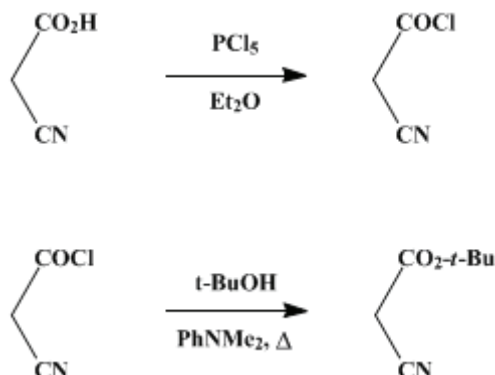


***t*-BUTYL CYANOACETATE**

[Cyanoacetic acid, *tert*-butyl ester]



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1. Procedure

In a 5-l., three-necked, round-bottomed flask equipped with a rubber- or mercury-sealed mechanical stirrer and a reflux condenser carrying a drying tube are placed 340 g. (4 moles) of [cyanoacetic acid](#) ([Note 1](#)) and 2 l. of anhydrous [ether](#). To the stirred solution, 834 g. (4 moles) of [phosphorus pentachloride](#) is added in portions through the third neck of the flask, which is sealed between additions. The mixture is cooled occasionally with an ice bath to prevent excessive refluxing, and, after the addition is complete, stirring is continued for 0.5 hour or until the [phosphorus pentachloride](#) dissolves completely. The reflux condenser is removed and replaced with apparatus for downward distillation ([Note 2](#)), and the [ether](#) is distilled from a water bath at 50–60° ([Note 3](#)), after which most of the [phosphorus oxychloride](#) is removed at reduced pressure (20–25 mm. with a bath temperature of 55–65°) ([Note 4](#)), the receiver being cooled in an ice-salt bath. The red, oily residue is dissolved in 200 ml. of [benzene](#) and the [benzene](#) and residual [phosphorus oxychloride](#) distilled under reduced pressure. This operation is repeated with 200 ml. of fresh [benzene](#) to ensure complete removal of [phosphorus oxychloride](#) ([Note 5](#)). The residue is then cooled to room temperature ([Note 6](#)) and is transferred to a 500-ml. pressure-equalized dropping funnel for immediate use in the following step.

The same 5-l. flask used in the preceding step is used again, without washing; it is fitted with a reflux condenser carrying a drying tube, a sealed mechanical stirrer, and the dropping funnel containing the acid chloride. In the flask are placed 296 g. (4 moles) of dry *t*-butyl alcohol ([Note 7](#)) and 484 g. (4 moles) of [dimethylaniline](#) in 600 ml. of anhydrous [ether](#) ([Note 8](#)). The acid chloride is added dropwise to the stirred solution, the mixture being cooled occasionally with an ice bath to prevent excessive refluxing. After the addition is complete, the reaction mixture is refluxed for 2 hours and then stirred gently at room temperature for 15 hours. Two liters of water is added with stirring, and the mixture is filtered with suction through a Büchner funnel fitted with a matting of glass wool ([Note 9](#)). The matting is washed with three 250-ml. portions of [ether](#) ([Note 10](#)). After separation of the combined ethereal layers, the aqueous layer is extracted twice with 250-ml. portions of [ether](#). The combined [ether](#) solutions are washed with successive portions of 2*N* [sulfuric acid](#) (a total of 1 l.) until free of [dimethylaniline](#), then with two 200-ml. portions of 2*N* [sodium carbonate](#) solution, and dried over [sodium carbonate](#). After removal of the [ether](#) by distillation, the residue is transferred to an alkali-washed flask and distilled at reduced pressure through a 20-cm. alkali-washed Vigreux column ([Note 11](#)). The yield of colorless product is 355–378 g. (63–67%) boiling at 67–68°/1.5mm. (90°/10 mm., 54–56°/0.3 mm), $n_D^{20} = 1.4198$.

2. Notes

1. [Cyanoacetic acid](#) of 98% purity, obtained from Kay-Fries Chemicals, Inc., was used.
2. A Claisen head with a condenser leading into a flask with a suction arm connected to a drying tube is suitable. Ground-glass joints are recommended.
3. A large bucket containing water and placed on a steam bath serves as a suitable water bath. The temperature is easily controlled between the limits mentioned.
4. The [ether](#) is removed from the receiving flask before the [phosphorus oxychloride](#) is distilled. A drying tube should be placed between the suction arm of the flask and the water pump, which serves as the source of suction. The reaction mixture may be stirred during the distillation of the oxychloride, or the stirrer may be removed and replaced with a capillary ebulliator tube to which is attached a balloon filled with dry [nitrogen](#).
5. The checkers found that the distillation with [benzene](#) ensures a more complete removal of [phosphorus oxychloride](#) which, if still present, interferes in the subsequent step and a lower yield of product results.
6. The submitters found that on several occasions, when the residue was not cooled before transfer, it began to generate considerable heat while standing in the dropping funnel and resulted in the total carbonization of the acid chloride.
7. The submitters dried the [t-butyl alcohol](#) by refluxing it over [calcium hydride](#) overnight and distillation in a moisture-free apparatus. The checkers found that stirring the [t-butyl alcohol](#) at 60–70° over [calcium hydride](#) for several hours and then distilling the alcohol, using an air condenser, is a satisfactory procedure. When the [t-butyl alcohol](#) is refluxed, the alcohol vapors condense and solidify (m.p. 24–25°) in the reflux condenser and cause clogging.
8. These reagents should be weighed out beforehand in order to prevent delay in commencing with this step.
9. The filtration removes some tarry resinous material which would otherwise interfere in the separation of the layers. The checkers found that unless the filtrate is recycled through the same matting several times, to remove practically all the tarry residue, the separation of layers and the subsequent extractions prove troublesome owing mainly to emulsion formation.
10. The checkers found that a considerable amount of product is withheld by the residue on the glass-wool matting. The product is extracted by placing the matting in a beaker, stirring with [ether](#), and filtering. This procedure is repeated twice, and the [ether](#) extracts are combined with the original filtrate.
11. The distilling flask and Vigreux column to be used should be washed with 25% aqueous [sodium hydroxide](#) solution, rinsed three times with water, and then dried. Alternatively, about 1 g. of anhydrous [potassium carbonate](#) may be added to the residue before distillation.

3. Discussion

[t-Butyl cyanoacetate](#) has been prepared from [t-butyl bromoacetate](#) and [potassium cyanide](#) in [methanol](#)² and from [t-butyl chloroacetate](#) and [potassium cyanide](#) in [methyl Cellosolve](#).³ The present method is an adaptation of that of Beech and Pigott⁴ and is similar to the *Organic Syntheses* preparation of [t-butyl acetate](#).⁵

4. Merits of Preparation

The present preparation employs a method of considerable scope which gives much better yields and is considerably less laborious than other methods for the preparation of [t-butyl cyanoacetate](#). The compound is of specific interest since, for example, it may be used in any reaction where [ethyl cyanoacetate](#) is used (condensation reactions, etc.), but it has the added advantage that the carbo-*t*-butoxy group, which may serve in conjunction with the α -cyano group to activate the α -hydrogens (for cyanoethylations, etc.), may be later removed simply by pyrolysis of the compound.⁶

References and Notes

1. University of Michigan, Ann Arbor, Mich.
2. B. Abramovich and C. R. Hauser, *J. Am. Chem. Soc.*, **64**, 2271 (1942).
3. Private communication, W. S. Johnson, University of Wisconsin.
4. W. F. Beech and H. A. Pigott, *J. Chem. Soc.*, 423, (1955).
5. C. R. Hauser, B. E. Hudson, B. Abramovitch, and J. C. Shivers, *Org. Syntheses*, Coll. Vol. **3**, 142

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6. S.-O. Lawesson, E. H. Larsen, and H. J. Jakobsen, *Arkiv Kemi*, **23**, 453 (1965).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

Benzene (71-43-2)

methanol (67-56-1)

ether (60-29-7)

sodium hydroxide (1310-73-2)

phosphorus pentachloride (10026-13-8)

sodium carbonate (497-19-8)

nitrogen (7727-37-9)

potassium cyanide (151-50-8)

Phosphorus Oxychloride (21295-50-1)

Ethyl cyanoacetate (105-56-6)

cyanoacetic acid (372-09-8)

dimethylaniline (121-69-7)

methyl Cellosolve (109-86-4)

t-butyl alcohol (75-65-0)

calcium hydride (7789-78-8)

t-BUTYL CYANOACETATE,
Cyanoacetic acid, tert-butyl ester (1116-98-9)

t-butyl acetate (540-88-5)

t-butyl chloroacetate (107-59-5)

t-butyl bromoacetate (5292-43-3)

