after two crystallizations from methanol, had mp 151–153° (other preparations,[24] mp 130–131°); nmr signals at τ 2.52 (C-11 aromatic H), 8.64 (d, J = 7 Hz, isopropyl), 8.82 (C-10 methyl), and 9.02 (d, J = 5 Hz, C-4 methyl).

Anal. Calcd for $C_{19}H_{26}N_2O_4$: C, 65.88; H, 7.56; N, 8.09. Found: C, 66.13; H, 7.81; N, 8.05.

Registry No.—**1a,** 2221-95-6; **1b,** 19402-16-5; **1f,** 1451-69-0; **1g,** 3749-83-5; **1h,** 19402-19-8; **1i,** 19407-09-1; **1j,** 19407-10-4; **1k,** 19407-11-5; **1m,** 19407-12-6; **1n,** 15821-26-8; **1p,** 19407-14-8; **1p** (2,4-dinitrophenylhydrazone), 19407-15-9; **1p** (semicarbazone), 19407-16-0; **2a,** 19407-17-1; **2a** (12,14-dinitro derivative), 19407-40-0; **2b,** 19407-18-2; **2b** (12,14-dinitro derivative), 19407-41-1; **2f,** 19407-19-3; **2f** (3,5-dinitrobenzoate), 3858-39-7; **2g,** 19407-21-7; **2h,** 19407-22-8; **2i,** 19407-23-9; **2i** (2,4-dinitrophenylhydrazone), 19407-24-0; **2j,** 19407-25-1; **2j** (3,5-dinitrobenzoate), 1451-73-6; **2k,** 19407-27-3; **2m,** 19407-28-4; **2n,** 19426-88-1; **2p,** 13601-88-2; **3,** 19407-30-8; 4α-methylamino-18-norabietane hydrochloride, 19407-31-9; 4α-dimethylamino-18-norabietane picrate, 19407-32-0.

Photochemistry of Isothiochroman-4-one[1–3]

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Received May 7, 1968

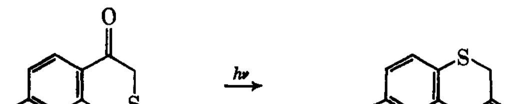
Irradiation of isothiochroman-4-one in cyclohexane (high pressure mercury lamp, Pyrex 7740 filter) produced thiochroman-3-one (21%). Under similar conditions 7-methoxy-, 8-methyl-, 3-methyl-, and 3,3-dimethylisothiochroman-4-one rearranged to 6-methoxy- (40%), 5-methyl- (30%), 2-methyl- (30%), and 2,2-dimethylthiochroman-3-one (37%), respectively. 1,2,3,4-Tetrahydro-1-keto-3-thiaphenanthrene failed to undergo the rearrangement reaction. Irradiation of 5-methyl-2,3-dihydro-2H,6H-thiopyran-3-one under similar conditions resulted in rearrangement to 2-(2-prop-1-enyl)-1-thietan-3-one (28–35%). The pathway for the photochemical conversion of isothiochroman-4-ones into thiochroman-3-ones is discussed.

Photochemistry.—The ultraviolet (uv) spectra of β-keto sulfides show evidence for charge transfer in the excited state as well as perturbation of the n,π* state of the carbonyl group.[5–7] Various interpretations of the spectral data have been discussed.[5–8] These effects are not observed in the spectra of β-keto sulfones.[9]

Only two reports have appeared on the photochemistry of β-keto sulfides. Schönberg, Fateen, and Omran[10] obtained radical coupling products (*e.g.*, bidesyl) in the photolysis of desyl aryl sulfides, and La Count and Griffin[11] found that phenacyl benzyl sulfide failed to give the thietanol product from α-hydrogen atom abstraction as did the oxygen analog, phenacyl benzyl ether.

Initial studies confirmed the indication that simple, acyclic β-keto sulfides undergo photochemical reaction involving homolytic cleavage of the α-carbon–sulfur bond. Photolysis of 2-*t*-butylmercaptocyclohexanone (**1**) in cyclohexane for 2 hr produced three products[12] corresponding to 22% of the starting material. Less than 10% **1** remained. The products were identified as di-*t*-butyl disulfide, cyclohexenone, and cyclohexanone and were formed in a ratio of 5:1.4:1. Photolysis in methanol gave the same products in somewhat better yield plus a small amount of 3-*t*-butylmercaptocyclohexanone which was probably formed from Michael addition of *t*-butylmercaptan to cyclohexanone.

In view of the product distribution resulting from β cleavage to radical pairs, it was decided to investigate systems in which the two functionalities were contained in the same ring system. The unsaturated system, isothiochroman-4-one (**2**), was selected. Irradiation of 0.2–0.4% solutions of **2** in cyclohexane or Genetron 113 (1,1,2-trichloro-1,2,2-trifluoroethane) with a Hanovia, Type L, 450-W mercury arc immersion lamp with a Pyrex filter, produced thiochroman-3-one (**5**) in yields of 19–21% and 1-thiaindane in 6% yield. The remainder of the starting material is converted into an amorphous polymeric material which gradually precipitated from the reaction mixture. In a similar fashion 7-methoxyisothiochroman-4-one (**3**) and 8-methylisothiochroman-4-one (**4**) were converted into 6-methoxythiochroman-3-one (**6**) and 5-methylthiochroman-3-one (**7**) in yields of 30 and 40%, respectively. These two examples establish that the sulfur atom in the thiochroman-3-one products is attached to the aryl carbon atom which held the carbonyl function in the starting isothiochroman-4-ones. Photolysis of



2, R = R′ = H
3, R = H; R′ = CH_3O
4, R = CH_3; R′ = H

5, R = R′ = H
6, R = H; R′ = CH_3O
7, R = CH_3; R′ = H

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(1) This work was previously reported in communication form.[2]

(2) W. C. Lumma, Jr., and G. A. Berchtold, *J. Amer. Chem. Soc.*, **89,** 2761 (1967).

(3) This research has been supported by National Science Foundation Grants No. GP-5761 and GP-7831.

(4) To whom inquiries should be sent. Alfred P. Sloan Fellow, 1963–1967.

(5) E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, **71,** 84 (1949).

(6) G. Bergson and A-L. Delin, *Ark. Kemi*, **18,** 489 (1961).

(7) G. Bergson, G. Claeson, and L. Schotte, *Acta Chem. Scand.*, **16,** 1159 (1962).

(8) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962, p 55.

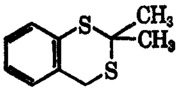
(9) E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, **71,** 231 (1949).

(10) A. Schönberg, A. K. Fateen, and S. Omran, *ibid.*, **78,** 1224 (1956).

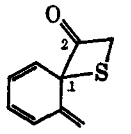
(11) R. B. La Count and C. E. Griffin, *Tetrahedron Lett.*, 1549 (1965).

(12) A complex mixture of high boiling material was also isolated, but the constituents were not characterized.

3-methylisothiochrom-4-one (**8**) and 3,3-dimethylisothiochroman-4-one (**9**) produced 2-methylthiochroman-3-one (**10**) and 2,2-dimethylthiochroman-3-one (**11**) in yields of 30 and 37%, respectively, thereby establishing that C-3 in the starting materials became C-2 in the products. (A product assigned structure **12** was also isolated from the photolysis of **9** in 6% yield.) This was also established by the photolysis of deuterated **2** prepared by base-catalyzed exchange with D_2O.

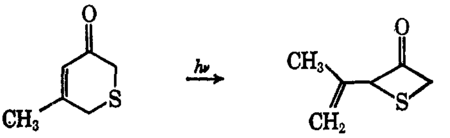


12



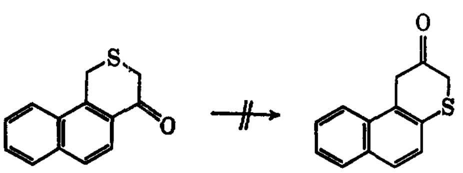
13

These results combined with the appearance of a weak absorption band at 1770 cm^{-1} in the infrared (ir) spectrum of solutions of **2** which had been irradiated for short periods of time suggest that **13** might be the initial photoproduct in the reaction. Excitation of the carbonyl group or the triene moiety in **13** could then result in cleavage of bond 1 and subsequent rearrangement to starting material or cleavage of bond 2 and rearrangement to product. Evidence for the intermediacy of **13** was obtained from the photolysis of 5-methyl-2,3-dihydro-2H,6H-thiopyran-3-one (**14**) which produced the thietanone **15** in yields of 28–35%. The stability of **15** under the conditions of the reaction suggests that excitation of the triene moiety of **13** is responsible for further rearrangement.



14 **15**

Irradiation of **2** with a 3500-Å[13] source resulted in the slow formation of polymeric material. Compound **3** was not produced but an absorption band appeared at 1770 cm^{-1} in the spectrum of the solution suggesting the formation of intermediate **13**. Since this suggests the 3500-Å source will effect n,π* excitation of **2** to form **13** but does not supply sufficient energy to excite the triene moiety in **13**[14] relative to other processes, it became of interest to investigate the photochemistry of **16** which, by analogy with 2-acetonaphthalene, should have a π,π* triplet of lower energy than its n,π* triplet.[15] Irradiation of **16** with either of the previously described light sources did not produce **17**; amorphous polymer was the only product observed. Although other explanations are possible, it appears most likely that an n,π* configuration may be necessary for the observed photochemical rearrangement.



16 **17**

Preparation of the Keto Sulfides.—The synthesis of **1** was accomplished from the reaction of sodium *t*-butylmercaptide with 2-chlorocyclohexanone in ethanol. The synthesis of **2**[16–19] and several methyl-substituted analogs[19,20] by the Friedel–Crafts cyclization of the corresponding arylmethylmercaptoacetic acids or acid chlorides has been reported previously. The isothiochroman-4-ones **2** and **4** were prepared by the known procedure,[17] and this method was also applied to the preparation of **3** and **16**. The nmr spectrum of **3** (see Experimental Section) establishes that the cyclization of *m*-methoxybenzylmercaptoacetic acid resulted in ring closure *para* to the methoxyl group to form **3** rather than *ortho* to the methoxyl group. The preparation of the necessary arylmethylmercaptoacetic acids is described in the Experimental Section. Isothiochroman-4-ones **8** and **9** were prepared by alkylation of the enolate anion of **2** with excess methyl iodide and were separated by column chromatography.

Compound **14** was prepared by cyclization of the sodium salt of S-2-methylallylmercaptoacetic acid[21] with excess oxalyl chloride followed by work-up with aqueous ammonia at 0°. The ketone was purified by distillation followed by column chromatography.

Structure Proof of Photochemical Products.—The structures of the products from irradiation of **1** were established by comparison of gas chromatographic retention times and ir spectra with those of authentic samples.

The structure of **5** from irradiation of **2** was established by synthesis of an authentic sample as outlined in Scheme I.

Thiosalicylic acid was alkylated in 92% yield with ethyl bromoacetate and 2 equiv of sodium ethoxide in ethanol to give **18** which was converted into the acid chloride in 82% yield with thionyl chloride. Reaction of the acid chloride in ether with excess diazomethane gave 95% crystalline diazo ketone **19**. A modified Wolff rearrangement of **19** in absolute ethanol with catalytic amounts of silver benzoate–triethylamine reagent[22] produced diester **20** in yields of 62–82%. The normal silver oxide catalyst was unsatisfactory. Dieckmann cyclization of **20** with excess sodium hydride in refluxing tetrahydrofuran afforded a mixture of crude β-keto ester **21** and **5** which could be hydrolyzed and decarboxylated to pure **5**. This material was identical in all respects with **5** obtained from irradiation of **2**. The thiaindan isolated from this irradiation was identical in all respects with an authentic sample.[23]

The structure of **6** from irradiation of **3** was identical in all respects with an authentic sample prepared as outlined in Scheme II.

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(13) Rayonet Photochemical Reactor with sixteen 3500-Å General Electric "black phosphor" lamps.

(14) The triene should show an absorption maximum at ~303 mμ.

(15) G. S. Hammond and P. A. Leermakers, *J. Amer. Chem. Soc.*, **84**, 207 (1962).

(16) A. K. Kiang and F. G. Mann, *J. Chem. Soc.*, 1909 (1951).

(17) C. C. Price, *et al.*, *J. Amer. Chem. Soc.*, **85**, 2278 (1963).

(18) J. von Braun and K. Weissbach, *Ber.*, **62**, 2416 (1929).

(19) P. Cagniant and D. Cagniant, *Bull. Soc. Chim. Fr.*, 1998 (1959).

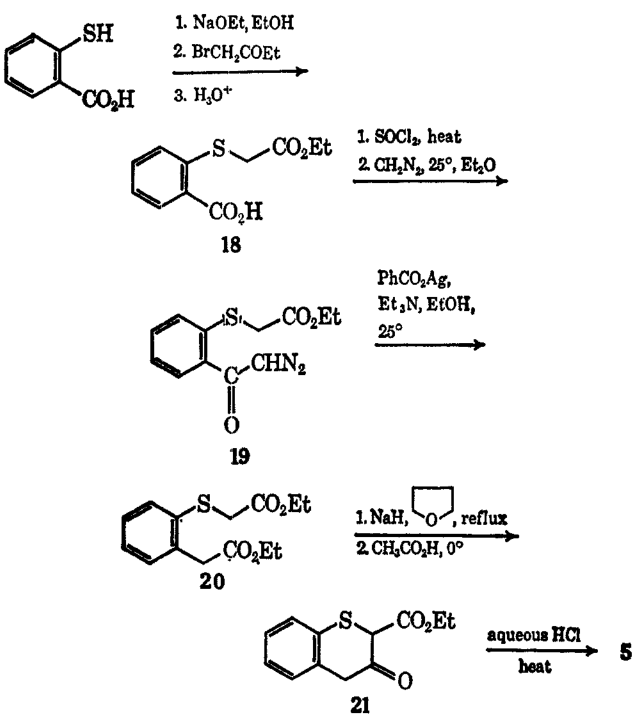
(20) P. Cagniant, G. Jecko and D. Cagniant, *ibid.*, 2225 (1961).

(21) Q. Soper, *et al.*, *J. Amer. Chem. Soc.*, **70**, 2849 (1948).

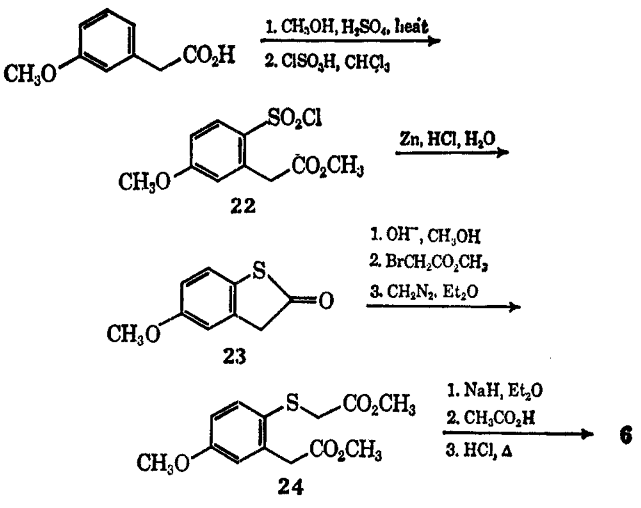
(22) M. S. Newman and P. F. Beal, III, *ibid.*, **72**, 5163 (1950).

(23) S. F. Birch, R. A. Dean, and E. V. Whitehead, *Inst. Petrol. J.*, **40**, 76 (1954).

Scheme I



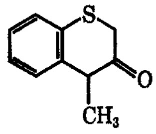
Scheme II



Chlorosulfonation of methyl *m*-methoxyphenylacetate gave the crystalline sulfonyl chloride **22** in 6–11% yield; the low yield is probably due to an unfavorable equilibrium with the corresponding sulfonic acid.[24] Structure **22** was assigned by analogy to the chlorosulfonation of anisole[25] and on the basis of reductive cyclization to the thiolactone **23** with zinc and hydrochloric acid in 18% yield. Esterification of **23** followed by alkylation with methyl bromoacetate produced **24** in 93% yield. Dieckmann cyclization of **24** followed by hydrolysis and decarboxylation gave a 9% yield of **6**.

The structure of **7** from irradiation of **3** is assigned by analogy to the formation of **6**.

The structure of **10** is confirmed by the intense peaks at *m/e* 122 and 121 in the mass spectrum due to fragmentation of the elements of methylketene from the molecular ion (*m/e* 122) and subsequent loss of a hydrogen atom (*m/e* 121). This fragmentation is expected for **10** but is unreasonable for the alternative structure **25**, the molecular ion of which should lose the elements of ketene rather than methylketene.

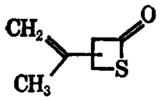


25

Loss of ketene and a methyl radical from the molecular ion of **25** is reasonable but this would lead to *m/e* 121 and no *m/e* 122. A similar argument confirms the structure of **11**.

The structure of the byproduct **12** from irradiation of **9** was assigned on the basis of its mass spectrum. The molecular ion at *m/e* 196 and the m + 1 and m + 2 peaks established the molecular formula as $C_{10}H_{12}S_2$. The principal fragment ions at *m/e* 181, 153, 122, and 121 show loss of CH_3, C_3H_6, C_3H_6S, and C_3H_7S, respectively, as a fragmentation pattern consistent with structure **12**.

The product from irradiation of **14** was established as **15** on the basis of the spectral data listed in the Experimental Section. These data rule out the alternative structures **26** as well as other isomeric structures.



26

Experimental Section[26]

2-*t*-Butylmercaptocyclohexanone (1).—This compound was prepared by a general procedure[27] from 2-chlorocyclohexanone (66.3 g, 0.50 mol) and a solution of *t*-butyl mercaptan (45.1 g, 0.50 mol) in ethanolic sodium ethoxide (from 11.5 g, 0.50 g-atom of sodium in 500 ml of absolute ethanol). There was obtained 12.0 g of a forerun, bp 25–68° (6 mm) and 59.4 g of colorless liquid, bp 68–116° (6–4.5 mm). The forerun contained a major component identified as ethyl cyclopentanecarboxylate by ir comparison. The higher boiling fraction was purified by distillation (spinning band) and gave 33.8 g (36%) of a colorless liquid: bp 123–124° (16 mm); $n^{20}D$ 1.4952; $\nu_{max}^{CHCl_3}$ 2950, 1700, 1459, 1368, 1336, 1313, 1283, and 916 cm^{-1}; λ_{max}^{EtOH} 245 mμ (ϵ 430) and 304 (294); nmr ($CDCl_3$) δ 3.43 (multiplet, 1 H), 3.03 (multiplet, 1 H), 1.94 (multiplet, 7 H), and 1.33 ppm (singlet, 9 H).

Anal. Calcd for $C_{10}H_{18}OS$: C, 64.46; H, 9.74; S, 17.21. Found: C, 64.30; H, 9.84; S, 16.75.

Photolysis of 1.—Irradiation[28] of **1** (5.00 g in 500 ml of cy-

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(24) F. Muth, "Methoden Der Organischen Chemie" (Houben-Weyl), Vol. 9, Georg Thieme Verlag, Stuttgart, 1955, p 573.

(25) M. S. Morgan and L. H. Cretcher, *J. Amer. Chem. Soc.*, **70**, 375 (1948).

(26) All melting points are corrected and boiling points are uncorrected. The ir spectra were recorded on a Perkin-Elmer Model 237 or 337 recording spectrophotometer. The uv spectra were recorded on a Cary Model 14 spectrophotometer. The nmr spectra were recorded on a Varian A-60 nmr spectrometer, and chemical shift data are given in parts per million (ppm) downfield from tetramethylsilane as an internal standard in CCl_4 or $CDCl_3$. Mass spectra were determined on a Consolidated Electrodynamics Model 21-130 or a Hitachi Perkin-Elmer Model RMU-6D (direct inlet) mass spectrometer with an ionizing potential of 68 V. The gas chromatographic analyses and isolations were made on an 8 ft × ¼ in. column with 20% SE-30 on neutral 60–80 mesh Chromosorb P (thermal conductivity detector) or a 12 ft × ¼ in. column of the same packing adapted to an Aerograph Hy-Fi Model 600 gas chromatograph with flame ionization detector. The drying agent in extraction procedures was $MgSO_4$ or Na_2SO_4, and solvents were removed at reduced pressure on a Büchi Rotovapor apparatus using a water bath at temperatures below 35° unless otherwise specified. Microanalyses were performed by Galbraith Laboratories, Inc., or S. M. Nagy and associate.

(27) C. K. Bradsher, F. C. Brown and R. J. Grantham, *ibid.*, **76**, 114 (1954).

(28) Hanovia Type L, 450-W, high pressure mercury lamp.

clohexane) with a Corex 9700 filter for 2 hr gave 4.06 g of a yellow oil after removal of the solvent. Distillation gave 1.10 g of material, bp ~65° (5 mm), and 0.65 g of higher boiling material, bp 120–125° (0.35 mm), which was not further examined. Analysis of the lower boiling fraction by vpc (10% SE-30 on Chromosorb P, 165°) showed the presence of three components in the ratio (area) 5.1:1.4:1, identified respectively as di-*t*-butyl disulfide, cyclohexenone, and cyclohexanone by peak enhancement and comparison of ir spectra with the spectra of authentic samples.

Isothiochroman-4-one (2).—Ketone **2** was prepared from S-benzylthioglycolic acid by a known procedure[17] in 24–26% yield, mp 59–60° (lit.[16] mp 59–60°).

7-Methoxyisothiochroman-4-one (3).—*m*-Methoxybenzyl chloride (prepared from *m*-methoxybenzyl alcohol by the method of Fuchs and Carlton[29]) was heated with an equivalent amount of thiourea in ethanol until the salt crystallized according to the procedure of Mndzhoyan and Aroyan.[30] Recrystallization from ethanol-ether gave the salt in 97% yield, mp 172.5–173.5°.

Anal. Calcd for $C_9H_{13}ClN_2OS$: C, 46.44; H, 5.63; Cl, 15.24; N, 12.04; S, 13.78. Found: C, 46.65; H, 5.70; Cl, 15.19; N, 11.93; S, 13.97.

Following the procedure of Mndzhoyan and Aroyan,[30] *m*-methoxybenzylmercaptoacetic acid was prepared by heating (80°) the isothiuronium salt (25.0 g, 0.107 mol) with chloracetic acid (15.1 g, 0.160 mol) in absolute ethanol (50 ml) under N_2 and treating the stirred mixture dropwise during 1 hr with a solution of NaOH (21.6 g, 0.54 mol) in ethanol (100 ml) and water (200 ml). The mixture was heated at 90–100° for 4 hr, the aqueous mixture was acidified with concentrated HCl (45 ml), and the oil which separated was extracted into ether. The ether layer was washed with water and saturated NaCl solution, dried ($MgSO_4$), and evaporated. Distillation of the crude oil gave 20.0 g (88%) of a colorless syrup: bp 159–167° (0.18 mm); $n^{21}D$ 1.5699; $\nu_{max}^{CHCl_3}$ 3500, 3400–2500, 1760, 1708, 1600, 1580, 1485, 1460, 1448, 1425, 1290, 1265, and 1150 cm^{-1}; λ_{max}^{EtOH} 275.5 mμ (ε 2230) and 282.5 (2010); nmr ($CDCl_3$) δ 11.1 (singlet, 1 H), 7.12 (multiplet, 4 H), 3.85 (singlet, 2 H), 3.82 (singlet, 3 H), and 3.12 ppm (singlet, 2 H).

Anal. Calcd for $C_{10}H_{12}O_3S$: C, 56.68; H, 5.70; S, 15.11. Found: C, 56.78; H, 5.91; S, 14.95.

Cyclization of this acid to **3** was effected by adding a mixture of phosphorus pentoxide (26.3 g, 0.185 mol) and "Hyflo-Super Cel" (15 g) to dry benzene (300 ml) containing absolute ethanol (1 ml) and heating this mixture under reflux for 1 hr during which time a solution of *m*-methoxybenzylmercaptoacetic acid (19.6 g, 0.0925 mol) in benzene (100 ml) was added. The mixture was refluxed for 1 hr longer, the hot benzene solution was decanted through a filter, and the dark residue was leached with boiling benzene. The combined benzene layers were washed with 1 *N* NaOH (two 100-ml portions), water, and saturated NaCl solution and dried ($MgSO_4$). Evaporation of the benzene and crystallization of the residue from ether–hexane gave 4.16 g of **3**, mp 96–97°. Starting acid (11.0 g) could be recovered by acidification of the basic washings with 6 *N* HCl. The yield of **3** based on recovered acid was 53%: $\nu_{max}^{CCl_4}$ 3050–2825, 1680, 1600, 1275, 1112, 1045, and 1020 cm^{-1}; λ_{max}^{EtOH} 229 (ε 11,000) and 285 (12,300); nmr (CCl_4) δ 8.16 (doublet, J = 9 cps, 1 H), 6.94 (doublet of doublets, J = 9 and 2.5 cps, 1 H), 6.75 (doublet, J = 2.5 cps, 1 H), 3.90 (broad singlet, 5 H), and 3.53 ppm (singlet, 2 H).

8-Methylisothiochroman-4-one (4).—This material was prepared by the procedure described for the preparation of **3** except that the acid was cyclized by the procedure of Price, *et al.*[17]

o-Methylbenzylisothiuronium bromide was prepared from *o*-bromoxylene in 92% yield: mp 169–170° (ethanol–ether); ν_{max}^{KBr} 1640, 1545, 1262, 788, 745, 734, 700, 670, 483, and 463 cm^{-1}.

Anal. Calcd for $C_9H_{13}BrN_2S$: C, 41.38; H, 5.20; Br, 30.60; N, 10.73. Found: C, 41.59; H, 5.20; Br, 30.75; N, 10.61.

o-Methylbenzylmercaptoacetic acid was prepared from the isothiuronium salt in 84% yield: bp 150.5–152° (1 mm) [lit.[20] bp 159° (2.5 mm)]; $\nu_{max}^{CCl_4}$ 3500–2500, 1710, 1488, 1420, and 1290 cm^{-1}.

Cyclization of the acid gave **4** in 21% yield: bp 100–101° (0.15 mm) [lit.[20] bp 182° (14.8 mm)]. The distilled ketone crystallized on standing as colorless needles: mp 50–51° (recrystallized from ether–pentane); $\nu_{max}^{CCl_4}$ 3050, 2960, 1687, 1587, 1455, 1282, and 1068 cm^{-1}.

3-Methylisothiochroman-4-one (8) **and 3,3-Dimethylisothiochroman-4-one** (9).—To a cooled solution (0°) of sodium (6.90 g, 0.30 g-atom) in absolute ethanol (300 ml) under N_2 was added **2** (16.4 g, 0.100 mol) with stirring until a clear, orange solution formed. Methyl iodide (42.6 g, 0.300 mol) was added rapidly with stirring. The ice bath was removed and the mixture was stirred for 3 hr at room temperature, after which a deep red color had developed. The mixture was immediately poured into a slurry of ice and 6 *N* HCl (100 ml) and the mixture was extracted with four 100-ml portions of ether. The combined ether extracts were washed with water, saturated Na_2CO_3 solution, and saturated NaCl solution and dried ($MgSO_4$). Evaporation of the solvent left 7.0 g of a dark red oil which was short path distilled to give a clear, deep red oil, 5.5 g, bp ~100° (0.2 mm). The nmr spectrum of this oil indicated ~45% dialkylated and ~55% monoalkylated ketone.

The mixture was separated by column chromatography (300 g of silicic acid, Merck reagent grade, 100–200 mesh). Elution with 10% ether–90% hexane gave 2.17 g (11%) of **9**; elution with 20% ether–80% *n*-hexane to pure ether gave 1.96 g (11%) of **8**. Recrystallization of **8** (ether–pentane) gave colorless needles, mp 52–53° (lit.[19] mp 51°). Distillation of **9** gave a colorless oil: bp 108° (1.5 mm); $n^{26}D$ 1.5841; $\nu_{max}^{CCl_4}$ 3050, 2980, 2930, 1685, 1603, 1480–1450, 1413, 1381, 1367, 1300, 1273, 1181, 1158, 1130, 1095, and 982 cm^{-1}.

Deuteration of 2.—A mixture of deuterium oxide (3.50 g, 0.175 mol), anhydrous Na_2CO_3 (35 mg), **2** (5.00 g, 0.0305 mol), and ethylene glycol dimethyl ether (21 ml, distilled from Na and then from $LiAlH_4$) was refluxed under N_2 for 17 hr. The mixture was cooled and diluted with ether and the ether solution was washed with five 50-ml portions of water and 50 ml of saturated NaCl solution and dried ($MgSO_4$). Evaporation on a steam bath gave 4 g of partially deuterated ketone, mp 58.5–59°. The mass spectrum showed the ketone to be 25% d_0, 24.5% d_1, 43.4% d_2, 6.9% d_3, and 0.2% d_4. The d_3 and d_4 species presumably arise from partial deuteration at C-1. That the deuteration is predominantly at C-3 was established by inspection of the fragment resulting from loss of thioformaldehyde from the molecular ion which indicated 10.1% monodeuteration at C-1.

1,2,3,4-Tetrahydro-1-keto-3-thiaphenanthrene (16).—This compound was prepared from 1-(chloromethyl)naphthalene by the same general procedure described for the preparation of **3**.

1-Naphthylisothiuronium chloride was prepared in 86–94% yield from 1-(chloromethyl)naphthalene and thiourea in hot ethanol: fuses at 227.5–228.5°, sealed tube (ethanol–ether); ν_{max}^{KBr} 1642, 1525, 1515, 1440, 795, and 770 cm^{-1}.

Anal. Calcd for $C_{12}H_{13}ClN_2S$: C, 57.02; H, 5.18; Cl, 14.03; S, 12.69. Found: C, 56.97; H, 5.34; Cl, 14.20; S, 12.43.

1-Naphthylmercaptoacetic acid was prepared in 80–93% yield from the thiuronium chloride: mp 110.5–111° (cyclohexane); ν_{max}^{KBr} 1703, 1595, 1510, 1425, 1395, 1307, 1218, 1160, 1133, 1017, 950, 800, and 775 cm^{-1}; λ_{max}^{EtOH} 224.5 mμ (ε 78,100) and 284 (8190); nmr ($CDCl_3$) δ11.7 (singlet, 1 H), 7.75 (multiplet, 7 H), 4.30 (singlet, 2 H), and 3.11 ppm (singlet, 2 H).

Anal. Calcd for $C_{13}H_{12}O_2S$: C, 67.21; H, 5.21; S, 13.81. Found: C, 67.10; H, 5.18; S, 13.61.

Cyclization of 1-naphthylmercaptoacetic acid (26.0 g, 0.112 mol) with phosphorus pentoxide (45.6 g, 0.321 mol) mixed with "Hyflo-Super Cel" (16 g) in 300 ml of refluxing benzene for 4 hr produced **16** which was purified by two sublimations [100° (0.1 mm)] and recrystallization from absolute ethanol to give 4.5 g (19%) of **16**: mp 125–126°; $\nu_{max}^{CHCl_3}$ 3050, 2860, 1685, 1342, 1275, and 1085 cm^{-1}; λ_{max}^{EtOH} 211.5 mμ (ε 30,100), 251 (39,700), 289 (8120) and 345 (2140); nmr ($CDCl_3$) δ 8.07 (doublet, J = 9 cps, 1 H), 7.66 (multiplet, 5 H), 4.21 (singlet, 2 H), and 3.50 ppm (singlet, 2 H).

Anal. Calcd for $C_{13}H_{10}O_5$: C, 72.86; H, 4.70; S, 14.97. Found: C, 72.97; H, 4.90; S, 14.89.

5-Methyl-2,3-dihydro-2H,6H-thiopyran-3-one (14).—S-(2-Methylallyl)mercaptoacetic acid[31] (60.0 g, 0.411 mol) and anhydrous $NaHCO_3$ (34.6 g, 0.411 mol) were heated (neat, 100°) in a nitrogen atmosphere until CO_2 was no longer evolved. Dry benzene (500 ml) was added and the mixture was refluxed

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(31) Q. Soper, *et al.*, *J. Amer. Chem. Soc.*, **70**, 2849 (1948).

16 hr. A Dean–Stark azeotrope trap was connected and reflux was continued until water no longer separated. The mixture was filtered; the filter cake was dried by suction and then in a steam-heated oven to yield 68.5 g (99%) of sodium salt.

A solution of oxalyl chloride (25 g, 0.20 mol) in dry benzene (50 ml) was cooled in an ice bath to 0–5°. The powdered sodium salt of S-(2-methylallyl)mercaptoacetic acid (16.8 g, 0.100 mol) was added in portions to the rapidly stirred oxalyl chloride by means of Gooch rubber addition tubing. The mixture was kept under a slight positive pressure of N_2, and the temperature was maintained at 10–20° during the addition. The mixture was then heated to reflux for 25 min, cooled, and filtered by suction. The dark red filtrate was shaken vigorously with a slurry of ice and concentrated ammonium hydroxide (20 ml). The organic layer was separated, washed with 1 *N* HCl (30 ml), saturated $NaHCO_3$ solution, water, and saturated NaCl solution, and dried ($MgSO_4$). Filtration and evaporation of the filtrate *in vacuo* left 6.0 g of a dark oil which was short path distilled to give a light yellow oil (3.8 g, 30%), bp 57–70° (0.15–0.40 mm).

The ir spectrum of this oil showed bands at 1680 and 1721 cm^{-1} for the conjugated and unconjugated isomers of 5-methyldihydropyran-3-one, respectively, with the former being the stronger band. Column chromatography of the crude material on silicic acid (Merck, reagent grade, 60 g), eluting first with benzene (225 ml) and then with 10% EtOAc–90% C_6H_6 gave, with the latter, mixed fractions (25 ml each) containing both isomers (0.26 g) and fractions containing 2.52 g of pure **14**. Distillation of the conjugated ketone gave a faintly yellow oil: bp 105–106° (6 mm); $n^{25}\mathrm{D}$ 1.5579; $\nu_{max}^{CCl_4}$ 3035, 2986, 2882, 1675, 1438, 1409, 1390, 1380, 1335, 1275, 1177, 1129, 1026, and 892 cm^{-1}; $\lambda_{max}^{isooctane}$ 231.5 mμ (ε 9340), 270 (302), and 347 (97.8); nmr (CCl_4) δ 5.74 (quartet, *J* = 1.5 cps, 1 H), 3.17 (broad singlet, 2 H), 3.08 (singlet, 2 H), and 1.99 ppm (broad singlet, 3 H).

Anal. Calcd for C_6H_8OS: C, 56.21; H, 6.29; S, 25.02. Found: C, 56.07; H, 6.31; S, 24.82.

Photolysis of 2. Run 1.—Irradiation[28] of **2** (2.00 g, 0.0122 mol) in 500 ml of cyclohexane with a Pyrex 7740 filter was carried out for a total of 16 hr. Periodic cleaning of the immersion well was essential owing to the formation of a coating of polymer. The ir spectra (CCl_4) of residues from evaporation of aliquots taken during the irradiation showed gradual disappearance of the band at 1685 cm^{-1} for starting material and formation of a new intense band at 1725 cm^{-1}. The murky solution was filtered and the clear filtrate evaporated leaving 0.72 g of crude residue. Chromatography of the residue on Florisil, eluting with *n*-hexane containing 0, 2.5, 5.0, and 10% ether gave, with the latter, 303 mg (15%) of an orange oil characterized as **5** by comparison with an authentic sample after purification by short-path distillation.

Run 2.—A similar irradiation[28] for 14 hr with a Corex 9700 filter gave 264 mg (13%) of **5**.

Run 3.—Irradiation of 200 mg of **2** in 50 ml of cyclohexane for 57.5 hr with a 3500-Å source[13] gave a murky mixture which was filtered, evaporated, and distilled (short path) to give 39 mg of an orange oil. The ir spectrum ($CHCl_3$) of this oil showed only weak absorption at 1720 and 1685 and moderately strong absorption at 1770 cm^{-1}. No pure products could be isolated from this residue.

Run 4.—Irradiation[28] of **2** (1.00 g, 6.10 mmol) in 500 ml of cyclohexane for 5 hr with a Pyrex 7740 filter, followed by filtration, evaporation, chromatography of the residue on silicic acid (50 g, elution with 10% ether–90% *n*-hexane), and distillation gave 192 mg (19%) of **5** which was identified by comparison with an authentic sample.

Run 5.—Irradiation[28] of **2** (1.00 g, 6.10 mmol) in "Genetron 113" (500 ml) for 8.25 hr with a Pyrex 7740 filter gave, after short-path distillation of the crude photoproduct, 301 mg of an orange oil which contained a major and a minor product. The minor product (6% corrected vpc yield) was collected by vpc and identified as 1-thiaindan by comparison with an authentic sample prepared as previously reported.[23] The major component (21% corrected vpc yield) was identified as thiochroman-3-one, **5**, by comparison with an authentic sample: $\nu_{max}^{CCl_4}$ 3084, 1723, 1468, 1443, 1385, 1253, 1236, 951, 500, and 440 cm^{-1}; $\lambda_{max}^{isooctane}$ 254 mμ (ε 6900) and 357 (150); nmr (CCl_4) δ 7.93–7.04 (multiplet, 4 H), 3.55 singlet, 2 H), and 3.15 ppm (singlet, 2 H).

Anal. Calcd for C_9H_8OS: C, 65.82; H, 4.91; S, 19.53. Found: C, 65.99; H, 4.80; S, 19.25.

Photolysis of 3, 4, 8, 9, and Deuterated 2.—Irradiation[28] of these materials with a Pyrex 7740 filter was carried out analogously to run 4 for **2** with 1.00 g of ketone in 500 ml of cyclohexane.

7-Methoxyisothiochroman-4-one (**3**) was irradiated for 3 hr. 6-Methoxythiochroman-3-one was isolated in 40% yield: $\nu_{max}^{CCl_4}$ 3050–2825, 1725, 1600, 1572, 1480, 1467, 1310, 1250, 1160, 1070, and 1030 cm^{-1}; λ_{max}^{EtOH} 251.5 mμ (ε 10,200) and 291 (1860); nmr (CCl_4) δ 7.40 (doublet, apparent *J* = 9 cps, 1 H), 6.82 (quartet, apparent *J* = 3 cps, 1 H), 6.74 (singlet, 1 H), 3.80 (singlet, 3 H), 3.64 (singlet, 2 H), and 3.22 ppm (singlet, 2 H).

8-Methylisothiochroman-4-one (**4**) was irradiated for 5 hr. 5-Methylthiochroman-3-one was isolated by vpc (corrected vpc yield was 30%): $\nu_{max}^{CCl_4}$ 3060, 2970, 2905, 1723, 1455, 1380, and 1225 cm^{-1}; λ_{max}^{EtOH} 209 mμ (ε 16,200), 247.5 (6760), and 287 (sh) (891); nmr (CCl_4) δ 7.17 (multiplet, 3 H), 3.58 (singlet, 2 H), 3.20 (singlet, 2 H), and 2.28 ppm (singlet, 3 H).

3-Methylisothiochroman-4-one (**8**) was irradiated for 4 hr. 2-Methylthiochroman-3-one (**10**) was isolated by vpc (corrected vpc yield was 30%): $\nu_{max}^{CCl_4}$ 3050, 2960, 2923, 1725, 1473, 1443, 1390, 1200, and 1073 cm^{-1}; λ_{max}^{EtOH} 210 mμ (infl) (45,700) and 246.5 (7580); nmr (CCl_4) δ 7.30 (multiplet, 1 H), 7.09 (multiplet, 3 H), 3.62 (singlet, 2 H), 3.28 (quartet, *J* = 7 cps, 1 H), and 1.36 ppm (doublet, *J* = 7 cps, 3 H).

3,3-Dimethylisothiochroman-4-one (**9**) was irradiated for 1 hr. The chromatographic fractions contained three components identified as (1) unreacted **9** (5% corrected vpc yield; (2) 2,2-dimethylthiochroman-3-one (**11**) [37% corrected vpc yield; $\nu_{max}^{CCl_4}$ 3055, 2972, 2929, 2855, 1715, 1468, 1437, 1377, 1358, 1244, 1140, 1122, and 1096 cm^{-1}; λ_{max}^{EtOH} 248 mμ (ε 6610); nmr (CCl_4) δ 7.21 (multiplet, 4 H), 3.74 (singlet, 2 H), and 1.38 ppm (singlet, 6 H)]; (3) 2,2-dimethyl-1,3-dithiatetralin (**12**) (6% corrected vpc yield).

Deuterated 2 was irradiated for 6 hr to give 270 mg (27%) of deuterated **5** which was shown by mass spectrometry to be 34% d_0, 43% d_1, 20% d_2, and 3% d_4 species. The corrected intensities of the peaks at *m/e* 123 and 122 corresponded to 2.2 and 1.5% monodeuterated species at *m/e* 122 and 121, respectively, in the undeuterated sample.

Photolysis of 5-Methyl-2,3-dihydro-2H,6H-thiapyran-3-one (14).—Irradiation[28] of a solution of **14** (1.00 g, 7.82 mmol) in cyclohexane (500 ml) for 2 hr with a Pyrex 7740 filter gave a slightly cloudy solution which was filtered and concentrated by evaporation. The pale yellow residue (0.87 g) was distilled (Klagen tube, pot temperature 100–110° (0.1 mm)] to give a nearly colorless oil (282–350 mg, 28–35%) which rapidly discolored on standing. The product was identified as **15** from its analytical and spectral data: $n^{25}\mathrm{D}$ 1.5193; $\nu_{max}^{CCl_4}$ 3082, 2978, 2918, 1780, 1641, 1448, 1397, 1374, 1168, 1127, and 910 cm^{-1}; λ_{max}^{EtOH} 245 mμ (ε 912) and 330 (166); nmr (CCl_4) δ 5.25 (multiplet, 1 H), 5.10 (multiplet, 1 H), 5.00 (doublet, *J* = 0.6 cps, 1 H), 4.14 (doublet–quartet, *J* = 14 and 0.6 cps, 2 H), and 1.85 ppm (finely split singlet, 3 H).

Anal. Calcd for C_6H_8OS: C, 56.21; H, 6.29; S, 25.02. Found: C, 56.51; H, 6.48; S, 24.78.

Photolysis of 1,2,3,4-Tetrahydro-1-keto-3-thiaphenanthrene (16). A.—Irradiation[28] of a solution of **16** (1.00 g, 4.68 mmol) in cyclohexane (500 ml) for 7 hr with a Pyrex 7740 filter gave a murky mixture which was filtered and the filtrate was evaporated. The solid residue was combined with the precipitate from the filtration (815 mg total) and sublimed [110° (0.15 mm)] to give 234 mg of pale yellow solid. Except for very weak bands at 1775 and 1720 cm^{-1}, the ir spectrum (CCl_4) of this material was identical with the spectrum of **16**.

B.—Irradiation[13] of a solution of **16** (501 mg, 2.34 mmol) in cyclohexane for 24 hr and evaporation of an aliquot gave a residue whose ir spectrum showed a strong band at 1685 for starting material and a moderately strong band at 1770 cm^{-1}. The reaction was not investigated further.

***o*-(Ethyl carboxymethylmercapto)benzoic Acid (18).**—To a stirred solution of Na metal (12.5 g, 0.542 g-atom) in absolute ethanol (750 ml) under N_2 was added thiosalicylic acid (41.7 g, 0.271 mol); a heavy, white precipitate formed immediately. The mixture was stirred for 30 min at room temperature and ethyl bromoacetate was added rapidly. A mildly exothermic reaction occurred with dissolution of the original precipitate and formation of a considerably less bulky precipitate. After refluxing for 1 hr, the mixture was cooled and treated with concentrated HCl (23 ml). Evaporation of the solvents left a rock hard residue which was ground to a powder with mortar and pestle. The powdered material was leached with 500 ml of hot water and collected by filtration as a buff powder (59.8 g, 92%). Recrystallization from ethanol–water gave colorless needles: mp 125.5–126.5°; $\nu_{\max}^{\mathrm{KBr}}$ 3500–3000, 1731, 1695, 1589, 1562, 1470, 1416, 1319, 1284, 1196, 1164, 1070, 1053, 1032, 895, 745, 699, 652, and 556 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 222 mμ (ϵ 20,400), 256.5 (7510) and 314 (2980); nmr ($CDCl_3$) δ 11.64 (singlet, 1 H), 8.23 (doublet, J = 8 cps, 1 H), 7.67–7.17 (multiplet, 3 H), 4.25 (quartet, J = 7 cps, 2 H), 3.78 (singlet, 2 H), and 1.27 (triplet, J = 7 cps, 3 H).

Anal. Calcd for $C_{11}H_{12}O_4S$: C, 54.98; H, 5.04; S, 13.35. Found: C, 54.84; H, 5.01; S, 13.31.

o-(Ethyl carboxymethylmercapto)diazoacetophenone (19).—A mixture of **18** (49.3 g, 0.205 mol) and $SOCl_2$ (65 ml) was refluxed on a steam bath for 30 min. The resulting deep red solution was evacuated with a water aspirator to remove excess $SOCl_2$ and the residue was distilled to give 43.5 g (82%) of clear, yellow acid chloride: bp 164–166° (1.5 mm), 140–142.5° (0.1 mm); $n^{30}\mathrm{D}$ 1.5868; $\nu_{\max}^{\mathrm{CCl_4}}$ 2980, 1766, 1735, 1587, 1455, 1272, 1200, 1131, 1031, 873, and 700 cm^{-1}; nmr (CCl_4) δ 8.33 (doublet, J = 7.5 cps, 1 H), 7.43 (multiplet, 3 H), 4.18 (quartet, J = 7 cps, 2 H), 3.67 (singlet, 2 H), and 1.25 (triplet, J = 7 cps, 3 H).

Anal. Calcd for $C_{11}H_{11}ClO_3S$: C, 51.06; H, 4.09; S, 12.40; Cl, 13.71. Found: C, 51.18; H, 4.17; S, 12.59; Cl, 13.74.

A solution of diazomethane[32] was prepared from 18.5 g of "EXR-101" and to this solution was added dropwise at 0° during 1 hr a solution of the acid chloride (6.45 g, 0.025 mol) in ether (50 ml). The solution was allowed to warm gradually to room temperature and stand for 38–40 hr. Removal of the ether at 30° left a bright yellow crystalline residue which was triturated with pentane and filtered to give 6.25 g (95%) of crude diazo ketone **19**, mp 67–70°. Recrystallization of a sample from ether–pentane gave tiny, yellow rhombs: mp 68–69°; $\nu_{\max}^{\mathrm{KBr}}$ 3107, 2978, 2957, 2103, 1739, 1727, 1605, 1583, 1460, 1353, 1292, 1167, 1019, 875, and 739 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 237 mμ (ϵ 16,900), 290 (10,900), and 326 (sh) (3260); nmr ($CDCl_3$) δ 7.63 (multiplet, 3 H), 7.39 (multiplet, 1 H), 6.00 (singlet, 1 H), 4.23 (quartet, J = 7.5 cps, 2 H), 3.75 (singlet, 2 H), and 1.23 (triplet, J = 7.5 cps, 3 H).

Anal. Calcd for $C_{12}H_{12}N_2O_3S$: C, 54.53; H, 4.58; N, 10.60; S, 12.13. Found: C, 54.37; H, 4.62; N, 10.80; S, 12.43.

Ethyl o-(Ethyl carboxymethylmercapto)phenyl Acetate (20).—A solution of $AgNO_3$ (5.90 g, 0.0298 mol) in water (100 ml) and a solution of sodium benzoate (5.00 g, 0.0298 mol) in water (100 ml) were mixed and the precipitate of silver benzoate was collected and washed with several portions of water on a suction funnel. The filter cake was broken up and dried *in vacuo* [75° (3 mm) for 24 hr and then 25° (0.1 mm) for 24 hr]. A solution of silver benzoate (2.00 g) in triethylamine (18.2 g, distilled from $LiAlH_4$) was prepared and stored in a vacuum-dried bottle fitted with a "no-air" stopper.

To a slurry of the diazo ketone **19** (2.00 g, 7.59 mmol) in 13 ml of absolute EtOH in a flask connected to a gas buret was added, dropwise with stirring at 25°, the silver benzoate–triethylamine reagent. Initially a few drops were added followed by portions necessary to maintain evolution of N_2. After addition of *ca.* 2.0 g of the reagent during 25 min, N_2 evolution had ceased and 160 ml of the gas (~90% of the theoretical) had been collected. The dark red mixture was refluxed with Norit for 5 min on a steam bath, cooled, diluted with an equal volume of EtOH, and filtered. Concentration of the filtrate *in vacuo* left a dark syrup which was dissolved in 100 ml of ether. The ether solution was washed with two 20-ml portions of saturated $NaHCO_3$ solution and 20 ml of saturated NaCl solution, dried, evaporated, and distilled to give 1.53 g (72%) of a clear, yellow liquid: bp 121–124° (0.15 mm); $n^{30}\mathrm{D}$ 1.5281; $\nu_{\max}^{\mathrm{CCl_4}}$ 3055, 2989, 1743, 1275, 1162, and 1038 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 250 mμ (sh) (ϵ 3500); nmr (CCl_4) δ 7.55 (multiplet, 1 H), 7.27 (multiplet, 3 H), 4.13 (quartet, J = 7 cps, 2 H), 4.08 (quartet, J = 7 cps, 2 H), 3.83 (singlet, 2 H), 3.50 (singlet, 2 H), 1.24 (triplet, J = 7 cps, 3 H), and 1.18 ppm (triplet, J = 7 cps, 3 H).

Anal. Calcd for $C_{14}H_{18}O_4S$: C, 59.55; H, 6.42; S, 11.36. Found: C, 59.71; H, 6.49; S, 11.52.

Ethyl Thiochroman-3-one-2-carboxylate (21).—Sodium hydride (2.30 g of an approximately 50% by weight dispersion in Nujol, *ca.* 0.048 mol) was washed with dry *n*-hexane by decantation under N_2 and suspended in tetrahydrofuran (100 ml, distilled from sodium hydride). To this slurry was added dropwise a solution of **20** (6.76 g, 0.024 mol) in 20 ml of dry tetrahydrofuran during 1 hr at 65–70°. The mixture was refluxed under N_2 for 7.5 hr and then cooled to room temperature. Absolute EtOH (2 ml) was added, the mixture was poured onto a slurry of ice (100 g) and glacial HOAc (7.5 ml), and the oily suspension was extracted with three 100-ml portions of ether. The combined ether layers were washed with water and with saturated NaCl solution, dried ($MgSO_4$), evaporated, and distilled to give two fractions, bp 119–132° (0.35–0.4 mm) and 132–137° (0.4–0.6 mm). Spectral data (ir and nmr) indicated that the lower boiling fraction (1.32 g) was a mixture (~1:1) of **21** and **5**, and the higher boiling fraction (2.71 g) was essentially pure β-keto ester **21** (combined yield 76%).

Evaporative distillation of the higher boiling fraction gave colorless product **21**: $\nu_{\max}^{\mathrm{CHCl_3}}$ 3500–2500, 3055, 2980, 1716, 1635, 1603, 1565, 1465, 1440, 1410, 1395, 1370, 1330, 1312, 1290, 1260, 1225, 1170, 1100, 1072, 1042, 1035, 950, 922, 890, 860, 650, and 578 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 229 mμ (ϵ 10,700), 261 (8900), and 299 (2610); nmr ($CDCl_3$) δ 7.5 (complex, 4 H), 4.45 and 4.42 (two quartets, J = 7.5 cps, 2 H), 1.38 (triplet, J = 7.5 cps, 3 H), and 3.85–3.42 and 12.6 ppm (multiplet and singlet, 3 H).

Anal. Calcd for $C_{12}H_{12}O_3S$: C, 60.99; H, 5.12; S, 13.57. Found: C, 61.09; H, 4.96; S, 13.76.

Thiochroman-3-one (5).—The mixture of β-keto ester **21** and ketone **5** obtained in the preparation of **21** was refluxed under N_2 with 50 ml of 20% HCl for 8.5 hr (bath temperature 140°). The mixture was cooled and extracted with ether. The ether extracts were washed with water, saturated $NaHCO_3$ solution, and saturated NaCl solution, dried ($MgSO_4$), and evaporated to give a red oil (3.55 g) which was chromatographed on Florisil (40 g). Elution with *n*-hexane gave 0.97 g of recovered **21** and with 10% ether–90% *n*-hexane gave 1.53 g of desired ketone **5**. Distillation of the ketone gave 1.30 g (41% based on recovered **21**) of a nearly colorless product, bp 98–99° (1.6 mm).

The ir spectrum of this material indicated that it still contained a trace of **21** which was removed by a second chromatography on Florisil followed by short-path distillation. The spectral data and vpc data of this ketone were identical with those of **5** obtained from irradiation of **2**.

Methyl 2-Chlorosulfonyl-5-methoxyphenylacetate (22).—A solution of *m*-methoxyphenylacetic acid (16.6 g, 0.10 mol) in methanol (50 ml) containing concentrated H_2SO_4 (4.5 ml) was refluxed for 4 hr on a steam bath. Water (100 ml) was added, the mixture was extracted with ether, and the ether extracts were washed with water, saturated $NaHCO_3$ solution, and saturated NaCl solution, dried, and evaporated. Distillation afforded 15.9 g (88%) of methyl *m*-methoxyphenylacetate: bp 107–108° (2 mm); $n^{28}\mathrm{D}$ 1.5130; $\nu_{\max}^{\mathrm{CCl_4}}$ 3000, 2950, 2835, 1744, 1603, 1587, 1493, 1469, 1455, 1438, 1265, 1153, 1060, 1048, 1021, 735, and 692 cm^{-1}; nmr (CCl_4) δ 7.05 (triplet, apparent J = 8 cps, 1 H), 6.68 (multiplet, 3 H), 3.84 (singlet, 3 H), 3.57 (singlet, 3 H), and 3.44 ppm (singlet, 2 H).

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.37; H, 6.66.

To a solution of methyl *m*-methoxyphenylacetate (29.0 g, 0.161 mol) in $CHCl_3$ (80 ml) under N_2 and cooled to −8° was added dropwise, with vigorous stirring, freshly distilled chlorosulfonic acid (38.5 g, 0.329 mol) while the temperature was maintained below 0°. The ice bath was removed and the mixture was stirred under N_2 for 1.25 hr while it was warmed to room temperature. The mixture was poured onto a slurry of ice and $CHCl_3$, the layers were separated, and the $CHCl_3$ layer was washed with two 75-ml portions of ice–water and dried (Na_2SO_4). Evaporation of the solvent left an oil which gave 5.0 g (11%) of white, crystalline **22** after trituration with pentane, mp 82–83°. The nearly pure product could be recrystallized from cyclohexane containing a little ether: mp 83–84°; $\nu_{\max}^{\mathrm{CHCl_3}}$ 3006, 2938, 2835, 1742, 1597, 1569, 1480, 1460, 1430, 1374, 1339, 1320, 1252, 1170, 1055, and 1000 cm^{-1}; nmr ($CDCl_3$) δ 8.03–6.97 (multiplet, 3 H), 4.13 (singlet, 2 H), 3.90 (singlet, 3 H), and 3.72 ppm (singlet, 3 H).

Anal. Calcd for $C_{10}H_{11}ClO_5S$: C, 43.09; H, 3.98; Cl, 12.72; S, 11.51. Found: C, 43.12; H, 4.11; Cl, 12.90; S, 11.45.

5-Methoxy-1-thiaindan-2-one (23).—The sulfonyl chloride **22** (4.91 g, 17.6 mmol) was added in portions to a vigorously stirred suspension of zinc dust (6.0 g) in water (16 ml) during 1 hr. Water (6 ml) was added and the stirred mixture was

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(32) J. A. Moore and D. E. Reed, *Org. Syn.*, **41**, 16 (1961).

heated to 60–80° (bath temperature) for 1 hr under N_2. During the heating period an additional 0.8 g of zinc dust was added in small portions. The mixture was cooled to 0–10° and a solution of 40 ml of concentrated HCl in 10 ml of water was added in small portions. After the mixture was stirred vigorously for 18 hr at 20°, a flocculent, gray precipitate had formed. An additional 4.0 g of zinc dust was added and the mixture was heated to gentle reflux under N_2 for 1 hr. The mixture was cooled, filtered through glass wool, and extracted with ether. The acidic aqueous layer was saturated with NaCl and extracted with ether. The combined ether extracts were washed with saturated NaCl solution, dried (Na_2SO_4), and evaporated to give a semisolid residue. Trituration with pentane gave solid **23** (0.56 g, 18%), mp 110–116°, which was purified by sublimation: mp 122–123°; $\nu_{\max}^{CHCl_3}$ 3010, 2945, 2905, 2830, 1712, 1601, 1578, 1469, 1429, 1304, 1225, 1150, 1080, 1033, and 1012 cm^{-1}; $\lambda_{\max}^{EtOH}$ 216 mμ (ϵ 11,100) 234.5 (11,100), 270.5 (5750), and 298 (934); nmr ($CDCl_3$) δ 7.19–6.81 (multiplet, 3 H), 3.89 (singlet, 2 H), and 3.79 (singlet, 3 H).

Anal. Calcd for $C_9H_8O_2S$: C, 59.98; H, 4.47; S, 17.79. Found: C, 59.94; H, 4.48; S, 17.88.

Methyl 2-(Methyl carboxymethyl)-4-methoxyphenylmercaptoacetate (24).—To a slurry of thiolactone **23** (226 mg, 1.26 mmol) in 5 ml of 80% methanol–water under N_2 was added solid KOH (160 mg, 2.85 mmol). The solution was stirred for 15 min at room temperature and methyl bromoacetate (301 mg, 1.97 mmol) was added. The mixture was stirred for 15 min at room temperature and then heated under reflux for 1 hr. Water (10 ml) and 6 *N* HCl (0.5 ml) were added and 5 ml of distillate was collected. The mixture was cooled and extracted with three 30-ml portions of ether. The combined ether extracts were washed with water and saturated NaCl solution, dried ($MgSO_4$), and evaporated to give a yellow oil. The oil was dissolved in 10 ml of ether; the solution was cooled to 0° and treated with a solution of diazomethane in ether (prepared from 715 mg N′-nitro-N-methyl-N-nitrosoguanidine and a mixture of 3 ml of 50% aqueous KOH and 18 ml of ether)[33] until a yellow color persisted. After the mixture was stirred for 10 min while it warmed to room temperature, the yellow color was carefully discharged with a few drops of glacial HOAc. The ether solution was diluted to 100 ml (ether), dried ($MgSO_4$), and evaporated to give 332 mg (93%) of **24**. A sample of this material was purified by short-path distillation [Klagen tube, bath temperature 210° (0.1 mm)] to give a nearly colorless oil: $\nu_{\max}^{CCl_4}$ 3003, 2954, 2838, 1742, 1596, 1569, 1480, 1467, 1433, 1335, 1300–1230, 1156, 1068, 1028, and 1008 cm^{-1}; nmr (CCl_4) δ 7.44 (doublet of doublets, $J = 7$ and 2 cps, 1 H), 6.74 (doublet, $J = 2$ cps, 1 H), 6.70 (doublet of doublets, $J = 7$ and 2 cps, 1 H), 3.81 (singlet, 2 H), 3.69 (singlet, 3 H), 3.60 (singlet, 3 H), 3.55 (singlet, 3 H), and 3.35 (singlet, 2 H).

Anal. Calcd for $C_{13}H_{16}O_5S$: C, 54.91; H, 5.67; S, 11.28. Found: C, 55.04; H, 5.77; S, 11.14.

6-Methoxythiochroman-3-one (6).—Sodium hydride (*ca.* 50% Nujol dispersion, 115 mg, *ca.* 2.4 mmol) was washed free of Nujol with three 5-ml portions of *n*-hexane under N_2 and 5 ml of ether was added. The vigorously stirred slurry was treated dropwise during 45 min with a solution of **24** (339 mg, 1.2 mmol) in ether (10 ml) containing 3 microdrops of methanol. A mildly exothermic evolution of H_2 took place after a short while with development of a light yellow color and formation of a copious gray to tan precipitate. Stirring at room temperature was continued for 0.5 hr longer and the mixture was heated under reflux for 1 hr (bath temperature 45°). The mixture was cooled and poured into a slurry of ice–water (20 g) and glacial HOAc (0.3 g). The layers were separated and the aqueous layer was extracted with three 50-ml portions of ether. The combined ether extracts were washed with water (20 ml), a mixture of saturated $NaHCO_3$ solution (2 ml) and water (8 ml), and saturated NaCl solution, dried (Na_2SO_4), and evaporated to give 285 mg (94%) of crude β-keto ester as an amber, partially crystallized oil (keto/enol forms, *ca.* 3:1).

The crude β-keto ester was heated under reflux with 1 ml of 6 *N* HCl (oil bath, 130–140°) under N_2 for 45 min. The mixture was cooled and poured into a solution of Na_2CO_3 (0.50 g) in water (9 ml). The mixture was shaken, the layers were separated, and the aqueous layer was extracted with three 50-ml portions of ether. The combined ether extracts were washed with 2 *N* NaOH (10 ml), water, and saturated NaCl solution, dried ($MgSO_4$), and evaporated to give a dark residue which was distilled (Klagen tube, *ca.* 0.6 mm) to give 17.1 mg of a light yellow oil. The major component was collected by vpc and was identical in all respects with the sample of **6** from irradiation of **3**.

Registry No.—**1,** 18926-31-3; **2,** 4426-76-0; **3,** 16994-31-3; **4,** 16994-30-2; **5,** 16895-58-2; **6,** 18926-35-7; **9,** 16994-33-5; **10,** 18926-36-8; **11,** 18926-37-9; **14,** 16994-29-9; **15,** 18926-39-1; **16,** 5254-94-4; **18,** 18926-41-5; **18** (acid chloride), 18926-42-6; **19,** 18926-43-7; **20,** 18926-44-8; **21,** 18926-45-9; **22,** 18944-99-5; **23,** 18926-46-0; **24,** 18945-00-1; *m*-methoxybenzylmercaptoacetic acid, 18926-47-1; *o*-methylbenzylisothiuronium bromide, 18926-48-2; *o*-methylbenzylmercaptoacetic acid, 18926-49-3; 1-napthylisothiuronium chloride, 18945-01-2; 1-napthylmercaptoacetic acid, 10404-24-7; 6-methoxythiochroman-3-one, 18926-35-7; 5-methylthiochroman-3-one, 18927-04-3; methyl *m*-methoxyphenylacetate, 18927-05-4.

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[33] A. F. McKay, *J. Amer. Chem. Soc.*, **70,** 1974 (1948).

Synthesis of New Indole Alkaloid Types

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Received October 4, 1968

A new series of compounds related to tubulosine has been synthesized. The designation "methylenebis type" is proposed for this general structural class. The compounds were prepared by condensing various esters represented by **5a** with homoveratrylamine or tryptamine; the resulting amides (*e.g.*, **6a**) were cyclized with phosphoryl chloride. Reduction of **7a** with sodium borohydride gave mixtures of the corresponding epimeric pair **8a**. This mixture was separated, and the major epimer was N-methylated *via* lithium aluminum hydride reduction of its N-formamide. The mass spectra of the compounds described showed fragmentation patterns analogous to those arising from emetine and tubulosine, thereby confirming the structures expected on the basis of the synthetic sequence.

For many years, the ipecacuanha alkaloids,[1] as represented by the pharmacologically important compound emetine[2] (**1a**), were the only compounds of the "methylenebis"[3] alkaloid type known to occur naturally. Members of this series possess benzoisoquinolizidine and isoquinoline moieties, connected by a methylene bridge.

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[1] H.-G. Boit, "Ergebnisse der Alkaloid-Chemie bis 1960," Akademie-Verlag, Berlin, 1961, p 370.

[2] The Merck Index, 7th ed, Merck and Co. Inc., Rahway, N. J., 1960, p 401.

[3] We propose the general designation "methylenebis type" for this class of alkaloids and related substances containing two discrete basic moieties connected by a methylene bridge.