



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.

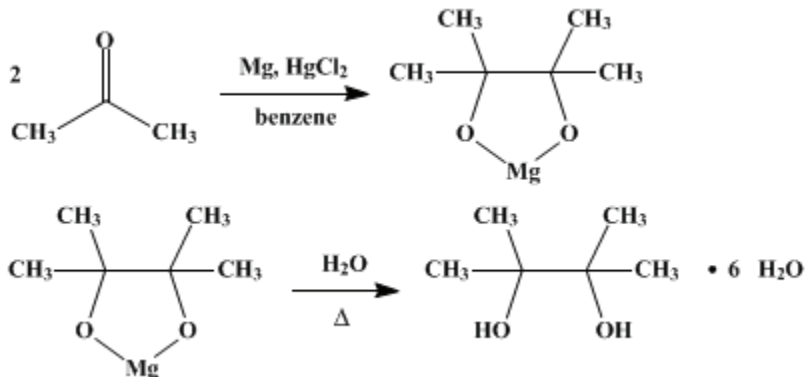
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 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.

Organic Syntheses, Coll. Vol. 1, p.459 (1941); Vol. 5, p.87 (1925).

PINACOL HYDRATE



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1. Procedure

In a 5-l. round-bottomed flask, fitted with a stopper holding a separatory funnel and an efficient reflux condenser (Note 1) closed at the top with a calcium chloride tube (Note 2), are placed 80 g. (3.29 atoms) of magnesium turnings and 800 cc. of dry benzene (Note 3). Through the dropping funnel is added gradually a solution of 90 g. of mercuric chloride in 400 g. (505 cc., 6.9 moles) of acetone (Note 4), carefully at first and then more rapidly after the reaction starts. The time of addition is about five to ten minutes (Note 5). Sometimes the reaction does not commence until a considerable proportion of the acetone solution of mercuric chloride has been added. In this case the reaction proceeds very vigorously when it does start, and the flask must be cooled in running water to avoid loss through the condenser. As soon as the first vigorous reaction is over, a mixture of 200 g. (258 cc., 3.45 moles) of acetone and 200 cc. of benzene is added (Note 6). When the reaction slows down, the flask is heated on a water bath until no further reaction is evident (about two hours). During this time the magnesium pinacolate swells until it fills the flask about three-fourths full. The flask is removed from the condenser and shaken until the reaction mass is well broken up (Note 7). The condenser is again attached and the heating continued for another hour.

Through the separatory funnel is then added 200 cc. of water, and the reaction mixture is heated for another hour. The flask should be shaken occasionally during this time. The reaction mixture is cooled to about 50° and filtered. The solid is returned to the flask and heated for ten minutes with a fresh 500-cc. portion of benzene to dissolve any remaining pinacol. The original filtrate and the second portion of benzene, after it is filtered from the magnesium hydroxide, are mixed and distilled to one-half the original volume in order to remove the acetone; the remaining benzene solution is treated with 300 cc. of water and cooled to $10\text{--}15^\circ$. The pinacol hydrate separates, and after about thirty minutes (Note 8) it is collected on a suction filter and washed with benzene, or better, the mixture is centrifuged in a basket centrifuge. The pinacol hydrate, air-dried at room temperature (Note 9), weighs 325–375 g. (43–50 per cent of the theoretical amount based on the magnesium used) (Note 2). The product melts at $46\text{--}47^\circ$. It is sufficiently pure for most purposes. Occasionally the product is slightly yellow. If such a product is dissolved in an equal weight of boiling water, treated with a little animal charcoal, filtered, and the filtrate cooled in ice, over 95 per cent of the material may be recovered in large white crystals (Note 10).

2. Notes

1. The condenser should have an inner tube with a fairly large diameter (12–15 mm.) in order to take care of the acetone vapors during the vigorous reaction.
2. The reaction mixture must be guarded carefully from moisture throughout the reaction; if moisture is present the magnesium becomes coated with oxide or hydroxide and the reaction does not take place

smoothly.

Scrupulous drying improves the yield of [pinacol hydrate](#) reported in these directions (G. A. Hill, private communication).

3. If a larger amount of [benzene](#) is used, the reaction is too slow in starting. Commercial [benzene](#) is satisfactory if it has been distilled and the first portion containing the water rejected.

4. The [acetone](#) used is the ordinary commercial grade dried over [calcium chloride](#). The dryness of the [acetone](#) is important and determines the time required for the reaction to start; if it is perfectly dry (two to three days over [calcium chloride](#) with occasional agitation) the reaction starts at once. See [Note 5](#), p. 239.

5. The reaction should be allowed to proceed with the maximum speed without loss of [acetone](#) through the condenser. If the reaction is made to run slowly, the yields are lower.

6. It is important that the second portion of [acetone](#) and [benzene](#) be added to the reaction mixture before the refluxing stops, as otherwise heat must be applied to start the reaction again.

7. Mechanical stirring is rendered somewhat difficult in the laboratory because the mass becomes almost solid at the end of the reaction. A centrifugal tube type stirrer will give satisfactory results.

8. Generally, from one-half to three hours are necessary for maximum crystallization. The shorter period is frequently sufficient if the cooling is thorough.

9. If dried at a temperature above that of the room, there is a tendency for the product to melt and for [pinacol](#) to be lost by volatilization.

10. The [pinacol hydrate](#) contains a small quantity of an organic mercury compound or compounds, the vapors of which are harmful. This contaminant may be removed by a thorough washing with [benzene](#) or preferably by melting under [benzene](#) and then cooling with stirring (H. S. King,¹ and H. B. J. Schurink, private communications). Alternatively, the contaminant can be destroyed by distilling with steam.²

3. Discussion

[Pinacol hydrate](#) can be prepared by the reduction of [acetone](#) by means of [magnesium amalgam](#),³ [aluminum amalgam](#),⁴ [sodium](#),⁵ [sodium amalgam](#),⁶ and electrolytically.⁷ The procedure described is a modification of that by Holleman.³ The catalyzed addition of [hydrogen peroxide](#) to [tetramethylethylene](#) also furnishes [pinacol](#).⁸ Satisfactory methods have been described for the preparation of anhydrous [pinacol](#).¹

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 462](#)
- [Org. Syn. Coll. Vol. 3, 312](#)

References and Notes

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2. Backer and Bottema, *Rec. trav. chim.* **51**, 295 (1932).
3. Couturier and Meunier, *Compt. rend.* **140**, 721 (1905); *Bull. soc. chim.* (3) **33**, 454 (1905); Richard and Langlais, *Bull. soc. chim.* (4) **7**, 454 (1910); Holleman, *Rec. trav. chim.* **25**, 206 (1906); Friedr. Bayer and Co., *Ger. pat.* 233,894 [*Frdl.* **10**, 1000 (1910–12)]; *Brit. pat.* **411** [*C. A.* **5**, 3152 (1911)]; Hofmann, Delbrück, and Meisenburg, *U. S. pat.* 1,039,739 and 1,039,740 [*C. A.* **6**, 3495 (1912)]; Kautschukges. "Bogatyr," *Fr. pat.* 459,313 [*C. A.* **8**, 2780 (1914)]; Berlin, *U. S. pat.* 1,703,220 [*C. A.* **23**, 1910 (1929)]; Calvert, *India Rubber Rev.* **26**, No. 9, 48 (1926) [*C. A.* **20**, 3685 (1926)]; King and Stewart, *Trans. Nova Scotian Inst. Sci.* **17**, 262 (1930) [*C. A.* **25**, 1799 (1931)].
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- 248,252 [Frdl. **10**, 999 (1910–12)].
6. Friedel, Ann. **124**, 327 (1862); Linnemann, Ann. Suppl. **3**, 375 (footnote) (1865).
 7. Merck, Ger. pat. 113,719 [Frdl. **6**, 22 (1900–02)]; Friedr. Bayer and Co., Ger. pat. 252,759 [Frdl. **11**, 538 (1912–14)].
 8. Milas and Sussman, J. Am. Chem. Soc. **58**, 1302 (1936).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

organic mercury compound or compounds

calcium chloride (10043-52-4)

Benzene (71-43-2)

magnesium,
magnesium turnings (7439-95-4)

aluminum (7429-90-5)

acetone (67-64-1)

sodium (13966-32-0)

hydrogen peroxide (7722-84-1)

mercuric chloride (7487-94-7)

magnesium hydroxide

Pinacol hydrate (6091-58-3)

magnesium pinacolate

pinacol (76-09-5)

tetramethylethylene (563-79-1)