

TABLE I

Compound	—Analytical wave length (μ)—		
	<i>ortho</i>	<i>meta</i>	<i>para</i>
Fluorotoluene	13.3	12.88	12.28
Chlorotoluene	13.4	12.96	12.42
Bromotoluene	13.42	13.0	12.48

eter with sodium chloride optics. Analyses were carried out by the standard base line technique with suitable corrections made for the interference of any isomer on the others by use of an electronic computer. Table I lists the analytical wave lengths used.

When other interfering materials were present (*e.g.* chlorobenzene in the chlorotoluene samples), the base line was sketched into approximate the absorption of the interfering component. Accuracy of the isomer ratios is within ± 3 relative per cent, as checked with mixtures of known composition.

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Reactions of *t*-Butyl Peresters. VI. Pyrolysis of α -Acyloxy Derivatives of Aliphatic Sulfides

GEORGE SOSNOVSKY AND HUGH J. O'NEILL

Armour Research Foundation of Illinois Institute of Technology, Chicago 16, Illinois

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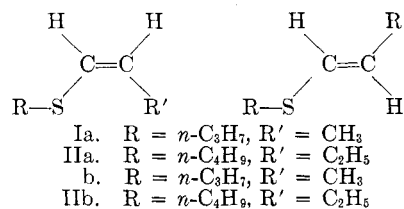
Benzoyloxy-substituted di-*n*-propyl sulfide and acetoxy- and benzoyloxy-substituted di-*n*-butyl sulfides were subjected to pyrolysis. The products in each case were two unsaturated sulfides. The products were analyzed by gas-liquid chromatography, infrared and ultraviolet spectroscopy, and n.m.r. It was concluded that the unsaturated sulfides are the *cis* and *trans* isomers of *n*-propyl 2-methylvinyl sulfide and *n*-butyl 2-ethylvinyl sulfide, respectively.

In preceding communications^{1,2} we reported a method of preparing α -acyloxy derivatives of straight-chain aliphatic and cyclic sulfides. The acyloxy derivatives were produced by the reaction of *t*-butyl peresters with sulfides in the presence of catalytic amounts of cuprous bromide. Similar studies with various sulfides were recently reported by Lawesson, Berglund, and Grönwall.^{3,4}

Until now all workers have assumed that the acyloxy group enters the position which is α to the sulfur atom. However, an alternative is possible. Although the α position may be favored, introduction of the acyloxy group into other positions along the methylene chain cannot be ruled out. If the acyloxy group does enter at other positions, the utility of our method would be seriously decreased. Because of this possibility we analyzed the composition of the products derived from the reaction of *t*-butyl peresters with two straight-chain aliphatic sulfides—namely, the di-*n*-propyl and the di-*n*-butyl sulfides. Since most acyloxy derivatives of aliphatic sulfides are sensitive to heat, they cannot be analyzed successfully by vapor phase chromatography. Therefore, we decided to investigate the composition of the products of pyrolysis of acyloxy derivatives and to make deductions on the basis of

these results about the nature of the initial acyloxy compounds.

If the acyloxy group entered exclusively into the α position, only one positional olefin would result on pyrolysis, with the possibility of both *cis* and *trans* isomers being formed. Di-*n*-propyl and di-*n*-butyl derivatives would then give the *cis* and *trans* isomers, Ia, Ib and IIa, IIb, respectively.



The second possibility is that the entering groups attack the β - or γ -carbon atom as well as the α -carbon and thereby produce a mixture of positional olefinic sulfides on subsequent pyrolysis. To solve this question the products of pyrolysis of the acyloxy derivatives of di-*n*-propyl and di-*n*-butyl sulfide were separated by gas-liquid chromatography and analyzed by infrared and ultraviolet spectroscopy and n.m.r.

The pyrolysis product of benzoyloxy-substituted di-*n*-propyl sulfide was resolved into two components by gas-liquid chromatography at 70°. The first (57% Ia) had a retention time of 5.9 minutes and the second (43% Ib) of 6.8 minutes. The pyrolysis product of the benzoyloxy derivative of di-*n*-butyl sulfide yielded two products by gas-liquid chromatography at 90°. The first (61% IIa) had a retention time of 12.8 minutes and the

(1) G. Sosnovsky, Abstracts of Papers presented at the 138th Meeting of the American Chemical Society, New York, September, 1960, p. 78P.

(2) G. Sosnovsky, *J. Org. Chem.*, **26**, 281 (1961); *Tetrahedron*, in press.

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

(4) S. O. Lawesson, C. Berglund, and S. Grönwall, *ibid.*, **15**, 249 (1961).

second (39% IIb) of 15.2 minutes. The pyrolysis product of the acyloxy derivatives of di-*n*-butyl sulfide also gave only two components. The retention times of these components indicated that they were identical to those obtained from the benzyloxy derivative. The first (58% IIa) had a retention time of 12.8 minutes and the second (42% IIb) of 15.2 minutes.

Infrared analysis of component Ia showed a characteristic absorption band at 663 cm^{-1} , while Ib could be identified by its absorption band at 936 cm^{-1} . These two frequencies were tentatively assigned as the ($=\text{C}-\text{H}$) out-of-plane deformation frequencies of *cis* and *trans* configurations, respectively. The analyses of components IIa and IIb showed characteristic absorption bands at 684 cm^{-1} and 939 cm^{-1} , which were also tentatively assigned as the *cis* and *trans* configurations of the *n*-butyl 2-ethylvinyl sulfide.

The ($\text{C}=\text{C}$) stretching frequencies for components Ia and IIa were at 1618 cm^{-1} and 1608 cm^{-1} , respectively, while those of components Ib and IIb were at 1627 cm^{-1} and 1612 cm^{-1} . The relatively low frequencies obtained for these bands indicate possible resonance interaction of a conjugated ethylenic bond, in this case with the sulfur atom, and therefore is indicative of an α olefinic linkage. Similar shifts toward lower frequencies for this same band were obtained for ethyl vinyl sulfide (1588 cm^{-1}).

The ultraviolet analyses (Figure 1) of the *cis*

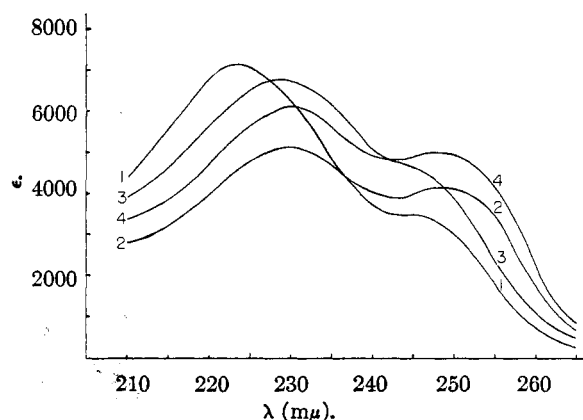


Fig. 1.—Ultraviolet absorption spectra: (1) *n*-propyl-2-methyl vinyl sulfide (*cis*); (2) *n*-propyl-2-methyl vinyl sulfide (*trans*); (3) *n*-butyl-2-ethyl vinyl sulfide (*cis*); (4) *n*-butyl-2-ethyl vinyl sulfide (*trans*).

isomers Ia and IIa gave absorption bands at 245 $\text{m}\mu$ (ϵ 3507) and 245 $\text{m}\mu$ (ϵ 4641), respectively, while the *trans* isomers Ib and IIb yielded bands at 249.5 $\text{m}\mu$ (ϵ 4134) and 248.5 $\text{m}\mu$ (ϵ 5002). These data are consistent with the views that the K bands for the *trans* isomer will be more intense and at a slightly higher wave length than those for the corresponding *cis* isomer.⁵ This is presumably because of maximal elongation and therefore a closer approach to coplanarity.

In an additional study, components IIa and IIb were transferred to sealed glass ampules under argon and heated for twenty-four hours at 150°, after which time they were removed and reexamined by both gas chromatography and infrared spectroscopy. Analysis by gas-liquid chromatography showed a complete redistribution to the original two components in both tubes. Thus, on heating, the isolated component IIa redistributed to form 47.8% IIa and 52.2% IIb, while the isolated component IIb yielded 49.2% IIa and 50.8% IIb.

The infrared tracings of the redistributed components were identical to those of the two initial components obtained by pyrolysis. This result confirms the fact that we are dealing with *cis-trans* isomers and not with positional unsaturated sulfides.

N.m.r. studies of components IIa and IIb were carried out as a means of differentiating positional and geometrical olefinic isomers and to confirm the *cis-trans* relationship of the two components. The samples were prepared for analysis by dilution in carbon tetrachloride and were analyzed by high-resolution n.m.r. Interpretation by Dr. R. Hoffman, Department of Physics, Uppsala University, confirmed the identity of the *cis* and *trans* isomers.

As a result of the identification of the resulting pyrolysis products of the acyloxy and benzyloxy derivatives of di-*n*-propyl and butyl sulfides, it may be reasonably assumed that the initial attack of the perester is at the α -carbon atom. This is based on the premise that if the initial attack were also at either the β - or the γ -carbon atom or if a random distribution of α , β , and γ esters were initially formed, a more or less random distribution of the resulting olefinic pyrolysis products would also be expected. The fact that such a distribution does not occur lends support to our views that a specific α -carbon attack is the main if not the sole target.

Experimental

The boiling points are uncorrected. The molecular weights were determined cryoscopically in benzene.

The separation and isolation of the olefinic components obtained from the pyrolysis of benzyloxy-substituted di-*n*-propyl sulfide and the acyloxy- and benzyloxy-substituted di-*n*-butyl sulfide were carried out on an Aerograph Model A-90-C gas chromatograph. The column consisted of coiled copper tubing 8 ft. \times $\frac{1}{4}$ in. containing 20 wt-% diethylene-glycol succinate on 60-80-mesh Chromosorb W. Helium was used as the carrier gas.

The trapping of the eluting material was performed with a Connecticut Instrument Corp. fraction collector equipped with a small conical glass bulb. Collection of the individual components was carried out by repeated separation on the column until approximately 40-50 mg. of each component was obtained. The trap was immersed in a Dewar flask and maintained at liquid nitrogen temperatures with the exit connected to a drying tube layered with argon to maintain an inert atmosphere. The isolated components were then

(5) (a) A. Smakula and A. Wasserman, *Z. phys. chem.*, **A155**, 353 (1931). (b) R. S. Mulliken, *Z. chem. phys.*, **7**, 364 (1939). (c) C. Wiegand and E. Merkel, *Ann.*, **587**, 242 (1947). (d) H. H. Schlubach and A. Braun, *ibid.*, **627**, 28 (1959).

characterized by elemental analysis, molecular weight, infrared and ultraviolet spectrometry, and, in the case of IIa and IIb, high-resolution n.m.r. studies. The purity of the isolated fractions was checked by reinjection into the instrument. The purity of components Ia and Ib was calculated to be 94.8% and 93.9%, respectively, while the values for components IIa and IIb were 96.5% and 97.3%. There was no attempt made to purify further the olefins by repeated separations, since the initial purity would suffice for characterization purposes and since it was known that the only impurity present was the corresponding olefinic component.

The infrared analyses were performed on the Perkin-Elmer Model 21 double-beam spectrophotometer using a beam condenser assembly and a microcavity cell (0.05 mm.). The components were collected directly in the cavity cell using the fraction collector and scanned between 2 and 15 μ using sodium chloride optics.

The ultraviolet analyses of the isolated components were carried out on a Cary Model 14 ultraviolet recording spectrophotometer. The samples were weighed out in capillary tubes and quantitatively transferred to 10-ml. volumetric flasks containing spectroscopic grade isoöctane. The individual components were then scanned between 200 and 400 m μ .

Pyrolysis of Benzoyloxy-Substituted Di-*n*-propyl Sulfide.—Benzoyloxy-substituted di-*n*-propyl sulfide,² 22 g. (0.0925 mole), was heated for 2 hr. at 130–140°/10 mm. The volatile products were condensed in a trap chilled with a mixture of Dry Ice and 2-propanol. The residue yielded 6.3 g. (57%) of benzoic acid. The liquid condensate was distilled without fractionation and yielded 5 g. (46.5%) of a colorless liquid, b.p. 50°/22 mm., n_D^{20} 1.4754. This liquid (A) was fractionated by vapor phase chromatograph.

Reaction of *t*-Butyl Perbenzoate with Di-*n*-butyl Sulfide and Pyrolysis of Benzoyloxy-Substituted 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 reaction mixture was cooled and washed with 2 *N* sodium carbonate solution to remove benzoic acid (4 g. 16.7%). Contrary to the experience of Lawesson and co-workers,⁴ we could not purify the benzoyloxy derivative by distillation at 0.1 mm.; benzoic acid was eliminated upon distillation. Instead, we removed most of the excess *n*-butyl sulfide by the use of a high-vacuum (10⁻⁴ mm.) pump at room temperature. The remaining oil, 42 g. of n_D^{20} 1.5093, was heated to 115–120°/10 mm. for 2 hr. The products were 17.5 g. (76%) of a liquid, b.p. 66–67°/12 mm., n_D^{20} 1.4737, plus 15.5 g. (81%) of benzoic acid. The liquid (B) was fractionated by vapor phase chromatography.

Gas-Liquid Chromatography of Vinyl Sulfides (A) Obtained from Benzoyloxy-Substituted Di-*n*-propyl Sulfide.—The liquid A was fractionated by vapor phase chromatography at 70°, and the flow rate of the carrier gas (helium)

was 40 ml./min. Two products were obtained. The first (57%), retention time 5.9 min., n_D^{20} 1.4754, was analyzed as follows. Found: C, 62.11; H, 10.49; S, 27.90; mol. wt., 115. Calcd. for C₆H₁₂S: C, 62.04; H, 10.41; S, 27.60; mol. wt., 116. The second (43%), retention time 6.8 min., n_D^{20} 1.4761, was analyzed as follows. Found: C, 62.22; H, 10.38; S, 27.99; mol. wt., 117. Calcd. for C₆H₁₂S: C, 62.04; H, 10.41; S, 27.60; mol. wt., 116.

Gas-Liquid Chromatography of Vinyl Sulfides (B) Obtained from Benzoyloxy-Substituted Di-*n*-butyl Sulfide.—The liquid (B) was fractionated by vapor phase chromatography at 90° and a flow rate of 75 ml./min. Small amounts of *n*-butyl sulfide (5.5% of the total sample) and two unsaturated sulfides were obtained. The first sulfide (61%), retention time 12.8 min., n_D^{20} 1.4722, was analyzed as follows. Found: C, 66.61; H, 11.35; S, 21.77; mol. wt., 140. Calcd. for C₈H₁₆S: C, 66.63; H, 11.18; S, 22.19%; mol. wt., 144. The second compound (39%), retention time 15.2 min., n_D^{20} 1.4742, was analyzed as follows. Found: C, 66.46; H, 10.90; S, 22.52; mol. wt., 146. Calcd. for C₈H₁₆S: C, 66.63; H, 11.18; S, 22.19%; mol. wt., 144.

Reaction of *t*-Butyl Peracetate with Di-*n*-butyl Sulfide and Pyrolysis of Acetoxy-Substituted Di-*n*-butyl Sulfide.—Acetoxy-di-*n*-butyl sulfide, 10 g. (0.049 mole) prepared from *t*-butyl peracetate and *n*-butyl sulfide with cuprous bromide at 80°, b.p. 64–66°/0.55 mm., n_D^{20} 1.4525, was subjected to pyrolysis at 150–175°/760 mm. The products obtained were 2.9 g. (98%) o acetic acid and 5.5 g. (78%) of unsaturated sulfides, b.p. 63–64°/9–10 mm., n_D^{20} 1.4740. The sulfides (C) were fractionated by vapor phase chromatography.

Gas-Liquid Chromatography of Vinyl Sulfides (C) Obtained from Acetoxy-Substituted Di-*n*-butyl Sulfide.—Vapor phase chromatographic fractionation yielded 58% of a product with a retention time of 12.8 min. and 42% of a product with a retention time of 15.2 min. The infrared spectrum and refractive indices of these products were identical with those obtained from the benzoyloxy derivatives.

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