It is, therefore, of interest to describe a simple method for the preparation of the heretofore difficultly accessible thiol ester, *t*-butyl S-methyl thiolcarbonate, undoubtedly the best of the currently available intermediates for the preparation of *t*-butyl carbazate,[5] precursor of one of the most important carbo-*t*-butoxylating agents, *t*-butyl azidoformate.[10,11]

An earlier described synthesis[3] of *t*-butyl S-methyl thiolcarbonate suffers from the disadvantage that expensive, relatively inaccessible gaseous carbonyl sulfide is required. It has now been shown that the thiol ester is readily obtained by reaction of commercially available methyl chlorothiolformate[12] with *t*-butyl alcohol in refluxing chloroform in the presence of pyridine.[13] The corresponding S-phenyl ester was also obtained in analogous fashion in 61% yield from phenyl chlorothiolformate. Use of *t*-butyl S-phenyl thiolcarbonate might offer some advantage over the use of the methyl ester in the preparation of *t*-butyl carbazate by virtue of its increased reactivity toward hydrazine. The greater acidity of benzenethiol *vs.* phenol allows clean separation of the resultant *t*-butyl carbazate and the coproduct benzenethiol thus avoiding a difficulty which arises in the use of the corresponding oxygen analog, *t*-butyl phenyl carbonate.[3,6]

Experimental[14]

t-Butyl S-Methyl Thiolcarbonate.—To a solution of 53.6 ml. of pyridine and 62.6 ml. of *t*-butyl alcohol in 200 ml. of chloroform which was stirred mechanically at room temperature there was added dropwise over 15–20 min. 66.4 g. of methyl chlorothiolformate.[12] The mixture was stirred and refluxed for 24 hr. and then washed in a separatory funnel with two 200-ml. portions of water, three 100-ml. portions of 5% hydrochloric acid, and finally 100 ml. of 1 *M* sodium bicarbonate. The solution was dried over magnesium sulfate and most of the solvent removed by distillation at atmospheric pressure followed by the use of a water aspirator.

Distillation of the residue gave 61.5 g. (69%) of the ester, b.p. 62–65° (24 mm.). Redistillation through a 30-cm. helices-packed column gave 50 g. (56%) of the ester, b.p. 60–63° (24 mm.), lit.[3] b.p. 60–62° (20 mm.). Conversion of this ester to *t*-butyl carbazate by heating in an oil bath at 105–110° for 24 hr. has already been described.[3]

t-Butyl S-Phenyl Thiolcarbonate.—A solution of 62.6 ml. of *t*-butyl alcohol and 53.6 ml. of pyridine dissolved in 200 ml. of chloroform was treated at room temperature with stirring over a period of 10 min. with 103.4 g. (81.6 ml.) of phenyl chlorothiolformate.[12] The solution was refluxed with stirring for 55 hr. and worked up essentially as given for the corresponding methyl ester. Distillation from an ordinary Claisen flask gave 70 g. (61%) of the thiol ester, b.p. 88.5° (1.2 mm.) to 102° (1.9 mm.). A center cut for analysis, distilled through a 30-cm. helices-packed column (95% recovery) had b.p. 86° (0.9 mm.).

Anal. Calcd. for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71. Found: C, 63.23 H, 7.02.

Conversion of *t*-Butyl S-Phenyl Thiolcarbonate to *t*-Butyl Carbazate.—A mixture of 21 g. of *t*-butyl S-phenyl thiolcarbonate and 10 g. of 64% hydrazine was heated in a water bath to 85–90° with swirling for a few minutes until the two phases coalesced. The resulting solution was warmed in the water bath at 75–80° for 3 hr. and then poured into a solution of 8 g. of sodium hydroxide in 250 ml. of water. The resulting cloudy mixture was treated with decolorizing carbon at room temperature with occasional stirring for 1 hr. and filtered. The clear filtrate was extracted with ether in a continuous extractor for 48 hr.

Evaporation of the dried (magnesium sulfate) ether extract from a water bath with the aid of a water aspirator gave a colorless oil which solidified on cooling or seeding to give 10.5–11 g. (80–83%) of snow white crystals of *t*-butyl carbazate, m.p. 39.5–41° (lit.[6] m.p. 41–42°).

(5) Other methods which have been recommended for the synthesis of *t*-butyl carbazate involve acylation of hydrazine by means of *t*-butyl phenyl carbonate,[6] *t*-butyl *p*-nitrophenyl carbonate,[7,8] and N-*t*-butyloxycarbonylimidazole.[9]

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(14) Analyses are by Galbraith Laboratories, Knoxville, Tenn.

Reductions of 3,6-Diphenyl-*s*-tetrazine[1,2]

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Received January 16, 1963

In the course of attempting to prepare 3,6-bis(hydroxymethyl)-*s*-tetrazine *via* the reduction of 3,6-bis(carboxy)-*s*-tetrazine with lithium aluminum hydride, it became apparent that the tetrazine ring was cleaved. In order to facilitate the study of this reduction, 3,6-diphenyl-*s*-tetrazine[2] (I) was utilized instead of the 3,6-bis(carboxy)-*s*-tetrazine since the former is much easier and cheaper to prepare.

When I is slowly added to an ether solution of lithium aluminum hydride, there is an immediate loss of red color. Hydrolysis of the reaction mixture gives a yellow, ether-soluble product. This product has been identified as benzalazine by means of melting point, nitrogen analysis, and mixture melting point with an authentic sample of benzalazine. The infrared spectrum of this material is identical with that of benzalazine.

Hydrazine is identified as one of the products by the addition of benzaldehyde to the aqueous hydrolyzate. A yellow solid is recovered from this reaction and is identified as benzalazine. Ammonia is not observed as a product of the reduction. Sodium borohydride gives essentially the same results in this reaction. The reaction of I with sodium dithionite gives only 1,2-dihydro-3,6-diphenyl-*s*-tetrazine.[2,3] The reduction of this dihydrotetrazine with lithium aluminum hydride gives benzalazine. Benzalazine is not changed when an ether solution of it and lithium aluminum hydride are refluxed overnight. The reduction of 3,6-diphenyl-*s*-tetrazine or 1,2-dihydro-3,6-diphenyl-*s*-tetrazine with zinc dust and acetic acid gives 3,5-diphenyl-1,2,4,4*H*-triazole.[4] This triazole is not changed when it is warmed with lithium aluminum hydride overnight.

(1) Supported by a grant (CY3908) from the National Cancer Institute, National Institutes of Health, Department of Health, Education, and Welfare, Bethesda, Md. Presented at the Southwest Regional Meeting of the American Chemical Society, Dallas, Tex., December, 1962.

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Experimental

Reduction of 3,6-diphenyl-s-tetrazine (II). (A) Lithium Aluminum Hydride Reduction.—A 1-l. three-necked flask was fitted with a nitrogen inlet tube, stirrer, and a condenser topped with a calcium chloride drying tube which in turn was connected to a water trap. The flask was charged with 3.0 g. of lithium aluminum hydride and 250 ml. of ether. A steady stream of nitrogen was passed through the flask and a solution of 10 g. (0.043 mole) of 3,6-diphenyl-s-tetrazine[5] in 100 ml. of anhydrous ether was added as rapidly as possible through the condenser. There was an immediate loss of purple color. The mixture was refluxed on a steam bath for 1 hr.

The mixture was cooled and 15 ml. of water was added dropwise. This was followed by the addition of 250 ml. of 10% sulfuric acid. The yellow ether layer was separated, dried over sodium sulfate, and the ether evaporated. A yellow solid (6.8 g.) was collected, m.p. 92–93°. This was identified as benzalazine.

Treatment of II with nitric acid did not produce the characteristic purple color of tetrazines. The material did not depress the melting point of an authentic sample of benzalazine[6] and infrared spectrum was identical with that of benzalazine.

Anal. Calcd. for $C_{14}H_{12}N_2$: N, 13.45. Found: N, 13.62.

A 10-ml. sample of the aqueous hydrolyzate from above was heated on a steam bath with 0.1 ml. of benzaldehyde. A yellow solid soon separated and was identified as benzalazine, m.p. 92–93°. The infrared spectrum was also identical with that of benzalazine.

(B) Sodium Borohydride Reduction.—This reduction was carried out in the same manner as A except that methanol was used as a solvent. Five grams of II gave 2.2 g. of benzalazine, m.p. 91–93°.

(C) Sodium Dithionite Reduction.—A solution of 3 g. (0.013 mole) of II, 20 ml. of water, and 15.6 ml. of 4.6 *N* sodium hydroxide was warmed on a steam bath and 6 g. of sodium hydrosulfite added over a period of 15 min. The mixture was stirred and heated until all of the purple color disappeared. The mixture was cooled, filtered, and the precipitate was washed with benzene. The product, m.p. 183–184° (closed tube) and 190–192° (open tube), was identical with 1,2-dihydro-3,6-diphenyl-s-tetrazine[5] which had been previously prepared by the reduction of 3,6-diphenyl-s-tetrazine with hydrogen sulfide.[7]

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Some Reactions of Hexaphenyldilead

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Received January 24, 1963

At elevated temperatures, hexaphenyldilead is decomposed into tetraphenyllead and elemental lead, two moles of starting material yielding three moles of tetraphenyllead.[2] In the presence of acids, however, decomposition of hexaphenyldilead takes place at room temperatures.[3,4]

Halogen acids cleave, in a stepwise sequence, two of the phenyllead bonds in tetraphenyllead to yield, in the first step, benzene and triphenyllead halide. Triphenyllead halide in turn further reacts to form additional benzene and diphenyllead dihalide (reactions 2 and 3). Hexaphenyldilead, in comparison, when treated with halogen acids yields lead halide as well as triphenyllead halide, diphenyllead dihalide, and benzene.

We were interested in two aspects of these reactions: (a) if hexaphenyldilead decomposes to tetraphenyllead in the molar ratio of 2:3, why the combined yield of the products, triphenyllead halide and diphenyllead dihalide, has never been reported to surpass 50%[3,4] and (b) how it is possible to form lead halide in view of the fact that it is not formed under similar conditions in the reaction of either tetraphenyllead, triphenyllead chloride, or diphenylleaddi halide with halogen acids.

We have found that hexaphenyldilead, in the presence of two molar equivalents of acetic acid, did not react at room temperature when *n*-heptane or benzene were used as solvents. At reflux temperatures, however, the reaction proceeded smoothly. The products obtained were benzene (90% based on acetic acid), lead acetate (41%), tetraphenyllead (25%), triphenyllead acetate (18%), and some unchanged hexaphenyldilead (3%). When hexaphenyldilead was refluxed in acetic acid, however, lead acetate and diphenyllead diacetate were the only products isolated. In a similar manner, excess thiolacetic acid reacted with hexaphenyldilead yielding similar amounts of analogous compounds.

In accounting for the products formed, we have considered the following reaction scheme.

$$Ph_6Pb_2 \rightleftharpoons [2Ph_3Ph] \longrightarrow Ph_4Pb + [Ph_2Pb] \quad (1)$$

$$Ph_4Pb + HOAc \longrightarrow Ph_3PbOAc + PhH \quad (2)$$

$$Ph_3PbOAc + HOAc \longrightarrow Ph_2Pb(OAc)_2 + PhH \quad (3)$$

$$[Ph_2Pb] + 2HOAc \longrightarrow Pb(OAc)_2 + 2PhH \quad (4)$$

The initial assumption is that hexaphenyldilead is thermally decomposed in the presence of acetic acid to tetraphenyllead and the relatively unstable diphenyllead. In the presence of less than an excess of acetic acid, reactions 2 and 4 are competitive, thus accounting for the formation of lead acetate, tetraphenyllead, and triphenyllead acetate. In the presence of excess acetic acid, reactions 2 and 3 go to completion and the final products are diphenyllead diacetate and lead acetate (*via* reaction 4).

Since triphenyllead acetate and diphenyllead diacetate are thermally stable under the conditions used, the accounting for the formation of lead acetate by an alternate reaction to reaction 4, such as a disproportionation of the triphenyllead acetate and diphenyllead diacetate, was ruled out. As no hydrogen evolution was observed during the reaction, it appeared equally unlikely that the formation of lead acetate occurred from reactions of elemental lead and acetic acid or between a triphenyllead hydride intermediate and acetic acid.

Hexaphenyldilead has been reported to react with oxygen to yield triphenyllead oxide.[5,6] In an analogous reaction with sulfur, we obtained triphenyllead sulfide in 59% yield; however, it was interesting to note that detectable amounts of tetraphenyllead and diphenyllead sulfide could be identified as by-products. This lends support to the reaction sequence given, particu-

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