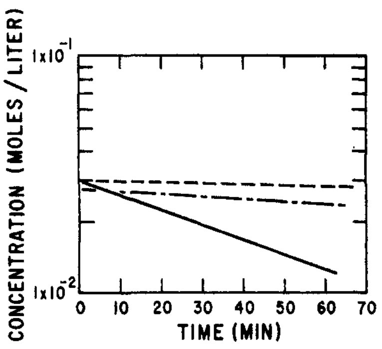

Figure 4.—Effect of the addition of nitric oxide and nitrosyl chloride on the rate of reaction of 2-chloro-2-nitrosobutane in benzene: ———, NO, $k = 1.4 \times 10^{-2}$ min^{-1}; - - - -, NOCl, $k = 4.3 \times 10^{-4}$ min^{-1}; -·-·-·, no addition, $k = 4.6 \times 10^{-4}$ min^{-1}. Experiments were conducted in the absence of oxygen.

In dilute solutions of 2-chloro-2-nitrosobutane in oxygen-free methanol, the primary process of greatest importance is eq 2. The radicals abstract hydrogen from the solvent to produce the oxime and hydrogen chloride. Not only is the oxime hydrochloride the dominant product, but traces of formaldehyde can be detected by gas chromatography of the reaction products.

In concentrated oxygen-free methanol solutions of 2-chloro-2-nitrosobutane, 2,3-butanedione monooxime was formed as well as 2-butanone oxime. The dinitrone reported by Baldwin and Rogers[3] was detected only if the photolysis products were not analyzed immediately.

In tetrahydrofuran the primary process of importance is probably eq 2. The rate of reaction and quantum yields are increased relative to the other solvents (see Table I). The abstraction of hydrogen from cyclic ethers results in the formation of an intermediate α-alkoxy radical which can then combine with another radical to form a stable product or ring opening can occur with the formation of a carbonyl compound.[16] These free-radical pathways result in the increase in reaction rate and apparent quantum efficiency.

The mechanism for the photodecomposition of 2-chloro-2-nitrosobutane solutions proceeds in essentially the same manner as the reaction in benzene (see Table I).

In summary, the fate of the excited 2-chloro-2-nitrosobutane molecule depends on solvent and concentration. The competing paths, eq 2 and 3, are the important primary processes. Selectivity in product occurs in oxygen-saturated solutions, but not in oxygen-free systems. In the absence of oxygen the excited molecule can either experience deactivating collisions or react to form free radicals. These free radicals undergo further reactions to produce products dependent on the nature of the radical, not the source of the free radical. In the presence of oxygen the excited molecule reacts very rapidly with oxygen to form 2-chloro-2-nitrobutane and only traces of products of free-radical origin.

The use of laser light sources removes many experimental problems encountered in ordinary photochemical work. As was to be expected, the low-power lasers used did not directly give rise to products different from common light sources, but the fact that the time of photolysis could be drastically shortened lessened the interference from dark side reactions and simplified product analysis.

Registry No.—2-Chloro-2-nitrosobutane, 681-01-6.

(16) R. S. Davidson, *Quart. Rev.* (London), **21**, 249 (1967).

Derivatives of Thiacyclobutene (Thiete). IV.[1] Thermal Decomposition of a Naphthothiete Sulfone. An Oxidation–Reduction Reaction and Formation of a Cyclic Sulfinate Ester (Sultine)[2-4]

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Received October 16, 1968

Pyrolysis of 3,8-diphenyl-2H-naphtho[2,3-*b*]thiete 1,1-dioxide, 1, at 360–400° for 5 min in a nitrogen atmosphere gives two principal organic products which are thiophene derivatives: 14H-benzo[*b*]benzo[3,4]fluoreno[2,1-*d*]thiophen-14-one (2) and 14H-benzo[*b*]benzo[3,4]fluoreno[2,1-*d*]thiophene (3). Sulfur dioxide is not evolved in any significant amounts and no evidence for formation of a naphthocyclopropene was observed. When the pyrolysis is done in the presence of 9,10-dihydroanthracene, the reaction took a completely different course yielding 78–81% cyclic sulfinate ester or sultine, 4,9-diphenyl-3H-naphth[2,3-*c*]-2,1-oxathiole 1-oxide (6). The cyclic sulfinate by itself decomposes on pyrolysis to the two thiophene derivatives obtained from the naphthothiete sulfone.

Pyrolysis of sulfones usually gives sulfur dioxide and products derived formally from radicals formed on the departure of sulfur dioxide.[5] Examples of pyrolysis of four-membered-ring sulfones (thietane sulfones) are limited. Dodson and Klose found that sulfur dioxide was lost from either *cis*- or *trans*-2,4-diphenylthietane 1,1-dioxide to give a mixture of *cis*- and *trans*-1,2-diphenylcyclopropane in which the *trans* isomer predom-

(1) Paper III: D. C. Dittmer and J. M. Balquist, *J. Org. Chem.*, **33**, 1364 (1968).

(2) This work was aided by Grant GP 5513 of the National Science Foundation and Grant CA08250 of the National Cancer Institute, National Institutes of Health.

(3) Reported at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, p 101-O.

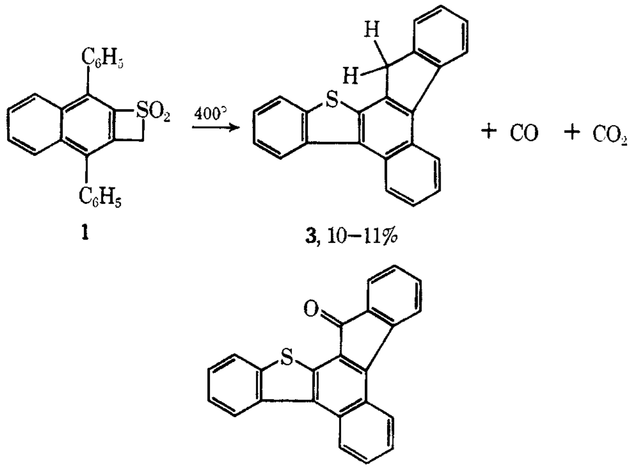
(4) For further details, see R. S. Henion, Ph.D. Thesis, Syracuse University, 1967.

(5) Reviewed in ref 4 and by J. L. Kice, "The Chemistry of Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, London, England, 1966, p 115.

inated.[6] Truce and Norell pyrolyzed 2-phenyl-3,3-diethoxythietane 1,1-dioxide and obtained ethyl cinnamate, which they suggested was formed by way of 2-phenyl-1,1-diethoxycyclopropane.[7] Middleton pyrolyzed 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane 1,1-dioxide with loss of sulfur dioxide and formation of 2,2,3,3-tetrakis(trifluoromethyl)thiirane.[8] Hoffmann and Sieber heated naphtho[1,8-*bc*]thiete 1,1-dioxide and obtained perylene and unidentified carbonyl compounds; *in vacuo* a cyclic sulfinate ester was isolated.[9]

Rearrangement of acyclic sulfones and cyclic sulfones (five membered) to sulfinates was suggested to explain ions observed in the mass spectra of sulfones,[10] and other similar rearrangements have been reported.[11] Loss of carbon monoxide has been observed also.[11a,b]

Pyrolysis of Naphthothiete Sulfone 1 Neat.—Heating 3,8-diphenyl-2H-naphtho[2,3-*b*]thiete 1,1-dioxide (1) for 5 min at 400° in a nitrogen atmosphere gave five organic products (indicated by thin layer chromatography) in addition to carbon monoxide which had been reported previously.[12] We now wish to report that the two major organic products are the scarlet 14H-benzo[*b*]benzo[3,4]fluoreno[2,1-*d*]thiophen-14-one (2) and colorless 14H-benzo[*b*]benzo[3,4]fluoreno[2,1-*d*]thiophene (3), the pyrolysis reaction taking an entirely different course from those reported earlier. Analysis of the gases evolved shows them to be mainly carbon monoxide (14–20% based on starting sulfone) and carbon dioxide (6–18%) with lesser amounts of water, hydrogen sulfide, carbon oxysulfide, and sulfur dioxide. Relatively more sulfur dioxide was obtained at lower temperatures. No evidence was obtained for a naphthocyclopropene which might have been expected if the pyrolysis had proceeded as observed with those five-membered cyclic sulfones which yield benzocyclobutene derivatives[13] and the four-membered sulfones which yield cyclopropanes.[6–8]



1

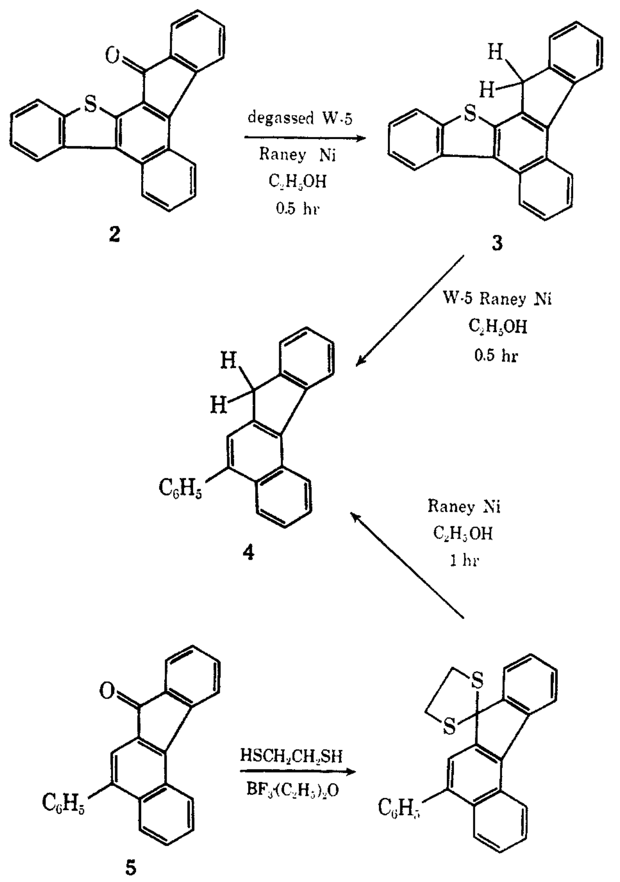
3, 10–11%

2, 30–33%

Structure Proof of Ketone 2 and Fluorene 3.—The infrared, ultraviolet, visible, and mass spectroscopic data are consistent with structures 2 and 3, and chemical evidence provides further proof for them.[14]

When fluorene 3 was refluxed with W-5 Raney nickel (hydrogen rich) in ethanol, 5-phenyl-7H-benzo[*c*]fluorene, 4, a known compound,[15] was formed which also was prepared by desulfurization of the ethylene dithioketal of 5-phenyl-7H-benzo[*c*]fluorenone (5) (Scheme I).

SCHEME I



This fluorenone was prepared as described previously.[16] Fluorene 3 also was obtained when ketone 2 was refluxed with partially degassed W-5 Raney nickel in ethanol. Although reduction of a carbonyl group to a methylene group by Raney nickel is known,[17] this appears to be the first case where a carbonyl group is reduced without a concomitant desulfurization by the Raney nickel. Raney nickel also is reported to renuce alcohols to alkanes under mild conditions.[18] If fluorenone 2 was refluxed for 5 hr with hydrogen-rich Raney nickel, desulfurization occurred accompanied by reduction of the carbonyl group and the naphthalene

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(6) R. M. Dodson and G. Klose, *Chem Ind.* (London), 450 (1963).

(7) W. E. Truce and J. R. Norell, *J. Amer. Chem. Soc.*, **85**, 3236 (1963).

(8) W. J. Middleton, U. S. Patent 3,136,781 (1964); *Chem. Abstr.*, **61**, 5612 (1964).

(9) R. W. Hoffmann and W. Sieber, *Angew. Chem. Intern. Ed. Engl.*, **4**, 786 (1965); *Ann. Chem.*, **703**, 96 (1967).

(10) S. Meyerson, H. Drews, and E. K. Fields, *Anal. Chem.*, **36**, 1294 (1964), and references cited therein.

(11) (a) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **88**, 2836 (1966); (b) J. H. Bowie, D. H. Williams, S.-O. Lawesson, J. Ø. Madsen, C. Nolde, and G. Schroll, *Tetrahedron*, **22**, 3515 (1966); (c) Q. N. Porter, *Aust. J. Chem.*, **20**, 103 (1967); (d) R. D. Chambers and J. A. Cunningham, *Chem. Commun.*, 583 (1967); (e) D. C. Dittmer and F. A. Davis, *J. Org. Chem.*, **32**, 3872 (1967).

(12) D. C. Dittmer and N. Takashina, *Tetrahedron Lett.*, 3809 (1964).

(13) M. P. Cava and A. A. Deana, *J. Amer. Chem. Soc.*, **81**, 4266 (1959).

(14) The physical data are given in the Experimental Section and are fully discussed in ref 4.

(15) A. Etienne and A. Le Berre, *C. R. Acad. Sci., Paris*, **239**, 176 (1954).

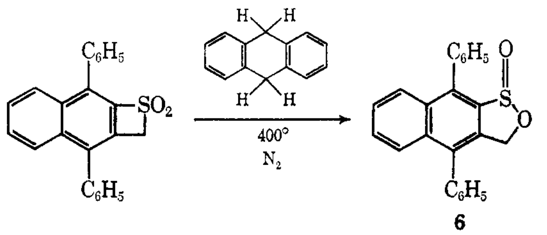
(16) R. Weiss and A. Abeles, *Monatsh.*, **61**, 162 (1932).

(17) G. N. Rao, B. D. Tilak, and K. Venkataraman, *Proc. Indian Acad. Sci.*, *A*, **38**, 244 (1953); *Chem. Abstr.*, **49**, 1003 (1955).

(18) For examples, see W. A. Bonner, J. A. Zderic, and G. A. Casaletto, *J. Amer. Chem. Soc.*, **74**, 5086 (1952); J. A. Zderic, M. E. C. Rivera, and D. C. Linon; *ibid.*, **82**, 6373 (1960); E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 3363 (1962).

nucleus.[19] An impure red oil was obtained in which a carbonyl group was present (infrared absorption around 1710 cm^{-1}). A mass spectrum of this crude oil indicated the presence of ions at *m/e* 306 which is the mass to charge ratio for the molecular ion of ketone **5** expected from the desulfurization of ketone **2**.

Pyrolysis of Naphthothiete Sulfone 1 in the Presence of 9,10-Dihydroanthracene.—When thiete sulfone **1** was heated in the presence of a twofold excess of 9,10-dihydroanthracene, the reaction took a completely different course. A good yield (78–81%) of cyclic sulfinate[20] **6** (4,9-diphenyl-3H-naphth[2,3-*c*]-2,1-oxathiole 1-oxide) was obtained. Cyclic sulfinates or sultines are rare, only a few examples in addition to **6** having been reported.[9,21] Recently, treatment of a thietane sulfone with *t*-butoxymagnesium bromide was reported to yield a sultine.[21a] The rearrangement of sulfones to sultines may occur while the mass spectra of cyclic sulfones are being obtained[10,11] and in the pyrolysis of a thiete sulfone.[9] The reverse rearrangement of acyclic sulfinates to sulfones is fairly common[22a] although only one example of such a rearrangement involving a sultine is known.[9] The interconversion of a sulfoxide and a sulfenic ester has been postulated.[22b]

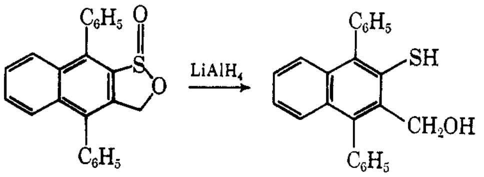


6

The infrared spectrum of sultine **6** shows absorption at 1120 and 940 cm^{-1} in agreement with absorptions reported for esters of sulfinic acids.[23] The ultraviolet absorption (λ_{max} 246, 304, 333 mμ) is similar to that of naphthothiete sulfone **1**, and the intense absorption of the diphenylnaphthalene chromophore overwhelms the weaker absorption around 240–250 mμ attributed to sulfinate esters.[23] The proton nmr spectrum ($CDCl_3$, relative to tetramethylsilane) shows a multiplet at δ 7.00–8.00 (aromatic protons, relative area 14) and an AB pattern (relative area 1.7), J = 14 Hz, with the low-field absorption centered at δ 5.98 and the high-field absorption centered at δ 5.31. The magnitude of the nonequivalence of the methylene protons may be attributed in part to the diamagnetic anisotropy of the S=O group which deshields the proton *cis* to the sulfinyl oxygen as has been observed in cyclic sulfite esters.[24]

Similarities exist between the mass spectra of sultine **6** and naphthothiete sulfone **1**, an indication that both have some structural features in common. The sulfone may rearrange to the sultine prior to fragmentation in the mass spectrometer. The base peak of the sultine is the parent ion at *m/e* 356, but that of thiete sulfone **1** is at *m/e* 291, the latter fragment possibly representing a naphthocyclopropenium cation analogous to similar ions seen in the mass spectra of benzothiete sulfone.[11e] The sultine shows an intense peak at *m/e* 308 (parent −SO) which is not very pronounced in the spectrum of sulfone **1** indicating that **1** does not decompose exclusively by rearrangement to sultine **6** before fragmentation in the spectrometer.

Reduction of the sultine with lithium aluminum hydride gave 1,4-diphenyl-3-hydroxymethyl-2-naphthalenethiol. The proton nmr spectrum of the naphthalenethiol was consistent with its structure. The chemical shift of the methylene protons is of the magnitude expected for methylene protons adjacent to oxygen rather than to sulfur.[12,25] At about −40° the nmr spectrum showed a broadened singlet at δ 4.66 (methylene protons) and a poorly resolved triplet at δ 2.12, the latter absorption indicating the slower exchange of the hydroxylic proton.



In the mass spectrum of the naphthalenethiol, the most abundant fragment was at *m/e* 324 corresponding to the parent ion minus water, a mode of decomposition characteristic of *o*-hydroxybenzyl alcohol.[26]

Pyrolysis of Sultine 6.—When the sultine was heated in the absence of 9,10-dihydroanthracene at 380–400° for 5 min in a nitrogen atmosphere, gases were evolved, and the mixture became dark red. The scarlet fluorenone **2** and fluorene **3** were obtained in yields of 21.2 and 7.8%, respectively. This result, in conjunction with the evidence from mass spectrometry, suggests that the sultine may have been an intermediate in the pyrolysis of naphthothiete sulfone **1**.

Pyrolysis of the thiete sulfone may involve initial scission of the sulfur–carbon bond to give an intermediate (dipolar or diradical in character) which may yield the sultine by formation of an oxygen–carbon bond (Scheme II). Loss of water and two hydrogen atoms

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(19) The reduction of aromatic rings in Raney nickel desulfurization has been observed: W. Davies and Q. N. Porter, *J. Chem. Soc.*, 459 (1957).

(20) By analogy with the nomenclature of cyclic esters of sulfonic acids which are called sultones, we suggest that the cyclic esters of sulfinic acids be called sultines. The word "sultine" is derived by replacing the "o" in sultone with an "i" to indicate that a sulfinic acid and not a sulfonic acid is involved. We are indebted to a luncheon conversation with C. S. Greene over soup and crackers for this suggestion about nomenclature.

(21) (a) R. M. Dodson, P. D. Hammen, and R. A. Davis, *Chem. Commun.*, 9 (1968). (b) K. S. Dhami, *Chem. Ind.* (London), 1004 (1968); E. N. Givens and L. A. Hamilton, *J. Org. Chem.*, **32**, 2857 (1967); E. Baumann and G. Walter. *Ber.*, **26**, 1124 (1893). A sultine structure proposed for anthraquinone-1-sulfenic acid is believed to be incorrect: H. Z. Lecher and E. M. Hardy, *J. Org. Chem.*, **20**, 475 (1955); J. A. Barltrop and K. J. Morgan, *J. Chem. Soc.*, 4245 (1956); T. C. Bruice and A. B. Sayigh, *J. Amer. Chem. Soc.*, **81**, 3416 (1959). Sultones and other ring systems containing sulfur and oxygen have been reviewed recently: D. S. Breslow and H. Skolnik, "Multisulfur and Sulfur and Oxygen Five- and Six-membered Heterocycles," parts I and II, Interscience Publishers, New York, N. Y., 1966.

(22) (a) J. Kenyon and H. Phillips, *J. Chem. Soc.*, 1676 (1930); C. L. Arcus, M. P. Balfe, and J. Kenyon, *ibid.*, 485 (1938); A. C. Cope, D. E. Morrison, and L. Field, *J. Amer. Chem. Soc.*, **72**, 59 (1950); A. H. Wragg, J. S. McFadyen, and T. S. Stevens, *J. Chem. Soc.*, 3603 (1958); D. Darwish and R. McLaren, *Tetrahedron Lett.*, 1231 (1962); D. Darwish and E. A. Preston, *ibid.*, 113 (1964); E. Ciuffarin, M. Isola, and A. Fava, *J. Amer. Chem. Soc.*, **90**, 3595 (1968). (b) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *ibid.*, **88**, 3138 (1966); E. G. Miller, D. R. Rayner, and K. Mislow, *ibid.*, 3139.

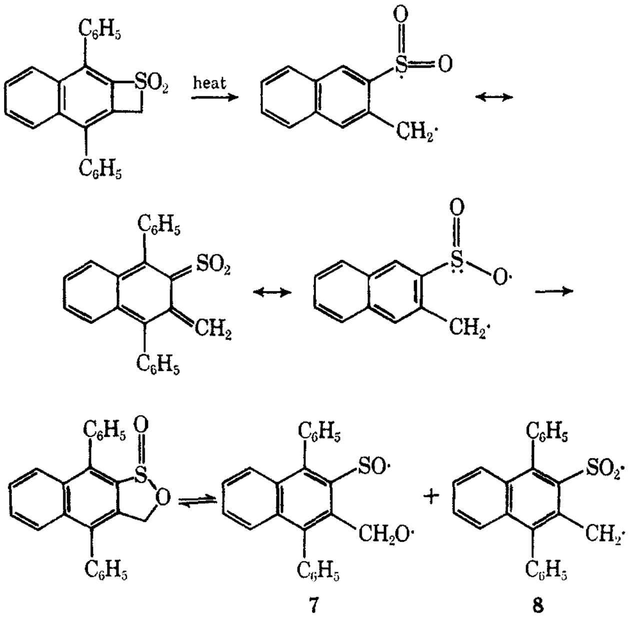
(23) M. Kobayashi and N. Koga, *Bull. Chem. Soc. Jap.*, **39**, 1788 (1966); B. Bonini, S. Ghersetti, and G. Modena, *Gazz. Chim. Ital.*, **93**, 1222 (1963); S. Detoni and D. Hadzi, *J. Chem. Soc.*, 3163 (1955).

(24) J. G. Pritchard and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **83**, 2105 (1961); R. S. Edmundson, *Tetrahedron Lett.*, 1649 (1965).

(25) For comparisons of the chemical shifts of $-CH_2OH$ and CH_2SH groups, see "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., Vol. 1, No. 101, 102; "Sadtler Standard Nuclear Magnetic Resonance Spectra," Sadtler Research Laboratories, Inc., Philadelphia, Pa., No. 276.

(26) J. S. Shannon, *Aust. J. Chem.*, **15**, 265 (1962).

SCHEME II



from intermediate **7** or two hydroxyl groups from intermediate **8**, both losses accompanied by cyclizations, could give fluorenone **2** and fluorene **3**, respectively.[27] The loss of oxygen from the sulfur atom is analogous to the loss in the pyrolysis of sulfoxides to sulfides.[28] The carbon monoxide observed in the pyrolysis of thiete sulfone **1** may be formed by decarbonylation of fluorenone **2**. Thermal decomposition of sulfinic acids yields small amounts of carbon monoxide, carbon dioxide, and water.[29] Alternatively, sulfur dioxide may be evolved only to react subsequently with intermediates derived from the naphthalene nucleus.

The role of 9,10-dihydroanthracene in preventing further decomposition of sultine **6** in pyrolysis is unclear. It apparently is not acting as a diluent because the pyrolysis proceeded normally to **2** and **3** when the 9,10-dihydroanthracene was replaced by anthracene or *p*-terphenyl. Various excited states of reactant or intermediates may be involved and the dihydroanthracene may interact with one of these to prevent extensive rearrangement. Further investigation into the mechanism of these transformations is in progress.

Experimental Section

Melting points were obtained on a Fisher-Johns melting point apparatus (uncorrected) or a Herschberg melting point apparatus using Anschütz precision thermometers (corrected). Infrared spectra were taken on either a Perkin-Elmer Model 137 infrared spectrophotometer or on a Perkin-Elmer Model 521 grating spectrophotometer. The infrared absorptions are reported as weak (w), medium (m), and strong (s). Ultraviolet spectra were obtained on a Perkin-Elmer Model 202 ultraviolet spectrophotometer. The absorptions are reported in millimicrons and the intensity of the absorptions in ϵ; the actual absorbance value is given in cases where the molecular weight was not known or the sample was not weighed. Proton nuclear magnetic resonance (nmr) spectra were obtained on a Varian Model A-60 nmr spectrometer. Nmr absorptions are reported as δ values and tetramethylsilane was used as an internal standard unless stated otherwise. Microanalyses were performed at Galbraith Laboratories, Knoxville, Tenn., or at Alfred Bernhardt Microanalytisches Laboratorium in Max-Planck Institut für Kohlenforschung, Mülheim, West Germany. Molecular weight determinations were done by vapor pressure osmometry in an appropriate solvent, by the Rast method or by mass spectrometry. Mass spectra were performed by Morgan-Schaffer Corp., Montreal, Quebec, Canada, or at the Department of Chemistry, Syracuse University, Syracuse, N. Y. In all cases, a Perkin-Elmer Hitachi Model RMU-6D single focusing spectrometer was used at an ionizing voltage of 70 eV.

Pyrolysis of 3,8-Diphenyl-2H-naphtho[2,3-*b*]thiete 1,1-Dioxide.—A 100-ml, three-necked, round-bottomed flask was fitted with a gas inlet stopcock in each of the side necks and a standard taper stopper in the center neck. 3,8-Diphenyl-2H-naphtho[2,3-*b*]thiete 1,1-dioxide[12,30] (2.00 g, 5.62 × 10^{-3} mol) was placed in the flask which was flushed with Linde high-purity dry nitrogen for 5 min. The outlet may be connected to a gas bubbler or, if the gases are to be collected, to a 100-ml syringe. Heating of the flask is done with a metal bath (Wood's metal alloy or a mixture of tin and lead) which was heated with a Bunsen burner. The temperature of the bath was measured with a partial immersion (76 mm) thermometer. Nitrogen flow through the flask was maintained until the sulfone melted (259°), and then was reduced until there was a slight positive pressure. The sulfone was heated from about 180 to 360° in 4–6 min, and then for 5 min from 360 to 400°. Decomposition of the sulfone started at about 370–380° with the appearance of a red color in the flask. The flask was removed from the metal bath and cooled as a stream of nitrogen was passed through the flask.

The pyrolyzed mixture was dissolved in a minimum of chloroform and separated by column chromatography on a column of Woelm acidic alumina, activity grade I. A column 1.5 × 50 cm is sufficient to effect the separation. Elution with benzene gave, after recrystallization from benzene, white crystals of 14H-benzo[*b*]benzo[3,4]fluoreno[2,1-*d*]thiophene (**3**, 0.21 g, 6.52 × 10^{-4} mol, 11% yield), mp 233°. Changing the solvent to chloroform caused elution of a broad red-brown band, which when recrystallized from chloroform gave 14-H-benzo[*b*]benzo[3,4]fluoreno[2,1-*d*]thiophen-14-one (**2**, 0.60 g, 1.78 × 10^{-3} mol, 31.5% yield), mp 265°.

Anal. Calcd for $C_{23}H_{12}OS$ (**2**): C, 82.13; H, 3.60; S, 9.52; mol wt, 336. Found: C, 81.88; H, 3.59; S, 9.33; mol wt, 336 (mass spectrometry).

Anal. Calcd for $C_{23}H_{14}S$ (**3**): C, 85.69; H, 4.38; S, 9.93; mol wt, 322. Found: C, 85.56; H, 4.41; S, 9.65; mol wt, 322 (mass spectrometry).

Fluorenone **2** has the following properties: infrared (KBr) 3050 w, 1705 s, 1600 m, 1540 m, 1460 m, 1445 w, 1390 m, 1325 m, 1290 w, 1195 m, 1090 m, 1080 w, 945 m, 890 m, 770 s, 725 s, 710 m, 660 cm^{-1} s; ultraviolet ($CHCl_3$) 253 mμ (sh) (ϵ 3.75 × 10^4), 271 (6.40 × 10^4), 305 (sh) (3.50 × 10^4), 314 (4.20 × 10^4), 333 (1.40 × 10^4), and 347 (9.53 × 10^3); mass spectrum[31] *m/e* 338 (8.34%, isotope peak), 337 (26.05%, isotope peak), 336 (100.00%, parent ion), 308 (16.24%, P − CO), 307 (7.52%), 306 (13.19%), 305 (2.44%), 291 (6.09%), 276 (5.28%, $C_{22}H_{12}^+$), 263 (5.39%, $C_{21}H_{11}^+$), 168 (12.39%, $C_{23}H_{12}OS^{2+}$), 154 (11.78%), 153 (10.15%).

Fluorene **3** has the following properties: infrared (KBr) 3015 w, 2870 w, 1548 m, 1520 m, 1467 s, 1460 s, 1446 m, 1435 m, 1419 w, 1395 m, 1375 m, 1335 m, 1305 m, 1300 m, 1115 s, 1070 w, 1040 w, 1025 w, 940 w, 850 m, 765 s, 715 s, 710 s, 665 m, 630 s; ultraviolet ($CHCl_3$) 251 mμ (ϵ 4.20 × 10^4), 259 (4.08 × 10^4), 277 (2.69 × 10^4), 298 (9.69 × 10^3), 311 (1.40 × 10^4), 334 (sh) (1.88 × 10^4), 348 (3.06 × 10^4), and 367 (3.17 × 10^4); mass spectrum *m/e* 324 (8.42%, isotope peak, 323 (26.65%), isotope peak), 322 (100.00%, parent ion), 321 (47.10%), 320 (7.38%), 319 (14.03%), 289 (6.68%), 161 (15.78%, $C_{23}H_{14}S^{2+}$), 160.5 (15.41%), 160 (7.04%), 159.5 (11.93%).

Because of the low solubility of **2** and **3** in common nmr solvents (such as $CDCl_3$, dimethyl-d_6 sulfoxide, and benzene-d_6) no nmr spectra of good quality were obtained for either of these compounds.

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(27) Speculative mechanisms can be written for these transformations.

(28) I. D. Entwistle and R. A. W. Johnstone, *Chem. Commun.*, 29 (1965); D. G. Barnard-Smith and J. F. Ford, *ibid.*, 120 (1965); W. Carruthers, I. D. Entwistle, R. A. W. Johnstone, and B. J. Millard, *Chem. Ind.* (London), 342 (1966).

(29) E. Wellisch, E. Gipstein, and O. J. Sweeting, *J. Org. Chem.*, **27**, 1810 (1962).

(30) L. A. Paquette, *ibid.*, **30**, 629 (1965).

(31) Only fragments which were 5% of the base peak or greater are included in this tabulation and in others, except for *m/e* 305. Percentages are relative to the intensity of the base peak.

The mass spectrum of 5-phenyl-7H-benzo[*c*]fluorenone[16] (5) was obtained for the purpose of comparison with that of fluorenone 2: *m/e* 307 (24.75%, isotope peak), 306 (100.00%, parent ion), 305 (15.00%), 278 (7.19%, P − CO), 277 (20.60%), 276 (34.70%), 275 (5.46%), 274 (9.29%), 153 (7.02%, $C_{23}H_{14}O^{2+}$), 138.5 (10.40%), 138 (35.90%), 137 (10.30%), 126 (7.38%), 125 (8.56%).

Analysis of the Gases.—The analysis of the gases obtained in the pyrolysis was done by mass spectrometry. The samples of naphthothiete sulfone 1 were pyrolyzed in evacuated Pyrex bulbs (volume 65 ± 1 cm^3). Weighed samples of 1 were transferred into the bulbs which were then evacuated to less than 0.03 mm and sealed. The samples (each about 1.40×10^{-3} mol) were pyrolyzed and the composition and quantities (mole per cent) of the components in the gas mixture are given in Table I.

Table I

Mass Spectral Analysis Data of Volatile Products from Pyrolysis of Naphthothiete Sulfone 1

	Mole per cent of total gases			
Product	Run 1[a] (heated 5 min at 380–400°)	Run 2[b] (heated 5 min at 380–400°)	Run 3[a] (heated 0.5 min at 350–360°)	Run 4[c] (heated 5 min at 295–305°)
H_2O	1.4	6.4	18.4	43.6
CO	59.1	40.9	48.8	5.9
H_2S	3.9	12.3	0.2	0
CO_2	29.1	36.8	20.9	0.9
COS	1.2	1.8	1.2	0
SO_2	0.5	0.1	5.3	15.3

[a] Bulb pressure after pyrolysis was 110 mm. [b] Bulb pressure after pyrolysis was 190 mm. [c] Bulb pressure after pyrolysis was 22 mm.

Reduction of 14H-Benzo[*b*]benzo[3,4]fluoreno[2,1-*d*]thiophen-14-one (2) with Hydrogen-Poor Raney Nickel.—A suspension of W-5 Raney nickel[32] (5–6 g) was degassed slightly by refluxing it for 15 min in absolute ethanol. Solid 2 (0.213 g, 6.34×10^{-4} mol) was added and refluxed with the degassed nickel for 0.5 hr. The hot mixture was filtered and the residual nickel washed on the filter with hot chloroform (300 ml). The dry nickel residue was not pyrophoric. The orange filtrate was evaporated to dryness on a steam bath under a stream of air. The residue was dissolved partially in chloroform and the solid inorganic compounds were removed by filtration. Recrystallization from chloroform and a few milliliters of 95% ethanol gave 83 mg of an impure orange solid. The third crop of crystals was sublimed at 95° (0.03 mm) to give an impure sublimate (5.1 mg) and a residue of impure fluorene 3 (34.9 mg). The residue was recrystallized from methanol–chloroform (4:1) to give pure 3 (15.4 mg), mp 237–238° uncor. This sample of 3 had infrared and ultraviolet spectra identical with those of the fluorene obtained in the pyrolysis of naphthothiete sulfone 1. The first and second crops of crystals were chromatographed on a column (35 × 1 cm) of Woelm neutral alumina, activity grade I. Elution with benzene gave fluorene 3, which was recrystallized from methanol–chloroform (4:1) to give orange crystals (27 mg). The total yield of crude 3 was 30.4%. Although 3 is white when pure, the slight orange color here is due to a slight trace of fluorenone 2, which was detected by mass spectrometry.

Elution with chloroform gave a red band of impure 2 (14.9 mg). Recrystallization gave pure 2 (8.2 mg), mp 264–68° uncor. The sample of 2 recovered was compared with the starting material and found to have identical infrared and ultraviolet spectra. Further elution of compounds from the column with chloroform or chloroform–ethanol (3:1) gave only 19.4 mg of an unidentified oil.

Desulfurization of 14H-Benzo[*b*]benzo[3,4]fluoreno[2,1-*d*]-thiophen-14-one (2) with Hydrogen-Rich Raney Nickel.—Fluorenone 2 (0.204 g, 6.08×10^{-4} mol) was refluxed with 10–12 g of W-5 Raney nickel[32] in 95% ethanol (100 ml) for 5 hr. The hot mixture was cooled slightly, then filtered under vacuum and the residual nickel washed with 250 ml of hot chloroform. The nickel was still pyrophoric. The filtrate was evaporated to dryness, and the residue taken up in chloroform to yield 183 mg of an oil. The chloroform-insoluble material was taken up in 95% ethanol to yield 26 mg of a crude solid. The oil gave more of the solid on cooling, which when combined with the crude solid above (26 mg) and recrystallized from chloroform–ethanol gave 13.4 mg of an unknown compound, mp 210–220°.

The oil was chromatographed on Woelm acidic alumina, activity grade I, on a 45 × 1 cm column. Elution with petroleum ether (bp 30–60°) and benzene gave a yellow oil (75 mg) and elution with chloroform gave a red oil (90 mg). The yellow oil gave the following analysis.

Anal. Calcd for $C_{23}H_{26}$: C, 91.33; H, 8.67; mol wt, 302. Found: C, 91.18; H, 8.50; mol wt, 304.

It had the following properties: infrared (KBr) 3045 m, 3010 m, 2915 s, 2845 s, 1600 m, 1515 m, 1460 m, 1440 s, 1400 m, 1335 w, 1260 m, 1085 m, 1070 m, 1025 m, 945 w, 870 w, 850 m, 765 s, 730 s, 700 cm^{-1} s; ultraviolet spectrum ($CHCl_3$) 254, 278 (weak), 290 (sh), 331 (sh), and 345 mμ (sh) (the two weak bands at 345 and 331 mμ may be due to impurities originating with starting material 2); nmr ($CDCl_3$) δ 0.89 (complex), 1.25 (singlet), 1.82 (complex), 2.72 (complex), 3.34 (complex), 3.82 (complex), 7.38 (complex), and 7.88 (complex). The ratio of the hydrogens at δ 7.38 and 7.88 to the rest of the hydrogens is 33:58.

The impure red oil gave the following analysis.

Anal. Calcd for $C_{23}H_{24}O$: C, 87.30; H, 7.64; mol wt, 316.5. Found: C, 84.35, 84.55; H, 12.63, 12.64; mol wt, 510, 520.

The red oil had the following properties: infrared (KBr) 3055 w, 3010 w, 2925 s, 2850 m, 1710 s, 1600 m, 1495 w, 1445 m, 1395 m, 1200 m, 755 s, and 700 cm^{-1} s; ultraviolet ($CHCl_3$) 257, 293 (sh), and 345 mμ (broad sh).

Synthesis of 5-Phenylbenzo[*b*]naphtho[1,2-*d*]thiophene.—This compound was prepared in order to compare its spectra with those of 3. 1,4-Diphenylnaphthalene[16,33] (1.500 g, 5.35 mmol) and sulfur (177 mg, 5.5 mmol) were melted together at 178° for 0.5 hr. Anhydrous aluminum chloride (42 mg, 0.313 mmol) was added in 21-mg quantities at 15-min intervals. The reaction became quite dark when the aluminum chloride was added. Heating in the oil bath was continued for 3.5 hr with occasional shaking of the reaction mixture. After the reaction mixture had cooled, 50 ml of water was added and the aqueous mixture was extracted with three 50-ml portions of benzene, to yield a dark red solution. The solvent was evaporated and the red oil chromatographed on a column (2.5 × 90 cm) of Woelm acidic alumina, activity grade I. The compound can be eluted with either benzene or carbon tetrachloride. Only the colorless eluent was found to give the desired product. After recrystallization from chloroform–ethanol, a white compound, mp 195.2–196° cor (179 mg, 5.78×10^{-4} mol, 10.8% yield), was obtained.

Anal. Calcd for $C_{22}H_{14}S$: C, 85.13; H, 4.55; mol wt, 310. Found: C, 85.30; H, 4.67; mol wt, 310 (mass spectrometry).

The compound had the following properties: infrared (KBr), 3010 w, 1490 w, 1465 w, 1440 w, 1430 m, 1338 m, 1160 w, 1015 w, 985 w, 873 m, 778 m, 760 m, 745 s, 730 m, and 695 cm^{-1} s; ultraviolet ($CHCl_3$) 249 mμ (ε 5.08×10^4), 258 (5.78×10^4), 281 (4.67×10^4), 305 (2.18×10^4), 321 (sh) (8.48×10^3), and 353 (4.03×10^3); mass spectrum *m/e* 312 (7.00%, isotope peak), 311 (24.81%, isotope peak), 310 (100.00%, parent ion), 309 (24.7%), 308 (35.3%), 306 (5.4%), 280 (10.5%), 155 (11.6%, $C_{22}H_{14}S^{2+}$), 154.5 (10.5%), 154 (15.5%), 153 (7.4%).

Desulfurization of 14H-Benzo[*b*]benzo[3,4]fluoreno[2,1-*d*]-thiophene (3) with Raney Nickel.—A mixture of 3 (150 mg, 4.66×10^{-4} mol) was refluxed in 95% ethanol (50 ml) with W-5 Raney nickel[32] (5–6 g) for 0.5 hr. The mixture was then filtered and the residual nickel washed with hot benzene (350 ml). The solvent was evaporated on a steam bath under a stream of air and the oily residue was recrystallized from methanol–ligroin (bp 40–60°) in two crops for a total of 95 mg of a compound, mp 128–130° cor (lit.[15] mp 128°). The melting point was not depressed when mixed with an authentic sample of 5-phenyl-7H-benzo[*c*]fluorene (4). It also had infrared and ultraviolet spectra identical with those of the authentic material. Fluorene 4 had the following properties: infrared (KBr) 3090 w, 3040 w, 2920 w, 1590 w, 1490 m, 1460 m, 1440 w, 1395 m, 1335 m, 1205 w, 1020 w, 945 m, 910 w, 872 m, 785 w, 769 s, 755 s, 745 m, 710 s, 698 s, and 640 cm^{-1} s; ultraviolet ($CHCl_3$) 247, 330, and 345 mμ.

Synthesis of 5-Phenyl-7H-benzo[*c*]fluorene (4).—A mixture of 5-phenyl-7H-benzo[*c*]fluorenone,[16] 5 (1.00 g, 3.27×10^{-3} mol), and 1,2-ethanedithiol (20 ml) was warmed on a steam bath until the ketone dissolved. Boron trifluoride–ethyl etherate (15 ml) was added to the warm solution and the mixture was allowed to stand for 15 min. Methanol (50 ml) was added

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(32) H. R. Billica and H. Adkins, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 176.

(33) C. Dufraisse and R. Priou, *Bull Soc. Chim. Fr.*, **5**, 502 (1938).

and the solution cooled to give white crystals of the dithioketal (1.25 g, crude). The crude product was recrystallized from ethanol–benzene (10:1) to give pure dithioketal (0.69 g, 55% yield), mp 219–222° uncor.

Anal. Calcd for $C_{25}H_{18}S_2$: C, 78.52; H, 4.74; mol wt, 382. Found: C, 78.37; H, 4.90; mol wt, 382 (mass spectrometry).

The dithioketal (0.500 g, 1.31 × 10^{-3} mol) and W-5 Raney nickel (10–11 g) were refluxed in absolute ethanol (200 ml) for 1 hr. The warm mixture was filtered and the nickel washed with hot chloroform (200 ml). The residual nickel was not pyrophoric. The solution was evaporated to dryness on a steam bath under a stream of air. The residue was taken up in chloroform (200 ml) and the insoluble inorganic compounds removed by filtration. The chloroform was evaporated and the residue recrystallized from methanol–chloroform (10:1) to give slightly off-white crystals (268 mg, 70% yield), mp 126–29° uncor (lit.[15] mp 128°).

Anal. Calcd for $C_{23}H_{16}$ (4): C, 94.48; H, 5.52; mol wt, 292. Found: C, 94.38; H, 5.51; mol wt, 280 (Rast), 292 (mass spectrometry).

Fluorene 4 had the following properties: nmr ($CDCl_3$) δ 7.15–8.55 (complex multiplet, aromatic protons), 3.97 (singlet, methylene protons); infrared (KBr) 3040 w, 1600 w, 1590 w, 1510 w, 1492 m, 1460 m, 1440 w, 1395 m, 1333 m, 1205 w, 1065 w, 1020 w, 998 w, 945 s, 910 w, 872 m, 855 w, 785 w, 769 s, 755 s, 745 m, 710 s, 695 s, and 635 m cm^{-1}; ultraviolet ($CHCl_3$) 246 mμ (ε 3.25 × 10^4), 330 (2.06 × 10^4), and 343.5 (2.09 × 10^4).

Pyrolysis of 3,8-Diphenyl-2H-naphtho[2,3-*b*]thiete 1,1-Dioxide (1) with 9,10-Dihydroanthracene.—A mixture of sulfone 1 (2.017 g, 5.66 × 10^{-3} mol) and 9.10-dihydroanthracene (2.321 g, 12.88 × 10^{-3} mol) (Aldrich Chemical Co., recrystallized once from 95% ethanol) was pyrolyzed as described previously for neat 1. The slightly orange solid which was obtained was dissolved in a minimum amount of carbon tetrachloride and chromatographed on a column (2 × 50 cm) of Woelm acidic alumina, activity grade I. A mixture of 9,10-dihydroanthracene (78–84%) and anthracene (22–16%) (total recovery of the combined compounds was 83%) was eluted with carbon tetrachloride. A yellow band was eluted with chloroform–ethanol (20:1), and recrystallized (with decolorization with activated carbon) from 95% ethanol to give the slightly yellow sultine (6) (78–81% yield), mp 202.4–203° cor.

Anal. Calcd for $C_{23}H_{16}O_2S$ (6): C, 77.50; H, 4.52; S, 8.99; mol wt, 356. Found: C, 77.40; H, 4.62; S, 8.84; mol wt, 356 (mass spectrometry).

Sultine 6 has the following properties: infrared (KBr) 3020 w, 2900 w, 1585 w, 1508 w, 1490 w, 1440 m, 1405 w, 1364 m, 1325 w, 1270 w, 1175 w, 1120 s, 1070 w, 1020 w, 995 w, 948 s, 920 m, 835 m, 765 s, 740 s, 700 s, 680 s, and 665 cm^{-1} s; nmr ($CDCl_3$) δ 7.00–8.00 (complex multiplet, aromatic protons), 5.98 (doublet), and 5.32 (doublet, J_{AB} = 14 Hz); ultraviolet (C_2H_5OH) 239 (ε 5.70 × 10^4), 300.5 (1.4 × 10^4), and 333 (5.98 × 10^3).

Lithium Aluminum Hydride Reduction of Sultine 6.—A suspension of the sultine (0.5 g, 1.4 × 10^{-3} mol) in anhydrous ethyl ether (30 ml) was added to a slurry of lithium aluminum hydride (0.53 g, 14 mmol) in anhydrous ethyl ether (50 ml) stirred with a magnetic stirring bar. The addition and reaction were done in a nitrogen atmosphere. After the addition (0.5 hr) the slurry was refluxed for 5 hr. Excess hydride was destroyed with water (30 ml) which contained about 1 ml of concentrated hydrochloric acid. The decomposed mixture was neutralized to pH 5–6 with aqueous sodium hydroxide and extracted with four 100-ml portions of benzene, and the benzene evaporated on a steam bath under a stream of air. The yellowish residue was taken up in methanol and filtered with decolorizing carbon, and water was added to the filtrate to the cloud point. Cooling of the solution gave a yellow solid (0.248 g, 60% yield), mp 234.4–236° cor.

Anal. Calcd for $C_{23}H_{18}OS$: C, 80.67; H, 5.30; S, 9.36; mol wt, 342. Found: C, 80.97; H, 5.47; S, 9.38; mol wt, 342 (mass spectrometry).

The reduction product had the following properties: infrared (KBr) 3520 w, 3400 m, 3050 w, 3020 w, 2930 w, 2870 w, 2550 w, 1595 w, 1540 w, 1500 w, 1490 m, 1440 m, 1365 m, 1320 w, 1270 w, 1170 w, 1042 m, 1020 w, 980 w, 915 w, 810 w, 760 m, 750 m, 735 m, and 695 cm^{-1} s; ultraviolet (C_2H_5OH) 231 mμ (ε 2.75 × 10^4), 253 (3.22 × 10^4), 278 (sh) (8.95 × 10^3), 292.5 (8.13 × 10^3), 304 (7.85 × 10^3), and 346 (sh) (1.79 × 10^3); nmr ($CDCl_3$) δ 7.16–7.76 (complex multiplet, aromatic protons), 4.66 (singlet, $-CH_2-$), 3.88 (singlet, –SH), and 2.12 (singlet, –OH); relative areas 14:2:1:1, respectively. The mass spectra of naphthothiete sulfone 1 and sultine 6 are compared in Table II.

TABLE II
MASS SPECTRAL DATA FOR
NAPHTHOTHIETE SULFONE 1 AND SULTINE 6[a]

m/e	% of base peak		Possible ion formula	M+ – fragment
	1	6		
358		8.23	Isotope peak	
357	11.42	26.50	Isotope peak	
256	43.02	100.00	$C_{23}H_{16}O_2S^+$	M^+
339		6.32	$C_{23}H_{15}OS^+$	$M^+ - 17$
338		10.20	$C_{23}H_{14}OS^+$	$M^+ - 18$
337		6.32	$C_{23}H_{13}OS^+$	$M^+ - 19$
336		7.29	$C_{23}H_{12}OS^+$	$M^+ - 20$
321		6.32		$M^+ - 35$
311		6.32	$C_{22}H_{15}S^+$	$M^+ - 45$
310		9.71	$C_{22}H_{14}S^+$	$M^+ - 46$
309		19.89	$C_{22}H_{13}S^+$	$M^+ - 47$
308	10.05	53.85	$C_{23}H_{16}O^+$	$M^+ - 48$
307	5.44	29.10	$C_{23}H_{15}O^+$	$M^+ - 49$
293	13.85	10.70	$C_{22}H_{13}O^+$	$M^+ - 63$
292	66.97	45.60	$C_{23}H_{16}^+$	$M^+ - 64$
291	100.00	76.75	$C_{23}H_{15}^+$	$M^+ - 65$
290	29.13	21.84	$C_{23}H_{14}^+$	$M^+ - 66$
289	52.24	35.40	$C_{23}H_{13}^+$	$M^+ - 67$
288	5.98		$C_{23}H_{12}^+$	$M^+ - 68$
287	11.42	6.32	$C_{23}H_{11}^+$	$M^+ - 69$
281		7.77		$M^+ - 75$
280	5.71	28.64	$C_{22}H_{16}^+$	$M^+ - 76$
279		16.99	$C_{22}H_{15}^+$	$M^+ - 77$
278		9.71		$M^+ - 78$
277	10.60	15.52	$C_{22}H_{13}^+$	$M^+ - 79$
276	16.32	25.73	$C_{22}H_{12}^+$	$M^+ - 80$
274		7.29		$M^+ - 82$
265		6.80		$M^+ - 91$
263	7.62	8.25	$C_{21}H_{11}^+$	$M^+ - 93$
252		5.34		$M^+ - 104$
234		5.38		$M^+ - 122$
216		5.34		$M^+ - 140$
215	31.83	23.88	$C_{17}H_{11}^+$	$M^+ - 141$
213	8.16	6.32		$M^+ - 143$
203		10.70	$C_{16}H_{11}^+$	$M^+ - 153$
202		11.65	$C_{16}H_{10}^+$	$M^+ - 154$
200		5.34		$M^+ - 156$
189		5.83		$M^+ - 167$
154.5		5.83		
154		16.99	$C_{23}H_{16}O^{2+}$	
153		7.29	$C_{23}H_{14}O^{2+}$	
145.5	7.07	7.77	$C_{23}H_{15}^{2+}$	
145	20.92	22.32	$C_{23}H_{14}^{2+}$	
144.5	23.61	22.32	$C_{23}H_{13}^{2+}$	
144	6.54	6.80	$C_{23}H_{12}^{2+}$	
143.5	9.79	8.74	$C_{23}H_{11}^{2+}$	
138.5		10.70	$C_{22}H_{13}^{2+}$	
138	16.01	23.30	$C_{22}H_{12}^{2+}$	
137		7.29		$M^+ - 219$
132		5.34		$M^+ - 224$
131.5	9.25	12.12	$C_{21}H_{11}^{2+}$	
126		5.83		$M^+ - 230$
125		7.77		$M^+ - 231$
113		5.34		$M^+ - 243$
83	5.71			$M^+ - 263$
77		5.83		$M^+ - 279$
31		6.32		$M^+ - 325$
28		8.25	N_2^+, CO^+, or C_2H_4	
18		7.77	H_2O^+	

[a] Only those fragments which were 5% of the base peak or greater are included in this table.

Pyrolysis of Sultine 6.—Cyclic sulfinate 6 (0.61 g, 1.71 × 10^{-3} mol) was placed in a 100-ml, three-necked, round-bottomed flask with a gas inlet and outlet stopcock in the side necks of the flask, and a standard taper stopper in the center neck. The flask was flushed with Linde high-purity dry nitrogen as it was heated up to 360°. The nitrogen flow was reduced to a slight positive pressure (the outlet may be connected to a mercury-filled bubbler) and the metal bath heated to 360–400° for 5 min. At about 375–380° [temperature measured with a partial (76 mm) immersion thermometer] a sudden evolution of gas was observed, and the compound became dark red. An analysis of the gases was not done. The pyrolyzed compound was cooled in a nitrogen atmosphere, dissolved in a minimum amount of carbon tetrachloride, and separated on a column (2 × 47 cm) of Woelm acidic alumina, activity grade I. Elution with ethanol-carbon tetrachloride (1:9) and with carbon tetrachloride alone gave fluorenone 2 (122 mg, 3.63 × 10^{-4} mol, 21.2% yield) and fluorene 3 (43 mg, 1.34 × 10^{-4} mol, 7.8% yield), identified by comparison of their ultraviolet and infrared spectra with those of 2 and 3 produced in the normal pyrolysis of naphthothiete sulfone 1.

Registry No.—1, 979-37-3; 2, 19639-51-1; 3, 19639-52-2; 4, 19639-53-3; 4 (dithioketal), 19639-54-4; 6, 19639-55-5; reduction product of 6 ($C_{23}H_{16}OS$), 19639-56-6; 5-phenylbenzo[*b*]naphtho[1,2-*d*]thiophene, 19639-57-7.

The Reaction of Phenyllithium with 1-Halo-2-butenes[1]

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Phenyllithium reacted with *cis*- and *trans*-1-chloro-2-butene and *trans*-1-bromo-2-butene and gave a mixture of 3-phenyl-1-butene, *cis*- and *trans*-1-phenyl-2-butene, and *cis*- and *trans*-1-methyl-2-phenylcyclopropane. The ratio of the isomeric cyclopropanes was similar to that obtained from the addition of phenyllithium to 3-methylcyclopropene and confirmed the formation of this compound in the reaction. Phenylsodium and phenylmagnesium bromide in their reactions with the 1-halo-2-butenes gave only the three olefins.

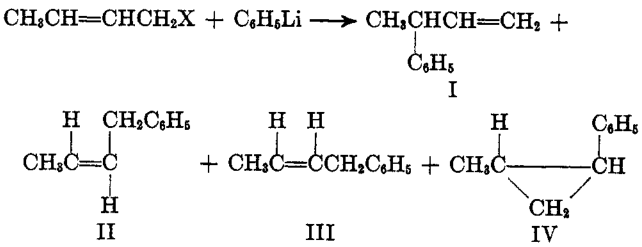
Two mechanisms have been offered for the formation of cyclopropanes in the reaction of phenyllithium with allylic halides. The first of these suggested an attack of the phenyl carbanion on the β-carbon atom of the halide followed by an intramolecular cyclization to the cyclopropane.[2] The second one suggested the formation of a carbene followed by cyclization to a cyclopropene which reacts with phenyllithium and forms the cyclopropane.[3] Results with deuterated allyl chloride and allyl-1-^{14}C chloride[4] have confirmed the second mechanism for the formation of the cyclopropane.

In this paper studies are reported on the course of the reaction between phenyllithium and 1-halo-2-butenes and the stereochemistry of the cyclopropane produced. The first mechanism would be expected to produce only *trans*-1-methyl-2-phenylcyclopropane and the second offers the possibility of a mixture of *cis* and *trans* isomers.

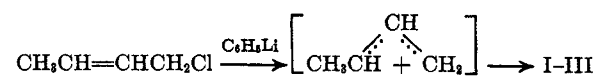
The results obtained for the reaction of phenyllithium with *cis*- and *trans*-1-chloro-2-butene and *trans*-1-bromo-2-butene, and of phenylsodium with *trans*-1-chloro-2-butene are listed in Table I.

Examination of the results in Table I indicates that *cis*- and *trans*-1-methyl-2-phenylcyclopropane (IV) are formed together with 3-phenyl-1-butene (I), *trans*-1-phenyl-2-butene (II), and *cis*-1-phenyl-2-butene (III) in the reaction of phenyllithium with 1-halo-2-butenes (Scheme I). Phenylsodium in the same reaction did not form any detectable cyclopropane. The cyclopropane formed varied in yield with the conditions used and was by vpc analysis better than 93.9% *trans;* the *cis* compound was present in amounts of 6.1% or less. The high ratio of *trans* to *cis* isomers would suggest that the first mechanism was operating but a study of the reaction of 3-methylcyclopropene with phenyllithium found the same ratio of isomeric cyclopropanes. The results therefore confirm the second mechanism for the formation of the cyclopropanes and are in agreement with the results of Magid and Welch.[4]

SCHEME I



An interesting sidelight on the reaction was the formation of a small percentage of *cis*-1-phenyl-2-butene (III) in the reaction of phenyllithium with *trans*-1-chloro-2-butene and a small amount of the corresponding *trans* olefin in the reaction involving *cis*-1-chloro-2-butene. A similar behavior was found with phenylsodium and *trans*-1-chloro-2-butene. This isomerization is consistent with the ionization mechanism proposed for the reaction of phenyllithium and 1-chloro-2-butene.[5] The stereochemistry of the allylic cation could be altered by an internal return of the halide ion to form the 3-halo-1-butene followed by ionization of this halide.



$$CH_3CH{=}CHCH_2Cl \xrightarrow{C_6H_5Li} \left[CH_3\overset{CH}{CH} + CH_2\right] \longrightarrow \text{I–III}$$

The effect of solvents on the ratio of the products obtained indicates that a complex between the phenyl-

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[1] Abstracted in part from the Ph.D. Theses of B. J. Studnicka, 1966, and A. R. Zigman, 1968.

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[3] (a) R. M. Magid and J. G. Welch, *J. Amer. Chem. Soc.*, **88**, 5681 (1966); (b) J. G. Welch and R. M. Magid, *ibid.*, **89**, 5300 (1967).

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[5] S. J. Cristol, W. C. Overhults, and J. S. Meek, *ibid.*, **73**, 813 (1951).