Alkylation of Sulphur Imides

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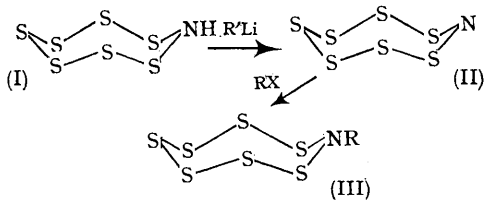
ALTHOUGH a variety of methods for the preparation of *N*-acyl derivatives of heptasulphur imide have been reported,[1] *N*-alkyl derivatives have not previously been available. We now report a general synthesis for primary and secondary alkyl derivatives of (I).

Alkylation of (I) occurred when S_7N^- (II),[2] as its lithium salt, was used to effect nucleophilic substitution on alkyl halides. (II) was generated by reacting (I) with alkyl-lithium reagents, in anhydrous tetrahydrofuran, at low temperatures. Methyl, ethyl, and allyl iodide, as well as benzyl bromide, were then reacted with (II) to give moderate yields (55%) of S_7NR (III). Isopropyl iodide reacted to give a 12% yield of (III) while no reaction was apparent with t-butyl iodide. The benzyl derivative was a solid of m.p. 44—45°; the other derivatives were oils. All were fairly stable at room temperature with the exception of the benzyl derivative which, when solid, decomposed in a week to ten days. Solutions, however, were substantially more stable.

The alkylimides were purified by chromatography on silica gel using hexane as eluant. Products, (III), were eluted directly after sulphur and had R_F values of: 0·42 for methyl, 0·42 for ethyl, 0·38 for allyl, 0·19 for benzyl, and 0·42 for isopropyl (*cf.* 0·52 for sulphur). Characterization of the alkylimides was by elemental analysis, molecular weight, ¹H n.m.r., and i.r. spectroscopy. In all cases the alkyl group was found to be on the nitrogen, and the eight-membered ring remained intact. The latter is of interest since the reactions were carried out under strongly basic conditions.



During the preparation of (II) considerable addition of the alkyl-lithium reagent to S–N and/or S–S bonds occurred in competition with proton abstraction. This competitive reaction gave rise, after alkylation, to mixtures of dialkylpolysulphanes and sulphur as by-products. The ratio of proton abstraction to addition was found to increase as the temperature was lowered. Once formed (II) persisted in solution at room temperature for several days and regenerated (I) when added to cold aqueous acid.

When the 1,4-isomer of hexasulphur di-imide[3] was treated with a 1M-equivalent of ethyl-lithium followed by methyl iodide, the products isolated after chromatography on silica gel were *N*-methylhexasulphur di-imide and *NN'*-dimethylhexasulphur di-imide in a ratio of approximately 2:1. In addition to unreacted hexasulphur di-imide, some sulphur and dialkylpolysulphanes were also formed. R_F values on silica gel with carbon disulphide as eluant were 0·71 for dimethyl, 0·53 for methyl, and 0·35 for unsubstituted hexasulphur di-imide (*cf.* 0·82 for sulphur). Characterization was by mass spectra, i.r. and n.m.r. spectroscopy. Only a few disubstituted derivatives of hexasulphur di-imides have been previously prepared[1a,4] while monosubstituted derivatives have not been reported.

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[1] (*a*) M. Becke-Goehring and W. Koch, *Z. Naturforsch*, 1952, **7b**, 634; (*b*) A. Meuwsen and F. Schlossnagel, *Z. anorg. Chem.*, 1953, **271**, 226; (*c*) J. E. Colchester, P. Tavs, and H. J. Schulze-Steinen, *J. Chem. Soc.*, 1963, 4918; (*d*) H. G. Heal and J. Kane, *J. Chem. and Eng. Data*, 1965, **10**, 386; (*e*) H. Garcia, *Compt. rend.*, 1966, **263**, *C*, 1362.

[2] M. Becke-Goehring and B. Schwarz, *Z. anorg. Chem.*, 1958, **296**, 3.

[3] H. G. Heal, *Nature*, 1963, **199**, 371; H. Heal and J. Kane, *Nature*, 1964, **203**, 971; J. C. Van de Grampel and A. Vos, *Rec. Trav. chim.*, 1965, **84**, 599.

[4] R. C. Brasted and J. S. Pond, *Inorg. Chem.*, 1965, **4**, 1163.