

Notes

A Simple, Convenient, and Efficient Method for the Synthesis of Isocyanates from Urethanes

V. L. K. Valli and H. Alper*

Department of Chemistry, University of Ottawa,
10 Marie Curie, Ottawa, Ontario, Canada K1N 6N5

Received May 12, 1994

There has been significant interest in the manufacture of isocyanates due to their commercial value as precursors to polyurethane elastomers, agrochemicals, adhesives, and reaction injection mouldings (RIM),¹ among other applications. The elimination of alcohol from a urethane² constitutes a simple approach to isocyanates. The patent literature is considerable on this subject,^{3,4} and the most widely used methods include thermal decomposition reactions with excess powdered boron or bismuth,^{3k} and germanium oxide,^{3g} effected at high temperatures (greater than 300 °C). Using these stringent conditions, decomposition of the substrate or product can occur, resulting in poor yields of isocyanates. Hence, the development of a mild, efficient procedure for the dealcoholysis of urethanes (eq 1) would provide a superior approach, compared with existing methodologies, in the synthesis of polyurethanes.



The isolation of an isocyanate from urethane is complicated by the tendency of formed isocyanate (RNCO) and alcohol (R¹OH) to recombine easily as shown in the equilibrium reaction (eq 1). The absence of a reverse addition results in easy isolation of an isocyanate. We wish to report the use of chlorocatecholborane as a reagent for the interception of the components of the

Table 1. Conversion of Urethanes to Isocyanates

Entry	Substrate	Product ^a	ν_{CO} (cm ⁻¹)	Yield (%)
1			2273	99
2			2273	100
3			2274	100 ^c
4			2268	100
5			2266	100
6			2264	98
7			2264	100
8			2266	99
9			2261	98
10			2272	96
11			2274	100
12			2271	100 ^e
13			2255	96
14			2258	97
15			2259	96

(1) (a) George, W. *The ICI Polyurethanes Book*, Ed 2, 1990, Published jointly by ICI and John Wiley & Sons, N.Y. (b) Moore, R.; Whelchel, W. C.; Russel, D. D. *Polyurethane World Congress 1991*, 863. (c) Seneker, S. D.; Rosthauser, J. W.; Markusch, P. H. *34th Annual Polyurethane Technical and Marketing Conference*, Oct 21st, 1992, p588. (d) Ozaki, S. *Chem. Rev.* 1972, 72, 464.

(2) Valli, V. L. K.; Alper, H. *J. Am. Chem. Soc.* 1993, 115, 3778.

(3) (a) Kumagai, Y.; Takano, T. Japanese Patent JP 01 135 753; *Chem. Abstr.* 1990, 112, 36703b. (b) Takano, T.; Kumagai, Y.; Iwata, K. Japanese Patent JP 01 113 358; *Chem. Abstr.* 1990, 112, 21453w. (c) Takano, T.; Kumagai, Y.; Iwata, K. Japanese Patent JP 01 121 259; *Chem. Abstr.* 1989, 111, 195580e. (d) Takano, T.; Kumagai, Y.; Iwata, K. Japanese Patent JP 63 150 255; *Chem. Abstr.* 1989, 110, 58270u. (e) Spohn, R. J. GB Pat. Appl. GB 2 113 673; *Chem. Abstr.* 1984, 100, 7361k. (f) Spohn, R. J. Ger. Pat. DE 3 204 973; *Chem. Abstr.* 1983, 99, 213033u. (g) Okuda, S. Japanese Patent JP 57 158 747; *Chem. Abstr.* 1983, 99, 105872h. (i) Okuda, S. Japanese Patent JP 57 159 751; *Chem. Abstr.* 1983, 98, 160402j. (k) Okuda, S. Japanese Patent JP 57 158 746; *Chem. Abstr.* 1983, 98, 144386b.

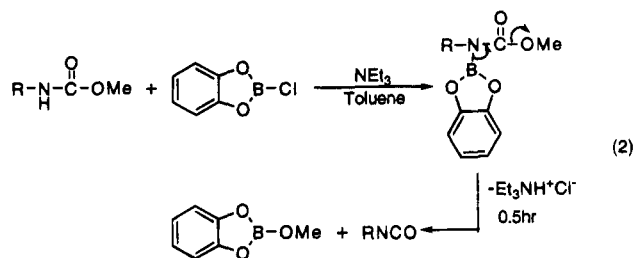
(4) (a) Fukuoka, S.; Aoki, T. Japanese Patent JP 60 237 058; *Chem. Abstr.* 1986, 104, 207855u. (b) Henson, T. R.; Timberlake, J. F. U.S. Pat. 4 294 774; *Chem. Abstr.* 1982, 96, 7220n. (c) Merger, F.; Towae, F. Ger. Pat. 2 942 542; *Chem. Abstr.* 1981, 95, 63133c. (d) Merger, F.; Nestler, G.; Towae, F. Ger. Pat. 2 942 542; *Chem. Abstr.* 1981, 95, 62946h. (e) Merger, F.; Towae, F. Ger. Pat. 2 942 503; *Chem. Abstr.* 1981, 95, 25869p.

(5) Disteldorf, J.; Huebel, W.; Wolf, W. Ger. Pat. DE 3 151 855; *Chem. Abstr.* 1983, 99, 176959c.

^a Products were characterized by comparison of spectral data (IR, NMR, MS) and retention times (GC) with authentic materials in most cases. Isocyanates in entries 1–6, 9, 10, and 12 were commercially available. Isocyanates 7, 8,^{1b} and 11⁴ are known compounds. ^bYields were characterized by gas chromatography. ^c Isolated yield, 91%. ^d Dytek-A-diisocyanate. ^e Isolated yield 96%. ^f Jeffamine triisocyanate, x + y + z = 83. ^g Jeffamine D-400 diisocyanate, x = 5–6. ^h Jeffamine D-2000 diisocyanate, y = 33 avg.

alcohol from the urethane in the presence of triethylamine as a base (eq 2).

The entire sequence shown in eq 2 occurs rapidly in a one-pot reaction. For instance, refluxing *p*-tolylurethane with chlorocatecholborane and triethylamine in toluene for 10 min afforded *p*-tolyl isocyanate in 99% yield. The present transformation is simple and highly selective and



no side products such as amines were detected. The reaction can also be performed in other nonpolar solvents including pentane or benzene and is highly efficient in the case of other alkylurethanes. For example, *p*-tolylethylurethane is comparable in reactivity with *p*-tolylmethylurethane, affording 100% conversion to *p*-tolyl isocyanate. The generality of the method has been assessed using a variety of aromatic, aliphatic, and alicyclic urethanes. A series of mono- and diurethanes were subjected to dealcoholysis in the same manner as *p*-tolylmethylurethane to give the corresponding mono- and diisocyanates (Table 1). Industrially valuable diisocyanates were obtained in excellent yields, including toluene-2,4- and 2,6-diisocyanates (TDI), *p*-phenylene-diisocyanate (PPDI), Jeffamine D-400 and D-2000 diisocyanates, and Jeffamine T-5000 triisocyanate (Jeffamine: polymer with a "polypropyleneoxy" backbone).

Triethylamine is required to effect dehydrochlorination from the urethane and chlorocatecholborane. In fact, in the absence of triethylamine, the same reaction affords amines from urethanes instead of isocyanates as the primary product.⁶

In conclusion, isocyanates are formed in excellent yield when urethanes are treated with chlorocatecholborane and triethylamine.

Experimental Section

General Procedure for the Preparation of Isocyanates from Urethanes. The urethane (1 mmol) was dissolved in dry toluene (2 mL), triethylamine (1.2 mmol) was added, and the mixture was refluxed for 5 min (N_2 atmosphere). Chlorocatecholborane (1.2 mmol) was added and the mixture was refluxed for another 5 min. After the addition of chlorocatecholborane, an instantaneous reaction was observed and a white cloudy solid material appeared in the reaction flask (due to the formation of $Et_3NH^+Cl^-$). The reaction was monitored by infrared spectroscopy and gas chromatography. The product isocyanate was isolated by vacuum distillation under an N_2 atmosphere or derivatized as ureas using amines, or as other alkylurethanes by reaction with a different alcohol. In case of di- and triurethanes, correspondingly double and triple the amounts of chlorocatecholborane and triethylamine were used.

Acknowledgment. We are grateful to the Institute for Chemical Science and Technology, the University Research Incentive Fund, and the Natural Sciences and Engineering Research Council for support of this research. We thank duPont Canada for providing a sample of Dytek-A, Texaco for the sample of Jeffamine T-5000, and Dow Chemical Canada for the samples of Jeffamine D-400 and D-2000.

(6) Boeckman, R. K.; Potenza, J. C. *Tetrahedron Lett.* **1985**, 26, 1411.