Organic Syntheses

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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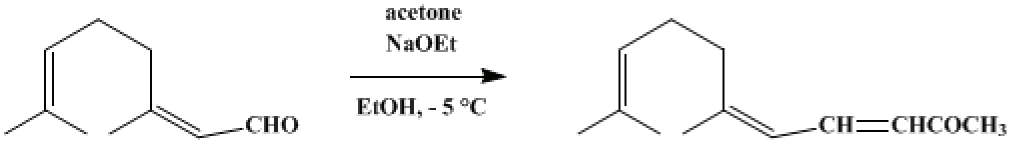
PSEUDOIONONE



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1. Procedure

A. *Purification of citral.* In a 4-l. bottle are placed 1 l. of water, 1 kg. of crushed ice, 450 g. of anhydrous sodium sulfite (or an equivalent amount of hydrated sodium sulfite), 320 g. of sodium bicarbonate, and 270 g. (304 ml., 1.78 moles) of commercial citral (Note 1). A tightly fitting stopper is securely wired into place, and the bottle is shaken thoroughly for 5–6 hours. The solution, which contains very little unchanged citral, is extracted twice with 300-ml. portions of ether (Note 2).

A 5-l. round-bottomed flask is fitted with a 1-l. dropping funnel, the mouth of which is connected to a tube passing through the stopper of the flask, and the whole apparatus is rigidly attached to a shaker (Note 3). About one-half of the sulfite solution is placed in the flask and covered with 800 ml. of ether. In the dropping funnel is placed 800 ml. of 10% aqueous sodium hydroxide. Shaking is begun, and when the contents of the flask are thoroughly mixed, the sodium hydroxide solution is admitted in a thin continuous stream over a period of about 1 hour. After all the sodium hydroxide solution is added, shaking is continued for not longer than 5 minutes, and the mixture is then poured into a large separatory funnel. The aqueous layer is drawn off and the ether layer is set aside. The aqueous layer is returned to the separatory funnel, covered with 300 ml. of ether, and shaken with an additional 200 ml. of 10% aqueous sodium hydroxide. After separation, the aqueous layer is extracted once with 150 ml. of ether, and the combined ether extracts are then dried over anhydrous sodium sulfate.

The remaining half of the sulfite solution is subjected to the same treatment, and the total ether extract, after drying, is evaporated on a water bath. The residue is then distilled under reduced pressure, yielding 200–215 g. of almost colorless citral which boils at 84–85°/2 mm. (93–95°/5 mm.).

B. *Pseudoionone.* In a 2-l. round-bottomed flask, fitted with a mechanical stirrer, a dropping funnel, and a thermometer, are placed 203 g. (230 ml., 1.33 moles) of pure citral and 800 g. (110 ml., 13.8 moles) of acetone (C.P., dried over anhydrous potassium carbonate). The mixture is cooled to −5° (or below) in an ice-salt bath, vigorous stirring is begun, and there is added through the dropping funnel a cold solution of 9.2 g. (0.4 mole) of sodium in 200 ml. of absolute ethanol. The solution of sodium ethoxide is added at the maximum rate which will permit maintenance of the temperature at −5° or below (rapid dropping). After the addition is complete, stirring is continued for 3–4 minutes. A solution of 30 g. (0.2 mole) of tartaric acid in 200 ml. of water is added, and the mixture is *immediately* steam-distilled to remove the excess acetone. A white precipitate may form when the tartaric acid is added, but this disappears during the steam distillation (Note 4). The mixture in the distilling flask is cooled in an ice bath, and the upper layer (about 380 ml.) is then removed and refluxed vigorously for 5–6 hours with three times its volume of 25% aqueous sodium bisulfite.

After cooling, the mixture is extracted twice with 200-ml. portions of ether to remove any material that has not reacted with the bisulfite. One-half of the aqueous solution is placed in the shaking extractor together with 650 ml. of ether. The calculated amount of 10% aqueous sodium hydroxide (1 mole of sodium hydroxide per mole of sodium bisulfite used) is now added as described for purification of the citral. Shaking is continued for 15 minutes after the addition of the alkali is complete (Note 5). The layers are separated (Note 6); the aqueous layer is returned to the separatory funnel and covered with 200 ml. of ether. After 100 ml. of 10% sodium hydroxide has been added, the mixture is vigorously shaken, and then the aqueous layer is removed and extracted with another 200-ml. portion of ether. The two ether extractions, one with addition of sodium hydroxide and one without, are repeated. The second half of the bisulfite solution is subjected to the same treatment as the first half, and all the ether extracts are combined (Note 7) and dried over anhydrous sodium sulfate. The ether is removed on the water bath, and the residual yellow-green oil is distilled under reduced pressure, yielding 120–130 g. (45–49% based upon 210 g. of pure citral) of pale yellow pseudoionone, boiling at 114–116°/2 mm. (124–126°/4 mm.).

2. Notes

1. Unless a pure pseudoionone free from isomers is wanted, it is not necessary to perform the elaborate purification of citral, or the elaborate purification of pseudoionone. The checkers, using commercial citral obtained from the Florasynth Laboratories, Inc., New York, found 90% of it to boil over a 3° range between 100° and 103°/7 mm. Using a solution of 203 g. of this distilled citral in 1 l. of commercial acetone, the checkers proceed as follows: The citral solution is cooled in an ice-salt bath to −10°, and one-fourth of the solution is forced, by dry compressed air, into a 500-ml. round-bottomed three-necked flask, fitted with a stirrer, dropping funnel, and an adjustable outlet tube long enough to reach to the bottom of the flask. The temperature is maintained at 0° to −5° while one-fourth of a solution of 9.2 g. of sodium in 200 ml. of absolute ethanol is added dropwise. After all the base is added, stirring is continued for 3 minutes, and then the reaction mixture is forced over into one-fourth of a solution of 33 g. of tartaric acid in 200 ml. of water. The elapsed time, from the addition of the first drop of base until the mixture is forced into the acid, is 14 minutes. The condensation is repeated three times more, and the combined acidified mixture is steam-distilled until 1 l. of distillate is obtained. It is important that the solution should remain slightly acid during steam distillation. The material remaining in the flask is cooled, the layers are separated, and the aqueous layer is extracted with ether. The combined organic layers are dried over sodium sulfate and then distilled. The yield of pseudoionone boiling at 123–124°/2.5 mm. is 177.8 g. (70% based upon the citral). By carrying out the condensation in small batches, the temperature is much more easily controlled and the yields are greatly improved. This pseudoionone, when catalytically reduced in a bomb, gave hexahydro-pseudoionol, boiling at 124–128°/10 mm., in a yield of more than 90%.
2. In handling these large quantities, much better results are obtained if extractions, etc., are carried out in portions.
3. A pressure outlet may be used, but the arrangement outlined here is quite sufficient. Citral and pseudoionone are both rapidly polymerized by contact with aqueous sodium hydroxide. This apparatus continuously provides an intimate mixture of the sulfite solution with the ether. On decomposition, the free carbonyl compound is immediately extracted and prolonged contact with sodium hydroxide is thus avoided.
4. From the completion of addition of the sodium ethoxide solution to the steam distillation, fast work is advantageous, and all equipment should be in readiness before the addition is started. Allowing the solution to stand before addition of the tartaric acid may cause darkening and formation of gummy material. It is important that the solution should remain slightly acid during the steam distillation.
5. The pseudoionone bisulfite addition product, unlike that of citral, apparently decomposes rather slowly; if the separation is made too soon, some undecomposed bisulfite compound is left in solution. This is later decomposed and, in contact with the alkali, polymerizes to a dark red gum.
6. The checkers obtained three layers at this point—a lower aqueous layer, a dark red oily layer, and the upper ether layer. The ether layer was removed and the other two layers were returned for further treatment. The dark oily layer gradually disappeared during the subsequent extractions.
7. The checkers washed these ether extracts with a little water to ensure removal of any basic material.

3. Discussion

Pseudoinone has been prepared by the condensation of citral and acetone, using as condensing agent a saturated solution of barium hydroxide,[1] a solution of sodium ethoxide in ethanol,[2,3] or metallic sodium.[4] Impure products have been obtained from citral and acetone, using alcoholic sodium hydroxide as the condensing agent,[4] and by treatment of oil of lemon grass and acetone with bleaching powder, cobalt nitrate, and alcohol.[5,6,7]

Pseudoionone, together with methylpseudoionone, has been obtained by oxidation of geraniol by acetone or methyl ethyl ketone in the presence of an aluminum alcoholate.[8] It has also been prepared from linaloöl.[9]

References and Notes

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

Pseudoionone

pseudoionone bisulfite

methylpseudoionone

aluminum alcoholate

ethanol (64-17-5)

potassium carbonate (584-08-7)

ether (60-29-7)

sodium sulfite (7757-83-7)

sodium hydroxide (1310-73-2)

sodium bicarbonate (144-55-8)

sodium sulfate (7757-82-6)

sodium bisulfite (7631-90-5)

acetone (67-64-1)

sodium (13966-32-0)

sodium ethoxide (141-52-6)

tartaric acid (87-69-4)

barium hydroxide (17194-00-2)

methyl ethyl ketone (78-93-3)

citral (5392-40-5)

cobalt nitrate

geraniol (106-24-1)