methanol (300 ml) gave 1.10 g (0.00576 mole, 36%) of yellow crystals, mp ~260° dec.

Anal. Calcd for $C_{10}H_9NOS$: C, 62.78; H, 4.75; N, 7.32; S, 16.76. Found: C, 62.59; H, 5.10; N, 7.22; S, 16.74.

Desulfurization of 1-Methyl-2-mercapto-4(1H)-quinolinone (16) with Raney Nickel Alloy.—Raney nickel alloy (3.0 g) was added in small portions in the course of 5 hr to a stirred, boiling solution of 1-methyl-2-mercapto-4(1H)-quinolinone (500 mg, 0.0026 mole) in a mixture of 10% sodium hydroxide (30 ml) and ethanol (15 ml). Water (50 ml) was added and most of the ethanol removed by concentration of the solution to about half its volume. The aqueous layer was saturated with sodium chloride and extracted five times with dichloromethane while the solid residue was extracted overnight with dichloromethane. The combined extracts were dried over anhydrous sodium sulfate and concentrated to dryness to give 0.34 g of a solid which consisted of two major components by tlc. As with the Raney nickel alloy reduction of compound 9 described above, one component was 1-methyl-4(1H)-quinolinone, while the other unidentified component was shown not to be 1-methyl-5,6,7,8-tetrahydro-4(1H)-quinolinone. The crude product (0.34 g) was purified by chromatography (Florisil and ethyl acetate–methanol 1:1) to give 0.24 g (0.0015 mole, 57%) of 1-methyl-4(1H)-quinolinone, which was identical with an authentic sample[27] as judged by a mixture melting point determination, by comparison of infrared and nmr spectra, and by tlc.

1-Methylisatin-2-anil (19).—A solution of dimethyloxosulfonium 2-(methylamino)benzoylmethylide (450 mg, 0.002 mole) and nitrosobenzene (430 mg, 0.004 mole) in absolute ethanol (40 ml) was refluxed for 1 hr, excess ethanol was removed, and the resulting red oil was dissolved in chloroform and passed through a column of Florisil. Evaporation of the eluate gave a red solid which was crystallized from 100 ml of petroleum ether (bp 60–70°) to give 300 mg (61%) of the anil as dark red needles, mp 129.5–131° (lit.[18] mp 132°).

The anil (500 mg) was hydrolyzed by heating under reflux for 1 hr in 50 ml of 2 *N* hydrochloric acid.[18] Cooling and neutralization of the solution with sodium bicarbonate resulted in the separation of crude 1-methylisatin (140 mg, 41%), which melted at 127–130° after recrystallization from water. The compound was identical with an authentic sample of 1-methylisatin by a mixture melting point determination, by comparison of infrared spectra, and by tlc.

2-Methylamino-α-chloroacetophenone (22).—Dimethyloxosulfonium 2-(methylamino)benzoylmethylide (1.00 g, 0.00444 mole) was stirred in a mixture of 150 ml of saturated sodium chloride solution and 5 ml of 2 *N* hydrochloric acid for 3 hr. The reaction mixture was then extracted overnight with dichloromethane, the extract dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The residue was chromatographed over a large column of silica gel with chloroform. Elution of the first yellow band and evaporation of the chloroform eluate provided 300 mg (37%)[29] of yellow crystalline 2-methylamino-α-chloroacetophenone, mp 81–82.5°. The infrared spectrum showed an N-H band at 3340 cm^{-1} and a C=O band at 1650 cm^{-1}. The nmr spectrum ($DCCl_3$) exhibited a three-proton doublet at 2.90 ppm (J = 5 cps) (NCH_3), a two-proton singlet at 4.59 ppm (CH_2), and a four-proton aromatic multiplet between 6.5 and 7.8 ppm. The N-H signal was not observed.

Anal. Calcd for $C_9H_{10}ClNO$: C, 58.86; H, 5.49; Cl, 19.35; N, 7.63. Found: C, 58.92; H, 5.51; Cl, 19.30; N, 7.58.

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[29] No attempt was made to find optimum conditions for this reaction.

A New Rearrangement of Sulfonium Ylides

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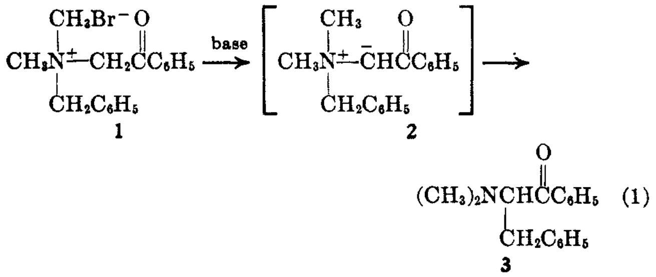
Alkyl- or arylmethylphenacylsulfonium ylides rearrange in boiling water to produce α-(alkyl- or arylthio)-methoxystyrenes rather than alkyl or aryl α-methylphenacyl sulfides as expected by a Stevens rearrangement. Alternate reactions occur under these conditions depending upon the structure of the S-ylides including alkyl migration, elimination, or hydrolysis. S-Ylides stabilized by two carbonyl groups do not react under the above conditions. The newly discovered molecular rearrangement and alternative reactions of S-ylides are discussed in terms of ylide structure and mechanism.

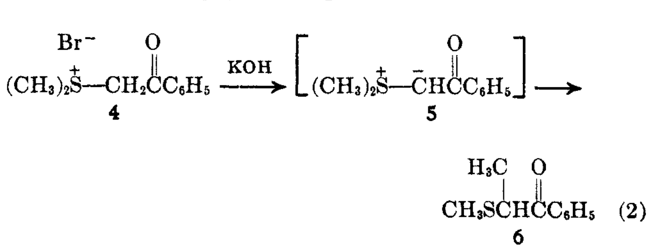
The Stevens rearrangement[1] of ammonium salts (*e.g.*, **1**) has been extensively studied. This electrophilic, intramolecular 1,2 rearrangement presumably involves an intermediate ylide (**2**). An example of the reaction, outlined in eq 1, leads to amine (**3**).



$$CH_3\overset{CH_2Br^-}{\underset{CH_2C_6H_5}{\overset{+}{N}}}-CH_2\overset{O}{\overset{\|}{C}}C_6H_5 \xrightarrow{\text{base}} \left[CH_3\overset{CH_3}{\underset{CH_2C_6H_5}{\overset{+}{N}}}-\overset{-}{C}H\overset{O}{\overset{\|}{C}}C_6H_5\right] \longrightarrow (CH_3)_2N\underset{CH_2C_6H_5}{CH}\overset{O}{\overset{\|}{C}}C_6H_5 \quad (1)$$

1 2 3

Sulfonium salts similarly rearrange, *via* ylides, to sulfides.[2] For example, Bohme and Krause[3] report that dimethylphenacylsulfonium bromide (**4**), refluxed with an equivalent of 1 *N* potassium hydroxide for 5 hr, gave methyl α-methylphenacyl sulfide (**6**) *via* the ylide **5** (eq 2). The product **6** was characterized



$$\overset{Br^-}{(CH_3)_2\overset{+}{S}}-CH_2\overset{O}{\overset{\|}{C}}C_6H_5 \xrightarrow{KOH} \left[(CH_3)_2\overset{+}{S}-\overset{-}{C}H\overset{O}{\overset{\|}{C}}C_6H_5\right] \longrightarrow CH_3S\overset{H_3C}{CH}\overset{O}{\overset{\|}{C}}C_6H_5 \quad (2)$$

4 5 6

by synthesis of authentic material from α-bromopropiophenone and methyl mercaptan and by oxidation to the sulfone.[3]

In the course of a study of S-ylide chemistry this base rearrangement of dimethylphenacylsulfonium bromide was repeated as described by Bohme and Krause. The molecular weight and analysis of the product oil, bp 95° (1 mm), do indeed correspond to $C_{10}H_{12}OS$, but the infrared and nmr spectra (Table I) suggest α-(methylthio)methoxystyrene (**7**) rather than methyl α-methylphenacyl sulfide (**6**).[4] The product

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[1] (a) H. E. Zimmerman, "Molecular Rearrangements," P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 378. (b) M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p 279.

[2] T. Thompson and T. S. Stevens, *J. Chem. Soc.*, **55**, 69 (1932).

[3] H. Bohme and W. Krause, *Chem. Ber.*, **82**, 426 (1949).

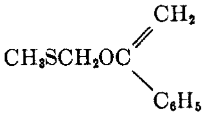
[4] K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1689 (1966).

TABLE I

COMPARISON OF SPECTRA OF **7** AND **6**

7		**6**	
ArH	τ 2.60[a] five protons, multiplet	ArH	τ 2.38 five protons, multiplet
CH_2	τ 5.12 two protons, singlet	CH	τ 5.67 one proton, quartet (J = 6.5 cps)
$=CH_2$	τ 5.26 one proton, doublet (J = 3 cps)	CH_3	τ 8.12 three protons, singlet
$=CH_2$	τ 5.80 one proton, doublet (J = 3 cps)	CH_3	τ 8.48 three protons, doublet (J = 6.5 cps)
CH_3	τ 7.92 three protons, singlet		
	$\nu^{CO\,b}$ 1600–1750 cm^{-1} (weak absorption)		ν^{CO} 1670 cm^{-1} (strong absorption)

[a] Nmr spectra taken neat (TMS standard). [b] Infrared spectra taken in $CHCl_3$.



$CH_3SCH_2OC(=CH_2)C_6H_5$

7

7 was further characterized by reaction with bromine to quantitatively give bromomethyl methyl sulfide and phenacyl bromide (eq 3). Similarly hydrogen

$$7 + Br_2 \longrightarrow CH_3SCH_2Br + BrCH_2COC_6H_5 \qquad (3)$$

bromide gave a quantitative yield of bromomethyl methyl sulfide and acetophenone (eq 4). These reac-

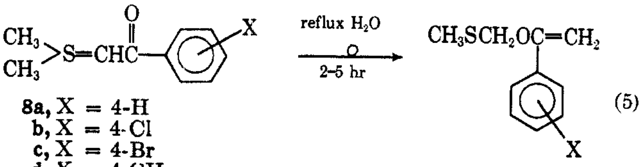
$$7 + HBr \longrightarrow CH_3SCH_2Br + CH_3COC_6H_5 \qquad (4)$$

tions are characteristic of an enol ether such as **7**.

A Stevens-type rearrangement did not occur as reported[3] with this simple dimethyl sulfonium salt **4**. This observation and the suggestion of the intermediacy of the sulfur ylide **5** in the reaction initiated further study.

The ylide[5,6] **5** rearranged, after 5-hr reflux in water without added base, to **7** in 66% yield. Longer reaction times gave the product **7** contaminated with acetophenone but no benzoic acid. Exhaustive hydrolysis of the salt **4** with concentrated potassium hydroxide gave trimethyl sulfonium hydroxide and benzoic acid.[3] The reaction is, then, dependent upon the reaction conditions and base concentration but, as carried out to produce **7**, does involve an ylide intermediate.

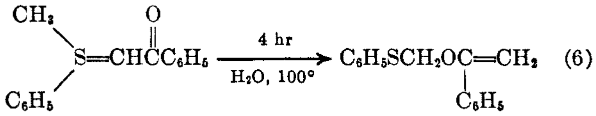
A series of ylides (**8a–e**) under reflux in water produced α-(methylthio)methoxystyrenes (**9a–e**) *via* the new rearrangement (eq 5). The products **9** were light brown oils with the properties listed in Table II.



8a, X = 4-H
b, X = 4-Cl
c, X = 4-Br
d, X = 4-CH
e, X = 3,4-benzo

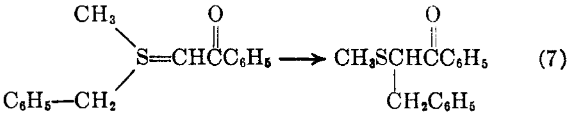
9

One S-methyl group is necessary, but not sufficient, for the rearrangement of sulfonium ylides. Although 2-(methylphenylsulfuranylidene)acetophenone[7] (**10**) rearranges to the corresponding enol ether **11** (eq 6), 2-(benzylmethylsulfuranylidene)acetophenone (**12**) gave the expected[8] product **13** (eq 7) of the Stevens rearrangement upon refluxing in water. We have, however, verified the observations of Ruiz[9] that treatment of benzylmethylphenacylsulfonium bromide with sodium methoxide in refluxing methanol gives the vinyl ether, α-(methylthio)-α-(phenyl)methoxystyrene. 2-(Methylpropylsulfuranylidene)acetophenone (**14a**) under the above conditions gave ~40% 1-(propylthio)methoxystyrene and ~60% methyl phenacyl sulfide (**15a**). When both S-methyl groups are replaced by ethyl or propyl groups (**14b–c**) the only product observed was the sulfide (**15b** and **c**); presumably olefin was also formed (eq 8).



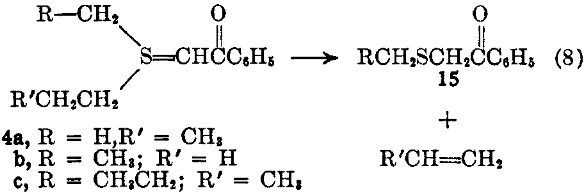
$$(CH_3)(C_6H_5)S{=}CHCOC_6H_5 \xrightarrow[H_2O,\ 100^\circ]{4\ hr} C_6H_5SCH_2OC(C_6H_5){=}CH_2 \qquad (6)$$

10 **11**



$$(CH_3)(C_6H_5CH_2)S{=}CHCOC_6H_5 \longrightarrow CH_3SCH(CH_2C_6H_5)COC_6H_5 \qquad (7)$$

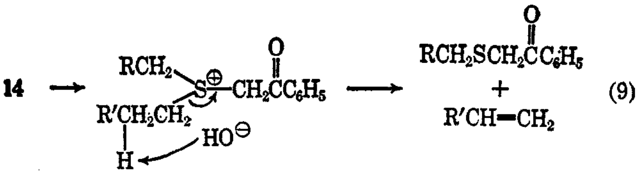
12 **13**



$$(RCH_2)(R'CH_2CH_2)S{=}CHCOC_6H_5 \longrightarrow RCH_2SCH_2COC_6H_5\ (\mathbf{15}) + R'CH{=}CH_2 \qquad (8)$$

14a, R = H, R′ = CH_3
b, R = CH_3; R′ = H
c, R = CH_3CH_2; R′ = CH_3

An ylide may undergo base-calatyzed elimination (**14** → **15**) *via* the sulfonium hydroxide [10] **16** (see eq 9).



$$\mathbf{14} \longrightarrow (RCH_2)(R'CH_2CH_2)\overset{\oplus}{S}{-}CH_2COC_6H_5\ \ HO^{\ominus} \longrightarrow RCH_2SCH_2COC_6H_5 + R'CH{=}CH_2 \qquad (9)$$

16

The elimination reaction is completely favored if R = C_2H_5, R′ = CH_3 or R = CH_3, R′ = H but is comparable in rate with the molecular rearrangement if R = H and R′ = CH_3. This result must be due to decreased stability of an α carbanion in groups larger than CH_3. Formation of a β carbanion leads to elimination; formation of an α carbanion produces enol ether **9**.

S-Ylides which possess readily hydrolyzed groups undergo hydrolysis rather than rearrangement. Thus ethyl 2-(dimethylsulfuranylidene)acetate[11] (**17**) and N,N-diethyl 2-(dimethylsulfuranylidene)acetamide[11] (**19**) gave dimethylacetothetin (**18**) in 100 and 47%

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(5) A. W. Johnson and Ronald T. Amel, *Tetrahedron Letters*, No. 8, 819 (1966).

(6) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1966).

(7) H. Nozaki, M. Takaku, and K. Kondo, *Tetrahedron*, **22**, 2145 (1966).

(8) F. Krollpfeiffer and H. Hartman, *Chem. Ber.*, **83**, 91 (1950).

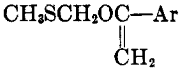
(9) E. B. Ruiz, *Acta Salmanticensia, Ser. Cienc.*, **2**, No. 7 (1958).

(10) The base may be hydroxide from reaction of ylide with water or the ylide itself. Whereas the ylide acts as the base, the reaction, of course, may be inter- or intramolecular. Alternately, displacement of the sulfide by hydroxide to form alcohol is possible.

(11) A. J. Speziale, C. C. Tung, K. W. Ratts, and A. N. Yao, *J. Am. Chem. Soc.*, **87**, 3460 (1965).

TABLE II

PROPERTIES OF α-(METHYLTHIO)METHOXYSTYRENES

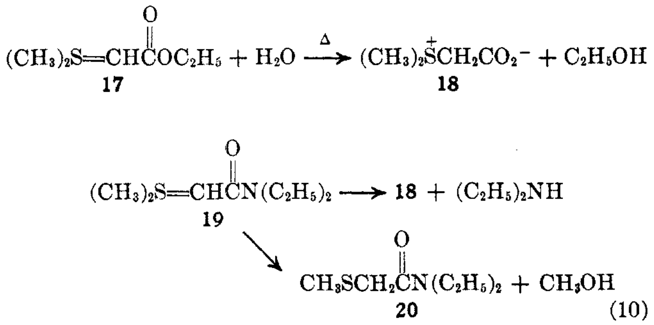


$$CH_3SCH_2O\underset{\underset{CH_2}{\|}}{C}{-}Ar$$

Ar	Reflux time, hr	Yield, %	Bp, (mm)	Nmr spectra,[a] τ (CDCl₃) CH₃	CH₂	=CH₂	ArH	Anal. Calcd, % C	H	S	X	Mol wt	Found, % C	H	S	X	Mol wt
C_6H_5	5	66	95° (1)	7.92 s	5.12 s	5.26 d (J = 3 cps) 5.80 d (J = 3 cps)	2.60 m	66.62	6.71	17.79		180	66.41	6.55	17.66		183
4-Br–C_6H_4	2	64	119° (0.4)	7.90 s	5.15 s	5.25 d (J = 3 cps) 5.85 d (J = 3 cps)	2.69 s	46.34	4.28	12.37	30.84		46.10	4.14	12.12	31.06	
4-Cl–C_6H_4	2	50	96° (0.3)	7.88 s	5.02 s	5.26 d (J = 3 cps) 5.74 d (J = 3 cps)	2.12 q	55.94	5.17	14.93	16.51	215	55.79	5.30	14.77	16.24	220
4-C_6H_5–C_6H_4	5	84	[b]	7.88 s	5.08 s	5.24 d (J = 3 cps) 5.78 d (J = 3 cps)	2.55 m	74.96	6.29	12.51			75.20[c]	6.32[c]	12.73[c]		
2-$C_{10}H_7$	2	57	[b]	7.88 s	5.10 s	5.18 d (J = 3 cps) 5.75 d (J = 3 cps)	2.38 m	73.00	6.12	13.92		230	72.90[c]	6.18[c]	13.82[c]		237

[a] Tetramethylsilane internal reference; all areas integrate correctly; s = singlet, d = doublet, q = quartet, m = multiplet. [b] Decomposes upon distillation. [c] Analytical sample obtained directly without distillation.

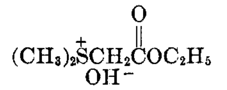
yield, respectively (eq 10). The amide, which is less completely hydrolyzed, also produced N,N-diethyl 2-(methylthio)acetamide (**20**). The ylides **17** and **19** are much more reactive than are phenacyl ylides **8**. For example, the ester- and amide-stabilized ylides undergo reaction with aldehydes[4] and Schiff bases[11] and must be prepared under nonaqueous conditions.[4] The sensitivity to water may be due to the facile hydrolysis of these species. Thetin formation from ethyl 2-(dimethylsulfuranylidene)acetate (**17**) and N,N-diethyl 2-(dimethylsulfuranylidene)acetamide (**19**) may proceed *via* normal hydrolysis of the corresponding sulfonium hydroxides **21**.



$$\underset{\mathbf{17}}{(CH_3)_2S{=}CH\overset{\overset{O}{\|}}{C}OC_2H_5} + H_2O \xrightarrow{\Delta} \underset{\mathbf{18}}{(CH_3)_2\overset{+}{S}CH_2CO_2^-} + C_2H_5OH$$

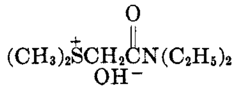
$$\underset{\mathbf{19}}{(CH_3)_2S{=}CH\overset{\overset{O}{\|}}{C}N(C_2H_5)_2} \longrightarrow \mathbf{18} + (C_2H_5)_2NH$$

$$\searrow \underset{\mathbf{20}}{CH_3SCH_2\overset{\overset{O}{\|}}{C}N(C_2H_5)_2} + CH_3OH \qquad (10)$$



$$(CH_3)_2\overset{+}{S}CH_2\overset{\overset{O}{\|}}{C}OC_2H_5 \quad OH^-$$

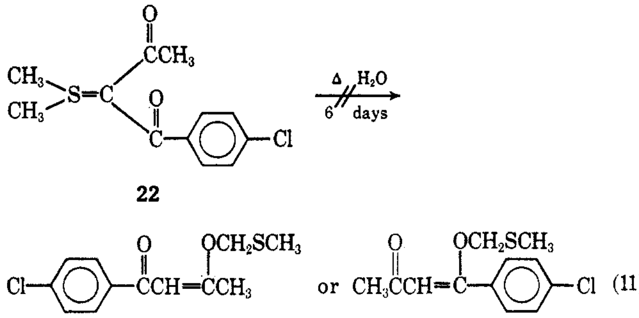
21a



$$(CH_3)_2\overset{+}{S}CH_2\overset{\overset{O}{\|}}{C}N(C_2H_5)_2 \quad OH^-$$

21b

In contrast S-ylides which are stabilized by two ketone groups are extremely stable species and do not readily rearrange. Ylide **22**, prepared from **8c** and acetic anhydride, was unchanged upon refluxing for 6 days in water (eq 11).



22

(11)

The rearrangement of **8a** to **9a** requires a proton-donating solvent. The reaction was complete in water in 2–5 hr but in ethanol only after 66 hr. A much slower decomposition occurred in DMSO and THF.[4] The effect of temperature was not determined.

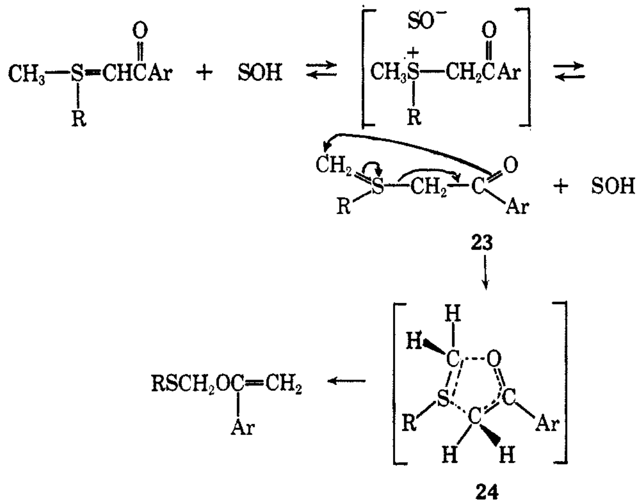
A postulated mechanism for the rearrangement (**8** → **9**) is given in Scheme I.

The initial equilibrium favors the starting ylide, but the presence of **23** leads *via* transition state **24** to the product, an enol ether. The initial tautomerization is supported by (1) the requirement for a proton-donating solvent and (2) the reluctance of very stable ylides to rearrange. The decreased basicity of extremely stable ylides does not favor the protonated intermediate. If the rearrangement of **8b** is effected in D_2O the product is completely deuterated at the vinyl positions with no deuterium in the methyl or methylene groups of **9b**. This means that the intermediate **23** (R = CH_3; Ar = 4-Br–C_6H_5), if it is in the reaction pathway, must rearrange to vinyl ether much faster than it reprotonates.

The rearrangement can occur *via* a transition state **24** because of the ability of sulfur to accept electrons simultaneously from one bond and release them in a second bond in an energy situation where sulfur already has ten electrons. This ability is due to the polarizability and low-lying d orbitals of sulfur.

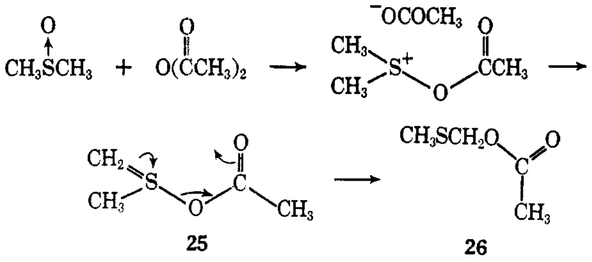
A particular ylide under hydrolytic conditions may

SCHEME I



undergo rearrangement to **9**, sulfur to carbon alkyl migration, elimination of sulfides, hydrolysis of functional groups, or, if too stable, no reaction. In all cases the path taken is a logical consequence of the expected behavior of the ylide carbanion.

The Pummerer reaction,[12] which leads to acetoxy sulfides,[13] **26** (eq 12), bears a close analogy to the reaction **8** → **9**. The intermediate **25** resembles **4** except that oxygen replaces CH$_2$. The mechanism of these rearrangements is interesting since, in the extreme, oxygen attack occurs at "the wrong end" of the S═CH$_2$ dipole.



(12)

Experimental Section[14]

Sulfonium Ylides.—The sulfonium ylides were prepared by the method of Ratts and Yao[6] except for 2-(methylphenylsulfuranylidene)acetophenone which was prepared by the method of Nozaki, Takaku, and Kondo[7] and 3-(dimethylsulfuranylidene)-4′-chlorobenzoylacetone which was prepared as an amber oil by the method of Johnson.[5] The nmr spectrum of **22** exhibited peaks at τ 2.77 (ArH, singlet, five protons), 7.22 (CH$_3$S, singlet, six protons), and 8.02 (CH$_3$CO, singlet, three protons). 2-(Dimethylsulfuranylidene)-4′-chloroacetophenone (**8c**) mp 106–107°, was obtained in 64% yield.

Anal. Calcd for C$_{10}$H$_{11}$ClOS: C, 55.94; H, 5.16; S, 14.93. Found: C, 55.80; H, 4.99; S, 14.79.

2-(Dimethylsulfuranylidene)acetonaphthone (**8e**), mp 71–72°, was obtained in 64% yield.

Anal. Calcd for C$_{14}$H$_{14}$OS: C, 73.00; H, 6.12; S, 13.92. Found: C, 72.82; H, 6.18; S, 13.73.

2-(Benzylmethylsulfuranylidene)acetophenone (**12**), mp 76–78°, was prepared in 60% yield.

Anal. Calcd for C$_{16}$H$_{16}$OS: C, 74.96; H, 6.29; S, 12.51. Found: C, 74.72; H, 6.11; S, 12.28.

2-(Diethylsulfuranylidene)acetophenone (**14b**), 2-(dipropylsulfuranylidene)acetophenone (**14c**), and 2-(methylpropylsulfuranylidene)acetophenone (**14a**) were obtained as unstable amber oils,[15] in 95, 100, and 78%, respectively, which upon treatment with hydrogen bromide regenerated the sulfonium salts in high yield.

Rearrangement of Ylides.—The general procedure used is illustrated by the rearrangement of 2-(dimethylsulfuranylidene)-acetophenone. The above ylide (3.8 g, 0.02 mole) was added to water (45 ml) and refluxed for 5 hr. The cooled mixture was extracted twice with 50-ml portions of ether and the ether extract concentrated to give 2.5 g (66%) of α-(methylthio)methoxystyrene. The nmr and infrared spectra of this material was unchanged upon distillation (see Table II). In some instances the reaction period was reduced to 2 hr.

Rearrangement of 2-(Methylphenylsulfuranylidene)acetophenone (10).—The above ylide (4.8 g, 0.02 mole) was refluxed with water for 4 hr. The cooled mixture was extracted twice with 50-ml portions of methylene chloride and the extract dried over magnesium sulfate and concentrated to give 4.1 g of oil (86%). The nmr spectrum of the crude oil exhibited peaks at τ 2.65 (ArH, multiplet, ten protons), 4.67 (CH$_2$, singlet, two protons), 5.16 (═CH$_2$, doublet, one proton), and 5.70 (doublet, one proton, J = 3 cps). Distillation of the sample on a Nester–Faust spinning-band column partially decomposed the product.

Rearrangement of 2-(Benzylmethylsulfuranylidene)acetophenone (12).—A solution of 2-(benzylmethylsulfuranylidene)-acetophenone (9.0 g, 0.035 mole) in water (200 ml) was refluxed for 5 hr. The solution became turbid and was extracted with ether. The ether extract was dried over magnesium sulfate and evaporated to dryness, leaving a yellow oil (8.4 g). Fine white crystals separated from the oil upon standing. A small amount of ether was added, and upon filtering and washing the mixture with ether, a white crystalline compound (0.1 g), mp 204–207°, was obtained. The infrared spectrum showed ν^{CO} 1670 cm^{-1} in Nujol. The nmr spectrum showed peaks at τ 2.42 (ArH, multiplet, five protons), 5.25 (–CH–, singlet, one proton and 8.20 (–CH$_3$–) singlet, three protons).

Anal. Calcd for C$_{18}$H$_{18}$O$_2$S$_2$: C, 65.42; H, 5.49; S, 19.41; mol wt 330. Found: C, 65.48; H, 5.42; S, 19.28; mol wt, 324.

The solution from which the crystals were filtered was concentrated and vacuum distilled. The first two fractions at 38–83° (0.3 mm) consisted of mixtures of acetophenone and benzyl methyl sulfide. The main fraction distilled at 145–150° (0.3 mm) (lit.[8] 152° (0.4 mm)) giving pure product (3.9 g, 43%). The infrared spectrum showed ν^{CO} 1670 cm^{-1} in CHCl$_3$. The nmr spectrum showed peaks at τ 2.42 (ArH, multiplet, ten protons), 5.62 (–CH–, triplet, one proton), 4.75 (–CH$_2$–, multiplet, two protons), and 8.05 (–CH$_3$–, singlet, three protons).

Anal. Calcd for C$_{16}$H$_{16}$OS (256.36): C, 74.96; H, 6.29; S, 12.51. Found: C, 74.93; H, 6.32; S, 12.73.

The oil crystallized on standing to yield a white crystalline solid, mp 59–60° (lit.[8] mp 55–60°). The infrared and nmr spectra were identical and unchanged from the distilled oil, 2-methylthio-3-phenylpropiophenone.

Benzylmethylphenacylsulfonium bromide (3.4 g, 0.01 mole) was added to 10 ml of methanol in which 0.23 g (0.01 g-atom) of sodium was previously dissolved. The solution was refluxed 2.5 hr and concentrated to an orange solid. Methylene chloride (50 ml) was added and the mixture filtered. The orange filtrate was concentrated to an oil, the nmr spectrum of which exhibited the following bands characteristic of α-(methylthio)benzyl α-styryl ether: z 2.50 (ArH, multiplet, ten protons), 3.76 (–CH, one proton), 5.19 (═CH$_2$, doublet, J = 3 cps, one proton, 5.80 (doublet J = 3 cps one proton), 7.94 (CH$_3$S, singlet, three protons).

Oxidation of 2-Methylthio-3-phenylpropiophenone. Formation of 2-Methylsulfonyl-3-phenylpropiophenone.—To the solution of 2-methylthio-3-phenylpropiophenone (3 g, 0.0117 mole) in 5:1 acetic acid solution (25 ml) was added dropwise and slowly hydrogen peroxide (3 g, 0.026 mole, 30%). The solution was cooled and the addition temperature was kept between 0 and 5°. The solution was warmed to 45° and the reaction immediately occurred with evolution of heat. The reaction mixture was immediately cooled and stirred at room temperature for 1 hr. The solution was then poured into a beaker of ice and a white solid precipitated. The white solid was filtered off giving the product (3.8 g, 100%), mp 105–119°. The infrared spectrum showed

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[12] (a) R. Pummerer, *Chem. Ber.*, **42**, 2282 (1909); (b) R. Pummerer, *ibid.*, 1401 (1910).

[13] F. G. Bordwell and B. M. Pitt, *J. Am. Chem. Soc.*, **77**, 572 (1955).

[14] Microanalyses were performed by Galbraith Laboratories, Inc. The infrared spectra were determined on a Perkin-Elmer Infracord and the nmr spectra on a Varian A-60 spectrometer.

[15] K. W. Ratts, *Tetrahedron Letters*, No. 39, 4707 (1966).

bands for C=O and SO_2 groups (see below) and the nmr spectrum showed peaks indicative of the products (see below). The white solid was recrystallized from ether giving a white crystalline solid (1.5 g, 44%), mp 128–131° (lit.[8] mp 129°). The infrared spectrum showed ν^{CO} 1670 cm^{-1}, ν^{SO_2} 1320, 1225 cm^{-1} in $CHCl_3$. The nmr spectrum showed peaks at τ 2.25 (ArH, multiplet, ten protons), 4.88 (–CH–, triplet, one proton), 6.48 ($-CH_2-$, doublet, two protons), and 7.04 ($-CH_3$, singlet, three protons). The crystals were further recrystallized from ether giving the analytical sample, mp 138–139°, of 2-methylsulfonyl-3-phenylpropiophenone.

Anal. Calcd for $C_{16}H_{16}O_3S$ (288.36): C, 66.64; H, 5.60; S, 11.12. Found: C, 66.47; H, 5.48; S, 10.96.

Rearrangement of Other Ylides. A. 2-(Diethylsulfuranylidene)acetophenone (14b).—The above ylide (20.8 g, 0.1 mole) was added to water (225 ml) and the mixture refluxed 5 hr. The aqueous phase was decanted from the red oil which was taken up in methylene chloride, dried over magnesium sulfate, and concentrated to 1.8 g. Nmr analysis indicated this was a mixture containing ethyl phenacyl sulfide (see below), starting ylide (see ref 15), acetophenone, and small amounts of α-(1-ethylthio)-ethoxystyrene ($CH_3(C{=})H$, τ 4.47 quadruplet, J = 6 cps; —C(=)H, τ 5.45 doublet, J = 3 cps; —C(=)H, τ 5.82 doublet, J = 3 cps; CH_3-C, τ 8.24 doublet, J = 6 cps). Distillation of the above sample yielded only ethyl phenacyl sulfide and acetophenone and intractable residues. The aqueous layer was extracted three times with 100-ml portions of methylene chloride, the extract dried over magnesium sulfate and concentrated to 14.5 g (70%) of starting ylide. This ylide was refluxed in water 15.5 hr. The solution was cooled and extracted with three 100-ml portions of methylene chloride. The extract was dried over magnesium sulfate and concentrated to give only ethyl phenacyl sulfide (by nmr analysis, see below).

B. Diethyl phenacyl sulfonium Bromide with Aqueous Potassium Hydroxide.—Diethylphenacylsulfonium bromide (54.0 g, 0.187 mole) was added to 195 ml of 1 N potassium hydroxide in 250 ml of water and heated to reflux over 1.5 hr, maintained for 5 hr, and allowed to stand overnight. The mixture was extracted with three 100-ml portions of ether which was concentrated to give 7.0 g of an oil. This oil by nmr analysis is a mixture of acetophenone and ethyl chloride (three 100-ml portions) which was concentrated to give 15.9 g of an oil which by nmr analysis was 2-(diethylsulfuranylidene)acetophenone.

Repetition of the above procedure with 162.0 g of salt, 750 ml of H_2O, and 585 ml of 1 N KOH gave 75.0 g of oil upon ether extraction. The combined ether extracts from the above experiments (82.0 g) were distilled to give 5.8 g, bp <50° (0.35 mm) (acetophenone); 0.7 g, bp 50–87° (0.35 mm); 42.8 g, bp 87–103° (0.35 mm), 32% (ethyl phenacyl sulfide).

Anal. Calcd for $C_{10}H_{12}OS$: S, 17.76. Found: S, 17.76.

The nmr spectrum showed peaks at τ 9.10 (CH_3, three protons, triplet), 7.90 (CH_2, two protons, quartet), 6.58 (CH_2, two protons, singlet), 2.70 (ArH, five protons, multiplet). The infrared spectrum showed ν^{CO} at 1670 cm^- (neat). There was obtained 26.0 g of dark, undistillable residue.

Attempted Rearrangement of 2-(Dipropylsulfuranylidene)-acetophenone (14c).—2-(Dipropylsulfuranylidene)acetophenone (11.8 g, 0.05 mole) in water (112 ml) was refluxed for 5 hr. Upon cooling the mixture was extracted with two 100-ml portions of ether and the ether extract dried over magnesium sulfate and concentrated to 7.8 g of red oil. Distillation of the oil gave 4.3 g (44%) of phenacyl propyl sulfide, bp 95–100° (0.15 mm).

Anal. Calcd for $C_{11}H_{14}OS$: S, 16.51. Found: S, 16.39.

The nmr spectrum showed peaks at τ 2.04 (ArH, two protons) and 2.66 (ArH, three protons, multiplets), 6.23 (CH_2, two protons, singlet), 7.53 (CH_2, two protons, triplet), 8.54 (CH_2, two protons, septuplet), 9.16 (CH_3, three protons, triplet).

Phenacyl Propyl Sulfide.—Sodium (2.3 g, 0.1 g-atom) was dissolved in methanol (40 ml) and propanethiol (7.6 g, 0.1 mole) added. Phenacyl bromide (19.9 g, 0.1 mole) was added and the mixture was allowed to stand 2 hr, and heated on the steam bath for 1 hr. The mixture was filtered and the residue washed with methanol. The filtrate was concentrated and distilled to give 14.6 g of product, bp 100° (0.15 mm), identical with that obtained in the above experiment.

Rearrangement of 2-(Methylpropylsulfuranylidene)acetophenone (14a).—The above ylide (20.8 g, 0.1 mole) was added to water (200 ml), refluxed for 4.5 hr, then allowed to stand at room temperature overnight. The mixture was extracted with three 100-ml portions of ether and the extract dried over magnesium sulfate and concentrated to 9.2 g of oil. The nmr spectrum indicated a 60:40 mixture of 1-(propylthio)methoxystyrene and methyl sulfide, with traces of acetophenone. Distillation of this oil at 0.3 mm gave acetophenone and mixtures of sulfide and styrene derivatives (by nmr analysis, see below).

Distillation of the combined mixtures on a spinning-band column yielded an analytical sample of α-(propylthio)methoxystyrene, bp 107–108° (0.7 mm).

Anal. Calcd for $C_{12}H_{16}OS$: C, 69.21; H, 7.75; S, 15.37. Found: C, 69.23; H, 7.88; S, 16.15.

The nmr spectrum exhibited peaks at τ 2.50 (multiplet, ArH, five protons) 5.08 (singlet, CH_2, two protons) 5.25 (doublet, $=CH_2$, one proton, J = 3 cps), 5.80 (doublet, $=CH_2$, one proton, J = 3 cps), 7.45 (triplet, CH_2, two protons, J = 7 cps), 8.50 (septuplet, CH_2, two protons, J = 7 cps), 9.14 (triplet, CH_3, three protons, J = 7 cps).

Rearrangement of N,N-Diethyl 2-(Dimethylsulfuranylidene)-acetamide (19).—A solution of the above ylide[16] (8.75 g, 0.05 mole) in water (250 ml) was refluxed for 2 hr. The colorless solution became light orange. The aqueous solution was cooled and extracted with ether. The ether extract was dried and evaporated to give an oil (2.0 g) which separated into two layers. The top layer of mineral oil was discarded. The lower layer was vacuum distilled and the main fraction collected at 59–62° (0.1 mm) and identified as N,N-diethyl 2-(methylthio)acetamide. The infrared spectrum showed ν^{CO} at 1640 cm^{-1} and the nmr spectrum showed peaks at τ 6.76 (singlet, CH_2 two protons), 6.65 (quadruplet, CH_2, four protons), 7.85 (singlet, CH_3, three protons), and 8.83 (multiplet, CH_3, six protons).

The aqueous layer was evaporated to yield a very viscous oil which eventually solidified. The solid was washed with ether giving a white solid (2.8 g, 47), mp 60°. The infrared spectrum showed broad ν^{OH} and ν^{CO} (see below). The white solid was crystallized from methanol–ethyl acetate giving a granular solid, mp 65–67°. The infrared spectrum showed ν^{CO} 3350 cm^{-1} and ν^{CO} 1675, 1600 cm^{-1} in Nujol. The nmr spectrum showed peaks at τ 4.88 (singlet OH), CH_2– at 5.40 (singlet, CH_2–, two protons), and 6.62 (singlet, CH_3, six protons) in D_2O. A solution of the crystals in water gave a negative chloride test with 5% aqueous silver nitrate solution. A mixture melting point with dimethylacetothetin hydrate was undepressed, 65–67°.

Rearrangement of Ethyl 2-(Dimethylsulfuranylidene)acetate (17).—A solution of ethyl 2-(dimethylsulfuranylidene)acetate[16] (7.4 g, 0.05 mole) in water (250 ml) was refluxed for 2 hr. The solution was cooled and extracted with ether. The ether extract was dried and evaporated, giving only mineral oil which was discarded. The aqueous layer was then evaporated to dryness. A white crystalline material was obtained (6.15 g), mp 64–67°. The nmr spectrum showed peaks at τ 4.90 (singlet, CH_2, five protons), 6.67 (singlet, $-CH_3$, six protons), 5.40 (singlet, $-CH_2-$, two protons), and 6.70 (singlet, $-CH_3-$, six protons) in CF_3COOH. The product was recrystallized from methanol–ethyl acetate and the melting point and infrared and nmr spectra were unchanged. A mixture melting point with dimethylacetothetin hydrate was undepressed, 65–67°. The pure recrystallized product was dried *in vacuo* at room temperature for 1 day. The crystals changed from colorless to white (opaque). The infrared and nmr spectra were exactly identical with those of dimethylacetothetin. The melting point of the dried product was 140–141°.

Anal. Calcd for $C_4H_8O_2S$ (120.17): C, 39.98; H, 6.71; S, 26.63. Found: C, 39.69; H, 6.87; S, 26.43.

Preparation of Dimethylacetothetin (18).—To the solution of carboxymethyldimethylsulfonium chloride (3.9 g, 0.025 mole) in water was added a suspension of silver oxide (5.79 g, 0.025 mole) in water. The mixture was stirred for 3–4 hr, and the black precipitate filtered off. The filtrate gave a negative chloride test with silver nitrate solution. The filtrate was evaporated. As the solution became more and more concentrated, a black solid started to precipitate. The solid was filtered off and the clear filtrate further evaporated. Finally a grayish solid residue (3 g) was obtained, which was dissolved in ethyl acetate–methanol and filtered repeatedly, until the filtrate was clear. Crystallization of the filtrate was induced by adding more ethyl acetate. The crystals obtained were hygroscopic, mp 48–55°. Repeated recrystallization gave dimethylacetothetin hydrate, mp 61–65°.

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[16] As prepared the mineral oil from the sodium hydride remained in the ylide sample.

The infrared and nmr spectra were identical with those of the compound obtained from N,N-diethyl 2-(dimethylsulfuranylidene)acetamide and a mixture melting point was also undepressed, 66–67°. The thetin was dried *in vacuo*, mp 138–140°.

Attempted Rearrangement of 2-(Dimethylsulfuranylidene)-acetyl-4′-chloroacetophenone (22).—The above ylide was added to 200 ml of water and the mixture refluxed for 6 days. The nmr spectrum of the insoluble oil was unchanged from starting material.

Solvent Effects.—The rearrangement of 2-(dimethylsulfuranylidene)acetophenone was repeated in absolute ethanol. Nmr spectra indicated complete reaction only after 66 hr. The solution was concentrated and the residue extracted with ether. Concentration of the ether gave 1-(methylthio)methoxystyrene in 81% yield. Heating the above ylide in DMSO for 13 days gave no rearranged product by nmr analysis.

Registry No.—**6**, 14236-72-7; **7**, 14439-02-2; **8c**, 14679-47-1; **8e**, 14679-48-2; **9a**, 14439-02-2; **9b**, 14680-04-7; **9c**, 14679-93-7; **9d**, 14679-94-8; **9e**, 14679-95-9; **11**, 14679-96-0; **12**, 14679-97-1; **13**, 14679-98-2; **15b**, 10271-55-3; **15c**, 14680-00-3; **18**, 4727-41-7; 2-methylsulfonyl-3-phenylpropiophenone, 3708-06-3; α-(propylthio)methoxystyrene, 14680-03-6; **20**, 14680-21-8.

Photochemical Decarboxylation of Acids with Thallium(III)

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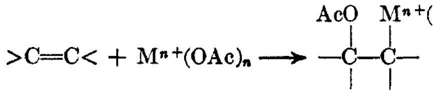
Tl(III) carboxylates generated by the facile metathesis of Tl(III) acetate and a variety of carboxylic acids are photolyzed at 2537 and 3500 A in benzene solutions. Photolysis yields Tl(I) carboxylate and CO_2 quantitatively together with products derived from the alkyl moiety of the acid. These are alkane, alkene, dialkyl and alkyl esters, and alkylbenzene. The relative amounts of each depend on the irradiating source. Alkyl dimers are formed in high yields with 2537-A light, whereas at 3500-A alkanes are the major products. These products are considered to arise from free alkyl radicals generated by photolytic homolysis of Tl(III) carboxylates stepwise to Tl(II) carboxylates, followed by further fragmentation to the Tl(I) product. The good yields of dimers particularly from primary acids using 2537-A irradiation is attributed to high local concentrations of radicals due to the instability of the Tl(II) species generated in an excited state. These alkyl radicals can be trapped by hydrogen donors of scavenged by Cu(II). The rearrangement of 5-hexenyl radical from 6-heptenoic acid to cyclopentylmethyl radical is not reversible and direct molecular processes do not obtain in the dimerization.

Thallium(III) acetate is an oxidant easily prepared from its readily obtainable oxide.[1] As the middle member of the post-transition triad, Hg, Tl, and Pb, Tl(III) exhibits properties intermediate between its isoelectronic analogs, Hg(II) and Pb(IV), toward organic substrates. Thus, arenes are more readily mercurated[2] than thallated,[3] and plumbation[4] occurs only in selected cases. Alkenes such as cyclohexene also react with this group of heavy metal carboxylates in approximately the same order of reactivity.[5] In most cases, products can be considered to arise *via* electrophilic addition of the metal moiety and acetate to the unsaturated linkage, followed by further reactions of the alkyl metal carboxylates.[6]



$$>C{=}C< + M^{n+}(OAc)_n \longrightarrow -\underset{|}{\overset{\overset{\textstyle AcO}{|}}{C}}-\underset{|}{\overset{\overset{\textstyle M^{n+}(OAc)_{n-1}}{|}}{C}}- \quad \text{etc.} \qquad (1)$$

On the other hand, in a variety of other types of oxidations, Pb(IV) acetate[6a] is a powerful, as well as versatile, oxidant under conditions in which neither Hg(II) nor Tl(III) acetates are effective. The mechanism of the facile decarboxylation of acids by Pb(IV) has been shown to be a free-radical chain process which can be induced thermally or photochemically.[7] The relevant propagation steps in the proposed mechanism are given by eq 2 and 3.[8] In this sequence a metastable Pb(III)[9] species plays an important role

$$R\cdot + RCO_2Pb(IV) \longrightarrow [R^+] + RCO_2Pb(III) \qquad (2)$$

$$RCO_2Pb(III) \longrightarrow Pb(II) + CO_2 + R\cdot \text{ etc.} \qquad (3)$$

in the oxidation. The oxidation of alcohols by Pb(IV) has also been shown to proceed *via* free radicals and Pb(III) intermediates are also implicated.[10]

The reactions of these heavy metal carboxylates with organic substrates superficially appear to involve at least two mechanisms: metallation which is *electrophilic* in character in contrast to electron transfer which is *free radical* in nature. In oxidation processes, the former may involve a direct 2-equiv oxidation of the metal moiety: Hg(II) → Hg(0),[11] Tl(III) → Tl(I),[5b] and Pb(IV) → Pb(II).[12] In electron-transfer reactions of Pb(IV), the oxidation which also requires 2 equiv over-all may proceed in two discrete 1-equiv steps: Pb(IV) → Pb(III) → Pb(II).

The electron-transfer mechanism is not common in chemistry of Tl(III) compounds. These are generally

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