Tetrahedron Letters,Vol.28,No.45,pp 5399-5402,1987 0040-4039/87 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

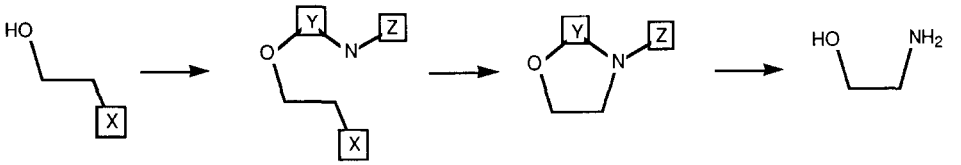
N-BENZOYLCARBAMATE CYCLIZATIONS

Spencer Knapp,* Paivi J. Kukkola, Shashi Sharma, and Sherrie Pietranico

Department of Chemistry, Rutgers The State University of New Jersey
New Brunswick, New Jersey 08903 USA

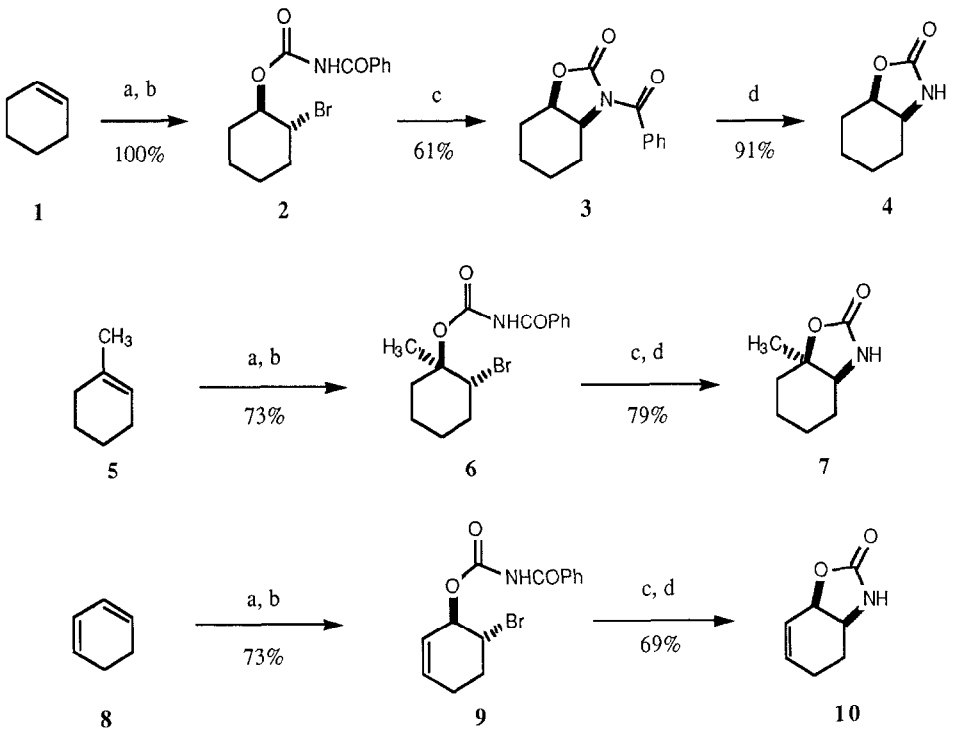
Summary: The anion of an alcohol derived N-benzoylcarbamate may be used to deliver nitrogen intramolecularly to electrophilic centers. This allows the stereocontrolled synthesis of a variety of amino-alcohol and amino-diol derivatives.

The device of intramolecular nitrogen delivery directed by a nearby hydroxyl group, shown schematically below, has been used for the synthesis of cis, vicinal amino-alcohols for a variety of connecting chains "Y", activating groups "Z", and leaving groups "X".[1] We suggest that the N-benzoylcarbamate derivative of an alcohol ("Y" = carbonyl, "Z" = benzoyl) shows several advantages in this role, and we offer some examples of its use for stereoselective synthesis of amino-alcohols from bromohydrins, diols, and epoxy-alcohols.



Alcohols, even hindered ones, are rapidly converted to their N-benzoylcarbamate derivatives by reaction with benzoylisocyanate[2] in carbon tetrachloride solution in the absence of a basic catalyst. Thus the bromohydrins[3] derived from cyclohexene (**1**), methylcyclohexene (**5**), and 1,3-cyclohexadiene (**8**) formed the N-benzoylcarbamate derivatives **2**, **6**, and **9**, respectively, in good yields without complications due to epoxide formation or solvolytic side reactions (Scheme 1). Cyclization of these three compounds to the cis-fused N-benzoyl-oxazolidinones, e. g. **3**, occurred upon treatment with NaH in THF. Base treatment readily removed the benzoyl groups, giving the oxazolidinones **4**,[4] **7**, and **10**. Of course, stronger base treatment can lead directly to the free amino-alcohol when this is desired. This four step sequence applied to an alkene constitutes an overall cis-oxyamination procedure, complete with all the benefits (face selectivity, site selectivity) that normally attend bromohydrin formation.

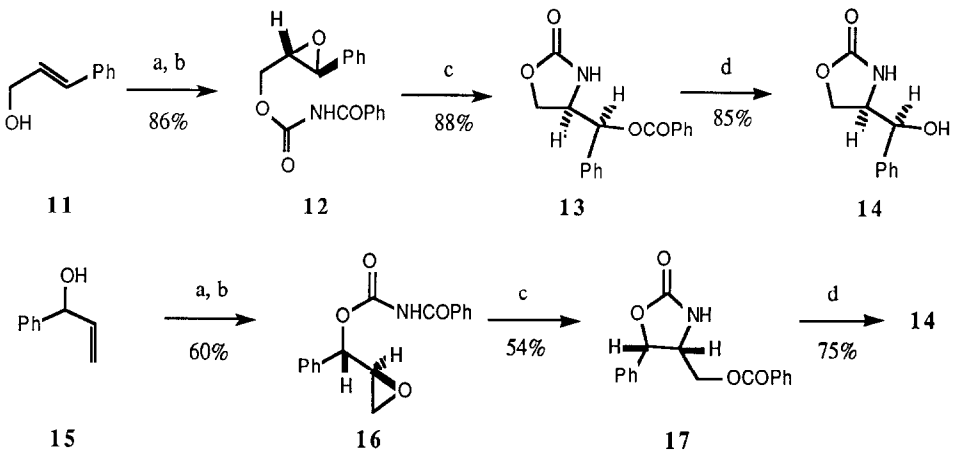
Scheme 1.



Reagents: (a) NBS, H_2O, 0^o to 25^o; (b) PhCONCO, CCl_4, 25^o; (c) NaH (1.25 equiv), THF, reflux; (d) LiOH, H_2O, THF, 25^o.

A similar sequence applied to the synthesis of amino-diols is shown in Scheme 2. Conversion of cinnamyl alcohol **11** to its N-benzoylcarbamate derivative followed by epoxidation gave **12**. Cyclization was induced by treatment with a fraction of an equivalent of NaH, leading to the oxazolidinone **13**, whose benzoyl has migrated from N to O. Removal of the benzoyl group as before gave the protected amino-diol **14**. The same sequence applied to phenylvinylcarbinol (**15**) also gave **14**, but by a different path. Epoxidation of the N-benzoylcarbamate derivative of **15** was selective (2:1) for the *threo* product **16**. Cyclization of **16** was accompanied by N to O benzoyl migration (despite steric interaction of the phenyl ring with the newly formed oxidomethyl group) but no rearrangement to **13** occurred. Hydrolytic removal of the benzoyl group of **17**, however, caused rearrangement of the *cis* , disubstituted oxazolidinone to the monosubstituted oxazolidinone **14**.

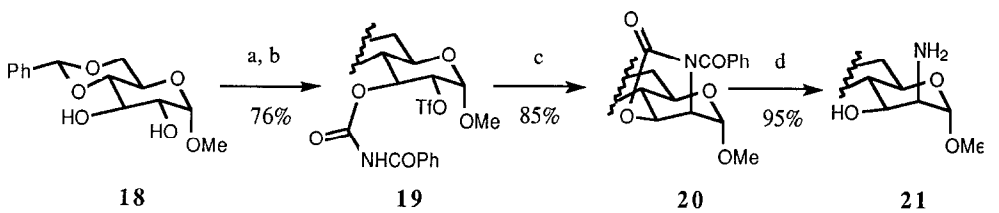
Scheme 2.



Reagents: (a) PhCONCO, CCl_4, 25°C; (b) mCPBA, CH_2Cl_2, 25°C; (c) NaH (0.25 equiv), THF, reflux; (d) LiOH, H_2O, THF, 25°C.

Finally, the use of an alcohol derived triflate as the leaving group "X" is illustrated by the conversion of glucose derivative **18** to the corresponding methyl 2-amino-2-deoxy-mannopyranoside **21**,[5] a sugar to aminosugar transformation[6] (Scheme 3).[7]

Scheme 3.



Reagents: (a) Tf_2O, pyr, CH_2Cl_2, -78° to 0°; (b) PhCONCO, CH_2Cl_2, 25°; (c) NaH (1.25 equiv), THF, 0°; (d) NaOH, H_2O, reflux.

Acknowledgments: We are grateful to the Charles and Johanna Busch Memorial Fund for financial support of this work, and to Dr. Dinesh V. Patel for helpful discussions. The 400 MHz NMR spectrometer was purchased with partial support from NSF Grant CHEM-8300444.

References and Notes

1. Recent examples: (halonium) Knapp, S.; Lal, G. S.; Sahai, D. *J. Org. Chem.* **1986**, *51*, 380. Knapp, S.; Patel, D. V. *Ibid.* **1984**, *49*, 5072. Knapp, S.; Patel, D. V. *J. Amer. Chem. Soc.* **1983**, *105*, 6985. Cardillo, G.; Orena, M.; Sandri, S.; Tomasini, C. *Tetrahedron* **1986**, *42*, 917. Bongini, A.; Cardillo, G.; Orena, M.; Sandri, S.; Tomasini, C. *J. Chem. Soc., Perk. I* **1986**, 1339, 1345. Bongini, A.; Cardillo, G.; Orena, M.; Sandri, S.; Tomasini, C. *J. Chem. Soc., Perk. I* **1985**, 935. Cardillo, G.; Orena, M.; Sandri, S.; Tomasini, C. *J. Org. Chem.* **1984**, *49*, 3951. Bongini, A.; Cardillo, G.; Orena, M.; Sandri, S.; Tomasini, C. *Tetrahedron* **1983**, *39*, 3801. Cardillo, G.; Orena, M.; Porzi, G.; Sandri, S. *J. Chem. Soc., Chem. Commun.* **1982**, 1308. Fraser-Reid, B.; Pauls, H. W. *J. Org. Chem.* **1983**, *48*, 1392. Fraser-Reid, B.; Pauls, H. W. *J. Chem. Soc., Chem. Commun.* **1983**, 1031. Hirama, M.; Iwashita, M.; Yamazaki, Y.; Ito, S. *Tetrahedron Lett.* **1984**, *25*, 4963. Sammes, P. G.; Thetford, D. *Ibid.*, **1986**, *27*, 2275. (epoxides) Minami, N.; Ko, S. S.; Kishi, Y. *J. Amer. Chem. Soc.* **1982**, *104*, 1109. Julina, R.; Herzig, T.; Bernet, B.; Vasella, A. *Helv. Chim. Acta* **1986**, *69*, 368. Bernet, B.; Vasella, A. *Tetrahedron Lett.* **1983**, *24*, 5491. Roush, W. R.; Adam, M. A. *J. Org. Chem.* **1985**, *50*, 3752. Roush, W. R.; Brown, R. J. *Ibid.* **1982**, *47*, 1371. Schubert, J.; Schwesinger, R.; Knothe, L.; Prinzbach, H. *Liebigs Ann. Chem.* **1986**, 2009. (mercuronium) Harding, K. E.; Stephens, R.; Hollingsworth, D. R. *Tetrahedron Lett.* **1984**, *25*, 4631. Guiliano, R. M.; Deisenroth, T. W.; Frank, W. C. *J. Org. Chem.* **1986**, *51*, 2304. (conjugate) Hirama, M.; Nishizaki, I.; Shigemoto, T.; Ito, S. *J. Chem. Soc., Chem. Commun.* **1986**, 393. Hirama, M.; Shigemoto, T.; Yamazaki, Y.; Ito, S. *Tetrahedron Lett.* **1985**, *26*, 4133. Hirama, M.; Shigemoto, T.; Ito, S. *Ibid.* **1985**, *26*, 4137. Hirama, M.; Shigemoto, T.; Yamazaki, Y.; Ito, S. *J. Amer. Chem. Soc.* **1985**, *107*, 1797. (palladium) Trost, B. M.; Sudhakar, A. R. *J. Amer. Chem. Soc.* **1987**, *109*, 3792.

2. A solution of benzoylisocyanate was conveniently prepared by heating a mixture of benzoyl chloride, silver cyanate, and carbon tetrachloride at reflux for 12 h. The solution was cooled, filtered, and added to a solution of the alcohol as needed. Speziale, A. J.; Smith, L. R. *J. Org. Chem.* **1962**, *27*, 3742. McGrew, L. A.; Sweeny, W.; Campbell, T. W.; Foldi, V.S. *Ibid.* **1964**, *29*, 3002. Gilman, H.; Hofferth, B.; Melvin, H. W. *J. Amer. Chem. Soc.* **1950**, *72*, 3045.

3. Dalton, D. R.; Dutta, V. P.; Jones, D. C. *J. Amer. Chem. Soc.* **1968**, *90*, 5498. Sisti, A. J. *J. Org. Chem.* **1970**, *35*, 2670.

4. Compound **4**: mp 57-58°, lit. 54-55°. Herweh, J. E.; Foglia. T. A.; Swern, D. *J. Org. Chem.* **1968**, *33*, 4029.

5. Compound **21**: mp 121-122°, $[\alpha]_D$ +42° (c 0.4, $CHCl_3$); lit. mp 109-110°, $[\alpha]_D$ +40° (c 0.79, $CHCl_3$). Bukhari, S. T. K.; Guthrie, R. D.; Scott, A. I.; Wrixon, A. D. *Tetrahedron* **1970**, *26*, 3653.

6. Barton, D. H. R.; Motherwell, W. B. *J. Chem. Soc., Perk. I* **1980**, 1124. Cerny. I.; Trnka, T.; Cerny, M. *Coll. Czech. Chem. Commun.* **1983**, *48*, 2386.

7. Characterization of new compounds (mp, selected IR in cm^{-1}): **2**, 127-128°, 3260, 1760, 1680; **3**, 115-116°, 1780, 1675; **6**, 103-105°, 3260, 1750, 1690; **7**, 50-51°, 3275, 1750; **9**, 121-123°, 3250, 1760, 1690; **10**, 86-88°, 3250, 1750; **12**, 110-111°, 3260, 1760, 1700; **13**, 54-56°, 3260, 1750, 1730; **14**, 140-142°, 3370, 1795, 1715; **16**, 123-124°, 3260, 1760, 1700; **17**, 158-160°, 3200, 1745, 1720; **19**, 157-159° (dec), 3300, 1780, 1690; **20**, 111-113°, 1790, 1690. The structure assignments are all consistent with 400 or 200 MHz NMR spectra. Yields shown are isolated yields of pure compounds following chromatography or crystallization.

(Received in USA 20 July 1987)