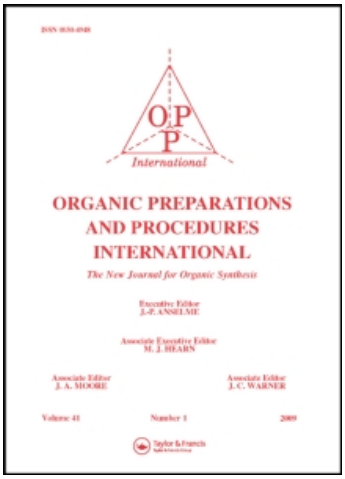

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PREPARATION OF N,N'-DIALKYLUREAS

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OPPI BRIEFS

(By James A. Moore, Associate Editor)

PREPARATION OF N,N'-DIALKYLUREAS

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The reaction of phenyl carbonate with primary amines such as methylamine, ethylamine and n-butylamine, gave the corresponding ureas in yields of 71, 85 and 82% respectively.[1] The products are pink colored but melt at the correct temperature and can be used as such in further reactions. The less expensive guiacol carbonate when used instead of phenyl carbonate, in

$$(C_6H_5O)_2CO + 2RNH_2 \longrightarrow RNHCONHR + 2C_6H_5OH$$

the preparation of N,N'-dimethylurea gave a comparable yield but required a much longer steam distillation time to remove the guiacol.

EXPERIMENTAL

N,N'-Dimethylurea.- To a vigorously stirred solution of 40% aqueous methylamine (195 ml) cooled in an ice bath, was added phenyl carbonate (214 g) in small portions. The temper-

ature was kept at 20-25° during the addition which required 40-50 min. The resulting solution was allowed to stand at room temperature for 24 hrs, heated at 100° for 4 hrs and then steam distilled until the distillate gave only a faint color with ferric chloride. About 9 to 12 ℓ. of steam distillate was obtained.

The solution in the distillation flask was treated with concentrated ammonium hydroxide (1 ml) and evaporated to dryness under reduced pressure using a water aspirator. Further drying was accomplished by treating the resulting solid with a mixture of benzene (100 ml) and absolute ethanol (50 ml) and evaporating to dryness under reduced pressure. The solid (74 g) obtained when recrystallized from benzene gave 62 g (70%) of N,N'-dimethylurea melting at 105-106°, lit.[3] 99.5-100°. Further purification by extraction of the urea (30 g) with absolute ether using a Soxhlet extractor gave 27 g of white crystals melting at 108-109° (corr).

N,N'-Diethylurea.- This urea was prepared using a mixture of 70% ethylamine (180 ml) and water (20 ml). The solid obtained after steam distillation and removal of the water was dissolved in hot ethyl acetate and the resulting solution was cooled. The diethylurea (75.3 g) obtained in this way was pink colored and melted at 109-111°. Concentration of the filtrate gave an additional 20.5 g of a red colored sample. The deep red ethyl acetate filtrate was chromatographed using silica gel with benzene and ethyl acetate as eluents and gave 9.2 g of the urea. The combined samples when recrystallized from acetone gave 88 g (76%) of a pale pink solid melting at

110-111°, lit.[3] 112°. Trituration with hot petroleum ether (b.p. 60-68°) gave white crystals with the same melting point.

The acetone filtrate upon removal of the solvent gave a red solid which upon sublimation under reduced pressure gave the urea. Recrystallization from a mixture of acetone and petroleum ether (b.p. 60-68°) gave 10.2 g (9%) of white crystals, mp. 110-111°.

N,N'-Di-n-butylurea.- This preparation was modified by using 146 g of n-butylamine dissolved in 90 ml of water. The N,N'-di-n-butylurea (178.4 g) was obtained from the steam distillation as a red colored solid insoluble in water. Recrystallization from acetone gave 158 g (92%) of a pale pink colored solid 74-75.5°, lit.[3] 70.5-71°.

REFERENCE

1. Ureas have been prepared from the amine and either phosgene [W. Marckwold, Ber., 23, 3207 (1890)], carbon dioxide [F. Fichter and B. Becker, Ber., 44, 348 (1911)], urea [T. L. Davis and K. Blanchard, J. Am. Chem. Soc., 45, 1816 (1923)] or the corresponding isocyanate [A. Wurtz, Ann., 80, 347 (1851)]. Patents have been obtained on the procedure using phosgene [Mallinckrodt, U. S. Patent 2444023] and urea [T. L. Davis, U.S. Patent 1785730].