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-octadiene[15] 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 ± 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.

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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

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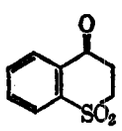
The preparation of several new γ-keto sulfones related to thiochroman-4-one 1,1-dioxide has been carried out by hydrogen peroxide oxidation of the corresponding cyclic sulfides. The preparation of the β-keto sulfone, isothiochroman-4-one 2,2-dioxide, is also described. Ultraviolet irradiation of these 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 Johnson[1] 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 shown[2] 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-dioxide[4] **1** and several monosubstituted thiochromanone



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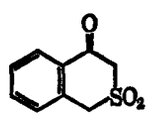


10

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-one[2] were the subject of our investigation into the effect of the $-SO_2-$ 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).

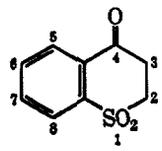
Results and Discussion

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).

TABLE I
MONOSUBSTITUTED THIOCHROMAN-4-ONE 1,1-DIOXIDES



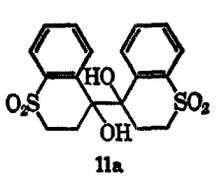
Substituent	Compd no.	Mp, °C	Yield, %	Formula	Calcd, % C	Calcd, % H	Calcd, % S	Found, % C	Found, % H	Found, % S
None	1	130–131[a]	80	$C_9H_8O_3S$	...	...	...	...	...	...
2-Methyl	2	127–128[b]	83	$C_{10}H_{10}O_3S$	57.1	4.8	15.2	57.25	4.9	15.2
3-Methyl	3	146–147[b]	42	$C_{10}H_{10}O_3S$	57.1	4.8	15.2	57.2	4.8	15.25
5-Methyl	4	130–132[c]	85	$C_{10}H_{10}O_3S$	57.1	4.8	15.2	57.1	4.8	15.2
7-Methyl	5	159–160[b]	50	$C_{10}H_{10}O_3S$	57.1	4.8	15.2	57.1	4.85	15.1
8-Methyl	6	124–125[b]	50	$C_{10}H_{10}O_3S$	57.1	4.8	15.2	57.1	4.8	15.25
2-Carbomethoxy	7	111–112[c]	60	$C_{11}H_{10}O_5S$	52.0	3.9	12.6	51.9	3.8	12.6
3-Carbomethoxy	8	152–153[c]	70	$C_{11}H_{10}O_5S$	52.0	3.9	12.6	51.8	4.0	12.6
8-Carbomethoxy	9	133–134[c]	91	$C_{11}H_{10}O_5S$	52.0	3.9	12.6	51.8	4.1	12.5

[a] Lit.[4] mp 130–132°. [b] Recrystallized from ethanol. [c] Recrystallized from methanol.

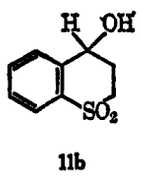
desired oxidation at the sulfur atom. When the carboxylic acid was first esterified, however, oxidation with excess hydrogen peroxide in acetic acid proceeded normally to produce the sulfone.

Ultraviolet irradiation of thiochroman-4-one 1,1-dioxide **1** in acetonitrile or benzene in a quartz vessel produced no change in the starting material after several hours. However, when the irradiation was conducted in a solvent like methanol which is much more likely to act as a hydrogen donor to the excited C=O group, photochemical reduction of the γ-keto sulfone took place, with the formation of the corresponding pinacol **11a** in 31% yield after 18 hr. No starting ketone was recovered, nor any other identifiable product, the remaining material being viscous and polymeric in nature.

The pinacol **11a** was characterized by a very high melting point (275°) and extremely low solubility in all the usual organic solvents. The infrared spectrum (Nujol) revealed bands at 3420 (OH), 1280 (asymmetric SO_2), and 1165 cm^{-1} (symmetric SO_2), but nmr data were not obtained because of solubility difficulties. The mass spectra of this pinacol and of the other pinacols listed in Table II appeared to be somewhat unusual and we plan to make this the subject of a separate publication. The analytical data (Table II) were in accord with both the reduction product **11a** and the thiochromanol **11b** arising from simple reduction of the ketone. Authentic thiochroman-4-ol 1,1-dioxide **11b** was prepared by sodium borohydride reduction[5] of the corresponding ketone, and was clearly not identical (Table III) with our photoreduction product.



11a



11b

Additional evidence for the pinacol structure **11a** was obtained by oxidation with sodium dichromate in sulfuric acid which afforded the starting ketone **1** in 60% yield, thus ruling out the possibility that any skeletal rearrangement had occurred during the photoreduction. Finally, thiochroman-4-one 1,1-dioxide could be reduced with activated zinc dust in acetic acid to a product which was identical in melting point, mixture melting point, and infrared spectrum with our photochemical reduction product.

The other sulfones listed in Table I and isothiochroman-4-one 2,2-dioxide **10** were then subjected to irradiation under essentially similar conditions in dilute (<1%) methanolic solution and the results are summarized in Table II.

It was not felt necessary to synthesize all the corresponding simple reduction products **11b–20b**, so that in Table III are listed only some examples of secondary alcohols obtained by sodium borohydride reduction which serve to emphasize the obvious distinction from the pinacols listed in Table II.

No products other than the pinacols have been detected in any of the above irradiations. Little starting material could be recovered and the residues obtained on removal of the insoluble pinacol were almost entirely polymeric in nature. In a comparative study it was found that isothiochroman-4-one 2,2-dioxide **10** when irradiated in quartz gave comparable amounts of pinacol about five times faster than the same solution irradiated in Pyrex. In the only case (compound **1**) where isopropyl alcohol was used as solvent, it was found to produce no easily observable enhancement in the rate of pinacol formation, while it suffered from the disadvantage of being a much poorer solvent for the sulfone than methanol. Although no serious attempts to optimize the conditions of pinacol formation have been made, our most recent experiments with the use of alternative solvents such as chloroform or 2-butylamine show that the reaction times may be substantially reduced (to as little as 1 hr). The isolated yields of pinacols, however, remained almost the same.

The photochemical reduction of aromatic ketones to produce pinacols is a familiar reaction.[6,7] The reaction seems to be relatively insensitive in the present series to the electronic effects of substituents, although the absence of pinacol formation where there is a carbomethoxy group located at the 8 position (**9**), *meta* oriented to the carbonyl function, may be significant.

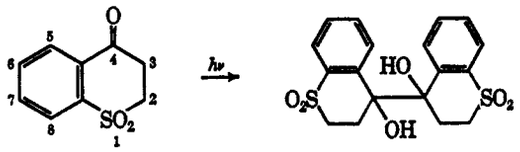
(5) F. J. Lotspeich, *J. Org. Chem.*, **30**, 2068 (1965).

(6) See, for example, S. G. Cohen and R. J. Baumgarten, *J. Amer. Chem. Soc.*, **89**, 3471 (1967), and references contained therein.

(7) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 139 ff.

TABLE II

PINACOLS OBTAINED BY PHOTOCHEMICAL REDUCTION OF THIOCHROMANONE SULFONES[a]

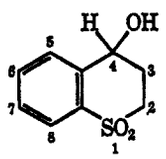


Starting ketone	Irradiation time, hr	Pinacol compd no.	Yield,[b] %	Mp,[c] °C	Calcd, % C	Calcd, % H	Calcd, % S	Found, % C	Found, % H	Found, % S
1	18	11a	31	275	54.8	4.6	16.25	54.5	5.0	16.2
2-CH_3, 2	5	12a	23	295	55.7[d]	5.3[d]	14.85[d]	56.1	5.5	14.7
3-CH_3, 3	7	13a	15	235	55.7[d]	5.3[d]	14.85[d]	55.7	5.4	14.9
5-CH_3, 4	24	14a	*e*	...	...	...	...	...	...	...
7-CH_3, 5	12	15a	17	273	56.9	5.2	15.2	57.1	5.2	15.2
8-CH_3, 6	20	16a	17	265	56.9	5.2	15.2	56.75	5.2	15.3
2-$COOCH_3$, 7	8	17a	13	290	51.8	4.3	12.55	51.6	4.2	12.5
3-$COOCH_3$, 8	60	18a	5[f]	223	51.8	4.3	12.55	51.9	4.35	12.5
8-$COOCH_3$, 9	6	19a	*g*	...	...	...	...	...	...	...
10	0.7	20a	30	305	54.8	4.6	16.25	54.6	4.5	16.3

[a] All irradiations were conducted in methanol. [b] Actual isolated yield. [c] All recrystallized from dimethyl sulfoxide. [d] Crystallized as a hemihydrate. [e] Unchanged starting material recovered. [f] 50% starting material recovered. [g] Only polymeric material obtained.

TABLE III

THIOCHROMANOLS BY SODIUM BOROHYDRIDE REDUCTION



Substituent	Compd no.	Mp, °C	Yield, %	Formula	Calcd, % C	Calcd, % H	Calcd, % S	Found, % C	Found, % H	Found, % S
None	11b	95–96[a,b]	40[c]	$C_9H_{10}O_3S$	...	...	...	...	...	...
3-Methyl	13b	117–118[a]	55	$C_{10}H_{12}O_3S$	56.6	5.7	15.1	56.4	5.7	15.2
8-Carbomethoxy	19b	114–115[a]	44	$C_{11}H_{12}O_5S$	51.6	4.7	12.5	51.6	4.55	12.4
Isothiochroman-4-ol 2,2-dioxide	20b	*d*	55	$C_9H_{10}O_3S$	...	...	...	*e*	*e*	*e*

[a] Recrystallized from benzene. [b] Lit.[5] mp 95–97°. [c] Reaction carried out in methanol–dioxane reportedly gives better yields. [d] Boiling point *ca.* 145° (0.1 mm). [e] Because of the high boiling point and consequent slight decomposition a satisfactory analysis could not be obtained. The infrared spectrum ($CHCl_3$) showed bands at 3580 (OH), 1350 (asymmetric SO_2), and 1135 (symmetric SO_2), and no carbonyl band; nmr ($CDCl_3$), τ 6.65 d (2 H, J = 5.2 cps), 6.17 s (OH, disappears upon shaking with D_2O), 5.78 d (2 H, J = 6.5 cps), 4.85 t (1 H, J = 5.2 cps), 2.43–3.01 m (4 H aromatic)—all in accord with the expected structure.

It was, however, noted that the ketone was completely destroyed in this instance, being converted quantitatively into polymeric material in 6 hr, so that, until we possess information on the nature of the competing polymerization mechanism, any definite conclusions would be unwarranted.

Further reference to Table II reveals that large amounts of starting material were recovered in the case of the 5-methyl and 3-carbomethoxy substituents, and this fact, together with the failure to form pinacols to any extent in these cases, suggests that steric inhibition is at its maximum in these two cases, as one would expect. The steric crowding of the adjacent carbonyl due to the planar 5-methyl substituent is obviously greater than that due to the 3-methyl substituent, which can adopt the pseudo-axial orientation. There is at present no evidence to distinguish between steric hindrance to the formation of a ketyl radical by hydrogen abstraction and steric hindrance to the coupling of the ketyl radicals so formed.

Further work is planned to extend this investigation to more elaborate keto sulfones derived from the isothiochroman-4-one series, and an investigation of the irradiation of keto sulfoxides related to the keto sulfones studied in the present account is already under way.

Experimental Section

The infrared spectra were recorded on a Perkin-Elmer Model 237B grating spectrometer and the nmr spectra on a Varian A-60 instrument, with tetramethylsilane as internal standard. Microanalyses were carried out in the laboratory of A. B. Gygli, Toronto. All melting points and boiling points are uncorrected.

Preparation of Monosubstituted Derivatives of Thiochroman-4-one.[8]—2-Methylthiochroman-4-one and 3-methylthiochroman 4-one[4] were prepared by the base-catalyzed addition of thiophenol to crotonic acid and methyl α-methacrylate, respectively, followed by ring closure with concentrated sulfuric acid. 5- and 7-methylthiochroman-4-one[9] were both obtained by the sulfuric acid cyclization of the reaction product of *m*-thiocresol and β-propiolactone. Chromatography of the mixture on grade I alumina and elution with *n*-hexane–benzene (60:40) gave first the liquid 5-methyl isomer, followed by the solid 7-methyl isomer, in the ratio of 5:3.

8-Methylthiochroman-4-one[10] was prepared by the method of Hurd and Hayao, starting from *o*-thiocresol and β-propiolactone.

(8) J. C. Petropoulos, M. A. McCall, and D. S. Tarbell, *J. Amer. Chem. Soc.*, **75**, 1130 (1953).

(9) I. Degani, R. Fochi, and G. Spunta, *Boll. Sci. Fac. Chim. Ind. Bologna*, **24** [2–3], 75 (1966); *Chem. Abstr.*, **66**, 46292n (1967).

(10) C. D. Hurd and S. Hayao, *J. Amer. Chem. Soc.*, **76**, 5065 (1954).

2-Carbomethoxythiochroman-4-one[11] was prepared by the addition of thiophenol to diethyl maleate, followed by hydrolysis. Cyclization of the resulting succinic acid, followed by reesterification, gave the desired product.

3-Carbomethoxythiochroman-4-one[12] was prepared from thiochroman-4-one by methoxalylation and decarbonylation of the resulting α-keto ester. All the above thiochromanones agreed closely in melting point (or boiling point) with the reported values.

8-Carbomethoxythiochroman-4-one.—Methyl *o*-mercaptobenzoate[13] (5.7 g, 0.034 mol) was mixed with β-propiolactone (3.0 g, 0.04 mol) and heated at 100–110° for 8 hr. After cooling, extraction with hot petroleum ether (bp 60–70°)–benzene mixture gave needle-shaped crystals of β-(2-carbomethoxythiophenoxy)propionic acid (5.0 g, 61%), mp 99–100°.

Anal. Calcd for $C_{11}H_{12}O_4S$: C, 55.00; H, 5.00; S, 13.33. Found: C, 55.17; H, 5.28; S, 13.28.

The acid (2.0 g, 0.008 mol) was cyclized to the corresponding thiochromanone by addition to polyphosphoric acid, prepared from phosphorus pentoxide (10.0 g, 0.07 mol) and phosphoric acid (12 ml), at 100°. After heating for 2 hr, the mixture was allowed to stand at room temperature for 6 hr, poured into ice–water, and extracted with ether. The combined extracts were washed ($NaHCO_3$, H_2O), dried, and evaporated. The oil originally obtained soon solidified and on recrystallization from benzene gave white crystals (0.36 g, 20%), mp 66–67°, used without further purification for conversion into the sulfone.

Preparation of the Thiochromanone Sulfones (1–9).—These were all prepared by oxidation of the appropriate thiochromanone with hydrogen peroxide. The analytical data, melting points, and yields for these compounds are collected in Table I. Infrared and nmr spectra were in accord with expectation. To illustrate the general method and the relevant spectral data, we describe the preparation of 8-methylthiochroman-4-one 1,1-dioxide **6**.

8-Methylthiochroman-4-one (2.0 g, 0.011 mol) was dissolved in acetic acid (8 ml) and 30% hydrogen peroxide (8 ml, 0.1 mol) was added. After heating at 100° for 45 min, the product **6** (50%), mp 124–125°, was collected by cooling and diluting with water (an essentially similar result was obtained without heating, if the reactants were allowed to stand overnight): infrared ($CHCl_3$) 1705 (CO), 1325 (asymmetric SO_2), and 1155 cm^{-1} (symmetric SO_2); nmr ($CDCl_3$), τ 7.27 s (CH_3); symmetric multiplet centered at 6.48 ($2CH_2$), 1.95–2.50 m (3 H aromatic.)

Isothiochroman-4-one 2,2-Dioxide 10.—Isothiochroman-4-one[2] (5.0 g, 0.03 mol), prepared by the P_2O_5 cyclization of S-benzylthioglycolic acid, was dissolved in a mixture of acetic acid (50 ml) and acetic anhydride (20 ml). The solution was cooled to 0° and 30% hydrogen peroxide (35 ml, 0.44 mol) was added slowly with stirring. The mixture was stirred for a further 4 hr at 25°, cooling in ice from time to time when the temperature showed signs of rising. Dilution with water and extraction with methylene chloride led on evaporation to a solid product, recrystallized from acetone (2.5 g, 42%), as white crystals: mp 163–164°; infrared ($CHCl_3$) 1695 (CO), 1335 (asymmetric SO_2), and 1125 cm^{-1} (symmetric SO_2); nmr (acetone-d_6), τ 6.25 (slight splitting, $J < 2$ cps, CH_2), 5.90 (CH_2), 2.90–3.33 m (3 H), 2.47–2.68 m (1 H).

Anal. Calcd for $C_9H_8O_3S$: C, 55.10; H, 4.08; S, 16.33. Found: C, 54.98; H, 3.94; S, 16.36.

Irradiation of the Keto Sulfones.—Ultraviolet irradiations were normally carried out in quartz vessels, using a 125-W medium-pressure Hanovia mercury lamp, in an atmosphere of nitrogen. The results of these experiments and data on the pinacols obtained are recorded in Table II. The following example will serve to illustrate the general method.

2-Carbomethoxythiochroman-4-one 1,1-dioxide (0.9 g) was irradiated in degassed methanol (150 ml). After 8 hr, the ketonic carbonyl band at about 1700 cm^{-1} in the infrared spectrum had completely disappeared. Evaporation of the solvent, followed by the addition of acetone, led to the formation of a white solid (pinacol), mp 289–290°, in 13% yield. Chromatography of the residual gummy material on silica gel led only to traces of unreacted starting material and to intractable gums.

(11) F. Bossert, *Ann. Chem.*, **680**, 40 (1964).
(12) T. Moriwake, *J. Med. Chem.*, **9**, 163 (1966).
(13) British Patent 767,027 (1967) (Schenley Industries, Inc.); *Chem. Abstr.*, **51**, 17998e (1957).

TABLE IV

ULTRAVIOLET SPECTRAL DATA[a] ON KETO SULFONES 1–10

Compound	λ_{max}, mμ (ε)		
Thiochroman-4-one 1,1-dioxide (**1**)	246 (9,500)	286 (1,600)	294 (1,400)
Isothiochroman-4-one 2,2-dioxide (**10**)	251 (11,000)	291 (1,700)	300 (1,500)
2-Methylthiochroman-4-one 1,1-dioxide (**2**)	246 (13,100)	286 (2,300)	294 (2,100)
3-Methylthiochroman-4-one 1,1-dioxide (**3**)	245 (8,600)	285 (1,400)	293 (1,300)
5-Methylthiochroman-4-one 1,1-dioxide (**4**)	247 (7,800)	294 (2,600)	303 (2,300)
7-Methylthiochroman-4-one 1,1-dioxide (**5**)	258 (11,800)	283 (2,100)	294 (1,700)
8-Methylthiochroman-4-one 1,1-dioxide (**6**)	250 (9,000)	294 (2,500)	302 (2,300)
2-Carbomethoxythiochroman-4-one 1,1-dioxide (**7**)	246 (9,200)	285 (1,800)	293 (1,700)
3-Carbomethoxythiochroman-4-one 1,1-dioxide (**8**)	235 (12,000)	...	309 (10,000)
8-Carbomethoxythiochroman-4-one 1,1-dioxide (**9**)	240 (8,100)	287 (1,000)	295 (900)

[a] All spectra were recorded in methanolic solution on a Unicam SP-800 spectrophotometer.

Ultraviolet spectral data on keto sulfones **1–10** is given in Table IV above.

Reduction of Thiochroman-4-one 1,1-Dioxide with Zinc in Acetic Acid.—The zinc dust (0.2 g, 0.003 g-atom) used in this reaction was first moistened with copper sulfate solution. Thiochroman-4-one 1,1-dioxide (0.2 g, 0.001 mol) was then heated with the zinc at 100° in 75% aqueous acetic acid (10 ml) for 15 min. The white insoluble solid so obtained was washed with concentrated hydrochloric acid to remove any unreacted zinc. This solid (0.11 g, 55%) had mp 273–274° on recrystallization from dimethyl sulfoxide, undepressed on admixture with the pinacol obtained by irradiation, and the infrared spectra of the two samples were superimposable.

Oxidation of Pinacol 11a with $Na_2Cr_2O_7$–H_2SO_4.—The pinacol (130 mg) obtained from thiochroman-4-one 1,1-dioxide by irradiation was mixed with water (0.2 ml) and treated with a solution of sodium dichromate (0.12 g) and sulfuric acid (0.13 g) in water (0.5 ml) at 55° for 2 hr. At this point, acetic acid (2 ml) was added, and after continued stirring for 1 hr, the white insoluble pinacol had completely disappeared. The mixture was diluted with water, and the product extracted with methylene chloride. Washing of the extracts ($NaHCO_3$, H_2O), drying, and evaporation gave a white solid (78 mg, 60%), mp 128–129°, undepressed on admixture with a genuine sample of thiochroman-4-one 1,1-dioxide.[4] The infrared spectra of the two samples were identical.

$NaBH_4$ Reduction of the Keto Sulfones.—The thiochromanols prepared by this procedure are listed in Table III. Compounds **11b**, **13b**, and **20b** were prepared using Lotspeich's procedure.[5] This was felt to be unsuitable for the reduction of keto esters and the following method was used in the case of 8-carbomethoxythiochroman-4-one 1,1-dioxide **9**.

Compound **9** (230 mg, 0.9 mmol) was dissolved in 95% ethyl alcohol (25 ml) to which had been added boric acid (0.1 g). Sodium borohydride (120 mg, 3.1 mmol) was then added in small amounts with stirring, and the mixture allowed to stand for 3 hr. Removal of the ethanol under vacuum and dilution with water was followed by acidification with dilute HCl. Extraction with ether led to the isolation of 8-carbomethoxythiochroman-4-ol 1,1-dioxide **19b** (100 mg, 44%), described further in Table III.

Oxidation of Thiochroman-4-one-2-carboxylic Acid with H_2O_2.—This compound (100 mg) was treated with acetone (5 ml) and 30% hydrogen peroxide (1 ml) and allowed to remain at 25° for 2 days. The yellow crystals (15 mg, 15%) which had appeared near the end of this time were collected by filtration, washed with benzene, and recrystallized from acetic acid, mp 233–234°.

Anal. Calcd for $C_{10}H_8O_5S$: C, 58.25; H, 2.91; S, 15.53. Found: C, 58.33; H, 2.84; S, 15.43.

The infrared spectrum of this compound showed bands (KBr) at 3450 (free OH), 3000–2400 (bonded OH), 1750 and 1715 cm^{-1} (monomeric and dimeric COOH and 1600 cm^{-1} (CO) but no bands characteristic of SO or SO_2. From this information and the

analytical data it was considered to be 4-thiochrom-one-2-carboxylic acid, lit.[14] mp 234–235°.

Registry No.—**2**, 16808-50-7; **3**, 16723-50-5; **4**, 16723-52-7; **5**, 16723-53-8; **6**, 16723-54-9; **7**, 16723-55-0; **8**, 16723-56-1; **9**, 16723-57-2; **10**, 16723-58-3; **11a**, 16723-59-4; **11b**, 2765-44-8; **12a**, 16723-60-7; **13a**, 16723-61-8; **13b**, 16723-68-5; **15a**, 16723-62-9; **16a**, 16723-63-0; **17a**, 16723-64-1; **18a**, 16723-65-2; **19b**, 16723-69-6; **20a**, 16723-66-3; 8-carbomethoxythiochroman-4-one, 16723-70-9; β-(2-carbomethoxythiophenoxy)propionic acid, 16723-72-1; 4-thiochromone-2-carboxylic acid, 16723-71-0.

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Chemistry of Aliphatic Disulfides. XVII. Studies on the Alkoxide Cleavage of 3,6-Dibenzoyl-1,8-diphenyl-4,5-dithia-1,8-octanedione[1,2]

RICHARD G. HISKEY AND AVERY J. DENNIS[3]

The Venable Chemical Laboratory, The University of North Carolina, Chapel Hill, North Carolina 27514

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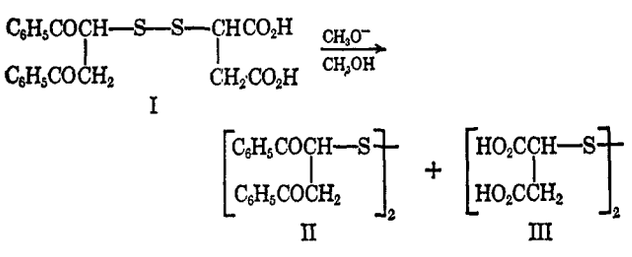
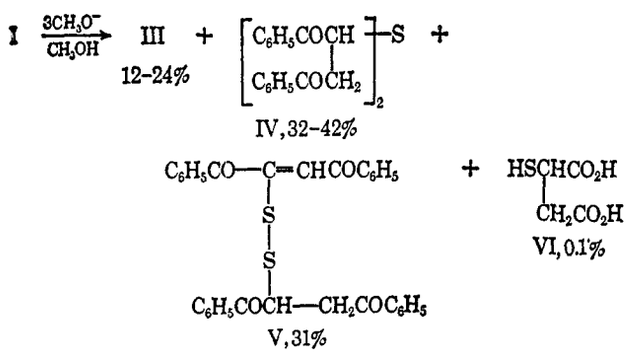
Treatment of 3,6-dibenzoyl-1,8-diphenyl-4,5-dithia-1,8-octanedione (II) with potassium ethoxide in ethanol provides 3,5-dibenzoyl-1,7-diphenyl-4-thia-1,7-heptanedione (IV) and potassium 1,4-diphenyl-2-butene-1,4-dione-2-mercaptide (VII) as the major products. A mechanism for cleavage of II involving α elimination of a mercaptide is proposed. Compound II is shown to be formed by disulfide interchange during the alkoxide cleavage of 6,7-dibenzoyl-3-carboxyl-4,5-dithiaheptanoic acid (I).

In a previous study,[4] the alkoxide cleavage of 6,7-dibenzoyl-3-carboxy-4,5-dithiaheptanoic acid (I) was examined. The products (III–V) formed by the action of 3 equiv of methoxide ion on I suggested that I was initially converted into 3,6-dibenzoyl-1,8-diphenyl-4,5-dithia-1,8-octanedione (II) and 2,2′-dithiosuccinic acid (III). Although II could not be

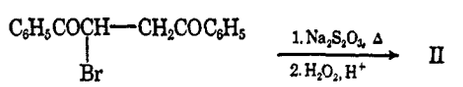


isolated, its presence was implied by the formation of IV and V, which were presumably produced by the action of methoxide ion on II. Since III was present as the tetrasodium salt, further cleavage of the negatively charged disulfide by methoxide should be minimal and indeed III was isolated in reasonable yield.



Although the mechanism for base-catalyzed disulfide interchange (I → II + III) has not been rigorously established, the process probably involves the direct attack of base on the sulfur–sulfur bond rather than initial abstraction of hydrogen atoms α or β to the disulfide bond. The further decomposition of II, however, seemed likely to involve α and/or β elimination of mercaptide.[5,6] Thus a study of the action of alkoxide on II might be expected to provide data on the relative importance of these two pathways and give some indication of the favored route for base-catalyzed decomposition of symmetrical and unsymmetrical disulfides.

Ethoxide Cleavage of II.—The desired substrate, II, was prepared by oxidation of the corresponding Bunte salt. The oxidation provided a mixture of diastereo-



isomers which were readily separated by fractional recrystallization to give a 49% yield of an isomer, mp 115–116°, and a 14% yield of an isomer, mp 137°. Both isomers were cleaved by the action of alkoxide under similar conditions and no significant differences in product analysis were observed.

Treatment of II with 1 equiv of potassium ethoxide in ethanol provided 3,5-dibenzoyl-1,7-diphenyl-4-thia-1,7-heptanedione (IV) in 71.6% yield and potassium 1,4-diphenyl-2-butene-1,4-dione-2-mercaptide (VII) in

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(2) For part XVI of the series, see R. G. Hiskey and A. J. Dennis, *J. Org. Chem.*, **33**, 563 (1968).

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