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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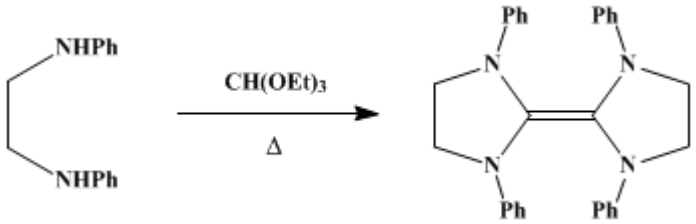
BIS(1,3-DIPHENYLIMIDAZOLIDINYLIDENE-2)

[$\Delta^{2,2'}$-Bis(1,3-diphenylimidazolidine)]



Submitted by H.-W. Wanzlick[1]
Checked by D. J. LaFollette and Ronald Breslow.

1. Procedure

In a 250-ml. round-bottomed flask equipped with a gas-inlet tube and reflux condenser 20 g. (0.094 mole) of N,N'-diphenylethylenediamine (1,2-dianilinoethane) (Note 1) and 100 ml. of purified triethyl orthoformate (Note 2) are heated by an oil bath under nitrogen (Note 3) for 5 hours. The oil bath is maintained between 190° and 200°, and water is allowed to stand in the condenser. The water in the condenser begins to boil slowly, and the alcohol which is produced is allowed to escape (Note 4). The reaction product which crystallizes during the reaction is filtered after cooling and washed with ether. There is obtained 19–20 g. (91–95%) of product, m.p. 285° (dec.) (Note 5).

2. Notes

1. 1,2-Dianilinoethane, containing water of crystallization, is best dried by melting under vacuum.
2. Commercial material, distilled.
3. The nitrogen is dried by passing it through concentrated sulfuric acid. It must be nearly oxygen-free; otherwise 1,3-diphenylimidazolidinone-2 is formed, and its removal by recrystallization results in a decreased yield.
4. An air condenser may also be employed.
5. The melting range depends on the rate of decomposition during heating. The checkers observed that in an evacuated capillary there is darkening from 270° to 290°, and fairly sharp melting at 299–300°. The product is autoxidizable and is best stored under dry nitrogen. Preparations which have oxidized on standing may be purified by digesting and washing with methylene chloride.

3. Discussion

This amino olefin was first prepared by thermal elimination of chloroform from 1,3-diphenyl-2-trichlormethylimidazolidine,[2] and later by the procedure described here.[3,4] It can also be made by treatment of 1,3-diphenylimidazolinium salts with strong bases.[5,6]

4. Merits of the Preparation

The procedure described is the simplest one known. All other methods also employ 1,2-dianilinoethane as starting material. This method, however, converts it directly into the amino olefin in one step.

The preparative value of this compound lies in the surprising fact that bis(1,3-diphenylimidazolidinylidene-2) behaves in many reactions (*e.g.*, with aromatic aldehydes,[2,7] and with carbon acids[2,7,8,9]) as if it dissociated to form a "nucleophilic carbene." The hydrolytic cleavage of these derived imidazolidine derivatives makes possible the preparation of formyl compounds, so that the amino olefin can be considered as a potential carbonylation reagent. In many reactions it is not

necessary to isolate the reagent, as it may be produced *in situ*.[10] It should be pointed out, however, that the reaction of the amino olefin with aldehydes and carbon acids does not actually involve prior dissociation to the carbene, but it is convenient, from a preparative point of view, to describe it in these terms.[6]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 7, 162

References and Notes

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

Bis(1,3-diphenylimidazolidinylidene-2)

$\Delta^{2,2'}$-Bis(1,3-diphenylimidazolidine)

sulfuric acid (7664-93-9)

ether (60-29-7)

chloroform (67-66-3)

nitrogen (7727-37-9)

triethyl orthoformate (122-51-0)

carbene (2465-56-7)

methylene chloride (75-09-2)

1,2-dianilinoethane,
N,N'-diphenylethylenediamine (150-61-8)

1,3-diphenylimidazolidinone-2

1,3-diphenyl-2-trichlormethylimidazolidine

1,3-diphenylimidazolinium