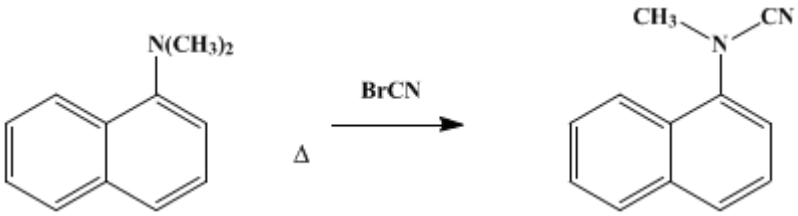
Organic Syntheses, Coll. Vol. 3, p.608 (1955); Vol. 27, p.56 (1947).

N-METHYL-1-NAPHTHYLCYANAMIDE

[Cyanamide, methyl-(1-naphthyl)-]



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1. Procedure

Caution! Cyanogen bromide is highly toxic. This preparation should be carried out under a good hood.

A mixture of 171 g. (1 mole) of dimethyl-α-naphthylamine (Note 1) and 125 g. (1.2 moles) of cyanogen bromide[1] in a 1-l. flask (Note 2) is heated under reflux on the steam bath for 16 hours (Note 3). The cooled reaction mixture is added to 2.5 l. of dry ether, and the insoluble quaternary salt (Note 4) is filtered. The ether filtrate is extracted with four 800-ml. portions of approximately 15% hydrochloric acid solution (Note 5) and washed with five 500-ml. portions of water. The ether solution is dried with 30–35 g. of anhydrous calcium sulfate (Drierite). After filtration, the solvent is removed by distillation at atmospheric pressure on the steam bath; the residue is fractionated under reduced pressure. The yield of pale yellow oil, boiling at 170–171°/1 mm. (185–187°/3 mm.), amounts to 115–122 g. (63–67%) (Note 6).

2. Notes

1. Better yields are obtained by dealkylating the tertiary amine in this manner than by starting with the secondary amine. In a similar manner, N-ethyl-1-naphthylcyanamide, b.p. 165–168°/2 mm., is obtained in a 48% yield from diethyl-α-naphthylamine; the yield from the secondary amine is only 25%.
2. Ground-glass equipment is preferable.
3. In order to avoid loss of cyanogen bromide an efficient condenser must be used and the heating should be very gradual at first.
4. About 10 g. of α-naphthyltrimethylammonium bromide, m.p. 160°, is generally obtained.
5. About 25 g. of crystalline dimethyl-α-naphthylamine hydrochloride may be recovered by efficient chilling of the hydrochloric acid extracts.
6. The N-methyl-1-naphthylcyanamide turns dark green upon standing exposed to the air for several days. It may be preserved in sealed, evacuated ampoules in the absence of light.

3. Discussion

The preparation described is based on the method of von Braun and co-workers.[2]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 609

References and Notes

1. *Org. Syntheses* Coll. Vol. **2**, 150 (1943).
2. Von Braun, Heider, and Muller, *Ber.*, **51**, 281 (1918).

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

dimethyl-α-naphthylamine

diethyl-α-naphthylamine

dimethyl-α-naphthylamine hydrochloride

hydrochloric acid (7647-01-0)

ether (60-29-7)

calcium sulfate (7778-18-9)

Cyanogen bromide (506-68-3)

N-Methyl-1-naphthylcyanamide,
Cyanamide, methyl-(1-naphthyl)- (53663-33-5)

N-ethyl-1-naphthylcyanamide

α-naphthyltrimethylammonium bromide