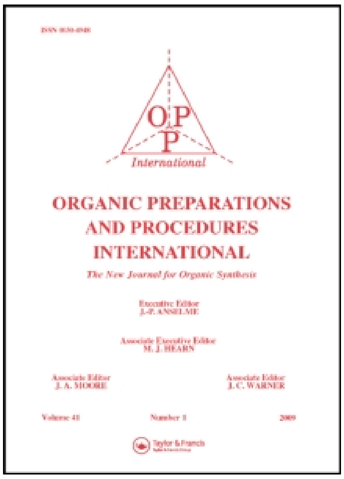


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

A NEW SIMPLIFIED METHOD FOR THE PREPARATION OF N,N'-DIPHENYLUREA

Kevin Tran[a]; K. Darrell Berlin[a]
[a] Department of Chemistry, Oklahoma State University, Stillwater, OK

To cite this Article Tran, Kevin and Berlin, K. Darrell(2004) 'A NEW SIMPLIFIED METHOD FOR THE PREPARATION OF N,N'-DIPHENYLUREA', Organic Preparations and Procedures International, 36: 1, 71 — 73
To link to this Article: DOI: 10.1080/00304940409355373
URL: http://dx.doi.org/10.1080/00304940409355373

5. K. Koguro, T. Oga, S. Mitsui, and R. Orita, *Synthesis*, 910 (**1998**).

6. R. K. Russell and W. V. Murray, *J. Org. Chem.*, **58**, 5023 (1993).

7. E. F. George and W. D. Riddell, *US Patent*, 3,865,570 (1973); *CA*: **80**: 23539y (1974).

8. J. Boibin, S. Husinec and S. Z. Zard, *Tetrahedron*, **51**, 11737 (1995).

****

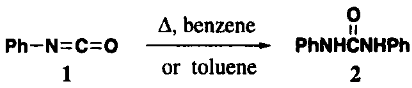
A NEW SIMPLIFIED METHOD FOR THE PREPARATION OF *N,N'*-DIPHENYLUREA

Submitted by (08/06/03)

Kevin Tran and K. Darrell Berlin*

Department of Chemistry, Oklahoma State University
Stillwater, OK 74078

Ureas constitute a family of organic molecules of great interest.[1] *N,N'*-Diphenylurea (**2**, carbanilide) is widely used in numerous applications.[2-10] Consequently, the synthesis of **2** has been the subject of several previous studies[11-18] utilizing a variety of solvents and metallic inorganic catalysts. However, these methods required large excesses of solvents, long reaction times, tedious work-ups, and elaborate purification procedures. Since **2** is relatively expensive, we have developed a new, inexpensive and clean approach to prepare **2** from phenyl isocyanate (**1**) in anhydrous benzene or toluene.[19] The approach is attractive because of its simplicity, ease of operation, and high yield of a very pure product **without** recrystallization. Moreover, no catalyst is required, and the reaction time is short. The Table below contains pertinent results which are the average of two separate experiments.



$$\underset{\mathbf{1}}{\text{Ph--N=C=O}} \xrightarrow[\text{or toluene}]{\Delta,\ \text{benzene}} \underset{\mathbf{2}}{\text{PhNH}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{NHPh}}$$

Table. Self-condensation of Phenyl Isocyanate (**1**) in benzene and toluene to N,N'-Diphenylurea

Solvent	Yield (%)	mp (°C)
Benzene	62	239-240, *lit*[2] mp 238-240°C
Toluene	62	241.5-242

EXPERIMENTAL SECTION

Commercial (Aldrich) phenyl isocyanate (**1**) was used directly. Solvents were dried (24 h) over molecular sieves (3A). Glassware was oven-dried overnight before use. IR spectra were recorded on a Perkin-Elmer 2000 FT-IR unit. NMR spectra were recorded on a Varian Gemini 2000 HR spectrometer (300 MHz) operating at 300.09 MHz (^{1}H) and 75.46 MHz (^{13}C). Mps were taken on a Thomas-Hoover apparatus and are uncorrected.

Typical Procedure.-In a 15 mL, 3-necked, round-bottomed flask equipped with a condenser, a magnetic stirring bar, and a N_2 inlet was placed a solution of phenyl isocyanate (**1**, 0.031 g, 0.26 mmol) in anhydrous benzene (2 mL) [or toluene][19] which was then heated under gentle reflux with stirring for 30 min. Heating was discontinued, but stirring was maintained until the flask had cooled to RT. The organic solution was washed with water (2 mL) and then brine (2 mL). After separation of the organic layer, and the aqueous layer was extracted with anhydrous ether (5 mL). The combined organic layer/extracts were dried (Na_2SO_4), and evaporation of the solvent under vacuum gave a white solid in good yield and high purity (see *Table*). Reactions scaled up to 1.0 g gave similar results. Performing the reaction in toluene avoids the use of benzene which has been classified as a moderate carcinogen.[20] A highly crystalline product, mp. 242-243°C, could be obtained if the solvents were allowed to evaporate slowly at RT over 2-3 days. However, the overall yield of **2** was low for reasons not clear at this time. The sample of **2** from toluene was slightly purer than that from benzene. TLC analysis with ethyl acetate:ether (1:3, 1:5, and 1:8) showed one spot for **2** obtained from runs in benzene or toluene. The IR, ^{1}H NMR and ^{13}C NMR spectra of **2** were identified by comparison with those reported for *N,N'*-diphenylurea.[13,21]

FT-IR (KBr) 3324 (N-H); 1646 (C=O), cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 8.66 (s, N-*H*); 7.43-7.45 (d, 2 H, Ar-*H*); 7.24-7.29 (t, 2 H, Ar-*H*); 6.93-6.97 (t, 1 H, Ar-*H*); ^{13}C NMR (DMSO-d_6): δ 152.55 (C=O); Ar-C: 139.74, 128.77, 121.76, 118.14.

Acknowledgments.- We thank the College of Arts and Sciences, Oklahoma State University, for partial support. We gratefully acknowledge support by grant KC2-2288 of the U.S. Civilian R&D Foundation for the Independent States of the Former Soviet Union.

REFERENCES

1. K. D. M. Harris, *Chem. Soc. Revs.*, **26**, 279 (1997).
2. L. He, R. Zhuo, F. Cai, and A. Lu, *J. Nat. Sci.*, **3**, 126 (1998).
3. T. Karmkar, M. Mukherjee, and D. P. Chakraborty, *Curr. Sci.*, **55**, 828 (1986).
4. M. C. Mok, S. Kim, D. J. Armstrong, and D. W. S. Mok, *Proc. Nat. Acad. Sci. USA.*, **76**, 3880 (1979).
5. N. P. Tatarintsev, Russian Patent RU 2179804 (2002); *Chem. Abstr.*, **137**, *29031* (2002).

6. G. K. Goldwin and A. D. Webster, *J. Hort. Sci.*, **53**, 283 (1978).

7. M. G. Vigorita, R. Ficarra, P. Ficarra, and A. Tommassini, *Bollettino Chimico Farmaceutico*, **120**, 278 (1981); *Chem. Abstr.*, **96**, 6135 (1982).

8. V. N. Serova, O. A. Cherkasova, E. N. Cherezova, N. A. Mukmeneva, and V. P. Arkhireev, *Russian Polymer News*, **6**, 1 (2001); *Chem. Abstr.*, **136**, 217556 (2002).

9. Y. Maekawa, T. Miwa, Y. Okabe, G. Rames-Langlade, and T. Ueno, *Macromolecules*, **33**, 6794 (2000).

10. M. A. Reid, A. Ferrante, D. Hunter, and W. P. Hackett, USA. PCT Int. Appl. January 24, 2002, 14pp. WO 0205638; *Chem Abstr.*, **136**, 130223 (2002).

11. J. L. J. Blanco, C. S. Barria, J. M. Benito, C. O. Mellet, J. Fuentes, F. S. Gonzalez, and J. M. G. Fenandez, *Synthesis*, **11**, 1907 (1999).

12. J. Chen, D. Shi, W. Chai, J. Chen, w. Chen, and T. Kao, *Chin. Chem. Lett.*, **4**, 943 (1993); *Chem. Abstr.*, **120**, 297633 (1994).

13. J. Pihuleac and L. Bauer, *Synthesis*, **1**, 61 (1989).

14. A. Flamini, A. M. Giuliani and N. Poli, *Tetrahedron Lett.*, **28**, 2169 (1987).

15. G. Süss-Fink and G. Herrmann, *Angew. Chem., Intern. Ed.* **25**, 570 (1986).

16. F. B. Fulton and J. Warkentin, *Can. J. Chem.*, **65**, 1177 (1987).

17. a) I. S. Blagbrough, N. E. Mackenzie, C. Ortiz, and A. I. Scott, *Tetrahedron Lett.*, **27**, 1251 (1986). b) N. E. Mackenzie, J. P. G. Malthouse, and A. I. Scott, *Biochem. J.*, **226**, 601 (1985).

18. M. M. Mojtahedi, M. R. Saidi, and M. Bolourtchian, *J. Chem. Res. (S)*, **12**, 710 (1999).

19. It is evident that the glassware and/or solvents and/or nitrogen contained sufficient water to allow for the conversion to the urea or that an intermediate may be converted to the urea during the aqueous wash of the reaction mixture.

20. L. Bretherick, "*Hazards in the Chemical Laboratory*", p. 120, The Royal Society of Chemistry, London, Chapter 7, 1981.

21. The IR, ^{1}H NMR, and ^{13}C NMR spectra of the *N,N'*-diphenylurea obtained were identical to those from the National Institute of Materials and Chemical Research, Japan, at www.aist.go.jp and those in *The Aldrich Library of ^{1}H NMR and ^{13}C NMR Spectra*, Vol. 2, p. 1418, Aldrich Chemical Company, Milwaukee, WI, 1993.

****