hydrogen selenide to give 9.5 g (92%) of 2-naphthylmethyl diselenide. Recrystallization from ethanol gave yellow needles, mp 134–135.5 °C: NMR ($CDCl_3$) δ 3.9 (s, 2, $-CH_2Se$), 7–7.8 (m, 7, $C_{10}H_7$). Anal. Calcd for $C_{22}H_{18}Se_2$: C, 60.01; H, 4.12; Se, 35.87. Found: C, 59.89; H, 4.16; Se, 35.83.

Bis(9-anthrylmethyl) Diselenide. 9-Anthraldehyde (9.69 g, 47 mmol) was reacted in a similar fashion with morpholine hydrochloride and sodium hydrogen selenide to yield 11.9 g (90%) of 9-anthrylmethyl diselenide as a yellow crystalline solid upon recrystallization from toluene, mp 193–195 °C (dec). Anal. Calcd for $C_{30}H_{22}Se_2$: C, 66.68; H, 4.10; Se, 29.22. Found: C, 66.65; H, 4.08; Se, 29.25.

Bis(1-dodecyl) Diselenide. Dodecylaldehyde (8.66 g, 47 mmol) was reacted with morpholine HCl and NaHSe as described in method II. After reduction, the resulting product was extracted with CH_2Cl_2 and dried over Na_2SO_4. The solvent was removed in vacuo and the yellow oily residue crystallized from cold ethanol to give 8.5 g (73%) of dodecyl diselenide. Recrystallization from acetone yielded a yellow solid, mp 29.5–30.5 °C (lit.[28] mp 30.5–31 °C): NMR ($CDCl_3$) δ 0.9 (t, 3, CH_3–), 1.3 (s, 20, $-CH_2-$), 3.0 (t, 2, $-CH_2$–Se). IR spectra showed no bands other than those for the alkyl groups in the region 4000–625 cm^{-1}.

Bis(4,4′-*N*,*N*-diethylaminobenzyl) Diselenide. *p*-Diethylaminobenzaldehyde (9.33 g, 47 mmol) was reacted with morpholine hydrochloride, sodium hydrogen selenide, and additional sodium borohydride in the manner described previously. The reaction mixture was extracted with chloroform, washed with water, and dried over $MgSO_4$. Evaporation of solvent in vacuo gave a yellow oil. Dissolved in acetone, the oil was acidified with 5% HCl/EtOH solution to precipitate the *p*-diethylaminobenzyl diselenide·2HCl (8.67 g, 67%) as a yellow crystalline salt, mp 200–202 °C (dec): NMR ($CDCl_2$) δ 1.2 (t, 6, $-CH_3$), 3.6 (b, 4, $-CH_2$–N–), 3.9 (s, 2, $-CH_2$–Se–), 7.2–7.9 (m, 4, Ar). Anal. Calcd for $C_{22}H_{34}N_2Cl_2Se_2$: C, 47.58; H, 6.17; N, 5.04; Cl, 12.77; Se, 28.44. Found: C, 47.33; H, 6.37; N, 4.89; Cl, 12.74; Se, 28.37.

Bis(*p*-methylbenzyl) Diselenide. *p*-Tolualdehyde (6.0 g, 50 mmol) was combined with 4.3 g (50.4 mmol) of piperidine in 70 mL of absolute ethanol and hydrogen selenide as described by method I. Approximately 0.60 g of $NaBH_4$ (13.2 mmol) was added to this solution giving a orange-yellow reaction mixture. The resulting yellow product was recrystallized from methanol and gave yellow needles, 7.8 g (85%) of *p*-methylbenzyl diselenide, mp 61–62 °C: NMR ($CDCl_3$) δ 2.3 (s, 3, CH_3–), 3.73 (s, 2, $-CH_2$Se–), 7.04 (s, 4, Ar). Anal. Calcd for $C_{16}H_{18}Se_2$: C, 52.19; H, 4.93; Se, 42.88. Found: C, 52.18; H, 5.01; Se, 42.82.

Registry No.—Benzaldehyde, 100-52-7; benzyl diselenide, 1482-82-2; *N*,*N*′-benzylidenedipiperidine, 2538-76-3; 4,4′-benzylidenedimorpholine, 6425-08-7; dibenzyl-α,α′-d_2 diselenide, 65915-28-8; bis(1-naphthylmethyl) diselenide, 53391-04-1; 1-naphthaldehyde, 66-77-3; bis(2-naphthylmethyl) diselenide, 53391-03-0; 2-naphthaldehyde, 66-99-9; bis(9-anthrylmethyl) diselenide, 61098-92-8; 9-anthraldehyde, 642-31-9; bis(1-dodecyl) diselenide, 10564-87-1; dodecylaldehyde, 112-54-9; bis(4,4′-*N*,*N*-diethylaminobenzyl) diselenide·2HCl, 65915-29-9; *p*-diethylaminobenzaldehyde, 120-21-8; bis(*p*-methylbenzyl) diselenide, 65915-30-2; *p*-tolualdehyde, 104-87-0; H_2Se, 7783-07-5; NaHSe, 12195-50-5; NaDSe, 12175-25-6.

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Iodonium Ylides. The Action of Thiols on Phenyl Dimedonyl Iodone. Oxidation–Reduction vs. Substitution

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The reactions of phenyl dimedonyl iodone (**1**) with various thiophenols, methanethiol, and hydrogen sulfide were studied. With thiophenol, the major process is oxidation–reduction to diphenyl disulfide (**6**) (73%), dimedone (**7**) (70%), and iodobenzene (99%). A 15% yield of phenyl 2-dimedonyl sulfide (**8**), a product of "substitution", was also obtained. The oxidation of thiophenol by **1** apparently proceeds by initial protonation of the latter by the former and subsequent electron transfer from the resulting thiophenoxide ion to the conjugate acid of **1**. The general reaction does not change with para-substituted thiophenols. However, the *ratio* of substitution/oxidation is dependent on the electron-donating capacity of the substituent. With methanethiol the gross reaction is the same. The action of hydrogen sulfide on **1** was reinvestigated, and the spirosulfide **2** (41%), dimedone (**7**) (28%), and 2,2′-bis(dimedonyl) sulfide (**29**) (12%) were obtained.

Introduction

Phenyl dimedonyl iodone (**1**), a stable iodonium ylide,[1] reacts with either phenyl isothiocyanate or methyl isothiocyanate to give low yields of the spirosulfide **2**.[2] Since 5,5-dimethylcyclohexane-1,2-thio,3-trione (**3**) is a possible precursor to **2**, we attempted to prepare authentic **3** by the treatment of **1** with hydrogen sulfide.[2] The thiotrione was not obtained, but the spirosulfide was isolated in 40% yield. We subsequently became interested in the reactions of other sulfhydryl compounds, specifically methanethiol and various thiophenols, with phenyl dimedonyl iodone and now report

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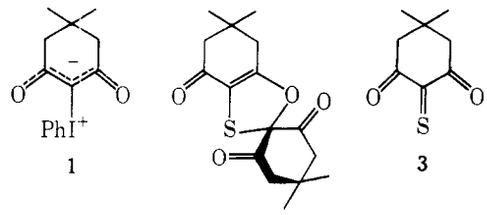
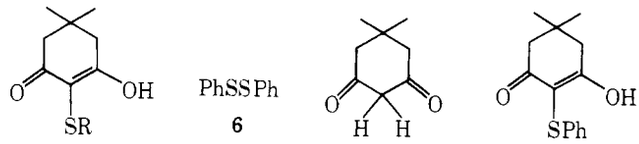


1 2 3

that the oxidation of thiols by 1 is a dominant but not exclusive process.

Results and Discussion

In view of the known ability of diaryliodonium salts to arylate nucleophiles,[3-8] it was anticipated that 1 would react with organic thiols to give primarily sulfides (4). In fact, such sulfides were usually minor products. The reaction of 1 with thiophenol (5) in dichloromethane at ice bath temperature gave diphenyl disulfide (6), dimedone (7), and 2-thiophenoxydimedone (8) in *isolated* yields of 73, 70, and 15%, respectively, and iodobenzene in 99% yield (determined by GC analysis in a separate experiment).

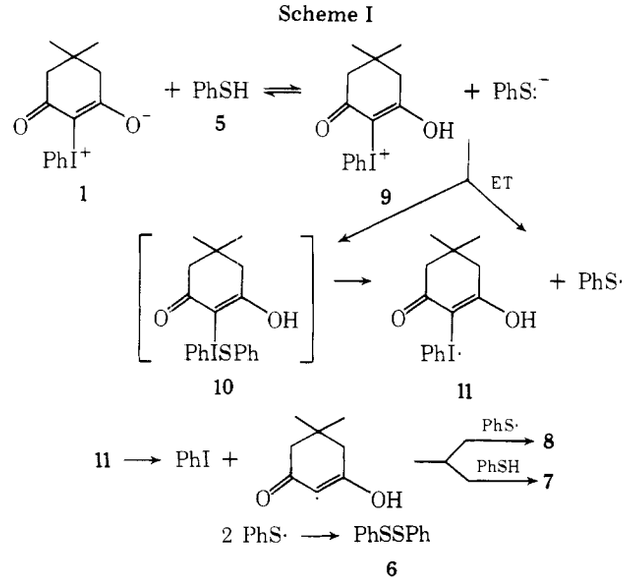


4 6 7 8

The formation of 6, 7, 8, and iodobenzene from 1 and thiophenol may be rationalized by (a) reversible protonation of 1 by thiophenol to give the phenyl-2-dimedonyliodonium ion (9) and thiophenoxide ion; (b) *formal* electron transfer (ET) from the latter species to 9 to give phenyl-2-dimedonyliodine radical (11) and thiophenoxyl radical; and (c) homolytic decomposition of 11 followed by various radical abstraction and combination processes (Scheme I). A similar ET mechanism was proposed by Beringer to account for the arylation of indandionate ions by diaryliodonium salts.[9,10]

The reaction between 1 and 5 is complete within minutes and thus the equilibrium constant (K_p) for the protonation of 1 by 5 in dichloromethane has not been determined. However, the pK_a of 9 as the tosylate salt has been measured in aqueous ethanol and is reasonably insensitive to changes in solvent composition (0.72 in pure water, 1.42 in 50% ethanol, and 1.48 in 85% ethanol).[11] The pK_a of thiophenol in 95% ethanol has been reported to be ~9.3.[12] If it is assumed that the pK_a of 9 is ~1.5 in 95% ethanol, a K_p value of 6.33×10^{-9} can be computed for that solvent.

Scheme I



1 + PhSH ⇌ 5 + 9 + PhS:⁻

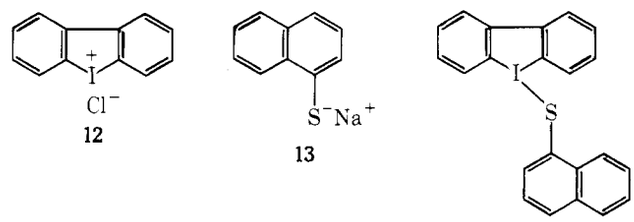
1 → 9 (ET)

9 → 10 + 11 + PhS·

11 → PhI + 8 (PhS·) + 7 (PhSH)

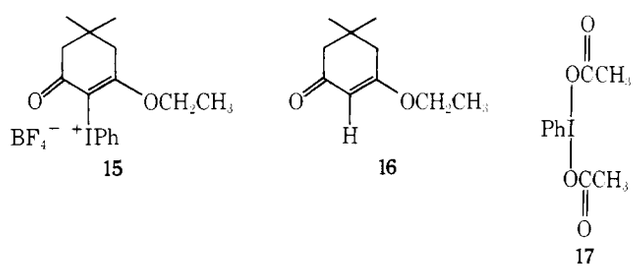
2 PhS· → PhSSPh 6

The susceptibility of thiophenoxide ion to electron-transfer oxidation is well known. For example, Meyers and Hsu have recently studied such oxidations by the triphenylmethyl cation.[13] The ET process may actually proceed through the covalent iodine(III) intermediate **10**, which suffers subsequent iodine–sulfur bond homolysis. That covalent iodine(III) compounds can decompose by free-radical pathways is an established fact.[7,14,15] The formation of a sulfur–iodine(III) bond may find precedent in the work of Sandin and his coworkers, who isolated a *stable adduct* when diphenyleneiodonium chloride (**12**) was allowed to react with sodium α-naphthalenethiolate (**13**).[16] A structure for the adduct was not proposed, but the iodine(III) structure **14** seems highly probable.



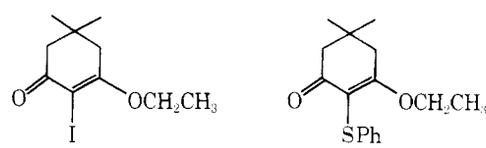
12 13 14

The following experiments indicate that the ET process requires the simultaneous presence of 9 and thiophenoxide ion. Thus, 1 did not react with methyl phenyl sulfide in dichloromethane, and analogy dictates that electron transfer from *un-ionized* thiophenol to 1 must be unlikely. When the known iodonium salt, phenyl-2-(3-ethoxy-5,5-dimethyl-2-cyclohexenonyl)iodonium tetrafluoroborate (**15**), prepared by the condensation of 3-ethoxy-5,5-dimethyl-2-cyclohexenone (**16**) with iodosobenzene diacetate (**17**) in fluoroboric acid[17] and a model for 9, was treated with thiophenol, there was again no reaction. Even when the electron acceptor 15 is present, thiophenol does not function as an electron donor. Similarly, when 1 was treated with sodium thiophenoxide (the electron donor) in acetonitrile, there was no reaction.



15 16 17

Finally, 15 reacted rapidly with sodium thiophenoxide in acetonitrile at ice bath temperature. After the sodium tetrafluoroborate was removed by filtration (89% yield), the crude product mixture was separated by column chromatography on Florisil to give diphenyl disulfide (**6**; 73%), 2-iodo-3-ethoxy-5,5-dimethyl-2-cyclohexenone (**18**; 38%), 3-ethoxy-5,5-dimethyl-2-cyclohexenone (**16**; 5%), and 2-thiophenoxy-3-ethoxy-5,5-dimethyl-2-cyclohexenone (**19**; 17%). The yield of iodobenzene, determined in a separate experiment, was 57%.



18 19

Formal electron transfer from the thiophenoxide ion to 15

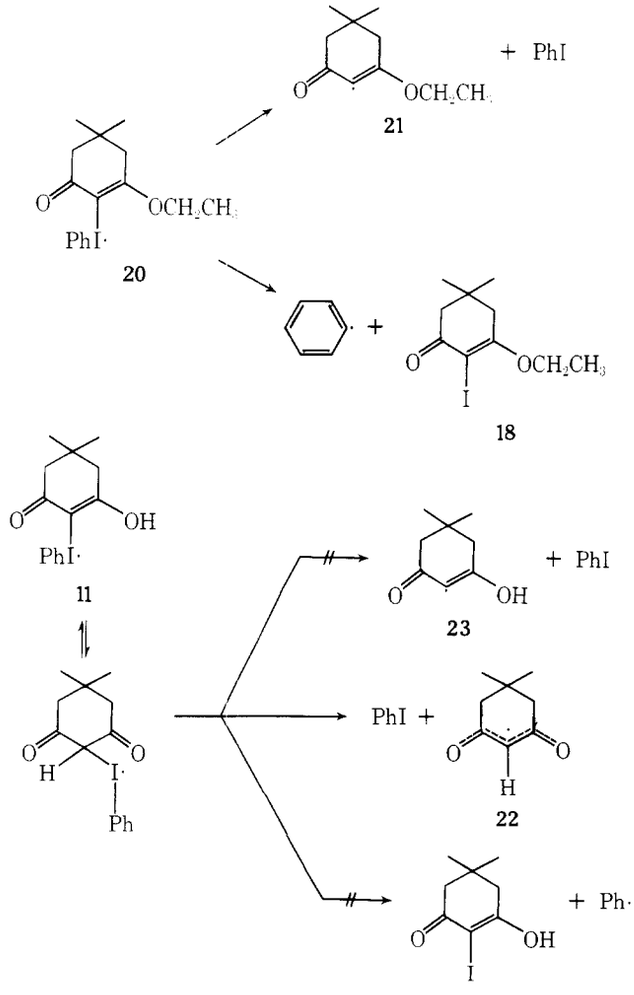
Table I.[a] Product yields (%) from Reactions of 1 with Various Thiophenols

Thiophenol	Registry no.	% disulfide	Registry no.	% sulfide	Registry no.	% 7[b]	% PhI[c]	σ	Subst/oxid product
p-NO_2	1849-36-1	80.5	100-32-3	0		43	97	+0.778	0
p-Cl	106-54-7	82.5	1142-19-4	10	66102-84-9	86	99	+0.227	0.120
H	108-98-5	73	882-33-7	15	61908-09-6	70	99	0.000	0.205
p-CH_3	106-45-6	72	103-19-5	32	66102-85-0	62	100	−0.170	0.444
p-OCH_3	696-63-9	65	5335-87-5	43	66102-86-1	46	94	−0.268	0.661
O-COOH	147-33-3	95	119-80-2			73			

[a] In the Experimental Section, the sulfides are numbered as **8** (X = H), **8a** (X = NO_2), **8b** (X = Cl), **8c** (X = CH_3), and **8d** (X = OCH_3); the disulfides are numbered as **6** (X = H), **6a** (X = NO_2), **6b** (X = Cl), **6c** (X = CH_3), and **6d** (X = OCH_3). [b] Registry no.: 126-81-8. [c] Registry no.: 591-50-4.

in this reaction to give the iodine radical **20** seems reasonable. However, a significant difference between the decomposition modes of the proposed iodine radicals **11** and **20** is apparent. In **11**, the dimedonyl–iodine bond cleaves to the near exclusion of the phenyl–iodine bond (99% PhI), but in **20** both bonds cleave (57% PhI, 38% **18**). Since *cyclic* vinyl radicals such as **21** are electronically analogous and comparable in energy to the phenyl radical, the formation of both types of radicals from the common precursor **20** is expected and is consistent with the facts. However, the absence of a similar competition in the homolytic collapse of **11** is surprising and points to the involvement of the enolic hydrogen atom. If, for example, that hydrogen is transferred from oxygen to vinyl carbon either before or during decomposition of **11**, the π-radical **22** would be generated instead of the vinyl radical **23.** It is possible that **22** would be sufficiently more stable than either **23** or the phenyl radical to be formed selectively, and this would account for the absence of 2-iododimedone in the product mixture (Scheme II).

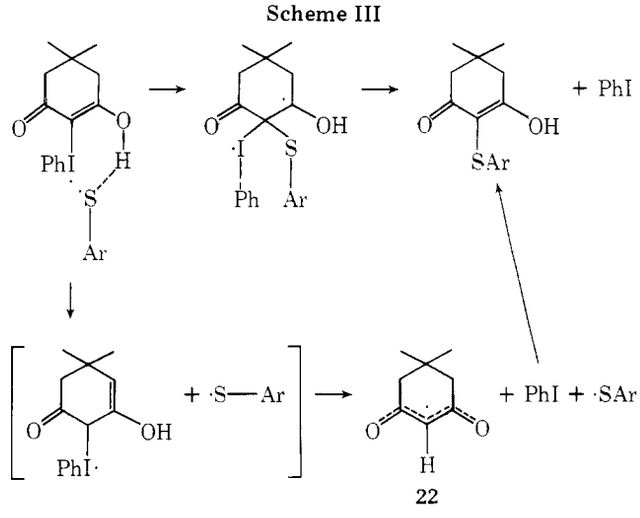
Scheme II



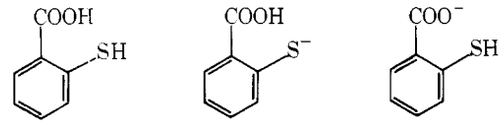
However, an even more complete mechanistic rationale is needed to accommodate the following observations. When **1** was allowed to react with various substituted thiophenols, the yield of substitution product decreased and the yield of oxidation product increased with an increase in electrophilicity of para substituents. The results are summarized in Table I, where the indicated yields are based on isolation except for those of iodobenzene, which were determined by GC analysis. Also in Table I, the ratios (substitution product/oxidation product) are compared to Hammett's σ constants. The correlation between the two is not linear, but a regular dependence is evident; e.g., as the substituent constants increase the indicated ratios decrease.

These results suggest that the substitution products arise primarily from caged radical pairs and that the redox products arise from radicals which have diffused into the bulk solvent (Scheme III). Implicit in this assumption is the suggestion that electrophilic substituents promote diffusion while nucleophilic substituents inhibit it. Perhaps the substitution products, when they are formed in a solvent cage, arise by direct attack of the thiyl radicals on the carbon–carbon double bond of **11** and subsequent elimination of iodobenzene from the intermediate diradical (Scheme III). It seems plausible that the thiophenoxy radicals might be held in proximity to that double bond by hydrogen bonding and, since their basicity decreases with an increase in electrophilicity of X, diffusion would become increasingly more competitive, and the yields of substitution product would diminish. We wish to emphasize, however, that at least a small part of the substitution product probably arises by the coupling of radicals which have diffused into the bulk solvent, and, in that case, radical **22** may be involved.

Scheme III



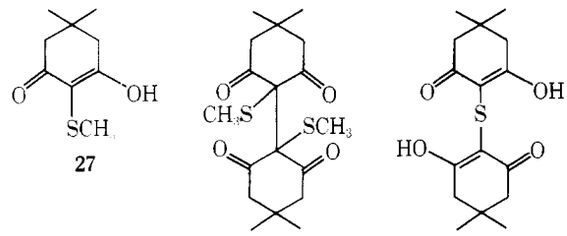
The oxidation of 2-carboxythiophenol (**24**) by **1** deserves comment. It seems clear that while protonation of **1** by the carboxyl function in **24** is a likely process, protonation of **1** by the sulfhydryl group of **24** leads to the observed products.



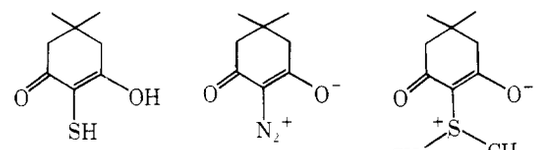
24 **25** **26**

That is, the electron donor is probably the thiophenoxide ion **25** and not the carboxylate ion **26.**

The oxidation–reduction reactions are not restricted to aromatic thiols. When iodonium ylide **1** was allowed to react with methanethiol in dichloromethane at ice bath temperature, the products included **7** (42%) and 2-thiomethoxydimedone (**27**; 33%). No attempt was made to isolate dimethyl disulfide, but its odor in the reaction mixture was unmistakable. At room temperature, the yield of **27** decreased to 17%, and an oxidation product (**28**) was isolated in 18% yield.



27 **28** **29**



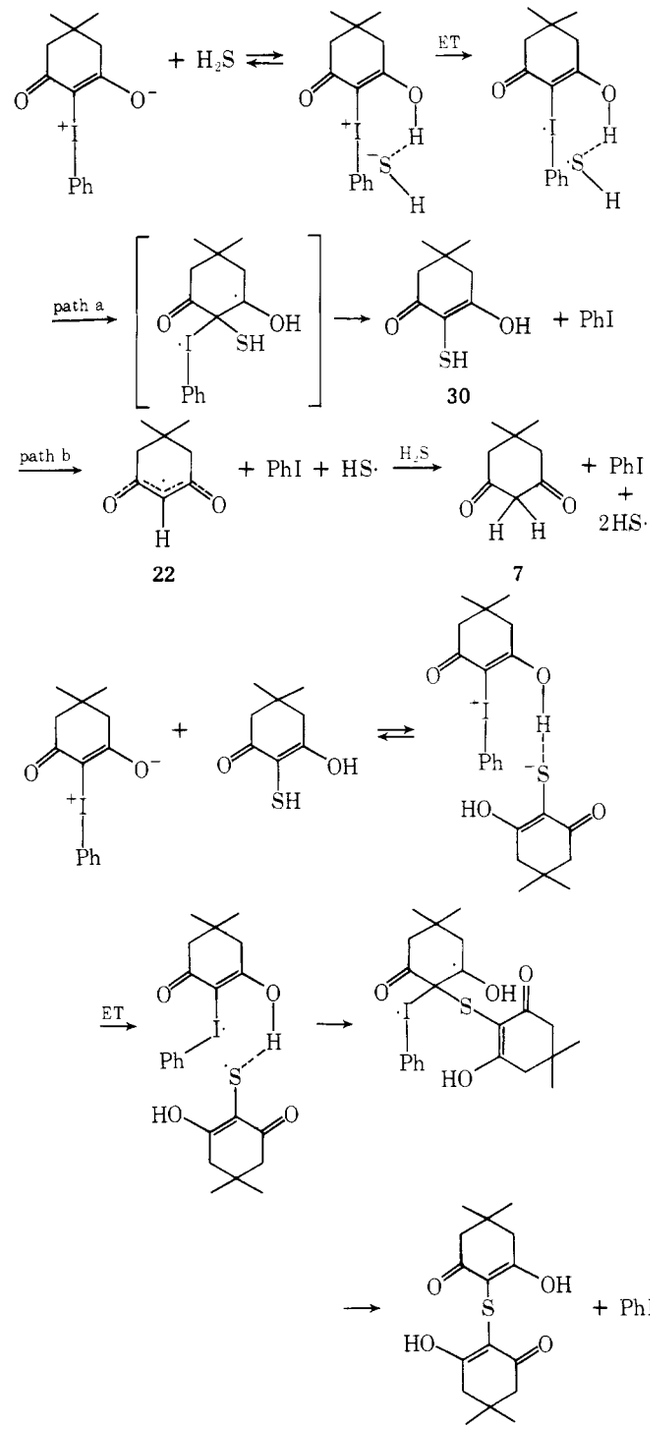
30 **31** **32**

(compound **28** was isolated in 58% yield from **27** and basic potassium ferricyanide). The mechanism for this reaction is probably the same as for **1** and thiophenol. However, in this case, the ratio of reduction (**7**) to substitution (**27**) is significantly lower (1.27 vs. 4.67 for thiophenol).

The reaction between **1** and hydrogen sulfide has been reinvestigated, since only **2** had been previously identified.[2] When a solution of **1** was saturated at room temperature with hydrogen sulfide, a rapid reaction ensued. The crude product mixture was chromatographed on Florisil to give the expected cyclic sulfide **2** (41%), **7** (28%), and 2,2-bisdimedonyl sulfide (**29**; 12%). Inasmuch as **2** and **29** may be viewed as substitution products, the ratio of reduction product to substitution product was 0.53, even lower than with methanethiol. The formation of **7** and **29** from **1** and hydrogen sulfide may proceed as indicated in Scheme IV, where electron transfer is again central. We also suggest that 2-mercaptodimedone (**30**) may be a direct precursor to **29.**

It is instructive to compare the reactivity of **1** toward thiophenol with that of other dimedonyl ylides. When a solution of 2-diazodimedone (**31**)[18] and thiophenol in dichloromethane was allowed to stand at room temperature for 24 h, there was no apparent reaction; compound **31** was recovered (93%). The dimethylsulfonium ylide (**32**)[19,20] was recovered in 95% yield from a similar reaction mixture after 24 h. The failure of compounds **31** and **32** to react with thiophenol may indicate that they are not sufficiently basic to provide threshold concentrations of their conjugate acids. Alternatively, the conjugate acids of **31** and **32** may exhibit reduction potentials

Scheme IV



sufficiently high that electron transfer from the thiophenoxide ion would be thermodynamically unfavorable. In the case of **32,** the second explanation seems more likely, since **32** is more basic than **1.**[6]

Experimental Section

General. ^{1}H NMR spectra (60 MHz) were recorded on a Varian Model A-60 NMR spectrometer (with Me_4Si as an internal standard), IR spectra on a Perkin-Elmer Model 337 spectrophotometer, and UV spectra on a Cary-17 UV–vis–IR spectrophotometer. ^{1}H NMR spectra (300 MHz) were recorded on a Varian Model HR-300 NMR spectrometer at The University of Akron's NMR Center. GC analyses were conducted on Hewlett-Packard Model 5750 and F&M Model 700 gas chromatographs. A 10 ft × ⅛ in. stainless steel column packed with 5% silicone rubber (UCC-982-methyl vinyl) on 80–100 mesh Chromsorb G and a 10 ft × 2 mm (i.d.) column of Sp-1000 on 100–120 Chromosorb WAW were utilized. Elemental compositions were de-

termined by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points are uncorrected.

Iodobenzene yields for reactions of **1** with various thiophenols and for **15** with sodium thiophenoxide were determined by GC analysis with durene as internal standard in experiments separate from those in which other products were isolated.

The column chromatographic separations discussed herein were conducted on Florisil. The elution fractions were generally about 300 mL in volume, and after solvent removal the fraction residues were subjected to NMR analysis. The specified solvent compositions refer to the solvent added at the top of the column and not that collected from the bottom of the column.

Sodium thiophenoxide,[21] **1**,[1,22] **15** (60%, mp 160–162 °C),[17] **31** (81%, mp 104–106 °C),[18,29] and **32** (79%, mp 169–171 °C)[19,20] were prepared by literature procedures. Compound **16** (83%, mp 57–58 °C)[23] was prepared by $TsOH \cdot H_2O$ catalyzed "esterification" of **7** with ethanol. Compounds **6** and **7** were generally identified by melting point and/or NMR analysis. The NMR spectra of the authentic materials were available for comparison.

Reactions of 1 with Various Thiophenols. The reaction conditions and workup procedure for the reaction of **1** with thiophenol are given below in detail. For other thiophenols, conditions and workups were *similar*, but not identical.

Thiophenol. To a solution of **1** (9.13 g, 26.7 mmol) in CH_2Cl_2 (80 mL), cooled in an ice bath, was added a solution of thiophenol (6.00 g, 54.5 mmol) in CH_2Cl_2 (80 mL) over a period of about 1 min. The reaction mixture was allowed to stir at ice bath temperature for 1 h and subsequently evaporated to dryness. The crude, pale yellow solid (9.1 g) which remained was recrystallized from ethyl acetate (60 mL) and yielded 2.36 g of **7** as long, white needles, mp 145 °C. The filtrate was evaporated to dryness, the residue was taken up in CH_2Cl_2 (10 mL), and the resulting solution was subjected to column chromatography on Florisil (~200 g); 17 fractions were collected: fractions 1–5 (cyclohexane = C_6H_{12}), 6–9 (Et_2O/C_6H_{12}, 2:8), 10–11 (Et_2O/C_6H_{12}, 5:5), 12–13 (Et_2O), 14 (Et_2O/CH_3CO_2Et, 5:5), 15 (CH_3CO_2Et), 16 (CH_2Cl_2), 17 (EtOH). Fractions 1–3 gave **6** (4.32 g), 6–13 gave **8** (0.993 g), and 16 gave **7** (0.145 g). The crude solid from fractions 14 and 15, containing **7** and **8**, was recrystallized from ethyl acetate and gave 0.12 g of **7** (mp 146 °C).

Crude **6** (4.31 g) was recrystallized from methanol as fine, white needles (yield 3.90 g, mp 59–61 °C), crude **7** (2.62 g) was recrystallized from ethyl acetate as long, white needles (yield 2.34, g, mp 149–151 °C), and crude **8** (0.99 g) was recrystallized from cyclohexane as fine, white needles (yield 0.87 g, mp 120–121 °C).

***p*-Nitrothiophenol:** 9.261 g (27 mmol) of **1**, 8.34 g (54 mmol) of *p*-nitrothiophenol, 200 mL of CH_2Cl_2, chromatographic workup. Products were **6a** (6.694 g, 80.5%), mp 178 °C [lit.[24] mp 182 °C], and **7** (1.636 g, 43%).

***p*-Chlorothiophenol:** 9.267 g (27.02 mmol) of **1**, 7.758 g (54.06 mmol) of *p*-chlorothiophenol, 200 mL of CH_2Cl_2, chromatographic workup. Products were: **6b** (6.406 g, 83%), recrystallized from CH_3OH as yellowish scales, mp 68–69 °C [lit.[25] mp 70–71 °C]; **8b**, recrystallized from cyclohexane (0.759 g, 10%), mp 133–134 °C; and **7** (crude yield 3.268 g, 86%).

***p*-Methylthiophenol:** 9.261 g (27 mmol) of **1**, 8.964 g (54 mmol) of *p*-methylthiophenol, 200 mL of CH_2Cl_2, chromatographic workup. Products were: **6c** (4.767 g, 72%), mp 46–48 °C [lit.[26] mp 47–48 °C]; **7** (2.353 g, 62%) and **8c** (2.248 g, 32%).

***p*-Methoxythiophenol:** 9.261 g (27 mmol) of **1**, 7.56 g (54 mmol) of *p*-methoxythiophenol, 200 mL of CH_2Cl_2, chromatographic workup. Products were: **6d** (4.874 g, 65%), green liquid [lit.[26] mp 44 °C]; **7** (1.74 g, 46%); and **8d** (3.24 g, 43%).

2-Carboxythiophenol. A solution of **1** (3.179 g, 9.3 mmol) in CH_2Cl_2 (50 mL) was mixed with a solution of **24** (3.294 g, 21.4 mmol) in CH_3OH (50 mL). Mild heat evolution was observed. The reaction mixture, which became cloudy within 1 min, was allowed to stir at room temperature for 0.5 h. The tan insoluble powder which had formed during that period was then isolated, washed with CH_2Cl_2 (~10 mL), dried, and identified by ^1H NMR analysis as 2,2′-bis(carboxydiphenyl) disulfide: yield, 2.681 g (84%). The filtrate was concentrated and gave 2.739 g of a yellow solid, which was treated with hot ethyl acetate; 0.361 g of the disulfide remained undissolved. The total yield of the disulfide was 95%. When the solution was allowed to cool, dimedone (**7**) crystallized in needles: yield, 0.953 g (73%); mp 146–148 °C.

Characterization of 8: NMR ($CDCl_3$) δ 1.10 [s, 6, $C(CH_3)_2$], 2.47 (s, 3.92, 2 CH_2), 7.18 (s, 5.04, arom), ~8.4 (br s, 1.22, enol OH): IR (KBr) 3.95 (v br band 3.2–5.1 similar to dimedone OH), 6.41 μm (vs); IR ($CHCl_3$) 3.06 (OH), 6.14 μm (conjugated C=O); UV (CH_3OH) λ_{max} 248 (ϵ 19 765), 280 nm (sh tailing to 325 nm, ϵ 7092).

Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.49; S, 12.91. Found: C, 68.01; H, 6.50; S, 12.64.

Characterization of 8b: white powder (from cyclohexane); mp 133–134 °C; NMR ($CDCl_3$) δ 1.1 [s, $C(CH_3)_2$], 2.48 (s, 2 CH_2), 7.14 (br "s", arom), 7.8 (br s, enol OH, exchanges with D_2O); IR ($CHCl_3$) 3.06 (OH), 6.35 μm (conj C=O); UV (CH_3OH) λ_{max} 262 nm (ϵ 7375).

Anal. Calcd for $C_{14}H_{15}O_2Cl$ S: C, 59.47; H, 5.31; Found: C, 59.62; H, 5.56.

Characterization of 8c: white powder (from cyclohexane); mp 101–103 °C; NMR ($CDCl_3$) δ 1.08 [s, $C(CH_3)_2$], 2.25 (s, CH_3), 2.45 (s, 2 CH_2), 7.07 (br s, arom), 7.85 (br s, enol OH, exchanges with D_2O); IR ($CHCl_3$) 3.06 (OH), 6.36 μm (conj C=O); UV (CH_3OH) λ_{max} 254 nm (ϵ 10 420).

Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.9. Found: C, 68.34; H, 7.04.

Characterization of 8d: mp 109–110 °C (from cyclohexane); NMR ($CDCl_3$) δ 1.07 [s, $C(CH_3)_2$], 2.44 (s, 2 CH_2), 3.73 (s, OCH_3), ~6.67–7.35 (m, arom), 8.00 (br s, enol OH, integrates for 0.5 H, exchanges with D_2O); IR ($CHCl_3$) 3.03 (OH), 6.33 μm (conj C=O); UV (CH_3OH) λ_{max} 254 nm (ϵ 9687).

Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.75; H, 6.47. Found: C, 65.12; H, 6.64.

Reaction of 15 with Sodium Thiophenoxide. To a solution of **15** (8.08 g, 17.6 mmol) in CH_3CN (60 mL), cooled in an ice bath, was added a suspension of sodium thiophenoxide (2.43 g, 18.4 mmol) in CH_3CN (60 mL). The reaction mixture cleared immediately and turned bright yellow, but it became pale yellow, and a white precipitate formed. The reaction mixture was allowed to stir for an additional 1 h at ice bath temperature and, upon subsequent filtration, gave 0.73 g of $NaBF_4$ as a white solid. The pale yellow filtrate was evaporated to dryness and the residue was triturated with CH_2Cl_2 (60 mL), which gave an additional 0.996 g of the insoluble $NaBF_4$. The pale yellow CH_2Cl_2 solution was then concentrated to a wet solid, which was subjected to column chromatography on Florisil (~200 g), 23 fractions being collected: fractions 1–4 (C_6H_{12}), 5–8 (Et_2O/C_6H_{12}, 1:9), 9 (Et_2O/C_6H_{12}, 2.8), 10–11 (Et_2O/C_6H_{12}, 5:5), 12–17 (Et_2O/C_6H_{12}, 8:2), 18–19 (Et_2O), 20–21 (Et_2O/CH_3CO_2Et, 5:5), 22–23 (CH_3CO_2Et). Fractions 1–3 gave **6** (1.466 g), 8–15 gave **18** contaminated with some **16** (wt 2.49 g), and 18–21 gave mostly **19** (1.056 g).

The solids from fractions 8–15 were combined (2.49 g) and washed with two 10-mL portions of ethanol. A white solid (1.01 g), identified as 2-iodo-3-ethoxy-5,5-dimethyl-2-cyclohexenone (**18**), remained undissolved. The ethanol solution, when concentrated to half-volume, yielded an additional 0.55 g of **18**, which was isolated by filtration. The filtrate was then evaporated to dryness, and the residue, upon trituration with ethanol (3 mL), gave 0.28 g of **18**. The resulting ethanol solution was concentrated to a wet, brown solid which was shown by ^1H NMR analysis to be a 1:1 mixture of **16** and **18**. This material was triturated with ether (5 mL) and 0.096 g of **18** was obtained. Thus, the total *isolated* yield of **18** was 1.95 g.

The ether solution from the above trituration was transferred to a molecular still, the solvent was evaporated under a nitrogen stream, and the crude residue was distilled: bp 90–95 °C (~1 mm). In this way, 0.153 g of a thick, light yellow liquid, shown by ^1H NMR analysis to be 3-ethoxy-5,5-dimethyl-2-cyclohexenone (**16**) contaminated with trace impurities, was obtained.

The liquids from fractions 18–21 were combined and, after 2 days under ambient conditions, solidified to a yellow, crystalline material. This crude solid was triturated with two portions (10 mL, 5 mL) of ether and gave 0.801 g of 2-thiophenoxy-3-ethoxy-5,5-dimethyl-2-cyclohexenone (**19**) as a white powder.

Characterization of 18: NMR ($CDCl_3$) δ 1.12 [2, 6, $C(CH_3)_2$], 1.43 (t, J = 7 Hz, $-CH_2\mathbf{CH_3}$), 2.43 (s, 2.3, CH_2), 2.57 (s, 2.1, CH_2), 4.23 (q, J = 7 Hz, 2.1, $-\mathbf{CH_2}CH_3$); IR (KBr) 6.12 (conj C=O), strong bands at 6.45, 7.38, 7.72, and 8.09 μm; UV (CH_3OH) λ_{max} 283 nm (ϵ 9417).

Anal. Calcd for $C_{10}H_{15}O_2I$: C, 40.84; H, 5.15; I, 43.15. Found: C, 40.84; H, 5.30; I, 43.30.

Compound **18** has previously been reported by Neiland and Vanag.[27] It gradually (~2 weeks) decomposes upon storage at room temperature.

Characterization of 19: mp 93–95 °C; NMR ($CDCl_3$) δ 1.12 [s, $C(CH_3)_2$], 1.19 (t, J ~7 Hz, $-OCH_2\mathbf{CH_3}$), 2.37 (s, CH_2), 2.57 (s, CH_2), 4.13 (q, J ~7 Hz, $-\mathbf{OCH_2}CH_3$), 7.14 (*apparent* s, aromatic hydrogens). The resonances at δ 1.12 and 1.19 overlap and were, therefore, integrated together. Also, the combined integration of the ring methylene singlets is reported. NMR integration: theoretical, 9:4:2:5; experimental 9:4.15:1.85:4.77. IR (KBr) 6.10 (C=O of an α,β-unsaturated ketone with a β-OCH_2CH_3 substituent), strong bands at 6.46, 7.37, 7.81, and 8.05 μm; UV (CH_3OH) λ_{max} 252 (ϵ 21 406), plateau at 279 nm (ϵ 2702).

Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.24; S, 11.60. Found: C, 69.80; H, 7.34; S, 11.57.

Reaction of 1 with Methanethiol at ~0 °C. A solution of **1** (8.35 g, 24.4 mmol) in CH_2Cl_2 (200 mL) was cooled in an ice bath and subjected, for 10 min, to a stream of methanethiol. During that time, the yellow color of the ylide solution was discharged. The reaction mixture was then evaporated to a crude solid which was dissolved in hot ethyl acetate (60 ml). Upon cooling, the ethyl acetate solution yielded 1.01 g of **7** as long, colorless needles. The filtrate was concentrated to dryness, and the residue was subjected to column chromatography on Florisil, 18 fractions being collected: fraction 1 (C_6H_{12}), 2–8 (Et_2O/C_6H_{12}, 2:8), 9–12 (Et_2O/C_6H_{12}, 5:5), 13 (Et_2O/C_6H_{12}, 8:2), 14 (Et_2O), 15–16 (CH_3CO_2Et), 17 (CH_2Cl_2), 18 (EtOH). Fractions 1–2 gave a mixture (0.44 g) of **27** and **28**, 3–12 gave **27** (1.131 g), and 13–17 gave a mixture (1.063 g) of **7** and **27**.

The solids (1.064 g) from fractions 13–17 were combined and dissolved in hot ethyl acetate (20 mL). That solution, upon cooling, gave **7** as fine white needles: yield, 0.355 g; mp 149 °C. From the filtrate, a second crop of dimedone (mp 148 °C, 0.072 g) was obtained. Thus, the total *isolated* yield of **7** was 1.441 g (42%).

The filtrate was concentrated to dryness, and the residue was crystallized from cyclohexane (20 mL). There was obtained 0.369 g of crystals, mp 84–86 °C, identified as 2-thiomethoxydimedone (**27**). The total isolated yield of **27**, including the material from fractions 3–12, was 1.500 g (33%). Finally, the combined samples of crude **27** (1.500 g) were recrystallized from cyclohexane as fine white needles: yield, 1.330 g; mp 85–86 °C.

Reaction of 1 with Methanethiol at Room Temperature. A solution of **1** (10.394 g, 30.4 mmol) in CH_2Cl_2 (120 mL) was saturated for 10 min with a stream of methanethiol at room temperature. Once again, the yellow color of the ylide solution was discharged. The reaction mixture was then concentrated to a white solid residue which was taken up in hot ethyl acetate (80 mL). The hot solution, upon cooling to room temperature, gave 1.524 g of fine white needles (mp ~148–149 °C) identified as **7**.

The filtrate was evaporated to dryness, and the residue was subjected to column chromatography on Florisil. The products were **7** (1.897 g, 44.5%), **27** (0.963 g, 17%), and **28** (0.887 g crude, 15.7%, mp 143–145 °C).

Characterization of 27: NMR ($CDCl_3$) δ 1.10 [s, 6, $C(CH_3)_2$], 2.14 (s, 2.9, $-SCH_3$), 2.44 (s, 4, 2 CH_2), 8.08 (br s, 0.8, OH); IR (KBr) 4.2 (enol OH, v br band from 3 to 5 μm similar to spectrum of **7**), 6.46 (very intense), 7.43, 7.68, 7.98 μm (very strong band with three maxima); IR ($CHCl_3$) 3.08 (OH), 6.06 (conj C=O), 6.31 μm (C=C); UV (CH_3OH; 3.95×10^{-5} M) λ_{max} 248 (ϵ 8377), 281 nm (8909); UV (CH_3OH; 4.94×10^{-5} M) λ_{max} 247 (ϵ 8382), 279 nm (7289); UV (CH_3OH; 9.88×10^{-5} M) λ_{max} 248 (ϵ 9081), 286 nm (sh, ϵ 5528).

Anal. Calcd for $C_9H_{14}O_2S$: C, 58.03; H, 7.58; S, 17.21. Found: C, 58.34; H, 7.56; S, 17.07.

Characterization of 28. The crude product was recrystallized from cyclohexane as white crystals (0.761 g, mp 143–145 °C): NMR ($CDCl_3$, 300 MHz, 55 °C) δ 1.18 [s, $C(CH_3)_2$], 2.33 (s, $-SCH_3$), 2.38 (d, $-CH_2-$, J = 14 Hz), 3.35 (d, $-CH_2-$, J = 14 Hz). The doublet at δ 2.38 overlaps with the singlet at δ 2.33. Therefore, the two resonances were integrated together. NMR integration: theoretical, 6:5:2; experimental, 6:5:2. IR ($CHCl_3$) 5.89 (~1690 cm^{-1}, C=O), sh at 5.79 μm.

Anal. Calcd for $2(C_9H_{14}O_2S) - 2H$: C, 58.35; H, 7.07; S, 17.31. Found: C, 58.21; H, 7.47; S, 17.20.

Oxidation of 2-Thiomethoxydimedone (27). To a solution of **27** (0.142 g, 0.764 mmol) in CH_2Cl_2 (5 mL) was added 5 mL of basic potassium ferricyanide solution. The two-phase mixture was allowed to stir under nitrogen for 20 h at room temperature and more CH_2Cl_2 (10 mL) was added. The CH_2Cl_2 layer was then isolated, dried ($MgSO_4$), and concentrated to a white powder, mp ~140 °C, identified by NMR analysis as **28**: yield, 0.083 g; 58%.

Reaction of 1 with Hydrogen Sulfide. A solution of **1** (11.68 g, 34.1 mmol) in CH_2Cl_2 (150 mL) was cooled in an ice bath and saturated with H_2S. The reaction mixture, which had become bright yellow, was allowed to stir at ~0 °C for 30 min and was subsequently evaporated to dryness. The residue, a bright yellow solid, was dissolved in hot ethyl acetate (50 mL). As the solution cooled, it gave long crystalline needles which were isolated, washed with ethyl acetate, and dried; yield, 1.77 g. NMR analysis of the solid revealed the presence of two components, **7** and **29**. Recrystallization of the mixed solids from absolute ethanol gave 0.63 g of 2,2′-thiobisdimedone (**29**) as fine needles; mp 229–231 °C [lit. mp 230–231 °C]. The filtrate was evaporated to dryness, and the white solid which remained was recrystallized from ethyl acetate, two crops of material being isolated; yield 0.72 g, 0.14 g. This product was identified as dimedone (**7**) by its melting point (149–150 °C) and by ^1H NMR analysis.

The original ethyl acetate filtrate was concentrated to dryness, and the material which remained was subjected to column chromatography on Florisil, 24 fractions being collected; fractions 1–2 (C_6H_{12}), 3–5 (Et_2O/C_6H_{12}, 2:8), 6–13 (Et_2O/C_6H_{12}, 3:7), 14–15 (Et_2O/C_6H_{12}, 5:5), 16–17 (Et_2O/C_6H_{12}, 8:2), 18–19 (Et_2O), 20–22 (Et_2O/CH_3CO_2Et, 5:5), 23–24 (CH_3CO_2Et). Fractions 1–8 gave **2** (1.961 g), 9–12 gave *mostly* **2** (0.289 g), 13 gave 0.027 g of mostly **7**, and 14–23 gave 0.840 g of **7** with unknown contaminants.

The solids from fractions 9–12 (0.289 g) were combined and recrystallized from 1:1 (v/v) cyclohexane/CH_2Cl_2, and 0.192 g of **2** was obtained. Thus, the total isolated yield of **2**, including the material from fractions 1–8, was 2.156 g (41%).

The combined solids from fractions 14–23 (0.839 g) were dissolved in hot ethyl acetate. Upon cooling, the solution yielded light yellow needles (0.424 g, mp 148–150 °C) which were isolated and recrystallized from ethyl acetate as long white needles; yield, 0.369 g; mp 149–150 °C. These were identified as **7**. The initial filtrate was concentrated to pale yellow needles which were recrystallized from ethyl acetate as fine, white needles (0.123 g, mp 149–150 °C) also identified as **7**. Thus, the total isolated yield of **7** was 1.36 g (28%).

The final filtrate above was then concentrated to a yellow solid (0.302 g) which was recrystallized from cyclohexane. In this way, 0.173 g of an unknown solid was obtained as a yellow powder; mp 184–185 °C. Although this material has not been identified, its elemental composition has been determined and is the same as that of compound **2**.

Characterization of 2,2′-Thiobisdimedone (29). This material has been reported as a product from the reaction of dimedone with dimethoxy disulfide in the presence of potassium *tert*-butoxide.[28] However, only its melting point has been reported, and, for that reason, we report its characterization here: NMR ($CDCl_3$) δ 1.06 (s, 12 H), 2.40 (s, 8 H), 10.14 (s, 2 H), exchangeable with D_2O; IR ($CHCl_3$) 6.16 (C=CC=O), 3.25 μm (OH).

Anal. Calcd for $C_{16}H_{22}O_4S$: C, 61.91; H, 7.14; S, 10.33. Found: C, 61.96; H, 7.20; S, 10.55.

Control Experiments: (1) **24** (3.438 g), CH_3OH (50 mL), 3 days, ambient conditions; 3.363 g (98%) of **24** recovered. (2) Thiophenol (5 mL), CH_2Cl_2 (50 mL), 3 days, ambient conditions; only 0.054 g (1%) of **6** obtained. (3) **1** (3.42 g), benzoic acid (2.53 g), CH_2Cl_2 (40 mL), 20 h at room temperature; 2.84 g (83%) of **1** recovered. (4) **15** (2.66 g), thiophenol (1.492 g), CH_3CN (40 mL), 20 h at room temperature; 2.448 g (92%) of **15** recovered. (5) **1** (1.038 g), sodium thiophenoxide (0.544 g), CH_2Cl_2 (40 mL), 20 h at room temperature; 0.509 g (94%) sodium thiophenoxide recovered; 0.988 g (94%) of **1** recovered. (6) **31** (1.826 g), thiophenol (3.012 g), CH_2Cl_2 (35 mL), 24 h at room temperature; 1.699 g (93%) of **31** recovered. (7) **32** (1.613 g), thiophenol (2.018 g), CH_2Cl_2 (30 mL), 24 h at room temperature; 1.539 g (95%) of **32** recovered.

Registry No.—**1**, 35024-12-5; **2**, 56995-07-4; **15**, 2580-24-7; **16**, 6267-39-6; **18**, 66102-87-2; **19**, 66102-88-3; **27**, 64897-93-4; **28**, 66102-89-4; **29**, 66102-90-7; **31**, 1807-68-7; **32**, 7039-33-0; sodium thiophenoxide, 930-69-8; methanethiol, 74-93-1; hydrogen sulfide, 7783-06-4.

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Ring Transformations of Heterocyclic Halogeno Compounds with Nucleophiles. 39.[1] Carbon-13 and Proton Nuclear Magnetic Resonance Investigations on the Mechanism of the Ring Transformation Reaction of Pyrimidines into *s*-Triazines[2]

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Treatment of 4-chloro-2-dimethylaminopyrimidine (**1a**) and its 5-phenyl derivative (**1b**) with potassium amide in liquid ammonia and subsequent workup of the reaction mixtures lead to the formation of 2-dimethylamino-4-methyl-*s*-triazine and 4-benzyl-2-dimethylamino-*s*-triazine, respectively. By extensive ^{13}C NMR investigations of both reaction mixtures in liquid ammonia containing potassium amide, a number of unstable intermediates could be identified: from **1a** the 1:1 anionic σ complex **2a** and the anionic open-chain intermediate aminoethynyldiazabutadiene **3**; from **1b**, the σ complex **2b** and the anionic aminodiazabutadiene **7**, but also a redox product of **7**, i.e., the cyanoaminoazabutadiene **8**. Based upon the results of a deuterium labeling experiment it is assumed that the conversion of **7** into **8** occurs by an intramolecular oxidation–reduction process.

Several papers have been published concerning σ-adduct formation between the nucleophilic amide ion and the parent diazines,[3] as well as some of their derivatives, containing a leaving group (Cl, Br, SCH_3, and SO_2CH_3).[4-8]

The results of these studies show that in the absence of a leaving group the σ complex is stable and does not undergo a subsequent reaction[3,5] but that in the presence of such a leaving group, however, further reactions beyond the stage of the σ adduct can occur.[4-8]

A reaction which has attracted our interest for several years is the ring transformation of 2-substituted 4-chloropyrimidines into 2-substituted 4-methyl-*s*-triazines by potassium amide in liquid ammonia.[9] ^1H- and ^{13}C-NMR spectroscopy indicated that the first step in this ring interconversion is the formation of a 1:1 anionic σ complex **2a** in which the amide ion is thus not attached to C-4, the carbon bearing the halogen substituent, but to C-6.[5,6] More examples of this unexpected addition behavior have been found with other diazines.[4,8]

We have investigated by ^{13}C-NMR spectroscopy two reactions in particular, i.e., the ring transformation of 4-chloro-2-dimethylaminopyrimidine (**1a**) into 2-dimethylamino-4-methyl-*s*-triazine (**5a**) (yield 80% with potassium amide) and the hitherto unknown conversion of 4-chloro-2-dimethylamino-5-phenylpyrimidine (**1b**) into 4-benzyl-2-dimethylamino-*s*-triazine (**5b**) (yield 60% with potassium amide), specially aiming to obtain information about intermediates beyond the stage of the σ adduct.

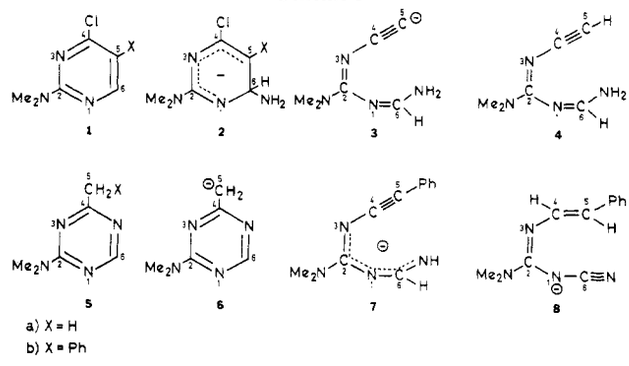
Results and Discussion

4-Chloro-2-dimethylaminopyrimidine (1a). From the results of our studies we reached the conclusion that the conversion of **1a** into **5a** occurs by the following reaction sequence **1a** → **2a** → **3** → **4** → **5a** (see Scheme I). Evidence for this mechanism is based on the following data. Addition of **1a** to 2 equiv of potassium amide in liquid ammonia gives the σ adduct **2a** (see Table I). Surprisingly we observed that when the excess of potassium amide is raised to 4 equiv and the reaction time is prolonged, the ^{13}C-NMR spectrum of the resulting reaction mixture is completely different from that of the σ complex **2a.** The new spectral data have been assigned to the intermediate aminoethynyldiazabutadiene anion **3** (see Table I). Two sharp signals at δ 113.3 and 118.5 have been attributed to the acetylenic carbons C-4 and C-5 and two signals at δ 168.4 (J_{C-H} = 157 Hz) and 166.0, both being broadened, to C-2 and C-6, respectively.[10] The broadening observed for the resonances of C-2 and C-6 may well find its cause in *E–Z* isomerism around the N-1–C-6 double bond.

Also the ^1H-NMR spectrum of a solution, obtained by reaction of **1a** with 4 equiv of KNH_2/NH_3 for 30 min, confirms the formation of intermediate **3.** Besides the sharp singlet at δ 2.62 of the dimethylamino substituent, a very broad adsorption band around δ 8 belonging to H-6 is found.

Intermediate **3** is found to be stable for at least 5 h under the reaction conditions. Under these conditions no indication of the formation of the ultimate reaction product 2-dimethylamino-4-methyl-*s*-triazine (**5a**) could be obtained. However, when the reaction mixture was quenched with ammo-

Scheme I



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