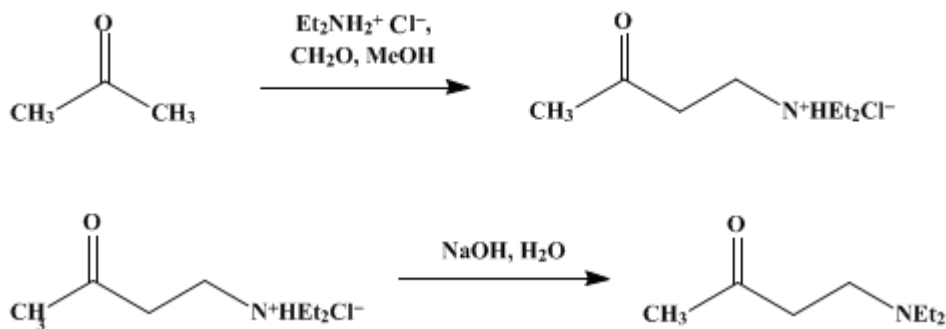


## 1-DIETHYLAMINO-3-BUTANONE

### [2-Butanone, 4-diethylamino-]



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Checked by William S. Johnson and Duane Zinkel.

### 1. Procedure

In a 3-l. round-bottomed flask equipped with a reflux condenser (Note 1) are placed 176 g. (1.60 moles) of diethylamine hydrochloride (Note 2), 68 g. (2.26 moles) of paraformaldehyde, 600 ml. (8.2 moles) of acetone, 80 ml. of methanol, and 0.2 ml. of concentrated hydrochloric acid. The mixture is heated for 12 hours at a moderate to vigorous rate of reflux (Note 3). The light-yellow solution, in which a small amount of gelatinous solid remains, is cooled, and a cold solution of 65 g. of sodium hydroxide in 300 ml. of water is added. The mixture is extracted with three 200-ml. portions of ether, the combined extracts are washed with two 150-ml. portions of saturated sodium chloride solution, and the washes are re-extracted with two 150-ml. portions of ether.

The combined ether solutions are dried overnight with about 80 g. of anhydrous sodium sulfate, filtered, and then distilled under reduced pressure (5 to 12 mm.) (Note 4) through a 20-cm. asbestos-wrapped Vigreux distilling column, with an efficient water-cooled condenser (Note 5). After the solvent and a small fore-run have been distilled, 150–171 g. (66–75%) of 1-diethylamino-3-butanone is collected as a light-yellow to nearly colorless liquid, b.p. 63–67°/7mm. (75–77°/15mm.),  $n_D^{25}$  1.4300–1.4310. The product may contain a small amount of 1,1-bis(diethylaminomethyl)acetone (the bis-Mannich base), which can interfere with some uses of this product. Refractionation gives relatively pure material, 142–161 g. (62–70%), b.p. 72–75°/10mm.,  $n_D^{25}$  1.4301–1.4307,  $d_4^{25}$  0.8626,  $M_D$  (found) 43.2–43.3,  $M_D$  (calcd.) 43.1 (Note 6).

### 2. Notes

1. Ground-glass joints are desirable.
2. A good grade of commercial diethylamine hydrochloride (Eastman Kodak white label grade or Matheson, Coleman and Bell) is satisfactory without purification.
3. At first some bumping may occur if the heating is too vigorous; mechanical stirring may reduce this, but does not improve the yield. The submitters found an electrically heated oil bath or a steam bath to be satisfactory, but *not a heating mantle*.
4. If the temperature of distillation is too high, or if a heating mantle is used, decomposition to methyl vinyl ketone may occur. The submitters used an electrically heated oil bath and prefer pressures below 12 mm. to minimize decomposition. A more elaborate fractionating column necessitating a higher bath temperature or prolonged heating is also undesirable. If the material stands more than one or two days before distillation it may decompose.
5. Unless the condenser is efficient, some product will be lost; a Dry Ice-cooled trap located between the receiver and the pump is recommended.
6. This product gave satisfactory analytical values: Calcd. for C<sub>8</sub>H<sub>17</sub>NO: C, 67.1; H, 12.0. Found: C,

67.2; H, 11.9. The neutral equivalent of various samples, titrated potentiometrically with standard hydrochloric acid solutions, ranged between 144 and 145 (calcd. 143.2).

### 3. Discussion

1-Diethylamino-3-butanone has been prepared by the Mannich reaction,<sup>2,3,4,5,6,7</sup> and by the condensation of methyl vinyl ketone with diethylamine hydrochloride in the presence of acetic anhydride.<sup>8</sup> The present procedure is a modification of that described by Wilds and Shunk.<sup>5</sup>

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### References and Notes

1. University of Wisconsin, Madison, Wisconsin.
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  3. du Feu, McQuillin, and Robinson, *J. Chem. Soc.*, **1937**, 53.
  4. Tuda, Hokusima, and Oguri, *J. Pharm. Soc. Japan*, **61**, 69 (1941) [*C. A.*, **36**, 3154 (1942)].
  5. Wilds and Shunk, *J. Am. Chem. Soc.*, **65**, 469 (1943).
  6. Spaeth, Geissman, and Jacobs, *J. Org. Chem.*, **11**, 399 (1946).
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### Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

hydrochloric acid (7647-01-0)

methanol (67-56-1)

ether (60-29-7)

acetic anhydride (108-24-7)

sodium hydroxide (1310-73-2)

sodium chloride (7647-14-5)

sodium sulfate (7757-82-6)

acetone (67-64-1)

1-Diethylamino-3-butanone,  
2-Butanone, 4-diethylamino- (3299-38-5)

1,1-bis(diethylaminomethyl)acetone

diethylamine hydrochloride (660-68-4)

methyl vinyl ketone (78-94-4)

paraformaldehyde (30525-89-4)

