323. *Reversible Formation and Solvolysis of Tertiary Alkyl Sulphides in Acetic Acid–Perchloric Acid.*

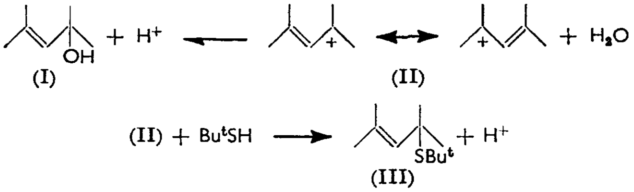
By M. E. CAIN, M. B. EVANS, and D. F. LEE.

Reactions providing a new route to di-t-alkyl sulphides and a novel method of cleaving suitably constituted C–S–C structures are described. The tertiary alkenyl sulphide (III) is readily obtained by condensation of 2-methylpropane-2-thiol with 2,4-dimethylpent-3-en-2-ol in glacial acetic acid. Tertiary alkyl sulphides can be similarly prepared if perchloric acid is present, although di-t-alkyl sulphides undergo competing acid-catalysed solvolysis, leading to equilibria.

Sulphides containing strongly electron-releasing alkenyl groups may be solvolysed in wet acetic acid, formation of diene and subsequently its cyclic dimer eventually leading to almost complete removal of the sulphide.

REACTION of 2,4-dimethylpent-3-en-2-ol (I) with 2-methylpropane-2-thiol in glacial acetic acid at room temperature for 24 hr. gives t-butyl 1,1,3-trimethylbut-2-enyl sulphide (III).

At higher temperatures the main product is the diene dimer obtained in previous attempts to prepare this sulphide.[1] The smoothness of this reaction is a reflection of the rapid formation of the highly resonance-stabilised [2] carbonium ion (II) by the relatively few protons available from autoprotolysis of the solvent.



The possible application of this method to the preparation of alkyl t-alkyl and di-t-alkyl sulphides has been studied. The former may be prepared from t-alkyl halide and sodium or cuprous [3] mercaptide, or by acid-catalysed addition of alkanethiol to olefin,[4] while the latter are usually prepared by addition of t-alkanethiol or hydrogen sulphide to a tertiary alkanol or olefin in the presence of Lewis [5] or proton [6] acids. We have found these methods unsatisfactory for the preparation of higher di-t-alkyl sulphides, while di-t-butyl sulphide so obtained [6] has always contained a small inseparable amount (2—5%) of unsaturated impurities, characterised by infrared absorption at 890 cm.$^{-1}$ ($R_2C{:}CH_2$).

RESULTS

Preparation of Sulphides.—Acetic acid was retained as solvent, the acid strength being increased by addition of perchloric acid (0·5M). The water added in the perchloric acid solution was removed by adding the calculated quantity of acetic anhydride. The yields obtained from various thiols and alkanols under standard conditions (see Experimental) are shown in Table 1.

TABLE 1.

Reaction of thiols (1·2M) with alcohols (1·0M) in acetic acid containing perchloric acid (0·5M) at room temperature for 24 hr.

ROH	R'SH	RSR' Yield [a] (%)	RSR' Isolated yield (%)
EtOH	Bu^{t}SH	0	—
Pr^{i}OH	Bu^{t}SH	0	—
Bu^{t}OH	EtSH	86	68
Bu^{t}OH	Pr^{i}SH	88	76
Bu^{t}OH	Bu^{t}SH	69	58
$CMe_2Et{\cdot}OH$	$CMe_2Et{\cdot}SH$	47	26
CMeEtPr^n·OH	Bu^{t}SH	—	34
CMeEtPr^n·OH	CMeEtPr^n·SH	—	20 [b]
5-Methyltetradecan-5-ol	Bu^{t}SH	—	20

[a] By gas–liquid chromatography of crude product. [b] Yield increased under different conditions (see Experimental).

Kinetics of Di-t-butyl Sulphide Formation.—Analysis of the reaction between 2-methylpropan-2-ol and 2-methylpropane-2-thiol by gas–liquid chromatography (see Experimental) is shown in the Figure. A first-order rate plot gave the reaction velocity constant $k_1 = 11{\cdot}4 \times 10^{-4}$ sec.$^{-1}$ at 25°.

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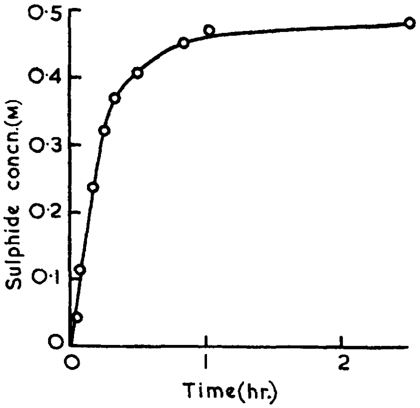
[1] B. Saville, *J.*, 1962, in the press.
[2] Rosenbaum and Symons, *J.*, 1961, 1.
[3] Adams and Ferretti, *J. Amer. Chem. Soc.*, 1959, **81**, 4927.
[4] Lawesson, Berglund, and Grönwall, *Acta Chem. Scand.*, 1961, **15**, 249.
[5] van Riemsdijk, van Steenis, and Waterman, *J. Inst. Petroleum*, 1951, **37**, 265.
[6] Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 84.

Product Distribution in the Preparation of t-Butyl t-Pentyl Sulphide.—Gas–liquid chromatography of the crude product obtained from both possible alcohol–thiol systems showed the following compositions:

Reactants	Total yield of sulphides (%)	Sulphide concns., moles % of product		
		Bu^t_2S	$CMe_2Et{\cdot}SBu^t$	$(CMe_2Et)_2S$
$CMe_2Et{\cdot}OH$; Bu^tSH	61	31	49	20
Bu^tOH; $CMe_2Et{\cdot}SH$	59	26	46	28

Acid-catalysed Solvolysis of Sulphides.—*Di-t-butyl sulphide.* Low yields from preparative runs and the deviation of the reaction curve from first order at high extents of reaction (see Figure) suggested competing solvolysis of the sulphide. Gas–liquid chromatography of samples isolated from an acetic acid solution of the sulphide (1·0M), water (1·0M), and perchloric acid (0·5M) after 1 hr. at 25° confirmed the presence of 2-methylpropane-2-thiol. The equilibrium was studied in identical solutions after 24 hr. at three temperatures:



Formation of $Bu_2{}^tS$ from Bu^tOH (0·5M) and Bu^tSH (2·5M) in acetic acid containing perchloric acid (0·25M) at 25°.

Temp.	15°	25°	35°
Sulphide concn. (M)	0·698	0·640	0·572
Equilibrium const. (K)	0·187	0·317	0·560

Values of the equilibrium constant, K, were obtained from the expression

$$K = [ROH][RSH]/[H_2O][RSR],$$

and a plot of log K against $1/T$ gave a straight line, from which the value of ΔH, the difference in activation energies of the forward and the back reaction, was found to be 9·9 kcal./mole.

In the presence of Linde molecular sieve 4A as drying agent (0·2 g./ml.) the equilibrium sulphide concentration at 25° was 0·698M.

TABLE 2.

Extent of acid-catalysed solvolysis of $Bu^tSR{\cdot}HClO_4$ concns. (M): A, 0·5; B, 0·005; C, 0.

R	Sulphide cleaved (%)					
	A		B		C	
	4 hr.	24 hr.	4 hr.	24 hr.	4 hr.	24 hr.
Et	—	0	—	—	—	—
Pr^i	—	0	—	—	—	—
$CH_2{:}CH{\cdot}CH_2{\cdot}$	0	0	0	0	0	0
$CHMe{:}CH{\cdot}CHMe{\cdot}$	22	37	4	18	0	8
$CMe_2{:}CH{\cdot}CHMe{\cdot}$	52	84	12	19	7	8
$CMe_2{:}CH{\cdot}CMe_2{\cdot}$	—	99	—	99	—	48

Other sulphides. Solvolyses were carried out at three perchloric acid concentrations with sulphide (1·0M) and water (1·0M) in acetic acid at 25° as shown in Table 2.

Di-t-butyl selenide. This compound was more resistant to solvolysis than the corresponding sulphide; the equilibrium concentration of selenide after 24 hr. at 25° under the conditions used for the sulphide was 0·89M.

DISCUSSION

Preparation of Sulphides.—In the condensing medium chosen, the anhydrous acid solvent increases proton availability, tertiary carbonium ions rapidly being liberated; as expected, neither ethanol nor propan-2-ol gave any reaction. The formation of di-t-butyl sulphide is virtually complete in an hour in this medium, and the 24-hour reaction period chosen for convenience in this work may be substantially reduced without loss of yield. It is important that no excess of acetic anhydride be present since this reacts rapidly with thiol under these conditions to give the thiolacetate (providing, incidentally, a simple route to t-butyl thiolacetate, although yields are lower than claimed for the usual more tedious method [7]). Except in the case of unsymmetrical di-t-alkyl sulphides (see below) it is possible to isolate undistilled products of 90—95% purity if care is taken to remove higher-boiling impurities from the " AnalaR " light petroleum used for extraction. The method is also applicable to selenides and was particularly useful for the preparation of di-t-butyl selenide, previous attempts with sulphuric acid as solvent having given low yields of impure material.[8]

Equilibria in Acid-catalysed Sulphide Solvolysis.—Previous examples of acid-catalysed solvolysis of sulphides have usually involved the triphenylmethyl group and halogen acids.[9] A notable exception is the mercuric chloride-assisted cleavage of (t-alkylthio)-acetic acids,[10] which were prepared by the reverse reaction from 2-methylpropan-2-ol and mercaptoacetic acid in hydrochloric acid. The observation of an equilibrium in sulphide solvolysis is, however, entirely new.

The solvolysis of di-t-butyl sulphide by the wet acid seems remarkable since sulphur is usually assigned a low proton affinity, and one might expect the positions of the corresponding equilibria

$$\mathrm{Bu^tOH} + \mathrm{H^+} \rightleftharpoons \mathrm{Bu^tOH_2^+}$$

and

$$\mathrm{Bu^t_2S} + \mathrm{H^+} \rightleftharpoons \mathrm{Bu^t_2SH^+}$$

to be such that the concentrations of the conjugate acid species would be $\mathrm{Bu^tOH_2^+} \gg \mathrm{Bu^t_2SH^+}$. To account for the comparable ease of formation of the intermediate t-butyl cation from both alcohol and sulphide, either the strongly electron-releasing t-butyl groups must confer a very high basicity on the sulphur atom, or $\mathrm{Bu^tSH^+}$ must be a better leaving group from carbon in S_N1 ionisations than $\mathrm{OH_2^+}$. Absence of cleavage of isopropyl t-butyl sulphide favours the former explanation, since $\mathrm{Pr^iSH^+}$ would be a better leaving group than $\mathrm{Bu^tSH^+}$.

In the preparation of t-butyl t-pentyl sulphide from both possible alcohol–thiol mixtures an almost statistical distribution of the three possible sulphides is obtained, the symmetrical sulphide derived from the thiol in excess being obtained in slightly higher yield than expected. Obviously the slight difference in stability of the t-butyl and t-pentyl cations is insufficient to affect significantly the direction of cleavage of the protonated intermediate. However, if stability differences were large, specific cleavage might occur, enabling single products to be obtained by using the alcohol giving the more stable carbonium ion. The formation of mixed products accounts for the very low yields observed for the other unsymmetrical sulphides described, and prevented the isolation of a pure sample of t-butyl t-pentyl sulphide.

The greater stability of di-t-butyl selenide than of the sulphide is of interest, although

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[7] Rylander and Tarbell, *J. Amer. Chem. Soc.*, 1950, **72**, 3021.

[8] Woodbridge, personal communication.

[9] Tarbell and Harnish, *Chem. Rev.*, 1951, **49**, 1; *J. Amer. Chem. Soc.*, 1952, **74**, 1862.

[10] Holmberg, *Arkiv Kemi, Min., Geol.*, 1942, **15***A*, No. 22; *Chem. Abs.*, 1944, **38**, 2945.

again the occurrence of solvolysis is somewhat surprising as selenium should have an even lower proton-affinity than sulphur. The difference between sulphides and selenides appears to be less sharp than that between sulphides and ethers, since di-t-butyl ether is reported to be extremely sensitive to acids, cleavage occurring immediately in the presence of dilute hydrochloric acid.[11] All three compounds illustrate the special reactivity which develops when *two* t-butyl groups are attached to a hetero-atom.

The unsaturated sulphides examined provide further evidence of the importance of electron-releasing substituents in solvolysis (Table 2). Although allyl t-butyl sulphide is unaffected, the rate of solvolysis increases with the introduction of methyl substituents into the allyl group. The reaction is, however, complicated by gradual displacement of the equilibrium to give diene and, subsequently, its dimer. Thus t-butyl 1,1,3-trimethylbut-2-enyl sulphide gave entirely the cyclic dimer, 3,3,5,5-tetramethyl-*p*-mentha-1,8-diene, in the presence of perchloric acid, and even in wet acetic acid the sulphide concentration fell continuously, 82% being lost after 43 days. The high yield obtained in the preparation of this sulphide is almost certainly due partly to the formation of two layers under the particular conditions used, and would probably be increased by using shorter reaction times.

Anomalous behaviour of sulphur compounds with strongly electron-releasing groups attached to sulphur has previously been noted in these laboratories. Di-t-butyl sulphoxide, and sulphoxides containing substituted allyl groups, show significant antioxidant activity,[12] thermal instability,[13] and abnormal reactivity towards t-butyl hydroperoxide.[14] It seems probable that these anomalies may arise from drastic modification of the basicity of the sulphur atom by electron-releasing substituents, and comparisons of sulphoxide basicities may provide a clearer understanding of these results. Since certain of the unsaturated sulphides used here are similar to the cross-linked structures present in natural rubber vulcanisates,[15] it is possible that the cleavages reported may provide a useful chemical probe in the elucidation of the finer details of structural differences in various rubber vulcanisates now in progress.

EXPERIMENTAL

Materials.—Reagents were of " AnalaR " grade, including perchloric acid used as the 72% aqueous solution. Light petroleum (b. p. 30—40°) was fractionated to remove higher-boiling impurities, the fraction of b. p. $<34°$ being used. 2-Methylbutane-2-thiol and 3-methylhexane-3-thiol were prepared through the thiouronium bromides.[16] 2-Methylpropane-2-selenol was kindly supplied by Mr. D. T. Woodbridge. 3-Methylhexan-3-ol and 5-methyltetradecan-5-ol were prepared from the appropriate methyl ketones by the Grignard reaction. Other alcohols and thiols were commercial materials, redistilled where necessary to 96% purity (gas–liquid chromatography).

Quantitative Analysis of Sulphides.—Gas–liquid chromatograms were obtained with an apparatus [17] involving columns packed with 5% w/w Silicone fluid 704 on Celite (60—72 mesh). Sulphides were identified [18] and their concentrations determined by using inert n-alkanes (C_{10}—C_{13}) as internal standards. Samples were prepared as follows. Aqueous 10% sodium hydroxide (10 ml.) and an aliquot part (10 ml.) of a 1·5% solution of the standard in n-heptane were placed in a separatory funnel (100 ml.) which was cooled under the tap. An aliquot part (1—3 ml.) of the reaction mixture was run in, the time when the pipette was half-empty being taken as the reaction time in the kinetic run. The funnel was stoppered, then shaken under the cooling water, and the contents were acidified with 2N-hydrochloric acid (25—30 ml.) and again

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[11] Smutny and Bondi, *J. Phys. Chem.*, 1961, **65**, 546.
[12] Barnard, Bateman, Cain, Colclough, and Cunneen, *J.*, 1961, 5339.
[13] Colclough and Cunneen, *Chem. and Ind.*, 1960, 626; and unpublished work.
[14] Colclough and Cunneen, unpublished work.
[15] Bateman, Glazebrook, Moore, Porter, Ross, and R. W. Saville, *J.*, 1958, 2838.
[16] Lee, B. Saville, and Trego, *Chem. and Ind.*, 1960, 868.
[17] Smith, " Gas Chromatography," Butterworths Scientific Publns., London, 1960, p. 114.
[18] Evans and Smith, *J. Chromatog.*, 1961, **6**, 293.

shaken. The lower layer was run off and the heptane solution dried ($MgSO_4$) before analysis. Results were obtained as the mean of at least four chromatograms, and control experiments showed that the accuracy was better than 3%.

Preparation of Sulphides.—The general method is described, followed by modified methods used for certain compounds. Analytical data for the new compounds are given in Table 3. All were >97% pure (gas–liquid chromatography).

General method. Into a 100-ml. volumetric flask containing acetic acid (*ca.* 30 ml.) was weighed perchloric acid solution (7·0 g.), followed by acetic anhydride (11·1 g.), the flask being cooled and shaken till the exothermic reaction ceased. The thiol (0·12 mole) and alcohol (0·10 mole) were added, the former always producing a yellow colour, and the mixture made up to the mark with acetic acid. After 24 hr. it was poured into saturated brine (250 ml.), the layers were separated, the aqueous layer was washed with redistilled light petroleum (3 × 50 ml.), and the combined organic layers were washed with saturated sodium hydrogen carbonate solution (2 × 50 ml.) and water (2 × 50 ml.), and dried ($MgSO_4$). For di-t-alkyl sulphides the solution was passed down a 40 × 3 cm. alumina-packed column, which was subsequently washed with more light petroleum (*ca.* 300 ml.). The solvent was removed by continuous distillation from a 50-ml. flask through a 40 × 1·5 cm. column packed with multi-turn glass helices, and the residue was distilled.

t-Butyl 1,3,3-*trimethylbut*-2-*enyl sulphide.* 2,4-Dimethylpent-3-en-2-ol (0·1 mole) and 2-methylpropane-2-thiol (0·12 mole) were dissolved in acetic acid (0·5 mole) and set aside overnight; two layers were formed. The mixture was worked up as in the general method, including chromatography on alumina.

Di-(1-*ethyl*-1-*methylbutyl*) *sulphide.* A mixture of perchloric acid solution (2·1 ml.), acetic anhydride (5·7 ml.), and 3-methylhexane-3-thiol (6·6 g.) was cooled to −40° and 3-methylhexan-3-ol (5·8 g.) added slowly with stirring, the mixture being allowed to warm sufficiently to ensure homogeneity (*ca.* −20°). It was stored at −20° for 18 hr., then water (20 ml.) and light petroleum (50 ml.) were added, followed by enough aqueous 10% sodium hydroxide to make the mixture alkaline. Subsequent working up was carred out as in the general method.

TABLE 3.

			Found (%)			Required (%)		
Sulphide	B. p./mm.	n_D^{20}	C	H	S	C	H	S
$(CMe_2Et)_2S$	79°/12	1·4688	69·1	12·8	18·3	68·9	12·7	18·4
$CMeEtPr^n{\cdot}SBu^t$	86—87°/11	1·4668	69·9	12·6	16·5	70·2	12·8	17·0
$(CMeEtPr^n)_2S$	125—127°/11	1·4781	73·0	13·2	13·9	73·0	13·1	13·9
$Me{\cdot}[CH_2]_9{\cdot}CMePr^n{\cdot}SBu^t$	125—126°/0·5	1·4712	75·9	13·1	11·0	75·9	13·4	10·7

t-Butyl Thiolacetate.—A solution (100 ml.) of 2-methylpropane-2-thiol (0·1 mole) and acetic anhydride (0·1 mole) in the usual perchloric–acetic acid mixture was left for 24 hr. before being worked up by the general method. The product (8·3 g., 63%) had b. p. 84°/130 mm., n_D^{20} 1·4535 (Found: C, 54·5; H, 9·10; S, 24·0. Calc. for $C_6H_{12}OS$: C, 54·5; H, 9·15; S, 24·25%), the purity being >99·5%.

Di-t-butyl Selenide.—This was prepared by a slightly modified method from 2-methylpropane-2-selenol (0·045 mole) and 2-methylpropan-2-ol (0·09 mole) in the usual perchloric–acetic acid mixture (50 ml.), all solutions being flushed with nitrogen. The crude product was distilled, to give the colourless *selenide* (4·8 g., 65%), b. p. 54°/16 mm., n_D^{20} 1·4755 (Found: C, 50·0; H, 9·6; Se, 41·0. $C_8H_{18}Se$ requires C, 49·8; H, 9·4; Se, 40·9%), which had a purity of >98%.

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THE NATURAL RUBBER PRODUCERS' RESEARCH ASSOCIATION, 48—56 TEWIN ROAD,
WELWYN GARDEN CITY, HERTS.
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