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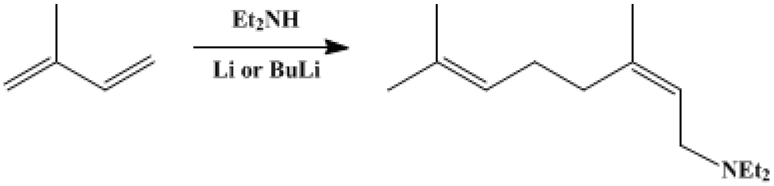
# TELOMERIZATION OF ISOPRENE WITH DIALKYLAMINE: *N,N*-DIETHYLNERYLAMINE

### [2,6-Octadien-1-amine, *N,N*-diethyl-3,7-dimethyl-, (*Z*)-]



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Checked by Alan J. Chalk, Laszlo V. Wertheimer, and Gabriel Saucy.

## 1. Procedure

A 100-mL glass autoclave (Note 1) is charged with 34 g (0.50 mol) of isoprene (Note 2) and 7.3 g (0.10 mol) of diethylamine (Note 3) under nitrogen (Note 4). The contents are cooled to 3–5°C using an ice–salt bath, and 3.7 mL (0.006 mol) of a 1.62 *M* solution of butyllithium in hexane (Note 5) is added dropwise by syringe while stirring. The resulting slightly yellow solution is blanketed carefully with dry nitrogen, and the vessel is sealed. The solution is heated to 65°C and stirred for 13 hr. The vessel is then cooled using an ice–salt bath, the contents are poured into 15 mL of water, and the organic layer is separated. The aqueous phase is extracted with 30 mL of diethyl ether. The organic layers are combined, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure with a rotary evaporator. The residual liquid is distilled under reduced pressure (Note 6) to afford 16.1–18.0 g (77–86%) of *N,N*-diethylnerylamine as a colorless liquid, bp 83–84°C (1.5 mm) (Note 7) and (Note 8).

## 2. Notes

1. The glass autoclave must be used with appropriate precaution. A pressure of about 20 psi is generated, so a low-positive-pressure reactor, such as a shielded Fischer-Porter Bottle (Fischer and Porter Company, Lab-Coest Division, Warminster, PA18974), can be used instead. Alternatively, the reaction may be carried out without pressure equipment in 3 days.[2]
2. Isoprene, obtained from Aldrich Chemical Company, Inc. (also available from Nakarai Chemicals, Ltd. in Japan), was dried over Linde 4A molecular sieves for at least 1 day and freshly distilled prior to use.
3. Diethylamine, obtained from Aldrich Chemical Company, Inc., was distilled from calcium hydride before use.
4. A slow stream of dry nitrogen was passed through an inverted funnel that was placed over the vessel.
5. Butyllithium in hexane was obtained from Aldrich Chemical Company, Inc. (also available from Nakarai Chemicals, Ltd. in Japan), and titrated before use.[3] Lithium (0.055 g, 0.0079 g-atom), cut into small pieces (ca. 2 mm), can be used in place of the butyllithium-hexane solution.
6. A forerun (1.4–0.6 g) boiling at 52–56°C (16 mm) consists mainly of *N,N*-diethyl-2-methyl-2-butenylamine and *N,N*-diethyl-3-methyl-2-butenylamine.
7. GLC analysis (7% Apiezon L on 60–80-mesh Gaschrom Q, 3 mm × 3 m, 170°C) showed that the product is over 99% isomerically pure. The spectral properties of *N,N*-diethylnerylamine are as follows: IR (neat) $cm^{-1}$: 1660, 1200, 1165, 1050, 830; $^1H$ NMR ($CDCl_3$) δ: 1.03 (t, 6 H, *J* = 7, $CH_3$-), 1.45–1.7 (m, 6 H, $CH_3$-C=), 2.02–2.2 (m, 4 H, -$CH_2$-C=), 2.50 (q, 4 H, *J* = 7, -N-$CH_2$-), 3.05 (d, 2 H, *J* = 6.5, -N-$CH_2$-C=), 4.9–5.5 (m, 2 H, -CH=).
8. The submitters report that similar reactions of isoprene with dimethylamine (55°C, 10 hr) and dipropylamine (65°C, 15 hr) afforded *N,N*-dimethylnerylamine (69%), bp 85–86°C (9 mm) and *N,N*-dipropylnerylamine (77%), bp 86–87°C (1 mm), respectively.

## 3. Discussion

The procedure described here is essentially that reported earlier[4] and modified by subsequent experience.[5] It is a simple, general method for the synthesis of an *N,N*-dialkylnerylamine from isoprene and a dialkylamine. *N,N*-Dialkylnerylamines can also be prepared by the reaction of a dialkylamine with neryl chloride[6] by a modification of Sandler's method.[7] However, pure nerol, the starting material of neryl chloride, is expensive, and not easily available commercially. The present method illustrates a mild and convenient one-step reaction for the preparation of an *N,N*-dialkylnerylamine. In addition, the starting materials are readily accessible, the reaction proceeds stereoselectively, and the yields of the product are generally high. This process consists of the initial addition of lithium dialkylamide to isoprene, followed by the propagation of the resulting intermediate, and the termination by dialkylamine.

*N,N*-Dialkylnerylamines serve as convenient precursors for naturally occurring acyclic monoterpenes such as linalool,[8] citronellal,[9] and citral.[10]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 8, 183

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## References and Notes

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

diethyl ether (60-29-7)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

diethylamine (109-89-7)

dimethylamine (124-40-3)

lithium (7439-93-2)

butyllithium (109-72-8)

ISOPRENE (78-79-5)

hexane (110-54-3)

citral (5392-40-5)

calcium hydride (7789-78-8)

Linalool (78-70-6)

neryl chloride

nerol (106-25-2)

citronellal (106-23-0)

N,N-Diethylnerylamine,
2,6-Octadien-1-amine, N,N-diethyl-3,7-dimethyl-, (Z)- (40137-00-6)

dipropylamine (142-84-7)

butyllithium-hexane

N,N-diethyl-2-methyl-2-butenylamine

N,N-diethyl-3-methyl-2-butenylamine

N,N-dimethylnerylamine

N,N-dipropylnerylamine