

[CONTRIBUTION FROM THE COATES LABORATORIES OF LOUISIANA STATE UNIVERSITY]

The Preparation of Di-*t*-butyl Carbonate and *t*-Butyl Chlorocarbonate¹

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No carbonate containing two tertiary alkyl groups, and only one tertiary alkyl chlorocarbonate have been reported²; moreover, this latter compound was not isolated and was identified only by derivatives. The preparation of two such substances, namely, di-*t*-butyl carbonate and *t*-butyl chlorocarbonate, is described herein.

The properties of these two substances are quite different. Di-*t*-butyl carbonate is stable at its boiling point, can be sublimed, and is not easily saponified. It does not react with concentrated ammonium hydroxide at 150°, nor with phenylhydrazine at 185°. On the other hand, *t*-butyl chlorocarbonate decomposes appreciably at 10° and is very easily hydrolyzed. It reacts violently with substances such as dimethylaniline, quinoline, pyridine and triethylamine, giving the corresponding amine hydrochloride and gaseous products. It also reacts with primary and secondary amines, giving urethans. *t*-Butyl carbamate, *t*-butyl *N*-*p*-tolylcarbamate and *t*-butyl *N*-phenylcarbamate were prepared in this way. The thermal decomposition of the chlorocarbonate gave one mole each of carbon dioxide, hydrogen chloride and isobutylene for each mole of chlorocarbonate decomposed, with no detectable trace of *t*-butyl chloride.

Experimental

All analyses herein reported are the average of at least two determinations.

Di-*t*-butyl Carbonate.—A suspension of sodium *t*-butoxide in dioxane was prepared by refluxing 60 g. of *t*-butanol and 600 ml. of dioxane over 17.3 g. of sodium wire until the sodium had reacted completely. The stirred suspension was kept at 60–85° while 36.9 g. of gaseous phosgene was introduced over a period of an hour and fifteen minutes.

The mixture was stirred for one hour at 65° and poured into two liters of ice and water. The crystalline material which separated was filtered off, melted with warm water, washed three times with water and filtered. The oil was distilled under vacuum. Recrystallization from ethanol-water gave flaky, white crystals of di-*t*-butyl carbonate (yield 40.5%, m. p. 39.5–40.5°, b. p. 158.0° at 767.2 mm.).

Anal. Calcd. for C₈H₁₈O₃: C, 62.04; H, 10.41; sap. eq., 174.2. Found: C, 62.23; H, 10.63; sap. eq., 173.8.³

***t*-Butyl Chlorocarbonate.**—To a solution of 165 g. of phosgene in 200 ml. of *n*-butane was added 93.5 g. of powdered sodium *t*-butoxide. The mixture was stirred vigorously at –60° during the addition, which required five hours. The mixture was stirred one-half hour longer, allowed to stand several hours, and filtered through a layer of crystalline silica on fritted glass. Butane and excess phosgene were evaporated under vacuum at –30

to –15°. The resulting product was distilled and a fraction which boiled at 4–16° at 1.5–8 mm. was collected. This fraction was treated with 8.5 g. of thionyl chloride at –70°, then placed under water aspirator vacuum for two hours at –20°. Liquid bromine was added until a faint yellow color persisted. The liquid was again distilled, and a fraction which boiled at 3–6° at 1–3.5 mm. was collected. This product was treated with 3 g. of thionyl chloride and with bromine as before. A final distillation gave pure *t*-butyl chlorocarbonate (yield 20.4%, b. p. 3–4° at 0.9–1.7 mm.).

Anal. Calcd. for C₅H₉O₂Cl: C, 43.97; H, 6.64; Cl, 25.96. Found: C, 43.7; H, 6.86; Cl, 25.79.

***t*-Butyl *N*-Phenylcarbamate.**—To 1 g. of aniline in 40 ml. of cold ethyl ether, 1 g. of *t*-butyl chlorocarbonate was added. The mixture was allowed to stand fifteen minutes in an ice-bath, 30 ml. of water was added, and most of the ether was evaporated with a heat lamp and a stream of dry air. Two ml. of 6 *N* nitric acid was added, after which the remaining ether was evaporated with air. Recrystallization of the resulting product from petroleum ether (b. p. 63–70°) gave white crystals of *t*-butyl *N*-phenylcarbamate (m. p. 136.3–136.5°, mixed m. p. 136.2–136.5°, literature value⁴ 136.0).

Anal. Calcd. for C₁₁H₁₅O₂N: N, 7.25. Found: N, 7.14.

***t*-Butyl *N*-*p*-Tolylcarbamate.**—This compound was prepared from *t*-butyl chlorocarbonate and *p*-toluidine by the same procedure described above. The product was recrystallized from petroleum ether (b. p. 63–70°) until the m. p. became reproducible at 92.0–92.8°.

Anal. Calcd. for C₁₂H₁₇O₂N: N, 6.76. Found: N, 6.64.

***t*-Butyl Carbamate.**—To 20 ml. of cold concentrated ammonium hydroxide was added slowly 5 g. of *t*-butyl chlorocarbonate. The resulting crystals were filtered off and recrystallized until the melting point became reproducible at 108.0–108.5°.

Anal. Calcd. for C₅H₁₁O₂N: N, 12.0. Found: N, 11.9.

Thermal Decomposition of *t*-Butyl Chlorocarbonate.—Weighed samples of *t*-butyl chlorocarbonate were heated in 200-ml. bulbs at 170° for thirty-six hours. To determine hydrogen chloride and carbon dioxide, samples were absorbed in 0.1 *N* sodium hydroxide, and the resulting solution titrated to the phenolphthalein end-point, then to the methyl orange end-point with 0.1 *N* nitric acid. Isobutylene was determined by absorbing samples in standard 0.1 *N* bromine solution and titrating the excess standard 0.1 *N* bromine solution with standard sodium thiosulfate.

Anal. Moles product per mole *t*-butyl chlorocarbonate: carbon dioxide, 0.999; hydrogen chloride, 0.983; isobutylene, 0.985.

Summary

1. Di-*t*-butyl carbonate has been prepared. It is a very stable, unreactive solid which sublimes readily.

2. *t*-Butyl chlorocarbonate has been prepared. It begins to decompose at 10°, and hydrolyzes extremely readily.

3. Two new urethans, *t*-butyl carbamate, and *t*-butyl *N*-*p*-tolylcarbamate have been prepared.

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(1) Taken from the Ph.D. Dissertation of James W. Rogers, August, 1947.

(2) E. Merck, German Patents 254,417, 254,472; *Chem. Zentr.*, **84**, I, 346 (1913).

(3) In order to determine the saponification equivalent, it was necessary to treat samples with solutions of potassium hydroxide and barium chloride, in triethylene glycol for nine hours at 175°.

(4) Knoevenagel, *Ann.*, **297**, 148 (1897).