819. *The Reactions of Organic Derivatives of Elements Capable of Valency-shell Expansion. Part V.* A Comparison of the Near-ultra-violet Absorptions of Unsaturated Derivatives of Nitrogen, Phosphorus, and Sulphur with those of their Saturated Analogues.*

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Absorption spectra, in the near-ultra-violet region, of compounds mentioned in the title have been measured and the results found to correspond to the conclusions reached in Part I.* There is an increase in the intensity of absorption (compared with the saturated analogues) with the unsaturated derivatives of elements capable of valency-shell expansion, together with a marked bathochromic effect. Both effects are dependent on concentration and an explanation based on the association of the derivatives is advanced. As expected, saturated and unsaturated quaternary ammonium salts in neutral solution do not show these differences. Intense general absorption occurs with unsaturated bisalkylthio-compounds, which appears to arise from the sharing of the *p* electrons of the sulphur atom with the propene system. No such phenomenon is noticed with sulphonium chlorides.

AN attempt is made in this paper to ascertain whether the absorption, in the near-ultra-violet region, of saturated and unsaturated derivatives of the following classes can be *empirically* correlated with conclusions reached in Part I regarding the ability of certain elements to expand their valency shells. The compounds considered are : (*a*) unsaturated substances known to form mobile tautomeric systems or to contain " active " hydrogen (quaternary ammonium salts, disulphonyl- and tetrasulphonyl-propenes, disulphamoyl-propenes); (*b*) unsaturated substances believed to be mobile [propene-1 : 3-(diquaternary phosphonium) salts]; (*c*) unsaturated polar compounds where the mobility, if present at all, is only slight (propene-1 : 3-disulphonium salts); and (*d*) 1 : 3-bisalkylthio- and 1 : 1 : 3 : 3-tetrakisalkylthio-propenes which are neither tautomeric nor contain " active " hydrogen. Comparison is made between the saturated and the corresponding unsaturated derivatives in each case, and whilst great accuracy is not claimed for the observations, the differences are greater than any possible experimental errors. The most suitable solvent was 95% ethanol (Leighton, Cary, and Schipp, *J. Amer. Chem. Soc.*, 1931, **53**, 3017), although it suffered from the disadvantage of having an appreciable absorption below 210 mμ which added to the uncertainties of transmission measurements in this region. Tables 1—4 show that in most cases Beer's law was not applicable, this aspect being discussed in connection with Tables 5 and 6. All samples were dried over phosphoric oxide and measurements were made on a " Unicam " S.P. 500 spectrophotometer, with fused quartz cells and 10-mm. path length.

TABLE 1. *Maximum extinction coefficients for propane- and propene-*1 : 3-*diammonium, -diphosphonium, and -disulphonium chlorides,* $CH_2(CH_2R)_2$ *and* $CH_2R{\cdot}CH{:}CHR$.

	Saturated			Unsaturated		
R	Concn. (10^4 mole/l.)	$\lambda_{max.}$ (mμ)	log ε	Concn. (10^4 mole/l.)	$\lambda_{max.}$ (mμ)	log ε
$NEt_3\}Cl$	200—7·6	210—205	1·84—2·17	166—2·4	212—205	2·00—2·69
$PPr_3\}Cl$	119—6·0	210—208	2·19—2·75	117—2·0	230—213	2·30—3·79
$SBuMe\}Cl$	126—0·9	208—206	1·73—2·76	182—7·3	214—208	2·05—2·50

The non-applicability of Beer's law is quite clear from Table 1. The increase in the bathochromic effect and in the intensity of absorption of the unsaturated phosphorus compounds compared with those of the saturated derivatives is much more marked than with the other two pairs and suggests that there is some parallelism with the interaction of the double bond postulated for phosphorus but not for nitrogen or tervalent sulphur

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* Parts I—IV, preceding papers.

derivatives (Part I). The 1 : 3-disulphonium salts were difficult to obtain pure because aqueous solutions of the trimethylene derivatives, in particular, tended to develop an odour of sulphide on concentration even at room temperature. Since sulphides are strongly absorptive in the near-ultra-violet region, the measured optical densities of the sulphonium chlorides are probably rather too high.

TABLE 2. *Maximum extinction coefficients for* (a) 1 : 3-*bisalkylsulphonyl-*, (b) 1 : 3-*disulphamoyl-* ($R_2N\cdot SO_2\cdot$), (c) 1-*methyl*-1 : 3-*disulphamoyl-*, *and* (d) 1 : 1 : 3-*tetrakisethylsulphonyl-propane and -propene.*

	Saturated			Unsaturated		
	Concn. (10⁴ mole/l.)	$\lambda_{max.}$ (mμ)	log ε	Concn. (10⁴ mole/l.)	$\lambda_{max.}$ (mμ)	log ε
(*a*) Transparent	—	—	—	29·9—0·7	222—208	2·79—3·76
(*b*) R = Et	7·1—0·7	212—206	2·02—2·55	9·3—0·9	234—220	3·45—3·81
(*b*) R = H	—	—	—	18·4—1·8	218—212	2·93—3·50
(*c*)	—	—	—	10·0—0·3	242—218	3·20—4·07
(*d*) Transparent	—	—	—	1·3	206 & 286	3·76 & 4·50

All the unsaturated derivatives shown in Table 2 are tautomeric and the increased intensity of their absorption corresponds to the conclusion reached in Part I that " quadricovalent " sulphur adjacent to a double bond tends to expand its valency shell.

TABLE 3. *Maximum extinction coefficients for* (a) 1 : 3-*bisethylthio- and* (b) 1 : 1 : 3 : 3-*tetrakisethylthio-propane and -propene, and* (c) *bisethylthio- and* (d) *bisphenylthio-methane.**

	Saturated			Unsaturated.		
	Concn. (10⁴ mole/l.)	$\lambda_{max.}$ (mμ)	log ε	Concn. (10⁴ mole/l.)	$\lambda_{max.}$ (mμ)	log ε
(*a*)	15·7—1·3	212—206	2·89—3·22	1·40—1·0	252—254	3·76—3·85
(*b*)	26·3—2·1	214—208	2·79—3·48	5·0—1·5	212—206	3·59—3·52
	—	238—234	3·04—3·26	—	272—265	3·24—3·39
(*c*)	5·0	214	2·96	—	—	—
	—	238	2·96	—	—	—
(*d*)	—	—	—	—	205	4·3
				—	255	4·03

* Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 84.

In the range of concentrations studied for the substances of Table 3 a fairly close adherence to Beer's law was observed. Whilst the saturated sulphides exhibit a rapid decrease of absorption as the wave-length increases above 220 mμ and in this respect resemble allyl sulphide (log ε 3·33), the unsaturated analogues show a high absorption (log ε >3·0) up to 300 mμ. The saturated and unsaturated bisthioacetals give absorption curves nearly identical with those of bisethylthio(and other bisalkylthio)-derivatives (cf. Fehnel and Carmack, *loc. cit.*) and bisphenylthiomethane, the second absorption maxima appearing to result from interaction of the adjacent thio-groups since ethyl sulphide has not a maximum at this point.

TABLE 4. *Maximum extinction coefficients for benzyl and phenyl derivatives of quaternary nitrogen and phosphorus.*

	Concn. (10⁴ mole/l.)	$\lambda_{max.}$ (mμ)	log ε		Concn. (10⁴ mole/l.)	$\lambda_{max.}$ (mμ)	log ε
$CH_2Ph\cdot NMe_3Cl$	13·8—0·6	218—210	3·19—4·08	$Ph\cdot NMe_3Cl$	6·4—0·06	214—207	2·44—3·71
	—	263—264	2·63—3·46		—	259	2·34
$CH_2Ph\cdot PPr_3Cl$	12·5—0·5	221—210	3·55—4·11	Ph_3PO * ...	—	224	4·33
	—	260	3·58—3·41		—	266	3·38

* Jaffe and Friedman, *J. Amer. Chem. Soc.*, 1947, **69**, 2714. Figures for trialkylphenylphosphonium chlorides are not available, but trimethylphenylphosphonium *iodide* has an absorption similar to that of triphenylphosphine oxide at the higher maximum (Bowden and Braude, *J.*, 1952, 1068).

In the benzyl series exemplified in Table 4 nitrogen and phosphorus have nearly identical absorptions; the difference noticed in the phenyl derivatives is not inconsistent with the formation of π-bonds by the absorption of nuclear electrons into the *d* shell of the phosphorus atom (Part I).

General Discussion.—The non-applicability of Beer's law to the measurements described above has been encountered by other workers, *e.g.*, for triphenylsulphonium bromide in chloroform solution (Bonner, *ibid.*, 1952, **74**, 5078), where it was ascribed to molecular association. The bathochromic effect, which increases with concentration and is accompanied by a diminution of the molecular extinction coefficient, makes comparison between different classes of compounds impracticable unless a standard concentration is employed throughout. Considerations of solubility and the relative inaccuracy in the measurement of optical densities other than those which lie between 0·1 and 1·0 limit the use of identical concentrations, and it is difficult to weigh exactly non-crystalline materials such as the " onium " chlorides. Nevertheless Table 5, which lists the various groups in order of their optical densities, enables certain reasonable deductions to be made. The compounds used for construction of Table 5 are all trimethylene derivatives and the occurrence of some interaction between terminal groups is shown by a comparison of optical densities of solutions (5×10^{-4} mole/l. in *cyclo*hexane) of bisethylthiomethane and 1 : 1 : 3 : 3-tetrakisethylthiopropane (see Table 5*b*). The density of the latter is rather more than twice that of the former at corresponding wave-lengths. The effect of unshared *p* electrons in the case of the last two groups in Table 5*a* is very noticeable. Its absence in the case of the sulphonium salts leads to the very much smaller optical density.

TABLE 5. *Measured optical densities of groups attached to saturated chains.*

(*a*) Group	Concn. (10^4 mole/l.)	$\lambda_{max.}$ (mμ)	Optical density (max.)	(*a*) Group	Concn. (10^4 mole/l.)	$\lambda_{max.}$ (mμ)	Optical density (max.)
$C\cdot SO_2\cdot Bu$	6·96	—	0	$C\cdot SBuMe\}Cl$	6·31	209	0·184
$C(SO_2Et)_2$	6·31	206	0·045	$C\cdot PPr_3\}Cl$	5·96	208	0·337
$C\cdot SO_2\cdot NR_2$	7·13	211·5	0·075	$C\cdot SBu$	6·29	267	0·763
$C\cdot NEt_3\}Cl$	7·56	206	0·113	$C(SEt)_2$	5·25	210	1·140

	Optical density at mμ stated			
(*b*) Compound	240	230	220	214
$Et_2S\cdot CH_2\cdot SEt_2$	0·335	0·305	0·256	0·459
$(EtS)_2CH\cdot CH_2\cdot CH(SEt)_2$	0·905	0·840	0·645	0·945

If the maximum values of the optical densities of the unsaturated derivatives in a particular region, irrespective of the actual wave-lengths, are considered, it is seen (Table 6) that there is a decrease in the case of the sulphonium compounds, a slight increase for the quaternary ammonium salts, and a large increase in all the other cases. The relatively low concentration of the unsaturated sulphide is responsible for the small change in intensity of absorption for this compound.

TABLE 6. *Measured optical densities of groups attached to unsaturated chains.*

Group	Concn. (10^4 moles/l.)	$\lambda_{max.}$ (mμ)	Optical density (maximum)	Δ *
$C\cdot NEt_3^+$	6·96	205	0·137	+0·02
$C\cdot SBuMe^+$	7·28	208	0·231	0·05
$C\cdot SO_2\cdot Bu$	7·52	216	1·31	1·31
$C(SO_2\cdot Me)_2$	6·50	208	1·38	1·33
$C\cdot PPr_3^+$	5·87	214	1·79	1·45
$C(SEt)_2$	5·0	212	1·95	0·84
$C\cdot SO_2\cdot NEt_2$	9·3	234	2·62	2·54
$C\cdot SBu$	1·4	252	0·810	0·05

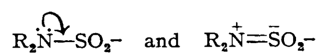
* Approx. difference between saturated and unsaturated derivatives.

In all the cases considered, a rise in the concentration is accompanied by a fall in the molecular extinction coefficient but this is less pronounced for sulphides, thioacetals, and sulphonium salts. A marked increase in the wave-length of maximum absorption occurs with derivatives of elements where utilisation of *d* orbitals has been postulated, and since this is dependent on concentration it may be the result of association between two or more molecules. This is especially noticeable in the case of the propenylenediphosphonium salts (Table 1) where the maximum absorption for high concentrations (0·0117 mole/l.) is at 230 mμ, which is reduced to 213 mμ when the solution is diluted about fifty times.

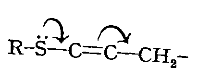
Association can be of two kinds. The first involves terminal groups only and appears to be marked by increased intensity of absorption with practically no change of wavelength. This is illustrated by both the saturated and the unsaturated ammonium salts (Table 1) at moderate concentrations and is in conformity with the association of quaternary ammonium salts found by Kraus and Vingee (*ibid.*, 1934, **56**, 511) to occur in quite low concentrations (0·01—0·0001N) both in dioxan and in benzene.

A second type of association involves the propene chain and depends on the possibility of expansion of the valency shell of the central atom of the terminal group. The easy interconversion of the disulphones, which does not involve the kinetically free ions (Rothstein, *J.*, 1937, 317), was considered to involve transitional structures such as:

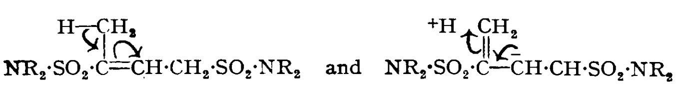
and possibly should include other structures in which more than two molecules take part. The sulphamoyl derivatives (Table 2) which exhibit, to a small degree, the same bathochromic effect, contain " active " hydrogen and appear to be mobile in certain circumstances (Part III). The effect, however, is smaller than with sulphones; this is not unexpected since the unshared electrons on the nitrogen atoms would tend to counteract the effects shown in the sulphones and give rise to mesomerism between structures of the type



$R_2\ddot{N}-SO_2-$ and $R_2\overset{+}{N}=\overset{-}{S}O_2-$



Apart from reasons already mentioned, the choice of a polar solvent had the advantage of utilising an environment where solvation of the hydrogen ion would assist in its separation and so increase delocalisation of the electrons of the propene system. Solvent, however, should have less influence on sulphides and thioacetals (Table 3), where the non-bonding electrons on sulphur are available both for promotion on the *d* level or alternatively can be absorbed into the propene system (see inset). The energy required for the former process is probably too high for its occurrence since neither the bis- nor the tetrakis-alkylthiopropenes show any tendency to part with a proton to form an anion (this paper and Part IV, respectively). This is also true for sulphonium compounds (p. 4024) as might be expected from the discussion in Part I. This non-formation of π-bonds is probably the reason for the narrow absorption bands that are found for these substances. The same effect is noticed in the sulphonamides where the presence of the non-bonding nitrogen electrons tends to raise the promotional energies required to utilise the *d* orbitals of sulphur by the π-electrons of the carbon–carbon double bond; and it is significant that the narrowest absorption bands are shown by the *N*-unsubstituted sulphonamides. A similar decrease in absorption is observed in the case of the butenylene disulphonamides, where the methyl group tends to prevent the formation of an anion and also stabilises the π-electrons in the 2 : 3-positions (Part III) by resonance involving the structures:



EXPERIMENTAL

Quaternary Ammonium Salts.—*NNNN'N'N'*-Hexaethyl-2-hydroxytrimethylenediammonium dibromide was prepared by boiling a solution of glycerol 1 : 3-dibromide with an excess of ethanolic 33% triethylamine under reflux and precipitating the product with dry ether. It crystallised from ethanol–ligroin (b. p. 60—80°) in needles, m. p. 243—244° (Found: C, 43·0; H, 8·7; Br, 38·4. Calc. for $C_{15}H_{36}ON_2Br_2$: C, 42·9; H, 8·6; Br, 38·1%). The corresponding *dipicrate* separated from acetone–ethanol in needles, m. p. 229—230° (Found: C, 45·2; H, 5·7; N, 15·7. $C_{27}H_{40}O_{15}N_8$ requires C, 45·3; H, 5·6; N, 15·6%).

The above bromide (21 g.) was dehydrated under reflux for 15 hr. with phosphorus pentachloride (25 g.) and chloroform (100 c.c.). The product was mixed with water and extracted with ether, and the aqueous layer first neutralised with sodium hydroxide, then slightly acidified with hydrochloric acid, and evaporated to dryness. The residue was extracted with ethanol, the liquid filtered, and the filtrate reduced to a syrup on the steam-bath. Treatment with sodium picrate solution afforded *NNNN'N'N'-hexaethylpropenylene-1 : 3-diammonium dipicrate,* which crystallised from absolute ethanol in needles, m. p. 225° (Found: C, 46·7; H, 5·1; N, 16·0. $C_{27}H_{38}O_{14}N_8$ requires C, 46·4; H, 5·4; N, 16·0%). Another sample which after repeated crystallisations had m. p. 215° afforded a similar analysis (Found: C, 46·5; H, 5·4; N, 15·6%). Since propenylenediammonium picrates do not show a depression of m. p. in admixture (Ingold and Rothstein, *J.*, 1931, 1666) these may have been different geometrical isomerides.

The quaternary diammonium dichloride was obtained by acidifying the dipicrate with concentrated hydrochloric acid and, after removal of the picric acid, extracting the filtrate with benzene (three times). Finally the aqueous layer was boiled with activated vegetable charcoal and filtered, and the solvent removed on the steam-bath. Final desiccation over phosphoric oxide afforded a colourless amorphous solid. Its structure was shown by oxidation to carboxymethyltriethylammonium chloride by using the above chloride (4 g.), sodium permanganate (6 g.), sodium carbonate (2 g.), and water (100 c.c.) (cf. Ingold and Rothstein, *loc. cit.*). Two recrystallisations of the picrate from water completely eliminated unchanged diammonium salt and the m. p. was 195—196° (Found: C, 43·5; H, 5·2; N, 14·2, 14·5. Calc. for $C_{14}H_{20}O_9N_4$: C, 43·3; H, 5·2; N, 14·7%).

Sulphur Compounds.—Derivatives of bisethylthiopropane. A solution of 1 : 3-bisethylthio-2-hydroxypropane (18 g.) in benzene (20 c.c.) was treated dropwise with thionyl chloride (8 c.c.). Reaction occurred in the cold and was completed by warming the mixture with a further 2 c.c. of the reagent for 10 min. on the steam-bath. *2-Chloro-1 : 3-bisethylthiopropane* (18·2 g., 92%) so obtained had b. p. 127°/10 mm. (Found: C, 42·9; H, 7·5. $C_7H_{15}ClS_2$ requires C, 42·3; H, 7·6%). Oxidation with 30% hydrogen peroxide furnished the corresponding sulphone which crystallised from ethyl acetate–ligroin (b. p. 60—80°) in needles, m. p. 82—83°. It was identical (mixed m. p.) with that obtained by replacement of hydroxyl in the corresponding hydroxy-sulphone (Rothstein, *loc. cit.*) (Found: C, 32·4; H, 5·8. Calc. for $C_7H_{15}O_4ClS_2$: C, 32·0; H, 5·7%).

Alkylation. 2-Chloro-1 : 3-bisethylthiopropane was dissolved in an equal weight of nitromethane, and excess of methyl iodide added. After a week, the product was extracted with water, and the aqueous layer washed with ether and then reduced to a small volume by distillation in a vacuum. The residual syrup furnished *2-chloro-SS'-diethyl-SS'-dimethyltrimethylenedisulphonium dipicrate* which separated from dilute ethanol in prisms, m. p. 136° (Found: C, 36·9; H, 3·8; S, 9·3. $C_{21}H_{25}O_{14}N_6ClS_2$ requires C, 37·0; H, 3·7; S, 9·4%). The *chloroplatinate,* m. p. 204°, crystallised from water (Found: C, 16·3; H, 3·3; Pt, 30·5. $C_9H_{21}Cl_7S_2Pt$ requires C, 17·0; H, 3·3; Pt, 30·7%). When the chloro-disulphonium dichloride was mixed at room temperature with one mol. of sodium methoxide in ethanolic solution, a halogen-free substance was obtained, which yielded a styphnate crystallising from alcohol in fine needles, m. p. 187° (decomp.). The styphnate was unsaturated to permanganate and was acid to sodium hydrogen carbonate solution. The analytical figures were unsatisfactory and a structure could not be assigned to the substance (Found: C, 34·9, 34·3; H, 3·3, 3·4; S, 7·3; N, 12·4%).

1 : *3-Bisethylthiopropene.*—(a) *Preparation.* The chloro-sulphide (20 g.) was slowly added to a solution of potassium (16 g., 50% excess) in *tert.*-butyl alcohol (150 c.c.), and the mixture boiled under reflux for 2 hr. The cooled liquid was mixed with water, to dissolve precipitated potassium chloride, and the solution extracted with ether and dried with successive small quantities of anhydrous potassium carbonate, the saturated aqueous solution of the reagent which separated being drawn off each time. The *tert.*-butyl alcohol was removed by fractional distillation at 100 mm., leaving the residual 1 : *3-bisethylthiopropene,* b. p. 105°/9 mm. (13·3 g., 82%) (Found: C, 52·2; H, 8·5; S, 39·6. $C_7H_{14}S_2$ requires C, 51·9; H, 8·6; S, 39·5%). Oxidation with 30% hydrogen peroxide afforded the corresponding disulphone, m. p. 117°, identified by comparison (mixed m. p.) with an authentic specimen (Rothstein, *loc. cit.*) (Found: C, 37·4; H, 6·3. Calc. for $C_7H_{14}O_4S_2$: C, 37·2; H, 6·2%). Like the other bisalkylthiopropenes described below, it could be neither *C*-alkylated nor condensed with benzaldehyde.

(b) *Methylation.* The disulphide was converted into the *SS'*-dimethiodide with methyl iodide, and an aqueous solution thereof was shaken with an excess of silver chloride. Filtration and distillation in a vacuum afforded a syrup which furnished *SS'-diethyl-SS'-dimethylpropenylene-1 : 3-disulphonium dipicrate,* separating from ethanol in prisms, m. p. *ca.* 185°, very soluble in both ethanol and water (Found: C, 38·4; H, 4·0; S, 9·0. $C_{21}H_{24}O_{14}N_6S_2$ requires C, 38·9; H, 3·7; S, 9·7%). An acid styphnate crystallising from ethanol in needles, m. p. 167° (decomp.), was obtained; it depressed the m. p. of styphnic acid but all the carbon analyses were low (Found: C, 35·4; H, 4·1; S, 8·9; N, 12·2%). The disulphonium dichloride was stable to 30% hydrogen peroxide and resisted alkylation with sodium ethoxide and methyl iodide. No condensation product with benzaldehyde could be obtained, the unchanged sulphonium salt being recovered.

Preparation of 1 : 3-*Bisbutylthio-derivatives.*—Addition of a solution of 1 : 3-dichlorohydrin (190 g.) in ethanol (200 c.c.) to an ethanolic solution of sodium *n*-butyl sulphide (from 127 g. of *n*-butanethiol) gave 1 : 3-*bisbutylthio-2-hydroxypropane*, b. p. 126°/0·3 mm. (143 g., 88%) (Found: C, 56·7; H, 9·9; S, 27·7. $C_{11}H_{24}OS_2$ requires C, 56·0; H, 10·3; S, 27·1%). Oxidation with hydrogen peroxide afforded 1 : 3-*bisbutylsulphonyl-2-hydroxypropane*, which separated from ethyl acetate in plates, m. p. 138—139° (Found: C, 44·4; H, 7·7; S, 21·2. $C_{11}H_{24}O_5S_2$ requires C, 44·0; H, 8·0; S, 21·3%). A benzene solution of the hydroxy-sulphide (59 g.) with thionyl chloride (20 g.) afforded 1 : 3-*bis*-n-*butylthio-2-chloropropane*, b. p. 130°/0·5 mm. (46 g., 72%) (Found: C, 51·3; H, 8·5; Cl, 14·0. $C_{11}H_{23}ClS_2$ requires C, 51·9; H, 9·0; Cl, 13·9%), and an unidentified fraction, b. p. 95°/0·5 mm. Oxidation of either fraction furnished 1 : 3-*bis*-n-*butylsulphonyl-2-chloropropane*, m. p. 105° (from ethyl acetate) (Found: C, 41·3; H, 6·9. $C_{11}H_{23}O_4ClS_2$ requires C, 41·6; H, 6·9%).

1 : 3-Bisbutylthio-2-chloropropane (46 g.) was converted into 1 : 3-*bis*-n-*butylthiopropene*, b. p. 104—106°/0·1 mm., by a boiling solution of potassium (9 g.) in *tert.*-butyl alcohol (Found: C, 60·4; H, 10·4; S, 29·4. $C_{11}H_{22}S_2$ requires C, 60·6; H, 10·1; S, 29·4%). The corresponding 1 : 3-*bis*-n-*butylsulphonylpropene* separated from ethyl acetate in prisms, m. p. 80—81° (Found: C, 46·5; H, 8·0; S, 22·8. $C_{11}H_{22}O_4S_2$ requires C, 46·8; H, 7·8; S, 22·7%).

Methylation of Bis-n-*butylthiopropene.*—The disulphide (10 g.) was left with methyl iodide (20 c.c.) in the dark for 24 hr. Nitromethane (10 c.c.) was then added and the mixture kept for a further 24 hr. Water was added, the organic layer separated, and the aqueous layer washed with chloroform and shaken for 12 hr. with silver chloride (40 g.). After filtration the liquid was evaporated to a small bulk in a vacuum at 30°, a syrup being obtained which crystallised in a vacuum-desiccator over phosphoric oxide to a highly deliquescent solid. Derivatives needed care in preparation owing to their great solubility in both water and ethanol. SS′-*Di*-n-*butyl*-SS′-*dimethylpropenylene*-1 : 3-*disulphonium dipicrate* crystallised from ethanol in prisms, m. p. 68—69° (Found: C, 41·9; H, 5·0; N, 12·1. $C_{25}H_{32}O_{14}N_6S_2$ requires C, 42·5; H, 4·5; N, 11·9%). The *distyphnate* separated from ethanol in needles, m. p. 71—72° (Found: C, 39·9; H, 4·6; S, 9·2; N, 11·6. $C_{25}H_{32}O_{16}N_6S_2$ requires C, 40·7; H, 4·3; S, 8·7; N, 11·3%), which dissolved in sodium hydrogen carbonate solution.

Preparation of 1-*Butylthio*-3-*ethylthio-derivatives.*—An ethanolic solution of 1-chloro-3-ethylthiopropan-2-ol (82 g.) was slowly added to a stirred solution of sodium *n*-butyl sulphide (from 54 g. of *n*-butanethiol), and the reaction completed on the steam-bath for 20 min. Fractionation of the product yielded a small amount of bis-*n*-butylthiopropan-3-ol (presumably from some unchanged dichlorohydrin in the starting material), the main product being 1-n-*butylthio*-3-*ethylthiopropan*-2-*ol*, b. p. 105—107°/0·1 mm. (74 g.) (Found: C, 51·5; H, 9·6; S, 30·1. $C_9H_{20}OS_2$ requires C, 51·9; H, 9·6; S, 30·8%). Oxidation yielded 1-n-*butylsulphonyl*-3-*ethylsulphonylpropan*-2-*ol*, crystallising from ethyl acetate in prisms, m. p. 120° (Found: C, 40·2; H, 7·5; S, 23·8. $C_9H_{20}O_5S_2$ requires C, 39·7; H, 7·3; S, 23·5%). The chloro-disulphide with thionyl chloride in benzene afforded 1-n-*butylthio*-2-*chloro*-3-*ethylthiopropane*, b. p. 112°/0·05 mm. (92%) (Found: C, 48·0; H, 8·8; Cl, 16·0. $C_9H_{19}ClS_2$ requires C, 47·7; H, 8·4; Cl, 15·6%), oxidised to 1-n-*butylsulphonyl*-2-*chloro*-3-*ethylsulphonylpropane*, m. p. 73° (from ethyl acetate) (Found: C, 37·3; H, 7·0; S, 22·0. $C_9H_{19}O_4ClS_2$ requires C, 37·2; H, 6·6; S, 22·0%). Impure products were obtained when the bisalkylthiopropane was converted into the unsaturated sulphide. The latter, and the corresponding sulphone and sulphonium salts, were prepared by another method (to be described later).

Saturated Sulphur Derivatives.—1 : 3-*Bis*-n-*butylthiopropane*, obtained in 87% yield from trimethylene bromide and sodium *n*-butyl sulphide, had b. p. 161°/11 mm. (Found: C, 60·1; H, 11·6; S, 28·9. $C_{11}H_{24}S_2$ requires C, 60·0; H, 10·9; S, 29·1%). The corresponding 1 : 3-*bis*-n-*butylsulphonylpropane*, m. p. 158°, crystallised from ethyl acetate (Found: C, 46·8; H, 8·3; S, 22·2. $C_{11}H_{24}O_4S_2$ requires C, 46·5; H, 8·5; S, 22·5%). The dimethiodide was obtained by boiling 1 : 3-bis-*n*-butylthiopropane with a solution of methyl iodide in nitromethane, and was converted into the *dipicrate*, which separated from dilute alcohol in plates, m. p. 153—154° (Found: C, 42·7; H, 4·8; N, 11·8; S, 8·7. $C_{25}H_{34}O_{14}N_6S_2$ requires C, 42·5; H, 4·8; N, 11·9; S, 9·1%).

Preparation of Benzylammonium and Benzylphosphonium Salts.—Benzyltrimethylammonium picrate was recrystallised several times and converted into the chloride, m. p. 232° (decomp.), which was dried over phosphoric oxide (Found : C, 64·4; H, 8·1; Cl, 20·0. Calc. for $C_{10}H_{16}NCl$: C, 64·7; H, 8·6; Cl, 19·7%).

Equimolecular quantities of benzyl chloride and tri-*n*-propylphosphine (Part II) were boiled under reflux in ethanol, and the very deliquescent phosphonium salt precipitated with dry ether. This yielded *benzyltri*-n-*propylphosphonium picrate*, needles (from ethanol), m. p. 105° (Found : C, 55·0; H, 6·0. $C_{22}H_{30}O_7N_3P$ requires C, 55·1; H, 6·2%). Treatment with hydrochloric acid yielded the *chloride*, m. p. 168° (Found : C, 67·5; H, 9·8; Cl, 11·9. $C_{16}H_{28}ClP$ requires C, 67·0; H, 9·8; Cl, 12·4%).

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