mp 174.5–177° (lit.[4] mp 176–177°; nmr (d_6-acetone) 6.2 and 6.6 (s, s, H_2C=C) and 7.8 and 8.25 (d, d, J = 9 Hz, 4-nitrophenyl) as well as absorption for the acidic hydrogen.

Registry No.—**1**, 104-03-0; **2**, 13797-13-2; **5**, 24886-58-6; **8**, 24886-59-7; **8** HCl, 24886-60-0; 2,4-dinitrophenylacetic acid, 643-43-6; 2-(4-nitrophenyl)-1,3-di(N-piperidino)propane, 24886-61-1.

Acknowledgment.—The authors wish to thank Dr. J. J. Cawley and Dr. W. W. Zajac, Jr. for helpful suggestions during the course of this work.

Photochemical Reactions of Phenacyl- and Benzylsulfonium Salts[1]

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Phenacylsulfonium tetrafluoroborates (**1**, **5**, **7**, **9**, and **11**) on irradiation afford products resulting from homolytic cleavage of the phenacyl carbon–sulfur bond. Benzylsulfonium tetrafluoroborates (**13**, **22**, **24**, **29**, and **32**) on irradiation afford products resulting from both homolytic and heterolytic cleavage of the benzyl carbon–sulfur bond where the heterolytic cleavage is the major pathway. β-Keto sulfonium fluoroborates (**44** and **46**) on irradiation in methanol are converted to polymeric products. Syntheses are described for all photochemical products previously unreported.

The photolysis of dimethylphenacylsulfonium bromide in water was recently reported.[3] Irradiation of the salt in methanol for 1 hr in these laboratories also produced acetophenone (51%) and phenacyl bromide (<5%) but no significant amount of *p*-bromodibenzoylethane which was reported to be the major product (25%) on irradiation in water.[3] Furthermore, irradiation of phenacyl bromide in methanol under similar conditions for 1 hr produced acetophenone (41%) indicating that acetophenone must arise in part, if not completely, from phenacyl bromide as an intermediate.[4] In view of this involvement of bromide ion in the photolysis, the tetrafluoroborate salt of dimethylphenacylsulfonium ion and other aroylsulfonium ions was irradiated in order to prevent anion involvement whether the cleavage of the carbon–sulfur bond was heterolytic or homolytic. The nonpolymeric products formed are listed in Table I.

Acetophenone (**2**) was the sole product from photolysis of **1** in methanol, but the coupling product **3** was observed in *t*-butyl alcohol and acetonitrile and the rearrangement product **4** was observed in low yield in *t*-butyl alcohol. In similar fashion **5**, **7**, and **9**, on irradiation in methanol, were converted to **6**, **8**, and **10**, respectively. Tetrafluoroborate salt **11** follows a similar reaction course in methanol and water.

The presence of the phenacyl dimer **3** in solvents other than methanol is in line with the increased difficulty of abstraction of a hydrogen atom by a radical from the other solvents.[5] An excited-state solvolysis of the sulfonium salts in methanol to form the corresponding α-methoxy ketone can not be discarded since α-methoxyacetophenone rapidly photolyzed in methanol to form **2**.[6] On the other hand, α-hydroxyacetophenone gave no monomeric products on irradiation in water and thus would not appear to be an intermediate in the irradiation of **1** or **11** in water. This would appear to eliminate an excited-state solvolysis as the reaction pathway of the BF_4^- salts in water.

The isolation of **12** from the photolysis of **11** rules out a Norrish type II process for the formation of **2**[7] since the $C_3H_7CH{=}S^+C_4H_9$ formed in such a process would be converted to $C_3H_7CH(OR)CHSC_4H_9$ (R = CH_3 in methanol, R = H in water).

The data from irradiation of the BF_4^- salts are most consistent with a radical pathway involving initial homolytic cleavage to the phenacyl radical[8,9] and the dialkylsulfinium cation radical.[10–12] Diarylsulfinium cation radicals are probably involved in the photolytic decomposition of triarylsulfonium salts.[14] The dimethylsulfinium cation radical formed from photolysis of **1** (in *t*-butyl alcohol) may lose H^+ to form $\cdot CH_2CSH_3$

(1) This research has been supported by National Science Foundation Grant No. GP-7831 and by National Institutes of Health Grant No. AI-09300.

(2) National Institutes of Health Predoctoral Fellow, 1965–1968.

(3) T. Laird and H. Williams, *Chem. Commun.*, 561 (1969).

(4) Irradiation of phenacyl chloride in ethanol affords only acetophenone (53%); J. C. Anderson and C. B. Reese, *Tetrahedron Lett.*, 1 (1962),

(5) (a) V. K. Schwetlich, R. Karland and J. Jentzsch, *J. Prakt. Chem.*, **22**, 113 (1963), report the rate of hydrogen atom abstraction by *t*-butoxy radicals to decrease in the following order: $CH_3OH > CH_3CN > (CH_3)_3OH$. (b) Water is known to be a poor hydrogen atom donor: A. Becket and G. Porter, *Trans. Faraday Soc.*, **59**, 2039 (1963).

(6) R. B. LaCount and C. E. Griffin, *Tetrahedron Lett.*, 1549 (1965), report that photolysis of α-methoxyacetophenone in benzene gives 3-phenyl-3-oxethanol (10% yield). P. Yates and A. G. Szabo, *ibid.*, 485 (1965), report obtaining the same product (29% yield) in benzene on irradiation for 12 hr. A detailed study of the photochemistry of α-alkoxyacetophenones has appeared recently: F. D. Lewis and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 311 (1970).

(7) This assumes **2** and **12** are formed in the same reaction process.

(8) The study by R. L. Huang and P. Williams, *J. Chem. Soc.*, 2637 (1958), indicates that phenacyl radicals are probably more reactive than benzyl radicals.

(9) Acetophenone, one of the products of the photolytic decomposition of dimethylsulfonium phenacylide [B. M. Trost, *J. Amer. Chem. Soc.*, **89**, 138 (1967)] and diazoacetophenone [D. O. Cowan, *et al.*, *J. Org. Chem.*, **29**, 1922 (1964)] in alcohols, presumably arose *via* phenacyl radicals formed from hydrogen atom abstraction by benzoyl carbene.

(10) Cation radicals of this type have been produced by the oxidation of aryl sulfides in concentrated H_2SO_4:[11] H. J. Shine, *et al.*, *J. Org. Chem.*, **32**, 1901 (1966), and references cited therein; A. Zweig, *et al.*, *Tetrahedron Lett.*, 1821 (1963).

(11) Reviews on the formation of sulfur cation radicals have appeared: (a) U. Schmidt, in "Organosulfur Chemistry," M. J. Jannsen, Ed., Interscience Publishers, New York, N. Y., 1967, p 75; (b) H. J. Shine, in ref 11a, p 93.

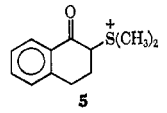
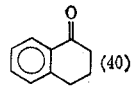
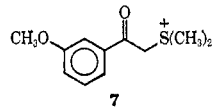
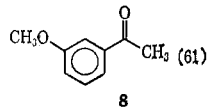
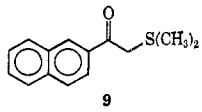
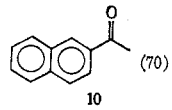
(12) Although the anodic oxidation of dialkyl sulfides is reported to produce a single wave representing removal of two electrons,[13] Zweig, *et al.*, (ref 10) cite convincing evidence for formation of the cation radical from dithiohydroquinone dimethyl ether by electrochemical oxidation.

(13) M. M. Nicholson, *J. Amer. Chem. Soc.*, **76**, 2539 (1954); V. Drushel and J. F. Miller, *Anal. Chem.*, **29**, 1456 (1957).

(14) J. W. Knapczyk and W. E. McEwen, *J. Amer. Chem. Soc.*, **91**, 145 (1969).

TABLE I

PRODUCTS FROM IRRADIATION OF PHENACYLSULFONIUM TETRAFLUOROBORATES

Salt	Solvent	Time, hr	Products (% yield)
$C_6H_5\overset{O}{\overset{\|}{C}}CH_2\overset{+}{S}(CH_3)_2$ 1	CH_3OH	6.2	$C_6H_5COCH_3$ (82) 2
1	$(CH_3)_3COH$	3	2 (33), $C_6H_5\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}C_6H_5$ 3 (16), $C_6H_5\overset{O}{\overset{\|}{C}}CH_2CH_2SCH_3$ 4 (5)
1	CH_3CN	5	2 (60), 3 (14%)
 5	CH_3OH	12.7	 (40) 6
 7	CH_3OH	8	 (61) 8
 9	CH_3OH	20	 (70) 10
$PhC(=O)CH_2\overset{+}{S}(n\text{-butyl})_2$ 11	CH_3OH	4.5	2 (48), $(n\text{-butyl})_2S$ (29) 12
11	H_2O	2	2 (16), 3 (14), 12 (29)

which would couple with the phenacyl radical to form the minor product **4**. The dimethyl sulfide isolated from photolysis of dimethylphenacylsulfonium bromide[3] and the di-*n*-butyl sulfide from **11** probably do not arise from hydrogen atom abstraction from water or methanol by the α-thioalkyl radical since such radicals are more stable than their oxygen analogs.[5a,15] A more reasonable explanation for formation of the dialkyl sulfide would be abstraction of a hydrogen atom by the dialkylsulfinium ion followed by loss of a proton.

The photolysis of benzylsulfonium tetrafluoroborates in methanol gives solvolytic products and radical products in line with conclusions drawn in previous photochemical studies of benzyl derivatives.[16] The sulfonium tetrafluoroborates studied are listed in Table II. Photolysis of **13** in methanol gives the solvolytic product **14** and the radical coupling product **15**. No toluene is observed as a radical abstraction product; benzyl radicals are known to prefer to couple rather than abstract hydrogen atoms.[17] Product **14** was found to photolyze slowly, but this did not account for the observed products **16–18** which undoubtedly arise from secondary reactions of **14**. It has been shown that a variety of radical initiators will abstract a hydrogen atom from the benzylic carbon of **14** to form an intermediate radical which fragments to **16**, or dimerizes to **18**.[18] Monomethyl ether **17** undoubtedly arose from coupling of the intermediate radical from **14** with the benzyl radical. Photolysis of **13** in *t*-butyl alcohol gave only **19** and **15**. No secondary products are formed owing to the steric inhibition to benzylic hydrogen atom abstraction by the *t*-butyl group of **19**.

The dibenzylmethylsulfonium salt, **22**, on irradiation gave a product mixture similar to that of **13**, except in this case the sulfur-containing product **23** was also isolated. Photolysis of **23** in methanol for 2 hr (80% reaction) gave **15** in 19% yield. Consequently, some of **15** formed during the photolysis of **22** may arise as a secondary product from **23**.

In view of Zimmerman's conclusions[16] on the enhancing effect of *m*-methoxy substitution on the photochemical solvolysis of benzylic systems, salt **24** was irradiated. The enhanced rate of reaction of **24** *vs.* that of **13** probably reflects only the more intense absorption of **24**. A longer irradiation for **24** rapidly decreased the yield of **25** and several unidentified secondary products appeared. Although the ratio of heterolytic/homolytic cleavage products would appear to decrease from **13** to **24**, the extent of secondary reactions that may be leading to polymer formation can not be determined and no conclusions can be drawn concerning the adequacy of Zimmerman's theoretical model. The formation of **28** from **24** probably involves coupling of the *p*-methoxybenzyl radical with the α-thioalkyl radical, $\cdot CH_2SCH_3$, derived from homolytic cleavage as suggested above.

Irradiation of salts **29** and **32** in methanol gave similar results. The major product from **29** is the photochemical solvolysis product **30**. The formation of **31** is explained in terms of a secondary photochemical reaction of **30** analogous to the photolysis of benzyl methyl sulfide described above except that the product is that resulting from hydrogen atom abstraction rather than radical coupling. Irradiation of **32** gives the solvolytic product **33** and the secondary product **34**. It is interesting to note that **33** preferentially cleaves to the substituted 2-phenylethyl radical and the thiyl radical

(15) S.-O. Lawesson and C. Berglund, *Acta Chem. Scand.*, **15**, 36 (1961).
(16) H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, **85**, 915 (1963).
(17) W. A. Waters in "Vistas in Free Radical Chemistry," W. A. Waters, Ed., Pergamon Press, New York, N. Y., 1959, p 151.
(18) R. E. Lovins, L. J. Andrews, and R. M. Keefer, *J. Org. Chem.*, **30**, 4150 (1965).

TABLE II

PRODUCTS FROM IRRADIATION OF BENZYLSULFONIUM TETRAFLUOROBORATES

Salt	Solvent	Time, hr	Products (% yield)
$PhCH_2\overset{+}{S}(CH_3)_2$ **13**	CH_3OH	3.5	$PhCH_2OCH_3$ (25), $PhCH_2CH_2Ph$ (3), PhCHO (9), **14** **15** **16**; $PhCH(OCH_3)CH_2Ph$ (8), $PhCH(OCH_3)CH(OCH_3)Ph$ (7) **17** **18**
13	$(CH_3)_3COH$	2.3	$PhCH_2OC(CH_3)_3$ (33), **15** (4) **19**
13	CH_3CN	24	$PhCH_2NHC(=O)CH_3$ (70), $PhCH_2C_6H_4CH_3$ (7) **20** **21**
$(PhCH_2)_2\overset{+}{S}CH_3$ **22**	CH_3OH	1.2	**14** (23), **15** (8), **16** (5), **17** (7), **18** (4), $PhCH_2SCH_3$ (26) **23**
CH_3O-C_6H_3-$CH_2\overset{+}{S}(CH_3)_2$ **24**	CH_3OH	0.25	CH_3O-C_6H_4-CH_2OCH_3 (53), **25**; CH_3O-C_6H_4-CH_3 (4), **26**; CH_3O-C_6H_4-CH_2-CH_2-C_6H_4-OCH_3 (8), **27**; CH_3O-C_6H_4-$CH_2CH_2SCH_3$ (5) **28**
$\overset{+}{S}$-CH_3 **29**	CH_3OH	2.5	CH_2SCH_3, CH_2OCH_3 (18), **30**; CH_3, CH_2OCH_3 (14) **31**
$\overset{+}{S}$-CH_3 **32**	CH_3OH	3	$CH_2CH_2SCH_3$, CH_2OCH_3 (17), **33**; CH_2CH_3, CH_2OCH_3 (5) **34**

rather than to the substituted benzyl radical and the α-thioalkyl radical. That **34** is formed from **33** was established by irradiation of **33** in methanol which gave **34** as the only nonpolymeric product.

Although poor leaving groups deter excited-state solvolysis,[18] the photolysis of **13** in acetonitrile suggests that excited-state solvolysis occurs in solvents of low nucleophilicity. Amide **20** must result from hydrolysis of the nitrilium salt,[19] $PhCH_2N^+{\equiv}CCH_3$, during the work-up procedure. Since radicals add to the carbon atom of nitriles,[20] **20** must arise from heterolytic cleavage rather than homolytic cleavage. The hydrocarbon **21**, however, may arise from the benzyl radical.

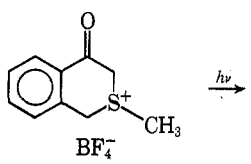
The above results clearly indicate that irradiation of phenacylsulfonium salts leads to homolytic cleavage whereas benzylsulfonium salts undergo predominantly heterolytic cleavage. Clearly, excitation of the benzylsulfonium salts leads to an initial π^*,π state. Whether the π^*,π state or the π^*,n state of the phenacylsulfonium salts is responsible for the observed reactions has not been determined. The π^*,n triplet state of phenacylsulfonium salts **1**, **5**, **7**, and **11** is of lower energy than the π^*,π triplet state, whereas the reverse is probably the case for **9**.[21] Nonetheless, the reaction course for **9** appears to be the same as the other phenacyl sulfonium salts studied.

(19) H. Meerwein, *et al.*, *Chem. Ber.*, **89**, 209 (1956), report the isolation of a number of nitrilium salts, all of which rapidly hydrolyzed to amides.

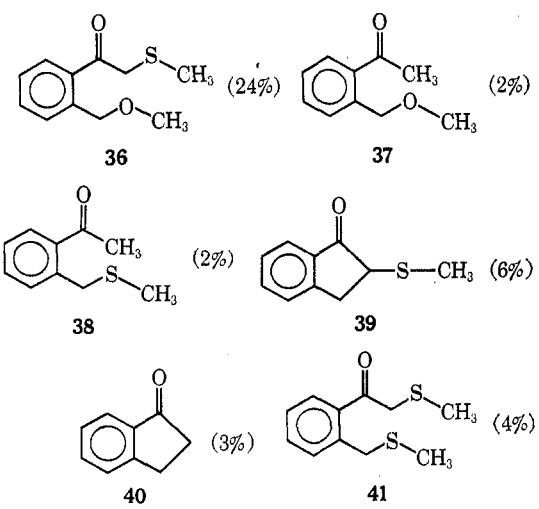
(20) J. R. Shelton and C. W. Uzelmeir, *J. Amer. Chem. Soc.*, **88**, 5222 (1966).

(21) By analogy to 2-acetonaphthalene: G. S. Hammond and P. A. Leermakers, *ibid.*, **84**, 207 (1962).

Irradiation of **35**, which is both a phenacyl and a benzylsulfonium salt, in methanol for 4.5 hr (84% reaction) led to products readily explained in terms of the



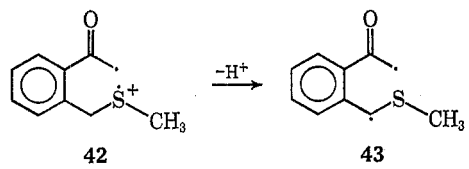
35



36 (24%) **37** (2%) **38** (2%) **39** (6%) **40** (3%) **41** (4%)

above results. Solvolytic displacement at the benzylic carbon–sulfur bond leads to the major product **36**; product **37** is formed from **36** by a secondary homolytic

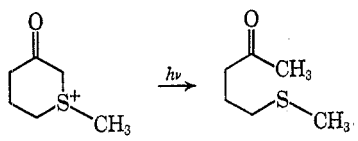
cleavage.[22] Homolytic cleavage, as observed for phenacyl sulfonium salts, leads to **42** which is converted to **38** by hydrogen atom abstraction and to **39** by loss of H^+ to **43** which ring closes. Indanone (**40**) is formed



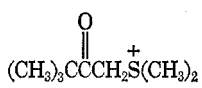
42 **43**

from **39** in an analogous fashion to the secondary photolysis of **36** to **37**. Several reasonable pathways explain the formation of **41**.

Irradiation of β-ketosulfonium salt **44** in methanol for 20 hr gave **45** in low yield (2%) as the sole nonpolymeric product. Tetrafluoroborate salt **46** gave no



44 **45**



46

monomeric products on irradiation in methanol for 38 hr (43% decomposition).

Experimental Section[23]

Photochemical Studies.—Photolyses were conducted in the Rayonet "Photochemical Reactor."[24] The materials photolyzed are listed in Table III. The irradiations were carried out in a Pyrex vessel with a 3000-Å source (source a) or in a quartz vessel with a 2537-Å source (source b). The reaction vessels were equipped with a magnetic stirring bar, a gas dispersion tube, and a reflux condenser. Tubes sealed with "no air" stoppers served as convenient reaction vessels for small quantities of material. Photochemical solvents were dried and distilled directly into the photolysis vessel under N_2. Methanol (Baker "Reagent") was dried by reaction with Mg turnings; *t*-butyl alcohol (Eastman Organic Chemicals) was distilled from $LiAlH_4$; acetonitrile (Eastman Organic Chemicals, "Spectrograde") was distilled from P_2O_5. The solutions were degassed prior to irradiation with a moderate stream of N_2 for at least 2 hr.

All photolyses were monitored by analysis (tlc or glpc) of samples withdrawn at convenient intervals of time. For photolyses monitored by glpc, a known amount of hydrocarbon standard[25] was added before irradiation.

TABLE III
PHOTOCHEMICAL STUDIES

Compound irradiated (wt, g)	Solvent (vol, ml)	Source	Time, hr	Amount of compound recovered
$PhCOCH_2\overset{+}{S}(CH_3)_2Br^-$ (1.222)	CH_3OH (450)	a	7.5	0
$PhCOCH_2Br$ (0.483)	CH_3OH (300)	a	3	<10
1 (0.515)	CH_3OH (350)	a	6.2	0
1 (0.186)	*t*-butyl alcohol (900)	a	3	0
2 (0.375)	CH_3CN (300)	a	5	0
5 (1.35)	CH_3OH (450)	a	12.7	0
7 (0.803)	CH_3OH (300)	a	8	0
$PhCOCH_2OCH_3$ (0.222)	CH_3OH (75)	a	2	0
9 (0.125)	CH_3OH (300)	a	20	0
11 (0.750)	CH_3OH (300)	a	4.5	0
11 (0.554)	H_2O (300)	a	2	0
$PhCOCH_2OH$ (0.080)	H_2O (25)	a	2	87
13 (0.612)	CH_3OH (500)	b	3.5	0
13 (0.187)	*t*-butyl alcohol (600)	b	2.3	0
13 (0.622)	CH_3CN (500)	b	24	0
$PhCH_2OCH_3$ (0.196)	CH_3OH (60)	b	4	58
22 (1.12)	CH_3OH (500)	b	1.2	0
24 (0.583)	CH_3OH (500)	b	0.25	0
29 (1.058)	CH_3OH (450)	b	2.5	12
32 (1.97)	CH_3OH (500)	b	3	34
32 (0.715)	CH_3CN (300)	a	4	0
33 (0.010)	CH_3OH (1)	b	0.75	20
$PhCH_2SCH_3$ (0.157)	CH_3OH (60)	b	2	20
35 (1.93)	CH_3OH (450)	a	4.5	16
44 (0.475)	CH_3OH (500)	b	20	0
46 (1.060)	CH_3OH (450)	b	38	57

After irradiation of the salts, the solution was concentrated to *ca.* half its original volume, an equal volume of $CHCl_3$ or ether was added and the solution was concentrated. If a solid separated, the solution was cooled and the solid was recovered by filtration. The process was repeated until no more solid was recovered. In all cases in which pure material was obtained the recovered solid was unreacted starting material. If a weighed quantity of standard had not been added previously, it was added at this point. The solution was washed with H_2O, dilute $NaHCO_3$, saturated NaCl, and dried. The residue was analyzed by glpc. All products listed were identified by collection from glpc and comparison with an authentic sample. Yields were determined

(22) Acyclic β-keto sulfides have been shown to cleave in this fashion: J. R. Collier and J. Hill, *Chem. Commun.*, 700 (1968), and references cited therein.

(23) Infrared spectra were taken on a Perkin-Elmer Model 237 or 337 spectrophotometer. Ultraviolet spectra were taken on a Cary Model 14 spectrophotometer. The nmr spectra were taken on a Varian A-60 or T-60 spectrometer and are reported in parts per million downfield from TMS at 0.00. Mass spectra were run on a Perkin-Elmer Hitachi RMU-6D spectrometer with an ionizing potential of 80 eV. Melting points were taken on a Thomas–Hoover "Uni Melt" and are corrected. Boiling points are uncorrected. Gas chromatographic analyses and isolations were performed on an F & M Model 810 research chromatograph (thermal conductivity detector) utilizing 4 ft × 1/4 in. columns packed with either 15% SE-30 on neutral 60–80 mesh Chromosorb P or 15% Carbowax 20M on the same support. In general reactions were conducted under an atmosphere of N_2 and $MgSO_4$ was used to dry organic extracts. Microanalyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, or Galbraith Laboratories, Knoxville, Tenn.

(24) Model RPR100 (Southern New England Ultraviolet Co., Middletown, Conn.): reactor barrel, 10 in. (diameter) by 15 in. (depth) with 16 lamps in a circular bank.

(25) *n*-Dodecane (Matheson Co.), *n*-tetradecane and *n*-octadecane (Columbia Organic Chemicals Co.), or *n*-heptadecane (Aldrich Chemical Co.).

from calibrated glpc curves. Table III lists the pertinent data that was not adequately described in Tables I or II or elsewhere in the discussion section. The products listed in Tables I and II were not formed when the salts were dissolved in methanol and were allowed to stand in the absence of light.

Preparation of Tetrafluoroborate Salts. Method A.—A solution of 10–25 mmol of $AgBF_4$ in 25–30 ml of ethanol was added dropwise with stirring to a solution containing an equivalent amount of sulfonium bromide in 300–350 ml of ethanol and the mixture was stirred for 1 hr. The mixture was filtered, the solid was washed with hot methanol, and the filtrate and washings were combined and concentrated to a residue that was recrystallized from ethanol.

Method B.—The preparation of sulfonium tetrafluoroborates from the corresponding sulfides involved preparation of a solution of 5–20 g of trimethyloxonium tetrafluoroborate[26] in 20–100 ml of nitromethane in a flask sealed with a "no air" stopper. The required sulfide, neat or in a small quantity of solvent, was added to the well-stirred solution. In some cases a vigorous exothermic reaction ensued which was moderated by occasional immersion in an ice bath. The solution was stirred 30–60 min at room temperature and was allowed to stand in the refrigerator overnight. If crystallization occurred, the product was claimed by filtration; if it did not, the solvent was removed and a small quantity of ether was added to the residue, which then usually crystallized. The crude salt was recrystallized from an appropriate solvent.

Dimethylphenacylsulfonium Tetrafluoroborate (1).—Salt 1 was prepared in 57% yield from dimethylphenacylsulfonium bromide[27] by method A: mp 168.5–170°; uv max (CH_3OH) 249 nm (ε 12,700) and 285 (2240); nmr (acetone-d_6) δ 3.18 (s, 6), 5.55 (s, 2), 7.55–7.87 (m, 3) and 8.01–8.21 (m, 2).

Anal. Calcd for $C_{10}H_{13}BF_4OS$: C, 44.79; H, 4.89; S, 11.96. Found: C, 44.85; H, 4.99; S, 12.18.

1,2-Dibenzoylethane (3) was prepared from benzene and succinoylchloride:[28] mp 144–146° (lit.[28] mp 144–145°).

3-(Methylthio)propiophenone (4) was prepared in 74% yield from 3-chloropropiophenone and $NaSCH_3$: mp 35–37° (lit.[29] mp 35–36°).

1-Oxo-1,2,3,4-tetrahydronaphthalenyldimethylsulfonium Tetrafluoroborate (5).—2-Bromo-1-tetralone[30] (45.5 g, 0.202 mol) was added to a cold (0°) solution of 0.244 mol of $NaSCH_3$ in 150 ml of absolute ethanol. The solution was stirred overnight at room temperature, concentrated, and poured into water. The mixture was extracted with ether, and the combined extracts were washed with water, saturated NaCl solution, and dried. The crude residue was distilled to give 6.8 g (23%) of 1-tetralone[31] (6) and 17.8 g (46%) of 2-methylthio-1-tetralone as a pale yellow oil: bp 88–90° (0.09 mm); ir (CCl_4) 1682 cm^{-1}; uv max (CH_3OH) 248 nm (ε 10,000), 279 (2420) and 327 (630); nmr (CCl_4) δ 2.05 (s, 3), 2.05–3.45 (m, 5), 6.88–7.55 (m, 3), and 7.77–8.12 (m, 1); mass spectrum *m/e* (rel intensity) 192 (19), 146 (100), 145 (42), 118 (33), 115 (39) and 90 (30).

Anal. Calcd for $C_{11}H_{12}OS$: C, 68.71; H, 6.29; S, 16.68. Found: C, 68.46; H, 6.29; S, 16.67.

2-Methylthio-1-tetralone was converted in 71% yield to 5 by method B: mp 114–116°; ir (KBr) 1682 and 1125–1035 cm^{-1}; uv max (CH_3OH) 254 nm (ε 12,500) and 303 (2610); nmr (dimethyl sulfoxide-d_6) δ 2.33–3.44 (m, 4), 2.83 (s, 3) 2.95 (s, 3), 5.10 (d of d, 1, J = 12 and 5.5 Hz), and 7.13–7.97 (m, 4).

Anal. Calcd for $C_{12}H_{15}BF_4OS$: C, 49.00; H, 5.14; S, 10.90. Found: C, 49.14; H, 5.17; S, 11.18.

***m*-Methoxyphenacyldimethylsulfonium Tetrafluoroborate** (7).—Solid 2-bromo-*m*-methoxyacetophenone (25.0 g, 0.109 mol) (Aldrich Chemical Co.) was added to a cold (0°) solution of $NaSCH_3$ in 150 ml of ethanol and the solution was stirred for 5 hr at room temperature. Water was added and the solution was concentrated and poured into ether. The aqueous layer was removed and extracted with ether. The combined ether extracts were washed with water, saturated NaCl solution, and dried. The crude residue was distilled to give 2.33 g (14%) of *m*-methoxyacetophenone (8), bp 57–59° (0.08 mm) [lit.[32] bp 125° (14 mm)], and 14.1 g (66%) of 2-methylthio-*m*-methoxyacetophenone: bp 93–95° (0.08 mm); ir (CCl_4) 1677 cm^{-1}; uv max (CH_3OH) 250 nm (ε 6580), 307 (2450) and 345 (495); nmr (CCl_4) δ 2.00 (s, 3) 3.57 (s, 2), 3.67 (s, 3), and 6.77–7.50 (m, 4); mass spectrum *m/e* (rel intensity) 196 (18), 150 (15), 135 (100), 107 (33), 94 (18), 92 (21), 79 (11), 77 (32), 64 (18), 63 (15), 61 (17), 50 (10), 47 (14), 46 (11), 45 (20), and 43 (16).

Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.19; H, 6.16; S, 16.34. Found: C, 61.31; H, 6.31; S, 16.49.

2-Methylthio-*m*-methoxyacetophenone was converted in 79% yield to 7 by method B: mp 163–165°; ir (KBr) 1678 cm^{-1}; uv max (CH_3OH) 220 nm (ε 19,500), 256 (9090), and 312 (3510); nmr (dimethyl sulfoxide-d_6) δ 2.95 (s, 6) 3.82 (s, 3), 5.37 (s, 2) and 7.13–7.67 (m, 4).

Anal. Calcd for $C_{11}H_{15}BF_4O_2S$: C, 44.31; H, 5.07; S, 10.76. Found: C, 44.51; H, 5.11; S, 10.95.

(2-Naphthoyl)methyldimethylsulfonium Tetrafluoroborate (9).—A solution of 8.6 g (0.034 mol) of 2-bromoacetonaphthalene (Aldrich Chemical Co.) in 50 ml of acetone containing 2 ml of water was cooled to 0° and treated with 5 ml of dimethyl sulfide. The solution was stirred 10 min at 0°, warmed to room temperature, and stirred an additional hour. The white precipitate was filtered and recrystallized from ethanol to give 5.10 g (48%) of the sulfonium bromide: mp 133–135° dec; ir (KBr) 1678 cm^{-1}. The bromide was converted in 36% yield to the tetrafluoroborate by method A; mp 157.5–159.5°; ir (KBr) 1672 and 1125–1035 cm^{-1}; uv max (CH_3OH) 233 nm (ε 31,200), 244 (32,100), 253 (36,400), 287 (11,620), 296 (11,860), 317 (4230) (sh), and 332 (3090); nmr (dimethyl sulfoxide-d_6) δ 3.03 (s, 6), 5.53 (s, 2), 7.47–8.27 (m, 6) and 8.73 (s, 1).

Anal. Calcd for $C_{14}H_{15}BF_4OS$: C, 52.85; H, 4.75; S, 10.08. Found: C, 52.65; H, 4.83; S, 10.33.

Di-*n*-butylphenacylsulfonium Tetrafluoroborate (11).—Salt 11 was prepared from phenacyl bromide and di-*n*-butyl sulfide followed by conversion to the tetrafluoroborate salt by method A using the overall procedure described for the preparation of 1. The bromide salt was obtained in 31% yield: mp 90–92° (lit.[33] mp 88–89°). The tetrafluoroborate salt 11 was obtained in 80% yield: mp 81.5–83°; ir (KBr) 1688 and 1120–1020 cm^{-1}; uv max (CH_3OH) 247 nm (ε 11,400) and 288 (4300); nmr (dimethyl sulfoxide-d_6) δ 0.73–2.13 (m, 14), 3.17–3.60 (m, 4), 5.40 (s, 2), and 7.50–8.23 (m, 5).

Anal. Calcd for $C_{16}H_{25}BF_4OS$: C, 54.55; H, 7.15; S, 9.10. Found: C, 54.34; H, 7.08; S, 9.36.

Benzyldimethylsulfonium tetrafluoroborate (13) was prepared in 71% yield from benzyl methyl sulfide by method B: mp 101–103° (ethanol); ir (KBr) 1125–1030 cm^{-1}; uv max (CH_3OH) 254 nm (ε 221), 260 (302), 265 (314), and 271 (232); nmr (acetone-d_6) δ 2.90 (s, 6), 4.73 (s, 2) and 7.30–7.70 (broad s, 5).

Anal. Calcd for $C_9H_{13}BF_4S$: C, 45.02; H, 5.46; S, 13.36. Found: C, 45.12; H, 5.47; S, 13.52.

1,2-Diphenyl-1-methoxyethane (17).—1,2-Diphenylethanol (5.00 g, 0.252 mol; Eastman Organic Chemicals) was added all at once to a suspension of 1.78 g of a 61% mineral oil dispersion of NaH (0.0453 mol) in 50 ml of ether. The mixture was stirred at reflux for 4 hr, cooled to 0°, and excess CH_3I (5 ml) was added. The suspension was stirred at room temperature overnight and treated with water, and the layers were separated. The aqueous layer was extracted with ether and the combined ether extracts were washed with water and saturated NaCl solution and were dried. The ether was removed under reduced pressure, and the mixture partially crystallized when a few milliliters of hexane were added. The crystalline material was filtered from the solution and recrystallized from hexane giving 1.40 g of starting material. The filtrate was passed over 150 g of alumina (Woelm, activity I). The desired product (17) was eluted with hexane, following a forerun of mineral oil, and was short-path distilled giving 1.84 g (45%) of 17. The spectra data of this product were identical with that previously reported.[34]

***meso*-1,2-Dimethoxy-1,2-diphenylethane** (18) was prepared in 78% yield from *meso*-1,2-diphenyl-1,2-ethanediol[35] by the same procedure used to prepare 17 except that tetrahydrofuran was used in place of ether as the solvent: mp 141–143° (lit.[36] mp 140–142°).

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Benzyl *t*-butyl ether (19) was prepared in 59% yield as previously described:[37] bp 85–86° (9 mm) [lit.[37] bp 206–208° and 38–41° (0.5 mm)[38]].

N-Benzylacetamide (20) was obtained in 59% yield from benzylamine and acetyl chloride: mp 61–63° (lit.[39] mp 60–61°).

Dibenzylmethylsulfonium tetrafluoroborate (22) was prepared in 56% yield from dibenzyl sulfide (Eastman Organic Chemicals) by method B: mp 115–116.5° (from acetone–ether); ir (KBr) 1125–1140 cm^{-1}; uv max (CH_3OH) 253.5 nm (ϵ 538), 260 (655), 265 (631), and 271 (430); nmr (acetone-d_6) δ 2.82 (s, 3), 4.87 (AB pattern, 4, J = 18 Hz) and 7.18–7.72 (m, 10).

Anal. Calcd for $C_{15}H_{17}BF_4S$: C, 56.98; H, 5.42; S, 10.14. Found: C, 56.99; H, 5.35; S, 10.19.

***m*-Methoxybenzyldimethylsulfonium Tetrafluoroborate** (24).—*m*-Methoxybenzyl bromide[40] was converted in 79% yield to *m*-methoxybenzyl methyl sulfide by the same procedure described for the preparation of 2-methylthio-1-tetralone: bp 62–63° (0.08 mm); ir (CCl_4) 1268 cm^{-1}; uv max (CH_3OH) 275 nm (ϵ 2230) and 282.5 (2030); nmr (CCl_4) δ 1.85 (s, 3), 3.50 (s, 2), 3.62 (s, 3), and 6.46–7.32 (m, 4); mass spectrum *m/e* (rel intensity) 168 (17), 122 (21), 121 (100), 91 (53), 78 (57), 77 (41), 65 (26), 63 (23), 52 (24), 51 (37), and 45 (27).

Anal. Calcd for $C_9H_{12}OS$: C, 64.24; H, 7.19; S, 19.06. Found: C, 64.43; H, 7.17, S, 19.30.

m-Methoxybenzyl methyl sulfide was converted in 53% yield to **24** by method B: mp 59–61° (from ethanol); ir (KBr) 1175–950 cm^{-1}; uv max (CH_3OH) 278 nm (ϵ 3110) and 283 (3020); nmr (acetone-d_6) δ 2.97 (s, 6), 3.82 (s, 3), 4.72 (s, 2), and 6.85–7.53 (m, 4).

Anal. Calcd for $C_{10}H_{15}BF_4OS$: C, 44.46; H, 5.60; S, 11.87. Found: C, 44.30; H, 5.46; S, 12.06.

***m*-Methoxybenzyl methyl ether** (25) was prepared in 55% yield from *m*-methoxybenzyl bromide[40] and $NaSCH_3$ in methanol: bp 50–52° (0.38 mm) [lit.[41] bp 52–53° (0.3 mm)].

1,2-Bis(*m*-methoxyphenyl)ethane (27) was prepared in 60% yield as previously reported:[42] bp 142–145° (0.3 mm) [lit.[43] bp 203–205° (10 mm)].

2-Methylthio-*m*-methoxyethylbenzene (28).—A mixture of 9.03 g (0.0461 mol) of 2-methylthio-*m*-methoxyacetophenone, 65 ml of diethylene glycol, 8 ml of hydrazine hydrate (99–100%), and 2.50 g of KOH was heated slowly to 110–120°, maintained at that temperature for 1 hr, and then heated at 170–190° for 1 hr. The solution was cooled, treated with water, and extracted with several portions of ether. The combined ether solutions were washed with saturated NaCl solution and dried. The crude mixture was distilled to give 2.6 g of a low-boiling [bp 28° (0.02 mm)] forerun consisting of a mixture and the desired product **28** (1.01 g) in 12% yield: bp 64–65° (0.02 mm); ir (CCl_4) 2915, 1601, 1490, 1262, 1153, and 1053–1045 cm^{-1}; uv max (CH_3OH) 273 nm (ϵ 1870) and 278 (1660); nmr (CCl_4) δ 2.00 (s, 3), 2.37–2.90 (m, 4), 3.67 (s, 3), and 6.43–7.20 (m, 4); mass spectrum *m/e* (rel intensity) 182 (40), 134 (37), 121 (44), 91 (31), and 61 (100).

Anal. Calcd for $C_{10}H_{14}OS$: C, 65.89; H, 7.74; S, 17.59. Found: C, 66.06; H, 7.69; S, 17.80.

2-Methyl-1,3-dihydroisothianaphthenium tetrafluoroborate (29) was prepared in 68% yield from 1,3-dihydroisothionaphthene:[44] mp 146.5–148° (from ethanol); ir (KBr) 1142–1033 cm^{-1}; uv max (CH_3OH) 252 nm (ϵ 164), 257.5 (228), 263.5 (298), and 271 (271); nmr (acetone-d_6) δ 2.92 (s, 3), 4.95 (AB pattern, 4, J = 16.5 Hz) and 7.25–7.75 (m, 4).

Anal. Calcd for $C_9H_{11}BF_4S$: C, 45.40; H, 4.66; S, 13.47. Found: C, 45.48; H, 4.82; S, 13.68.

***o*-(Methylthio)methylbenzyl Methyl Ether** (30).—*o*-(Methylthio)methylbenzoic acid (6.0 g, 0.033 mol) was esterified with ethanol and H_2SO_4 by standard procedures to give in 89% yield ethyl *o*-(methylthio)methylbenzoate: bp 82.5–85° (0.13 mm); ir (CCl_4) 1725 cm^{-1} uv max (C_2H_5OH) 227 nm (ϵ 10,250) and 282 (1350); nmr (CCl_4) δ 1.28 (t, 3, J = 7 Hz) 1.83 (s, 3) 4.01 (s, 2) 4.25 (q, 2, J = 7 Hz), 7.00–7.33 (m, 3) and 7.70–7.95 (m, 1); mass spectrum *m/e* (rel intensity) 210 (39), 165 (34), 164 (56), 149 (100), 135 (61), 133 (67), 118 (23), 90 (19), and 77 (20).

Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.71; S, 15.25. Found: C, 62.80; H, 6.68; S, 15.10.

To 720 mg (19.0 mmol) of $LiAlH_4$ in 10 ml of ether at 0° was added dropwise a solution of 3.77 g (18.0 mmol) of ethyl *o*-(methylthio)methylbenzoate in 10 ml of ether. The mixture was stirred for 3 hr at room temperature and was then treated successfully with 1 ml of ethyl acetate, 2 ml of water, and 10 ml of 5% HCl. The aqueous layer was extracted twice with ether and the combined ether layers were washed with saturated solutions of $NaHCO_3$ and NaCl and then dried. The crude product was chromatographed on 25 g of silicic acid with $CHCl_3$. The first fractions contained some unreacted ester. The later fractions were combined and distilled to give 1.73 g (57%) of *o*-(methylthio)methylbenzyl alcohol: bp 84–87° (0.1 mm); ir (CCl_4) 3605, 3460 (broad), and 1010 cm^{-1}; uv max (CH_3OH) 240 nm (ϵ 953) (sh), 261 (479), 267 (331) (sh), 272 (226) (sh) and 290 (16); nmr ($CDCl_3$) δ 2.80 (s, 3), 3.57 (s, 2), 4.25–4.67 (broad s, 1; disappears on addition of D_2O), 4.56 (s, 2) and 7.00–7.35 (m, 4); mass spectrum *m/e* (rel intensity) 168 (5), 167 (4), 135 (24), 121 (18), 120 (100), 119 (47), 91 (41), and 77 (26).

Anal. Calcd for $C_9H_{12}OS$: C, 64.24; H, 7.19; S, 19.06. Found: C, 64.06; H, 7.08; m, 19.30.

To a suspension of 850 mg of 61% mineral oil dispersion of NaH (21.6 mmol) in 50 ml of ether was added 1.26 g (7.49 mmol) of *o*-(methylthio)methylbenzyl alcohol. The mixture was stirred for 6 hr and 0.55 ml of CH_3I was added to the thick paste. Stirring was continued overnight. Ethanol and then water were added cautiously to the mixture. The aqueous layer was extracted with ether and the combined ether layers were dried. The crude product was chromatographed over 10 g of silicic acid. The mineral oil was eluted with hexane, the desired product **30** with 10% ether–hexane, and starting material with 1% methanol–ether. Fractions containing **30** were short-path distilled to give 81 mg (6%) of pure **30**: ir (CCl_4) 1102 cm^{-1}; uv max (CH_3OH) 242 nm (ϵ 947) (sh), 262 (510) (sh), 274 (226) (sh) and 289 (33); nmr (CCl_4) δ 1.73 (s, 3), 3.13 (s, 3), 3.17 (s, 2), 4.33 (s, 2), and 7.00 (m, 4); mass spectrum *m/e* (rel intensity) 135 (42), 134 (100), 119 (40), 105 (28), 104 (17), 91 (27), and 77 (9).

Anal. Calcd for $C_{10}H_{14}OS$: C, 65.89; H, 7.74; S, 17.59. Found: C, 66.04; H, 7.84; S, 17.74.

***o*-Methylbenzyl methyl ether** (31) was prepared in 58% yield as previously described: bp 86–87° (20 mm) [lit.[45] bp 97° (32 mm)]; ir (CCl_4) 1098 cm^{-1}; nmr (neat) 2.14 (s, 3), 3.17 (s, 3), 4.21 (s, 2), and 6.90–7.37 (m, 4); mass spectrum *m/e* (rel intensity) 136 (12), 135 (10), 121 (22), 105 (48), 104 (100), 91 (16), and 77 (15).

2-Methylisothiochromanium tetrafluoroborate (32) was prepared in 66% yield from isothiochromate[46] by method B: mp 94–96° (from ethanol); ir (KBr) 1125–1030 cm^{-1}; uv max (CH_3OH) 262 nm (ϵ 245), 265 (240) (sh), and 271 (192); nmr (dimethyl sulfoxide-d_6) δ 2.53 (s, 3), 2.70–3.93 (m, 4), 4.47 (AB pattern, 2, J = 15 Hz), and 7.40 (s, 4).

Anal. Calcd for $C_{10}H_{13}BF_4S$: C, 47.64; H, 5.20; S, 12.72. Found: C, 47.82; H, 5.35; S, 12.82.

***o*-(2-Methylthio)ethylbenzyl Methyl Ether** (33).—A solution of 2.60 g (0.0103 mol) of **32** and 8.0 g (0.059 mol) of $NaOAc \cdot 3H_2O$ in 50 ml of water was refluxed for 2.5 days. The pH of the solution was maintained between 6–7 by the addition of dilute KOH solution as necessary. An oil gradually separated. The mixture was treated with methanol and dilute KOH solution, refluxed for 1 hr, cooled, and extracted with ether. The combined ether extracts were washed with water and saturated NaCl solution and dried. The crude residue was chromatographed over 20 g of alumina (Woelm, activity I). Elution with 10% ether–hexane gave 63 mg of by-products. Elution with 1% methanol–ether gave 166 mg of *o*-(2-methylthio)ethylbenzyl alcohol: ir (CCl_4) 3610, 3510 (broad) and 1003 cm^{-1}. The alcohol (126 mg, 0.69 mol) was added to a suspension of 163 mg of a 61% mineral oil dispersion of NaH (4.1 mmol) in 10 ml of tetrahydrofuran. The mixture was refluxed for 1 hr, cooled, treated with 50 μl of CH_3I, refluxed for 1 hr and cooled. Water was added cautiously and

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the aqueous layer was extracted with ether. The combined ether layers were washed with saturated NaCl solution and dried. The major component (**33**) was collected by glpc: ir (CCl_4) 1103 cm^{-1}; uv max (CH_3OH) 260 nm (ϵ 320), 266 (306) (sh), and 271 (246); nmr (CCl_4) δ 2.00 (s, 3), 2.37–3.03 (m, 4), 3.23 (s, 3), 4.33 (s, 2), and 7.07 (s, 4); mass spectrum *m/e* (rel intensity) 196 (44), 149 (15), 148 (20), 147 (25), 121 (39), 117 (97), 116 (100), 115 (31), 105 (48), 104 (18), 91 (27), 77 (15), 61 (50), and 45 (18).

Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.21; S, 16.34. Found: C, 67.35; H, 8.14; S, 16.24.

o-Ethylbenzyl Methyl Ether (34).—A mixture of 2.34 g (0.014 mol) of **37**, 3 ml of hydrazine hydrate (99–100%), 1.0 g of KOH, and 50 ml of diethylene glycol were heated at 110–120° for 1 hr and then warmed to 180–190° and maintained at that temperature for 2 hr. The distillate was collected in a Dean–Stark water separator. The cooled mixture was poured into water and extracted with ether. The combined ether layers were washed with saturated NaCl solution and dried. The crude product was distilled to give 1.35 g (63%) of **34**: bp 24–25° (0.03 mm); ir (CCl_4) 1098 cm^{-1}; uv max (CH_3OH) 263 nm (ϵ 238) and 271 (204); nmr (CCl_4) δ 1.13 (t, 3, J = 7.5 Hz), 2.60 (q, 2, J = 7.5 Hz), 3.20 (s, 3), 4.33 (s, 2), and 6.83–7.37 (m, 4); mass spectrum *m/e* (rel intensity) 150 (1), 149 (2), 121 (16), 119 (23), 118 (100), 117 (43), 91 (18), and 77 (12).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.42. Found: C, 80.16; H, 9.62.

2-Methyl-4-oxoisothiochromanium tetrafluoroborate (35) was prepared in 71% yield from isothiochroman-4-one[47] by method B: mp 158.5–59.5° (from 9:1 ethanol–methanol); ir (KBr) 1690 and 1025–1125 cm^{-1}; uv max (CH_3OH) 254 nm (ϵ 6760), 294 (1950), and 315 (1270) (sh); nmr (dimethyl sulfoxide-d_6) δ 2.83 (s, 3), 4.48 (AB pattern, 2, J = 15 Hz), 4.85 (AB pattern, 2, J = 15 Hz) and 7.37–8.12 (m, 4).

Anal. Calcd for $C_{10}H_{11}BF_4OS$: C, 45.14; H, 4.17; S, 12.05. Found: C, 45.10; H, 4.08; S, 12.26.

o-Methoxymethyl-2-methylthioacetophenone (36).—Bromine (1.89 g, 0.0118 mol) in 10 ml of CS_2 was added dropwise over a 30-min period to a cold (−5°) solution of 1.22 g (0.0744 mol) of **37** in 10 ml of CS_2. The solution was stirred for 10 min, and water and ether were added. The organic layer was removed and washed with water, dilute $NaHSO_3$ solution, dilute $NaHCO_3$ solution, and saturated NaCl solution. The solvent was removed at 0° and the residue was dissolved in 20 ml of absolute ethanol. The solution was added all at once to a cold (0°) solution of 0.012 mol of $NaSCH_3$ in 15 ml of ethanol. The solution was warmed to room temperature, stirred for 30 min, and treated with water. The solution was extracted with several portions of ether, and the combined ether extracts were washed several times with water and saturated NaCl solution and dried. The residue was chromatographed over 100 g of silicic acid. The product, eluted with 5% ether in hexane, was short-path distilled to give 793 mg (51%) of **36**: ir (CCl_4) 1671 cm^{-1}; uv max (CH_3OH) 243 nm (ϵ 7780), 278 (2130) and 320 (802) (sh); nmr (CCl_4) δ 2.08 (s, 3), 3.40 (s, 3), 3.58 (s, 2), 4.68 (s, 2), and 7.08–7.82 (m, 4); mass spectrum *m/e* (rel intensity) 210 (5), 119 (32), 105 (14), 103 (12), 91 (60), 90 (14), 89 (15), 77 (26), 65 (15), 63 (13), 61 (12), 51 (18), and 45 (16).

Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.71; S, 15.25. Found: C, 63.00; H, 6.82; S, 15.37.

o-(Methoxy)methylacetophenone (37).—The procedures of Ramsden, *et al.*,[48] and Newman and Booth[49] were adapted to reaction of the Grignard reagent of *o*-chlorobenzyl methyl ether[50] with acetic anhydride to produce **37** in 48% yield: bp 46–47° (0.06 mm); ir (CCl_4) 1685 cm^{-1}; uv max (C_2H_5OH) 242 nm (ϵ 8290) and 284 (1130); nmr (neat) δ 2.43 (s, 3), 3.33 (s, 3), 4.73 (s, 2), and 7.10–7.80 (m, 4); mass spectrum *m/e* (rel intensity) 164 (47), 149 (68), 131 (100), 103 (48), 91 (37), 77 (32), and 43 (44).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.36. Found: C, 72.92; H, 7.43.

o-(Methylthio)methylacetophenone (38).—Authentic **38** was prepared by Dr. R. E. Kohrman in these laboratories.[51]

2-Methylthioindan-1-one (39).—The ethylene ketal of 2-bromoindan-1-one[52] (7.09 g, 0.0276 mol) was added all at once to a solution of 0.052 mol of $NaSCH_3$ in 50 ml of ethanol; the mixture was stirred overnight at room temperature and was then refluxed for 1 hr. Water (20 ml) and concentrated HCl (10 ml) were added, and the solution was refluxed for 3 hr, cooled, and poured into ether. The ether layer was washed several times with water, dilute $NaHCO_3$ solution, and saturated NaCl solution and was dried. Glpc analysis showed the presence of 1-indanone and two major components that were collected from SE-30. The lower-boiling component was not investigated. The other component, **39**, was purified by glpc: ir (CCl_4) 1717 cm^{-1}; uv max ((CH_3OH) 248 nm (ϵ 12,500), 290 (2480) and 345 (367); nmr (CCl_4) δ 2.16 (s, 3), 2.33–3.77 (m, 3), and 7.10–7.77 (m, 4); mass spectrum *m/e* (rel intensity) 178 (15), 135 (23), 134 (15), 133 (12), 132 (100), 131 (45), 103 (31), 102 (22), 91 (22), 89 (12), 77 (35), 76 (16), 75 (13), 74 (12), 63 (15), 51 (27), 50 (20), and 45 (15).

Anal. Calcd for $C_{10}H_{10}OS$: C, 67.38; H, 5.65. Found: C, 67.10; H, 5.87.

o-(Methylthio)methyl-2-methylthioacetophenone (41).—Excess methanethiol (*ca.* 25 g) was condensed by means of a Dry Ice condenser in a flask containing 1.0 g (0.043 g-atom) of Na. One drop of methanol was added and the contents of the flask were stirred at 0° until no further reaction was evident (*ca.* 1 hr). Compound **35** (0.672 g, 2.52 mmol) was added to the gray suspension and the mixture was stirred for 30 min at 0°, refluxed for 30 min, and cooled to 0°. Cold ether (25 ml) was added, the mixture was allowed to warm to room temperature, and it was stirred overnight. Water (10 ml) was added and the ether solution was washed several times with water and saturated NaCl solution and dried. Compound **41** was collected from the crude product mixture by glpc and was short-path distilled: ir (CCl_4) 1680 cm^{-1}; uv max (CH_3OH) 241 nm (ϵ 7890), 275 (1900) and 320 (586) (sh); nmr (CCl_4) δ 1.93 (s, 3), 2.13 (s, 3), 3.57 (s, 2); 3.88 (s, 2), and 7.00–7.83 (m, 4); mass spectrum *m/e* (rel intensity) 226 (7), 179 (12), 166 (12), 165 (100), 131 (19), 119 (15), 118 (16), 91 (11), 90 (13), and 89 (10).

Anal. Calcd for $C_{11}H_{14}OS_2$: C, 58.37; H, 6.23; S, 28.33. Found: C, 58.19; H, 6.12; S, 28.16.

1-Methyl-3-oxotetrahydrothiopyranium tetrafluoroborate (44) was prepared in 36% yield from tetrahydrothiopyran-3-one[53] by method B: mp 153.5–155.5° (from acetone–ether); ir (KBr) 1730 and 1125–1025 cm^{-1}; uv max (CH_3OH) 261 nm (31.6); nmr (acetone-d_6) δ 2.50–2.90 (m, 4), 3.11 (s, 3), 3.50–4.10 (m, 2), and 4.20 (AB pattern, 2, J = 15 Hz).

Anal. Calcd for $C_6H_{11}BF_4OS$: C, 33.05; H, 5.09; S, 14.71. Found: C, 32.81; H, 4.98; S, 14.96.

2-Thiaheptan-6-one (45) was prepared in 67% yield as previously described: bp 83–84° (8 mm) [lit.[54] bp 90–92° (18 mm)].

(2-Oxo-3,3-dimethyl)butyldimethylsulfonium tetrafluoroborate (46) was prepared in 81% yield from 5,5-dimethyl-2-thiahexan-4-one[55] by method B: mp 107.5–109° (from ethanol); ir (KBr) 1705 and 1125–1010 cm^{-1}; uv max (CH_3OH) 278 nm (49.4); nmr (dimethyl sulfoxide-d_6) δ 1.13 (s, 9), 2.83 (s, 6), and 4.92 (s, 2).

Anal. Calcd for $C_8H_{17}BF_4OS$: C, 38.72; H, 6.94; S, 12.93. Found: C, 38.59; H, 6.84; S, 13.15.

Registry No.—**1**, 24806-57-3; **5**, 24806-58-4; **7**, 24806-59-5; **9**, 24806-60-8; **11**, 24806-61-9; **13** 24806-62-0; **22**, 21529-86-2; **24**, 24806-64-2; **28**, 24807-41-8; **29**, 24806-65-3; **30**, 24807-42-9; **31**, 15018-12-9; **32**, 24806-66-4; **33**, 24807-44-1; **34**, 24807-45-2; **35**, 24806-67-5; **36**, 24807-46-3; **37**, 24807-47-4; **39**, 24807-48-5; **41**, 24807-49-6; **44**, 24806-68-6; **46**, 24806-69-7; 2-methylthio-1-tetralone, 24807-50-9; 2-methylthio-*m*-methoxyacetophenone, 24807-51-0; *m*-methoxybenzyl methyl sulfide, 24807-52-1; ethyl *o*-(methylthio)methylbenzoate, 24807-53-2; *o*-(methylthio)methylbenzyl alcohol, 24807-54-3.

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