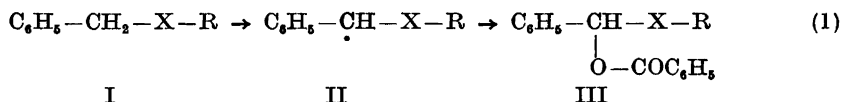# Studies on Peroxy Compounds VIII *

## The Preparation of Acylals and Related Compounds by Copper Salt Catalyzed Reaction of t-Butyl Perbenzoate with Simple Ethers and Sulphides

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The thermal decomposition of t-butyl perbenzoate in the presence of simple ethers and sulphides has been studied. Cuprous chloride has been shown to have a stabilizing effect on the intermediate radical. Instead of dimerization of the substrate, the benzoyloxy group is introduced in the α-position. The benzoates of anisole, phenetole, t-butyl iso-butyl ether, n-butyl-allyl ether, sec-butyl allyl ether, t-butyl allyl ether and di-n-butyl ether have thus been prepared. In the last mentioned case, the corresponding α-butoxy compound has also been formed; the mechanism of this is discussed. Likewise, the benzoyloxy compounds of phenyl methyl sulphide, phenyl ethyl sulphide, t-butyl ethyl sulphide, n-butyl allyl sulphide and di-n-butyl sulphide have been smoothly prepared. When the last mentioned compound was heated, benzoic acid was split off, resulting in an α,β-unsaturated sulphide. Similarly, when attempts were made to purify the benzoyloxycompound of phenyl n-amyl sulphide, benzoic acid was split off with the formation of the unsaturated sulphide.
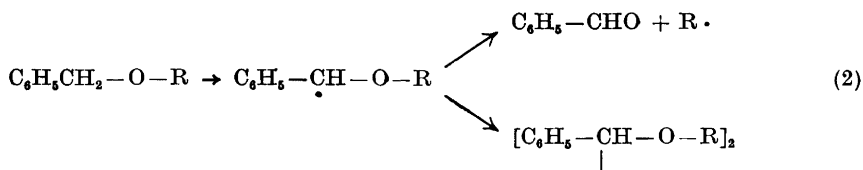
In two earlier papers [1,2] in this series, Lawesson and Berglund have shown that benzyl ethers or sulphides do not undergo fragmentation or dimerization when treated with t-butyl perbenzoate in the presence of catalytic amounts of cuprous chloride but instead, the benzoyloxy group is introduced according to the following equations:

$$C_6H_5-CH_2-X-R \rightarrow C_6H_5-\overset{\bullet}{C}H-X-R \rightarrow C_6H_5-CH-X-R \qquad (1)$$
$$\underset{\text{I}}{} \qquad\qquad \underset{\text{II}}{} \qquad\qquad \underset{\text{III}}{\overset{|}{O-COC_6H_5}}$$

$$X = O, S; \ R = \text{alkyl, aryl}$$
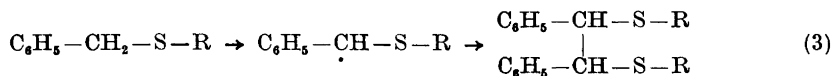
* Part VII: Ref.[2]

This gives a method of preparing acylals [3] of different types. That the copper salt in some way stabilizes the radical II is in keeping with the fact that in its absence a free radical II (X = O), obtained by heating benzyl ethers with $t$-butyl peroxide, either undergoes fragmentation, dimerization or both, according to the following [4]:

$$C_6H_5CH_2-O-R \rightarrow C_6H_5-\overset{\bullet}{C}H-O-R \nearrow \quad C_6H_5-CHO + R\cdot$$
$$\searrow \quad [C_6H_5-CH-O-R]_2$$
$$\qquad\qquad\qquad | \qquad\qquad\qquad (2)$$

A benzyl sulphide when treated in the same way, gives a free radical II (X = S) which, probably due to the sulphur atom, does not undergo fragmentation but only dimerizes [2,5]:

$$C_6H_5-CH_2-S-R \rightarrow C_6H_5-\overset{\bullet}{C}H-S-R \rightarrow \begin{array}{c} C_6H_5-CH-S-R \\ | \\ C_6H_5-CH-S-R \end{array} \qquad (3)$$

The question arises, which hydrogen is removed from the benzyl compound? As the most stable radical is preferentially formed, it is clear that the hydrogen abstraction is mainly from the $CH_2$-group between the phenyl group and the hetero atom, the extensively delocalized odd electron in II resulting in a resonance-stabilized radical.
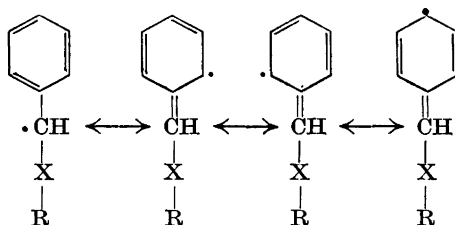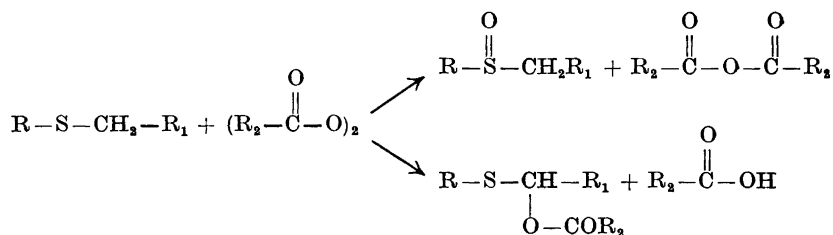


In the case of benzyl sulphides, the stabilization of the radical II (X = S) might also be explained by the following mesomeric interaction [6,7].

$$C_6H_5-\overset{\bullet}{C}H-\overset{..}{\underset{..}{S}}-R \longleftrightarrow C_6H_5-CH=\overset{\bullet}{\underset{..}{S}}-R$$
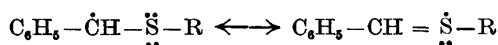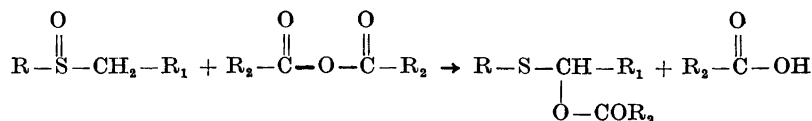
The reaction of certain acyl peroxides with simple ethers was first investigated by Cass [8-10] who, by studying the decomposition of benzoyl peroxide in diethyl ether, isolated 1-ethoxy-1-benzoyloxy ethane and benzoic acid as main products. The kinetics of this reaction has also been elucidated by Nozaki and Bartlett [11] and the mechanism recently worked out by Denney and Feig [12]. It may be concluded from these investigations that a hydrogen is preferentially removed from the $\alpha$-carbon and that the intermediate radical formed does not undergo any fragmentation whatsoever.

Recently, Johnston and Williams [13] have studied the reaction of $t$-butyl peroxide with aromatic compounds with side chains and found that toluene, for instance, gives dibenzyl smoothly with a stabilized benzyl-type radical as an intermediate. However, anisole gives only polymeric material, probably due to the fact that the intermediate free radical is extremely short-lived and not stabilized by resonance. Sosnovsky [14] and the present authors [15] have studied the reaction between $t$-butyl perbenzoate and di-$n$-butyl ether in the presence of cuprous salts.

Apart from the studies made recently by us [2,5] only one other investigation of the reaction between peroxides and sulphides has been reported up till now. Horner and Jürgens [16] found as late as 1956 that diacyl peroxides with sulphides give the corresponding sulphoxide and the $\alpha$-acyloxy compound of the sulphide. The peroxide is thereby converted into the anhydride and acid, respectively, according to the following formulas:

$$R-S-CH_2-R_1 + (R_2-\overset{\overset{\displaystyle O}{\|}}{C}-O)_2 \nearrow \quad R-\overset{\overset{\displaystyle O}{\|}}{S}-CH_2R_1 + R_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_2$$

$$\searrow \quad R-S-\underset{\underset{\displaystyle O-COR_2}{|}}{CH}-R_1 + R_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

The Pummerer reaction [17-19] between a sulphoxide and an anhydride gives also an acyloxy compound:

$$R-\overset{\overset{\displaystyle O}{\|}}{S}-CH_2-R_1 + R_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_2 \rightarrow R-S-\underset{\underset{\displaystyle O-COR_2}{|}}{CH}-R_1 + R_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$
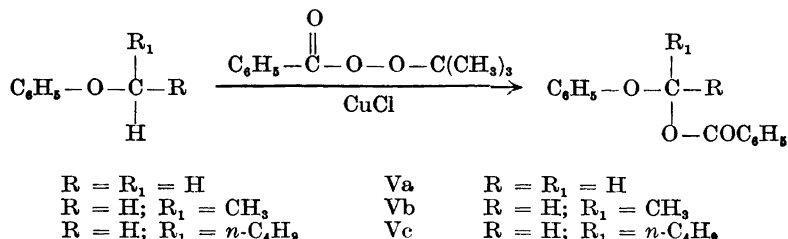
To complete the project previously outlined [20] we describe in this paper the results of the reaction of $t$-butyl perbenzoate with simple ethers and thioethers. The general idea of our earlier investigations has been to show that the presence of cuprous chloride is of primary importance in the decomposition rate of the perester as well as for stabilizing the formed radical of the substrate. We have confirmed earlier results that $t$-butyl perbenzoate decomposes slowly on heating alone, whereas the presence of cuprous chloride greatly accelerates rupture of the oxygen-oxygen bond. The stabilizing effect is easily understood by referring to eqns. 1—3. As has been pointed out by Cass for the case of simple ethers and by Horner for the case of sulphides the corresponding ether or sulphide radicals are relatively stable and the effect of the cuprous salt is supposed to prevent dimerization.

In our investigations, a dilute perbenzoate solution was added to the preheated substrate admixed with catalytic amounts of cuprous chloride and the consumption of the peroxy compound was then followed by titration or by infra-red measurements. Generally, the substrate was kept at a rather low

temperature in order to prevent decomposition of the benzoyloxy compound. After the benzoic acid, invariably formed, was extracted, the remainder was fractionated giving the acylals.
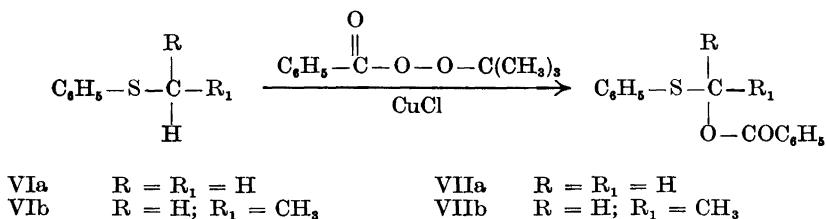
Johnston's and William's result [13] that anisole when heated with *t*-butyl peroxide, does not give any well-defined products is the only published example which we know where complications arise. We have therefore also investigated a series of compounds of similar type.

*Phenyl alkyl ethers.* Anisole IVa and phenetole IVb give the corresponding benzoyloxy compound Va and Vb smoothly.

$$C_6H_5-O-\underset{\underset{H}{|}}{\overset{\overset{R_1}{|}}{C}}-R \quad \xrightarrow[\text{CuCl}]{C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-C(CH_3)_3} \quad C_6H_5-O-\underset{\underset{O-COC_6H_5}{|}}{\overset{\overset{R_1}{|}}{C}}-R$$

| | |
|---|---|
| IVa | R = R$_1$ = H |
| IVb | R = H; R$_1$ = CH$_3$ |
| IVc | R = H; R$_1$ = *n*-C$_4$H$_9$ |

| | |
|---|---|
| Va | R = R$_1$ = H |
| Vb | R = H; R$_1$ = CH$_3$ |
| Vc | R = H; R$_1$ = *n*-C$_4$H$_9$ |

In the case of anisole, only one structure is possible as the benzoyloxy group does not enter a common non-activated aromatic substrate. The position of the benzoyloxy group in Vb was established by hydrolysis which gave acetaldehyde. Furthermore we were unable to isolate any benzoate when phenyl *iso*propyl ether was used as substrate. As cumene [21] and 2-phenylbutane [22] do give the benzoyloxy compound, steric hindrance is apparently not the cause of this failure. We are rather inclined to believe that the instability of the benzoate formed causes it to decompose during the reaction. When phenyl *n*-amyl ether IVc was used as the substrate the benzoate Vc was obtained in rather low yield, and attempts to purify the compound for anlyses were futile.

*Phenyl alkyl sulphides* were also investigated and from phenyl methyl sulphide VIa and phenyl ethyl sulphide VIb the corresponding benzoates VIIa and VIIb were obtained.
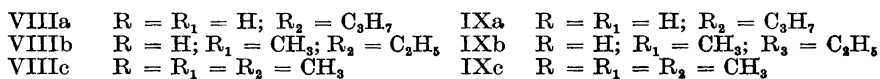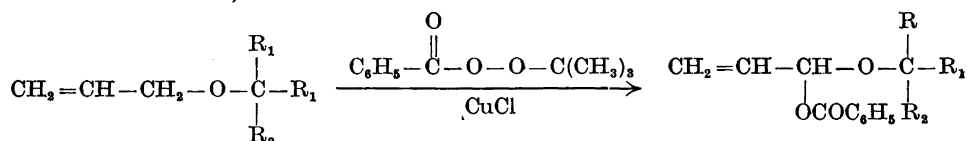
$$C_6H_5-S-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-R_1 \quad \xrightarrow[\text{CuCl}]{C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-C(CH_3)_3} \quad C_6H_5-S-\underset{\underset{O-COC_6H_5}{|}}{\overset{\overset{R}{|}}{C}}-R_1$$

| | |
|---|---|
| VIa | R = R$_1$ = H |
| VIb | R = H; R$_1$ = CH$_3$ |

| | |
|---|---|
| VIIa | R = R$_1$ = H |
| VIIb | R = H; R$_1$ = CH$_3$ |

Phenyl *iso*propyl sulphide did not give any isolable benzoyloxy compound either. In the case of phenyl *n*-amyl sulphide (VI R = H; R$_1$ = *n*—C$_4$H$_9$) all attempts to purify the formed benzoate were futile. Decomposition occurred

and benzoic acid was split off, giving an unsaturated sulphide according to the following scheme:

$$C_6H_5-S-CH-CH_2-CH_2-CH_3 \xrightarrow{\Delta} C_6H_5-S-CH=CH-CH_2-CH_2-CH_3$$
$$|$$
$$O-COC_6H_5$$
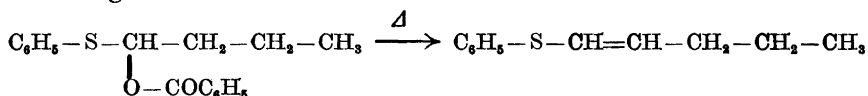
Phenyl allyl sulphide did react normally with *t*-butyl perbenzoate, infra-red measurements showing a benzoate to be present in the crude product, but all attempts to get a pure neutral product by distillation proved futile.

*Di-alkyl ethers.* All ethers except those having only one hydrogen on the α-carbons gave the corresponding benzoyloxy compound smoothly. Thus *t*-butyl *sec*-butyl ether and di-*iso*propyl ether gave no benzoate even when the reaction temperature was low. Quantitative yields of benzoic acid were isolated, indicating that the acylal formed is unstable and decomposes even at a moderate temperature. The allylic ethers investigated gave the benzoyloxy compound rapidly and although a few of them are quite unstable in air it was possible to get them in a pure state. *n*-Butyl allyl ether VIIIa thus gave the benzoate IXa,

$$CH_2=CH-CH_2-O-\underset{\underset{R_2}{|}}{\overset{\overset{R_1}{|}}{C}}-R_1 \xrightarrow[\text{CuCl}]{C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-C(CH_3)_3} CH_2=CH-\underset{\underset{OCOC_6H_5}{|}}{\overset{\overset{R}{|}}{CH}}-O-\underset{\underset{R_2}{|}}{\overset{}{C}}-R_1$$

| VIIIa | R = R$_1$ = H; R$_2$ = C$_3$H$_7$ | IXa | R = R$_1$ = H; R$_2$ = C$_3$H$_7$ |
| VIIIb | R = H; R$_1$ = CH$_3$; R$_2$ = C$_2$H$_5$ | IXb | R = H; R$_1$ = CH$_3$; R$_2$ = C$_2$H$_5$ |
| VIIIc | R = R$_1$ = R$_2$ = CH$_3$ | IXc | R = R$_1$ = R$_2$ = CH$_3$ |

*sec*-butyl allyl ether VIIIb the corresponding acylal IXb and finally *t*-butyl allyl ether VIIIc the corresponding benzoyloxy compound IXc. As the allylic position is more activated than the other α-position, the hydrogen is preferentially abstracted from here giving the corresponding acylal. Thus there is little doubt about the position of the benzoyloxy group in the case of IXa and IXc. However, some uncertainty was to be expected with respect to the *sec*-butyl allyl ether. As it is well-known that reactivity increases with decreasing C—H bond strength and increasing resonance stabilization of the radical produced, since hydrogen atoms are always substituted at rates which are in the order primary < secondary < tertiary, the tertiary hydrogen of the *sec*-butyl group could have been substituted besides one of the allylic hydrogens. However, the product isolated is certainly IXc as we have never been able to prepare a tertiary benzoate, though possibly the primary product could have been a mixture.
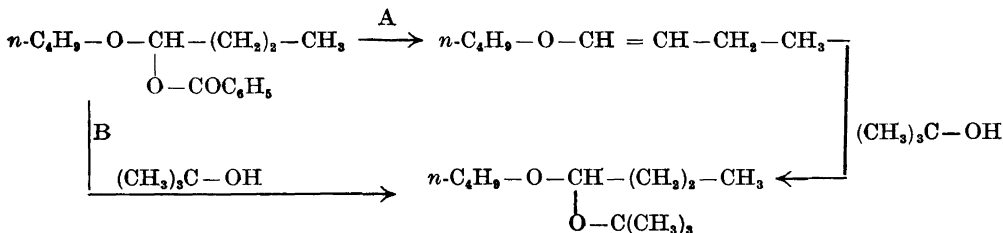
With di-*n*-butyl ether we were able to isolate the α-benzoyloxy compound X in 50 % yield [15] after a nine hours long reaction time.

$$CH_3-(CH_2)_3-O-\underset{\underset{OCOC_6H_5}{|}}{CH}-(CH_2)_2-CH_3$$
$$X$$
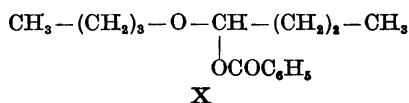
A careful investigation of the fore-runs revealed that a 15 % yield of an
a-butoxy compound XI* also had been formed.

$$CH_3-(CH_2)_3-O-CH-(CH_2)_2-CH_3$$
$$OR$$
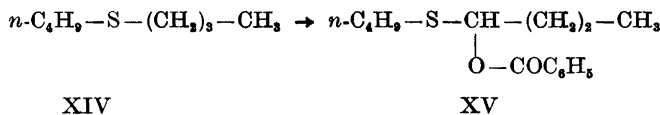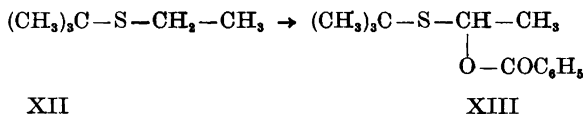
XIa  R $= n\text{-}C_4H_9$  ;  XIb  R $= t\text{-}C_4H_9$
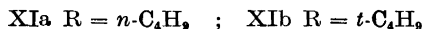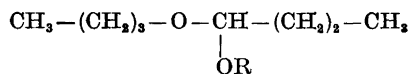
The benzoyloxy groups is supposed to substitute an a-hydrogen first
which compound then reacts with t-butanol to give the acetal XIb. We
have partly confirmed this as X when heated with t-butanol gives the t-butoxy
compound XIb. By heating X for 24—30 h benzoic acid is eliminated but an
unsaturated ether is not found and only ill defined products were formed.
This indicates that the Sosnovsky mechanism (route A) might be an over
simplification and before his interpretation is accepted a reinvestigation is
needed.

$$n\text{-}C_4H_9-O-CH-(CH_2)_2-CH_3 \xrightarrow{\ A\ } n\text{-}C_4H_9-O-CH=CH-CH_2-CH_3$$

O$-$COC$_6$H$_5$

B

(CH$_3$)$_3$C$-$OH

$$n\text{-}C_4H_9-O-CH-(CH_2)_2-CH_3$$
$$O-C(CH_3)_3$$

(CH$_3$)$_3$C$-$OH

Since it has been shown in an earlier investigation [2] that a benzoyloxy group
is displaced by an alkoxy group, route B might be considered as an alternative
to route A.

*Di-alkyl sulphides.* t-Butyl ethyl sulphide XII and di- n-butyl sulphide
XIV smoothly give the corresponding benzoyloxy compound XIII and XV.

$$(CH_3)_3C-S-CH_2-CH_3 \rightarrow (CH_3)_3C-S-CH-CH_3$$
$$O-COC_6H_5$$

XII                                    XIII

$$n\text{-}C_4H_9-S-(CH_2)_3-CH_3 \rightarrow n\text{-}C_4H_9-S-CH-(CH_2)_2-CH_3$$
$$O-COC_6H_5$$

XIV                                    XV

When t-butyl *iso*propyl sulphide was reacted with t-butyl perbenzoate in the
presence of cuprous chloride, quantitative yields of benzoic acid was isolated.
In contradistinction to the findings with the corresponding oxygen analog,
the benzoyloxy group in XV is not displaced by the alkoxy group when

* *Added in proof:* Lawesson and Berglund, (*Arkiv Kemi* (1961), *in press*) have shown
that this acetal is XIa,

heated with $t$-butanol or any other alcohol. Furthermore, when heated in benzene, benzoic acid is split off and an unsaturated sulphide XVI is formed.

$$CH_3(CH_2)_3-S-CH-(CH_2)_2CH_3 \xrightarrow{\Delta} CH_3(CH_2)_3-S-CH=CH-CH_2CH_3$$
$$\overset{|}{O}-CO-C_6H_5 \qquad\qquad XVI$$
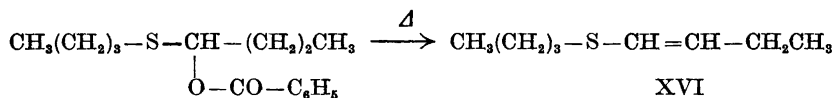
## EXPERIMENTAL

The reactions described were carried out in an atmosphere of nitrogen. All ethers and sulphides were distilled prior to use. Commercial (Light) $t$-butyl perbenzoate ($n_D^{20} = 1.5000$) was used. The progress of the reactions was followed either by titration according to the method of Silbert and Swern [23] or by IR-measurements. The infra-red spectra were recorded either on a Perkin-Elmer Model 21, double beam spectrophotometer or on a Perkin-Elmer Infracord. The analyses were made by Alfred Bernhardt, Mülheim (Ruhr), and The Analytical Department, Uppsala University. Boiling and melting points are uncorrected.

### Starting materials

*Preparation of ethers and sulphides.* The anisole, phenetole, $n$-butyl ether and iso-propyl ether used were of commercial grade. Phenyl—S—R (R = CH$_3$, C$_2$H$_5$, $i$-C$_3$H$_7$, CH$_2$—CH=CH$_2$, $n$-C$_5$H$_{11}$) were prepared by adding the appropriate chloride to sodium thiophenolate [24]. Phenyl—O—R′(R′ = $i$-C$_5$H$_7$, $n$-C$_9$H$_{11}$) were made by reacting the appropriate chlorides with sodium phenolate. $t$-Butyl—S—R″ (R″ = C$_2$H$_5$, $i$-C$_3$H$_7$) was prepared in a manner analogous to the synthesis of phenyl $t$-butyl sulphide by Ipatieff *et al.*[25] $t$-Butyl—O—R‴ (R‴ = $sec$—C$_4$H$_9$, $i$-C$_4$H$_9$) was prepared according to Lawesson and Yang [26] whilst allyl—O—R″″ (R″″ = $n$-C$_4$H$_9$, $sec$-C$_4$H$_9$) according to Talley *et al.*[27] Di-$n$-butyl sulphide was prepared by adding $n$-butyl bromide to $n$-butyl mercaptid and $t$-butyl allyl ether according to the general method by Norris and Rigby [28].

*Preparation of t-butyl-sec-butyl ether.* $t$-Butylperbenzoate (0.3 mole) in 200 ml of ether was slowly added to a vigorously stirred solution of $sec$-butylmagnesium bromide (0.5 mole in 200 ml of ether) at 0°—5°. Stirring was continued overnight, after which the mixture was poured into ice-water containing hydrochloric acid. After extraction with ether, washing with 2 M NaOH and water, the ether phase was dried. Distillation gave 21 g (54 %) of $t$-butyl $sec$-butyl ether $n_D^{20} = 1.3972$, b.p. 114—115°. (C 73.40; H 14.08. Calc. C 73.78; H 13.92.)

*Preparation of t-butyl isobutyl ether.* $t$-Butyl perbenzoate (0.4 mole) in 100 ml of ether was dropped to a Grignard reagent (0.6 mole) in 500 ml of ether at 0—5°. The work-up was performed as in the case of $t$-butyl $sec$-butyl ether. 30 g, yield 58 %, b.p. 110—111°C, $n_D^{20} = 1.3912$. (C 73.72; H 14.00. Calc. C 73.78; H 13.92.)

*Preparation of t-butyl allyl ether.* 174 g of allyl alcohol was added to a cooled mixture of 29.4 ml conc. sulphuric acid and 296 ml of water. The flask was warmed to 70° and $t$-butyl alcohol (30 ml) was added dropwise. The product was distilled slowly, the distillation temperature being maintained at 80° by the occasional addition of $t$-butanol, a total of 105 ml being added. The product was washed 15 times with water. When all the alcohol was removed the two layers separated immediately. The product was dried over Na$_2$SO$_4$, warmed with sodium to reflux temperature for one hour and distilled. 28 g of $t$-butyl allyl ether, b.p. 100°, $n_D^{20} = 1.4078$, was obtained. [Lit.[27] $n_D^{20} = 1.4011$].

*Preparation of t-butyl ethyl sulphide.* Into an ice-cold mixture of 220 g of sulphuric acid and 75 ml of water in a 500 ml flask equipped with a stirrer, gas-inlet tube and a reflux condenser was bubbled 15 g (0.26 mole) of *iso*butylene, followed by the dropwise addition of 15 g (0.21 mole) of ethyl mercaptan. The mixture was allowed to stand in the ice bath for half an hour whereupon crushed ice was added. The mixture was extracted three times with ether. The combined ether extracts were washed with 2 M NaOH and water

until neutral, dried over sodium sulphate and the ether driven off. 14 g (57 %) of the sulphide, b.p. 120°, $n_D^{20}$ = 1.4429, was obtained. [Lit. values [29], b.p. 120.4°, $n_D^{25}$ = 1.4390].

*Preparation of t-butyl isopropyl sulphide.* 35 g (0.61 mole) of *iso*butylene was added to a mixture of 220 g of conc. $H_2SO_4$ and 75 g of water in the apparatus described above, followed by 30 g (0.4 mole) of *iso*propyl mercaptan. The neutral and dry product was distilled giving 37 g (70 %) of the sulphide, b.p. 129—131°, $n_D^{20}$ = 1.4412.

Socony-Vacuum Laboratories report b.p. 40—42°/31—32 mm Hg.

## Reactions with *t*-butyl perbenzoate

*The reaction with anisole.* To a flask containing 50 ml (0.5 mole) of redistilled anisole ($n_D^{20}$ = 1.5178), 300 ml of dry benzene and 0.1 g of CuCl, was added 40 ml (0.2 mole) of *t*-butyl perbenzoate during ½ h. The mixture was maintained at gentle reflux for 23 h, when it was extracted with 2 M NaOH and washed with water till neutral. The alkaline washings gave 11.5 g of benzoic acid. Distillation of the dried organic solution gave 34 g of anisole, b.p. 60—65° / 20 mm Hg ($n_D^{20}$ = 1.5180), 2.3 g of benzoic acid, b.p. 80—100° / 0.1 mm Hg and the benzoyloxy compound, b.p. 135—140°/0.1 mm Hg. The last fraction solidified and part of it was recrystallized from petroleum ether. M.p. 35—36°. Yield 23 %. Distillation residue, 13 g. (C 73.74; H 5.35. Calc. C 73.67; H 5.30.)

*The reaction with phenetole.* 40 ml (0.2 mole) of *t*-butyl perbenzoate in 50 ml of benzene was added dropwise to 65 g (0.53 mole) of redistilled phenetole ($n_D^{20}$ = 1.5065) in 300 ml of benzene and 0.1 g of CuCl. The solution was maintained at gentle reflux for 20 h. After washing and drying in the usual manner 9.8 g of benzoic acid precipitated out. After the benzene and excess of phenetole had distilled off, 18 g (37 %) of *a*-benzoyloxy phenetole, b.p. 108—110°/0.05 mm Hg, $n_D^{20}$ = 1.5512, was obtained. (C 74.31; H 5.80. Calc. C 74.36; H 5.83.)

*Hydrolysis.* To a 4 g sample of Vb was added 50 ml of methanol and hydrochloric acid in slight excess. The mixture was allowed to stand for half an hour at 20° whereupon a solution of 2,4-dintrophenylhydrazine in hydrochloric acid was added. The mixture was shaken for 60 min, cooled and filtered. Acetaldehyde 2,4-dinitrophenyl hydrazone was obtained in 71 % yield, m.p. 165—167° after recrystallization from ethanol. Mixed melting point with an authentic sample of the acetaldehyde derivative showed no depression. A strong smell of phenol was apparent in the aqueous phase.

*The reaction with phenyl methyl sulphide.* 40 ml (0.2 mole) of *t*-butyl perbenzoate was added dropwise during 50 min. to a mixture of 150 ml of benzene, 35 g (0.28 mole) of redistilled thioanisole ($n_D^{20}$ = 1.5868) and 0.1 g of CuCl maintained at 70—75°. The reaction was complete after 5.5 h. The alkaline washings gave 3.4 g of benzoic acid. After drying and distilling off the benzene and excess of thioanisole, 23 g (47 %) of the benzoyloxy compound, b.p. 150—155°/0.15 mm Hg, $n_D^{20}$ = 1.5978, was obtained. Horner and Jürgens [16] had a b.p. of 145—146°/0.5 mm Hg.

*The reaction with phenyl ethyl sulphide.* 200 ml of benzene, 39 g (0.28 mole) of redistilled phenyl ethyl sulphide ($n_D^{20}$ = 1.5669) and 0.1 g of CuCl were placed in the reaction flask and maintained at an oil bath temperature of 110°. 30 ml (0.15 mole) of *t*-butylperbenzoate was added dropwise during 55 min. After 2.25 h, the reaction was complete. The mixture was worked up as usual, giving 4.2 g of benzoic acid from the alkaline washings. Distillation gave 24 g (62 %) of the benzoyloxy compound, b.p. 121—122°/0.1 mm Hg, $n_D^{20}$ = 1.5823. (C 69.90; H 5.58; S 12.36. Calc. C 69.75; H 5.46; S 12.39.)

*The reaction with phenyl n-amyl sulphide.* *t*-Butyl perbenzoate (0.2 mole) was added during 30 min. to a refluxing mixture of 150 ml of benzene, 68 g (0.38 mole) of phenyl *n*-amyl sulphide ($n_D^{20}$ = 1.5397) and 0.1 g of cuprous chloride. The reaction was complete after heating for 13 h at an oil bath temperature of 100°. The alkaline washings gave 6.3 g of benzoic acid. After distilling off the benzene and excess of sulphide at reduced pressure, the benzoyloxy compound decomposed at a distilling temperature of 100—120°/0.1 mm Hg, and 27 g of distillate were collected in the receiver. The distillate was taken up in

ether, washed with 2 M NaOH, then with water until neutral and dried. 9.1 g of benzoic acid was recovered from the alkaline washing. Distillation of the ether phase gave 12.5 g (35 %) of the unsaturated sulphide, b.p. 72—73°/0.3 mm Hg, $n_D^{20} = 1.5650$. (C 74.20; H 7.76; S 17.83. Calc. C 74.13; H 7.92; S 17.96.)

*The reaction with t-butyl isobutyl ether.* 0.1 mole of t-butyl perbenzoate was added during 20 min. to a mixture of 200 ml of benzene, 23 g (0.177 mole) of redistilled t-butyl isobutyl ether ($n_D^{20} = 1.3912$) and 0.1 g of cuprous chloride, maintained at an oil bath temperature of 120°. The reaction was complete, after 16 h, whereupon the mixture was worked up, giving 7 g of benzoic acid. The neutral and dry benzene solution was distilled giving 12 g of t-butyl isobutyl ether and 8.3 g (33 %) of the benzoyloxy compound, b.p. 53°/1.5 mm Hg, $n_D^{20} = 1.5042$. (C 71.17; H 8.60. Calc. C 71.97; H 8.86.)

*The reaction with n-butyl allyl ether.* t-Butyl perbenzoate (0.2 mole) was added dropwise to 51 g (0.45 mole) of n-butyl allyl ether and 0.1 g of cuprous chloride in 300 ml of benzene, maintained at 95°. Th reaction mixture was heated for 2 h, after which time no perester was present. Benzoic acid (12.5 g) was recovered from the alkaline washings. The neutral and dry benzene solution was distilled giving 16.6 g (35 %) of the benzoyloxy compound, b.p. 96—99°/0.05 mm Hg, $n_D^{20} = 1.4792$. (C 71.56; H 7.77. Calc. C 71.77; H 7.74.)

*The reaction with sec-butyl allyl ether.* t-Butyl perbenzoate (0.2 mole) was added during 30 min. to a refluxing mixture of 300 ml of benzene, 48 g (0.42 mole) of sec-butyl allyl ether and 0.1 g of cuprous chloride. After refluxing for 5.5 h at an oil bath temperature of 100°, the mixture was worked up as usual giving 7.5 g of benzoic acid. After distilling off the benzene and excess sec-butyl allyl ether, 20 g (43 %) of the benzoyloxy compound, b.p. 84—86°/0.05 mm Hg, $n_D^{20} = 1.4968$, was obtained. (C 71.27; H 7.68. Calc. C 71.77; H 7.74.)

*The reaction with t-butyl allyl ether.* To 28 g (0.24 mole) of t-butyl allyl ether ($n_D^{20} = 1.4078$) and 0.1 g of cuprous chloride in 150 ml dry benzene, maintained at an oil bath temperature of 105°, t-butyl perbenzoate (0.1 mole) in 25 ml benzene was added during 35 min. After heating for 2 h, titration showed that no perester was present. The mixture was worked up as usual, yielding 0.5 g benzoic acid. Fractionation gave 17 g (74 %) of the benzoyloxy compound, b.p. 94—96°/0.3 mm Hg, $n_D^{20} = 1.4863$. (C 71.24; H 7.45; Calc. C 71.77; H 7.74.)

*The reaction with di-n-butyl ether.* Into a flask containing 300 ml of dry benzene was introduced 52 g (0.4 mole) of di-n-butyl ether ($n_D^{20} = 1.4205$) and 0.1 g of cuprous chloride. t-Butyl perbenzoate (0.2 mole) dissolved in 50 ml of benzene was added during 10 min. and the mixture maintained at 90° for 9 h. After washing with 2 M sodium hydroxide and water in the usual way, the organic phase was dried over magnesium sulphate. The alkaline washings yielded 11 g of benzoic acid. The organic phase was fractionated under vacuum to give 6 g (15 %) of a-butoxy n-butyl ether, b.p. 59—60°/0.3 mm Hg, $n_D^{20} = 1.4182$. (C 71.23; H 12.75. Calc. C 71.23; H 12.95). Sosnovsky gives for 1-n-butoxy-1-t-butoxy butane b.p. 100°/17 mm Hg, $n_D^{25} = 1.4148$.

25 g (50 %) of a higher boiling fraction consisting of a-benzoyloxy di-n-butyl ether, b.p. 97—98°/0.3 mm Hg, $n_D^{20} = 1.4837$, was then obtained. (C 72.25; H 8.91. Calc. C 71.97; H 8.86.)

*Decomposition of a-benzoyloxy di-n-butyl ether in t-butanol.* 21 g (0.084 mole) of the benzoyloxy compound was heated during 15 h at 140° in 18 g (0.24 mole) of t-butanol. The solution was then dissolved in ether and extracted with 2 M NaOH, from which 7.5 g benzoic acid was recovered. The neutral and dry ether solution was fractionated giving 8.5 g (50 %) of the a-t-butoxy di-n-butyl ether, b.p. 92°/10 mm Hg, $n_D^{20} = 1.4183$. (C 71.34; H 13.00. Calc. C 71.23; H 12.95.)

*The reaction with t-butyl ethyl sulphide.* 0.1 mole of t-butyl perbenzoate was added dropwise to a mixture of 200 ml of benzene, 14 g (0.12 mole) of t-butyl ethyl sulphide ($n_D^{20} = 1.4429$) and 0.1 g of cuprous chloride at 125°. After 6.5 h, the reaction was complete and the mixture worked up as usual yielding 5.6 g of benzoic acid. The neutral

and dry benzene solution was distilled giving 12 g (50 %) of benzoate, b.p. 93—95°/0.4 mm Hg, $n_D^{20} = 1.5216$. (C 65.90; H 7.46; S 13.31. Calc. C 65.51; H 7.60; S 13.43.)

*The reaction with di-n-butyl sulphide.* 40 ml (0.2 mole) of *t*-butyl perbenzoate in 50 ml of benzene was added during 40 min. to a mixture of 200 ml of dry benzene, 0.1 g of cuprous chloride and 60 g (0.41 mole) of redistilled di-*n*-butyl sulphide ($n_D^{20} = 1.4540$) at 80°.] After 3 h the mixture was worked up as usual, giving 3.6 g of benzoic acid After distilling off the benzene and the excess of sulphide 35 g (66 %) of the benzoyloxy compound, b.p. 108—109°/0.2 mm Hg, was obtained. (C 67.57; H 8.09; S 11.98. Calc. C 67.63; H 8.31; S 12.02.)

*Decomposition of a-benzoyloxy di-n-butyl sulphide.* a) 8.5 g (0.032 mole) of *a*-benzoyloxy di-*n*-butyl sulphide was refluxed during 6 h with 30 ml abs. ethanol. The ethanol was then removed under vacuum, the residue taken up in ether and the benzoic acid (3.8 g) extracted with 2 M NaOH. Distillation gave 3 g of a compound, b.p. 76—79°/10 mm Hg, $n_D^{20} = 1.4730$. Horner and Kaiser [17] report b.p. 19.1°/0.3 mm Hg and $n_D^{20} = 1.4750$ for $C_4H_9-S-CH=CH-C_2H_5$.

b) 17 g (0.064 mole) of the benzoyloxy compound was refluxed with 75 ml of *t*-butanol during 9 h and the mixture worked up as above. 7.3 g of the unsaturated sulphide, b.p. 83°/15 mm Hg, $n_D^{20} = 1.4741$, was obtained.

*The reaction of t-butyl perbenzoate with n-butyl allyl sulphide.* 0.2 mole of *t*-butyl perbenzoate was added during 1 h to a mixture of 200 ml of benzene, 53 g (0.4 mole) of redistilled *n*-butyl allyl sulphide and 0.1 g of cuprous chloride, maintained at gentle reflux temperature (80°). The reaction was complete after 2 h. The mixture was worked up as usual, giving 4.3 g of benzoic acid. Fractionation gave 31 g (61 %) of the benzoyloxy compound, b.p. 122—124°/0.3 mm Hg, $n_D^{20} = 1.5380$. (C 66.53; H 6.71; S 12.61. Calc. C 67.17; H 7.25; S 12.79.)

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