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.

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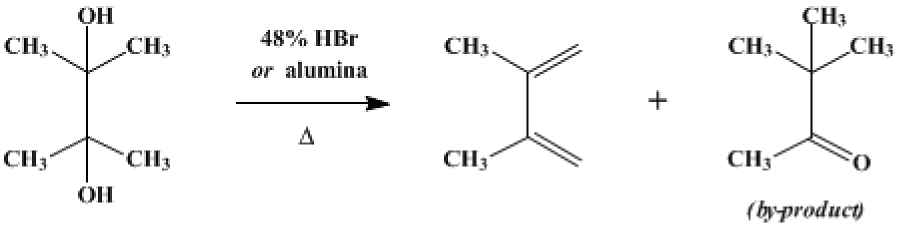
Organic Syntheses, Coll. Vol. 3, p.312 (1955); Vol. 22, p.39 (1942).

2,3-DIMETHYL-1,3-BUTADIENE

[1,3-Butadiene, 2,3-dimethyl- I. HYDROBROMIC ACID METHOD]



Submitted by C. F. H. Allen and Alan Bell.
Checked by R. L. Shriner and John C. Robinson, Jr..

1. Procedure

In a 2-l. round-bottomed flask, surmounted by a packed fractionating column (Note 1), is placed a mixture of 354 g. (3 moles) of pinacol (Note 2) and 10 ml. of commercial 48% hydrobromic acid. A few boiling chips are added, and the flask is then heated slowly with a colorless flame about 3 in. high (Note 3). The distillate is collected until the thermometer reads 95°; this requires about 2 hours when the rate of distillation is approximately 20–30 drops per minute. The upper, non-aqueous layer is washed twice with 100-ml. portions of water, 0.5 g. of hydroquinone is added, and the liquid is dried overnight with 15 g. of anhydrous calcium chloride. It is then fractionated as below, using the same column but a 1-l. flask (Note 4).

Yield	*Fraction*	*B.P.*	*Grams Per Cent*
2,3-Dimethylbutadiene	69–70.5°	135–147	55–60
Intermediate	70.5–105°	10–15	
Pinacolone	105–106°	66–75	22–25
Residue		7–8	

2. Notes

1. The column described in *Organic Syntheses*, **20**, 96, filled with glass helices, and wrapped with asbestos paper, is satisfactory. Carborundum may also be used as the filling, but a longer time is required for the distillation. Cold water is circulated through the cold finger.
2. The pinacol used was the commercially available material, or that obtained by dehydration of pinacol hydrate. This dehydration may be accomplished by adding 2 l. of benzene to 1 kg. of pinacol hydrate [*Org. Syntheses* Coll. Vol. **1**, 448 (1932), 459 (1941)], and distilling the water-benzene mixture. The lower layer is separated, and the upper benzene layer is returned to the distilling flask. This is repeated until the benzene distillate is clear. The anhydrous pinacol is then distilled, and the fraction boiling from 168° to 173° is collected. Depending upon the quality of the material used, 1 kg. of pinacol hydrate yields about 500 g. of anhydrous pinacol.
3. If too large a flame is used the column floods.
4. 2,3-Dimethylbutadiene can be kept, without appreciable change, for a limited time in a refrigerator. If it is not to be used reasonably soon, a little hydroquinone should be added as an inhibitor.

[II. ALUMINUM OXIDE METHOD]

Submitted by L. W. Newton and E. R. Coburn.
Checked by Nathan L. Drake and Richard Tollefson.

1. Procedure

A Claisen flask, provided with the usual capillary inlet for air, is connected to a Pyrex tube (Note 1) which is drawn out at one end and packed with 8-mesh alumina (Note 2). The tube is inserted in an electric furnace (Note 3) capable of maintaining a temperature of 420–470°; the temperature is measured by a thermometer placed alongside the tube in the furnace. The drawn-out end of the tube is connected by a rubber stopper to an efficient Pyrex coil-condenser, which is in turn connected by a rubber stopper to the first of two receivers, arranged in series and connected by a short length of rubber tubing. Each receiver consists of a 500-ml. filter flask, which carries an inlet tube (Note 4) extending somewhat more than halfway to the bottom of the flask. The first receiver is immersed in an ice-salt mixture (Note 5); the second is immersed in a Dry Ice-methanol mixture contained in a Dewar flask. The exit tube of the second receiver is connected to a manometer (Note 6) and to a water pump.

Pinacol (Note 7) or pinacolone is placed in the Claisen flask and is distilled, under the vacuum of a water pump, through the Pyrex tube, which is maintained at a temperature of 420–470°. About 100 g. of pinacol is distilled in 15 minutes, and then the apparatus is swept out by maintaining the reduced pressure for 15 minutes longer. The water and resinous material collected in the ice-cooled receiver are discarded (Note 8). The second receiver is removed from the cooling bath, and the product is allowed to melt. Two layers are formed; these are allowed to separate, and then the receiver is replaced in the cooling bath until the lower water layer is frozen. The crude dimethylbutadiene is then decanted. The yellow product is dried over anhydrous calcium sulfate and is fractionated (Note 9) through a Widmer or other column; the portion boiling at 67–70° is collected. The yield from 100 g. of pinacol is 55–60 g. (79–86%) (Note 10). The diene is best stored over a small amount of hydroquinone in a refrigerator.

2. Notes

1. The Pyrex tube should have a diameter of 3 cm. and a length of 70 cm.
2. The grade of alumina is important. With an ordinary grade of desiccator alumina, the checkers were unable to obtain the yields stated. The alumina employed successfully was Alorco activated alumina, from the Aluminum Ore Company, East St. Louis, Illinois. The catalyst darkens in use, but it can be kept in a clean and active condition by the following treatment: after each run, or at least after two or three runs, the tube is heated to 420–470°, and a slow stream of air is drawn through it until the alumina is white (2–5 hours).
3. A very convenient furnace can be constructed by wrapping a 3-ft. length of 1½-in. iron pipe with asbestos paper and winding a suitable heating element over this paper (about 47.5 ft. of No. 18 B. & S. gauge Nichrome wire). The whole is enclosed in a length of steam-pipe insulation. The temperature is controlled by a properly chosen Variac (variable transformer).
4. The inlet tube should have a diameter of 10 mm.
5. This receiver serves to collect most of the water and polymer formed.
6. Another receiver, consisting of a 3 by 30 cm. side-arm test tube, may be used. It is immersed in a Dewar flask and cooled with Dry Ice-methanol. Only a small amount of material is collected in this receiver.
7. Anhydrous pinacol can be prepared from pinacol hydrate [*Org. Syntheses* Coll. Vol. **1**, 448 (1932), 459 (1941)] by distillation. The material that boils at 172–178° is collected, and the distillate should be refractionated. It is more convenient, however, to prepare anhydrous pinacol from the hydrate by the method described in (Note 2) under part I (p. 313). Pinacol hydrate may be used as starting material; the yield will be slightly less than that obtained when the anhydrous material is used.
8. The contents of this receiver should be examined carefully for the presence of 2,3-dimethylbutadiene; the checkers usually found appreciable amounts present.
9. If the dehydration has been inefficient, some pinacolone (b.p. 107°) may be present in this product. The pinacolone may be distilled over the alumina again.
10. According to the submitters, the yield from 100 g. of pinacolone is 57–63 g. (70–77%).

3. Discussion

The most convenient method for preparation of 2,3-dimethylbutadiene involves the dehydration of pinacol. Many catalysts have been used, among them hydrobromic,[1] hydriodic,[1] and sulfuric acids;[2,3,4] sulfonic acids of the benzene[5] and naphthalene[6,7,8] series; acid potassium sulfate;[9] alum;[10] aniline hydrobromide;[1] iodine;[11] hot copper at 450–480°;[1] and alumina at 400°.[12,13,14] The diene has also been obtained by distillation of the product from the reaction between methylmagnesium iodide and ethyl α-methacrylate;[15] by treatment of tetramethylethylene dichloride with alcoholic potash;[4] from pinacol hydrochloride and sodium carbonate;[16] by the action of sodium or pyridine on α,α,β-trimethyl-βγ-dibromobutyric acid;[17] by passing 1,2,4-trimethyl-4-isopropenylcyclohexene over hot copper;[18] and by dehydration of dimethylisopropenylcarbinol with hydrochloric[19] or sulfuric acid.[17]

A patent reports the preparation of 2,3-dimethylbutadiene from trimethylethylene and formaldehyde in the presence of aqueous sulfuric acid.[20]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 310
- Org. Syn. Coll. Vol. 4, 795

References and Notes

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

α,α,β-trimethyl-βγ-dibromobutyric acid

sulfonic acids

ethyl α-methacrylate

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

Benzene (71-43-2)

formaldehyde (50-00-0)

potassium sulfate (37222-66-5)

hydroquinone (123-31-9)

HYDROBROMIC ACID (10035-10-6)

sodium carbonate (497-19-8)

copper (7440-50-8)

calcium sulfate (7778-18-9)

iodine (7553-56-2)

Pinacolone (75-97-8)

pyridine (110-86-1)

sodium (13966-32-0)

Naphthalene (91-20-3)

methylmagnesium iodide (917-64-6)

Pinacol hydrate (6091-58-3)

pinacol (76-09-5)

trimethylethylene (513-35-9)

2,3-DIMETHYL-1,3-BUTADIENE,
1,3-Butadiene, 2,3-dimethyl-,
2,3-Dimethylbutadiene (513-81-5)

dimethylbutadiene (926-56-7)

tetramethylethylene dichloride

pinacol hydrochloride

1,2,4-trimethyl-4-isopropenylcyclohexene

dimethylisopropenylcarbinol

aniline hydrobromide