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OXIDATION OF THIOLESTERS

SOME ASPECTS OF THE CHEMISTRY OF S-ACYLTHIOL S-OXIDES AND RELATED COMPOUNDS

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Abstract—In the ozone oxidation of thiolesters in 1,2-dichloroethane at room temperature, S-acylthiol S-oxides 3 are proposed as intermediates. The isolation of carboxylic acid anhydrides and dialkyl disulphides as the actual reaction products can be explained as resulting from the decomposition of the unstable S-acyl S-acyloxysulphonium salt 4 arising probably from the reaction of the intermediate S-acylthiol S-oxides with another mole of thiolester. However, in the case of hindered thiolesters, the S-acylthiol S-oxides formed rearrange, possibly via an S→O acyl shift, to the corresponding acyl sulphenates 12 which on further oxidation lead to the mixed carboxylic acid sulphonic acid anhydrides 13.

Although the oxidation of thiolesters has been object of some attention in the past, there has been little detailed work carried out in this field.

Oxidation of thiolesters $RC(O)SCH_2R'$ with peracetic acid in excess of acetonitrile was found to give the corresponding carboxylic acids when R and R′ are both aromatic. When R′ is aliphatic, R being either aromatic or aliphatic, a sulphonic acid $R'CH_2SO_3H$ and carboxylic acid RCOOH are formed.[1]

In general, potassium permanganate and hydrogen peroxide did not oxidize the thiolesters. However, Otto and Lueders[2] did obtain benzoic acid and benzylsuphonic acid from permanganate oxidation of benzyl thiolbenzoate in acetic acid.

The preparation of stable S-acylthiol S-oxides (α-keto sulphoxides) was reported by Barton *et al.*[3] who obtained them from oxidation of monothiocarbonates and monothiocarbamates with *m*-chloroperbenzoic acid. Compounds of this type have been postulated as possible intermediates in the oxidation of thiolesters either with N-bromosuccinimide or iodosobenzene in the presence of an alcohol.[4]

In a short communication, some results of the ozone oxidation of thiolesters were reported.[5] The action of ruthenium tetroxide was described as affording in some instances the corresponding acyl sulphonates.[6]

We wish now to report some new data concerning the oxidation of thiolesters by ozone. We believe that the obtained results, as well as the ones hitherto obtained through the use of other oxidants and until now left unexplained, can be understood on the basis of the intermediate formation of the unstable S-acylthiol S-oxides.

RESULTS AND DISCUSSION

Previous attempts to oxidize thiolesters by the action of ozonised oxygen at −25° in 1–3% solution in carbon tetrachloride were unsuccessful.[7] In the present work the thiolesters could be oxidized by passing a stream of ozonised oxygen (*ca.* 0.05 mmole of ozone/min) through a 5–10% solution of the compound in 1,2-dichloroethane at room temperature. Periodically, samples were taken and analysed by glc and IR spectroscopy. The reaction was considered complete when no more starting material could be detected. The thiolesters used are listed in Tables 1 and 2.

In the reaction with ozone, the primary and secondary S-alkyl esters of cyclohexanecarboxythiolic acid show a long induction period before the first modifications in the gas chromatogram or in the IR spectrum become apparent. They demand a high concentration of ozone and about 15 hr are needed to completely oxidize 10 mmole of the thiolester. However, only 0.45 mole of ozone are consumed by 1 mole of the compound. After evaporation of the solvent, the reaction product yields on distillation the corresponding dialkyl disulphide and cyclohexanecarboxylic acid anhydride (Table 1). Such a long induction period is also observed in the oxidation of t-butyl cyclohexanecarboxythiolate and n-butyl 2,2-dimethylthiolpropionate, though these compounds do not yield the same type of products (Table 2). Thiolbenzoates and phenylthiolacetates react quite rapidly with ozone. The reaction reaches completion after an average

Table 1. Ozonolysis of thiolesters RC(O)SR′ in 1,2-dichloroethane at room temperature: Carboxylic acid anhydrides and disulphides

R	R′	$(R-\overset{O}{\overset{\|}{C}})_2O$* (yield%)	R-S-S-R (yield%)
cyclo-C_6H_{11}	n-C_3H_7	85	84
	iso-C_3H_7	97	86
	n-C_4H_9	94	84
	Sec-C_4H_9	91	84
	n-C_6H_{13}	82	82
	cyclo-C_6H_{11}-CH_2	90	85

* Together with some cyclohexanecarboxylic acid

Table 2. Acyl sulphonates $RCOSO_3R'$ from ozonolysis of thiolesters $RCOSR'$ in 1,2-dichlorethane

R	R'	$RCOSO_3R'$* (yield %)	^{1}H-NMR (δ)
Ph	$\underline{n}$-C_4H_9	55	7.75(5H,s) 3.22(2H,t)1.80 (4H,m)0.99(3H,t)
	$\underline{s}$-C_4H_9	86	7.75(5H,s)3.31(1H,m)1.45 (3H,d)1.81(2H,m)0.99(3H,t)
	$\underline{t}$-C_4H_9	50	7.75(5H,s)1.46(9H,s)
$PhCH_2$	$\underline{n}$-C_4H_9	60†	7.32(5H,s)3.73(2H,s)3.21 (2H,t)1.81(4H,m)0.99(3H,t)
	$\underline{s}$-C_4H_9	70†	7.32(5H,s)3.73(2H,s)3.31 (1H,m)1.45(3H,d)1.81(2H,m) 0.99(3H,t)
	$\underline{t}$-C_4H_9	80†	7.32(5H,s)3.73(2H,s)1.46 (9H,s)
$\underline{t}$-C_4H_9	$\underline{n}$-C_4H_9	50	3.20(2H,t)1.80(4H,m)1.17 (9H,s)0.99(3H,t)
cyclo-C_6H_{11}	$\underline{t}$-C_4H_9	70	2.48(1H,m)2.10-1.10(11H,m) 1.46(9H,s)

* ir ν max (liq. film) 1780,1380,1180 cm^{-1}

† benzoic acid was also formed

consumption of 1.8 mole of ozone by 1 mole of thiolester. In that case the isolated products are the corresponding acyl sulphonates (*vide infra*).

All the reactions when carried out in the presence of an excess of methanol, yield the methyl ester of the corresponding carboxylic acid (80–90%) and the sulphonic acid (60–90%) with no significative change in the rate of thiolester consumption. This suggests that the initial attack of ozone on the thiolester must be the slowest step of the overall reaction, giving rise to a powerful acylating intermediate, as thiolesters do not react spontaneously with methanol under the reaction conditions in absence of ozone.

Although it was not possible to detect such an intermediate by chromatographic methods, the appearance of an IR band at 1080 cm^{-1} during the monitoring of the reaction, suggests the presence of a sulphoxide group and could be attributed to an S-acylthiol S-oxide 3. This type of intermediate could be detected by ^{1}H NMR spectroscopy, when the ozonolysis of methyl thiolacetate was carried out in a NMR tube using carbon tetrachloride as solvent and spectra were taken at regular intervals. The slow formation of acetyl methyl sulphoxide originates two new signals at δ 2.15 and δ 2.53, both singlets (Fig. 1). Its formation seems to be slower than thiolester consumption and the signal at δ 2.53

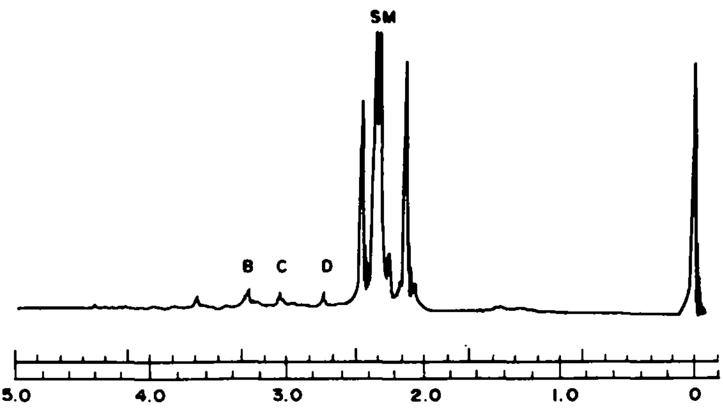


Fig. 1. ^{1}H NMR spectrum obtained during ozonolysis of methyl thiolacetate (SM) (0.104 g) in carbon tetrachloride (10 ml). The relative intensities of the sulphoxide and thiolester signals reach a maximum at this point. Singlets at δ 3.25 (B), 2.97 (C) and 2.70 (D) increasingly become more intense with the simultaneous disappearance of the sulphoxide and thiolester signals. They can be attributed to the formation of an S-acyl S-acyloxysulphonium salt 4 ($R=CH_3$).

attains a maximum intensity at an early point of the reaction. Thereafter it rapidly disappears to give place to a new set of singlets at δ 3.26, 2.97 and 2.70 together with the ones corresponding to acetic acid. This can be conveniently explained if we assume that beyond a certain concentration the S-acylthiol S-oxide enters further reaction at a higher rate than the one of its own formation. The high susceptibility of 3 to hydrolysis justifies the formation of acetic acid.

The ozonolysis of an equimolar mixture of n-propyl cyclohexanecarboxythiolate and n-butyl cyclohexanecarboxythiolate in identical conditions, affords di-n-propyl disulphide, n-propyl n-butyl disulphide and di-n-butyl disulphide in the proportion of 1:2:1 as shown by glc. Identically, methyl n-butanesulphonate can be identified by glc and tlc as one of the reaction products of the ozonolysis of a mixture of methyl cyclohexanecarboxylate and n-butyl cyclohexanecarboxythiolate.

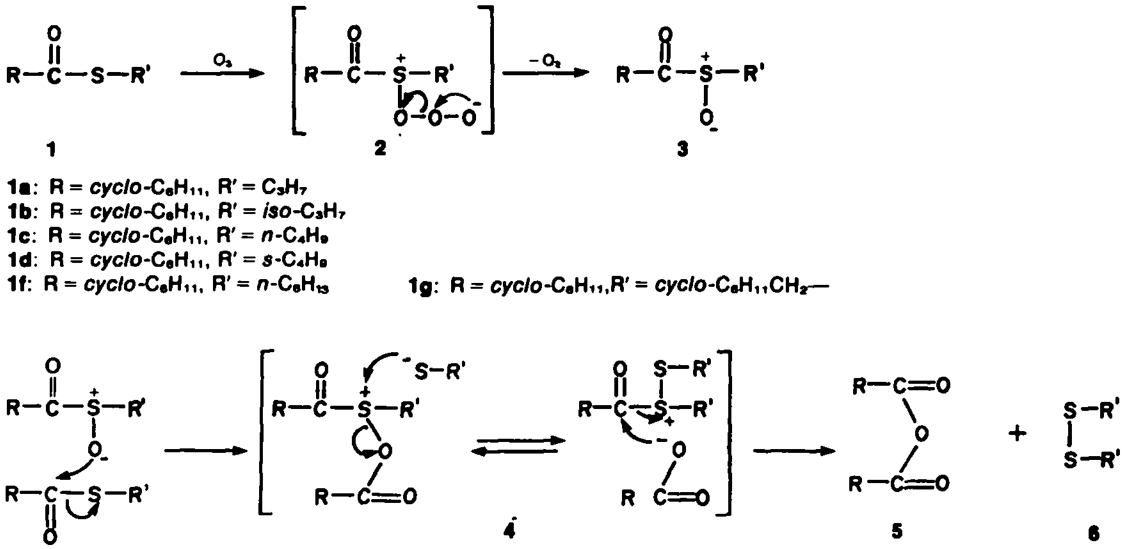
These results can be rationalized in terms of the mechanism outlined in Scheme 1: The initially formed ozone-thiolester adduct 2 after losing an oxygen molecule affords the S-acylthiol S-oxide 3. It is known that thiolesters possess good acylating properties that make them useful acylating reagents. Thus, in the presence of another mole of thiolester, 3 would be acylated at the O-atom of the sulphoxide group to originate an S-acyl S-acyloxysulphonium salt 4 which on work-up decomposes to the carboxylic acid anhydride 5 and the disulphide 6.

This mechanism is very well in accordance with the observed molar ratio of ozone consumption and also gives an explanation for the fact that disulphides, indeed, appear as products of the reaction, though they are not able to survive under the reaction conditions, being rapidly oxidized to the sulphonic acids as it is found in control experiments. Since it has been reported that the presence of strong electron-withdrawing groups α to a sulphur atom can prevent its oxidation by ozone[7] the formation of a sulphonium salt of the type 4 would account for that fact. The inability of thiolsulphonates to be oxidized by ozone under the reaction conditions seems to be a confirmation of this.

In a previous communication[8] it was shown that ethoxycarbonyl benzyl sulphoxide 7 was able to undergo acylation at the sulphoxide O-atom to afford S-acyl S-acyloxysulphonium salts of the type 4. Some of these could be isolated as BF_4^- as white pasty solids which rapidly decomposed at room temperature. They react with sodium mercaptides under nitrogen atmosphere to afford the corresponding anhydrides and disulphides (Scheme 2).

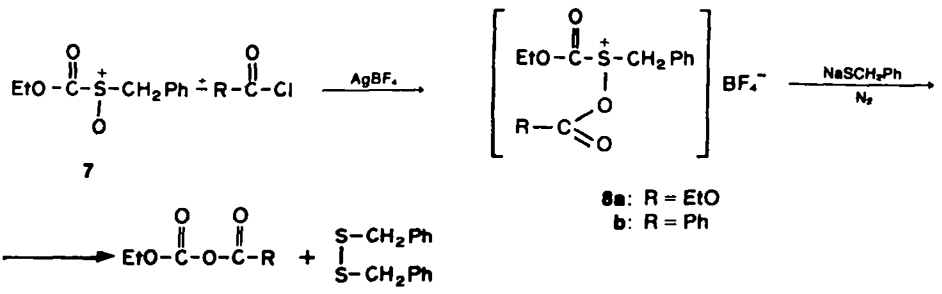
An interesting reaction is exemplified in Scheme 3. Though thiocarbonate O, S-diesters are known to be somewhat resistant to nucleophilic attack, ethoxycarbonyl benzyl sulphoxide 7 reacts with O-ethyl S-benzyl monothiocarbonate in 1,2-dichloroethane at reflux temperature to afford diethyl carbonate, dibenzyl disulphide and CO_2. However, as expected,[3] under these conditions and after 20 hr 80% of the thiolester are recovered.

The thiolesters listed in Table 2 do not follow the same



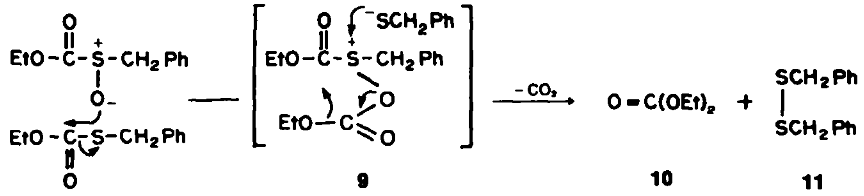
1a: R = cyclo-C_6H_{11}, R' = C_3H_7
1b: R = cyclo-C_6H_{11}, R' = iso-C_3H_7
1c: R = cyclo-C_6H_{11}, R' = n-C_4H_9
1d: R = cyclo-C_6H_{11}, R' = s-C_4H_9
1f: R = cyclo-C_6H_{11}, R' = n-C_8H_{17}
1g: R = cyclo-C_6H_{11}, R' = cyclo-$C_6H_{11}CH_2$—

Scheme 1.



8a: R = EtO
b: R = Ph

Scheme 2.



Scheme 3.

reaction path. After evaporation of the solvent under reduced pressure, a yellow to brown coloured liquid is obtained, which extensively decomposes on attempted distillation. Left in the air or by treatment with water it decomposes to the corresponding carboxylic acids and sulphonic acids which can be unequivocally identified by glc through their methylated products and by comparison with authentic samples. Their good acylating properties, IR (ν_{max} cm^{-1}, 1780, 1380, 1180) and ^{1}H NMR spectra are in agreement with the expected for the acyl sulphonates.[9,10]

As already stated, the thiolesters in this group exhibit a different behaviour towards ozone, depending on the presence or absence of a benzene ring in the acyl group. They lead, however, to the same type of reaction products. The influence .of the benzene ring can be related to its ability to release electrons to the C=O group, thus increasing the electron availability at the S atom. The formation of ozone–thiolester complexes with the participation of the benzene ring[11] could also contribute to explain the easier oxidation of thiolbenzoates and phenylthiolacetates.

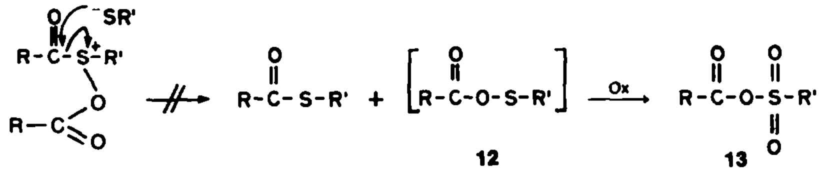
The fact that t-butyl cyclohexanecarboxythiolate and n-butyl 2,2-dimethylthiolpropionate also afford the acyl sulphonates on ozonolysis instead of the disulphides and the carboxylic acid anhydrides, speaks in favour of the influence of steric factors in the course of the reaction. For identical reasons it does not seem likely that the acyl sulphonates can arise from the attack of a mercaptide ion to the thiolcarbonyl group of an intermediate S-acyl S-acyloxysulphonium ion where steric requirements would be expected to play an important role (Scheme 4).

If we assume the initial formation of an S-acylthiol S-oxide in the reaction of ozone with thiolesters, the above considerations suggest that the nature of the reaction products depends on the ability of the unreacted thiolester to effect the acylation of 3. When this acylation takes place easily it gives an S-acyl S-acyloxysulphonium salt 4 which on work-up decomposes to the carboxylic acid anhydride 5 and the disulphide 6. With hindered thiolesters where, owing to steric or electronic reasons, this acylation step becomes more difficult, the S-acylthiol S-oxide preferentially rearranges via an S→O acyl shift to the corresponding acyl sulphenate 12. This is further oxidized to give the acyl sulphonate 13 (Scheme 5).

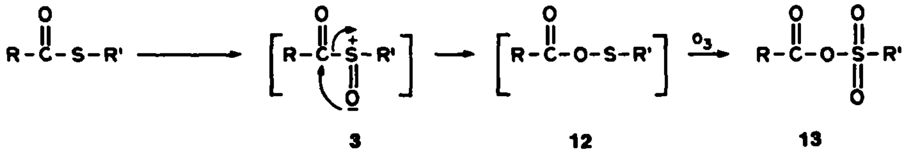
The fact that in this case 1.8 mole of ozone must supply 3 atoms of oxygen is in agreement with previous findings.[7]

It is interesting to note that benzyl phenylthiolacetate 14 reacts with ozone to give benzoic acid and phenylacetic acid in the ratio of 3:2 together with traces of benzaldehyde. When the reaction is carried out using carbon tetrachloride as solvent and ^{1}H NMR spectra are traced at frequent intervals the formation of a new singlet at δ 3.60 can be detected (phenylacetic acid shows a singlet at δ 3.54). These observations could be explained in terms of the mechanism outlined in Scheme 6.

The acyl sulphenate 16 formed by the rearrangement of the S-acylthiol S-oxide 15, owing to the acidity of the

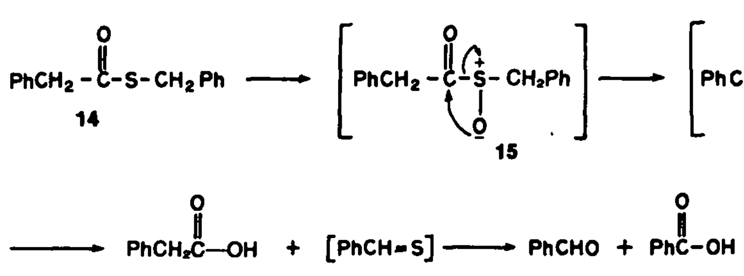


Scheme 4.



1h: R = Ph, R' = n-C_4H_9
1i: R = Ph, R' = s-C_4H_9
1j: R = Ph, R' = t-C_4H_9
1l: R = $PhCH_2$, R' = n-C_4H_9
1m: R = $PhCH_2$, R' = s-C_4H_9
1n: R = $PhCH_2$, R' = t-C_4H_9
1o: R = t-C_4H_9, R = n-C_4H_9
1p: R = $cyclo$-C_6H_{11}, R = t-C_4H_9

Scheme 5.



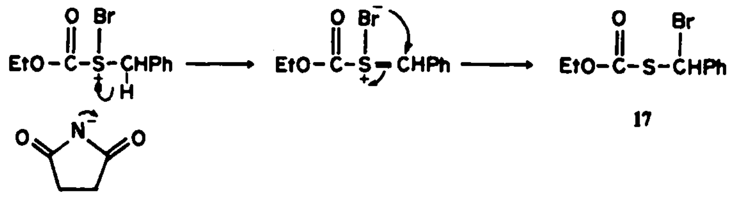
Scheme 6.

benzylic protons, could undergo an Ei-type reaction[12] to give the products.

Under the reaction conditions phenylacetic acid is oxidized to benzoic acid. In general benzyl groups are found to be sensitive to the action of ozone. Benzaldehyde and benzoic acid were also formed during the ozone oxidation of benzyl thiolbenzoate, benzyl cyclohexanecarboxythiolate, benzylsulphonic acid, α-toluenethiol and diphenyl disulphide.

The reaction of an alcohol with a mixture of ethyl thiolbenzoate and N-bromosuccinimide afforded an acylating intermediate, whose IR absorption bands at 1780 and 1180 cm^{-1}[14] are in agreement with the presence of an acyl sulphenate group. Since it is known that bromosulphonium ions react with hydroxylic compounds to afford sulphoxides,[13] the acyl sulphenate must originate from the rearrangement of the previously formed benzoyl sulphoxide.

That the reaction of N-bromosuccinimide with thiolesters affords the corresponding bromosulphonium salts, is demonstrated by allowing a mixture of O-ethyl S-benzyl thiocarbonate and N-bromosuccinimide in carbon tetrachloride to react at room temperature. After 7 days the expected Pummerer rearrangement product 17 is isolated in 79% yield.



Scheme 7.

When O-ethyl S-(p-nitrobenzyl) thiocarbonate is used, the corresponding bromo-derivative 18 is obtained in about the same yield after 5 days. The corresponding carbonates O,O-diesters do not react under these conditions.

These results are identical with those obtained by oxidation of sulphides with N-bromosuccinimide.[14]

EXPERIMENTAL

The thiolesters were prepared from the corresponding thiols and acyl chlorides by usual procedures and analysed correctly. CCl$_4$ and 1,2-dichloroethane (Uvasol, E. Merck, Darmstadt), were used after distillation over P$_2$O$_5$. ^{1}H NMR spectra were obtained at 60 MHz either with a Perkin-Elmer R12 instrument or with a Nuclear Magnetic Ressonance Ltd. (Bucks) instrument. TMS was used as an internal standard and the chemical shifts are reported in δ values. IR spectra were recorded by a Perkin-Elmer 700 instrument for monitoring purposes. The IR spectra of pure compounds were taken by a Perkin-Elmer F 11 gas chromatograph with N$_2$ as a carrier and FID detectors. Identifications were made by comparison with authentic samples in two different columns purchased from Perkin-Elmer: XE-60 on Chromosorb G AW-DMCS (ref. 496-3453) and Apiezon L on Chromosorb P (ref. 496-0751) were used. Tlc and Plc plates were prepared with silica gel GF$_{254}$ (E. Merck, Darmstadt). Capillary m.ps were taken with a Buechi instrument and are uncorrected.

In the general procedure a stream of ozonised O$_2$ (*ca.* 0.05 mmole of O$_3$/min) was passed through a 5–10% soln of the compound in 1,2-dichloroethane at room temp. At regular intervals, samples were taken and analysed by IR, glc and tlc. The reaction was considered complete when no more starting material could be detected. The solvent was then evaporated at reduced pressure and the residue was worked-up for isolation and identification of the reaction products.

Ozonolysis of n-butyl cyclohexanecarboxythiolate 1c. The thiolester (2 g, 10 mmole) was dissolved in 40 ml of 1,2-dichloroethane and ozonised for 15 hr. The solvent was evaporated at reduced pressure and the residue was dissolved in 20 ml of dry ether and dried over MgSO$_4$. After filtration, the ether was evaporated. The residue yielded two different fractions on distillation. The first fraction, b.p. 92°/11 mm Hg, was identified by IR, tlc, glc and ^{1}H NMR as di-n-butyl disulphide by comparison with an authentic sample, 0.75 g (84%). The second fraction, b.p. 126°/11 mm Hg, was found to be identical with an authentic sample of cyclohexanecarboxylic acid anhydride, 1.12 g (94%).

Identical results with other thiolesters are listed in Table 1.

Ozonolysis of sec-butyl thiolbenzoate 1l. The ozonolysis was carried out in a soln of sec-butyl thiolbenzoate (1.94 g, 10 mmole) in 40 ml of 1,2-dichloroethane for 6 hr. After evaporation of the solvent, a brownish-yellow liquid (3.2 g), ν_{max}, cm^{-1}, 1780, 1380, 1180 (^{1}H NMR see Table 2) was obtained. This was dissolved in 30 ml of dry ether and excess of diazomethane was bubbled into the soln. The ether was evaporated and the residue again dissolved in 30 ml of dry ether. 1 μl of this soln was injected in the gas chromatograph. Methyl benzoate and methyl n-butanesulphonate were identified by comparison with authentic samples and the corresponding peak areas were calculated. The ethereal soln was then evaporated and the residue dissolved in 30 ml of dry MeOH. The formation of methyl benzoate was detected by glc. Excess of diazomethane was bubbled into the methanolic soln, the solvent was evaporated and the residue dissolved in 30 ml of dry ether. 1 μl of this soln was injected in the gas chromatograph. Methyl benzoate and methyl n-butanesulphonate were identified as before and the corresponding peak areas were calculated. From the difference found in the peak areas before and after methanolysis the yield on benzoyl n-butanesulphonate was calculated (86%).

Other thiolesters reacted in the same way and the results are listed in Table 2.

Ozonolysis of thiolesters in the presence of methanol. The reactions of n-butyl cyclohexanecarboxythiolate 1c and n-butyl thiolbenzoate 1h can be taken as general examples: n-butyl cyclohexanecarboxythiolate (1 g, 5 mmole) was dissolved in 20 ml of 1,2-dichloroethane to which 1 ml (0.79 g, 25 mmole) of dry MeOH was added. After 18 hr, the solvent was evaporated and the residue was taken in 10 ml of ether and 10 ml of water. The ether layer was separated and the aqueous layer extracted twice with ether. The joined ethereal extracts were dried over $MgSO_4$, filtered and the ether evaporated. Distillation of the residue gave 0.64 g (90%) of methyl cyclohexanecarboxylate, b.p. 183°.

The residue obtained after evaporation of the aqueous phase was taken in 3 ml of glacial AcOH and again evaporated at reduced pressure, this operation being repeated twice. Distillation of the residue gave n-butanesulphonic acid b.p. 147°/0.5 mm Hg, 0.62 g (90%). The aniline salt had m.p. 159°, m.m.p. 159°. Methylation of the acid in methanolic solution with diazomethane afforded methyl n-butanesulphonate identical by IR, ^{1}H NMR, glc and tlc with an authentic sample.

In identical conditions, n-butyl thiolbenzoate 1h (1.94 g, 10 mmole), after 6 hr, gave methylbenzoate, b.p. 199° (1.22 g, 90%) and n-butanesulphonic acid (1.24 g, 90%).

Mixed ozonolysis of n-propyl cyclohexanecarboxythiolate 1a *and n-butyl cyclohexanecarboxythiolate* 1c. A soln of n-propyl cyclohexanecarboxythiolate (0.93 g, 5 mmole) and n-butyl cyclohexanecarboxythiolate (1 g, 5 mmole) in 40 ml of 1,2-dichloroethane was ozonised for 16 hr. The residue obtained after evaporation of the solvent showed the characteristic IR bands of cyclohexanecarboxylic acid anhydride ν_{max} cm^{-1}, 1810, 1740, 1070 and 1000. The mixture was treated with 15% NaOHaq and extracted twice with 20 ml of ether. The ethereal soln was dried over $MgSO_4$. Tlc showed the presence of di-n-propyl, n-propyl, n-butyl and di-n-butyl disulphides in the ratio 1:2:1 (by glc).

Mixed ozonolysis of n-butyl cyclohexanecarboxythiolate 1c *and methyl cyclohexanecarboxylate.* The reaction was carried out as before with a soln of n-butyl cyclohexanecarboxythiolate (1 g, 0.5 mmole) and methyl cyclohexanecarboxylate (1 g, 7 mmole) in 40 ml of 1,2-dichloroethane during 6 hr. On evaporation of the solvent the residue showed the characteristic IR bands of cyclohexanecarboxylic acid anhydride, ν_{max} cm^{-1} 1810, 1740, 1070 and 1000. After treatment with a 15% NaOHaq, it was extracted three times with 10 ml of ether, the etheral fractions were joined and dried over $MgSO_4$. This soln was used after filtration for glc analysis. Di-n-butyl disulphide and methyl n-butanesulphonate were identified by comparison with authentic samples and found to be present in the ratio 2.5:1 respectively. Identical results were obtained by tlc (eluent: CH_3Cl:n-hexane 3:7).

Ozonolysis of benzyl cyclohexanecarboxythiolate. The ozonolysis of 2.34 g (10 mmole) in 40 ml of 1,2-dichloroethane was carried out in 18 hr. The products were identified by tlc as being cyclohexanecarboxylic acid, benzoic acid, benzaldehyde, S-benzyl toluene-α-thiolsulphonate and benzylsulphonic acid by comparison with authentic materials. The residue obtained after evaporation of the solvent (2.5 g) was dissolved in 10 ml of ether and extracted with 5 ml of water. The aqueous fraction after evaporation yielded 0.009 g (0.5%) of benzylsulphonic acid. The ethereal fraction was extracted with a 5% NaOHaq. The aqueous layer was separated, acidified with a 10% HClaq and extracted with 10 ml of ether. The ether layer was separated, dried over $MgSO_4$ and the ether evaporated. The residue yielded on distillation cyclohexanecarboxylic acid, b.p. 105°–106°/4 mm Hg (0.73 g, 57%). The residue of the distillation was recrystallised from water and yielded benzoic acid m.p. 122° (0.37 g, 30%). The neutral ethereal fraction yielded a white solid which after recrystallisation (light petroleum-MeOH) gave S-benzyl toluene-α-thiolsulphonate, m.p. 107.5°–108.5°, ν_{max} (KBr) cm^{-1} 1330, 1120, ^{1}H NMR ($CDCl_3$), 4.03 (2H, s), 4.20 (2H, s), 7.33 (10H, s), identical with an authentic sample (0.83 g, 60%). The mother liquors after evaporation yielded benzaldehyde, identified by its 2,4-dinitrophenylhydrazone, m.p. 235°–236° (0.124 g, 4%), m.m.p. 235°–236°.

Ozonolysis of benzyl phenylthiolacetate 14. The ozonolysis of benzyl phenylthiolacetate during 6 hr followed by ^{1}H NMR spectroscopy, afforded benzoic acid and phenylacetic acid in the ratio 3:2 as calculated from the NMR spectrum, together with traces of benzaldehyde. The spectrum was identical to the one obtained from a mixture of the same compounds in identical proportions.

Synthesis of benzylethoxycarbonylbenzoyloxysulphonium tetrafluoroborate 8b. A soln of silver tetrafluoroborate (0.097 g, 0.5 mmole) in 5 ml of dry CH_2Cl_2 was added dropwise, with stirring, to a 5 ml soln of ethoxycarbonyl benzyl sulphoxide (0.106 g, 0.5 mmole) and benzoyl chloride (0.076 g, 0.5 mmole) in CH_2Cl_2, at − 10°. The AgCl ppt was filtered off and the solvent was evaporated under a stream of N_2. The residue after recrystallisation (EtOAc-light petroleum) gave white pasty crystals ν_{max} cm^{-1} (CH_2Cl_2), 1760, 1735, 1590, 1200, 1060, 1025, highly hygroscopic, that decomposed at room temp. When dissolved in CH_2Cl_2 at − 10° upon addition of an equimolar amount of $PhCH_2SNa$ in methanolic soln under N_2, O-methyl O-benzoyl carbonate (0.06 g, 63%), ν_{max} cm^{-1}, 1810, 1750, 1270, 1190, 1170, 1010, 700 and dibenzyl disulphide were obtained.

Synthesis of benzylethoxycarbonylethoxycarbonyloxy sulphonium tetrafluoroborate 8a. The reaction of ethoxycarbonyl benzyl sulphoxide (0.106 g, 0.5 mmole), ethyl chloroformate (0.054 g, 0.5 mmole) and silver tetrafluoroborate (0.097 g, 5 mmole) was carried out as described. It afforded benzylethoxycarbonylethoxycarbonyloxysulphonium tetrafluoroborate as white pasty crystals ν_{max} cm^{-1} (CH_2Cl_2) 1730, 1370, 1230, 1060, 1025. The reaction with $PhCH_2SNa$ afforded ethylcarbonate and dibenzyl disulphide identified by glc and tlc.

Reaction of thiolesters with N-*bromosuccinimide.* A mixture of N-bromosuccinimide (3.6 g, 20.4 mmole) and O-ethyl S-benzyl thiocarbonate (2.6 g, 13.6 mmole) in 50 ml of CCl_4 protected from light, was stirred at room temp. for 7 days. The formed succinimide was filtered off and recrystallised from alcohol, m.p. 125° (1.8 g, 90%). The filtrate was collected and the solvent evaporated. The distillation of the residue gave O-ethyl S-(α-bromobenzyl) thiocarbonate, 17 b.p. 91°–94°/0.15 mm Hg (2.9 g, 79%), IR ν_{max} cm^{-1} (CCl_4) 1730, 1450, 1150, ^{1}H NMR δ ($CDCl_3$) 1.19 (3H, t), 4.25 (2H, 9), 6.45 (1H, s), 7.30 (5H, m). (Found: C, 43.86; H, 4.22; Br, 29.86; S, 11.60. Calc. for $C_{10}H_{11}BrO_2S$: C, 43.65; H, 4.03: Br, 29.04; S, 11.65%).

In a similar reaction O-ethyl S-(*p*-nitrobenzyl) thiocarbonate gave 18 after 5 days, m.p. 79.5°–80° (2.5 g, 78%), IR ν_{max} cm^{-1}, 1725, 1610, 1530, 1345, 1150, ^{1}H NMR δ ($CDCl_3$) 1.38 (3H, t), 4.36 (2H, 9), 6.52 (1H, s), 7.84, 8.45 (4H, AB, J_{ab} = 10 Hz), (Found: C, 37.36; H, 3.11; Br, 24.76; N, 4.16; S, 10.19. Calc. for $C_{10}H_{10}BrNO_4S$: C, 37.51; H, 3.15; Br, 24.96; N, 4.37; S, 10.01%).

Reaction of O-ethyl O-benzyl carbonate with N-*bromosuccinimide.* The reaction was carried out as described above with 1.62 g (9 mmole) of O-ethyl O-benzyl carbonate and 2.4 g (13 mmole) of N-bromosuccinimide. After 8 days, work-up of the reaction mixture afforded N-bromosuccinimide m.p. 177°, 3.2 g (89%) and O-ethyl O-benzyl carbonate b.p. 71°–74°/0.7 mm Hg, 1.4 g (90%).

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