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REACTIONS OF t-BUTYL PERESTERS—IV

CUPROUS BROMIDE-CATALYZED REACTION OF PERESTERS WITH SULFIDES

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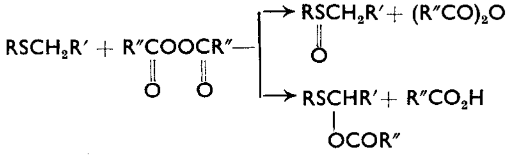
Abstract—Straight-chain aliphatic and cyclic sulfides reacted smoothly with t-butyl peracetate and t-butyl perbenzoate at 75–105° in the presence of catalytic amounts of cuprous bromide. The products obtained were the corresponding acyloxy derivatives, and there was no oxidation of the sulfur atom under the experimental conditions. Thus, α-acyloxy derivatives of diethyl-, di-n-propyl-, di-n-butyl sulfides, and of tetrahydrothiophene were prepared.

In the preceding publications[1,2] the reactions of t-butyl peresters with aliphatic and cyclic ethers in the presence of catalytic amounts of cuprous bromide were described. These studies were extended to straight-chain aliphatic sulfides and to tetrahydrothiophene. The results were reported briefly in subsequent communications.[3,4] Similar studies with sulfides were reported recently by Lawesson in Sweden.[5,6] Details of the preparation of acyloxy derivatives of sulfides are described in the present paper.

In the past the acyloxy sulfides were prepared by the following methods: from α-halosulfide and either acetic acid or sodium acetate,[7] from sulfides and lead tetraacetate,[8] from alkali mercaptides and chloromethylacetate,[9] from sulfides and diacyl peroxides,[8] and from sulfoxides and carboxylic acid anhydrides.[10,11,12]

Reaction of diacyl peroxide with sulfides usually gave a mixture of the corresponding sulfoxide and the α-acyloxy derivative.



$$RSCH_2R' + R''\underset{\underset{O}{\|}}{C}O\!O\underset{\underset{O}{\|}}{C}R'' \longrightarrow \begin{cases} R\underset{\underset{O}{\|}}{S}CH_2R' + (R''CO)_2O \\ RS\underset{\underset{OCOR''}{|}}{C}HR' + R''CO_2H \end{cases}$$

For example, reaction of tetrahydrothiophene and diacetyl peroxide gave the tetramethylene sulfoxide, acetic acid, acetic anhydride, and 2-acetoxytetrahydrothiophene.[8]

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[1] G. Sosnovsky, *J. Org. Chem.* **25**, 874 (1960).

[2] G. Sosnovsky, *Tetrahedron* **13**, 241 (1961).

[3] G. Sosnovsky, Abstract of Papers presented at the 138th Meeting of the American Chemical Soc., New York, September 1960, p. 78P.

[4] G. Sosnovsky, *J. Org. Chem.* **26**, 281 (1961).

[5] S. O. Lawesson and C. Berglund, *Acta Chem. Scand.* **15**, 36 (1961).

[6] S. O. Lawesson, C. Berglund and S. Grönwall, *Acta Chem. Scand.* **15**, 249 (1961).

[7] H. Böhme, H. Fischer and R. Frank, *Liebigs Ann.* **563**, 54 (1949).

[8] L. Horner and E. Jürgens, *Liebigs Ann.* **602**, 135 (1957).

[9] W. R. Kirner, *J. Amer. Chem. Soc.* **50**, 2446 (1928).

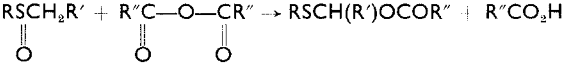
[10] R. Pummerer, *Ber. Dtsch. Chem. Ges.* **43**, 1401 (1910).

[11] L. Horner and P. Kaiser, *Liebigs Ann.* **626**, 19 (1959).

[12] L. Horner, *Liebigs Ann.* **631**, 198 (1960).

Similarly, reaction of tetrahydrothiophene and benzoyl peroxide resulted in the sulfoxide, 2-benzoyloxy tetrahydrothiophene,[8] benzoic acid, and benzoic acid anhydride. The reaction of benzoyl peroxide and di-n-butyl sulfide yielded the di-n-butyl sulfoxide only, but the presence of the α-acyloxy derivative was assumed on the basis of the composition of the hydrolysis products.[8] The formation of sulfoxides is not surprising since sulfides are known to react with various peroxy compounds such as hydrogen peroxide,[13] peracids,[13] and hydroperoxides[14] to give good yields of sulfoxides or sulfones. Therefore, from the point of view of preparation, the reaction of sulfides with diacyl peroxides is limited in scope.

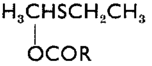
An excellent preparative method for the acyloxy derivatives of sulfides is the Pummerer reaction.[11] The starting materials are a sulfoxide and a carboxylic acid anhydride.



$$\mathrm{R\underset{O}{\underset{\|}{S}}CH_2R'} + \mathrm{R''\underset{O}{\underset{\|}{C}}{-}O{-}\underset{O}{\underset{\|}{C}}R''} \rightarrow \mathrm{RSCH(R')OCOR''} + \mathrm{R''CO_2H}$$

In the case of di-n-butyl sulfoxide, both acetic and benzoic acid anhydrides gave the unsaturated sulfide, $CH_3(CH_2)_3S\,CH = CH\,C_2H_5$, and no acyloxy compound was isolated.[11] We found[3,4] that t-butyl peracetate and t-butyl perbenzoate reacted smoothly at 75–105° with diethyl sulfide, di-n-propyl sulfide, di-n-butyl sulfide, and tetrahydrothiophene in the presence of catalytic amounts of cuprous bromide to give α-acyloxy derivatives. In contrast to the work with diacyl peroxides,[8] we observed no oxidation of the sulfur atom under the experimental conditions. The copper salt catalyst exerted a marked influence on the rate of reaction. Generally, in the absence of the catalyst the reaction was slower and smaller amounts of acyloxy compounds were obtained. Like the acyloxy derivatives of ethers,[1,2] the acyloxy derivatives of sulfides were sensitive to heat. Depending on experimental conditions, they gave either unsaturated sulfides or mercaptals. These results will be discussed in detail in a subsequent paper.

t-Butyl peracetate and t-butyl perbenzoate reacted smoothly with diethyl sulfide in the presence of cuprous bromide to give the α-acyloxy derivatives Ia and Ib, respectively, in moderate yields.

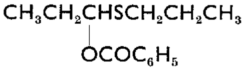


$$\mathrm{CH_3\underset{OCOR}{\underset{|}{C}}HSCH_2CH_3}$$

Ia $R = CH_3$
Ib $R = C_6H_5$

Under similar experimental conditions but in the absence of the catalyst, t-butyl perbenzoate was decomposed to give a high yield of benzoic acid (78 %), a small quantity of acetaldehyde diethylmercaptal, and an oil which did not give a well-defined product.

Reaction of di-n-propyl sulfide with t-butyl perbenzoate gave a high yield (78 %) of the benzoyloxy derivative II. In the absence of the catalyst a lesser amount of compound II was obtained.



$$\mathrm{CH_3CH_2\underset{OCOC_6H_5}{\underset{|}{C}}HSCH_2CH_2CH_3}$$

II

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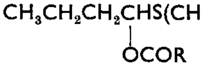
[13] R. B. Wagner and H. D. Zook, *Synthetic Organic Chemistry* p. 801. John Wiley, New York (1953).
[14] K. R. Hargrave, *Proc. Roy. Soc.* **A235**, 55 (1956).

Reaction of di-n-butyl sulfide with t-butyl peracetate and t-butyl perbenzoate gave the corresponding acyloxy compounds IIIa and IIIb in 44% and 78% yields, respectively. While the acetoxy compound (IIIa) could easily be purified by distillation, the benzoyloxy derivative (IIIb) decomposed on attempted distillation at 0·1 mm Hg. This finding is in agreement with that of Horner and Kaiser[11] and is in contrast to that of Lawesson.[5,6] After the excess of the starting di-n-butyl sulfide was removed under high vacuum for 24 hr, the remaining benzoyloxy compound was pyrolyzed at 115–120°/10 mm. The volatile product was shown by vapor phase chromatography to contain about 94 per cent of the α, β unsaturated sulfide (IV) plus 5 per cent of di-n-butyl sulfide. The di-n-butyl sulfide could not be removed from the product by conventional fractionation.



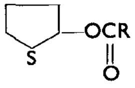
$$\underset{\text{OCOR}}{CH_3CH_2CH_2\underset{|}{C}HS(CH_2)_3CH_3}$$

IIIa $R = CH_3$
IIIb $R = C_6H_5$

$CH_3(CH_2)_3SCH{=}CHCH_2CH_3$

IV

Tetrahydrothiophene reacted rapidly at 90–105° with t-butyl peracetate and t-butyl perbenzoate in the presence of cuprous bromide to give the expected 2-acyloxy derivatives Va and Vb, respectively.



Va $R = CH_3$
Vb $R = C_6H_5$

The acetoxy derivative was readily distilled under reduced pressure, the refractive index of the product (n_D^{25} 1·4893) was in close agreement with that obtained by Horner and Kaiser[11] and Horner and Jürgens.[8] It was markedly different from that of tetramethylene sulfoxide (n_D^{23} 1·5201). The reaction of t-butyl peracetate with tetrahydrothiophene in the absence of the catalyst proceeded at a slower rate, and a smaller yield of compound Va was obtained. In contrast to the experience of Horner and Jürgens,[8] our attempts to distill the benzoyloxy derivative were unsuccessful. However, the refractive index (n_D^{25} 1·5650) of Vb was also different from that of the sulfoxide. On the basis of combustion, molecular weight, and infrared analysis, structure Vb was assigned to the benzoyloxy derivative of tetrahydrothiophene. In the absence of the catalyst tetrahydrothiophene reacted with t-butyl perbenzoate to give only a 38 per cent yield of Vb plus a 62 per cent yield of benzoic acid.

EXPERIMENTAL

t-Butyl perbenzoate and t-butyl peracetate (75% benzene solution, Lupersol No. 7) were purchased from the Lucidol Division, Wallace and Tiernan, Inc. The peresters were used without further purification, since in previous work the purified peresters gave indistinguishable results from those obtained with undistilled materials. The cuprous bromide used was an anhydrous, reagent-grade product. Progress of the reactions was followed by periodic infrared analyses. All experiments were carried out in an atmosphere of nitrogen gas. The reaction vessel was equipped with a stirrer and a reflux condenser and was connected to a gas meter. No gases were observed in the work reported. The boiling points are uncorrected. The molecular weights were determined cryoscopically in benzene. For further details see earlier publications.[15,16]

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[15] M. S. Kharasch, G. Sosnovsky and N. C. Yang, *J. Amer. Chem. Soc.* **81**, 5819 (1959).

[16] G. Sosnovsky and N. C. Yang, *J. Org. Chem.* **25**, 874 (1960).

Reactions of peresters with straight-chain aliphatic sulfides

t-Butyl peracetate with diethyl sulfide. t-Butyl peracetate (57 ml of a 75% benzene solution, 0·3 mole) was added over a period of 4 hr to a mixture of diethyl sulfide (40 ml, 0·35 mole), cuprous bromide (0·1 g, 0·35 mmole), and benzene (50 ml) maintained at 80°. After 60 hr of heating, the cooled reaction mixture was diluted with ether (50 ml) and extracted with 2 N sodium carbonate solution to remove acetic acid. The ethereal solution was washed with water, dried with anhydrous sodium sulfate, and concentrated at 10 mm Hg. The remaining oil was distilled at reduced pressure. The product obtained was: α-acetoxy diethyl sulfide (19·5 g, 44%), b.p. 70–72/20 mm, n_D^{25} 1·4468 (lit.[11] n_D^{22} 1·4490), $\nu_{C=O}$ 1730 cm^{-1}. (Found: C, 48·84; H, 8·30; S, 21·97; mol. wt. 146. Calc. for $C_6H_{12}O_2S$: C, 48·64; H, 8·16; S, 21·60; mol. wt. 148.)

t-Butyl perbenzoate with diethyl sulfide. t-Butyl perbenzoate (40 ml, 0·2 mole) was slowly added over a period of 2 hr to a mixture of diethyl sulfide (45 g, 0·5 mole), cuprous bromide (0·1 g, 0·35 mmole), and benzene (50 ml) maintained at 80–90°. After 26 hr the cooled reaction mixture was diluted with ether (50 ml) and extracted with 2 N sodium carbonate solution to remove benzoic acid (8 g, 33%). The ethereal solution was washed with water, dried with anhydrous sodium sulfate, and concentrated at 10 mm Hg. The remaining oil was repeatedly distilled at reduced pressure. The products obtained were: 4 g of residue and 13 g (31%) of α-benzoyloxy diethyl sulfide, b.p. 75°/0·1 mm (124–126°/10 mm), n_D^{25} 1·5266, $\nu_{C=O}$ 1715 cm^{-1}. (Found: C, 63·40; H, 6·98; S, 15·03; mol. wt. 216. $C_{11}H_{14}O_2S$ requires: C, 62·84; H, 6·98; S, 15·03; mol. wt. 216.)

t-Butyl perbenzoate with diethyl sulfide in the absence of cuprous bromide. When the preceding experiment was repeated in the absence of cuprous bromide a different result was obtained. The products were a large quantity of benzoic acid (18·5 g, 78%) and a small amount (2 g) of a liquid, b.p. 44°/1·3 mm (lit.[17,18] 186°/753 mm), n_D^{25} 1·5000 (lit.[17,18] n_D^{28} 1·4984), which analyzed as acetaldehyde diethyl mercaptal. (Found: C, 48·38; H, 9·38; S, 42·30; mol. wt. 145. Calc. for $C_6H_{14}S_2$: C, 47·98; H, 9·40; S, 42·62; mol. wt. 145.) The remaining oil (10 g), $\nu_{C=O}$ 1720 cm^{-1}, could not be distilled without severe decomposition at 95–105°/3·5 mm. It was not investigated further.

t-Butyl perbenzoate with di-n-propyl sulfide. t-Butyl perbenzoate (40 ml, 0·2 mole) was added dropwise to a mixture of di-n-propyl sulfide (45 ml, 0·3 mole), cuprous bromide (0·1 g, 0·35 mmole), and benzene (50 ml) maintained at 85–97°. After 8 hr of heating the reaction mixture was treated as usual. The products obtained were: recovered di-n-propyl sulfide (12 g, 0·1 mole), b.p. 138–142°, and *α-benzoyloxydi-n-propyl sulfide* (37 g, 78%), b.p. 90°/0·04 mm, n_D^{25} 1·5175, $\nu_{C=O}$ 1725 cm^{-1}. (Found: C, 65·59; H, 7·73; S, 13·74; mol. wt. 231. $C_{13}H_{18}O_2S$ requires: C, 65·53; H, 7·61; S, 13·47; mol. wt. 238.)

t-Butyl perbenzoate with di-n-propyl sulfide in the absence of cuprous bromide. A mixture of di-n-propyl sulfide (25 ml, 0·167 mole), t-butyl perbenzoate (20 ml, 0·1 mole), and benzene (25 ml) was heated at 105° for 16 hr. After the usual procedure the products obtained were: benzoic acid (5·0 g, 41·5%), recovered di-n-propyl sulfide (11 g, 0·94 mole), residue (1·2 g), and α-benzoyloxy di-n-propyl sulfide (12·5 g, 52%), b.p. 88–90°/0·04 mm, n_D^{25} 1·5175, $\nu_{C=O}$ 1725 cm^{-1}.

t-Butyl peracetate with di-n-butyl sulfide. t-Butyl peracetate (57 ml, 0·3 mole) was added to a mixture of di-n-butyl sulfide (98 ml, 0·575 mole), cuprous bromide (0·1 g, 0·35 mmole), and benzene (50 ml) maintained at 75–80°. After heating for 80 hr the reaction mixture was treated as usual. The products obtained were: recovered di-n-butyl sulfide (40 g, 0·275 mole), b.p. 37°/0·1 mm, n_D^{25} 1·4512; residue (5·4 g); and *α-acetoxydi-n-butyl sulfide* (27 g, 44%), b.p. 64–66°/0·55 mm, n_D^{25} 1·4525, $\nu_{C=O}$ 1730 cm^{-1}. (Found: C, 59·04; H, 9·80; S, 15·90; mol. wt. 192. $C_{10}H_{20}SO_2$ requires: C, 58·80; H, 9·87; S, 15·70; mol. wt. 204.)

t-Butyl perbenzoate with di-n-butyl sulfide. t-Butyl perbenzoate (40 ml, 0·2 mole) was added to a mixture of di-n-butyl sulfide (85 ml, 0·5 mole), cuprous bromide (0·1 g, 0·35 mmole), and benzene (50 ml) maintained at 85°. After 20 hr of heating the cooled reaction mixture was washed with 2 N sodium carbonate solution to remove benzoic acid (4 g, 16·7%). The excess di-n-butyl sulfide (40 g, 0·275 mole), b.p. 35–37°/0·5–0·1 mm, n_D^{25} 1·4512, was first removed with a mechanical pump and then with a diffusion pump (10^{-4} mm Hg) for 24 hr. The remaining benzoyloxy derivative (42 g, 78·5%, n_D^{25} 1·5093) was sensitive to heat and could not be distilled at 0·1 mm Hg. The benzoate was heated for 2 hr at 115–120°/10 mm Hg to give a liquid product (17·5 g, 77%) plus benzoic acid (15·5 g, 81%). The liquid was distilled without fractionation, b.p. 66–67°/12 mm, n_D^{25} 1·4732 (lit. n_D^{20} 1·4750,[6] n_D^{20}

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[17] E. E. Reid, *Organic Chemistry of Bivalent Sulfur* p. 334. Chemical Publishing Company. New York (1960).

[18] H. W. Post, *J. Org. Chem.* **5**, 244 (1940).

1·4730[11]). Vapour phase chromatography showed that the liquid contained about 94% of n-butyl 2-ethylvinyl sulfide, n_D^{25} 1·4737 contaminated with 5% of the starting di-n-butyl sulfide.

Reactions of peresters with a cyclic sulfide

t-Butyl peracetate with tetrahydrothiophene. t-Butyl peracetate (57 ml of a 75% benzene solution, 0·3 mole) was added over a period of 2 hr to a mixture of tetrahydrothiophene (45 ml, 0·5 mole), cuprous bromide (0·1 g, 0·35 mmole), and benzene (50 ml) maintained at 90°. After 6 hr of heating the cooled reaction mixture was treated as usual. The products obtained were: tetrahydrothiophene (10 g, 0·114 mole) b.p. 117–120°, n_D^{23} 1·5056; residue (2 g); and 2-acetoxytetrahydrothiophene (25 g, 56%), b.p. 60–62°/0·1 mm, n_D^{25} 1·4893 (lit.[8,11] n_D^{22} 1·4868), $\nu_{=O}$ 1735 cm^{-1}. (Found: C, 49·53; H, 7·16; S, 21·86; mol. wt. 141. Calc. for $C_6H_{10}O_2S$: C, 49·31; H, 6·90; S, 21·90; mol. wt. 146.)

t-Butyl peracetate with tetrahydrothiophene in the absence of cuprous bromide. A mixture of tetrahydrothiophene (45 ml, 0·5 mole), t-butyl peracetate (57 ml, 0·3 mole), and benzene (50 ml) was heated at 95° for 10 hr. The reaction mixture was treated as usual. The products obtained were: a mixture (7 g) of tetrahydrothiophene and t-butyl peracetate (1·5 g, by titration[15]); a fraction of unreacted t-butyl peracetate (5 g), b.p. 46°/13 mm, infrared spectrum identical with that of the starting material, $\nu_{C=O}$ 1775 cm^{-1}; unidentified residue (4·2 g); and 2-acetoxytetrahydrothiophene (17 g, 38·5%), b.p. 60°/0·1 mm, n_D^{25} 1·4899, $\nu_{C=O}$ 1735 cm^{-1}, infrared spectrum identical with that of an authentic sample, obtained from the preceding experiment.

t-Butyl perbenzoate with tetrahydrothiophene. t-Butyl perbenzoate (50 ml, 0·25 mole) was added to a mixture of tetrahydrothiophene (45 ml, 0·5 mole), cuprous bromide (0·1 g, 0·35 mmole), and benzene maintained at 95–105°. After 6 hr of heating the reaction mixture was treated as usual. The products obtained were: benzoic acid (7·7 g, 25·5%); recovered tetrahydrothiophene (15 g, 0·17 mole), b.p. 117–120°, n_D^{25} 1·5046; nondistillable 2-benzoyloxy tetrahydrothiophene (36 g, 69%), n_D^{25} 1·5650 (after chromatography on alumina), $\nu_{C=O}$ 1735 cm^{-1}. (Found: C, 63·13; H, 5·81; mol. wt. 198. Calc. for $C_{11}H_{12}O_2S$: C, 63·45; H, 5·81; mol. wt. 208.)

t-Butyl perbenzoate with tetrahydrothiophene in the absence of cuprous bromide. A mixture of tetrahydrothiophene (24 ml, 0·27 mole) and t-butyl perbenzoate (20 ml, 0·1 mole) was heated at 105° for 3 hr. After the usual procedure the products obtained were: benzoic acid (7·5 g, 62%), and 2-benzoyloxy tetrahydrothiophene (8 g, 38%), n_D^{23} 1·5656, infrared spectrum identical with that obtained in the preceding experiment.

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