Mercuric Ion-Catalyzed Hydration of Derivatives of 1,4-dichloro-2-butyne. Hydration of 1-Aryloxy-4-arylthio-2-butynes, 1,4-*bis*(Arylthio)-2-butynes, and 1,4-*bis*(Arylsulfonyl)-1-butynes.

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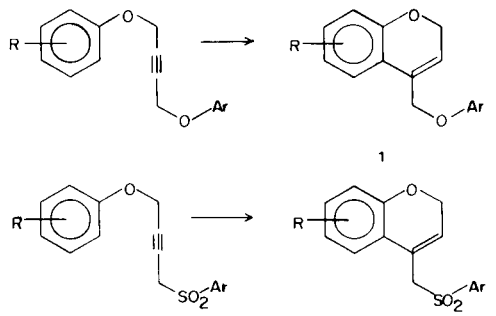
Received June 6, 1974

The mercuric ion-catalyzed hydration of 1,4-*bis*(arylthio)-2-butynes and 1-aryloxy-4-arylthio-2-butynes was studied. The 1,4-*bis*(arylsulfonyl)-2-butynes afforded 1,4-*bis*(arylsulfonyl)-2-butanones (**7**). The 1,4-*bis*(arylthio)-2-butynes afforded a variety of products in acetic acid among which were: 1,4-*bis*(arylthiomethyl)vinyl acetate (**18**); 1,4-*bis*(arylthio)-2-butanone (**15**); 1-(arylthio)-3-buten-2-one (**16**); and 1-(arylthio)-4-acetoxy-2-butanone (**17**). Ketone **15** eliminates arylthiol in an acidic medium yielding **16** which undergoes Michael addition of solvent to give **17**. Treatment of **7** with base in the presence of a nucleophile (ArSH) analogously leads to elimination of arylsulfinic acid, followed by Michael addition of arylthiol. Hydration of **5** in methanol cleanly gave 1-(arylthio)-4-methoxy-2-butanones (**19**). In contrast, 1-aryloxy-4-arylthio-2-butynes afforded chromenes (**8**) by intramolecular cyclization. No thiochromenes were formed in any of the examples investigated.

Hydration of alkynes has long evoked interest as a synthetic reaction of value (1). Catalyzed by mineral or Lewis acids and mercuric ion, the products of such hydration have variously afforded ketones (2), enol acetates (3), ketals (4), and heterocyclic ring products (5).

As part of our investigations (6) on the thermal rearrangements of 1,4-*bis*(aryloxy)-2-butynes, we reported (7) on the formation of the chormene **1** under conditions normally employed for the hydration of the triple bond. Such a facile ring closure was then extended to the synthesis of the chromene **3** from the butyne **2** (7a).



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2 3

Such facility of cyclization to chromenes in these reactions, prompted further inquiry along the following lines:

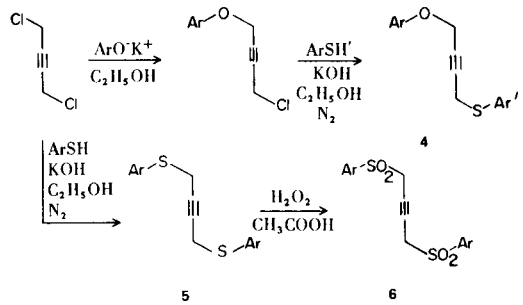
a) Can thiochromenes be synthesized analogously?

b) When using 1-aryloxy-4-arylthio-2-butyne, what is the extent of chromene versus thiochromene formation?

c) What are the likely intermediates, if any, in such ring closure?

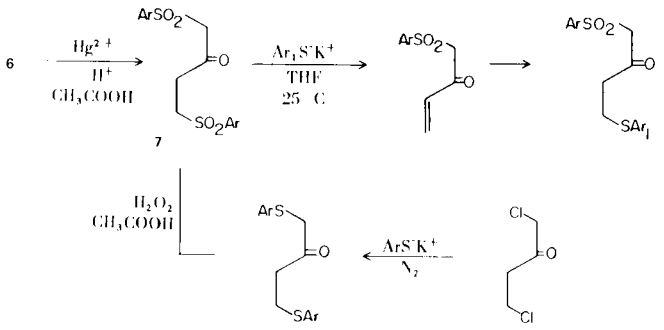
The present study provides answers for some of these questions in relation to the three systems **4**, **5**, and **6**. These were readily synthesized from 1,4-dichloro-2-butyne as shown in Scheme I.

Scheme I



Hydration of the alkyne **6** is clear-cut and simple. It provides emphatic evidence for the need for an *ortho*-activating function in the alkyne in order to observe any ring closure. Thus the product of hydration from **6** is ketone **7** obtained in high yields and purity. Structure **7** was also confirmed by an alternative synthesis as shown in Scheme II. Ketone **7** is extremely stable to the acidic

Scheme II

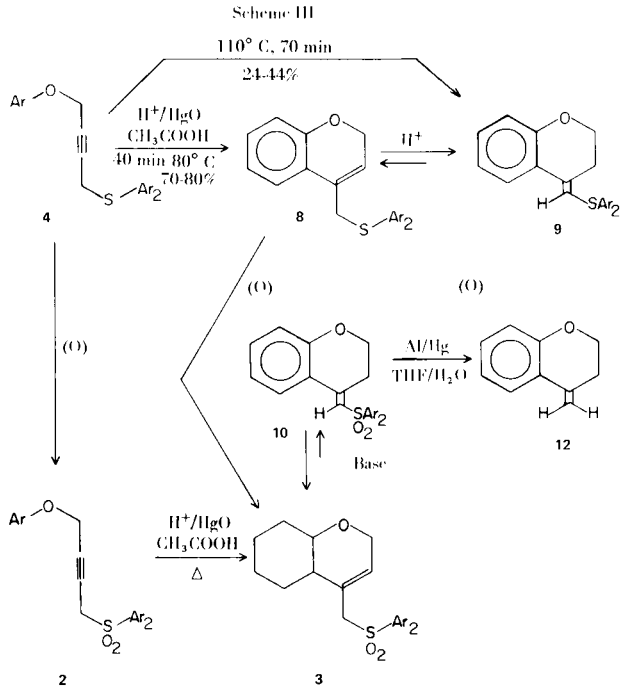


hydration conditions, although under mildly alkaline conditions, it is susceptible to an elimination-addition sequence (Scheme II).

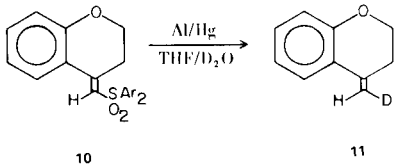
With such a clear demonstration of the need for an *ortho*-activating group to promote ring closures, the hydration of 1-aryloxy-4-arylthio-2-butynes was investigated using hot glacial acetic acid as solvent along with mercuric oxide and a trace of concentrated sulfuric acid as catalysts. From each of the five examples studied, a single product in yields of 24-44% was obtained. One of these sulfides was readily identified as the chromene **8** by its facile oxidation to the sulfone **3** reported earlier (7a). Each of the other four sulfides showed nmr spectra which were distinctly different from that of **8**. Oxidation of these sulfides with *m*-chloroperbenzoic acid afforded the appropriate sulfones **10**. Interestingly, chromatography of these sulfones over basic alumina (or treatment of a chloroform solution with dilute alkali in an nmr tube) resulted in a quantitative conversion into the Δ^3-chromenes (**3**). The sulfones **10** were, however, quite stable to chromatography over neutral alumnia. Isomerization of a vinylic sulfone into the corresponding allylic sulfone during chromatography has been observed previously (8). Additional corroboration of the vinyl sulfone structure in the sulfone **10** was readily secured by an aluminium-amalgam reduction of the vinyl sulfone to the 4-methylene chroman **12**. The hydration of 1-aryloxy-4-arylthio-2-butynes may thus be summarized as shown in Scheme III.

An interesting parenthetic observation in the formation of the chromenes is the fact that, both with the sulfides and the sulfones, the initial product of the cyclization is the Δ^3-chromene. Acid-catalyzed equilibration of the sulfide, however, results in conversion to the exomethylene compound. The geometrical disposition of the sulfone with respect to the benzene ring of the chromene may reasonably be expected to be trans, since it arises by acid-catalyzed equilibration of the endocyclic double bond to the exomethylene function. Added confirmation for this feature was secured in the following manner. Reduction

Scheme III



by aluminium amalgam in deuterium oxide at low temperature led to cleavage of the sulfone function and incorporation of a deuterium atom in its place. The nmr spectrum of this product, **12a**, readily revealed the site of the deuterium atom as shown below:

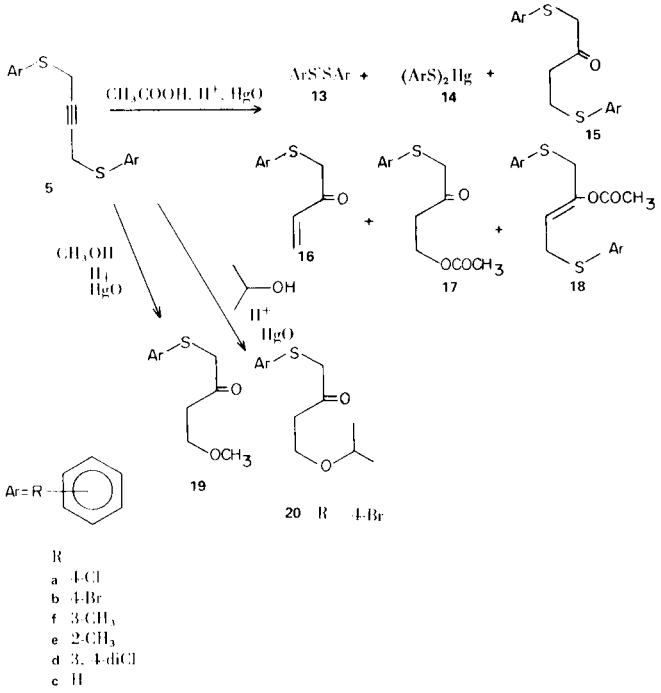


It is noteworthy that the specific location of deuterium was temperature dependent. Reduction of the sulfone at temperatures above 0° resulted in scrambling of the deuterium on the terminal methylene, leading to mixtures of **12a** and its geometrical isomer.

Aside from these intrinsically interesting observations, the hydration of 1-aryloxy-4-arylthio-2-butynes demonstrates a well defined preference for formation of a 6-membered *oxygen* heterocycle and none of a possible thiochromene derivative. The next question was whether a thiochromene would form at all, if there were no competing aryloxy function. This was very readily settled by hydration of 1,4-*bis*(arylthio)-2-butynes, **5**.

The hydration reaction, upon careful scrutiny gave no indication of thiochromene formation, but a host of other very interesting products were isolated which offered clues for the failure to form chromene. The six different products obtained from the hydration reaction are illustrated in Scheme IV. The isolation of the enol acetate **18** from

Scheme IV



the hydration is not surprising in view of early observations by Hennion (3). Ketone **15** could readily form by hydrolysis of the enol acetate. Elimination of the arylthiol from **15** was also anticipated based on literature observations (9) of expulsion of methanol or water during hydration of α-methoxy and α-hydroxyalkynes, respectively. The present study, however, provides the first example of elimination of arylthiol under these conditions. Formation of the ω-acetoxy ketone **17** may stem from Michael addition of acetic acid to the enone. Corroborative evidence for such a suggestion comes from the formation of the ω-alkoxy ketones **19** and **20** when the solvent was changed from acetic acid to methanol and 2-propanol, respectively. Hydration of the alkyne in these solvents was a cleaner reaction, resulting in the formation of one major product, the alkoxy ketone. Thus a study of the hydration of 1,4-*bis*(arylthio)-2-butynes has failed to reveal formation of thiochromenes. This failure indicates lesser activation of the site of ring closure by the sulfide sulfur than by oxygen in the aryl propynyl ethers. The facility of extrusion of the arylthiol function provides added diversionary pathways for participation by the solvent.

Despite these variations, the butynyl sulfides offer some clue to the overall mechanism of the ring closure under hydration conditions. Although ketonic products are obtained from the sulfides **5**, no ring closure derivatives are detected. This is contrasted to the fact that ring closure products are obtained from 1-aryloxy-4-arylthio-2-butynes and their sulfones, but no ketonic products are detected among the hydration products. Thus formation of the ketones and the chromenes may be by entirely separate pathways.

EXPERIMENTAL

Melting points were determided on a Thomas-Hoover capillary melting point apparatus or a Fisher-Johns hot stage and are uncorrected. Nmr spectra were obtained on a Varian A-60 spectrometer using deuteriochloroform with TMS = δ 0.00 (d = doublet, t = triplet, m = multiplet, td = triplet of doublets, bs = broad singlet). Ir spectra were recorded on a Perkin Elmer 621 spectrophotometer using a) potassium bromide pellets, b) neat (crystallized melts for solids) on sodium chloride plates, or c) carbon tetrachloride solution. Mass spectra were recorded at 20 and 70 ev. on a Hitachi-Perkin Elmer RMU-6E mass spectrometer. The mass spectra of **6** have been described in detail (10). All other compounds gave correct molecular ions and reasonable fragmentation patterns. The synthesis of 1-aryloxy-4-arylthio-2-butynes has been reported previously (7b).

General Procedure for Preparation of 1,4-*bis*(Arylthio)-2-butynes.

The appropriate thiophenol (0.1 mole) was dissolved in 50 ml. of 95% ethanol and the flask flushed with nitrogen. A solution of 5.6 g. potassium hydroxide in 70 ml. of 80% ethanol was added over *ca.* 20 minutes. The solution was stirred an additional 20-30 minutes, then addition of 6.1 g. (0.05 mole) 1,4-dichloro-2-butyne was initiated (add over 20 minutes). The mixture was stirred under a positive nitrogen pressure overnight at 25°. The mixture was then filtered. If the product was a liquid, the filtrate was rotary evaporated, the residue taken into ether (400 ml.), and worked up as for the solid sulfides. If the sulfide was a solid, the filtrate yielded small amounts of the sulfide and was generally discarded. Instead, the solid collected was stirred with water (400 ml.) and refiltered. The remaining solid was dissolved in ether (400 ml.) and washed with 5% potassium hydroxide solution followed by water (2 x 250 ml.). The ether layer was then dried (sodium sulfate) and evaporated to give the pure sulfides having the physical properties and yields listed in Table I.

General Prodecure for Preparation of 1,4-*bis*(Arylsulfonyl)-2-butynes.

The procedure (11) of Truce was used to prepare the sulfones listed in Table II from the corresponding sulfide in 75-85% yield.

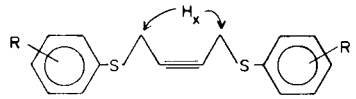
General Procedure for Hydration of 1-Aryloxy-4-arylthio-2-butynes.

A mixture of the title compound (10 g.), red mercuric oxide (2.6 g.), concentrated sulfuric acid (2-4 drops), and glacial acetic acid (50 ml.) was refluxed for 45-60 minutes. The mixture was cooled, diluted with ether (200 ml.) and filtered. The filtrate was diluted with an additional 200 ml. of ether and washed successively with 5% potassium hydroxide and water (2 x 200 ml.). Drying (magnesium sulfate or sodium sulfate) and solvent removal *in vacuo* gave a dark viscous liquid. This crude product was purified by filtration through netural alumina (2.5 x 15 cm) eluting with benzene/hexane. The compounds thus obtained as pale yellow oils are listed in Table III.

Osidation of **8a** with *m*-chloroperbenzoic acid (MCPBA) to the Corresponding Sulfone.

MCPBA (assumed 85%, 1.7 g.) in methylene chloride (150 ml.) was slowly added to a well stirred solution of 4-(4′-chlorophenylthiomethyl)-6-chloro-Δ^3-chromene, **8a**, (1.3 g.) in methylene

Table I



No.	R	M. p. (°C)	% Yield	Molecular Formula	Analysis Percent Calcd. C	Calcd. H	Found C	Found H	NMR (Hx only)
a	3,4-diCl	95-96.5	62	$C_{16}H_{10}Cl_4S_2$	47.0	2.5	46.9	2.3	3.55 (2H, s)
b	4-Cl	67-68	77	$C_{16}H_{12}Cl_2S_2$	55.5	3.6	55.7	3.6	3.55 (2H, s)
c	4-*t*-butyl	-	70	$C_{24}H_{30}S_2$		---			3.50 (2H, s)
d	3-Me	-	59	$C_{18}H_{18}S_2$		---			3.50 (2H, s)
e	4-Br	94-95.5	50	$C_{16}H_{12}Br_2S_2$	44.9	2.8	44.9	2.8	3.55 (2H, s)
f	2-Me	50-51	74	$C_{18}H_{18}S_2$	72.5	6.0	72.6	5.99	3.50 (2H, s)
g	4-Me	47.5-48.5	59	$C_{18}H_{18}S_2$	72.5	6.0	72.6	5.9	3.50 (2H, s)
h	H	46-47.5	66	$C_{16}H_{14}S_2$	71.0	5.2	71.0	5.0	3.50 (2H, s)
i	4-OMe	-	64	$C_{18}H_{18}O_2S_2$		---			3.48 (2H, s)

(a) A dash indicates the sulfide was an undistillable oil and was used without further purification.

Table II

1,4-Bisarylsulfonyl-2-butynes **6**

No.	R	M.p. (°C)	ν_{SO_2} (mc^{-1})	Molecular Formula	Analysis Percent Calcd. C	Calcd. H	Found C	Found H	NMR (b)
a (a)	H	158-159	1139, 1319	$C_{16}H_{14}O_4S_2$	57.5	4.2	57.4	4.3	7.57-8.10 (10H, M); 4.10 (4H, S); (ii).
b	4-Me	174-175	1149, 1316	$C_{18}H_{18}O_4S_2$	59.6	5.0	59.4	4.9	7.38-8.02 (8H, Q); 4.25 (4H, S); 2.54 (6H, S); (ii)
c	3-Me	116-118	1139, 1319	$C_{18}H_{18}O_4S_2$	59.6	5.0	59.6	4.9	7.38-7.83 (8H, M); 3.90 (4H, S); 2.42 (6H, S); (i)
d	2-Me	135-138	1124, 1316	$C_{18}H_{18}O_4S_2$	59.6	5.0	59.4	4.9	7.38-7.84 (8H, M); 3.90 (4H, S); 2.45 (6H, S); (i)
e	4-OMe	163-164.5	1121, 1325	$C_{18}H_{18}O_6S_4$	54.8	4.6	54.8	4.8	7.12-8.11 (8H, Q); 4.27 (4H, S); 4.03 (6H, S); (ii)
f	4-Cl	180-181	1139, 1319	$C_{16}H_{12}Cl_2O_4S_2$	48.0	3.50	48.0	3.5	7.51-8.05 (8H, Q); 3.93 (4H, S); (i)
g	4-Br	208-211	1121, 1325	$C_{16}H_{12}Br_2O_4S_2$	39.0	2.5	38.9	2.5	7.12-7.55 (8H, M); 3.50 (4H, S); (i)
h	4-*t*-Bu	195.5-196.5	1140, 1319	$C_{24}H_{30}O_4S_2$	65.0	6.8	65.0	6.8	7.45-8.05 (8H, M); 4.23 (4H, S); 1.39 (18H, S); (ii)

(a) Reported m.p., 158°; G. S. Pourcelot and P. Cadiot, *Bull. Soc. Chim. France*, 3024 (1966). (b) i = deuteriochloroform; ii = trifluoroacetic acid.

chloride (100 ml.) under reflux. After 3 hours more at reflux the cooled reaction mixture was treated with 5% sodium carbonate solution and then washed with water. Drying and solvent evaporation gave a white solid (105 g., 74%; m.p. 170-171°) identical spectroscopically with an authentic sample (7b) of 4-(4'-chlorophenylsulfonylmethyl)-6-chloro-Δ^3-chromene, **5a**.

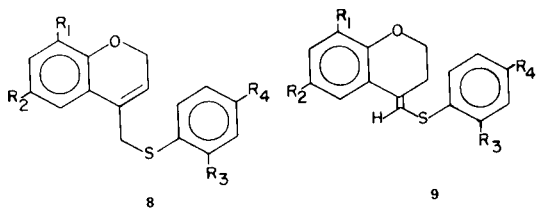
General Procedure for Oxidation of **9** to the Corresponding Sulfones **10**.

The procedure was similar to that described above but the reaction time varied. Starch-iodide test paper was used to indicate completion of the reaction (about 3 hours). The oils thus obtained solidified on cooling. Recrystallization gave the colorless crystalline sulfones listed in Table IV.

Rearrangement of **10** to **3**.

One tenth g. **10** was dissolved in 5 ml. of chloroform and placed on a 16 x 20 cm column of basic alumina (*p*H 9.5-10.5) for 25 minutes. Elution with chloroform quanitatively gave **3** identical (ir, nmr, m.p. m.m.p.) with authentic samples (7a).

Table III



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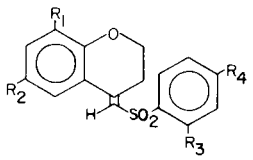
Cyclization Products from **4**, **8**, and **9**

No.	R_1	R_2	R_3	R_4	% Yield	NMR
8a	H	Cl	H	Cl	24	3.56 (s, 2H), 4.42-4.62 (d, 2H), 5.30-5.54 (t, 1H) 6.46-7.50 (m, 7H).
9b	H	CH_3	CH_3	H	37	2.21 (s, 3H), 2.36 (s, 3H), 2.66-2.96 (td, 2H), 4.03-4.32 (t, 2H), 6.60-7.50 (m, 8H).
9c	CH_3	H	CH_3	H	44	2.15 (s, 3H), 2.33 (s, 3H), 2.56-2.90 (td, 2H), 4.00-4.25 (t, 2H), 6.50-7.50 (m, 8H).
9d (a)	H	CH_3	H	Cl	27	2.18 (s, 3H), 2.52-2.83 (td, 2H), 3.92-4.20 (t, 2H) 6.50-7.40 (m, 8H).
9e	H	H	H	Cl	37	2.61-2.92 (td, 2H), 4.03-4.32 (t, 2H), 6.60-7.55 (m, 9H).

(a) This compound was obtained as a solid; m.p. 62-63.5°; *Anal.* Calcd. for $C_{17}H_{15}ClOS$: C, 67.5; H, 5.0. Found: C, 67.3; H, 5.0.

Table IV



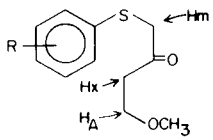
No.	R_1	R_2	R_3	R_4	Mp	Yield	NMR
a	H	CH_3	CH_3	H	127°	67%	2.23 (s, 3H), 2.65 (s, 3H), 3.01-3.33 (td, 2H) 4.00-4.30 (t, 2H), 6.63-7.55 (m, 7H), 7.99-8.23 (m, 1H).
b	CH_3	H	CH_3	H	119°	64%	2.10 (s, 3H), 2.78 (s, 3H), 2.99-3.30 (td, 2H), 3.97-4.28 (t, 2H), 6.55-7.50 (m, 7H), 7.90-8.20 (m, 1H).
c	H	CH_3	H	Cl	169-171°	65%	2.22 (s, 3H), 3.00-3.32 (td, 2H), 3.99-4.31 (t, 2H) 6.68-7.56 (m, 7H), 8.00-8.27 (m, 1H).

(a) $C_{18}H_{18}O_3S$: C, 68.8; H, 5.8. Found: C, 68.5; H, 5.72. (b) $C_{18}H_{18}O_3S$: C, 68.8; H, 5.8. Found: C, 69.0; H, 5.73. (c) $C_{17}H_{16}ClO_3S$: C, 61.0; H, 4.5. Found: C, 61.0; H, 4.61.

Rearrangement of **8** to **9**.

Hydration of sulfide **4c** for a shorter time (40 minutes) at slightly lower temperatures (85-95° on a steam bath) than described in Scheme III gave, after identical workup including filtration through neutral alumina, the chromene derivative **8c** in 62% yield (reactant and reagent quanities were the same as above). The nmr [2.12 (s, 3H), 2.28 (s, 3H), 3.58 (s, 2H), 4.47-4.64 (d, 2H, J = 3.1 Hz), 5.35-5.57 (t, 1H, J = 3.1 Hz), 6.57-7.35 (m, 7H)] is analogous to that of **8a**. This pale yellow oil (3.5 g.) was dissolved in 350 ml. of chloroform and 10.5 ml. of trifluoroacetic acid. The solution color immediately changed from pale yellow to deep red. After 105 minutes at reflux the cooled reaction mixture was stirred 5 to 10 minutes with 10% potassium carbonate (350 ml.). The chloroform layer (color returned to pale yellow after treatment with base) was washed with water (200 ml.), dried (magnesium sulfate) and evaporated to give 3.4 g. (97%) of **9**, spectroscopically (ir, nmr, and mass) identical with the compound obtained from hydra-

Table V



No.	R	M.p. or b.p. (°C)	% Yield	Molecular Formula	Analysis Percent Calcd. C	H	Found C	H	NMR (H_A, H_M, and Hx only) (a)
19a	4-Cl	26-27	56.0	$C_{11}H_{13}ClO_2S$	54.0	5.4	53.9	5.2	2.66-2.94 (2H, T, J = 6.2 Hz) 3.50-3.78 (4H, m)
19b	4-Br	34-34.7	73.8	$C_{11}H_{13}BrO_2S$	45.7	4.5	45.4	4.4	2.70-2.98 (2H, T, J = 6.2 Hz) 3.54-3.84 (4H, m)
19c	H	112-113/.02mm	54.6	$C_{11}H_{14}O_2S$	62.8	6.6	63.1	6.72	2.66-2.95 (2H, T, J = 6.2 Hz) 3.50-3.78 (4H, m)
19d	3,4-diCl	29-29.5	77.1	$C_{11}H_{12}Cl_2O_2S$	47.3	4.3	47.1	4.2	2.62-2.88 (2H, T, J = 6 Hz) 3.44-3.78 (4H, m)
19e	2-Me	102-104/.008mm	55,2	$C_{12}H_{16}O_2S$	64.2	7.2	64.5	7.3	2.72-2.98 (2H, T, J = 6.2 Hz) 3.55-3.81 (4H, m)
19f	3-Me	126-128/.55mm	53.9	$C_{12}H_{16}O_2S$	64.2	7.2	64.5	7.2	2.69-2.95 (2H, T, J = 6.2 Hz) 3.52-3.77 (4H, m)

No.	R	M.p.	% Yield	Molecular Formula	Analysis Percent Calcd. C	H	Found C	H	NMR (H_A, H_M, and Hx only) (a)
20	4-Br	38-39	64.6	$C_{13}H_{17}BrO_2S$	49.2	5.4	49.2	5.4	2.68-2.95 (2H, T, J = 6.2 Hz) 3.57-3.88 (4H, m)

(a) H_A and Hx partially overlap.

Table VI

1,4-Diarylsulfonyl-2-butanones (**7**)

$R\text{-}C_6H_4\text{-}SO_2\text{-}CH_2\text{-}C{\equiv}C\text{-}CH_2\text{-}SO_2\text{-}C_6H_4\text{-}R$

No.	R (a)	M.p.	% Yield	Molecular Formula	Analysis Percent Calcd. C	H	Found C	H	NMR (H_{AB} and Hz only)
a	H	113-115	83.8	$C_{16}H_{16}O_5S_2$	54.5	4.6	54.4	4.5	4.18 2.98-3.48 (4H, A_2B_2m)
b	4-Me	149-150	77.5	$C_{18}H_{20}O_5S_2$	56.8	5.3	56.6	5.2	4.01 (2H, s) 2.94-3.38 (4H, A_2B_2m)
c	3-Me	92-93	83.0	$C_{18}H_{20}O_5S_2$	56.8	5.3	56.7	5.2	4.17 (2H, s) 2.98-3.38 (4H, A_2B_2m)
d	2-Me	105.5-107	50.0	$C_{18}H_{20}O_5S_2$	56.8	5.3	56.7	5.3	4.21 (2H, s) 2.98-3.38 (4H, A_2B_2m)
e	4-OMe	117-118	88.5	$C_{18}H_{20}O_7S_2$	52.4	4.9	52.2	4.8	4.23 (2H, s) 3.00-3.50 (4H, A_2B_2m)
f	4-Cl	186-188	79.2	$C_{16}H_{14}Cl_2O_5S_2$	45.6	3.3	45.4	3.3	4.57 (2H, s) (b) 3.12-3.75 (4H, A_2B_2m)
g	4-*t*-butyl	202-204	74.2	$C_{24}H_{32}O_5S_2$	62.0	7.0	62.0	6.9	4.19 (2H, s) 3.12-3.42 (4H, A_2B_2m)

(a) All compounds gave ir $\nu(SO_2)$ = 1160, 1318 cm^{-1} and $\nu(C{=}O)$ = 1730 cm^{-1} (crystallized melts). (b) In trifluoroacetic acid solution.

tion of **4c** in refluxing acetic acid. Treatment of **8c** with concentrated sulfuric acid in chloroform gave gummy intractable material.

General Procedure for Hydration of 1,4-*bis*(Arylthio)-2-butynes in Acetic Acid.

The following procedure is typical: 2.6 g. (0.012 mole) of mercuric oxide was dissolved in hot glacial acetic acid (50 ml.). 1,4-*bis*-(4-bromophenylthio)-2-butyne (10 g., 0.023 mole) was added in one portion followed by 5 drops concentrated sulfuric acid. The mixture was warmed (*ca.* 90°) 45 minutes on a steam bath then allowed to stand 14 hours at 24°. After an additional hour heating on the steam bath, the cooled solution was filtered and diluted with ether (200 ml.). The filtrate was washed with 300 ml. of ice cold 5% potassium hydroxide solution. More ether (300 ml.) was added and the ether layer washed with water (2 x 300 ml.), dried (magnesium sulfate), and evaporated to give an oily brown solid. Addition of 60 ml. of ether and cooling at -20° overnight followed by rapid filtration gave 1.1 g. of 1,4-*bis*(4-bromophenylthio)-2-butanone; m.p. 127-128°; nmr: 2.73-3.28 (4H, A B m, $\Delta \nu / J \cong \sim 2$), 3.62 (2H, s), 7.05-7.59 (8H, m); $\nu_{C=O}$ = 1710 cm^{-1}; M^+ 444.

Anal. Calcd. for $C_{16}H_{14}Br_2OS_2$: C, 43.1; H, 3.2. Found: C, 43.2; H, 3.1. Chromatography of the remaining 6.8 g. of brown oil on 255 g. of Florisil gave in order of elution [eluting sequentially with 4:1 hexane:benzene (3 l.), 2:1 hexane:benzene (1.5 l.), 1:1 hexane:benzene (1 l.), 1:2 hexane:benzene (1.5 l.), benzene (1l.), and chloroform (2.5 l.)]:

a) 4-bromophenyldisulfide: (**13**) .3 g., m.p. 91-92°; spectroscopically identical to an authentic sample prepared by DMSO oxidation of 4-bromothiophenol (12).

b) unidentified, unstable oil: 0.25 g.

c) 1,4-*bis*(4-bromophenylthiomethyl) vinyl acetate (**18**): m.p. 65-66°; nmr: 2.05 (3H, s), 3.28-3.50 (2H, d, J = 7.5 Hz), 3.64 (2H, s), 5.11-5.45 (1H, 7, J = 7.5 Hz), 7.00-7.55 (8H, s); ir ν (C=O) = 1744 cm^{-1}; ν C-O-C = 1203 cm^{-1}; M^+ 486.

Anal. Calcd. for $C_{18}H_{16}Br_2O_2S_2$: C, 44.3; H, 3.3. Found: C, 44.5; H, 3.2.

d) 1,4-*bis*(4-bromophenylthio)-2-butanone (**15**): 1.0 g. (see physical data above).

e) 1-(4-bromophenylthio)-3-buten-2-one (**16**): 0.8 g. This yellow-orange oil could not be purified for elemental analysis, but spectral data fully substantiate the assigned structure; nmr: 3.68 (2H, s), 5.70-6.60 (3H, m), 7.00-7.58 (4H, m); ir: ν (C=O) = 1687, 1712 cm^{-1}, ν (C=CH) = 963 cm^{-1}; M^+ 256.

f) 1-(4-bromophenylthio)-4-acetoxy-2-butanone (**17**): 1.3 g., m.p. 41-42°, nmr: 1.98 (3H, s), 2.82-3.10 (2H, t, J = 7.2 Hz), 3.62 (2H, s), 4.23-4.52 (2H, t, J = 7.2 Hz), 7.14-7.64 (4H, m); ν (C=O) = 1715, 1750 cm^{-1}; M^+ 316.

Anal. Calcd. for $C_{12}H_{13}BrO_3S$: C, 45.4; H, 4.1. Found: C, 45.4; H, 3.9.

g) di(4-bromophenylthio)mercury (**14**): several early fractions were contaminated with this highly insoluble solid; m.p. 243-245°; M^+ 574, base peak 219 (at 70 ev.). Sodium borohydride reduction in alkaline THF gave a quantitative yield of 4-bromothiophenol spectroscopically identical to an authentic sample in addition to elemental mercury.

General Procedure for Hydration of 1,4-*bis*(Arylthio)-2-butynes in Methanol and 2-Propanol.

Mercuric oxide (6.75 g., 0.0312 mole) was added to a solution of concentrated sulfuric acid (5.3 ml.) and water (20 ml.). The mixture was stirred 5 minutes and then methanol (25 ml.) was added giving a bright yellow, opaque mixture. After heating the methanol mixture to reflux the sulfide (0.0268 mole) in tetrahydrofuran (20-50 ml.) was added in one portion. The mixture was then refluxed for 12-15 hours, cooled, and filtered. The filtrate was evaporated *in vacuo*, diluted with 500 ml. of water, and extracted with ether (3 x 150 ml.). The combined ether layers were washed with water (200 ml.), dried (magnesium sulfate), and evaporated. The yellow residue was then distilled [entries b and d (Table V) gave crystalline products directly and were not distilled] to give the 1-(arylthio)-4-methoxy-2-butanones listed in Table V.

Replacement of methanol with 2-propanol in the above procedure gave **20** (Table V).

General Procedure for Hydration of 1,4-*bis*(Arylsulfonyl)-2-butynes.

The sulfone (0.0475 mole) was dissolved in hot glacial acetic acid (25 ml.) then mercuric oxide (0.75 g., 0.00347 mole) followed by 2 drops of concentrated sulfuric acid was added. The mixture was warmed (90°) on a steam bath 4 hours, cooled, diluted with ether (200 ml.), and, after standing *ca.* 1 hour, filtered. The filtrate was washed with 5% potassium carbonate solution till neutral, then with water (2 x 250 ml.). Drying (sodium sulfate) and solvent removal gave a brown solid, which on recrystallization from ethanol gave the pure ketones listed in Table VI.

Reaction of 4-Chlorothiophenol with 1,4-*bis*(4-methoxyphenylsulfonyl)-2-butanone.

4-Chlorothiophenol (0.15 g.) and potassium hydroxide (0.64 g.) in THF (20 ml.) were stirred at 20° under nitrogen for 4 hours. 1,4-*bis*4-Methoxyphenylsulfonyl)-2-butanone in THF (20 ml.) was added dropwise and the solution stirred an additional 5 hours. The solvent was removed *in vacuo* and the residue taken into chloroform. Washing successively with potassium hydroxide solution and water and solvent evaporation gave a bronw solid which was recrystallized from methylene chloride/-hexane to give 1-(4-methoxyphenylsulfonyl)-4-(4-chlorophenylthio)-2-butanone (0.28 g., 72.9%); m.p. 86-88°; nmr: 3.08 (4H, A_2B_2m,$\Delta \nu$, J = ~0.3), 3.92 (3H, s), 4.17 (2H, s), 6.95-7.96 (8H, s); M^+ 384.

Anal. Calcd. for C H ClO S : C, 53.1; H, 4.4. Found: C, 53.0; H, 4.4.

Preparation of 1,4-*bis*(4-chlorophenylsulfonyl)-2-butanone.

4-Chlorothiophenol (1.0 g.) and potassium hydroxide (0.32 g.) in THF (30 ml.) were stirred at 20° under nitrogen for 4 hours. 1,4-Dichloro-2-butanone (12) (0.50 g.) in THF (10 ml.) was added dropwise and stirring continued an additional 2 hours. After removal of solvent *in vacuo* the residue (in 100 ml. of chloroform) was washed with 5% potassium hydroxide solution then with water. Drying (sodium sulfate) and solvent removal gave 1,4-*bis*(4-chlorophenylthio)-2-butanone (0.80 g.), 64.5%) as a white solid, m.p. 101-102°; nmr: 2.72-3.30 (4H, A_2B_2m, $\Delta \nu / J$ = ~2), 3.62 (2H, s), 7.29 (8H, s); M^+ 356.

Anal. Calcd. for $C_{16}H_{14}Cl_2OS_2$: C, 53.8; H, 3.9. Found: C, 54.0; H, 3.9.

MCPBA (assumed to be 85%, 0.69 g.) in methylene chloride (50 ml.) was added to a refluxing solution of 1,4-*bis*(4-chlorophenylthio)-2-butanone (0.357 g.) in methylene chloride (50 ml.). After 6 hours reflux, chloroform (100 ml.) was added and the solution washed with 5% potassium hydroxide solution and water. Drying (sodium sulfate), solvent removal and recrystallization from chloroform gave 1,4-*bis*(4-chlorophenylsulfonyl)-2-butanone (0.30 g., 71%) as a white solid; m.p. 186-188°; the

nmr of this sample was identical to that of entry f (Table VI).

Anal. Calcd. for $C_{16}H_{14}Cl_2O_5S_2$: C, 45.6; H, 3.3. Found: C, 45.3; H, 3.3.

REFERENCES

(1a) G. Dupont, *Ann. Chim. (Paris)*, **30**, 535 (1913); (b) "*The Total Synthesis of Natural Products,*" J. ApSimon, Ed., Wiley Interscience, New York, N. Y., p. 249 (1972); (c) G. Stork and R. Barch, *J. Am. Chem. Soc.*, **86**, 935 (1969).

(2) M. Miocque, N. M. Hung, and V. Q. Yen, *Ann. Chim. (Paris)* [13] **8**, 157 (1963).

(3) G. F. Hennion and D. B. Killian, *J. Am. Chem. Soc.*, **56**, 1130 (1934).

(4) M. F. Shostakovskii, A. V. Bagdanova, and G. I. Platnikova, *Russ. Chem. Rev.*, **33**, 66-77 (1964).

(5) H. G. Viehe, Chemistry of Acetylenes, Marcell Dekker, New York, N. Y., p. 267, (1969).

(6a) B. S. Thyagarajan, K. K. Balasubramanian, and R. Bhima Rao, *Tetrahedron Letters*, **21**, 1393 (1963); (b) K. C. Majumdar, B. S. Thyagarajan, and K. K. Balasubramanian, *J. Heterocyclic Chem.*, **10**, 159 (1973).

(7a) B. S. Thyagarajan, K. K. Balasubramanian, and R. Bhima Rao, *Tetrahedron*, **23**, 1893 (1967); (b) K. C. Majumdar and B. S. Thyagarajan, *J. Heterocyclic Chem.*, **9**, 389 (1972).

(8a) G. H. Posner and D. J. Brunelle, *J. Org. Chem.*, **38**, 2724 (1973); (b) D. E. O'Conner and W. I. Lyness, *J. Am. Soc.*, **86**, 3840 (1964).

(9a) S. G. Matsoyan, G. A. Chukhad Zhyan, and S. A. Vertanyan, *Chem. Abstr.*, **54**, 7545 (1960); (b) I. A. Poletaeva and O. F. Ginzberg, *Sh. Org. Khim.*, 440 (1968); (c) S. Karaev, V. Ibragimov, I. Shikhiev, *Chem. Abstr.*, **77**, 100881 (1973); (d) K. G. Golodova, S. I. Yakimovich, *Zh. Org. Khim.*, **8**, 2015 (1972).

(10) B. S. Thyagarajan, D. K. Bates, K. C. Majumdar, and P. K. Brown, *Int. J. Sulfur Chem., A,* in press.

(11) W. E. Truce, M. M. Boudakian, R. F. Heine, and R. J. McManimie, *J. Am. Chem. Soc.*, **78**, 2724 (1956).

(12) W. W. Epstein and F. W. Sweat, *Chem. Rev.*, 67, 247 (1967).

(13) G. Baddeley, H. T. Taylor, and W. Pickles, *J. Chem. Soc.*, 124 (1953).