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Chemistry of α,β-Unsaturated Thione Dimers. 3. Reactions of Thiochalcones and 2-Arylidene-1-thiotetralones with Cumulenes Containing a Carbon–Carbon Double Bond

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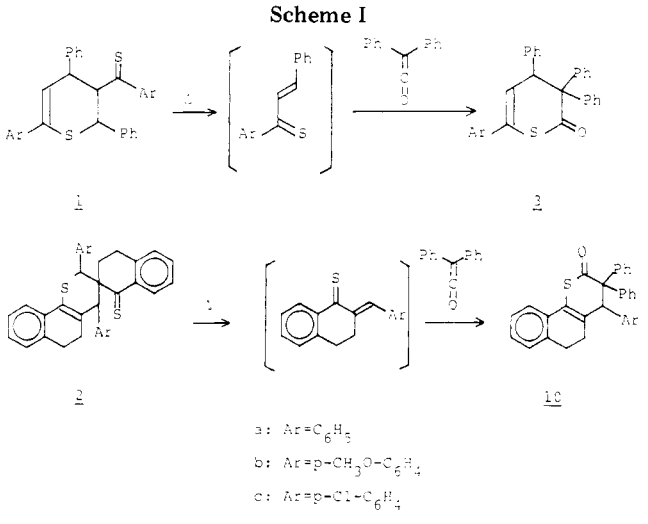
Thiochalcone, 4′-methoxythiochalcone, 2-benzylidene-1-thiotetralone, 2-(*p*-methoxybenzylidene)-1-thiotetralone, and 2-(*p*-chlorobenzylidene)-1-thiotetralone generated by the thermolysis of the corresponding thione dimer reacted as dienes with the cumulenes diphenylketene, fluorenylideneketene *N*-phenylimine, and tetraphenylallene. The reactions with diphenylketene and the allene gave the six-membered adduct via addition of the thione to the carbon–carbon double bond of the ketene and the allene. The reaction with the ketene imine gave two kinds of six-membered adducts: those via addition to the carbon–carbon double bond and those via addition to the carbon–nitrogen double bond.

Previously it was found that α,β-unsaturated thiones derived from thiochalcone (**1**) and 2-arylidene-1-thiotetralone (**2**) dimers readily underwent [4 + 2] cycloaddition reactions with dienophiles such as maleic anhydride, citraconic anhydride, styrene, norbornene, norbornadiene, and *n*-butyl vinyl ether.[1] In a continuation of the work we had an interest in the reaction of α,β-unsaturated thiones with cumulenes containing a carbon–carbon double bond which can participate as dipolarophiles or dienophiles in [4 + 2] and [2 + 2] cycloaddition reactions.[2] This report describes the results of the cycloaddition reactions of **1** and **2** with diphenylketene, fluorenylideneketene *N*-phenylimine, and tetraphenylallene.

The thermolysis of **1b** in the presence of diphenylketene gave the cycloadduct **3b**. The presence of the carbonyl group is indicated by a strong absorption at 1680 cm^{-1} in the IR spectrum. In the NMR spectrum, the doublets at 4.43 (J = 7.0 Hz) and 6.61 (J = 7.0 Hz) ppm are assigned to the benzylic and olefinic protons, respectively. The presence of one olefinic proton eliminates the possibility of four-membered structures **5b**, **6b**, **7b**, and **8b**, and the structure of **4b** is eliminated by the fact that the chemical shift of the benzylic proton of the product is close to that of dihydrothiopyran **9b**.[1] In the case of **1a**, the product **3a** could not be separated from diphenylketene dimer. The reaction with the other thione dimers **2** afforded the corresponding adduct **10**.

Scheme I



The reaction of **1b** with fluorenylideneketene *N*-phenylimine gave **11b** and **13b**, the structures of which were determined by ^{13}C NMR and ^{1}H NMR spectroscopy. The proton-noise-decoupled ^{13}C spectrum of **11b** showed the three alkyl carbon signals. The signals which appeared in the off-resonance decoupled spectrum were as follows: (1) a doublet at 52.9 ppm, (2) a quartet at 55.3 ppm, and (3) a singlet at 62.5 ppm. These signals correspond to the C-4 methine carbon, the methoxy carbon, and the C-3

(1) T. Karakasa and S. Motoki, *J. Org. Chem.*, **44**, 4151 (1979).
(2) L. Ghosez and M. J. O'Donnell, "Pericyclic Reactions", Vol. II, A. P. Marchand and R. E. Lehr, Eds., Academic Press, New York, 1977, p 79.

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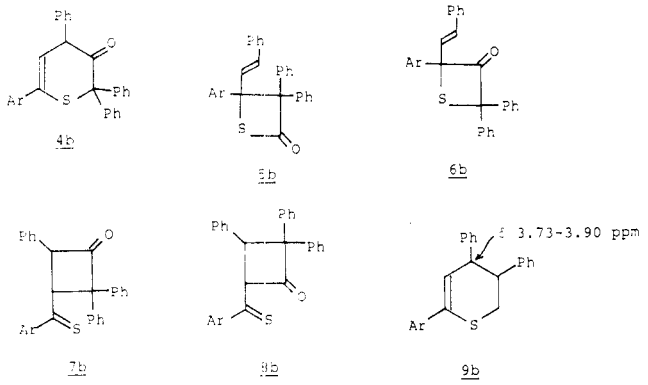
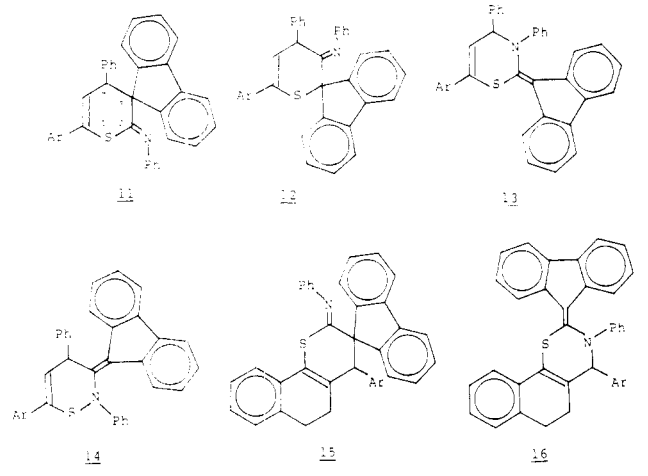
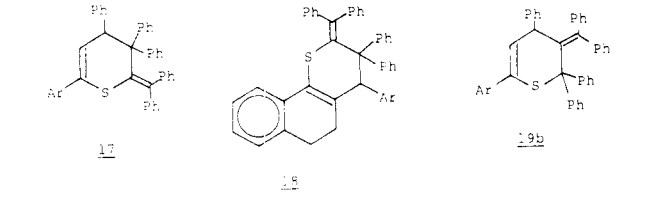


carbon, respectively. In the ^{1}H NMR spectrum, the doublets at 4.32 (J = 5.0 Hz) and 6.38 (J = 5.0 Hz) ppm are assigned to the benzylic and olefinic protons, respectively. The value of the chemical shift of the benzylic proton supports the proposed structure rather than its regioisomeric structure **12b**. Similarly, the structure of **13b** was determined by the ^{13}C NMR spectrum (two alkyl signals at 55.1 and 62.8 ppm corresponding to the methoxy and the C-4 carbons, respectively) and the ^{1}H NMR spectrum (the doublets at 5.92 (J = 7.0 Hz) and 6.40 (J = 7.0 Hz) ppm are assignable to benzylic and the olefinic protons, respectively). The reaction with the other thione dimers **1a** and **2** afforded the corresponding adducts (**11a**, **13a**, **15**, **16**).

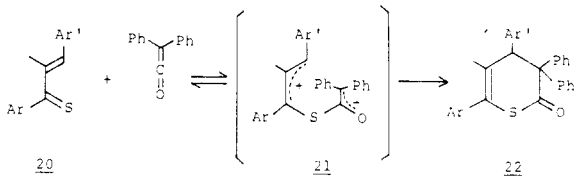


The thermolysis of **1b** with tetraphenylallene gave the adduct **17b**. The elemental analysis and mass spectrum are in agreement with the proposed structure **17b**. In the ^{1}H NMR spectrum, the doublets at 4.54 and 6.14 ppm are assigned to the benzylic and olefinic protons, respectively. The ^{13}C NMR spectrum showed the C-4 carbon signal at 56.8 ppm which supports the proposed structure rather than its regioisomeric structure **19b**. The reaction of **1a** and **2** with tetraphenylallene afforded the corresponding adducts **17a** and **18**.



We believe that the reactions of 1 and **2** with the ketene probably proceeded through formation of a zwitterionic intermediate. Indeed, during the reaction of **2** with diphenylketene we observed that the color of the reaction mixture changed from deep blue to pale yellow with

Scheme II



progress of the reaction. However, when the solvent was evaporated and ethanol was added to the residue after disappearance of the blue color, the color of the resultant solution turned from pale yellow to green. Evaporation of the ethanol gave a small amount of **2** and the corresponding ketone of **2**. The disappearance of the blue color of the reaction mixture indicates that almost all of **2** was consumed at that time, so appearance of the green color is considered to be due to the decompositon of the colorless intermediate **21** by ethanol because the product **22** is stable to ethanol. Perhaps, the sulfur atom in the α,β-unsaturated thione may be effective in favoring the stepwise mechanism due to the ability to stabilize the negative charge in an intermediate zwitterion **21**.[3] Similarly, the reaction of **1** and **2** with the keteneimine would proceed via a stepwise mechanism in analogy with the reaction with diphenylketene, because both of the fluorenylidene groups[4] in the keteneimine and the sulfur atom in the α,β-unsaturated thiones are expected to stabilize a zwitterionic intermediate. However, we have no positive evidence to support such a proposal[5] at present.

On the other hand, allenes have only weakly polarized double bonds and behave usually in a somewhat similar fashion to isolated olefinic double bonds.[2] Therefore, the reactions of **1** and **2** with the allene would proceed by a [4 + 2] concerted mechanism.

Experimental Section

All melting points are uncorrected. ^{1}H NMR spectra were recorded at 60 MHz on a JEOL JNM-PMX 60 spectrometer and at 100 MHz on a JEOL JNM-FX 100 spectrometer. Me_4Si was used as an internal standard. ^{13}C NMR spectra were recorded at 25 MHz on a JEOL JNM-FX 100 spectrometer with Me_4Si as an internal standard. IR spectra were obtained on a Hitachi Model 260-10 infrared spectrometer. Mass spectral data were obtained with a Hitachi RMU-7M double-focusing mass spectrometer. Thiochalcone, 4′-methoxythiochalcone, 2-benzylidene-1-thiotetralone, 2-(*p*-methoxybenzylidene)-1-thiotetralone, and 2-(*p*-chlorobenzylidene)-1-thiotetralone dimers were prepared and purified according to the method described previously.[6] Diphenylketene[7] and tetraphenylallene[8] were prepared by the methods described in the literature. Fluorenylideneketene *N*-phenylimine was prepared by the reaction of triphenylphospine–fluorenylidene with phenyl isocyanate:[9] yellow crystals; yield 64%; mp 85–86 °C; IR (Nujol) 2025 ($\nu_{C=C=N}$) cm^{-1}; mass spectrum (70 eV), m/e 267 (M^+, 100), 190 (58), 164 (66). Anal. Calcd for $C_{20}H_{13}N$: C, 89.86; H, 4.90. Found: C, 89.94; H, 4.73.

General Procedure for the Reactions with Diphenyl-

(3) It is known that the introduction of electron-donating groups on the diene and the presence of anion-stabilizing substituents on the ketene are expected to increase the stability of a dipolar intermediate which could then lead, at least partially, to either of the two possible six-membered-ring products.[2]

(4) A. Maercker, *Org. React.*, **14**, 278 (1965).

(5) Krow reported that diarylketene *N*-arylimines did not react as dienophiles in the [4 + 2] concerted cycloaddition reactions: G. R. Krow, *Angew. Chem., Int. Ed. Engl.*, **10**, 435 (1971).

(6) T. Karakasa and S. Motoki, *J. Org. Chem.*, **43**, 4147 (1978).

(7) E. C. Taylor, A. Mckillop, and G. H. Hawks, *Org. Synth.*, **52**, 36 (1972).

(8) W. Tadros, A. D. Sakla, and A. A. A. Hemy, *J. Chem. Soc.*, 2687 (1961).

(9) P. Froyen, *Acta Chem. Scand., Ser. B*, **28**, 586 (1974).

Table I. Reactions with Diphenylketene, Fluorenylideneketene *N*-Phenylimine, and Tetraphenylallene

product	reacn time, min	% yield	isolatn proced[a]	mp, °C
3b	75	11	A	145.5-147
10a	45	51	B	208-209
10b	20	35	A	169.5-170.5
10c	35	17	B	217-218
11a[b]	4	5[c]	C	257-259
13a[b]		5[c]		188
11b	12	23	C	221-222
13b		59		138-140
15a	12	39	C	211.5-213.5
16a		45		192-194
15b	8	50	C	208-209.5
16b		30		161-162
15c	18	58	C	275-276
16c		37		210-212
17a[b]	60	7[c]	C	165-167 dec
17b	80	59	C	160-161 dec
18a	35	83	C	191-192 dec
18b	15	50	C	191-193 dec
18c	45	99	A	209-210.5 dec

[a] See Experimental Section. [b] Thiochalcone dimer (synthesized for 10 mmol of chalcone) was obtained as a deep blue syrup and used without crystallization. [c] Based on chalcone.

ketene, Fluorenylideneketene *N*-Phenylimine, and Tetraphenylallene. A suspension of the α,β-unsaturated thione dimer (1.5 mmol) and the cumulene (3 mmol) in dry benzene (5 mL) was gently refluxed under a nitrogen atmosphere. The reaction times are given in Table I. The benzene was evaporated. Isolation of the products was performed by using several slightly different procedures.

Isolation Procedure A. The residue was recrystallized from a suitable solvent.

Isolation Procedure B. Ethanol was added to the residue. The solid product (crude adduct) which separated was isolated by filtration. The green filtrate was concentrated to give a mixture of the α,β-unsaturated thione dimer and the corresponding ketone.

Isolation Procedure C. The residue was chromatographed on Wakogel C-200 (silica gel 100–200 mesh) by eluting with benzene–ligroin.

6-(*p*-Methoxyphenyl)-3,3,4-triphenyl-3,4-dihydro-2*H*-thiopyran-2-one (3b): recrystallized from ethanol; IR (Nujol) 1680 (C=O) cm^{-1}; mass spectrum (70 eV), *m/e* 448 (M^+, 8), 254 (100), 253 (82), 239 (2), 223 (3), 194 (75), 151 (11); ^1H NMR ($CDCl_3$) δ 3.72 (s, 3 H), 4.43 (d, *J* = 7.0 Hz, 1 H), 6.61 (d, *J* = 7.0 Hz, 1 H), 6.38-7.62 (m, 19 H). Anal. Calcd for $C_{30}H_{24}O_2S$: C, 80.33; H, 5.39. Found: C, 80.62; H, 5.45.

3,3,4-Triphenyl-5,6-dihydrobenzo[*h*]thiochroman-2-one (10a): recrystallized from ethanol; IR (Nujol) 1680 (C=O) cm^{-1}; mass spectrum (70 eV), *m/e* 444 (M^+, 9), 250 (100), 249 (89), 194 (75); ^1H NMR ($CDCl_3$) δ 2.30–2.83 (m, 4 H), 4.15 (s, 1 H), 6.33–7.55 (m, 24 H). Anal. Calcd for $C_{31}H_{24}OS$: C, 83.75; H, 5.44. Found: C, 84.14; H, 5.42.

4-(*p*-Methoxyphenyl)-3,3-diphenyl-5,6-dihydrobenzo[*h*]-thiochroman-2-one (10b): recrystallized from ethanol; IR (Nujol) 1680 (C=O) cm^{-1}; mass spectrum (70 eV), *m/e* 474 (M^+, 7), 280 (100), 279 (63), 265 (24), 249 (53), 194 (70); ^1H NMR ($CDCl_3$) δ 2.32–2.88 (m, 4 H), 3.68 (s, 3 H), 4.13 (s, 1 H), 6.40–7.43 (m, 23 H). Anal. Calcd for $C_{32}H_{26}O_2S$: C, 80.98; H, 5.52. Found: C, 80.99; H, 5.70.

4-(*p*-Chlorophenyl)-3,3-diphenyl-5,6-dihydrobenzo[*h*]-thiochroman-2-one (10c): recrystallized from ethanol; IR (Nujol) 1680 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30–2.88 (m, 4 H), 4.15 (s, 1 H), 6.40–7.58 (m, 23 H). Anal. Calcd for $C_{31}H_{23}ClOS$: C, 77.73; H, 4.84. Found: C, 77.63; H, 4.79.

11a: recrystallized from benzene–ligroin; colorless crystals; mass spectrum (70 eV), *m/e* 491 (M^+, 6), 267 (100), 190 (18), 164 (26) [*m/e* 491.1682 (*m/e* calcd for $C_{35}H_{25}NS$ 491.1708)]. Anal. Calcd for $C_{35}H_{25}NS$: C, 85.51; H, 5.13. Found: C, 85.79; H, 5.33.

13a: recrystallized from benzene–ligroin; yellow crystals; mass spectrum (70 eV), *m/e* 491 (M^+, 3), 267 (100), 224 (26), 223 (58), 190 (48), 164 (54); ^1H NMR ($CDCl_3$) δ 6.00 (d, *J* = 7.0 Hz, 1 H), 6.58 (d, *J* = 7.0 Hz, 1 H), 6.77–8.52 (m, 23 H) [*m/e* 491.1708 (*m/e* calcd for $C_{35}H_{25}NS$ 491.1708)]. Anal. Calcd for $C_{35}H_{25}NS$: C, 85.51; H, 5.13. Found: C, 85.71; H, 5.11.

11b: recrystallized from benzene–ligroin; colorless crystals; mass spectrum (70 eV), *m/e* 521 (M^+, 4), 267 (100), 254 (6), 253 (12), 190 (21), 164 (29); ^1H NMR ($CDCl_3$) δ 3.77 (s, 3 H), 4.32 (d, *J* = 5.0 Hz, 1 H), 6.38 (d, *J* = 5.0 Hz, 1 H), 6.47-7.78 (m, 22 H). Anal. Calcd for $C_{36}H_{27}NOS$: C, 82.89; H, 5.22. Found: C, 82.79; H, 5.36.

13b: recrystallized from benzene–ligroin; yellow crystals; mass spectrum (70 eV), *m/e* 521 (M^+, 2), 267 (100), 254 (22), 253 (43), 190 (39), 164 (48); ^1H NMR ($CDCl_3$) δ 3.62 (s, 3 H), 5.92 (d, *J* = 7.0 Hz, 1 H), 6.40 (d, *J* = 7.0 Hz, 1 H), 6.68–8.52 (m, 22 H). Anal. Calcd for $C_{36}H_{27}NOS$: C, 82.89; H, 5.22. Found: C, 82.87; H, 5.10.

15a: recrystallized from benzene–ligroin; colorless crystals; mass spectrum (70 eV), *m/e* 517 (M^+, 7), 267 (100), 190 (14), 164 (18); ^1H NMR ($CDCl_3$) δ 1.97–2.70 (m, 4 H), 3.20 (s, 1 H), 5.97–7.85 (m, 22 H). Anal. Calcd for $C_{37}H_{27}NS$: C, 85.84; H, 5.26. Found: C, 85.57; H, 5.30.

16a: recrystallized from benzene–ligroin; yellow crystals; mass spectrum (70 eV), *m/e* 517 (M^+, 10), 267 (100), 250 (9), 249 (19), 190 (28), 164 (32); ^1H NMR ($CDCl_3$) δ 2.17–3.00 (m, 4 H), 5.70 (s, 1 H), 6.40–8.48 (m, 22 H). Anal. Calcd for $C_{37}H_{27}NS$: C, 85.84; H, 5.26. Found: C, 85.97; H, 5.35.

15b: recrystallized from benzene–ligroin; colorless crystals; mass spectrum (70 eV), *m/e* 547 (M^+, 11), 280 (2), 267 (100), 190 (14), 164 (16); ^1H NMR ($CDCl_3$) δ 2.03–3.07 (m, 4 H), 5.68 (s, 1 H), 6.60–8.53 (m, 21 H). Anal. Calcd for $C_{38}H_{29}NOS$: C, 83.33; H, 5.34. Found: C, 83.39; H, 5.57.

16b: recrystallized from benzene–ligroin; yellow crystals; mass spectrum (70 eV), *m/e* 547 (M^+, 9), 280 (7), 279 (12), 267 (100), 249 (7), 190 (25), 164 (26); ^1H NMR ($CDCl_3$) δ 2.17–2.92 (m, 4 H), 3.45 (s, 3 H), 5.70 (s, 1 H), 6.50–8.58 (m, 21 H). Anal. Calcd for $C_{38}H_{29}NOS$: C, 83.33; H, 5.34. Found: C, 83.34; H, 5.48.

15c: recrystallized from benzene–ligroin; colorless crystals; mass spectrum (70 eV), *m/e* 551 (M^+, 1), 267 (100), 190 (18), 164 (29). Anal. Calcd for $C_{37}H_{26}ClNS$: C, 80.49; H, 4.75. Found: C, 80.44; H, 5.05.

16c: recrystallized from benzene–ligroin; yellow crystals; mass spectrum (70 eV), *m/e* 551 (M^+, 4), 284 (5), 283 (9), 267 (100), 249 (9), 190 (22), 164 (28); ^1H NMR ($CDCl_3$) δ 2.13–3.07 (m, 4 H), 5.68 (s, 1 H), 6.60–8.53 (m, 21 H). Anal. Calcd for $C_{37}H_{26}ClNS$: C, 80.49; H, 4.75. Found: C, 80.44; H, 5.05.

3,3,4,6-Tetraphenyl-2-(diphenylmethylene)-3,4-dihydro-2*H*-thiopyran (17a): recrystallized from benzene–ligroin; mass spectrum (70 eV), *m/e* 548 (M^+), 344 (100), 267 (42), 224 (28), 223 (64); ^1H NMR ($CDCl_3$) δ 4.55 (d, *J* = 6.0 Hz, 1 H), 6.22 (d, *J* = 6.0 Hz, 1 H), 6.34–7.70 (m, 30 H). Anal. Calcd for $C_{42}H_{32}S$: C, 88.69; H, 5.67. Found: C, 88.70; H, 5.66.

6-(*p*-Methoxyphenyl)-3,3,4-triphenyl-2-(diphenylmethylene)-3,4-dihydro-2*H*-thiopyran (17b): recrystallized from benzene–hexane; mass spectrum (70 eV), *m/e* 598 (M^+), 344 (100), 267 (38), 254 (25), 253 (45); ^1H NMR ($CDCl_3$) δ 3.68 (s, 3 H), 4.54 (d, *J* = 6.0 Hz, 1 H), 6.14 (d, *J* = 6.0 Hz, 1 H), 6.23–7.68 (m, 29 H). Anal. Calcd for $C_{43}H_{34}OS$: C, 86.25; H, 5.72. Found: C, 86.01; H, 5.77.

3,3,4-Triphenyl-2-(diphenylmethylene)-5,6-dihydrobenzo[*h*]thiochroman (18a): recrystallized from benzene–ethanol; mass spectrum (70 eV), *m/e* 594 (M^+), 344 (100), 267 (39), 250 (42), 249 (77); ^1H NMR ($CDCl_3$) δ 2.08–2.54 (m, 4 H), 4.06 (s, 1 H), 6.18–7.98 (m, 29 H). Anal. Calcd for $C_{44}H_{34}S$: C, 88.85; H, 5.76. Found: C, 89.13; H, 5.82.

4-(*p*-Methoxyphenyl)-3,3-diphenyl-2-(diphenylmethylene)-5,6-dihydrobenzo[*h*]thiochroman (18b): recrystallized from ethanol; mass spectrum (70 eV), *m/e* 624 (M^+), 344 (100), 280 (33), 279 (46), 267 (49), 249 (30); ^1H NMR ($CDCl_3$) δ 2.08–2.56 (m, 4 H), 3.80 (s, 3 H), 4.01 (s, 1 H), 6.28–7.96 (m, 28 H). Anal. Calcd for $C_{45}H_{36}OS$: C, 86.50; H. 5.81. Found: C, 86.62; H, 5.95.

4-(*p*-Chlorophenyl)-3,3-diphenyl-2-(diphenylmethylene)-5,6-dihydrobenzo[*h*]thiochroman (18c): recrystallized from ethanol; mass spectrum (70 eV), *m/e* 628 (M^+), 344 (100), 284 (24), 283 (41), 267 (44), 249 (39); ^1H NMR ($CDCl_3$) δ 2.06–2.56 (m, 4 H), 4.08 (s, 1 H), 6.20–7.96 (m, 28 H). Anal.

Calcd for $C_{44}H_{33}ClS$: C, 83.99; H, 5.29. Found: C, 84.22; H, 5.44.

Registry No. **1a**, 67254-57-3; **1b**, 67314-93-6; **2a**, 67254-58-4; **2b**, 67254-59-5; **2c**, 67254-60-8; **3a**, 72478-72-9; **3b**, 72478-73-0; **10a**, 72478-74-1; **10b**, 72478-75-2; **10c**, 72478-76-3; **11a**, 72478-77-4; **11b**, 72478-78-5; **13a**, 72478-79-6; **13b**, 72478-80-9; **15a**, 72478-81-0; **15b**, 72478-82-1; **15c**, 72478-83-2; **16a**, 72478-84-3; **16b**, 72478-85-4; **16c**, 72478-86-5; **17a**, 72478-87-6; **17b**, 72478-88-7; **18a**, 72478-89-8; **18b**, 72478-90-1; **18c**, 72478-91-2; diphenylketene, 525-06-4; fluorenylideneketene *N*-phenylimine, 1749-21-9; tetraphenylallene, 1674-18-6.

Supplementary Material Available: NMR data for **11**, **13**, **15**, **16**, **17**, and **18** (4 pages). Ordering information is given on any current masthead page.

Reductive Coupling of Aromatic Sulfinate Salts to Disulfides[1,2]

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A variety of aromatic sulfinate salts undergo reductive coupling to disulfides in the presence of ethyl hypophosphite. Support for the intermediacy of sulfoxy sulfones and thiosulfonates has been obtained.

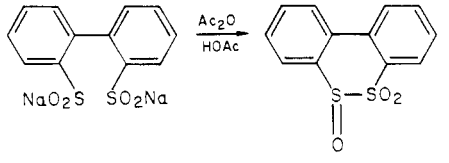
We wish to report a new method for the synthesis of disulfides by reductive coupling of sulfinate salts[4] through the agency of ethyl hypophosphite[5,6] (eq 1). Thus, simply

$$ArSO_2M + CH_3CH_2OP(O)H_2 \xrightarrow{Me_2SO} ArSSAr \quad (1)$$

allowing a sulfinate salt to react with ethyl hypophosphite in dimethyl sulfoxide (Me_2SO) overnight gives the corresponding disulfide (see Table I). For example, sodium benzenesulfinate is converted into phenyl disulfide in 64% yield. The reaction seems to be limited to aromatic sulfinate salts since all attempts to reduce aliphatic sulfinates[4] did not yield clean products. Purification by distillation or column chromatography resulted in low recovery of nonpolar material.

Although the mechanism of the conversion of eq 1 is not firmly established, a preliminary investigation has revealed some interesting facts. First, the use of excess ethyl hypophosphite or sulfinate salt lowers the yield of disulfide. For example, a 2:1 ratio of ethyl hypophosphite to sodium benzenesulfinate gives a 52% yield of phenyl disulfide. A 1:2 ratio of these reactants leads to a 36% yield of product. In addition, methyl hypophosphite, available from the ethyl ester by exchange with methanol,[5] also reduces sodium benzenesulfinate to phenyl disulfide in 73% yield. Diethyl phosphite does not react with sodium benzenesulfinate, nor does sodium benzenesulfonate give any organic soluble material when allowed to stir with ethyl hypophosphite in Me_2SO.

These results make sense in view of the recent report by Kice[7a] of intramolecular coupling of sulfinate salts by acetic anhydride (eq 2). Although no mechanism is proposed for this reaction, it is tempting to assume the formation of a mixed anhydride between the sulfinic acid and acetic acid[7b] which then "sulfenylates" the remaining sulfinate salt on sulfur. The analogous reaction in our system is shown in eq 3. Thus, ethyl hypophosphite acts

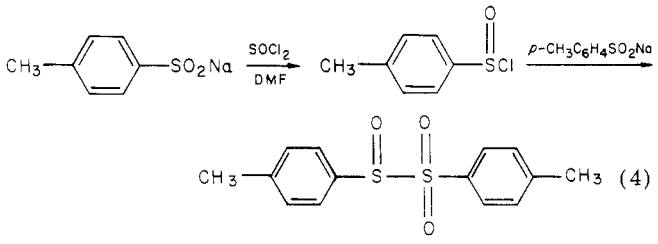


(2)

$$C_6H_5SO_2Na \xrightarrow{EtOP(O)H_2} C_6H_5S(O)OP(O)H_2 \xrightarrow{C_6H_5SO_2Na} C_6H_5S(O)S(O)_2C_6H_5 + NaOP(O)H_2 \quad (3)$$

as an efficient coupling reagent.[8] Diethyl phosphite apparently is unable to function in this way. Sulfonate salts cannot form sulfur–sulfur bonds and therefore do not couple.

A sulfoxy sulfone was prepared in order to test the feasibility of it as an intermediate (eq 4).[9] This sulfoxy sulfone was allowed to react with ethyl hypophosphite in Me_2SO under the usual conditions to give *p*-tolyl disulfide in 29% yield. Deoxygenation by a phosphorus-containing compound is not surprising since trivalent phosphorus is well-known to convert sulfoxides into sulfides.[10] In ad-



(4)

(1) A portion of this work was presented at the 30th Southeastern Regional Meeting of the American Chemical Society, Savannah, GA, Nov 8–10, 1978.

(2) Taken in part from the Ph.D. dissertation of Michael A. Reynolds, University of Georgia, 1979.

(3) Undergraduate research participant.

(4) Readily available from organolithium and Grignard reagents plus sulfur dioxide: Pinnick, H. W.; Reynolds, M. A. *J. Org. Chem.* **1979**, *44*, 160.

(5) Pinnick, H. W.; Reynolds, M. A. *Synth. Commun.* **1979**, *9*, 535.

(6) To our knowledge the only previous example of disulfide formation from compounds with sulfur in a high oxidation state is the report of the conversion of sulfonyl chlorides into disulfides by trichlorosilane and tri-*n*-propylamine: Chan, T. H.; Montillier, J. P.; Van Horn, W. F.; Harpp, D. N. *J. Am. Chem. Soc.* **1970**, *92*, 7224.

(7) (a) Chau, M. M.; Kice, J. L. *J. Org. Chem.* **1977**, *42*, 3265. (b) For a recent report of the preparation of a stable mixed carboxylic–sulfinic acid anhydride, see: Kohn, H.; Charumilind, P.; Simonsen, S. H. *J. Am. Chem. Soc.* **1979**, *101*, 5431.

(8) Acetic anhydride/acetic acid converts sodium benzenesulfinate into the sulfoxy sulfone in poor yield.

(9) (a) Brederick, H.; Wagner, A.; Beck, H.; Klein, R.-J., *Chem. Ber.* **1960**, *93*, 2736. (b) The intermediate sulfinyl chloride was not isolated.

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