

Studies on Peroxy Compounds VII *

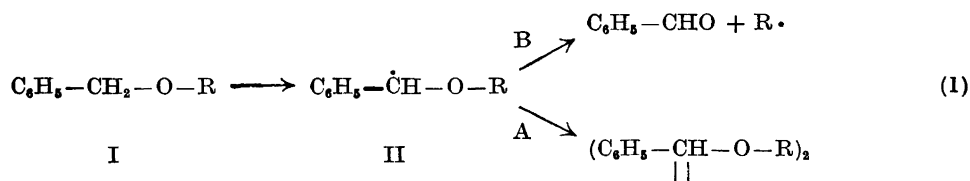
The Copper Salt Catalyzed Decomposition of *t*-Butyl Perbenzoate in the Presence of Benzyl Sulphides

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It has been shown that when *t*-butyl peroxide is decomposed in a benzyl sulphide, the benzyl radical formed dimerizes but no fragmentation is observed. When *t*-butyl perbenzoate is decomposed in the same types of substrates and with catalytic amounts of cuprous chloride present, no dimer but only the corresponding benzoyloxy compound is isolated. Also, when the perester is decomposed in the presence of benzyl alcohol, cuprous chloride has a stabilizing effect giving the dibenzyl acetal of benzaldehyde; without cuprous chloride, benzaldehyde is the sole product. Cuprous chloride has no effect in the case of benzyl mercaptan; dibenzyl disulphide is formed in both reactions. When the benzoyloxy compound of dibenzyl sulphide is heated stilbene is formed.

Recently Huang and coworker¹ showed by decomposing *t*-butyl peroxide in the presence of different benzyl ethers that the generated radical II either dimerizes, undergoes fragmentation or both as follows:

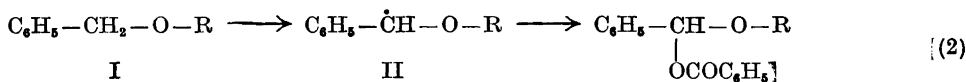


The reaction takes different courses depending upon the group R. As the reaction is not favoured if a very energetic radical R· is formed it is clear that for R = methyl or phenyl dimerization occurs exclusively (route A), thus revealing the high reactivity of the methyl and phenyl radicals. With R = ben-

* Part VI. Lawesson, S.-O. and Gröwall, S. *Acta Chem. Scand.* 14 (1960) 1445.

zyl, only fragmentation according to route B is observed, and with R = *i*-propyl *etc.* both fragmentation and dimerization occur which indicates that these radicals R· (R = C₂H₅, *i*-C₃H₇) are somewhere inbetween the methyl and phenyl ones on one side and benzyl on the other in regard to reactivity and stability.

Lawesson and Berglund^{2,3} have studied the copper salt catalyzed decomposition of *t*-butyl perbenzoate in the presence of benzyl ethers and found that the benzyloxy group is introduced according to the following formulas:



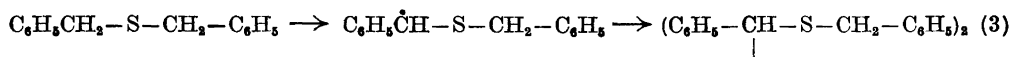
R = C₆H₅, CH₃, *i*-C₃H₇, *t*-C₄H₉

This would indicate that the intermediate radical II (eqn. 2) is in some way stabilized by the presence of the copper salt. No fragmentation or dimerization is observed. When dibenzyl ether is used as a substrate, the dibenzyl acetal of benzaldehyde is isolated, which is a rather unexpected result. We cannot give an exact explanation of this at present, but for reasons which appear in the sequel, a hypothesis is presented (see below).

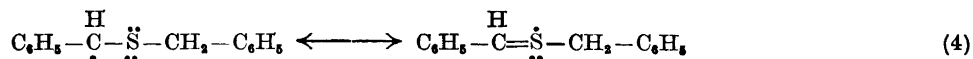
In connection with this it may be mentioned that Lawesson and Busch⁴ have investigated the reaction of acetals with radicals, and it has been shown that dibenzylacetal of benzaldehyde with *t*-butoxy radicals gives benzyl benzoate, benzaldehyde, dibenzyl and *meso*-dihydrobenzoin dibenzoate.

From the work of Lawesson and Berglund^{2,3}, the effect of cuprous salt has been shown to be of certain importance in modifying the course of the reaction when benzylic ethers (I) are transformed into the corresponding radicals (II) and then allowed to react with a benzyloxy radical. Our recently outlined research plan² was therefore continued, and this paper deals with the work on sulphur homologues of the benzyl ethers.

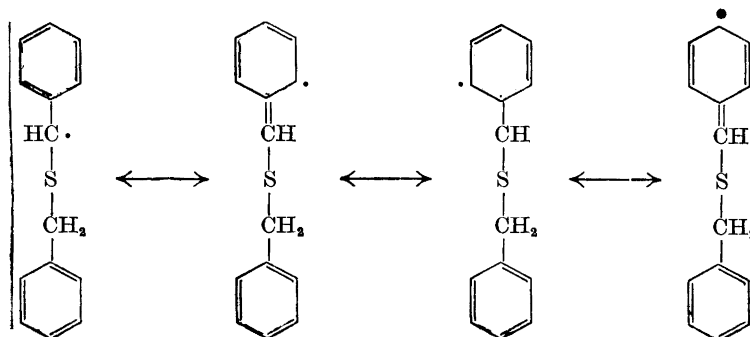
As a free radical of a benzyl ether dimerizes, fragments or both according to eqn. 1, it was of a special interest to ascertain how radicals of benzyl sulphides would react under similar conditions. From the work of Huang *et al.*¹, we know that for benzyl ether [R = benzyl (eqn. 1)] fragmentation is the main process. Therefore, it was logical to start with dibenzyl sulphide as an assumed extreme case. If the sulphide would react in the same way as the corresponding ether, thiobenzaldehyde (as a trimer) and dibenzyl would be the supposed products. We found that the only product, besides starting material, which could be isolated was the dimer according to the following formulas:



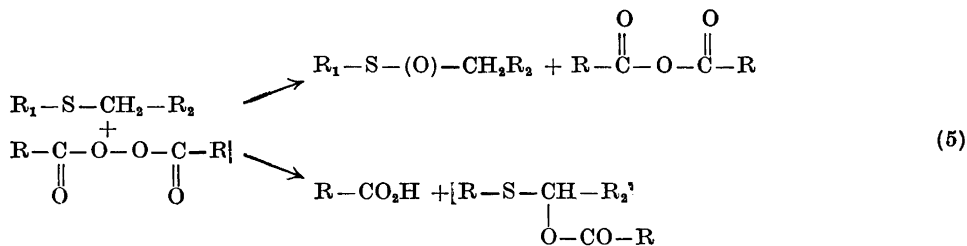
The illustrated difference between benzyl ethers and thio ethers may be explained as follows: sulphur but not oxygen can stabilize an unpaired electron on an adjacent carbon atom, and the following mesomeric interaction would explain the stabilization^{5,6}



The radical is further resonance stabilized, as the odd electron is extensively delocalized as follows:

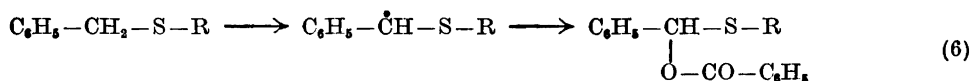


As radicals of benzyl sulphides do not undergo fragmentation but only dimerization, decomposition of peroxides in the presence of benzyl sulphides in contrast to benzyl ethers seems to be a simpler case. A survey of the literature shows that as late as 1957 Horner and coworkers⁷ investigated the reaction between diacyl peroxides and certain sulphides in chloroform whereby benzoic acid, benzoic anhydride, the sulphoxides and, in a few cases, the corresponding benzoyloxy compounds_▲ were isolated.



The only sulphide of benzylic type investigated was dibenzyl sulphide.

In our studies of copper salt catalyzed decomposition of *t*-butyl perbenzoate in the presence of different types of benzyl sulphides, we have found that the benzoyloxy group is introduced on the methylene group according to the following formulas:

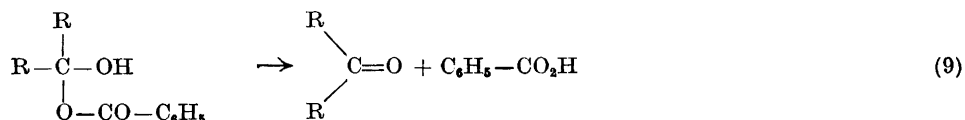
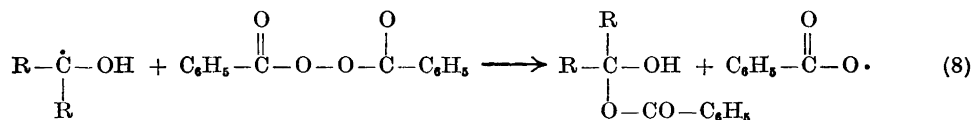
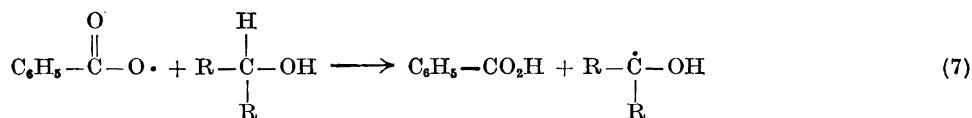


R = CH₃, C₂H₅, *i*-C₃H₇, *i*-C₄H₉, *t*-C₄H₉, C₆H₅

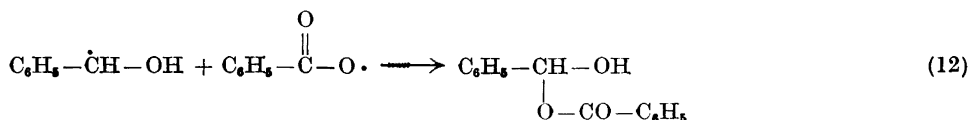
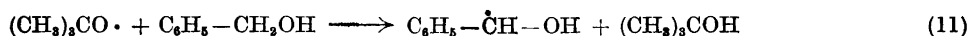
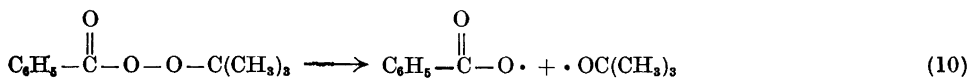
The principle of the method is to add *t*-butyl perbenzoate to a preheated benzene solution of the substrate in the presence of catalytic amounts of cuprous chloride. The temperature is maintained close to 80°C, and the reaction is followed by titration or by observation of the infra-red curves. The *t*-butyl perbenzoate carbonyl group absorbs at 1775 cm⁻¹, and the disappearance of this peak indicates the disappearance of the perester. After the formed benzoic acid is isolated by extraction, the benzoyloxy compound is isolated by extremely careful distillation. Too strong heat *etc.* can cause an immediate decomposition of the benzoyloxy compound, and like their corresponding ether homologues, these compounds are sensitive to air (oxygen); also when stored for six months in a closed vial over nitrogen, benzoic acid precipitates and a strong smell of thiobenzaldehyde is noticed.

In the case of dibenzyl sulphide, the reaction with *t*-butyl perbenzoate is quite normal. After the excess of substrate (dibenzyl sulphide) is distilled off from the reaction mixture, it is demonstrated by IR that the crude, neutral residue contains a benzoate. However, every attempt to purify it by distillation was futile as benzoic acid was always formed. By oxidizing the sulphide with potassium permanganate in glacial acetic acid, the corresponding sulphone was obtained and shown to be the authentic Horner compound⁷. In one experiment when an attempt was made to fractionate the benzoate using a 20 cm high column, *trans*-stilbene and benzoic acid were isolated. The formation of stilbene calls our attention to a paper by Bordwell and Cooper⁸ who isolated *trans*-stilbene from benzyl α -chlorobenzyl sulphone (actually an example of the Ramberg-Bäcklund reaction⁹⁻¹¹). We hope to continue our research on pyrolysis of α -benzoyloxy sulphides to find out more thoroughly the scope of our findings.

As there are some apparent differences between radicals of benzyl ethers and thioethers, we considered it pertinent to make a similar comparison between benzyl alcohol and benzyl mercaptan. With hydroxy compounds, similar investigations have been made earlier and Bartlett and Nozaki's results¹² are wellknown: induced decomposition of benzoyl peroxide in primary and secondary alcohols can be described by the following reaction scheme in agreement with other known radical reactions.



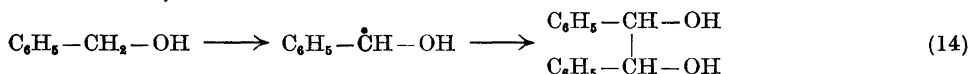
In our case, when *t*-butyl perbenzoate was decomposed in the presence of benzyl alcohol and catalytic amounts of cuprous chloride, the sole product which could be isolated was di-benzylacetal of benzaldehyde. The same product³ was obtained when *t*-butyl perbenzoate was decomposed in the presence of dibenzyl ether. From the work of Urry and coworkers¹³, it is also known that a *t*-butoxy radical abstracts a hydrogen attached to the carbon bearing the —OH; thus the following reaction scheme is postulated:



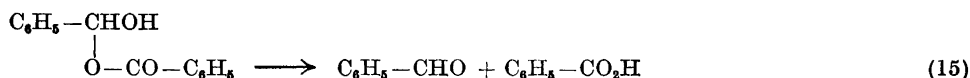
It is not probable that the intermediate radical in eqn. 11 should undergo fragmentation,



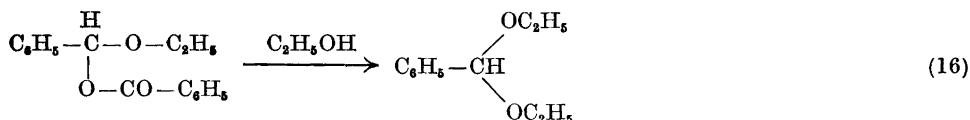
as this (eqn. 13) would lead to a high energy hydrogen radical. As no dimer is isolated, the copper salt stabilizes the radical and thus prevents a possible dimerization;



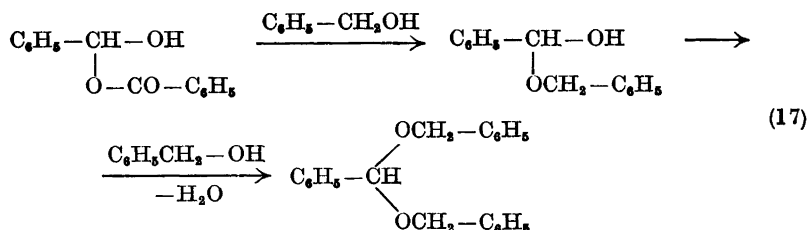
Instead, the stabilized benzyl radical with the benzoyloxy radical gives an acylal (eqn. 12), but the fate of this intermediate is unknown except that the final product has been characterized. As we have not been able to prepare dibenzyl acetal of benzaldehyde from benzaldehyde, benzyl alcohol and benzoic acid, the hypothesis that the acylal decomposes into benzaldehyde and benzoic acid is very uncertain.



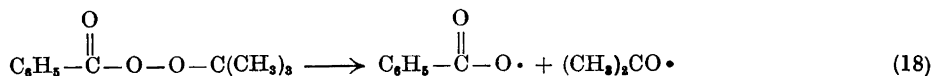
However, as we have now shown that reflux of ethanol with the benzoate of benzyl ethyl ether gives the acetal (eqn. 16),



it would not be out of order to envisage an exchange as follows:



When *t*-butyl perbenzoate is decomposed in benzyl alcohol but with no cuprous chloride present, no high-boiling product was isolated but only benzaldehyde. As *t*-butyl perbenzoate gives different kinds of radicals when heated,

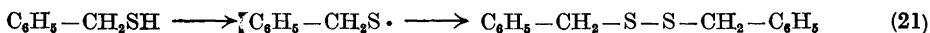


different alternatives are possible and no clear-cut reaction seems to be valid.

From the work of Bartlett *et al.*¹² the proposal of an acylal as an intermediate (*cf.* eqns. 7—9) has been made which then decomposes into the corresponding carbonyl compound and benzoic acid. Since the decomposition of the acylal according to eqn. 15 is prevented when cuprous chloride is present, this would indicate that also at that stage of the reaction transition metal salts are of a certain importance.

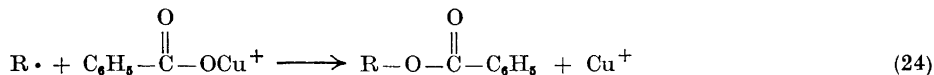
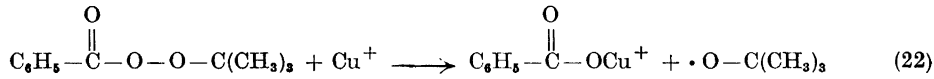
The results of Sosnovsky and Yang¹⁴ are different from ours in this case and their findings that benzaldehyde and benzoic acid are formed, when cuprous bromide is present, have not been observed by us.

In the case of benzyl mercaptan, the only product found was dibenzyl disulphide. The presence of copper salt seems to be of no importance in this case. The *t*-butoxy radical attacks on the S—H bond and not the C—H bond, and the proposal for the formation of disulphide under radical conditions is

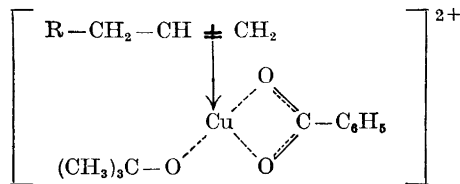


From the results presented in this investigation, the presence of copper salt leads to a different type of reactions. No conventional free radical intermediate seems to exist which would give the dimer, but a mechanism of a concerted type, where the copper salt is of a profound importance. Kharasch and Sosnovsky¹⁵ have shown that in olefins, transition metal salts such as copper or cobalt salts are effective but that zinc or magnesium salts are ineffective. In the case of copper salt, the valence is of no importance as the same

results are obtainable with cuprous or cupric salts. Based on cuprous salt, these authors offer an explanation of the copper salt catalysed decomposition of peresters in the presence of olefins according to the following formulas:



Denney *et al.*¹⁷, on the other hand, working solely with cupric salts suggest a complex between the cupric ion, a benzoyloxy, and a *t*-butoxy radical which then coordinates to the olefin. Probably in a concerted manner, the displacement of the allylic hydrogen by the benzoyloxy group follows the abstraction of the hydrogen atom by the *t*-butoxy radical.



At this point, neither of these mechanisms can be ruled out as two types of complexes might exist. However, in all our reactions, we have used cuprous chloride as a catalyst and have never observed divalent copper in the reaction mixture after the reaction has ended (determined by electron magnetic resonance). Further we have used divalent copper salt in one experiment and even in that case no divalent copper was observed. This would indicate that the Denney-complex in its present form might exist, but that the fate of it and the finer details of the mechanism are still unknown.

EXPERIMENTAL

The reactions between *t*-butyl perbenzoate and the benzyl sulphides were carried out in an atmosphere of dry, oxygenfree nitrogen. All sulphides were distilled prior to use. Commercial (Light) *t*-butyl perbenzoate ($n_D^{20} = 1.5000$) was used in all experiments without further purification. No reaction was considered complete unless the reaction mixture gave a negative peroxide test. The rate of the decomposition of the perester was followed by titration according to the method of Silbert and Swern¹⁸. The infra-red spectra measurements were made on a Perkin-Elmer Model 21, double beam spectrophotometer and an Infracord. The analyses were made by Alfred Bernhardt, Mülheim (Ruhr) and The Analytical Department, Uppsala University. Boiling and melting points are uncorrected.

Starting material

Preparations of sulphides. Benzyl-S-R (R = methyl, ethyl, *i*-propyl, *i*-butyl, *n*-butyl, benzyl) were prepared by adding the corresponding halogen compound to benzyl mercaptide¹⁹. Benzyl *t*-butyl sulphide was prepared in analogy with Ipatieff's *et al.*²⁰ preparation of phenyl *t*-butyl sulphide. Benzyl phenyl sulphide was prepared from thiophenol and benzylchloride²¹.

Benzyl t-butyl sulphide. 250 g of 75 % sulphuric acid was placed in a three-necked 500 ml flask, fitted with a mechanical stirrer, an inlet-tube to the bottom of the flask and a dropping funnel. The flask was surrounded by an ice-water bath. *Isobutylene* was bubbled through the rapidly stirred acid until 44 g (0.8 mole) was absorbed. Then, 43 g (0.35 mole) of benzyl mercaptan was added drop-wise. When the addition was complete, crushed ice was poured down into the flask while the flask still was surrounded by the ice-water bath. The solution was then twice extracted with ether. The ether extract was washed with water, alkali and water till neutral, then dried over anhydrous sodium sulphate and distilled. B.p. 114–115°C/10 mm Hg, $n_D^{20} = 1.5283$, Weight 54.5 g, Yield 87 %. Lit.²² report b.p. 115–116°C/15 mm Hg.

Experiments

The reaction of t-butyl perbenzoate and benzyl phenyl sulphide. A 500 ml three-necked flask was fitted with a stirrer, a dropping funnel and a reflux condenser, the top of which was connected to a gas collector. 200 ml of anhydrous benzene, 0.1 g of cuprous chloride and 37 g (0.185 mole) of benzyl phenyl sulphide (m.p. 40–42°C) were placed in the flask. The system was swept with nitrogen gas, and the flask was maintained at an oil bath temperature of 80°C. 20 ml (0.1 mole) of *t*-butyl perbenzoate in 50 ml of benzene was added dropwise during half an hour. A blue colour appeared rapidly, and the reaction progress was followed by titration of the peroxy compound in the following way: To a 2 ml sample of the solution were added 2 ml of a saturated sodium iodide solution and 10 ml of glacial acetic acid containing a trace of ferric chloride. The final solution was allowed to stand in the dark for 10 min, 50 ml of water was added, and then the iodine liberated was titrated with 0.1 M sodium thiosulphate. No gas evolution was observed. After 3.5 h, the reaction was complete. The solution was washed with a 2 M NaOH solution. The benzene phase was then washed with water until neutral and dried over sodium sulphate. The alkaline solution was acidified with 2 M HCl. The precipitated benzoic acid was filtered off, dried and weighed (1.3 g). From the organic phase, the benzene was removed under reduced pressure. In this and all following distillations, pure nitrogen was drawn through the capillary. The excess benzyl phenyl sulphide was first collected, b.p. 90–105°C/0.1 mm Hg. The benzyloxy compound was then collected at 165–170°C/0.05 mm Hg. The compound solidified, and part of it was recrystallized from ethanol and petroleum ether. The melting point was 64.5–65.5°C. 13.5 g. Yield 42 %. (Found: C 75.16; H 5.24; S 9.90. Calc. for $C_{26}H_{16}O_2S$ (320.19): C 74.99; H 5.03; S 9.99).

The reaction of t-butyl perbenzoate and benzyl methyl sulphide. 0.2 mole of *t*-butyl perbenzoate were added dropwise during 35 min to a refluxing benzene solution (300 ml), containing 53 g (0.375 mole) of redistilled benzyl methyl sulphide ($n_D^{20} = 1.5582$) and 0.1 g of cuprous chloride. The reaction was complete after 3 h at an oil bath temperature of 80°C. No gas was collected. The blue solution was extracted with a 2 M NaOH solution, washed with water until neutral and dried over sodium sulphate. From the alkaline washings 5.2 g of benzoic acid were obtained. After the solvent had been removed from the organic phase the residue was distilled and gave 30 g of the starting compound, b.p. 70–75°C/0.3 mm Hg. The benzyloxy compound was obtained at b.p. 140–145°C/0.1 mm Hg. Weight 39 g. Yield 76 %. The benzyloxy compound crystallized immediately and part of it was recrystallized from petroleum ether. M.p. 44–46°C. (Found: C 69.49; H 5.46; S 12.27. Calc. for $C_{15}H_{14}O_2S$ (258.22): C 69.79; H 5.42; S 12.39).

The reaction of t-butyl perbenzoate and benzyl ethyl sulphide. *t*-Butyl perbenzoate (0.2 mole) in 50 ml of anhydrous benzene was added dropwise to 65 g (0.43 mole) of benzyl ethyl sulphide ($n_D^{20} = 1.5508$) and 0.1 g of CuCl in 300 ml benzene, kept at an oil bath temperature of 80°C. After 2 h, the reaction was complete and no gas evolution was observed. The work-up was performed as above. The alkaline solution gave 4.5 g benzoic acid. Distillation of the organic phase first gave benzyl ethyl sulphide ($n_D^{20} = 1.5512$) 39 g and then the benzoate, b.p. 140–150°C/0.3 mm Hg. Weight 29 g. Yield 53 %. The benzyloxy compound crystallized, and part of it was recrystallized from petroleum ether. M.p. 29–32°C. (Found: C 70.73; H 6.03; S 11.71. Calc. for $C_{16}H_{16}O_2S$ (272.23): C 70.57; H 5.92; S 11.75).

The reaction of t-butyl perbenzoate and benzyl i-propyl sulphide. A flask containing 200 ml of anhydrous benzene, 0.1 g of CuCl and 40 g (0.28 mole) of redistilled benzyl *i*-propyl sulphide ($n_D^{20} = 1.5393$) was maintained at an oil bath temperature of 70°C. 0.1 mole of *t*-butyl perbenzoate in 25 ml of benzene was added during 15 min. Titration showed that the reaction was almost immediately complete, and the reaction mixture was cooled. The alkaline washings gave 3.5 g of benzoic acid. The neutral benzene solution was dried and the benzene and excess of sulphide was removed under reduced pressure. The rest solidified in contact with cold petroleum ether. After recrystallization the melting point was 28–29°C. Weight: 8 g. Yield 28 %. (Found: C 71.16; H 6.27; S 11.12. Calc. for $C_{17}H_{18}O_2S$ (286.24): C 71.31; H 6.34; S 11.17).

The reaction of t-butyl perbenzoate and benzyl i-butyl sulphide. *t*-Butyl perbenzoate (0.15 mole) was added dropwise to a refluxing benzene solution (200 ml) containing 59 g (0.33 mole) of benzyl *i*-butyl sulphide ($n_D^{20} = 1.5234$) and 0.1 g of cuprous chloride. After refluxing for 2 h at 80°C, the reaction was complete. No gas evolution was observed. The reaction mixture was washed with 2 M NaOH, then with water and finally dried over sodium sulphate. The alkaline solution was acidified and the precipitated benzoic acid dried and weighed (7.8 g). From the organic solution, benzene and excess of benzyl *i*-butyl sulphide were removed under reduced pressure. The benzoyloxy compound was obtained at 135–140°C/0.1 mm Hg. Weight 21 g. Yield 47 %. The product solidified and part of it was recrystallized from petroleum ether. M.p. 53–54°C. (Found: C 71.33; H 6.71; S 10.63. Calc. for $C_{18}H_{20}O_2S$ (300.25): C 71.98; H 6.71; S 10.66).

The reaction of t-butyl perbenzoate and benzyl t-butyl sulphide. In a flask containing 300 ml of anhydrous benzene were placed 50 g (0.28 mole) of redistilled benzyl *t*-butyl sulphide ($n_D^{20} = 1.5283$) and 0.1 g of cuprous chloride. 0.2 mole of *t*-butyl perbenzoate dissolved in 50 ml of benzene were added dropwise during 15 min to the benzene sulphide solution which was kept in an oil bath at a temperature of 75°C. After 45 min, the reaction was almost complete. No gas evolution was observed. After the solution had been washed with a 2 M NaOH solution and with water in the usual way, it was dried over sodium sulphate. Benzoic acid (3 g) was obtained from the alkaline washings. Benzene was removed from the organic phase, the remainder was distilled and benzyl *t*-butyl sulphide (18 g) was collected first, b.p. 114–120°C/10 mm Hg ($n_D^{20} = 1.5272$). The distillation residue, 39 g (65 %), crystallized in contact with cold petroleum ether M.p. 73–77°C. Recrystallization gave a m.p. of 77–78°C. (Found: C 71.75; H 6.75; S 10.55. Calc. for $C_{18}H_{20}O_2S$ (300.25): C 71.98; H 6.71; S 10.66).

The reaction of t-butyl perbenzoate and dibenzyl sulphide. In an oil bath with a temperature of 85°C were placed a flask containing 300 ml of benzene, 80 g (0.37 mole) of dibenzyl sulphide (m.p. 149°) and 0.1 g of CuCl. 0.2 mole of *t*-butyl perbenzoate in 50 ml of benzene was added dropwise. The reaction was complete after 2 h, 15 min. The alkaline washings gave 2.5 g of benzoic acid. The benzene and excess of the dibenzyl sulphide were removed. The residue was weighed and found to be 56 g. It was shown by infrared measurements to contain an ester group.

A. 15 g of the crude benzoyloxy compound of dibenzyl sulphide was distilled without any special precautions. At 175–195°C/0.2 mm Hg a red coloured crystalline fraction was obtained. The compound was dissolved in ether, washed with 2 M NaOH and water and dried. Benzoic acid (3.2 g) was precipitated from the alkaline washings. When ether was removed 2.7 g of a compound precipitated which was shown to be *trans*-stilbene by IR, elemental analysis and mixed melting point. Yield 32 %. (Found: C 93.15; H 6.67. Calc. for $C_{14}H_{21}$ (180.24): C 93.29; H 6.71). M.p. and mixed m.p. 123–124°C.

B. In another attempt to distil the compound under so mild conditions as possible no stilbene was obtained but only the expected benzoyloxy compound in a form not sufficiently pure for analyses. Every attempt to crystallize it was unsuccessful. Instead, the crude benzoyloxy compound was dissolved in acetic acid, and an excess of 4 % $KMnO_4$ solution was added. After extraction with chloroform, washing with water until neutral, removal of the solvent, the corresponding sulphone crystallized. After several recrystallizations the melting point was 121–123°C. Mixed melting point with the Horner compound was not depressed*.

* We wish to express our cordial thanks to Professor Dr. L. Horner for providing us with a sample of this material.

The reaction of dibenzyl sulphide and t-butylperoxide. In a 100 ml flask equipped with a mechanical stirrer and a reflux condenser were placed 23 g (0.108 mole) of dibenzyl sulphide and 10 g of *t*-butyl peroxide. The mixture was maintained at an oil bath temperature of 125°C for 53 h. By distillation, 11.5 g dibenzyl sulphide were recovered and from the residue 8.3 g of a product crystallized in contact with cold *i*-propyl ether. After several recrystallizations from *i*-propyl ether and also from ethanol, the melting point was found to be 133–134°C. The infra-red spectrum was mainly identical with that of the dibenzyl sulphide, and the compound was the dimer. (Found: C 78.41; H 6.20; S 14.87; mol. wt. in benzene 401. Calc. for $C_{28}H_{28}S_2$ (426.62): C 78.82; H 6.14; S 15.00).

The reaction of t-butyl perbenzoate and benzyl mercaptan. A flask containing 125 ml of anhydrous benzene, 0.1 g of CuCl and 27 g (0.22 mole) of redistilled benzyl mercaptan ($n_D^{20} = 1.5738$) was maintained at an oil bath temperature of 80°C. 20 ml (0.1 mole) of *t*-butyl perbenzoate in 15 ml of benzene was added dropwise during 10 min. The solution was at once discoloured and when the titration indicated that no perester was left, the solution was cooled immediately, and washed with 2 M NaOH and water. 12.5 g of benzoic acid was precipitated. After removing benzene, the distillation residue (22 g) solidified and was recrystallized from petroleum ether. M.p. 67–69°. The compound was dibenzyl disulphide which was demonstrated by mixed melting point (not depressed) and by identical infra-red spectra.

The reaction of t-butyl perbenzoate and benzyl alcohol. 54 g (0.5 mole) of benzyl alcohol and 0.1 g of cuprous chloride in 200 ml of benzene were heated to 105°C under a nitrogen atmosphere, and 0.2 mole of *t*-butyl perbenzoate was thereafter added dropwise during 30 min. After 5 h, all peroxide was consumed, and the work-up was performed in the usual way. Isolated benzoic acid was equal to 22.2 g. Of the starting material 31.8 g was recovered. No benzaldehyde could be isolated, and the main fraction of the acetal distilled at 150–155°C/0.05 mm Hg, $n_D^{20} = 1.5781$ (Lit.³: $n_D^{20} = 1.5776$). Yield 24 g. IR-spectra of dibenzyl acetal of benzaldehyde and the main fraction were superimposable.

The reaction of t-butylperbenzoate and benzyl alcohol without cuprous chloride. Benzyl alcohol, 108 g (1 mole) and 14 ml (0.07 mole) of *t*-butyl perbenzoate in 150 ml of benzene were reacted in the usual way for 9 h. The reaction mixture was extracted with 2 M NaOH and then with water until neutral and finally dried over $MgSO_4$. The alkaline washings gave 9 g of benzoic acid. The distillation gave 9 g of benzaldehyde.

The reaction of t-butyl peroxide with benzyl alcohol. 44 g of redistilled benzyl alcohol and 8 g of *t*-butyl peroxide were refluxed for 20 h at 130°C. Distillation gave starting material (smell of benzaldehyde) and a solid, which after recrystallization from ethanol gave 9 g (42 %) of mesohydrobenzoin, m.p. and mixed m.p. 135–136°C.

The reaction of an acylal with ethanol. The benzoyloxy compound of benzyl ethyl ether (95 g) was refluxed under a nitrogen atmosphere for 5 h with 30 ml of ethanol. The alcohol was then stripped off, ether was added and the benzoic acid was extracted with sodium bicarbonate (isolated benzoic acid = 4.2 g). The ether phase was washed until neutral with water, dried over sodium sulphate and distilled. The main fraction was obtained at b.p. 93–95°C/11 mm Hg Weight 3.2 g. IR and vapor phase diagrams of the last fraction showed that one pure compound had been isolated and was identical in all respects with the diethyl acetal of benzaldehyde.

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