

is, e.s.r. spectra do not at present provide an unequivocal means for distinguishing between $RO\cdot$ and $RO_2\cdot$ radicals. The difficulty is illustrated by our measurement of the principal g -values of the radical produced by the photolysis of a single crystal of α -tetralin hydroperoxide (Table I). The spectrum of this radical (average $g = 2.0155$) consists of a doublet with an isotropic splitting of about 9 gauss from which it would be tempting to conclude that it is the α -tetralyloxy radical ($C_{10}H_{11}O\cdot$). However, the possibility that it is the corresponding peroxy radical ($C_{10}H_{11}O_2\cdot$) with an appreciable spin density on both oxygen atoms³ cannot be entirely ruled out.

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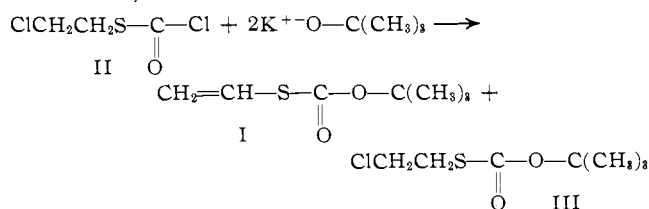
RECEIVED MAY 25, 1964

S-Vinyl-O-*t*-butyl Thiocarbonate. A New Route to Polymercaptans¹

Sir:

We wish to report the synthesis of S-vinyl-O-*t*-butyl thiocarbonate (I), a new monomeric precursor to polymercaptans containing a thermally removable or acid-labile sulfhydryl blocking group. This monomer can be utilized in the preparation of copolymers of polyvinyl mercaptan which contain acid- or base-sensitive substituents. These copolymers are being investigated as possible radiation prophylactics and as polymeric systems for enzymatic processes.

S-vinyl-O-*t*-butyl thiocarbonate² was synthesized by the following sequence of reactions: S-(β -chloroethyl) chlorothiоformate (II) was prepared from ethylene sulfide and phosgene according to the procedure of Ringsdorf and Overberger.^{2b} Addition of an ether solution of II (0.5 mole) to a solution of potassium *t*-butoxide (1.0 mole) in a 1:1 *t*-butyl alcohol-ether mixture at 20° resulted in concurrent esterification and dehydrohalogenation to produce I. Purification by fractional distillation afforded a 51.5% yield of S-vinyl-O-*t*-butyl thiocarbonate, b.p. 60.5–61° (15 mm.), n_D^{25} 1.4642 (lit.¹ n_D^{25} 1.4642), plus a 6% yield of S-(β -chloroethyl)-O-*t*-butyl thiocarbonate (III), b.p. 48–49° (0.5 mm.), n_D^{25} 1.4722 (lit.¹ n_D^{25} 1.4722).



S-Vinyl-O-*t*-butyl thiocarbonate polymerized readily in bulk or solution in the presence of free-radical initiators. The polymer was soluble in aromatic hydrocarbons and halogenated solvents and could be precipitated by addition to aliphatic hydrocarbons or methanol. A range of molecular weights could be prepared by varying catalyst concentrations but the

(1) This is the 27th in a series of papers concerned with new monomers and polymers; for the previous paper in this series see C. G. Overberger and W. H. Daly, *J. Org. Chem.*, **29**, 757 (1964).

(2) (a) Previously reported as a by-product from the dehydrohalogenation of S,S-(β -chloroethyl) dithiocarbonate [C. G. Overberger and W. H. Daly, ref. 1]; (b) H. Ringsdorf and C. G. Overberger, *Makromol. Chem.*, **44**, 418 (1961).

following discussion of hydrolysis procedures pertains specifically to a polymer with an intrinsic viscosity of 0.45. In copolymerization experiments the monomer has been shown to be similar in reactivity to the S-vinyl carbamates.³

The acid lability of the *t*-butyloxocarbonyl group has been utilized in peptide synthesis for the protection of amino substituents.⁴ Analogous reactivity was observed for the thiocarbonates. Treatment of a 1% solution of poly(S-vinyl-O-*t*-butyl thiocarbonate) in 6:1 chloroform-tetrachloroethane with anhydrous hydrogen bromide for 4 hr. resulted in an evolution of carbon dioxide and isobutylene and yielded a solution of polyvinyl mercaptan. The polymercaptan was isolated by precipitation using methanol as the non-solvent and purified by dissolution in dimethyl sulfide and reprecipitation. Mercaptan assay⁵ indicated that 84% removal of the *t*-butyloxocarbonyl group had occurred.

Recently the thermal removal of the *t*-butyloxocarbonyl group from glycidic esters,⁶ carbonic anhydrides,⁷ carbamates,⁸ and 1-N-carbo-*t*-butoxy-5-phenylpyrazolidone-3⁹ has been reported. Since the reaction appeared general and the thermal decomposition of S-methyl thiocarbonates was known,¹⁰ poly(S-vinyl-O-*t*-butyl thiocarbonate) was investigated. It was found that heating a 15% solution of polymer in N-methylpyrrolidone under nitrogen to 150° induced a vigorous evolution of carbon dioxide and isobutylene. The isobutylene was identified by the formation of N-*t*-butylbenzamide from benzonitrile *via* the Ritter reaction.¹¹ Quantitative determination of carbon dioxide by absorption on Ascarite indicated that 89% reaction had occurred after 2 hr. This was in good agreement with a mercaptan assay of 82% for the polyvinyl mercaptan solution. The polyvinyl mercaptan was soluble in dimethyl sulfoxide, N,N-dimethylformamide, dioxane, and 5% sodium hydroxide.

The relative mildness of the conditions required for hydrolysis and the freedom from side reactions makes this a very versatile procedure for the preparation of mercaptans. The remarkably low decomposition temperature and the formation of isobutylene suggests an intramolecular mechanism similar to that proposed for the Chugaev reaction.¹² A mechanism of this type should be quite general making the *t*-butyloxocarbonyl group a thermally removable protective group for a variety of substituents containing active hydrogens. Studies are now in progress to elucidate this mechanism and to extend the scope of the reaction.

Details of the copolymerization experiments and the oxidation of the polyvinyl mercaptan with molecular oxygen will be reported in the near future.

(3) H. Ringsdorf, N. Weinschenker, and C. G. Overberger, *ibid.*, **64**, 126 (1963).

(4) (a) F. C. McKay and N. F. Albertson, *J. Am. Chem. Soc.*, **79**, 4686 (1957); (b) G. W. Anderson and A. C. McGregor, *ibid.*, **79**, 6180 (1957).

(5) A modification of the procedure described by C. G. Overberger, J. J. Ferraro, and F. W. Orttung, *J. Org. Chem.*, **26**, 3458 (1961), was used.

(6) E. D. Blanchard, Jr., and G. Büchi, *J. Am. Chem. Soc.*, **85**, 955 (1963).

(7) C. J. Michejda and D. S. Tarbell, *J. Org. Chem.*, **29**, 1168 (1964).

(8) W. J. Bailey and J. R. Griffith, *Polymer Preprints*, **5**, 279 (1964).

(9) N. M. Weinschenker, B.S. Thesis, Polytechnic Institute of Brooklyn, 1964.

(10) E. Salomaa, *Ann. Acad. Sci. Fennicae Ser. II*, **94**, 1 (1959).

(11) J. J. Ritter and P. D. Minieri, *J. Am. Chem. Soc.*, **70**, 4045 (1948).

(12) (a) G. L. O'Connor and H. R. Nace, *ibid.*, **75**, 2118 (1953); (b) R. F. W. Bader and A. N. Bourns, *Can. J. Chem.*, **39**, 348 (1961).

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Synthesis of Tetraisoamylammonium Tetraisoamylboride. A Reference Electrolyte for the Evaluation of Single Ion Conductivities

Sir:

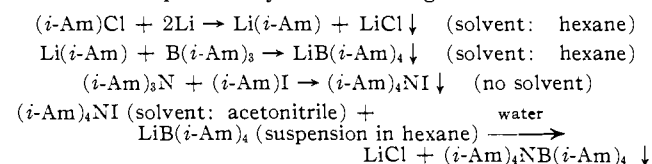
For the investigation of ion-solvent interactions, reliable values of single ion conductivities are invaluable. Ideally, precise transference number measurements are required for this purpose. However, in the majority of nonaqueous solvents serious experimental difficulties are encountered in such measurements, with the result that reliable transference numbers are available only for methanol, and, somewhat less reliably, for ethanol and nitromethane as solvents.¹ Consequently, for other solvents several investigators have estimated single ion conductivities indirectly, by assuming that in any given solvent the cation and anion of a salt such as tetrabutylammonium tetraphenylboride, $\text{Bu}_4\text{N}^+\text{BPh}_4^-$, or triisoamylbutylammonium tetraphenylboride, $(i\text{-Am})_3\text{BuNBPh}_4^-$,² will have equal mobilities. This assumption is justified as a first approximation, because the cation and anion are of approximately equal crystallographic size, and because (classical) solvation may be expected to be small since the ions are large and reasonably symmetrical, and the single charge is fairly well shielded. Methanol is the only solvent for which the applicability of these salts has been tested so far on a reliable scale derived from directly measured transference numbers. It was found² that the limiting equivalent conductivity of Ph_4B^- in methanol is 8% lower than that of Bu_4N^+ and agrees to within 1% with that of $(i\text{-Am})_3\text{BuN}^+$. On this basis Coplan and Fuoss recently have recommended the use of $(i\text{-Am})_3\text{BuNBPh}_4^-$ as a reference electrolyte for the indirect estimation of single ion conductivities in other solvents. However, models show that the average (effective) crystallographic radius of Ph_4B^- is somewhat smaller than that of Bu_4N^+ and considerably smaller (by ca. 10%) than that of $(i\text{-Am})_3\text{BuN}^+$. It is our opinion that although Ph_4B^- may be the best reference anion hitherto available, it is by no means ideal for this purpose. Some degree of classical solvation³ may occur with this anion in polar (even in nonhydrogen-bonding) solvents, since the phenyl groups are somewhat polarizable. More important, in a hydrogen-bonding solvent, such as methanol, hydrogen bonding of the solvent to the phenyl groups is conceivable, of the type described by Schleyer, *et al.*⁴ Such solvation could account for the fact that in methanol the mobility of Ph_4B^- is considerably lower than that of Bu_4N^+ , despite its somewhat smaller

crystallographic radius. Specific solvation must of course be absent if an ion is to serve as a reference in a variety of solvents.

We have succeeded in synthesizing the salt tetraisoamylammonium tetraisoamylboride, $(i\text{-Am})_4\text{NB}(i\text{-Am})_4$, and recommend it as a reference electrolyte for the evaluation of single ion conductivities. It has an advantage over previous salts used for this purpose in that its anion matches the cation closely in having virtually the same size, and particularly in that the anion should be much less susceptible to specific solvation effects than may be the case with Ph_4B^- . Furthermore, this salt is interesting *per se* in that it is an unusual boron compound. To our knowledge, no other tetraboride has been prepared with such large alkyl groups.

The applicability of this salt to the evaluation of single ion conductivities is now being tested in this laboratory by measuring its conductivity and those of an appropriate series of other salts in acetonitrile, acetone, and nitromethane. Preliminary results⁵ obtained in nitromethane agree with known transference numbers¹ to better than 0.1%. We are also attempting to measure transference numbers directly in acetonitrile and acetone.

The synthesis of $(i\text{-Am})_4\text{NB}(i\text{-Am})_4$ is difficult, but it was accomplished by the following series of reactions



Synthesis of Lithium Tetraisoamylboride.—Isoamyl-lithium was prepared by a modification of the procedure given by Gilman, *et al.*,⁶ for the preparation of similar compounds. The following changes were made in Gilman's procedure. (1) A magnetic stirrer and Dry Ice-acetone reflux condenser were used. (2) The reaction medium was hexane (Fisher Certified Reagent, dried over Drierite). The yield decreases in the order hexane, pentane, petroleum ether (b.p. 60–70°). (3) Filtration was conducted in an argon-filled drybox. The filtered solution (deep violet in color) was transferred in the drybox to a flask fitted with a serum cap and was then injected with triisoamylboron (Callery Chemical Co.). *Caution.* Triisoamylboron is air sensitive. Immediately upon injection, a dense white precipitate formed which could not be filtered without causing extensive decomposition. Consequently, the precipitate was stored under the supernatant liquid in a freezer until needed.

Synthesis of Tetraisoamylammonium Tetraisoamylboride.—Tetraisoamylammonium iodide was prepared by the method of Fuoss and Kraus.⁷ It was repeatedly recrystallized from a 1:8 acetone-water mixture and dried *in vacuo* at 60°. A solution of this salt in pure, anhydrous acetonitrile⁸ was added to the suspension of $\text{LiB}(i\text{-Am})_4$ in hexane, with careful exclusion of air. The suspension dissolved. After stirring for 2 hr., the

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(3) The decrease in the mobility of the ions caused by the relaxation effect induced by the motion of the ions in a polar medium need not be considered here, since the decrease presumably will be the same for the cation and anion of the reference electrolyte. This relaxation effect has been suggested by Fuoss and treated theoretically by R. H. Boyd and by R. Zwanzig [*J. Chem. Phys.*, **38**, 1603 (1963)].

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