



A New and Efficient Preparation of Carbodiimides from Ureas Using Dimethylphosgeniminium Chloride as a Dehydrating Agent

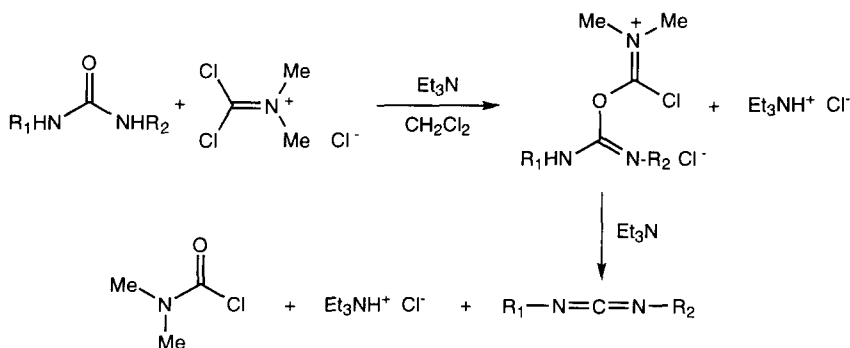
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Abstract: Dimethylphosgeniminium chloride was used as dehydrating agent for the preparation of carbodiimides from ureas. Copyright © 1996 Published by Elsevier Science Ltd

Carbodiimides are important reagents in synthetic chemistry. Amongst their numerous transformations, their use as efficient dehydrating agents is firmly established¹.

Although many good general methods are available for the preparation of carbodiimides from the corresponding thiourea², only a few methods are known for their conversion from the corresponding urea³. Herein, we report that the treatment of a variety of substituted ureas with dimethylphosgeniminium salts in the presence of triethylamine can afford directly the corresponding carbodiimides in excellent yields (Scheme 1, Table 1). The only side product of the reaction is N,N-dimethylcarbamoyl chloride and this can be easily removed by evaporation under reduced pressure.



Scheme 1

A typical procedure is described as follows. To a suspension of the urea (1eq.) and dimethylphosgeniminium salt (1eq.) in dichloromethane (0.3M) was added at 0°C under argon atmosphere a solution (0.3M) of triethylamine (2.1eq.) in dichloromethane. The reaction was followed by TLC (disappearance of the starting urea). After removal of the solvent, hexane was added to the reaction mixture and the resulting suspension was triturated for 30 minutes. The precipitated triethylammonium chloride

formed was filtered and the filtrate evaporated under reduced pressure. The resulting carbodiimides were sufficiently pure to be used as such but can be made analytically pure by column chromatography or short-path distillation. Various carbodiimides were prepared in very good yields as summarised in Table 1.⁴

Table 1: Preparation of carbodiimides

| Entry | R ¹ | R ² | Isolated yields (%) |
|-------|----------------|-------------------|---------------------|
| 1 | t-butyl | 1-naphtyl | 90 |
| 2 | cyclohexyl | 1-naphtyl | 75 |
| 3 | -(S)-MePh | phenyl | 86 |
| 4 | cyclohexyl | phenyl | 95 |
| 5 | -(S)-MePh | -(S)-MePh | 90 |
| 6 | cyclohexyl | cyclohexyl | 100 |
| 7 | t-butyl | t-butyl | 85 |
| 8 | 1-naphtyl | -(R)-(iPr)CHCOOEt | 100 |

This method has the advantage of providing the desired product rapidly and under extremely mild conditions, using a commercially available reagent.

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References and notes

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- (4) All new compounds have been fully characterised.

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