3-Methylthio-1,2,5,6-dibenz-1,3,5-cyclooctatriene (7).—To a boiling solution of 10.0 g of potassium hydroxide in 25 ml of absolute ethanol was added 20 mg (0.67 mmole) of **5a**. The reaction mixture was heated under reflux for 10 hr and then allowed to stand at room temperature for an additional 8 hr. The mixture was diluted with 50 ml of water and extracted with 100 ml of ether. The ether extract was washed with water, dried, and concentrated under reduced pressure to yield a gummy product. Crystallization from ethanol of the material thus obtained gave 120 mg (71%) of 3-methylthio-1,2,5,6-dibenz-1,3,5-cyclooctatriene (**7**), mp 72–73°. A second recrystallization from methanol afforded an analytical sample: mp 73.2–74.0°; λ_{max} 6.15 μ (C=C); λ_{max} 270 mμ (ϵ 8000). The nmr spectrum showed a multiplet centered at τ 2.93 (eight aromatic protons), a sharp singlet at 3.33 (one olefinic proton), a sharp singlet at 6.82 (four benzylic protons), and a sharp singlet at 7.68 (three protons of S-methyl group bonded to unsaturated carbon atom[28]).

Anal. Calcd for $C_{17}H_{16}S$: C, 80.90; H, 6.39; S, 12.71. Found: C, 80.94; H, 6.32; S, 12.35.

1.2,5,6-Dibenz-1,5-cyclooctadiene-3-one (8).—A mixture of 30 mg (0.12 mmole) of **7** and 5 ml of water containing 8 drops of concentrated sulfuric acid was heated under reflux for 68 hr. The reaction mixture was cooled to room temperature and extracted twice with 50-ml portions of ether. The combined ether extracts were washed successively with water and 5% sodium bicarbonate. Removal of the solvent from the dried ether extract gave 19 mg (72%) of 1,2,5,6-dibenz-1,5-cyclooctadien-3-one (**8**) as a white solid, mp 91–95°. Recrystallization from ligroin (bp 60–90°) afforded 12 mg (46%) of **8** as colorless needles, mp 95.0–95.5°. Admixture of ketone **8** with an authentic sample[10] did not change the melting point. Spectral comparison (ultraviolet and infrared) of the two ketones also confirmed their identity. The compound was further characterized by conversion to its 2,4-dinitrophenylhydrazone, mp 203–205° (lit.[10] mp 196–197°). The 2,4-dinitrophenylhydrazone prepared from the authentic sample of ketone **8** had mp 202–205° and was shown to be identical with the corresponding derivative of the ketone prepared by acidolysis of **7** by a mixture melting point determination and infrared spectral comparison.

3,7-Bis(methylthio)-1,2,5,6-dibenz-1,5-cyclooctadiene (9).—A stock solution of ethanolic sodium methyl mercaptide was prepared in the following way. Freshly cut sodium (1.26 g, 0.055 g-atom) was dissolved with stirring in 50 ml of absolute ethanol contained in a 100-ml, three-necked flask equipped with a magnetic stirrer, a reflux condenser capped with a calcium chloride drying tube, and a gas-inlet tube. Methyl mercaptan was bubbled through the resultant solution, which was cooled in an ice bath, until the solution no longer absorbed the gas. Excess methyl mercaptan was removed by allowing a gentle stream of nitrogen to bubble through the solution for 10 min. The solution was transferred quantitatively to a 100-ml volumetric flask and diluted to the mark with absolute ethanol. A 12.0-ml aliquot of this solution containing 0.46 g (6.58 mmoles) of sodium methyl mercaptide was added to a solution of 1.00 g (2.74 mmoles) of 3,7-dibromo-1,2,5,6-dibenz-1,5-cyclooctadiene (**10**)[9] in 70 ml of ethanol; the latter was warmed in a water bath initially in order to keep the dihalide in solution. The reaction mixture, protected from atmospheric moisture, was heated under reflux for 5 hr. The cloudy reaction mixture was cooled to room temperature and concentrated under reduced pressure, and the resulting residue was extracted twice with 50-ml portions of ether. The combined ether extracts were washed with water and dried. Removal of the ether on the steam bath afforded a white solid which was crystallized from methanol to afford 407 mg (50%) of 3,7-bis(methylthio)-1,2,5,6-dibenz-1,5-cyclooctadiene (**9**) as white needles, mp 94.5–95.0°. Its infrared spectrum was similar to that of isomer **5a**, but was not completely superimposable on the spectrum of the latter. The ultraviolet spectrum showed maximum absorption at λ_{max} 276 mμ (ϵ 425). The nmr spectrum showed a multiplet centered at τ 3.15 (eight aromatic protons), a multiplet centered at 6.50 (six benzylic protons), and a sharp singlet at 8.05 (six protons of S-methyl groups).

Anal. Calcd for $C_{18}H_{20}S_2$: C, 71.96; H, 6.71; S, 21.34. Found: C, 71.8; H, 6.8; S, 21.5.

Compound **9** was recovered unchanged in quantitative yield after treatment with hot ethanolic potassium hydroxide according to the procedure used above for converting isomer **5a** to triene **7**.

1,2,5,6-Dibenz-1,5-cyclooctadiene (**6**), mp 109–110°, was isolated in 69% yield by the desulfurization of a 100-mg quantity of **9** with approximately 2 g (two-thirds teaspoon) of activated Raney nickel[18] in 40 ml of absolute ethanol following the procedure described above for the preparation of **6** from **5a**. Hydrocarbon **6** was shown by a mixture melting point determination and infrared spectral comparison to be identical with an authentic specimen.[9]

N-Phenylmaleimide Adduct of Spiran 11.—A solution of 300 mg (1.00 mmole) of freshly prepared **11** in 10 ml of anhydrous tetrahydrofuran was treated with a solution of 173 mg (1.00 mmole) of N-phenylmaleimide in 5 ml of tetrahydrofuran. The reaction mixture was allowed to stand at room temperature for 24 hr and the solvent was then removed under reduced pressure. The yellow, gummy residue was taken up in a 1:1 mixture of ethanol-ethyl acetate and the resultant solution was heated with Norit and filtered, and the filtrate was refrigerated overnight. The cream-colored solid (140 mg, mp 202–208°) thus separated was recrystallized twice from the same solvent system to give 70 mg (15%) of analytically pure adduct **13** as glistening, white crystals, mp 212–213° dec. In the ultraviolet, **13** showed λ_{max} 261 mμ (ϵ 9400), consistent for a derivative of methyl vinyl sulfide [λ_{max} 230 mμ (ϵ 15,850) and 240 mμ (ϵ 10,000)][29] with its double bond exocyclic to a six-membered ring. The nmr spectrum (in dimethyl sulfoxide-d_6) showed the presence of an S-methyl group bonded to an olefinic carbon atom[28] (sharp singlet at τ 7.75) and the presence of an S-methyl group bonded to a saturated carbon atom (sharp singlet at τ 8.05). Additional bands were a multiplet at τ 2.70 (nine aromatic protons), a multiplet at 3.68 (three olefinic protons), a multiplet at 6.65 [eight protons, attributable to three benzylic protons, two allylic protons, two protons of succinimide moiety, and one proton of the nonbenzylic methylene group (the other proton was buried in the upfield S-methyl resonance at 8.05)].

Anal. Calcd for $C_{28}H_{27}NO_2S_2$: C, 71.01; H, 5.75; N, 2.96; S, 13.54. Found: C, 71.10; H, 5.67; N, 3.06; S, 13.02.

Thermal Isomerization of Spiran 11. Formation of 3,4-Bis(methylthio)-1,2,5,6-dibenz-1,5-cyclooctadiene (5a and 5b).—A 500-mg quantity (1.67 mmoles) of spiran **11** was heated in an

(28) In this investigation, all of the compounds (**5a**, **5b**, **9**, **11**, and **13**) containing S-methyl groups bonded to a saturated carbon atom showed a characteristic singlet in the range τ 8.00–8.14. Those compounds (**7**, **11**, and **13**) with S-methyl groups bonded to an olefinic carbon atom showed a characteristic peak in the range τ 7.68–7.75; similar values for the proton chemical shifts of S-methyl groups bonded to nitrile and carbonyl carbon atoms have been reported by G. R. Pettit, I. B. Douglass, and H. A. Hill, *Can. J. Chem.*, **42**, 2357 (1964).

(29) C. C. Price and J. Zomlefer, *J. Am. Chem. Soc.*, **72**, 14 (1950).

atmosphere of dry nitrogen at 150° for 1 hr. The resulting viscous, red oil was cooled to room temperature and taken up in 20 ml of boiling methanol. The yellow solution was treated with Norit, filtered, and refrigerated to give 290 mg of a white solid, mp 90–102°. Concentration of the mother liquor gave an additional 100 mg of white solid, mp 90–102°. Crystallization from methanol of the combined crops of solid afforded 275 mg (55%) of 3,4-bis(methylthio)-1,2,5,6-dibenz-1,5-cyclooctadiene (5b, mp 101–103°) as colorless needles. A second recrystallization from methanol gave an analytical sample of 5b, mp 102–103°. The infrared spectrum exhibited bands in the 5.13–5.95-μ range typical of an *ortho*-disubstituted benzene and was similar in many respects to the spectrum of the higher melting geometrical isomer (5a). In the ultraviolet 5b showed λ_{max} 274 mμ (ϵ 352). The nmr spectrum showed a multiplet of eight aromatic protons centered at τ 2.85, a sharp singlet of two protons geminal to the S-methyl groups at 5.73, a multiplet of four benzylic methylene protons centered at 6.80, and a sharp singlet of six protons of the S-methyl groups at 8.14.

Anal. Calcd for $C_{18}H_{20}S_2$: C, 71.96; H, 6.71; S, 21.34. Found: C, 71.63; H, 6.67; S, 21.07.

Following the procedure described above for the desulfurization of 5a to hydrocarbon 6, a 43-mg quantity (0.143 mmole) of 5b (mp 102–103°) was converted to 1,2,5,6-dibenz-1,5-cyclooctadiene (6) by reaction with approximately 1 (one-third teaspoon) of activated Raney nickel[18] in 20 ml of absolute ethanol at reflux temperature for 2 hr. The white, solid product (28 mg, mp 95–105°) was recrystallized twice from methanol to afford 12 mg (41%) of hydrocarbon 6 as colorless needles, mp 107.5–109°, not depressed on admixture with an authentic sample.[9] The hydrocarbon was further characterized by comparison of its ultraviolet and infrared spectra with those of the authentic specimen.

3-Methylthio-1,2,5,6-dibenz-1,3,5-cyclooctatriene (7, mp 72–73°) was prepared in 71% yield by treatment of 5b (100 mg, 0.33 mmole) with ethanolic potassium hydroxide at reflux temperature according to the procedure used above for converting 5a to triene 7. This material was identical in all respects with the triene obtained earlier from compound 5a.

The methanolic mother liquors from which 5b had been obtained above were combined, concentrated, and refrigerated for several days. The white solid which separated was fractionally crystallized from methanol to yield 75 mg (15%) of isomer 5a, mp 123–124°, as colorless prisms. This material was shown by a mixture melting point determination and infrared spectral comparison to be identical with a sample of 3,4-bis(methylthio)-1,2,-5,6-dibenz-1,5-cyclooctadiene (5a) prepared earlier by the reaction of phenyllithium with sulfonium iodide 4.

Formation of 1,2-Di-*o*-tolylethane (14). A. From Spiran 11. —A mixture of 140 mg (6.1 mg-atoms) of sodium wire (0.5 mm in diameter), 200 mg (0.67 mmole) of spiran 11, 10 ml of anhydrous ether, and 10 ml of liquid ammonia was stirred, while protected from atmospheric moisture, in a Dry Ice–acetone bath at −78° for 2 hr. The reaction mixture was then allowed to warm to room temperature in order to remove the ammonia, and the excess sodium was destroyed with ethanol. The mixture was diluted with 10 ml of water and the ether layer was separated. The aqueous layer was extracted twice with 20-ml portions of ether and the combined ether solutions were washed with water and dried. Removal of the solvent under reduced pressure gave 140 mg of a slightly yellow solid, mp 58–62°. Chromatography of this material on neutral alumina using hexane and hexane-benzene mixtures as eluents afforded 97 mg (69%) of 1,2-di-*o*-tolylethane (14) as white plates, mp 64–66° (lit.[11] mp 61–63°).

The melting point was not depressed upon admixture with an authentic sample.

B. From Spirodi-*o*-xylylene (12).—Treatment of a 150-mg quantity (0.72 mmole) of purified hydrocarbon 12 with a mixture of 10 ml of anhydrous ether, 10 ml of liquid ammonia, and 120 mg (5.2 mg-atoms) of sodium wire by the procedure described above gave, after chromatography, 80 mg (53%) of 14 as a white solid, mp 58–62°. One recrystallization from absolute methanol raised the melting point to 61–63°. No depression of the melting point was observed when this material was mixed with 1,2-di-*o*-tolylethane prepared above from 11; both preparations had identical infrared and ultraviolet spectra.

Formation of Spiro[5.5]-2,3-benz-6-methylundecane (15). A. From Spiran 11.—A suspension of 100 mg (0.33 mmole) of spiro compound 11, 6 g (2 teaspoons) of activated Raney nickel,[18] and 300 ml of absolute ethanol was stirred in a nitrogen atmosphere at room temperature[30] for 18 hr. The catalyst was removed by filtration and the filtrate was concentrated under reduced pressure. Evaporative distillation [85° at (1.0 mm)] of the resulting oil followed by preparative thin layer chromatography on silica gel with hexane as developer afforded 62 mg (87%) of spiro[5.5]-2,3-benz-6-methylundecane (15) as a colorless oil: $n^{24}D$ 1.5462; λ_{max}^{neat} 3.29 (m), 3.40 (s), 3.48 (s), 6.27 (w), 6.68 (m), 6.88 (s), 7.25 (m), 8.94 (w), 9.57 (w), 10.36 (w), 10.54 (w), 11.27 (w), 11.52 (w), 11.98 (w), 13.36 (s), and 14.06 (w) μ; λ_{max} 267 mμ (ϵ 562) and 274 mμ (ϵ 612). The nmr spectrum showed a sharp singlet at τ 3.10 (four aromatic protons), a multiplet centered at 7.30 (four benzylic protons), a multiplet centered at 8.33 (11 protons, consisting of nine cyclohexyl and two nonbenzylic methylene protons), and a broad singlet at 9.1 (three protons of methyl group).

Anal. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.65; H, 10.29.

B. From Spirodi-*o*-xylylene (12).—A mixture of 0.5 g of crude spirodi-*o*-xylylene,[11] 9 g (3 teaspoons) of activated Raney nickel,[18] and 400 ml of anhydrous ethanol was stirred in a nitrogen atmosphere at room temperature for 18 hr. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. Purification of the oily reaction product by the method used above afforded 74 mg of hydrocarbon 15: $n^{24}D$ 1.5462; λ_{max} 267 mμ (ϵ 577) and 274 mμ (ϵ 666). The infrared spectrum (neat) was identical with that of spiran 15 prepared above from 11 except for the presence of three additional very weak peaks at 7.88, 12.17, and 12.42 μ. The nmr spectrum was essentially the same as the spectrum of 15 prepared from 11 except for the one difference in the methyl region at τ 9.1 noted previously in the text. No distinction could be made by gas or thin layer chromatography between this material and that prepared from 11.[20]

(30) The temperature is critical. When the reaction was carried out at reflux temperature some 1,2,5,6-dibenz-1,5-cyclooctadiene (6) was isolated. Hydrocarbon 6 arises undoubtedly from desulfurization of 3,4-bis(methylthio)-1,2,5,6-dibenz-1,5-cyclooctadiene (5a and 5b) formed *in situ* by the thermal isomerization of spiran 11.