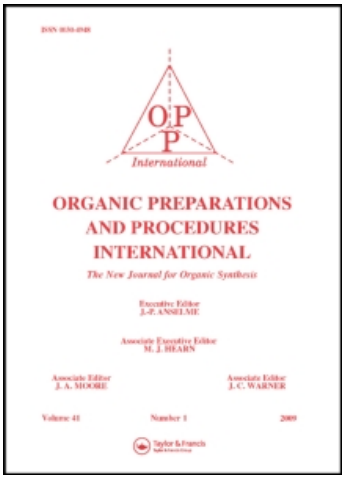

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

4(5)-METHYLIMIDAZOLIUM CHLORIDE

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To cite this Article Overberger, C. G. and Shen, C. M.(1969) '4(5)-METHYLIMIDAZOLIUM CHLORIDE', Organic Preparations and Procedures International, 1: 1, 1 — 3
To link to this Article: DOI: 10.1080/00304946909458338
URL: http://dx.doi.org/10.1080/00304946909458338

ORGANIC PREPARATIONS AND PROCEDURES 1(1), 1-3(1969)

4(5)-METHYLIMIDAZOLIUM CHLORIDE

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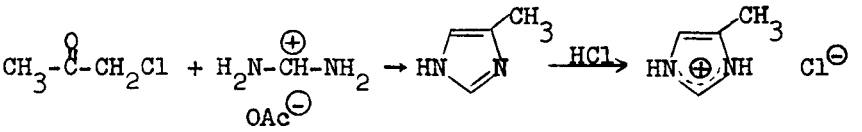

4(5)-Methylimidazole is conveniently prepared from chloro-2-propanone and formamidine acetate. This method is less time consuming and gives a higher yield of 4(5)-methylimidazole than the procedure of Windaus and Knoop.[1] The present procedure could be utilized as a general synthesis for 4-substituted imidazoles.

Experimental

4(5)-Methylimidazole Picrate To a solution of 50 g. (0.53 mole) formamidine acetate[2] in 300 ml. of diethylene glycol[3] heated at 135°, is added, with stirring and under anhydrous conditions, 16.6 g. (0.18 mole) of chloro-2-propanone[4] in 30 ml. diethylene glycol during a period of 4 hrs. The red-brown solution which forms is further heated at 135° for an additional 4 hrs. The solution is diluted to 500 ml. with water and is passed through a column of Dowex 50 x 8 (5 x 25 cm, H^+ form). After the column is washed with distilled water, 4(5)-methyl-

imidazole is obtained by elution with 0.1 N NH_4OH. Evaporation of the solvent gives a brown oil which is distilled at 90-5°/0.025 mm. yielding 4.0 g. (27.5%) of 4(5)-methylimidazole. This light-yellow liquid is dissolved in 200 ml. of boiling water and 9.0 g. of picric acid is added with stirring. Heating is continued until solution is complete. The yellow needles which separate on standing overnight at room temperature are filtered, washed with a small amount of water and air dried. The filtrate and washings are combined and heated and 1.0 g. of picric acid is added. The solution is cooled and the picrate is filtered. This procedure is repeated using 1.0 g. of picric acid each time until the air dried picrate melts below 150°. All fractions melting above 150° are combined and recrystallized from water (Norit) to yield 12.9 g. of light-yellow needles, m.p. 159-60. [lit.[1a] m.p. 159-60°].

4(5)-Methylimidazolium Chloride To a warm mixture of 40 ml. of hydrochloric acid solution (10 ml. of 37% hydrochloric acid and 30 ml. of water) and 80 ml. of benzene, is added 10.0 g. (0.032 mole) of the purified picrate. The mixture is vigorously agitated and the aqueous layer is then extracted 5 times with 50-ml. portions of benzene, treated with Norit, filtered and evaporated to dryness under reduced pressure giving a hygroscopic, white solid, m.p. 108-112°. 4(5)-Methylimidazolium chloride can be recrystallized from a small volume of absolute ethanol yielding colorless needles which deposit on cooling. Ethyl ether (twice the volume of absolute ethanol) is added to the suspension of crystals and the mixture is left in the refrigerator overnight. The colorless needles are filtered, washed with a small volume of ether and dried in vacuo over P_2O_5, giving 3.25 g. (84% yield) of the desired product, m.p. 113-114° [lit.[1b] m.p. 118°; lit.[5] m.p. 114°].

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3. Fisher reagent grade diethylene glycol was used without purification.

4. Eastman Kodak practical grade chloro-2-propanone was used without purification.

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(Received May 17, 1968)