A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

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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.

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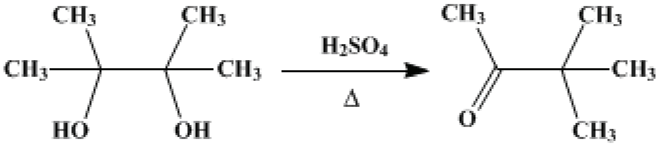
Organic Syntheses, Coll. Vol. 1, p.462 (1941); Vol. 5, p.91 (1925).

PINACOLONE



Submitted by G. A. Hill and E. W. Flosdorf.
Checked by C. S. Marvel and A. E. Gray.

1. Procedure

In a 2-l. round-bottomed flask, fitted with a stopper carrying a dropping funnel and a connection to a condenser set for distillation, are placed 750 g. of 6 *N* sulfuric acid (Note 1) and 250 g. of pinacol hydrate (Note 2). The mixture is then distilled until the upper layer of distillate ceases to increase in volume (Note 3). This requires about fifteen to twenty minutes. The pinacolone layer in the distillate is separated from the water and the water is returned to the reaction flask. First, 60 cc. of concentrated sulfuric acid is added to the water, and then a second 250-g. portion of pinacol hydrate. The distillation is repeated. This process is repeated twice more until 1 kg. (4.42 moles) of pinacol hydrate has been used (Note 4).

The combined pinacolone fraction is dried over calcium chloride, filtered, and fractionally distilled. There is first a small low-boiling portion; then the pinacolone comes over at 103–107°; and finally there is a higher-boiling portion which yields more pinacolone on redistillation. The yield from a run, as described, is 287–318 g. (65–72 per cent of the theoretical amount). This product occasionally turns slightly yellow on standing, but redistillation removes the color with almost no loss of product.

2. Notes

1. Phosphoric acid (50 per cent) or hydrated oxalic acid may be used to bring about this rearrangement. When these reagents are used, the reaction mixture should be boiled for three to four hours. A yield of pinacolone corresponding to 60–65 per cent of the theoretical amount is thus obtained.
2. The pinacol hydrate is the unrecrystallized product obtained as described on p. 459. The use of recrystallized pinacol hydrate increases the yield of pinacolone by about 4 per cent.
3. An oily layer always remains behind in the distilling flask.
4. Larger or smaller runs of pinacolone may be made without materially affecting the yield.

3. Discussion

Pinacolone can be prepared by heating pinacol hydrate with dilute sulfuric or dilute hydrochloric acid;[1] by treating anhydrous pinacol[2] with concentrated sulfuric acid at 0°; by heating pinacol or its hydrate with 5 per cent oxalic acid[3] for twelve hours, or with 50 per cent tartaric, phosphoric, or oxalic acid[3] for three to four hours. Pinacolone can also be prepared from pivalamide and methylmagnesium halides[4] and from *tert.*-butylmagnesium chloride and acetyl chloride[5] or sodium acetate.[6]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 81
- Org. Syn. Coll. Vol. 1, 524

References and Notes

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

sulfuric or dilute hydrochloric acid

pinacol or its hydrate

tartaric, phosphoric, or oxalic acid

methylmagnesium halides

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

sodium acetate (127-09-3)

acetyl chloride (75-36-5)

Oxalic acid (144-62-7)

Pinacolone (75-97-8)

phosphoric acid (7664-38-2)

Pinacol hydrate (6091-58-3)

pinacol (76-09-5)

pivalamide (754-10-9)

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