90% yield) was isolated: nmr[15] ($CDCl_3$) τ 2.81 (10 H s), 6.27–6.61 (2 H m) and 7.52–8.05 (4 H m).

Desulfurization of Compound 4.—Compound 4 (1.7 g, 0.0063 mol) was refluxed with about 4 g of Raney Ni W2 slurry in benzene for 4 hr. After filtration and evaporation of the benzene, 1.1 g of an oil was isolated. Analysis by glpc on columns A, B and C, using internal standards, showed that the mixture contained *trans*-1,2-diphenylcyclobutane (7), DL- and *meso*-2,3-diphenylbutane, and 1,4-diphenylbutane (6) in 62%, 27%, and 11% yield respectively. Using column C, *trans*-1,2-diphenylcyclobutane (7) was collected and the nmr spectrum obtained was identical with that of authentic material.

1,3-Diphenyl-3-butanol.—This compound was prepared by adding 12 g (0.10 mol) of acetophenone to an ether solution of Grignard reagent made from 27.7 g (0.15 mol) of β-phenylylthyl bromide and 5 g of magnesium. The reaction mixture was refluxed for 2 hr and worked up in the usual way. The crude alcohol was distilled at 136° (0.25 mm), giving on cooling an amorphous solid (12 g). The infrared spectrum showed the presence of an OH group and the absence of a carbonyl and bromide groups. This material was used without further purification.

1,3-Diphenylbutane (9).—1,3-Diphenyl-3-butanol (7.6 g, 0.034 mol) in 150 ml of glacial acetic acid was mixed with 0.1 g of 10% Pd–C at 45 psi of hydrogen for 15 hr. After filtration and evaporation of the acetic acid the mixture was chromatographed over silica gel with petroleum ether–CCl_4 (1:1) graduated slowly to CCl_4, affording 1,3-diphenylbutane (9) (3.5 g, 50% yield). The material was found to be glpc pure (column A, B, and C): n^{20} 1.5520; lit.[24] $n^{20}D$ 1.5525); nmr[15] τ 2.80–2.91 (10 H, m), 7.18–7.69 (3 H, m), 7.98–8.40 (2 H, m), and 8.80 (3 H, d).

Desulfurization of Compound 5.—Compound 5 (1.0 g) was refluxed with ~3 g of Raney nickel W2 in benzene for 15 hr. Filtration and evaporation gave 0.5 g (65%) of an oil and 0.3 g of 5. Analysis by glpc showed two compounds were present. The first fraction was identified as 1,3-diphenylbutane by comparing the retention times with an authentic sample on column A, B, and C. About 50 mg of the second fraction was collected from glpc column A and was identified as *trans*-1,3-diphenylcyclobutane: mass spectra (molecular ion) *m/e* 208; nmr τ 2.82 (10 H, s), 6.56 (2 H, p, J = 8.0 Hz), 7.60 (4 H, t, J = 8.0 Hz).

Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74; exact mass measurement of molecular ion, 208.1245. Found: C, 92.14; H, 7.55; exact mass measurement of molecular ion, 208.1252.

Attempted Epimimerization of Dimers 2 and 3.—Compounds 2 and 3 (150 mg) were each refluxed 12 hr with 1.2 g of sodium methoxide in 25 ml of methanol. Dimers 2 and 3 were recovered unchanged (glpc, column A; melting point and mixture melting point).

Registry No.—1, 825-44-5; 2, 25558-18-3; 3, 25558-19-4; 4, 25558-20-7; 5, 25558-21-8; 7, 7694-31-7; 9 (*trans*), 25558-23-0; bis(ethylene dithioketal) of dibenzoylethane, 25557-76-0.

Acknowledgments.—We wish to thank the National Research Council of Canada and the Petroleum Research Fund administered by the American Chemical Society for support of this work. Helpful discussions with Professors P. G. Farrell, D. F. R. Gilson, and J. P. Snyder are acknowledged. We also wish to thank Dr. Tony Davis for his generous help in running the Raman spectra.

The Chemistry of Small-Ring Sulfur Compounds. Thietanes and 1,2-Dithiolanes[1]

DAVID N. HARPP AND JOHN G. GLEASON[2]

Department of Chemistry, McGill University, Montreal, Canada

Received January 19, 1970

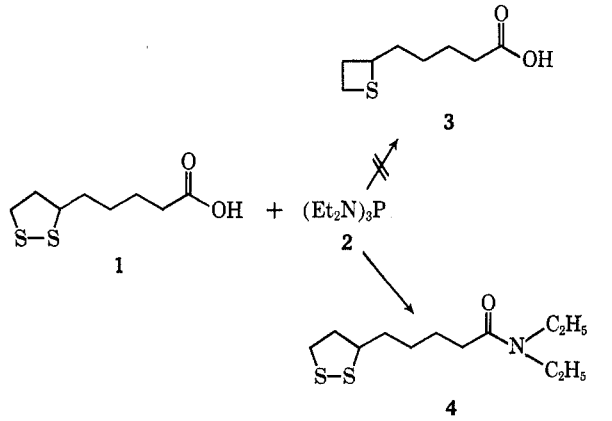
A variety of 1,2-dithiolanes undergo facile desulfurization with tris(diethylamino)phosphine (2) to give thietanes in good yield. By this method, the tetrahydropyranyl ester of α-lipoic acid afforded (after hydrolysis) thietane-2-valeric acid (3). 3H-1,2-Benzodithiole (17) did not give benzo[*b*]thiete (18) on desulfurization, but rather formed the dimeric sulfide (19). The tricyclic steroid 22 underwent rearrangement on desulfurization to afford the steroidal phosphine 25. The use of iodine–triethylamine in a new, modified procedure for the oxidation of propane-1,3-dithiols was found to be an excellent method for the preparation of 1,2-dithiolanes in high yield.

As part of our study on the selective desulfurization[3] of disulfides and related compounds, it occurred to us

$$R{-}S{-}S{-}R' + PR_3 \longrightarrow R{-}S{-}R' + S{=}PR_3$$

that the use of aminophosphines for the desulfurization of 5-membered disulfide rings (dithiolanes) could provide a new synthetic approach to thietanes.[4] Accordingly, the desulfurization of several dithiolanes was attempted and the results are summarized in Table I.

While the dithiolane, α-lipoic acid (1), a coenzyme in the biological oxidation of pyruvic acid, is readily available from natural sources, the corresponding thietane derivative, thietane-2-valeric acid (3), has only recently been prepared *via* a multistep synthesis.[5] However, attempts to obtain this derivative by the desulfurization of α-lipoic acid were unsuccessful. When α-lipoic acid (1) was treated with tris(diethylamino)-phosphine (2), no thietane derivative (3) was obtained. The main product, isolated in 78% yield, was the di-



(1) Organic Sulfur Chemistry. III. For part II, see D. N. Harpp and J. G. Gleason, *Tetrahedron Lett.*, 1447 (1969).

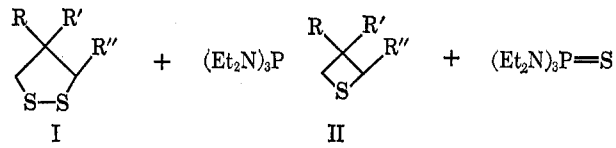
(2) Holder of an NRCC Studentship 1968–1969.

(3) D. N. Harpp, J. G. Gleason, and J. P. Snyder, *J. Amer. Chem. Soc.*, **90**, 4181 (1968).

(4) Although other methods for the synthesis of thietanes are available, the formation of polymer in these reactions is often competitive; see M. Sander, *Chem. Rev.*, **66**, 341 (1966); S. Ogawa, M. Morita, K. Donome, and K. Fujisawa, Japanese Patent 23937 (1967) [*Chem. Abstr.*, **69**, 35919 (1968)].

(5) (a) M. W. Bullock, U. S. Patent 2,788,355 (1957); *Chem. Abstr.*, **51**, 13909 (1957). (b) Sh. Yurugi, H. Yonemoto, and T. Fushimi, *Yakugaku Zasshi*, **80**, 169b (1960); *Chem. Abstr.*, **55**, 12288 (1961). (c) Sh. Yurugi and T. Fushimi, Japanese Patent 6532 (1962); *Chem. Abstr.*, **58**, 13916 (1963).

TABLE I



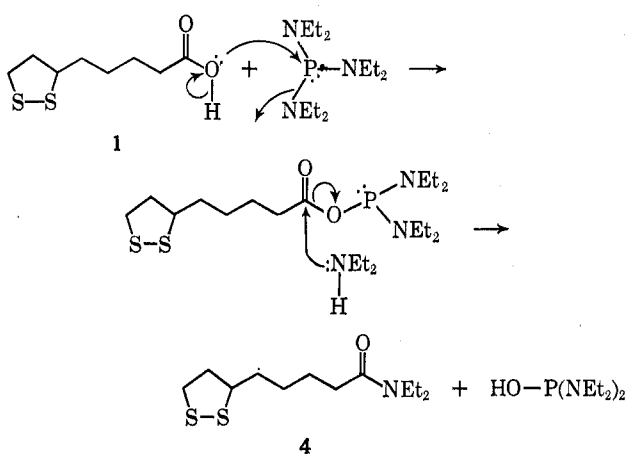
I II

Disulfide	R	R′	R″	Reaction time,[a] hr	Concentration of I, mol. l. $^{-1}$	Yield of II,[b] %
11	H	H	H	432	0.11	82[c]
12	C_6H_5	H	H	4[d]	0.22	87
16	=O		H	0.1	0.2	Polymer
5	H	H	$(CH_2)_4CONHC_6H_5$	1	0.4	64
7	H	H	$(CH_2)_4COOTHP$[e]	24[f,g]	0.8	80

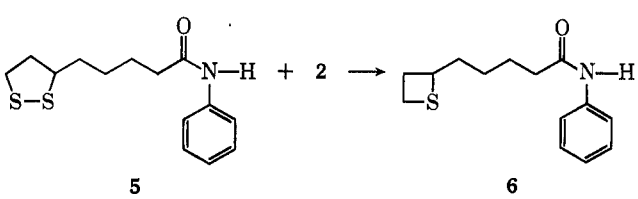
[a] In benzene solvent at room temperature, unless otherwise noted. [b] Yields reported are of crystallized or distilled thietane. [c] Isolated as mercuric chloride adduct. [d] In refluxing benzene. [e] THP = tetrahydropyran. [f] In ethyl acetate. [g] This long reaction time is probably unnecessary.

ethylamide of α-lipoic acid (**4**). The formation of amides from the reaction of carboxylic acids with alkylaminophosphines has been reported.[6] This reaction presumably involves displacement of the dialkylamine moiety by the carboxylic acid; subsequent rearrangement (Scheme I) affords the amide. When the carboxylic acid was masked by suitable protecting groups such as amides or esters, desulfurization proceeded unhindered. The anilide derivative of **1** was prepared; after 1 hr of stirring with the aminophosphine **2**, the yellow color of the disulfide was completely discharged and the absorption maxima at 332 mμ (characteristic of 1,2-dithiolanes)[7] disappeared. A new compound, **6**, mp 56–58°, was obtained in 68% yield (Table I).

SCHEME I



1 4



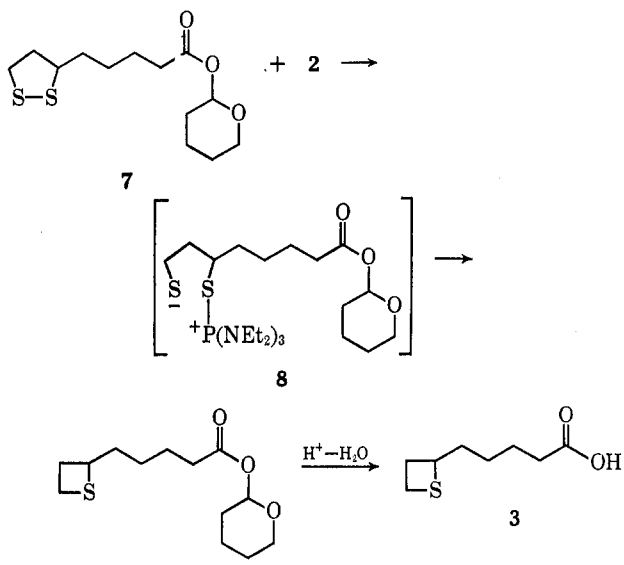
5 6

While the nmr and ir spectra of **6** were very similar to those of **5**, the mass spectrum exhibited a parent ion at *m/e* 249.1180 (calcd for $C_{14}H_{19}NOS$: 249.1198) and a fragmentation pattern consistent with the assigned thietane structure.

(6) R. Burgada, *Ann. Chim. (Paris)*, 347 (1963).

(7) G. Bergson, G. Claeson, and L. Schotte, *Acta Chem. Scand.*, **16**, 1159 (1962).

Similarly, the tetrahydropyranyl ester **7** was desulfurized to afford, after hydrolysis, thietane (**3**) in 82% yield. This desulfurization may proceed *via* an internal phosphonium salt of the type **8**, although other intermediates may be present (*vide infra*).



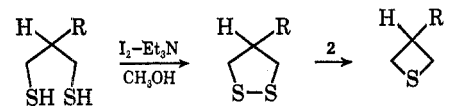
In order to examine the generality of this novel ring contraction, we required a convenient method of preparing 1,2-dithiolanes. Examination of the literature revealed that, except for a few alkyl-substituted dithiolanes, oxidation of bisthiols leads to extensive polymerization.[8] We have found that the use of triethylamine to maintain neutral conditions during iodometric oxidation of bisthiols greatly reduces polymerization. Thus, slow addition of a solution of triethylamine and bisthiol to an iodine solution provides both neutrality and high dilution, the latter being desirable for intramolecular cyclization of bisthiols. This procedure has permitted us to prepare a wide variety of cyclic disulfides in high yield.[9] This method is rapid and appears to be general.

Thus, the oxidation of 1,3-propanedithiol (**9**) with iodine in the presence of triethylamine followed by extraction with benzene afforded a solution of 1,2-dithiolane (**11**), free of polymer. Desulfurization of a 0.1 *M*

(8) For a general review on the preparation of 1,2-dithiolanes, see D. S. Breslow and H. Skolnik, "The Chemistry of Heterocyclic Compounds," Part I, Interscience, New York, N. Y., 1966, pp 313–345.

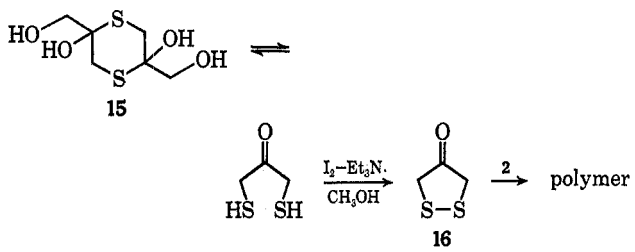
(9) Using this technique, five- to eight-membered cyclic disulfides, as well as a wide variety of acyclic disulfides, have been prepared in high yields.

solution of **11** provided thietane **13**, isolated as its mercuric chloride adduct, in 82% yield. Similarly, the



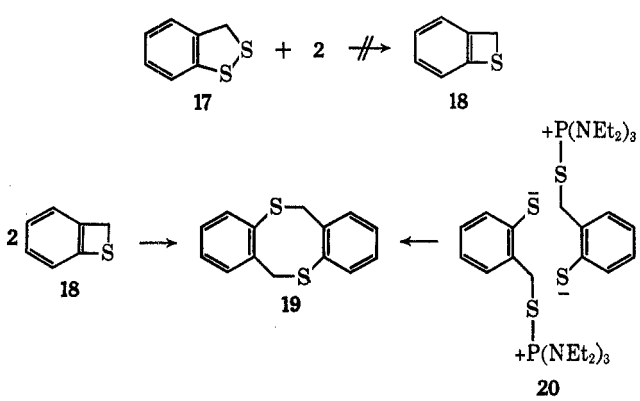
9, R = H; **10**, R = C_6H_5 **11**, R = H; **12**, R = C_6H_5 **13**, R = H; **14**, R = C_6H_5

dimer of dimercaptoacetone[10] (**15**) was oxidized to the corresponding disulfide **16**. Addition of phosphine,



however, effected immediate polymerization of this material and no characterizable compounds were isolated.

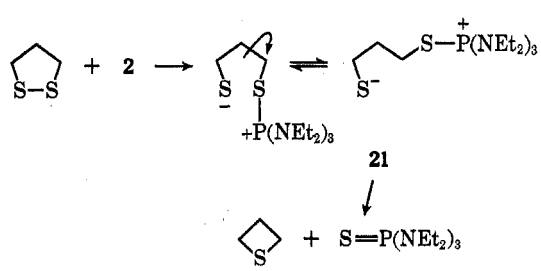
In addition, 4-phenyl-1,2-dithiolane (**12**) and 3H-1,2-benzodithiole (**17**) were readily prepared by the above method. Desulfurization of disulfide **12** gave 3-phenylthietane (**14**) in 85% yield. We had hoped that desulfurization of **17** would provide a simple synthesis of the unknown heterocycle, 2H-benzo[*b*]thiete (**18**). However, the only isolable product was the di-



mer of benzothiete, 6H,12H-dibenzo[*b*,*f*][1,5]dithioocin (**19**). This material could arise from either dimerization of benzothiete **18** or the phosphonium salt **20**.

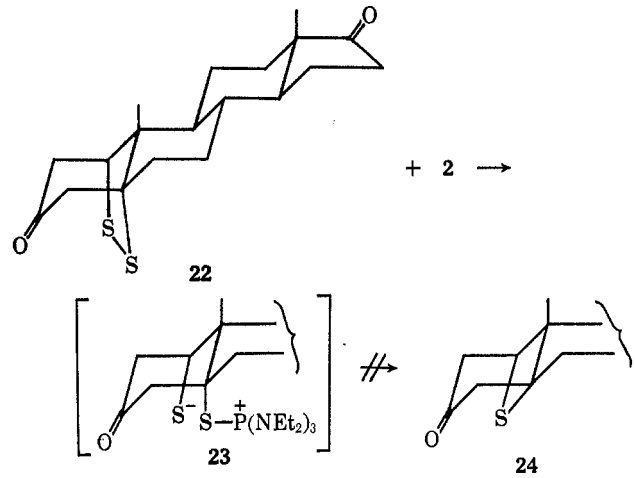
We have suggested[3] (Scheme II) that these desulfurization reactions proceed *via* an internal phospho-

SCHEME II

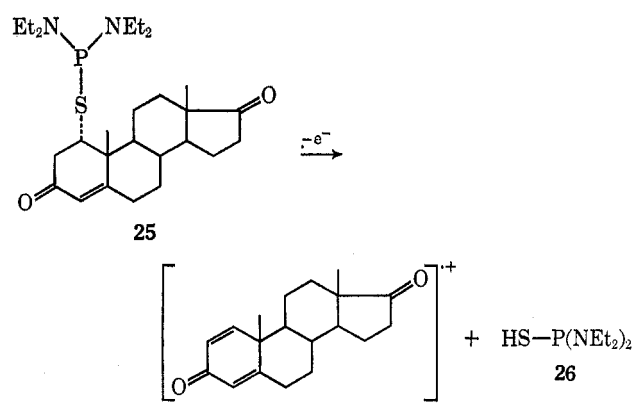


(10) L. Schotte, *Ark. Kemi*, **5**, 533 (1952).

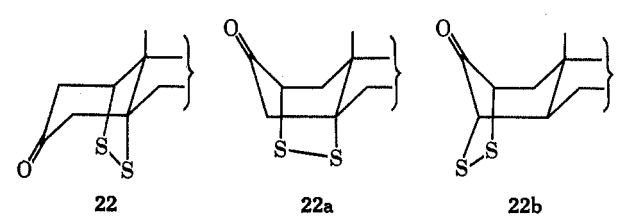
nium salt such as **21**. Of considerable interest is the desulfurization of the novel steroidal disulfide **22**[11,12] as rotation and subsequent SN2[13] decomposition are not



possible. Treatment of this disulfide with aminophosphine **2** did not provide either **23** or **24** but rather a new compound, **25**, $C_{27}H_{45}N_2O_2PS$ (exact mass calcd for $C_{27}H_{45}N_2O_2PS$, 492.2939; found, 492.2960), mp 200–201°. The presence of the Δ(4–5)-androstane-1,17-dione ring system was indicated by the infrared spectrum (1740 and 1670 cm^{-1}) and ultraviolet spectrum (λ_{max}^{MeOH} 228 mμ, ε 650) and the presence of only one olefinic proton at τ 4.2 in the nmr spectrum. The loss of a bis(dimethylamino)phosphine sulfide moiety **26** upon electron impact permitted the assignment of structure **25** for this compound.



(11) The synthesis of **22** has been reported;[12] however the presence of a 1,5 disulfide bridge was not rigorously demonstrated. A 100-MHz nmr double resonance experiment was used to show that the methine proton α to the disulfide (a quartet at τ 6.15) is part of an ABX spectrum where the AB portion is centered at τ 7.1. The chemical shift of the methylene (AB) portion of the ABX system rules out the possiblity of a 2,5 disulfide (**22a**) or 2,4 disulfide (**22b**) bridge.

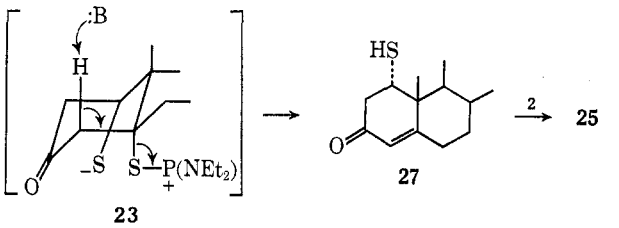


(12) R. C. Tweit and R. M. Dodson, *J. Amer. Chem. Soc.*, **81**, 4409 (1959).

(13) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, pp 294–296.

A mechanistic rationalization for the formation of **25** is depicted in Scheme III. The phosphonium salt **23**

SCHEME III



initially formed may undergo an elimination reaction to afford the thiol **27**. This thiol would then react[14] with the aminophosphine to provide **25**.

This interesting rearrangement might well be useful in preparing a variety of 1-α-androstane derivatives.

Experimental Section[15]

Tris(diethylamino)phosphine (2).—The procedure used was a modification of the method of Mark.[16] Thus, a solution of 43.0 g (3.4 mmol) of phosphorus trichloride in 3 l. of anhydrous ether was flushed with nitrogen and cooled to 10°; 150 g (2.06 mol) of diethylamine was added dropwise with vigorous stirring over 2 hr. The resulting suspension was stirred overnight, then refluxed for 0.5 hr. After cooling, the mixture was filtered and the filtrate evaporated to dryness. The residue was dissolved in 200 ml of hexane and treated with ac tivated charcoal, and the hexane removed under vacuum. The resulting oil was fractionated in vacuum to afford 50.2 g of **2** (65%), bp 80–84° (0.5 mm), n^{30}D 1.4695 (lit.[17] n^{30}D 1.465).

1,2-Dithiolane-3-valeric Acid Diethylamide (4).—A solution of 0.412 g (2.0 mmol) of **1** and 0.55 g (2.2 mmol) of tris(diethylamino) phosphine (**2**) in 2.5 ml of dry benzene was stirred for 4 hr. An oil which formed immediately upon addition of the phosphine slowly redissolved on stirring and a solid precipitated. The solvent was removed under vacuum and the residue was chromatographed over silica gel. Elution with methylene chloride afforded the diethylamide as a yellow oil, 0.42 g (80%), homogeneous on thin layer and gas chromatography: ir (film) 1640 cm^{-1} (tertiary amide); nmr (CCl_4) τ 6.70 (quartet, J = 7 Hz), 8.90 (triplet, J = 7 Hz), both observable above a broad envelope; mass spectrum parent ion m/e 261, fragments of 58, 115, 72 (Et_2N^+), 100, 128, 189, 228.

***dl*-1-2-Dithiolane-3-valeric Acid Anilide (5).**—α-Lipoic acid (**1**) was converted to its anilide (**5**) (aniline dicyclohexylcarbodiimide) in 75% yield: mp 69–71° (lit.[18] mp 72–73°); λ_{max}^{EtOH} 242 mμ (ϵ 30,200), 332 (363); ir (KBr) 3290 (NH), 1660 (amide I), 1540 (amide II), 690 cm^{-1} (aromatic); nmr ($CDCl_3$) τ 1.93 (broad singlet, 1 H, NH), 2.7 (complex multiplet, 5 H, aromatic), 6.48 (multiplet, 1 H, methine), 6.9 (multiplet, 2 H, $-CH_2-$S), broad multiplets centered at τ 7.8 and 8.5 accounting for remaining aliphatic protons; mass spectrum (150°), molecular ion at m/e 281.0919 (calcd for $C_{14}H_{19}NOS_2$: 281.0908), fragments of m/e 93, 135, 41, 55, 56, 148, 155.

Thietane-2-valeric Acid Anilide (6).—A solution of 1.129 g (4 mmol) of the anilide **5** and 1.10 g (4.4 mmol) of tris(diethylamino)phosphine (**2**) in 10 ml of benzene was stirred for 1 hr during which time the yellow color was discharged and the uv maximum at 332 mμ disappeared. The reaction mixture was allowed to stand overnight, the solvent removed under vacuum, and the residue chromatographed over Florisil. The phosphine sulfide was eluted with 1:1 methylene chloride-petroleum ether (bp 60–80°). Elution with methylene chloride afforded 0.634 g (64%) of colorless crystals, mp 51–54°, which after two crystallizations from cyclohexane afforded an analytical sample: mp 55–57°; ir (KBr) 3290 (NH), 1660 (C=O), 1540 (amide II), 760 and 690 cm^{-1} (aromatic); λ_{max}^{MeOH} 242 mμ (ϵ 24,900); nmr (CCl_4) broad multiplet at τ 2.7 (6 H, aromatic + NH) and aliphatic protons from 6.5–9.0; mass spectrum (150°), molecular ion at m/e 249.1180, (Calcd for $C_{14}H_{19}NOS$: 249.1198), fragments of m/e 93, 135, 41, 129.

Anal. Calcd for $C_{14}H_{19}NOS$: C, 67.44; H, 7.68; N, 5.62; S, 12.86. Found: C, 67.47; H, 7.64; N, 5.47; S, 12.85.

Thietane-2-valeric Acid (3).—A solution of 4.04 g (20 mmol) of **1** in 20 ml of dihydropyran was refluxed 3 hr. The solvent was removed under vacuum and the residue dissolved in 25 ml of ethyl acetate containing 5.5 g (22 mmol) of tris(diethylamino)phosphine (**2**). After stirring at room temperature for 24 hr, the solvent was removed under vacuum; 25 ml of dioxane and 25 ml of concentrated HCl were added; the solution was stirred for 18 hr. The solution was diluted with 200 ml of water and extracted with ether; the ethereal layer was extracted with 100 ml of a 5% sodium bicarbonate solution; the bicarbonate solution was carefully acidified and extracted with ether. After drying over anhydrous sodium sulfate, the ethereal solution was evaporated to dryness under vacuum to yield 2.82 g (80%) of **3** as a viscous yellow oil: bp 143° (0.1 mm); n^{27}D 1.5155; ir (film) 3020 (broad, OH), 1708 cm^{-1} (COOH); nmr (CCl_4) τ −1.63 (singlet, 1 H, COOH), multiplet at 6.0–9.2 accounting for 13 protons; mass spectrum (50°), parent ion at m/e 174, fragments of m/e 87, 41, 45, 55, 73, 80. The acid **3** was characterized as its anilide **6** (aniline, dicyclohexylcarbodiimide), mp 55–57°. This material was identical in all respects with the sample prepared by direct desulfurization of **5**.

1,2-Dithiolan-4-one (16).—A solution of 1.22 g (10 mmol) of dimercaptoacetone[19] (as its dimer) and 2.10 g (20 mmol) of triethylamine in 25 ml of methanol was added dropwise to a solution of 2.66 g (10.5 mmol) of iodine in 50 ml of methanol. The reaction mixture was filtered to remove 200 mg of polymer and the filtrate was diluted with 200 ml of benzene. After decolorization with a 10% solution of sodium thiosulfate and several washings with water, the solution was dried over magnesium sulfate and concentrated under vacuum to 50 ml to afford a golden yellow solution[19] of 1,2-dithiolan-4-one in benzene: nmr (benzene) τ 7.15 (singlet); $\lambda_{max}^{benzene}$ 340 mμ (sh) (ϵ 50), 325 (65), 312 (74), 300 (80).

Desulfurization of 1,2-Dithiolan-4-one (16).—To 50 ml of the above solution of **16** was added 2.50 g (10 mmol) of tris(diethylamino)phosphine (**2**). Immediately upon addition of the phosphine, the color changed from yellow to dark brown and a dark brown tar separated out of the solution. This tar was insoluble in all organic solvents tried.

1,2-Dithiolane (11).—A solution of 1.06 g (10 mmol) of 1,3-propanedithiol and 2.10 g (20 mmol) of triethylamine in 10 ml of methanol was added dropwise over 15 min to a solution of 2.66 g (10.5 mmol) of iodine in 25 ml of methanol. The resulting solution was diluted with 250 ml of benzene, decolorized with a 10% solution of sodium thiosulfate, washed with water, dried over magnesium sulfate, and concentrated under vacuum at 30–35° to less than a 50-ml volume, and the solution was transferred to a 50-ml volumetric flask and filled to volume with dry benzene. From the absorption at 330 mμ in the uv spectrum [lit.[20] λ_{max}^{MeOH} 330 mμ (ϵ 147)] the concentration of this solution was found to be 0.112 M corresponding to a yield of 56%: nmr (benzene) τ 7.70 (triplet, 2 H, J = 6 Hz), 8.65 (multiplet, 4 H).

Thiethane (13).—To 50 ml of a 0.112 M solution of **11** in benzene was added 2.50 g (10 mmol) of tris(diethylamino)phosphine (**2**). After standing in the dark for 18 days, the clear solution was added to 25 ml of a 20% solution of mercuric chloride in ethanol. After standing overnight, 1.6 g (82%) of a crystalline solid was obtained, mp 94–99° dec (lit.[21] mp 93–95° dec).

Desulfurization of 3H-1,2-Benzodithiole (17).—To a solution of 0.9 g (6.35 mmol) of 3H-1,2-benzodithiole[22] in 15 ml

(14) C. Stuebe and H. P. Lankelma, *J. Amer. Chem. Soc.*, **78**, 976 (1956).

(15) Melting points were determined on a Gallenkamp block and are corrected. Mass spectra were obtained on an AEI-MS-901B mass spectrometer at 70 eV and are reported in order of decreasing intensity.

(16) V. Mark, *Org. Syn.*, **46**, 42 (1966).

(17) D. Houalli, M. Sanchez, and R. Wolf, *Bull. Soc. Chim. Fr.*, 2368 (1965).

(18) L. J. Reed, M. Koike, M. E. Levitch, and F. R. Leach, *J. Biol. Chem.*, **232**, 143 (1958).

(19) Complete removal of solvent causes polymerization of the disulfide. For this reason, no further attempts were made to characterize this compound.

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of benzene was added slowly 1.88 g (7.6 mmol) of tris(diethylamino)phosphine (2). After 10 min, the benzene was removed under vacuum and the residue chromatographed over silica gel. Elution with 10% chloroform in hexane afforded 50 mg (7%) of 6H,12H-dibenzo[*b*,*f*][1,5]dithioocin as colorless crystals, mp 172–178°, which after crystallization from ethanol afforded colorless needles, mp 173–175° (lit.[24] mp 174–176°).

2-Phenyl-1,3-propanedithiol (10).—A solution of 4.6 g (10 mmol) of 2-phenyl-1,3-propanediol ditosylate[25] and 10 g (130 mmol) of thiourea in 50 ml of ethanol was refluxed for 4 hr; the ethanol was removed under vacuum and the residue refluxed under nitrogen with 10 g of sodium hydroxide in 50 ml of water for 12 hr. After careful acidification, the mixture was extracted with chloroform and the extract washed well with water, dried, and evaporated to dryness. The crude oil was fractionally distilled under vacuum to afford 1.0 g (55%) of a pale yellow oil: bp 76–78° (0.005 mm); nmr ($CDCl_3$) τ 2.70 (mulitplet, 5 H, aromatic), 6.0–7.4 (multiplet, 5 H), 8.7 (multiplet, 3 H, S–H). This crude dithiol was used without further purification.

4-Phenyl-1,2-dithiolane (12).—A solution of 1.4 g (7.6 mmol) of the dithiol 10 and 1.8 g (1.8 mmol) of triethylamine in 20 ml of methanol was added dropwise with stirring in a nitrogen atmosphere to a solution of 1.95 g (8 mmol) of iodine in 50 ml of methanol. The resulting solution was rapidly filtered and the filtrate cooled in dry ice until crystals formed. The crystals were filtered and washed well with cold methanol to afford 1.0 g (73%) of yellow crystals, mp 77–83°. Sublimation at 75° and 25-μ pressure afforded 488 mg of yellow crystals: mp 82–84°; ir (KBr) 1600, 1490, 1460, 775, and 705 cm^{-1} (aromatic); $\lambda_{max}^{benzene}$ 335 mμ (ϵ 143); nmr ($CDCl_3$) τ 2.66 (multiplet, 5 H, aromatic), 6.5 (multiplet, 5 H).

Anal. Calcd for $C_9H_{10}S_2$: C, 59.29; H, 5.53; S, 35.18. Found: C, 59.09; H, 5.50; S, 34.83.

3-Phenylthietane (14).—A solution of 400 mg (2.2 mmol) of 12 and 600 mg (2.4 mmol) of tris(diethylamino)phosphine (2) in 10 ml of benzene was refluxed 4 hr during which time the yellow color was discharged. The reaction mixture was evaporated to dryness and the residue chromatographed over silica gel. Elution with 1:1 hexane–chloroform afforded 280 mg (87%) of a colorless oil, homogeneous on thin layer and gas chromatography (LAC column at 190°): $n^{25}D$ 1.5895; ir (film) 1610, 1500, 1465, 760, 705 cm^{-1} (aromatic); nmr (CCl_4) τ 2.78 (5 H), 5.50 (multiplet, 1 H), 6.62 (multiplet, 4 H).

This material was characterized as its sulfone (H_2O_2, AcOH): mp 101–101.5°; ir (KBr) 1320, 1140 cm^{-1} (SO_2).

Anal. Calcd for $C_9H_{10}SO_2$: C, 59.29; H, 5.53; S, 17.59. Found: C, 59.67; H, 5.60; S, 17.84.

1α,5α-Epidithioandrostane-3,17-dione (22).—The method used was a modification of the procedure of Tweit and Dodson[12] in that triphenylphosphine was used to remove occluded sulfur from the crude product. This material was crystallized from acetone (33% yield): mp 210–214° (lit.[12] mp 210–214°); ir (KBr) 1730 (C_{17} C=O), 1710 cm^{-1} (C_3 C=O); λ_{max}^{MeOH} 364 mμ (ϵ 51), 280 sh (650), 262 (730); nmr[11] ($CDCl_3$) (100 MHz) τ 6.15 (quartet, 1 H, $J_{AX} + J_{BX} = 7$ Hz, $J_{AX} - J_{BX} = 1$ Hz), 9.10 (singlet, 3 H), 8.59 (singlet, 3 H), and a multiplet centered at about τ 7.5–6.9.

S-Bis(diethylamino)phosphino-1α-thioandrostan-4-ene-3,17-dione (25).—A suspension of 348 mg (1 mmol) of 1α,5α-epidithioandrostan-3,17-dione (22) in 5 ml of dry benzene containing 1.0 g (4 mmol) of tris(diethylamino)phosphine (2) was stirred overnight. The solvent was removed under vacuum and the residue chromatographed over silica gel. After elution of tris(diethylamino)phosphine sulfide with 95:5 dichloroethane–acetone, the product was eluted with 85:15 dichloroethane–acetone. Crystallization from hexane afforded 100 mg (20%) colorless crystals: mp 201–202°; ir (KBr) 1740 (C_{17} C=O), 1670 cm^{-1} (C=C—C=O); λ_{max}^{MeOH} 228 mμ (ϵ 6450), 280 (1470); mass spectrum, parent ion at *m/e* 492.2960 (Calcd for $C_{27}H_{45}N_2O_2PS$: 492.2939) with a fragment ion at *m/e* 284.1785 [$P^+ - (Et_2N)_2PSH$] (calcd for $C_{19}H_{24}O_2$: 284.1776).

Anal. Calcd for $C_{27}H_{45}N_2O_2PS$: C, 65.81; H, 9.21; N, 5.69. Found: C, 65.75; H, 9.02; N, 5.61.

Registry No.—**3,** 25636-58-2; **4,** 25636-59-3; **5,** 1027-31-2; **6,** 25636-60-6; **10,** 25636-61-7; **12,** 6133-92-2; **14,** 25636-63-9; **14** (sulfone), 25636-64-0; **16,** 25636-65-1; **22,** 25632-08-0; **25,** 25631-60-1.

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Aralkyl Hydrodisulfides.[1] XI. The Reaction with Amines

JITSUO TSURUGI, YASUO ABE, TAKESHIGE NAKABAYASHI, SHUNICHI KAWAMURA, TEIJIRO KITAO,[2] AND MITSUO NIWA[3]

Radiation Center of Osaka Prefecture, Shinke-cho, Sakai, Osaka, Japan

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Aralkyl hydrodisulfides were allowed to react with several amines at room temperature. The amines (morpholine, mono-, di-, and tri-*n*-butylamine, and piperidine) having pK_a values greater than 8.36 behave as bases. The products from 10 mmol of hydrodisulfide consisted of nearly 5 mmol of each hydrogen sulfide and diaralkyl disulfide, and 5 mg-atoms of sulfur, or, alternatively, nearly 5 mmol of hydrogen sulfide and fluctuating amounts of sulfur, diaralkyl disulfide, and polysulfides, the last of which were formed at the expense of the disulfide and sulfur. These results are satisfactorily explained by the basic mechanism reported previously and modified here. The amines (aniline, N,N-dimethylaniline, and pyridine) having pK_a values less than 5.17 behave as nucleophiles and gave hydrogen sulfide, arylalkanethiol, diaralkyl polysulfides, and disulfide, the last of which was formed at the expense of the thiol. These results are explained by the nucleophilic mechanism. 2,4-Lutidine having pK_a value of 6.79 seems to behave as a nucleophile.

It has been well known that amines behave as nucleophiles[4] toward octatomic sulfur or organic sulfur compounds. However, amines could behave as bases rather than nucleophiles in the presence of aralkyl hydrodisulfides which are weakly acidic. Our previous works have shown that nucleophiles such as phosphines,[5,6] phosphites[7] and arsines[8] attack aralkyl hydro-

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