

Reduction of Alkyl- and Arylacetylenes by an Electrochemical Method¹

ROBERT A. BENKESER AND CLINE A. TINCHER

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received February 12, 1968

It was established that dialkylacetylenes were reduced to *trans* olefins when an electric current was passed through a methylamine solution of lithium chloride and the acetylene. These *trans* olefins were arising directly from the reduction, since the corresponding *cis* olefins were not isomerized under the reaction conditions. Conjugated aromatic acetylenes could not be reduced selectively to aromatic olefins. Alkylbenzenes were the major product in such cases. A nonconjugated, terminal, aromatic acetylene was reduced principally to the aromatic olefin. Nonconjugated, internal aromatic acetylenes were reduced quite cleanly to the *trans* aromatic olefin. When 3-octyne was reduced in a divided electrochemical cell, extensive isomerization occurred, with the isomeric *trans* olefins predominating in the product. Potential pathways for the formation of these olefins were investigated.

The blue solution formed by dissolving sodium^{2,3} in liquid ammonia or lithium⁴ in certain low-molecular-weight amines has proved to be an excellent reagent for reducing dialkylacetylenes to *trans* olefins.

Dialkylacetylenes can also be reduced electrochemically to *cis* olefins⁵ at a spongy nickel cathode in an ethanol solution of sulfuric acid or potassium hydroxide.

Previously,¹ it was shown that aromatic compounds could be reduced electrochemically in either a divided or an undivided electrolytic cell in a solution of lithium chloride dissolved in methylamine. Alkylbenzenes in the undivided cell (anode and cathode compartments not separated) were reduced to dihydro products in excellent yield. In the divided cell (anode and cathode separated by asbestos) the same alkylbenzenes were reduced equally well to tetrahydro products.

In similar systems^{6a} polarographic studies^{6b} indicated that the aromatic compounds are being reduced by lithium metal formed *in situ* by the passage of the electric current.

The foregoing observations suggested that selective electrochemical reductions of alkyl- and arylacetylenes should be feasible in a methylamine solution of lithium chloride. A series of alkyl- and arylacetylenes was reduced in the undivided cell¹ to determine the nature and stereochemistry of the product. A representative dialkylacetylene was also reduced in the divided cell to test whether the nature of the reduction product is influenced by a change in cell design.

Dialkylacetylenes.—When samples of 2- and 3-octyne and 5-decyne were reduced in an undivided cell, by passage of the theoretical current to reduce one double bond, good yields of the *trans* olefins were obtained (see Table I). The stereochemistry of the products was established by comparing their physical properties (*e.g.*, infrared and nmr spectra and retention times on the gas chromatograph) with authentic samples.²

The observation that *cis* olefins are not isomerized under the conditions of the electrochemical reduction indicated that the *trans* olefins were formed directly and were not the result of an isomerization.

(1) This is paper X in a series entitled "Reduction of Organic Compounds by Lithium in Low Molecular Weight Amines." See *J. Amer. Chem. Soc.*, **86**, 5272 (1964), for the previous paper.

(2) K. N. Campbell and L. T. Eby, *ibid.*, **63**, 216, 2683 (1941).

(3) B. B. Elsner and P. F. M. Paul, *J. Chem. Soc.*, 3156 (1953).

(4) R. A. Benkeser, G. Schroll, and D. M. Sauve, *J. Amer. Chem. Soc.*, **77**, 3378 (1955).

(5) K. N. Campbell and E. E. Young, *ibid.*, **65**, 965 (1943).

(6) (a) I. Wender, H. W. Sternberg, and R. E. Markby, *J. Electrochem. Soc.*, **110**, 425 (1963); (b) *ibid.*, **113**, 1060 (1966).

TABLE I

ELECTROCHEMICAL REDUCTIONS OF DIALKYLACETYLENES

Compound	Yield, %	Olefin, %	Acetylene, %	Olefin composition, %	
				<i>trans</i>	<i>cis</i>
2-Octyne ^a	75	69	31	92	8
3-Octyne ^b	50	96	4	98	2
5-Decyne ^c	80	82	18	97	3
3-Octyne ^{d,e}	58	100	0	98	2

^a The product was analyzed on a Perkin-Elmer 226 capillary gas chromatograph using a 150-ft, 0.01-in.-diameter, UCON Polar column at 45°. ^b The product was analyzed on an Aerograph gas chromatograph using a 20-ft, 30% dibutyl tetrachlorophthalate column at 45°. ^c The product was analyzed on a F & M Model 500 gas chromatograph using a 14-ft, 25% β,β' -oxydipropionitrile column at 75°. ^d In this reduction the theoretical current to reduce two double bonds (38,600 C) was passed through the electrochemical cell. ^e The product was analyzed on an Aerograph gas chromatograph using a 25-ft, 25% β,β' -oxydipropionitrile column at 25°.

These results are in sharp contrast to those of Campbell and Young⁵ in that *trans* olefins are formed in our case instead of *cis*. It seems likely that the *cis* products observed⁵ were arising from a reduction on the surface of the spongy nickel cathode.⁷ Our stereochemical results would indicate that our reductions are *not* occurring on the cathode surface, but rather in solution. This supports the proposal^{6b} that the active reducing agent is lithium formed *in situ* and dissolved in the amine solvent. Reductions of acetylenes in the latter system have been shown⁴ to form *trans* olefins.

It was also established that internal olefins are relatively resistant to reduction in the undivided cell. Thus, 3-octyne was *not* reduced to *n*-octane by the passage of sufficient current to reduce two double bonds.

The electrochemical reduction of dialkylacetylenes to *trans* olefins has an advantage over the sodium-ammonia and lithium-ethylamine reductions in that direct handling of the alkali metals can be avoided. Also, the low cost of lithium chloride relative to lithium and the fact that it can be reused⁸ since it is in essence a current carrier make the electrochemical method rather attractive.

Arylacetylenes.—The electrochemical reduction of dialkylacetylenes to *trans* olefins and the electroreductions of aromatic compounds to dihydro aromatics¹ suggested that selective reductions of triple bonds in the presence of aromatic rings might be achieved electrochemically.

(7) C. L. Wilson, *Trans. Electrochem. Soc.*, **75**, 353 (1939).

(8) Unpublished studies by Dr. E. M. Kaiser of these laboratories.

TABLE II
ELECTROCHEMICAL REDUCTIONS OF AROMATIC ACETYLENES

Compound	Yield, %	Alkylbenzene, %	2,5-Dihydro-alkylbenzene, %	Aromatic olefin, %	2,5-Dihydro aromatic olefin, %	Recovered acetylene, %
$C_6H_5C\equiv CH^a$	80	45	1	4	0	50
$C_6H_5C\equiv C-C_2H_5^b$	80	43	2	11	0	44
$C_6H_5(CH_2)_2C\equiv CH^c$	80	8	0	64 ^d	13	15
$C_6H_5(CH_2)_2C\equiv C-CH_3^c$	62	0	0	65 ^e	10 ^f	25

^a The product was analyzed on an Aerograph gas chromatograph on a 20-ft, 25% Carbowax 1540 column at 135°. ^b The product was analyzed on a F & M Model 720 gas chromatograph using a 12-ft, 20% silicone oil 710 column at 180°. ^c The product was analyzed on Aerograph gas chromatograph using a 20-ft, 20% Zonyl E-7 column at 120°. ^d The nmr spectrum of 4-phenyl-1-butene (CCl_4) showed a five-proton singlet at τ 2.98, a one-proton multiplet at 4.40, a two-proton multiplet at 5.05, and a four-proton multiplet at 7.51. ^e The nmr spectrum of *trans*-5-phenyl-2-pentene (CCl_4) showed a five-proton singlet at τ 3.0, a two-proton multiplet at 4.70, a four-proton multiplet at 7.7, and a three-proton doublet at 8.4. The *cis* isomer (CCl_4) had a five-proton singlet at τ 2.96, a two-proton multiplet at 4.65, a four-proton multiplet at 7.55, and a three-proton doublet at 8.5. ^f The nmr spectrum of *trans*-5-(2,5-dihydrophenyl)-2-pentene (CCl_4) showed a two-proton multiplet at τ 4.32, a three-proton multiplet at 4.60, four-proton multiplets at 7.40 and 7.97, and a three-proton multiplet at 8.35.

When phenylacetylene and 1-phenyl-1-butyne were reduced in the undivided cell,¹ the major products were ethylbenzene and *n*-butylbenzene, respectively (see Table II), despite the passage of sufficient current to reduce only one double bond.⁹ These results parallel previous work⁴ wherein phenylacetylene was reduced to a mixture of ethylbenzene and styrene at a spongy nickel cathode.

Considerably greater selectivity was noted in the reduction of 4-phenyl-1-butyne. When the theoretical current to reduce one double bond was passed through an undivided cell containing this compound, the major product was 4-phenyl-1-butene. Only small amounts of *n*-butylbenzene and 4-(2,5-dihydrophenyl)1-butene formed as shown in Table II.

The ultimate in selectivity was achieved in the reduction of 5-phenyl-2-pentyne in the undivided cell, wherein the major product was *trans*-5-phenyl-2-pentene. Small amounts of 5-(2,5-dihydrophenyl)-2-pentene (see Table II) were also formed. It would seem that the electrochemical method holds promise for the selective reduction of nonconjugated, internal aromatic acetylenes. It is also evident that an aromatic ring is more readily reduced in such systems than an internal double bond as evidenced by formation of the *trans*-5-(2,5-dihydrophenyl)-2-pentene rather than *n*-amyl benzene.

Divided Cell Reduction of 3-Octyne.—To investigate the divided cell reduction of dialkylacetylenes, 3-octyne was reduced in an electrolytic cell where the anode and cathode compartments were separated by an asbestos divider.¹ Considerable isomerization occurred in this case, but, again, *trans* products predominated as shown in Table III.

TABLE III
DIVIDED CELL REDUCTION OF 3-OCTYNE

Products	Retention time (vpc), min
<i>trans</i> -2-Octene (33%)	173
<i>cis</i> -2-Octene (4%)	255
<i>trans</i> -3-Octene (37%)	154
<i>cis</i> -3-Octene + 1-octene (0.4%)	230
<i>trans</i> -4-Octene (24%)	140
<i>cis</i> -4-Octene (0.4%)	208
<i>n</i> -Octane (0.5%)	73

(9) It has been shown (unpublished work from this laboratory by S. Mela) that styrene is reduced to ethylbenzene under the reaction conditions.

The most likely agent causing the isomerization was deemed to be lithium methylamide. Since methylamine is the only source of protons during the electrochemical reduction, the formation of one molecule of olefin requires the formation of two molecules of lithium methylamide. It has been shown¹ that the function of the cell divider is to prevent the immediate destruction of lithium methylamide by the methylamine hydrochloride which forms at the anode. Thus, the lithium methylamide carries in solution to catalyze the isomerization of the organic compounds.

A possible explanation for the isomerization products observed, is that the acetylene is reduced to the *trans*-olefin first, which is then isomerized to the observed products. This possibility has not been entirely excluded, but investigations by Whiting and coworkers¹⁰ on the isomerization of *cis*- and *trans*-octenes by lithium alkylamide-ethylenediamine solutions suggest that the isomerization of *trans*-3-octene is not the major source of the reaction products observed.

The predominance of the *trans* olefins in the divided cell product suggested that 3-octyne itself was being isomerized, followed by a reduction of the isomeric acetylenes to the observed products. When 3-octyne was stirred in a lithium methylamide-methylamine solution to test this possibility, all the possible isomeric octynes were produced. Such base-catalyzed isomerizations of acetylenes are well documented¹¹ and are thought to proceed through allene intermediates. There remained the possibility that our divided cell products (Table III) were arising from a reduction of these allene intermediates rather than from the isomeric acetylenes. To check this point 1,2- and 2,3-octadiene were reduced in the undivided cell (to minimize their isomerization). The major product from the reduction of 1,2-octadiene was *trans*-2-octene (77%), while 2,3-octadiene yielded principally *trans*-2- and *trans*-3-octene in almost equal amounts.¹²

(10) M. D. Carr, J. R. P. Clarke, and M. C. Whiting, *Proc. Chem. Soc.*, 333 (1963).

(11) T. L. Jacobs, R. Akawie, and R. G. Cooper, *J. Amer. Chem. Soc.*, **73**, 1273 (1951); J. Bainvel, B. Wojtkowiak, and R. Romanet, *Bull. Soc. Chim. Fr.*, 978 (1963); J. H. Wotiz, W. E. Billups, and D. T. Christian, *J. Org. Chem.*, **31**, 2069 (1966).

(12) These results are rather different from the preliminary report [D. Devaprabhakara and P. D. Gardner, *J. Amer. Chem. Soc.*, **85**, 648 (1963)] of the reduction of 1,2- and 2,3-nonadiene by sodium in liquid ammonia. The former compound was reported to reduce principally to *cis*-2-nonene and the latter to a 50:50 mixture of *cis*- and *trans*-2-nonene. Since the reduction method employed was quite different from ours, further work will be needed to determine whether any real discrepancies exist.

The possibility existed that the intermediate allenes could be reducing at a much faster rate than the acetylenes, and, as a consequence, the products formed in the divided cell were arising predominantly from reduction of the allenes. In an attempt to shed light upon this point, a 50:50 mixture of 2-octyne and 1,2-octadiene was reduced only partially in the undivided cell. Analysis of the recovered starting material showed it to contain 37% 1,2-octadiene and 63% 2-octyne.

At first sight, this result would seem to indicate that 1,2-octadiene is reducing somewhat faster than 2-octyne. Such a conclusion is not necessarily valid, however, since it was found that the 1,2-octadiene is partially isomerized to 2-octyne during the electrochemical reduction. When pure 1,2-octadiene was reduced for half the theoretical time to reduce only one double bond, the recovered starting material contained 20% 2-octyne. The latter is definitely formed during the reduction, as 1,2-octadiene was not isomerized merely by lithium chloride in methylamine.

The above results suggest that, in the divided cell, 3-octyne is reduced to *trans*-3-octene and, as the lithium methylamide concentration gradually increases, the 3-octyne begins to isomerize to allenes and the isomeric octynes. Both the allenes and octynes are then reduced to the observed products.

Experimental Section

General Procedure for the Reduction of Dialkyl- and Aromatic Acetylenes in an Undivided Electrolytic Cell.—Dialkyl- and aromatic acetylenes were reduced in the undivided electrolytic cell previously described.¹ The cell was charged with 34 g (0.8 mol) of lithium chloride, 900 ml of anhydrous methylamine, and 0.1 mol of the acetylene to be reduced. A current of 2 A was passed through the cell for 2 hr and 40 min (19,300 C). At the end of this time the solvent was allowed to evaporate through a water condenser. The residue was hydrolyzed with 300 ml of water, and the aqueous solution was extracted with ether. The ether extracts were dried (CaSO₄); the solvent was ether. The ether extracts were dried (CaSO₄) and the solvent then removed. Distillation of the residue yielded the product, which was analyzed by vapor phase chromatography. The results for the reduction of 2-octyne,² 3-octyne,³ and 5-decyne² are summarized in Table I. The results obtained for phenylacetylene, 1-phenyl-1-butyne,¹³ 4-phenyl-1-butyne,¹⁴ and 5-phenyl-2-pentyne are shown in Table II.

Attempted Reduction of 3-Octyne (Undivided Cell, Excess Current).—Eleven grams (0.1 mol) of 3-octyne was reduced in the undivided electrolytic cell¹ by passing a current of 2 A through the system for 5 hr and 20 min (38,600 C). Distillation, following the usual work-up, afforded 6.0 g (58%) of product (bp 120°). The product composition is shown in Table I (entry 4).

5-Phenyl-2-pentyne.—4-Phenyl-1-butyne (116 g, 0.9 mol) was treated with 40 g (1.0 mol) of sodium amide dissolved in 800 ml of liquid ammonia followed by the addition of methyl iodide (200 g, 1.5 mol). The mixture was hydrolyzed with 6 N ammonium hydroxide, and the solvent was allowed to evaporate. Extraction with pentane was followed by the usual work-up. Distillation yielded 75 g (52%) of product, bp 101° (13 mm).

Anal. Calcd for C₁₁H₁₂: C, 91.61; H, 8.39. Found: C, 91.63; H, 8.60.

***cis*- and *trans*-5-Phenyl-2-pentyne.**—The *cis* isomer (5.2 g, 70%; bp 200°) was obtained by catalytic hydrogenation (60 psi; Raney nickel) of a solution of 5-phenyl-2-pentyne (7.5 g, 0.05 mol) in 60 ml of pentane. Analysis by vpc (Table II, footnote a) showed the product was 48% *cis*-5-phenyl-2-pentyne, 17% *trans*-5-phenyl-2-pentyne, and 35% *n*-amylbenzene. Each

of these components was isolated by vpc and identified by its nmr spectrum. The retention times of the *trans* isomer and *n*-amylbenzene also matched those of authentic samples.

Anal. Calcd for C₁₁H₁₄ (*cis*): C, 90.35; H, 9.65. Found: C, 90.42; H, 9.80.

The *trans* isomer (20 g, 55%; bp 200°) was prepared by coupling benzylmagnesium chloride [from 25 g (1 g-atom) of magnesium and 31.7 g (0.25 mol) of benzyl chloride in 700 ml of dry ether] with *trans*-crotyl chloride (23 g, 0.25 mol). Analysis by vpc (Table II, footnote a) showed the product was 71% *trans*-5-phenyl-2-pentyne, 11% *cis*-5-phenyl-2-pentyne, and 18% 4-phenyl-3-methyl-1-butene. Each of these components was isolated by vpc and its identity established by nmr spectra.

Anal. Calcd for C₁₁H₁₄ (*trans*): C, 90.35; H, 9.65. Found: C, 90.55; H, 9.75.

Electrochemical Reduction of 3-Octyne (Divided Cell).—3-Octyne (11 g, 0.1 mol) was placed in the cathode compartment of a divided electrolytic cell.¹ Current was passed through the cell for 2 hr and 40 min (19,300 C, 2 A). The solvent was evaporated through water condensers, and the residue in each half cell was hydrolyzed by the slow addition of water. The aqueous solutions were combined and the organic material isolated in the usual manner. Distillation yielded 5.2 g (47%) of product boiling at 121°. Analysis by vpc at 25° using three columns connected in series (β,β' -oxydipropionitrile-AgNO₃, 40%, 8 m; diethylene glycol-AgNO₃, 40%, 2 m; diethylene glycol-AgBO₃, 40%, 8 m) showed that the product consisted of the compounds listed in Table III. Identification was made by comparing retention times of each of the compounds with those of authentic samples. The latter were either commercially available (*n*-octane, 1-octene, *trans*-2-octene) or were synthesized by the method described in ref 2.

Isomerization of 3-Octyne.—Lithium methylamide (0.15 mol) was prepared by adding 1 g of lithium wire to a solution of methylamine containing a catalytic amount of ferric chloride. Then 3-octyne (10.0 g, 0.09 mol) was added, and the mixture was stirred for 2 hr and 40 min. The solvent was allowed to evaporate, and the residue was hydrolyzed (water). The organic material was worked up in the usual manner. Distillation afforded 3.5 g (35%) of product boiling at 132°. Analysis by vpc (17-ft, 20% dibutyl tetrachlorophthalate column at 72°) showed that the product contained all four isomeric octynes as adjudged by a comparison of retention times with authentic samples. The approximate product composition was 4-octyne (36%), 3-octyne (25%), 2-octyne (32%), and 1-octyne (12%).

Electrochemical Reduction of 1,2-Octadiene (Undivided Cell).—In a 200-ml three-neck flask fitted with a Dry Ice condenser and two (1.5 by 1.5 cm) platinum electrodes were placed in lithium chloride (8.5 g, 0.2 mol), 200 ml of methylamine, and 1,2-octadiene¹⁵ (3.0 g, 0.027 mol). A current of 1 A was passed through the cell for 1 hr and 27 min (5220 C). After the addition of 50 ml of diethyl ether, the solvent was allowed to evaporate through a water condenser. The residue was hydrolyzed, and the organic material was worked up in the usual manner. Distillation yielded 2.0 g (66%) of product boiling at 122°. Analysis by vpc (Perkin-Elmer 226 capillary gas chromatograph; 150-ft, 0.01-in.-diameter UCON Polar column at 55°) showed (comparison of retention times) that the product consisted of 1-octene (6%), *trans*-2-octene (63%), *cis*-2-octene (12%), and 1,2-octadiene and 2-octyne (6%). The retention time (minutes) of each product was 4.8, 5.3, 5.5, and 12.3, respectively.

Competitive Reduction of 1,2-Octadiene and 2-Octyne (Undivided Cell).—In the electrolytic cell described above, a mixture of 1,2-octadiene¹⁵ (3.0 g, 0.027 mol) and 2-octyne (3.0 g, 0.027 mol) was partially reduced by passing a current of 1 A through the system for 1 hr and 20 min (5220 C). Ether (75 ml) was added, and the solvent was evaporated. The usual work-up, followed by distillation, yielded 4.6 g (76%) of product boiling at 124–130°. Analysis by vpc (see previous conditions) showed that the product consisted of 1-octene (3%), *trans*-2-octene (43%), *cis*-2-octene (5%), 2-octyne (32%), and 1,2-octadiene (19%).

Partial Reduction of 1,2-Octadiene (Undivided Cell).—A 3-g (0.027 mol) sample of 1,2-octadiene¹⁵ was reduced in the undivided cell by passing a current of 1 A through the system for 40 min (2610 C). The usual work-up and distillation yielded 2.0 g (66%) of product boiling at 122–128°. Analysis by vpc (Perkin-Elmer 226 capillary gas chromatograph) using the conditions previously described, showed that the product consisted

(13) T. M. Morgan, *J. Chem. Soc.*, **29**, 162 (1876).

(14) J. R. Johnson and W. L. Mc Ewen, *J. Amer. Chem. Soc.*, **48**, 475 (1926).

(15) B. Wojtkowiak and R. Romanet, *Bull. Soc. Chim. Fr.*, 805 (1962).

of 1-octene (5%) *trans*-2-octene (39%), *cis*-2-octene (6%), 1,2-octadiene (40%), and 2-octyne (11%).

Attempted Isomerization of 1,2-Octadiene with Lithium Chloride.—A 3-g (0.027 mol) sample of 1,2-octadiene was stirred for 1 hr and 27 min in a solution of lithium chloride dissolved in methylamine. The usual work-up and distillation yielded 2.2 g (74%) of a product boiling at 130°. Analysis by vpc (capillary gas chromatograph described above) showed that the product contained only 1,2-octadiene.

Electrochemical Reduction of 2,3-Octadiene (Undivided Cell).—A 3-g (0.027 mol) sample of 2,3-octadiene¹⁵ was reduced in the undivided cell using the procedure described above for 1,2-octadiene. The organic material was worked up in the usual manner and distillation yielded 2 g (66%) of product boiling at 122°. Analysis on a Perkin-Elmer 226 gas chromatograph, using the conditions previously described, showed that the product consisted of *cis*- plus *trans*-3-octene (47%), *trans*-2-octene (48%), and *cis*-2-octene (5%). Analysis on an Aerograph gas chromatograph using a 25-ft, β,β' -oxydipropionitrile column at 30° showed the product composition to be *trans*-3-octene (45%),

cis-3- plus *trans*-2-octene (50%), and *cis*-2-octene (5%). The amount of *cis*-3-octene by difference is approximately $2 \pm 5\%$.

Registry No.—2-Octyne, 2809-67-8; 3-octyne, 15232-76-5; 5-decyne, 1942-46-7; phenylacetylene, 536-74-3; 1-phenyl-1-butyne, 622-76-4; 4-phenyl-1-butyne, 16520-62-0; 5-phenyl-2-pentyne, 16487-62-0; 4-phenyl-1-butene, 768-56-9; *trans*-5-phenyl-2-pentene, 16091-23-9; *cis*-5-phenyl-2-pentene, 16487-65-3; *trans*-5-(2,5-dihydrophenyl)-2-pentene, 16487-66-4; 1,2-octadiene, 1072-19-1; 2,3-octadiene, 16487-68-6.

Acknowledgment.—This research was sponsored by the Petroleum Research Fund of the American Chemical Society and by the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force under AFOSR Grant 822-67.

Photochemical Reduction of β - and γ -Keto Sulfones

IAN W. J. STILL AND M. T. THOMAS

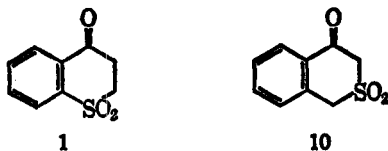
Department of Chemistry, University of Toronto, Toronto 5, Canada

Received March 6, 1968

The preparation of several new γ -keto sulfones related to thiochroman-4-one 1,1-dioxide has been carried out by hydrogen peroxide oxidation of the corresponding cyclic sulfides. The preparation of the β -keto sulfone, isothiochroman-4-one 2,2-dioxide, is also described. Ultraviolet irradiation of these keto sulfones in methanol has been found to lead in most cases to the corresponding pinacols, by bimolecular reduction of the carbonyl group. The photochemical reduction seems to be relatively insensitive to the substitution pattern, although the lack of reaction in two cases is attributed to steric effects of neighboring groups.

The photochemical reactions of the carbonyl group in sulfur-containing heterocyclic systems have not so far been investigated extensively. Berchtold and Johnson¹ recently reported the photochemical conversion of two cyclic γ -keto sulfides to ring-contracted β -thiolactones and speculated on the possibility of a charge-transfer mechanism being responsible. Ultraviolet irradiation of isothiochroman-4-ones has been shown² to give the corresponding thiochroman-3-ones as the major nonpolymeric products. Additional evidence for the possibility of charge-transfer interactions in cyclic γ -keto sulfides has also been obtained as a result of studies of the ultraviolet spectra of some cage compounds.³

In the present investigation we report the effect of ultraviolet irradiation on thiochroman-4-one 1,1-dioxide⁴ **1** and several monosubstituted thiochromanone



sulfones of the same series, most of which have not been previously reported. The sulfones were chosen to include examples of both electron-releasing (alkyl) and electron-withdrawing (carboalkoxyl) substituents at various sites in the thiochromanone system. These γ -keto sulfones and the β -keto sulfone **10** derived from

isothiochroman-4-one² were the subject of our investigation into the effect of the $-\text{SO}_2-$ group on the photochemical properties of the carbonyl function in such compounds. Ultraviolet data for the keto sulfones studied appear in the Experimental Section (Table IV).

Results and Discussion

The sulfones used in this investigation (Table I) were obtained from the corresponding sulfides by oxidation with hydrogen peroxide in hot acetic acid, except in the case of isothiochroman-4-one 2,2-dioxide **10** (see Experimental Section) where the use of a 5:2 mixture of acetic acid-acetic anhydride and lower temperatures gave much better yields.

Cyclization of the appropriate carboxylic acids to produce the required keto sulfides may be accomplished in several ways, but in general we have found concentrated sulfuric acid to be a satisfactory reagent for this purpose, with the exception of isothiochroman-4-one, which was best obtained using phosphorus pentoxide in benzene, and of 8-carbomethoxythiochroman-4-one, obtained using polyphosphoric acid. The 5- and 7-methylthiochroman-4-ones were obtained in yields of 35 and 20%, respectively, by the cyclization of β -(3'-methylthiophenoxy)propionic acid, and the isomers were separated by chromatography on alumina. When attempts were made to oxidize thiochroman-4-one-2-carboxylic acid to the corresponding sulfone without prior esterification, it was found that hydrogen peroxide in acetone at 25° produced the known 4-thiochromone-2-carboxylic acid in 15% yield. Such a dehydrogenation was rather unexpected, and indicates that internal hydrogen bonding may prevent the

(1) P. Y. Johnson and G. A. Berchtold, *J. Amer. Chem. Soc.*, **89**, 2761 (1967).

(2) W. C. Lumma, Jr., and G. A. Berchtold, *ibid.*, **89**, 2761 (1967).

(3) L. A. Paquette and L. D. Wise, *ibid.*, **89**, 6659 (1967).

(4) F. Arndt, *Chem. Ber.*, **58**, 1612 (1925).