Organic Syntheses

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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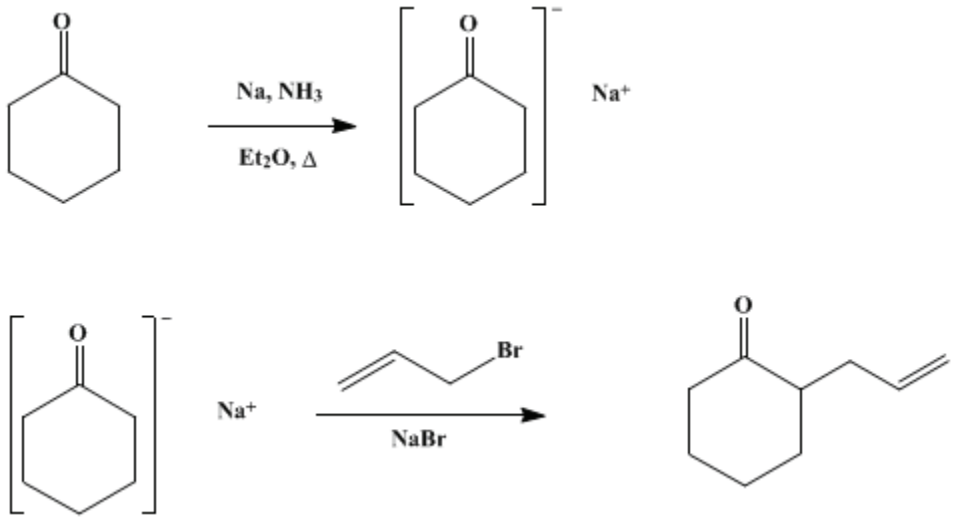
2-ALLYLCYCLOHEXANONE

[Cyclohexanone, 2-allyl-]



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1. Procedure

Approximately 1.5 l. of anhydrous liquid ammonia is introduced into a dry 5-l. three-necked flask fitted with a sealed mechanical stirrer and an efficient reflux condenser which is connected through a sodalime tube to a gas-absorption trap. Freshly cut sodium (47.2 g., 2.05 gram atoms) is converted to sodium amide by addition to the liquid ammonia in the presence of a small amount of ferric nitrate, according to p. 219. A 1-l. dropping funnel and a gas inlet tube connected to a source of dry nitrogen are attached to the third neck of the flask, and, after the blue color of the solution has disappeared and a gray suspension of sodium amide remains (Note 1), 1.2 l. of dry ether is added as rapidly as the rate of vaporization of ammonia will permit. The ammonia is removed by warming the flask on a steam bath until refluxing of the ether occurs. Cyclohexanone (Note 2) (220 g., 2.24 moles) is added through the dropping funnel (Note 3), and the mixture is stirred and heated under reflux on a steam bath for 3 hours. Nitrogen is then introduced through the gas inlet tube to maintain an inert atmosphere (Note 4), and the mixture is cooled in an ice bath. A solution of 246 g. (2.03 moles) of allyl bromide (Note 5) in 1 l. of anhydrous ether is added rapidly through the dropping funnel with stirring. If the reaction does not start soon after the completion of this addition the mixture is warmed cautiously on the steam bath. When the exothermic reaction has started it is controlled by cooling in the ice bath while refluxing continues for 20–30 minutes. The mixture is finally heated under reflux on the steam bath for 3 hours.

The mixture is cooled in an ice bath, any sodium or sodium amide which may remain in the necks of the flask is scraped into the reaction mixture with a spatula, and enough water is added to dissolve the sodium bromide. The ether layer is separated and combined with five 100-ml. ether extracts of the aqueous phase, washed with 150 ml. of saturated sodium chloride solution, and dried over anhydrous sodium sulfate. The ether is removed by distillation, and the residue is fractionated carefully under reduced pressure through a 4-ft. heated column packed with glass helices and fitted with a total-condensation variable take-off head. The yield of 2-allylcyclohexanone boiling at 90–92°/17 mm. is 153–174 g. (54–62%). In addition, 28–38 g. of unchanged cyclohexanone boiling at 51–52°/17 mm., 15–35 g. of diallylcyclohexanone boiling at 123–124°/17 mm., and small intermediate fractions are obtained.

2. Notes

1. The conversion of the sodium to sodium amide requires 30–90 minutes. More liquid ammonia may be added if too much is lost by vaporization before the conversion is complete.
2. Redistilled cyclohexanone, b.p. 154–156°, was used.
3. The submitters obtained equally good results by adding 80 g. (2.05 moles) of freshly prepared finely powdered sodium amide in portions to a solution of the cyclohexanone in 1.2 l. of dry ether, heating under reflux for 3 hours, and continuing the preparation in the manner described.
4. The submitters state that the yield is increased appreciably if a nitrogen atmosphere is maintained after this point. Loss of ether may be avoided by stopping the flow of nitrogen when refluxing begins.
5. Allyl bromide was dried over calcium chloride and redistilled, b.p. 70–71.5°.

3. Discussion

2-Allylcyclohexanone has been prepared by the direct alkylation of the sodium derivative of cyclohexanone with allyl iodide, sodium amide having been used in the preparation of the sodium enolate,[1] and by ketonic hydrolysis of ethyl 1-allyl-2-ketocyclohexanecarboxylate, prepared by alkylation of ethyl 2-ketocyclohexanecarboxylate.[2,3]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 25

References and Notes

1. Cornubert, *Ann. chim.*, [9] **16**, 145 (1921).
2. Cope, Hoyle, and Heyl, *J. Am. Chem. Soc.*, **63**, 1848 (1941).
3. Grewe, *Ber.*, **76**, 1075 (1943).

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

sodium enolate

calcium chloride (10043-52-4)

ammonia (7664-41-7)

ether (60-29-7)

Cyclohexanone (108-94-1)

sodium chloride (7647-14-5)

Allyl bromide (106-95-6)

sodium bromide (7647-15-6)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

allyl iodide (556-56-9)

sodium (13966-32-0)

sodium amide (7782-92-5)

ethyl 2-ketocyclohexanecarboxylate (1655-07-8)

2-Allylcyclohexanone,
Cyclohexanone, 2-allyl- (94-66-6)

ferric nitrate

diallylcyclohexanone

ethyl 1-allyl-2-ketocyclohexanecarboxylate

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