Table IV

Synthesis of Di-*sec*-alkylaluminum Hydrides from Aluminum, Hydrogen, and Nonterminal Olefins

Reactants		Activator compd., g.	Time, hr.	Temp., °C.	Pressure, atm.	Al conversion, %	Olefin recovered, moles	Product, g.
Olefin, moles	Al, g.-atoms							
3-Heptene, 2	1.1	*i*-Bu_2AlH, 17.5	23	120	200–250	76.7	0	$(sec\text{-}C_7H_{15})_2AlH$, 234
4-Nonene, 3.3	1.48	*i*-Bu_2AlH, 8 Al stearate, 1.5	22	120	185–330	76.2	0.97[a]	$(sec\text{-}C_9H_{19})_2AlH$, 336
6-Dodecene, 2.16	0.74	*n*-Dod_3Al, 37	14	120	170–330	82.5	0.88[b]	$(sec\text{-}C_{12}H_{25})_2AlH$,[c] 262
Cyclohexene, 4.4	2	*i*-Bu_2AlH, 8 Al stearate, 1.5	17	130	180–320	65	0[d]	$(C_6H_{11})_2AlH$,[e] 252

[a] Nonane content, 17.8%. [b] Dodecane content, 9.4%. [c] With consideration of the amount of $Al(n\text{-}C_{12}H_{25})_3$ used for the aluminum activation. [d] 146 g. of cyclohexane (1.7 moles), b.p. 80.5°, $n^{20}D$ 1.4270, was recovered, no cyclohexene. [e] Recrystallization from *n*-pentane gave 135 g. of colorless, crystalline product, m.p. 136° (uncor.), decomposition range 150–160°.

technik GmbH, Mülheim-Ruhr, West Germany) was employed. Prior attempts to utilize steel balls of other companies were unsuccessful and resulted in plating of the aluminum shot. The mill was charged, under argon, with aluminum shot (Th. Goldschmidt Co., Essen, West Germany), activator, and 150 ml. of a dry, inert diluent such as hexane, heptane, or *p*-xylene. The charge was ground on a vibrating ball-mill base for a period of 10–12 hr., and then discharged into a glass flask of suitable size. Usually one or two subsequent washings of the mill with 40–50 ml. each of the diluent were sufficient to remove all of the ground aluminum metal from the mill. Thereafter, the whole charge, including the diluent, was transferred from the flask to a stainless steel rocker bomb of 1-l. net capacity.

Olefin Feed.—Hydrogen was introduced into the rocker bomb at room temperature until pressures between 120–140 atm. were obtained, and the reactor was externally heated to the desired temperature. Then the olefins were added at half-hourly or hourly intervals in amounts of 25–65 ml., depending upon the time period necessary for the reactor pressure to become constant. A laboratory piston metering pump of an allowable operating pressure of 500 atm. was used for the feed operation.

Work-Up.—The excess hydrogen was slowly vented from the reaction vessel. The reaction mixture was quantitatively transferred from the autoclave to a glass flask, weighed, and separated from the nonreacted aluminum by filtration under argon. Subsequently, the diluent and nonreacted olefin were distilled from the organoaluminum reaction product at 13 mm. and/or 0.1 mm., respectively.

Characterization.—The methods employed for identification and analyses are described in the section on displacement reactions.

Neither 1-heptanol nor 1-nonanol were isolated from the products of oxidation and subsequent hydrolysis of the organoaluminum reaction products from the runs with 3-heptene and 4-nonene, respectively. The *sec*-dodecanol/dodecanone mixture obtained from the organoaluminum reaction product of the run with 6-dodecene contained, as expected, an amount of 1-dodecanol corresponding to the amount of $Al(n\text{-}C_{12}H_{25})_3$ activator used.

The results are summarized in Table IV.

Acknowledgment.—The author thanks Dr. H. Schirp for a stimulating discussion regarding this problem. All infrared analyses and all interpretations of infrared spectra in conjunction with this project were performed by Dr. H. van Raay, whose assistance and helpful cooperation are gratefully acknowledged.

Fused Aromatic Derivatives of Thiete and Thiete Sulfone[1]

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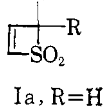
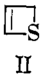
Derivatives of thiete (II), in which the double bond forms part of an aromatic system, have been prepared by the Diels–Alder addition of isobenzofurans to thiete sulfones, followed by dehydration and reduction. Limitations of the process are outlined. The stereochemistry of the Diels–Alder adducts has been elucidated by n.m.r. spectroscopy.

The recent interest in the chemistry of four-membered unsaturated sulfur heterocycles has led to two synthetic approaches to thiete 1,1-dioxides (I).[2,3] Neither thiete (II), the parent of the system, nor any of its derivatives, have been reported; several unsuccessful attempts to prepare II have, however, been documented.[4] The possible increased stability of the thiete anion (III) has already been discussed.[4] In view of our present general interest in the chemistry of unsaturated heterocyclic systems[1] and in an attempt to gain some insight into the chemical and physical properties of the thiete ring system in particular, the preparation of several fused aromatic derivatives of thiete was undertaken.



Ia, R=H
b, R=CH_3



II

III

Synthetic Procedure.—The synthetic scheme selected was based on the excellent diene characteristics of the isobenzofurans and the demonstrated dienophilic properties of thiete 1,1-dioxide (Ia).[4,5] When 1,4-diphenyl-2,3-benzofuran (IV) was condensed with Ib in refluxing xylene solution under a nitrogen atmosphere, there was obtained in 92.5% yield the expected adduct Va. The acid-catalyzed dehydration of Va proceeded

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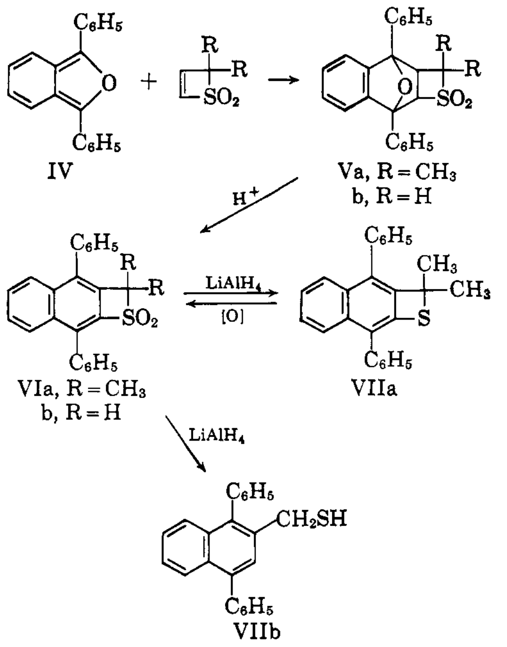
[1] Part XII of the series on Unsaturated Heterocyclic Systems. For part XI, see L. A. Paquette and L. D. Wise, *J. Org. Chem.*, **30**, 228 (1965).

[2] D. C. Dittmer and M. E. Christy, *ibid.*, **26**, 1324 (1961).

[3] W. E. Truce, J. R. Norell, J. E. Richman, and J. P. Walsh, *Tetrahedron Letters*, **No. 25**, 1677 (1963).

[4] D. C. Dittmer and M. E. Christy, *J. Am. Chem. Soc.*, **84**, 399 (1962).

[5] A similar independent study has been carried out by D. C. Dittmer, N. Takashina, and F. A. Davis, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 69S.

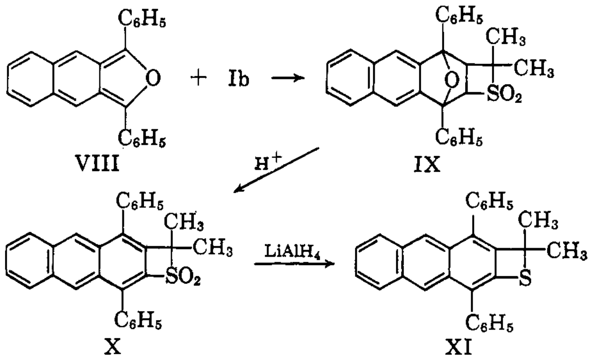


readily to give the 2H-naphtho[2,3-*b*]thiete 1,1-dioxide VIa in near quantitative yield. In confirmation of the structural assignment, the n.m.r. spectrum of VIa displayed only a singlet peak at δ 1.67 (methyl groups) and a complex multiplet centered at 7.48 (aromatic protons); that the substance was monomeric was adduced from a determination of its molecular weight.

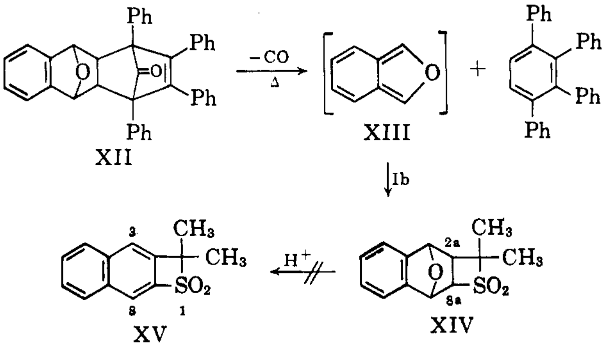
Lithium aluminum hydride reduction of VIa was *spontaneously exothermic*[6] and provided in 68% yield the thiete derivative VIIa which exhibited n.m.r. peaks at δ 1.75 (singlet, methyl groups) and 7.54 (aromatic protons). That no ring opening or skeletal rearrangement had occurred was established by reoxidation of VIIa to the starting sulfone with *m*-chloroperbenzoic acid.

A similar Diels–Alder condensation–dehydration sequence with Ia led to the fused thiete sulfone VIb in near quantitative over-all yield. Reduction of VIb with lithium aluminum hydride was likewise exothermic, but afforded a product which was *not* the desired thiete derivative. Instead, there resulted in 43.6% yield a product of over-reduction which has been assigned the mercaptan structure VIIb in accord with elemental analyses and with the following spectral properties. The proton magnetic resonance spectrum showed absorption at δ 1.68 (triplet, $J = 7$ c.p.s., -SH), 3.64 (doublet, $J = 7$ c.p.s., -CH$_2$-), and the 7.58 region (aromatic protons). Its ultraviolet spectrum was that expected of a 1,4-diphenylnaphthalene chromophore (see Experimental).

1,3-Diphenylnaphtho[2,3-*c*]furan (VIII) was found to react relatively more readily with Ib,[7] no doubt owing to the high reactivity of the 2,3-naphthoquinonoid system.[8] Dehydration of the resulting adduct IX afforded the sulfone X which was subsequently reduced in 90% yield to the 2H-anthra[2,3-*b*]thiete XI. The pertinent spectral properties of these compounds are in full agreement with the structural assignments and are listed in the Experimental section.



That the α,β-bonds of naphthalene possess appreciably greater double-bond character than the β,β-bonds is well known.[9] A very high degree of double-bond fixation in the α,β-positions has recently been observed in a naphtho[*b*]cyclobutadiene.[10] In an attempt to ascertain whether any substantial degree of double-bond fixation exists in the 2H-naphtho[2,3-*b*]thiete system, the synthesis of XV was attempted.[11] Generation of isobenzofuran (XIII) by the thermal decomposition of



XII in hot diglyme[12] containing Ib afforded in 98% yield the adduct XIV. This substance proved, however, to be remarkably resistant to acid hydrolysis; for example, XIV was recovered quantitatively after refluxing in methanolic hydrogen chloride for 18 hr.[13] When XIV was heated in glacial acetic acid containing small amounts of 48% hydrobromic acid for 30–120 min., starting material could likewise be recovered in 40–100% yields. The periods of longer reflux did in addition, however, yield a nonpolar substance which is not the desired XV. Its identity is presently being sought.

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[6] For a comparative study of the ease of reduction of sulfones to sulfides, see F. G. Bordwell and W. H. McKellin, *J. Am. Chem. Soc.*, **73**, 2251 (1951).

[7] Insight into the inferior dienophilic characteristics of the thiete 1,1-dioxides can be gained from the observations that, whereas VIII reacts *instantaneously* in solution with N-phenylmaleimide and 1,4-naphthoquinone,[1] it condenses completely with Ib only after approximately 24 hr. in refluxing benzene. However, in contrast to the ability of the aforementioned adducts to readily revert to their precursors in warm benzene,[1] the adduct IX is stable to these conditions. 1,4-Diphenyl-2,3-isobenzofuran (IV) did not react at an appreciable rate with Ib in refluxing benzene.

[8] M. P. Cava and J. P. Van Meter, *J. Am. Chem. Soc.*, **84**, 2008 (1962).

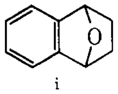
[9] *E.g.*, see L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p. 880.

[10] M. P. Cava, B. Hwang, and J. P. Van Meter, *J. Am. Chem. Soc.*, **85**, 4032 (1963).

[11] By analogy to the work of Cava, *et al.*,[10] the n.m.r. chemical shift of the aromatic protons at C-3 and C-8 of XV should appear considerably upfield from the remainder of the vinyl hydrogens if any double-bond fixation exists.

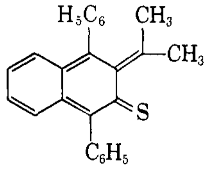
[12] L. F. Fieser and M. J. Haddadin, *J. Am. Chem. Soc.*, **86**, 2081 (1964).

[13] These conditions were similar to those employed by G. Wittig and L. Pohmer [*Ber.*, **89**, 1334 (1956)] in effecting the ready dehydration of i.

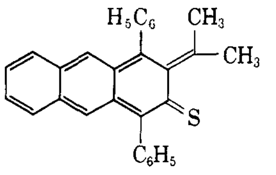


i

The thiete derivatives VIIa and XI are stable substances under normal conditions and have been stored for prolonged periods at room temperature without apparent change. This stability was not unanticipated. Whereas the instability of thiete (II) is presumably due to facile ring opening to thioacrolein, a similar mode of ring cleavage in VIIa and XI would have to yield the thioquinomethylene derivatives XVI and XVII, respectively. This process would be expected to be unfavorable from a thermodynamic point of view. We have obtained no evidence for this phenomenon, except perhaps to note that VIIa melts with decomposition while XI melts with gas evolution and decomposition.

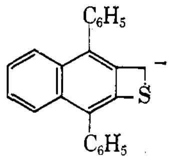


XVI



XVII

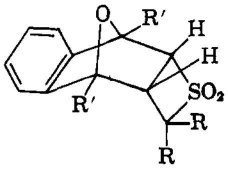
Unfortunately, our present inability to reduce VIb to the corresponding thiete has deterred our anticipated study of the potential aromatic properties of the related anion XVIII.



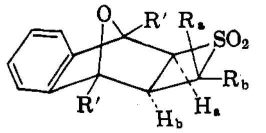
XVIII

Numerous attempts to induce photochemical extrusion of sulfur dioxide from VIa as a means of preparing naphthalenocyclopropane derivatives have shown VIa to be stable under the influence of the common light sources.

Stereochemistry of the Adducts.—The isobenzofuran–thiete sulfone adducts are capable of existing in either of the two possible configurations, XIX and XX. A decision as to whether they possess the *exo* or *endo* configuration might be expected to be readily attainable on the basis of n.m.r. evidence. Thus, Va exhibited doublet resonance lines centered at δ 2.96 (J = 8 c.p.s., H_b) and 4.88 (J = 8 c.p.s., H_a), and singlet peaks at 1.05 (methyl group at R_a) and 1.55 (methyl group at R_b). These data are explainable most readily in terms of the *exo* isomer XX. Accordingly, if the very reasonable assumption is made that the bridgehead phenyl (R′) groups in XX are twisted to minimize steric interactions and are therefore approximately in the plane of the oxygen bridge (see Figure 1), then the strong upfield shift (0.50 p.p.m.) of the axially oriented methyl group (R_a)[14] is readily attributable to the long-range shielding of the bridgehead phenyl substituent.[15] The magnitude of the induced field of the benzene ring has been shown to give rise to appreciable effects as distant as 5–6 Å. from the center of the ring[15]; models indicate that the distance of the axial methyl group from the bridgehead phenyl ring (see Figure 1) lies within this upper limit.



XIX



XX

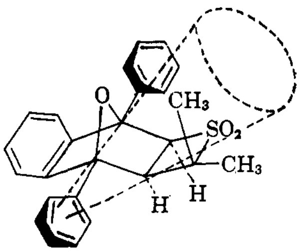


Figure 1.—Spatial distribution of substituents in the adduct VIa showing long-range shielding by the bridgehead phenyl group.

The n.m.r. spectrum of IX (for data, see Experimental) is a near duplicate of that of Va except for the aromatic region, and it therefore follows that IX likewise possesses the *exo* configuration.

It is interesting that the n.m.r. spectrum of XIV also provides strong evidence for the *exo* configuration, but by a rationale differing from that above. Thus, the methyl groups are displayed as singlets (δ 1.58 and 1.62), the cyclobutane protons as *doublets* centered at δ 2.23 and 4.27 (J = 7 c.p.s.), and the bridgehead protons as *singlets* at δ 5.48 and 5.73. That the bridgehead hydrogens are not coupled individually with the neighboring cyclobutane protons is a phenomenon that can be accommodated solely by the *exo* formulation. The relevant dihedral angles are seen from models to be approximately 90° and therefore from expectations based on the Karplus correlation, no spin–spin coupling should be observed. This lack of coupling between *endo* and bridgehead protons has proven general.[16] It should be noted that the chemical shifts of the two methyl groups in XIV, in the absence of the bridgehead phenyl groups, are located in the expected range.[14]

Approaches to Benzothiete Sulfones.—The stability of compounds VI and X prompted an investigation of the possibility of preparing the related benzothiete sulfone XXV. Although the goal was not realized, the recording of our results at the present time may perhaps serve to avoid duplication of effort. The cycloaddition of sulfene, generated from methanesulfonyl chloride and triethylamine,[17] to 1-dimethylaminocyclohexene (XXI) was found to yield the thietane dioxide XXII in 72.8% yield. Quaternization of XXII with methyl iodide, followed by Hofmann elimination, gave rise to the expected bicyclic thiete sulfone XXIV.[18] Thus far, attempts to aromatize XXIV to obtain XXV have not been successful. For example, although XXIV

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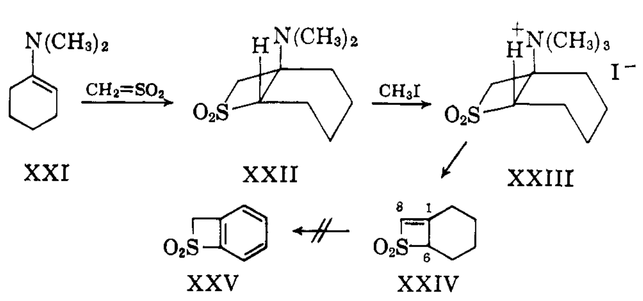
[14] The methyl groups in Ib were observed as a strong singlet at δ 1.63.[3]

[15] For other examples of long-range shielding by the benzene ring, see L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p. 117.

[16] *Cf. inter alia:* W. D. Kumler, J. N. Shoolery, and F. V. Brutcher, Jr., *J. Am. Chem. Soc.*, **80**, 2533 (1958); E. J. Corey, M. Ohno, S. W. Chow, and R. A. Scherrer, *ibid.*, **81**, 6305 (1959); H. E. Simmons, *ibid.*, **83**, 1657 (1961); J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *ibid.*, **85**, 2513 (1963); and J. Meinwald and Y. C. Meinwald, *ibid.*, **85**, 2514 (1963).

[17] For a recent leading reference, see L. A. Paquette, *J. Org. Chem.*, **29**, 2851 (1964).

[18] XXIV has recently been prepared by a similar route: *cf.* D. C. Dittmer and F. A. Davis, *ibid.*, **29**, 3131 (1964). The author wishes to thank Dr. Dittmer for informing him of his synthesis of XXIV prior to publication.



did react with elemental sulfur at approximately 180–200° to produce hydrogen sulfide, no tractable product could be obtained, even when the dehydrogenation was performed in an inert atmosphere. It was concluded that XXV is not stable at this elevated temperature. Furthermore, XXIV can be recovered quantitatively after prolonged reflux periods with chloranil in toluene and *t*-butyl alcohol. N-Bromosuccinimide bromination of XXIV gave rise to a noncrystalline orange oil[19] which when treated without purification with triethylamine in benzene afforded a viscous noncharacterizable red oil and a small quantity of recovered XXIV.

Experimental[20]

2a,3,8,8a-Tetrahydro-2,2-dimethyl-3,8-diphenyl-3,8-epoxy-2H-naphtho[2,3-*b*]thiete 1,1-Dioxide (Va).—A solution of 2.7 g. (0.01 mole) of 1,4-diphenyl-2,3-benzofuran[21] and 1.3 g. (0.01 mole) of 2,2-dimethylthiete 1,1-dioxide[1] in 3 ml. of xylene was refluxed for 24 hr. under an atmosphere of nitrogen. On cooling, a crystalline solid was obtained. Recrystallization of this material from benzene–hexane afforded 3.7 g. (92.5%) of light yellow solid, m.p. 258–259.5°. The analytical sample was obtained as large white prisms after further recrystallization from xylene, m.p. 259–260°, with formation of yellow color (reverse Diels–Alder?).

Anal. Calcd. for $C_{25}H_{22}O_3S$: C, 74.60; H, 5.51; S, 7.97. Found: C, 74.86; H, 5.60; S, 7.83.

2a,3,8,8a-Tetrahydro-3,8-diphenyl-3,8-epoxy-2H-naphtho[2,3-*b*]thiete 1,1-Dioxide (Vb).—A solution of 6.5 g. (0.024 mole) of 1,4-diphenyl-2,3-benzofuran and 2.5 g. (0.024 mole) of thiete 1,1-dioxide[2] in 7 ml. of xylene was refluxed for 24 hr. The cooled solution was treated with 10 ml. of hexane and there precipitated 8.9 g. (98.8%) of crude adduct, m.p. 167–190°. The analytical sample was obtained as a powdery white solid from benzene–hexane, m.p. 216.5–217°.

Anal. Calcd. for $C_{23}H_{18}O_3S$: C, 73.77; H, 4.84; S, 8.56. Found: C, 73.45; H, 5.16; S, 8.35.

2,3-Dimethyl-3,8-diphenyl-2H-naphtho[2,3-*b*]thiete 1,1-Dioxide (VIa).—A mixture of 4.8 g. (0.012 mole) of Va, 30 ml. of glacial acetic acid, and 3 ml. of 48% hydrobromic acid was refluxed for 2 hr. and allowed to cool to room temperature. The precipitated crystals were filtered, washed thoroughly with water, and dried to give 4.45 g. (96.7%) of white crystals, m.p. 228.5–230°. Recrystallization from benzene–hexane afforded pure white crystals: m.p. 229–229.5°; $\lambda_{\max}^{\mathrm{EtOH}}$ 241 mμ (ε 67,200), 310 (10,900), and 336 (6040).

Anal. Calcd. for $C_{25}H_{20}O_2S$: C, 78.09; H, 5.24; S, 8.34; mol. wt., 384. Found: C, 78.26; H, 5.27; S, 8.09; mol. wt., 377 (isothermally determined in $CHCl_3$).

3,8-Diphenyl-2H-naphtho[2,3-*b*]thiete 1,1-Dioxide (VIb).—A mixture of 750 mg. (2.0 mmoles) of Vb and 5 ml. of glacial acetic acid containing 0.5 ml. of 48% hydrobromic acid was refluxed for 1 hr. and cooled. The precipitated solid was filtered, washed with water, and dried. There was obtained 700 mg. (98.6%) of white solid, m.p. 255–256°. The analytical sample was obtained as short white blades from chloroform–hexane: m.p. 255.5–256.5°; $\lambda_{\max}$ 242 mμ (ε 62,800), 315 (14,300), and 338 (11,200).

Anal. Calcd. for $C_{23}H_{16}O_2S$: C, 77.50; H, 4.53; S, 9.00. Found: C, 77.71; H, 4.52; S, 8.83.

The chemical shift of the α-sulfonyl protons (singlet) was observed at δ 5.09.

2,2-Dimethyl-3,8-diphenyl-2H-naphtho[2,3-*b*]thiete (VIIa).—To a slurry of 1.0 g. (0.026 mole) of lithium aluminum hydride in 50 ml. of ether was slowly added 1.9 g. (0.005 mole) of VIa in small portions. A vigorous reaction was observed as the sulfone entered the slurry. After the completion of the addition, the mixture was stirred under reflux for 0.5 hr., cooled, and treated with 1 ml. of water, 1 ml. of 25% sodium hydroxide solution, and 3 ml. of water in that order. The precipitated salts were filtered and washed thoroughly with methylene chloride. The combined filtrates were evaporated to give 1.2 g. (68.2%) of white solid, m.p. 171.5–176°. Recrystallization of this material from benzene–hexane gave pure fluffy white needles: m.p. 179°; $\lambda_{\max}^{\mathrm{EtOH}}$ 221 mμ (ε 42,100), 232 (39,000), 258 (34,800), and 296 (10,350).

Anal. Calcd. for $C_{25}H_{20}S$: C, 85.18; H, 5.72. Found: C, 85.43; H, 5.82.

Oxidation of VIIa to VIa.—To a cold solution of 352 mg. (1.0 mmole) of VIIa in 15 ml. of chloroform was added in portions 380 mg. (2.2 mmoles) of *m*-chloroperbenzoic acid. The solution was stirred overnight at room temperature, washed with saturated aqueous sodium bicarbonate solutino, dried, filtered, and evaporated. The crystalline residue was dissolved in benzene and filtered to remove a small amount of insoluble material. The filtrate was treated with hexane and cooled to give 162 mg. of VIa, m.p. 222–224°; the infrared spectrum of this material was superimposable on that of an authentic sample.

Lithium Aluminum Hydride Reduction of VIb.—To a stirred slurry of 1.0 g. (0.026 mole) of lithium aluminum hydride in 50 ml. of ether was added 1.8 g. (0.005 mole) of VIb in small portions. An immediate exothermic reaction occurred with each addition. When the addition was completed, the mixture was refluxed for 0.5 hr., cooled, and decomposed as above. Evaporation of the filtrate afforded an oil which was crystallized from benzene–hexane to give 710 mg. (43.6%) of white solid, m.p. 140–142°. Further recrystallization from benzene–hexane afforded pure mercaptan VIIb as powdery white crystals, m.p. 143.5–144.5°, $\lambda_{\max}^{\mathrm{EtOH}}$ 237 mμ (ε 57,000) and 296 mμ (ε 12,150).

Anal. Calcd. for $C_{23}H_{18}S$: C, 84.62; H, 5.56. Found: C, 84.44; H, 5.58.

2a,3,10,10a-Tetrahydro-2,2-dimethyl-3,10-diphenyl-3,10-epoxy-2H-anthra[2,3-*b*]thiete 1,1-Dioxide (IX).—A solution of 1.6 g. (5.0 mmoles) of 1,3-diphenylnaphtho[2,3-*b*]furan (VIII)[8] and 0.73 g. (5.5 mmoles) of 2,2-dimethylthiete 1,1-dioxide in 10 ml. of benzene was refluxed on a steam bath under a nitrogen atmosphere for 24 hr. The hot solution was treated with hexane to the cloud point and allowed to cool. There was obtained 2.0 g. (91%) of white solid, m.p. 280–284°. Three recrystallizations of this material from benzene–hexane gave pure white prisms, m.p. 297.5–298.5°.

Anal. Calcd. for $C_{29}H_{24}O_3S$: C, 76.96; H, 5.35; S, 7.09. Found: C, 77.32; H, 5.59; S, 6.87.

The n.m.r. spectrum of IX displayed, in addition to the complex lines of the aromatic region, singlet peaks for the methyl groups at δ 1.08 and 1.57 and doublet lines (J = 8 c.p.s.) for the cyclobutane protons centered at 3.02 and 4.94.

2,2-Dimethyl-3,10-diphenyl-2H-anthra[2,3-*b*]thiete 1,1-Dioxide (X).—A mixture of 452 mg. (1.0 mmole) of IX and 3 ml. of glacial acetic acid containing 5 drops of 48% hydrobromic acid was heated under reflux for 1.5 hr. After cooling the mixture, the precipitated solid was filtered, washed thoroughly with water, and dried. There was obtained 430 mg. (100%) of yellow solid, m.p. 309–311°. Pure product was obtained as pale yellow crystals from benzene–hexane, m.p. 310–311°.

Anal. Calcd. for $C_{29}H_{22}O_2S$: C, 80.15; H, 5.10; S, 7.38. Found: C, 80.25; H, 5.22; S, 7.06.

In the n.m.r., the methyl groups of X comprised a singlet located at δ 1.68.

2,2-Dimethyl-3,10-diphenyl-2H-anthra[2,3-*b*]thiete (XI).—To a stirred slurry of 500 mg. of lithium aluminum hydride in 25 ml. of anhydrous ether was added 600 mg. (1.38 mmoles) of X in several portions. The mixture was refluxed with stirring for 1 hr. and was worked up as described above to give 500 mg. (90%) of a pale yellow solid, m.p. 105–110°. Pure product was obtained as yellow prisms after recrystallization from benzene–hexane, m.p. 128–130° (gas evolution).

Anal. Calcd. for $C_{29}H_{22}S$: C, 86.52; H, 5.51. Found: C, 86.52; H, 5.55.

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(19) Succinimide was also isolated in 95.7% yield.

(20) Melting points and boiling points are uncorrected. The n.m.r. spectra were obtained in deuteriochloroform with a Varian A-60 spectrometer utilizing tetramethylsilane as internal standard (TMS = δ 0). Ultraviolet spectra were determined in 95% ethanol on a Cary 14 recording spectrometer.

(21) M. S. Newman, *J. Org. Chem.*, **26**, 2630 (1961).

In the n.m.r. spectrum, the methyl groups of XI comprised a singlet located at δ 1.84.

2a,3,8,8a-Tetrahydro-2,2-dimethyl-3,8-epoxy-2H-naphtho[2,3-*b*]thiete 1,1-Dioxide (XIV).—A solution of 13.3 g. (0.025 mole) of XII[12] and 2.6 g. (0.02 mole) of 2,2-dimethylthiete 1,1-dioxide in 75 ml. of diglyme was heated under reflux with stirring for 16 hr. The cooled solution was evaporated under reduced pressure until a solid began to crystallize. The crude mixture was dissolved in benzene and chromatographed on Woelm neutral alumina. Elution with benzene–hexane (4:1) gave 9.55 g. (100%) of 1,2,3,4-tetraphenylbenzene, m.p. 188–190°. Elution with benzene-methanol (9:1) gave two fractions, m.p. 206–208° and m.p. 193–197°, weighing a total of 4.90 g. (98% yield). Pure adduct was obtained as white prisms from benzene, m.p. 207–208°.

Anal. Calcd. for $C_{13}H_{14}O_3S$: C, 62.37; H, 5.64; S, 12.81. Found: C, 62.13; H, 5.71; S, 12.83.

1-Dimethylamino-7-thiabicyclo[4.2.0]octane 7,7-Dioxide (XII).—To a stirred solution of 25.0 g. (0.20 mole) of 1-dimethylaminocyclohexene (XXI)[22] and 20.2 g. (0.20 mole) of triethylamine in 150 ml. of dioxane was slowly added dropwise 22.9 g. (0.20 mole) of methanesulfonyl chloride with external cooling to maintain the temperature at 30–40°. The entire procedure was conducted in a nitrogen atmosphere. Triethylamine hydrochloride began to precipitate from solution almost immediately. After standing at room temperature for 48 hr., the mixture was filtered, the salts were washed with a small additional amount of dioxane, and the filtrate was evaporated under reduced pressure. The resulting brown oil was chromatographed on Woelm neutral alumina; elution with ether-hexane (1:1) afforded 29.6 g. (72.8%) of an almost colorless oil.

A sample of this material was converted to its perchlorate salt in the usual manner, fat white blades from ethanol-ether, m.p. 235–236°.

Anal. Calcd. for $C_9H_{18}ClNO_6S$: C, 35.58; H, 5.97; N, 4.61. Found: C, 35.76; H, 6.09; N, 4.52.

A sample of the pure perchlorate was dissolved in water and the solution was made basic with concentrated ammonium hydroxide. Extraction with chloroform and molecular distillation gave a colorless oil, $n^{27.5}D$ 1.5120.

Trimethyl 7-Thiabicyclo[4.2.0]oct-1-yl Ammonium Iodide 7,7-Dioxide (XXIII).—A solution of 35.4 g. (0.174 mole) of XXII and 71 g. (0.50 mole) of methyl iodide in 300 ml. of ethanol was heated on a steam bath for 1.5 hr. and allowed to stand overnight at room temperature. The precipitated solid was filtered and dried to give 48.2 g. of methiodide, m.p. 204–205°. From the mother liquors, there was obtained an additional 4.4 g. (total yield, 87.4%) of white solid, m.p. 198–200°. Recrystallization from aqueous ethanol–ether gave pure XXIII, m.p. 241° dec.

Anal. Calcd. for $C_{10}H_{20}INO_2S$: C, 34.79; H, 5.84; N, 4.06. Found: C, 34.77; H, 5.92; N, 3.98.

7-Thiabicyclo[4.2.0]oct-8-ene 7,7-Dioxide (XXIV).—A warm solution (warmed for solubility reasons) of 10.4 g. (0.030 mole) of XXIII in 100 ml. of water was eluted through a column of Amberlite IRA-400 in its basic form until the eluates were no longer alkaline. Approximately 800 ml. of solution was collected. This aqueous solution was placed on a rotary evaporator at 35–40° for 30 min. to remove the major portion of the trimethylamine. The aqueous solution was extracted with chloroform and the combined organic layers were dried, filtered, and evaporated to give 4.4 g. (93.6%) of a colorless oil which rapidly crystallized, m.p. 67–72°. Recrystallization from ether and sublimation gave pure white solid, m.p. 89.5–90.5°.[23]

Anal. Calcd. for $C_7H_{10}O_2S$: C, 53.13; H, 6.37; S, 20.27. Found: C, 53.17; H, 6.40; S, 20.54.

The n.m.r. spectrum of XXIV showed a complex set of signals centered at δ 4.52 for the 6-proton and a doublet for the vinyl hydrogen at 6.32. The olefinic proton is coupled by slightly less than 1 cycle with the 6-proton across the ring.[24]

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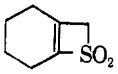
[22] E. P. Blanchard, Jr., *J. Org. Chem.*, **28**, 1397 (1963).

[23] N.m.r. examination of the mother liquors indicated that a small amount of a second component, probably ii, was present in the crude product. We have failed in our attempts to isolate this substance in a pure state, *i.e.*, free of XXIV.



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[24] Compare the spectrum of thiete sulfone (Ia).[3]

Sulfinate Esters. I. Their Preparation and Some Properties[1,2]

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Alkane- and arenesulfinate esters are made available for further study by a convenient new procedure. The synthesis involves converting a mercaptan, thiophenol, or disulfide to a sulfinyl chloride, which, without isolation, is caused to react with the appropriate alcohol. The crude esters thus prepared may be freed from sulfonyl chloride contaminants by treatment with an aromatic amine. Methyl methanesulfinate is slowly hydrolyzed by hot water, more rapidly in acid solution, and with great speed in the presence of alkali. It reacts readily with chlorine or bromine to form the corresponding methanesulfonyl and methyl halides. It also reacts with methylsulfur trichloride to form methyl chloride, methanesulfonyl chloride, and other products resulting from the secondary reaction of methanesulfenyl chloride with the ester.

The availability of a convenient method for preparing sulfinyl chlorides[3] has led us to investigate the preparation of sulfinate esters. These compounds have been prepared previously by a variety of methods, but that most commonly used is the reaction of an alcohol with a sulfinyl chloride. This is the method of choice, especially in view of the ease with which sulfinyl chlorides can be prepared.

Our early attempts to prepare esters by this method gave products which were contaminated with chlorine-containing impurities. These impurities could not be removed by fractional distillation and they seemed to be more resistant to hydrolysis than the esters themselves. The contaminants were finally identified as sulfonyl chlorides present in the sulfinyl chlorides used. In a recent Note[4] we pointed out that sulfinyl chlorides tend to disproportionate into sulfonyl and sulfenyl

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[1] Some of the esters here reported were prepared by Donald A. Koop, using conventional methods, for a thesis submitted in partial fulfillment of the requirements for the Ph.D., University of Maine, 1962.

[2] The following undergraduate students have assisted with experimental details of the work described: Stephen M. Belanger, Miriam L. Douglass, Thomas A. Foley, Alice L. Norton, and Judith A. Stearns.

[3] I. B. Douglass, B. S. Farah, and E. G. Thomas, *J. Org. Chem.*, **26**, 1996 (1961); *Org. Syn.*, **40**, 62 (1960).

[4] I. B. Douglass and D. A. Koop, *J. Org. Chem.*, **29**, 951 (1964).