



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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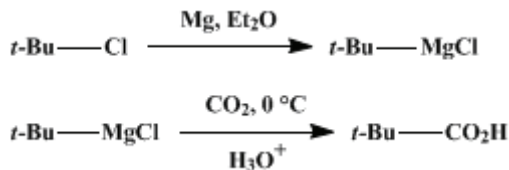
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.524 (1941); Vol. 8, p.104 (1928).

TRIMETHYLACETIC ACID

[Pivalic acid]

[(A) (from *tert.*- Butyl Chloride)]



Submitted by S. V. Puntambeker and E. A. Zoellner.

Checked by J. B. Conant and A. H. Blatt.

1. Procedure

In a 3-l. three-necked, round-bottomed flask, fitted with a mechanical stirrer and mercury seal, a 500-cc. separatory funnel, and an efficient reflux condenser, is placed 61 g. (2.5 atoms) of [magnesium turnings or powder](#) (Note 1). The [magnesium](#) is then covered with 200 cc. of anhydrous [ether](#). About 5 cc. of pure *tert.*-butyl chloride (with a crystal or two of [iodine](#)) is added to start the reaction. Stirring is begun, and a solution of 227 g. (2.5 moles) of pure *tert.*-butyl chloride (p. 144) in 1100 cc. of anhydrous [ether](#) is dropped slowly (Note 2) on the [magnesium](#) during six to eight hours. The reaction is practically complete when all the halide has been added, but stirring should be continued for fifteen minutes longer.

The reaction mixture is now surrounded by an ice and salt mixture. The separatory funnel is replaced by a two-holed rubber stopper containing a thermometer (bulb immersed in the reaction mixture) and a glass tube the outer end of which is connected to a mercury trap (Note 3). When the temperature of the reaction mixture has fallen to 0°, the condenser is replaced by a tube 10 mm. in diameter and adjusted so the end is 50 mm. above the surface of the reaction mixture. The reaction mixture is stirred and [carbon dioxide](#) is added through this tube directly from a cylinder after passing through two bottles containing concentrated [sulfuric acid](#). The [carbon dioxide](#) is added as rapidly as it is used up. The temperature is controlled by the rate of stirring and should not go above 8+. After two and one-half to three hours the temperature falls below 0°. Then the addition is continued for one-half hour under an excess pressure of 45 mm. (Note 3). The temperature falls to -3 to -5° at the end of this time, and the reaction is complete.

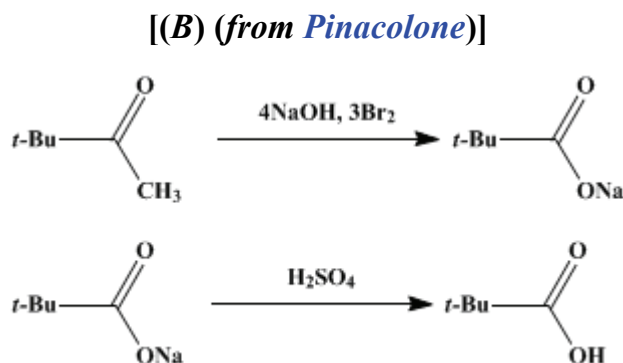
After the flask is surrounded with ice, the reaction mixture is hydrolyzed (Note 4) with 25 per cent [sulfuric acid](#), transferred to a 2-l. separatory funnel, and then the [ether](#) layer is separated (Note 4). The water layer is extracted with four 100-cc. portions of [ether](#). The combined [ether](#) extracts are then washed with four 100-cc. portions of 25 per cent [sodium hydroxide](#) solution to remove the [trimethylacetic acid](#) from the [ether](#).

The aqueous alkaline extract is heated to 100° to remove [ether](#) and volatile impurities. The solution is then cooled with ice and acidified with 25 per cent [sulfuric acid](#), and the organic acid separated. The water layer is distilled from a 2-l. flask until no more oily solution comes over. The distillate is saturated with salt, and the acid layer is separated. This water layer together with the low-boiling fraction from distillation of the crude [trimethylacetic acid](#) is distilled and the distillate salted out as before.

The combined acid layers are distilled from a 250-cc. Claisen flask connected to an air condenser, which in turn is connected to a side-arm flask cooled by running water. The [trimethylacetic acid](#) is collected at 162–165°/atm. press., 110–112°/124 mm. The yield, which depends somewhat on the form of [magnesium](#), is 157–162 g. (61–63 per cent of the theoretical amount based on *tert.*-butyl chloride) when ordinary [magnesium turnings](#) are used and 177–178 g. (69–70 per cent) when 200-mesh [magnesium powder](#) is used. The acid melts at 34–35°.

2. Notes

1. The yield of product depends to a considerable extent upon the form of [magnesium](#) used. Either the finer commercial grade of turnings should be used or the 30- to 200-mesh powdered [magnesium](#) that is kept in a tightly stoppered bottle when not in use. The powdered [magnesium](#) makes possible a 5–8 per cent increase in yield.
2. The rate of addition of the halide solution is important. The slower the rate, the better the yield. A delivery constant of the separatory funnel should be determined so that the solution can be added uniformly over a period of six to eight hours. A modified procedure for preparing [tert.-butylmagnesium chloride](#) has been described by Whitmore and Houk.¹
3. The mercury trap enables the operator to adjust the flow of the [carbon dioxide](#) according to the rate of absorption, and to apply a pressure of 45 mm. during the last half-hour. The pressure itself has practically no effect. The trap consists merely of a narrow glass test tube containing [mercury](#), and the tube is made to extend beneath the surface.
4. The hydrolysis of the reaction mixture and subsequent separation of the acid is the procedure given on [p. 362](#). [Sulfuric acid](#) should be added during the hydrolysis as long as any particles of [magnesium](#) are present. The water layer does not become clear, owing to solidification of the organic acid.



Submitted by L. T. Sandborn and E. W. Bousquet.
Checked by F. C. Whitmore and T. Otterbacher.

1. Procedure

In a 5-l. round-bottomed flask fitted with a mechanical stirrer is placed a solution of 330 g. (8.25 moles) of u.s.p. stick [sodium hydroxide](#) in 2.8 l. of water, and the solution is cooled to 0° in an ice-salt bath. To the well-stirred solution 480 g. (154 cc., 3 moles) of [bromine](#) is added from a separatory funnel at such a rate as to keep the temperature below 10° ([Note 1](#)) (fifteen to twenty minutes). The solution is cooled again to 0°, and 100 g. (1 mole) of [pinacolone](#) ([p. 462](#)) is added from a separatory funnel, the temperature being kept below 10°. After the solution is decolorized (about one hour) it is stirred for three hours at room temperature.

The flask is then fitted with a separatory funnel and a condenser for distillation, and heated with a Meker burner to steam-distil the [bromoform](#) and [carbon tetrabromide](#) ([Note 2](#)) and ([Note 3](#)).

The burner is then removed, the mixture is cooled to 50°, and 400 cc. of concentrated [sulfuric acid](#) ([Note 4](#)) is added through the separatory funnel. The heat of neutralization causes some [trimethylacetic acid](#) to distil with water. When all the acid is added the flask is heated again and the [trimethylacetic acid](#) comes over with about 400 cc. of water. When all the [trimethylacetic acid](#) (70–80 cc.) has distilled, a liquid heavier than water begins to come over. The distillation is stopped and the acid separated from the water in a separatory funnel and dried either with [calcium chloride](#) or by distilling with [benzene](#) which carries over all water ([Note 5](#)). The [trimethylacetic acid](#) is further purified by distillation under reduced pressure. It boils at 75–78°/20 mm.; melts at 34–35°; and the yield is 63–65 g.

The water layer is extracted with two 100-cc. portions of [ether](#). The combined [ether](#) solutions are

dried with [calcium chloride](#), the [ether](#) distilled, and the residue fractionated under reduced pressure, using a modified Claisen flask (p. 130). Ten to twelve grams may be obtained in this way. The total yield is 72–75 g. (71–74 per cent of the theoretical amount).

2. Notes

1. The temperature must be kept low during the reaction to prevent formation of [sodium bromate](#).
2. The reaction between [sodium hydroxide](#) and [tribromopinacolone](#) is not complete at room temperature. Heating in this manner, rather than separation in the cold, results in an increase of 10–15 per cent in the yield.
3. The [bromoform](#) passes over with the steam rather rapidly. In some runs some [carbon tetrabromide](#) was also obtained. Toward the end of the steam distillation a heavy oil that is more or less of a lachrymator may come over. This is undoubtedly brominated [pinacolone](#). The [bromoform](#) may be purified by distillation under reduced pressure. One run gave 115 g. of product, boiling at 78–79°/22 mm.
4. An equivalent amount of [hydrochloric acid](#) may be used without affecting the yield.
5. The [trimethylacetic acid](#) is dried very easily by distilling with about 50 cc. of [benzene](#) at ordinary pressure until all the water is removed, and then the residue is distilled under reduced pressure.

3. Discussion

[Trimethylacetic acid](#) can be prepared by the hydrolysis of *tert.*-butyl cyanide;² by the oxidation of dimethyl-2,2-propanol with [chromic acid](#);³ by the oxidation of [pinacolone](#) with [sodium hypobromite](#),⁴ [potassium hypochlorite](#),⁵ and [chromic acid](#);⁶ by the carbonation of *tert.*-butylmagnesium chloride;⁷ and by treatment of [butanol](#),⁸ [isobutanol](#),⁸ or [acetone](#)⁹ with [carbon monoxide](#) at high temperature and pressure.

References and Notes

1. Whitmore and Houk, J. Am. Chem. Soc. **54**, 3716 (1932).
2. Butlerow, Ann. **165**, 322 (1873).
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5. Böeseken, Rec. trav. chim. **29**, 99 (1910).
6. Friedel and Silva, Ber. **6**, 146, 826 (1873).
7. Bouveault, Compt. rend. **138**, 1108 (1904); Gilman and Zoellner, J. Am. Chem. Soc. **50**, 425 (1928), *ibid.* **53**, 1583 (1931), Rec. trav. chim. **47**, 1058 (1928).
8. E. I. du Pont de Nemours and Co., U. S. pat. 1,995,930 [C. A. **29**, 3353 (1935)]; Hardy, J. Chem. Soc. 362 (1936).
9. E. I. du Pont de Nemours and Co., U. S. pat. 2,037,654 [C. A. **30**, 3836 (1936)]; Hardy, J. Chem. Soc. 464 (1938).

Appendix

Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

dimethyl-2,2-propanol

[calcium chloride](#) (10043-52-4)

[sulfuric acid](#) (7664-93-9)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

ether (60-29-7)

sodium hydroxide (1310-73-2)

carbon monoxide (630-08-0)

magnesium,
magnesium turnings,
magnesium turnings or powder,
magnesium powder (7439-95-4)

bromine (7726-95-6)

mercury (7439-97-6)

carbon dioxide (124-38-9)

butanol (71-36-3)

iodine (7553-56-2)

acetone (67-64-1)

Pinacolone (75-97-8)

sodium bromate (7789-38-0)

chromic acid (7738-94-5)

tert.- Butyl Chloride,
tert.-BUTYL CHLORIDE (507-20-0)

bromoform (75-25-2)

isobutanol (78-83-1)

Trimethylacetic acid,
Pivalic acid (75-98-9)

carbon tetrabromide (558-13-4)

tribromopinacolone

sodium hypobromite

potassium hypochlorite

tert.- butyl cyanide (630-18-2)

tert.-butylmagnesium chloride,
tert.-butylmagnesium chloride (677-22-5)

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