very weak absorption (0 within our sensitivity) is observed. As expected, the *S*-(+) enantiomer yielded a mirror image reflected spectrum. The same sign CD band is observed in hexane and perfluoro-*n*-hexane solutions. This band obeys Beer–Lambert's rule, thus eliminating the possibility that hydrogen-bonded dimers are responsible for this band. This transition undergoes a small blue shift in solution where the peak is shifted from 251 nm in the gas phase to 246 nm in hexane solution. A similar blue shift, although somewhat larger, is obtained for the $n \rightarrow 3s$ Rydberg transition.

These observations lead us to believe that an excited state at an energy lower than the $n \rightarrow 3s$ is responsible for the observed signal. We believe this band to be the triplet component of the $n \rightarrow 3s$ Rydberg transition (whose singlet maximum is detected at 212 nm in the gas phase) for the following three reasons. Firstly, as we have already noted, this band precedes all the singlet states of the molecule. Secondly, the upper limit for the molar extinction coefficient of this transition is estimated as 0.2; singlet states, even forbidden, will have higher $\epsilon$ values through various borrowing mechanisms. Finally, the singlet–triplet energy splitting of 2-aminobutane is similar to that of ammonia and methylamine. The singlet–triplet splitting for the latter two compounds was determined[11] from the energy differences of the onset of the two transitions. It was found as 0.39 ± 0.1 eV for ammonia and 0.34 + 0.1 eV for methylamine. Taking the onset for the triplet at 262 nm and for the singlet at 247.5 nm yields a splitting of 0.28 eV for 2-aminobutane. The negative signal observed for this new state might also explain the negative optical rotation as expressed by the $[\alpha]_D$, since the $[\alpha]_D$ sign is associated with the CD sign of the first excited state. Whenever there is a mismatch between the sign of the $[\alpha]_D$ and the CD sign of the first excited state, higher excited states are then invoked to explain this mismatch. It is possible that in many cases triplets might be the explanation.

**Acknowledgment**. We thank D. Amar for helping with our measurements with the JASCO instrument.

---

[11] Abuain, T.; Walken, I. C.; Dance, D. F. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 641.

---

## New Chiral Auxiliaries for Thermal Cycloadditions

Dennis P. Curran,*[1] Kyu-Sung Jeong,[2] Timothy A. Heffner, and Julius Rebek, Jr.*[2]

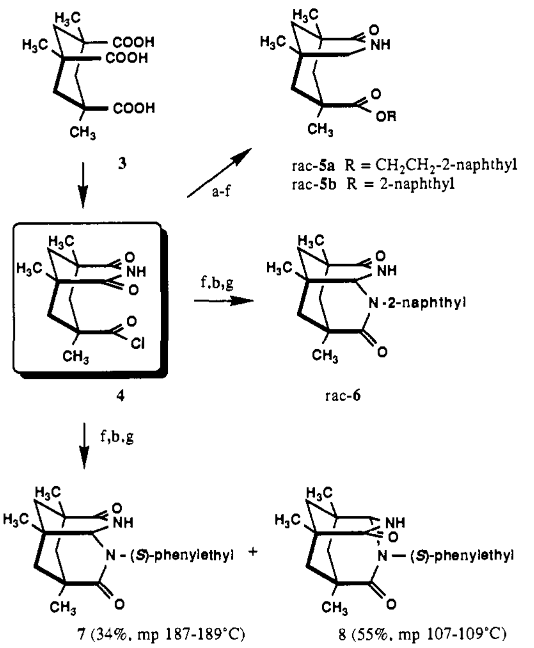
*Department of Chemistry, University of Pittsburgh*
*Pittsburgh, Pennsylvania 15260*

*Received July 6, 1989*

Although there are now several chiral acrylate derivatives that provide exceptionally high levels of asymmetric induction in Lewis acid promoted Diels–Alder reactions,[3] achieving these high levels of induction without the aid of a Lewis acid is often much more difficult. Because many important transformations are not subject to Lewis acid promotion, the development of new chiral auxiliaries that permit high levels of asymmetric induction in thermal addition and cycloaddition reactions of alkenes is an important goal.[3b,d]

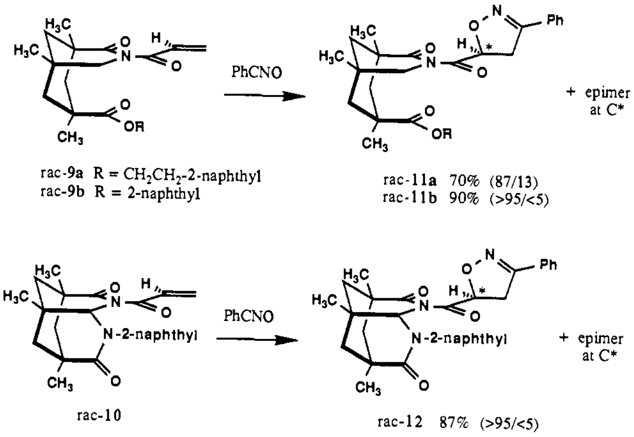
Cycloaddition reactions of nitrile oxides provide a challenge for the development of new chiral auxiliaries ($X_c$) because the interaction between the incoming nitrile oxide and the auxiliary is at a bare minimum: the forming ring in the transition state[4] is roughly planar, and the two atoms nearest the auxiliary (O and N) bear no substituents while the most remote atom (C) bears a lone substituent that projects away from the chiral auxiliary (see Figure 1).[5] Any chiral auxiliary that exhibits high asymmetric induction in a nitrile oxide cycloaddition might be generally useful for other thermal addition and cycloaddition reactions as well. Among the many auxiliaries that have been surveyed,[6] only

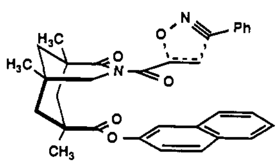
Scheme I[a]



[a] Steps: (a) MeOH; (b) NaBH$_4$, EtOH; (c) Et$_3$SiH, TFA; (d) NaOH; (e) SOCl$_2$; (f) ROH or RNH$_2$; (g) pTsOH, CH$_2$Cl$_2$.

Scheme II





transition state model for 9b

---

[1] Dreyfus Teacher-Scholar, 1985–1989; Recipient of a National Institutes of Health Career Development Award, 1987–1992.

[2] Current address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

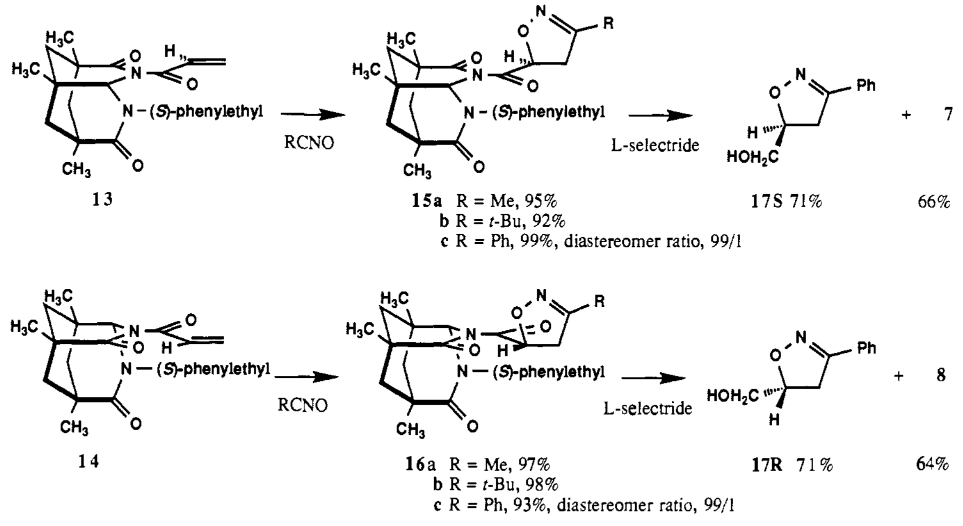
[3] Leading references: (a) Paquette, L. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, pp 456–478. (b) Helmchen, G.; Karge, R.; Weetman, J. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer-Verlag: Berlin, 1986; Vol. 4, pp 262–306. (c) Loncharich, R. J.; Schwartz, T. R.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 14. (d) Davies, S. G. *Chem. Br.* **1989**, *25*, 268. See also ref 6 and 8.

[4] Houk, K. N.; Duh, H.-Y.; Wu, Y.-D.; Moses, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 2754.

[5] Indeed, it is a characteristic of nitrile oxide cycloadditions to chiral acrylates that the degree of asymmetric induction does not depend on the nitrile oxide substituent. See ref 6 and 8.

[6] Recent examples and leading references: (a) Curran, D. P.; Kim, B. H.; Piyasena, H. P.; Loncharich, R. J.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 2137. (b) Olsson, T.; Stern, K.; Sundell, S. *J. Org. Chem.* **1988**, *53*, 2468.

Scheme III



13

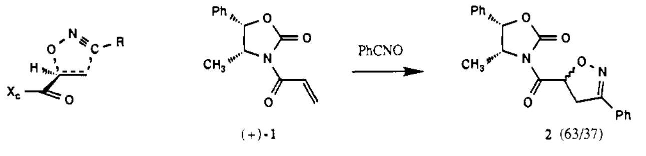
15a R = Me, 95%
b R = *t*-Bu, 92%
c R = Ph, 99%, diastereomer ratio, 99/1

17S 71% 66%

14

16a R = Me, 97%
b R = *t*-Bu, 98%
c R = Ph, 93%, diastereomer ratio, 99/1

17R 71% 64%



Transition state for an asymmetric nitrile oxide cycloaddition

*Evans' chiral imides:* the substituents are too far removed from the incoming nitrile oxide

**Figure 1.**

Oppolzer's chiral sultam[7] has shown consistently useful levels of asymmetric induction (typically 89/11 ± 3).[8] For example, Evans has shown that acrylimides like **1** are outstanding chiral auxiliaries for Lewis acid promoted Diels–Alder reactions,[9] yet we have found that cycloaddition of **1** with benzonitrile oxide gave a disappointing 63/37 ratio of diastereomeric cycloadducts **2** (stereostructures not determined). We contended that this poor selectivity was due not to insufficient conformer control[10] but to insufficient face shielding of the alkene by the chiral auxiliary. We now report that a new generation of chiral acrylimide derivatives with improved face-shielding capability provides heretofore unattainable levels of asymmetric induction in nitrile oxide cycloadditions.

The molecular skeleton of the new auxiliaries is derived from the commercially available Kemp[11] triacid **3**. Because full details will be published elsewhere,[12] the preparation of the auxiliaries is summarized very briefly in Scheme I. The imide acid chloride **4**[13] readily acylates amines or alcohols. Following standard reductive protocols, three racemic (*rac*-**5a**, *rac*-**5b**, and *rac*-**6**) and two optically active (**7** and **8**) auxiliaries were prepared. Acylation of the auxiliaries with acryloyl chloride[9b] typically occurred in 40–60% yield.

Cycloadditions of *rac*-**9a**, *rac*-**9b**, and *rac*-**10** with benzonitrile oxide were carried out by a standard procedure,[14] and in all cases, $\Delta^2$-isoxazolines were formed in excellent yields. The isolated yield of the major diastereomer (*rac*-**11a**, *rac*-**11b**, or *rac*-**12**) for each experiment is reported in Scheme II. While *rac*-**9a** provided only modest asymmetric induction (but still comparable to the best currently available levels), we were pleased to discover that *rac*-**9b** and *rac*-**10** provided unprecedented levels of diastereoselectivity. For the first time in our experience, the presence of a minor diastereomeric cycloadduct was not immediately obvious from inspection of the crude NMR spectrum.[15] A single-crystal X-ray diffraction structure of *rac*-**11b** proved that the expected diastereomer was produced in the cycloaddition (see transition-state model in Scheme II), and the relative stereostructures of *rac*-**11** and *rac*-**12** were assigned by analogy.

The results with the optically active chiral auxiliaries are summarized in Scheme III. Although acrylimides **13** and **14** are diastereomers (both contain an (*S*)-phenylethylamine subunit), they behave almost as if they are enantiomers. After cycloadditions with ethanenitrile oxide, 2,2-dimethylpropionitrile oxide, and benzonitrile oxide, pure diastereomeric cycloadducts **15a–c** and **16a–c** were isolated in 92–99% yields. In each cycloaddition, the degree of asymmetric induction was sufficiently high that the quantity of the minor diastereomer was difficult to determine by spectroscopic examination of the crude reaction mixture. However, the preparation of authentic samples of the expected minor diastereomers[16] allowed accurate quantitation (by HPLC analysis) for the benzonitrile oxide cycloadducts (**15c** and **16c**). In each case, about 1% of the minor diastereomeric cycloadduct (not shown) was formed when the cycloaddition was conducted at 25 °C.[17] To complete one cycle of the chiral auxiliary, **15c** and **16c** were cleaved by a standard procedure[7] with L-Selectride (Aldrich), to give optically pure 5-(hydroxymethyl)-$\Delta^2$-isoxazolines **17S** and **17R**, respectively. Each was readily separated from the intact bis(lactam) **7** or **8** by flash chromatography.

Optically pure 5-(hydroxymethyl)-$\Delta^2$-isoxazolines are important compounds because they are precursors for a variety of classes

---

[7] Oppolzer, W. *Tetrahedron* **1987**, *43*, 1969. The original printing of this excellent review contains printer errors. A version is reprinted in the Errata section of *Tetrahedron* **1987**, *43*(18).

[8] Curran, D. P.; Kim, B. H.; Daugherty, J.; Heffner, T. A. *Tetrahedron Lett.* **1988**, *29*, 3555. Curran, D. P.; Heffner, T. A., manuscript in preparation.

[9] (a) Evans, D. A. In *Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research, Vol. 27. Stereospecificity in Chemistry and Biology*; Robert A. Welch Foundation: Houston, 1984; pp 13–49. (b) Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238.

[10] Nonbonded interactions between the amide substituent and the *β*-acryloyl carbon prohibit s-trans rotamers of **1** while C–N rotamers are disfavored by the alignment of the dipoles of the two carbonyls. See ref 9a.

[11] Kemp, D. S.; Petrakis, K. S. *J. Org. Chem.* **1981**, *46*, 5140. Available from Aldrich Chemical Company.

[12] Jeong, K. S.; Paris, K.; Ballester, P.; Rebek, J., Jr., full paper in preparation.

[13] Askew, B.; Ballester, P.; Buhr, C.; Jeong, K. S.; Jones, S.; Paris, K.; Williams, K.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 1082.

[14] All cycloadditions were conducted at 25 °C. Triethylamine (0.055 mmol) was added to a solution of the chiral acrylate (0.050 mmol) and the hydroximic acid chloride (0.055 mmol) in ether (4 mL). After 16 h, the mixture was filtered and the crude product (obtained by evaporation) was purified by flash chromatography.

[15] Authentic samples of the minor diastereomeric cycloadducts were not available to permit an accurate estimate of the diastereomer ratio. We estimate that as much as (but not more than) 1–3% of a minor diastereomeric cycloadduct could have been present.

[16] Authentic mixtures of diastereomers were prepared by coupling racemic 3-phenyl-5-(chloroformyl)-$\Delta^2$-isoxazoline with optically pure **7** or **8**. The diastereomers exhibited characteristically different NMR resonances and were readily separated.

[17] In all cases, small resonances that we tentatively assigned to the minor diastereomers (the assignments were rigorous for **15c** and **16c**) were observed in the crude $^1$H NMR spectra. These resonances consistently integrated to 1–2% of the corresponding resonances of the major product in all six cycloadditions.

J. Am. Chem. Soc. **1989**, *111*, 9240-9241

of oxygenated organic molecules.[18] Thus, the new chiral imides **13** and **14** have immediate preparative value. Further studies will determine whether these auxiliaries will be generally useful for other types of thermal additions and cycloadditions. At present, we know that they show exceptional selectivity in asymmetric alkylations.[12] Lastly, we note that imides **7** and **8** possess an N-H bond in an asymmetric microenvironment, and preliminary studies on asymmetric protonations are very encouraging.[19]

**Acknowledgment.** We thank the Hoechst-Celanese Company for partial funding of this work.

**Supplementary Material Available:** Full details of the crystal structure of **11b**, procedures for the preparation of **13** and **14**, and tables giving spectroscopic characterization of all new compounds (18 pages). Ordering information is given on any current masthead page.

---

[18] (a) Curran, D. P. *Advances in Cycloaddition*; JAI: Greenwich, CT, 1988; pp 129-189. (b) Curran, D. P.; Heffner, T. A., manuscript in preparation.

[19] Rebek, J. R., Jr. *Angew. Chem., Int. Ed. Engl.*, in press.

---

# The Transition from Molecules to Solids: Molecular Syntheses of $Ni_9Te_6(PEt_3)_8$, $Ni_{20}Te_{18}(PEt_3)_{12}$, and NiTe

J. G. Brennan, T. Siegrist, S. M. Stuczynski, and
M. L. Steigerwald*

*AT&T Bell Laboratories*
*Murray Hill, New Jersey 07974*

*Received August 17, 1989*

Molecular precursors offer some attractive practical advantages in the synthesis of solid-state compounds. The intimate mixing of the elements that comes with the use of precursors allows lower reaction temperatures than the traditional ceramic preparative route, which in turn should allow for the preparation of solid-state phases that are inaccessible to the ceramic method. In order to exploit the precursor method to its fullest, it is important to characterize as completely as possible reactions that take the molecular starting materials to solid-state products. One straightforward method is the interception and characterization of reaction intermediates.[1] In most cases it is expected that these chemical species will not only be intermediates in the sense of reaction coordinate diagrams but also intermediate in size, describable as either large molecules or small fragments of the bulk. In this view, the study of the isolated chemical intermediates will give insight into both the chemistry of formation of a bulk solid and the evolution of the size-dependent physical properties.[1]

Trialkylphosphine tellurides are useful as organometallic equivalents of elemental tellurium for the preparation of solid-state metal tellurides.[2] The initial indication of the utility of phosphine tellurides is their ability to reversibly deposit zerovalent tellurium[3] (eq 1). This is reminiscent of the ease with which bis(cyclooctadiene)nickel ($Ni(COD)_2$) thermally liberates zerovalent nickel (albeit irreversibly)[4] (eq 2). The similarity between eq 1 and 2 raises the question as to whether the combination of $R_3PTe$ and $Ni(COD)_2$ would result in the formation of the solid-state compound[5] NiTe (eq 3).

$$Et_3PTe \rightleftharpoons Te + Et_3P \tag{1}$$

$$Ni(COD)_2 \rightarrow Ni + 2COD \tag{2}$$

$$Ni(COD)_2 + Et_3PTe \rightarrow NiTe_x \tag{3}$$

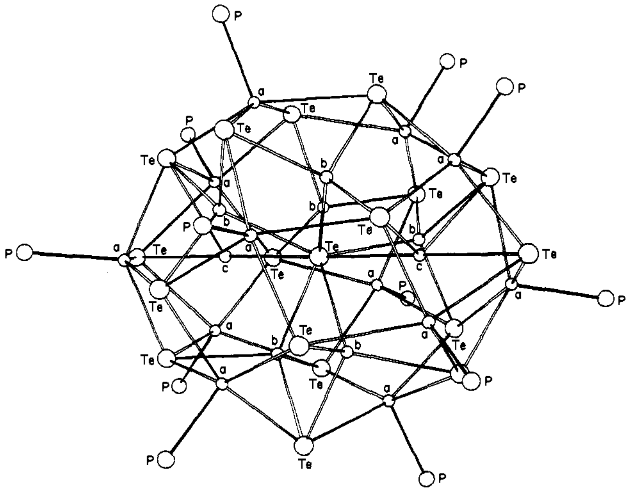


**Figure 1.** Structure of $Ni_{20}Te_{18}(PEt_3)_{12}$. The labels a, b, and c refer to $Ni_a$, $Ni_b$, and $Ni_c$, respectively. The ethyl groups are omitted for clarity. $Ni_a$ coordination is square-based pyramidal with Ni–Te distances between 2.55 and 2.69 Å and Ni–P distances approximately 2.2 Å. $Ni_b$ coordination is tetrahedral with Ni–Te distances between 2.45 and 2.64 Å. $Ni_c$ coordination is (very distorted) trigonal bipyramidal with two short (2.52–2.59 Å) and three long (2.8–2.9 Å) Ni–Te distances. The central Te–$Ni_c$–Te–$Ni_c$–Te array is almost exactly linear and contains the shorter Ni–Te bonds.

This communication describes the synthesis of the solid-state compound nickel telluride, NiTe, using these organometallic reagents as the sources of Ni and Te. In addition, we report the isolation and crystallographic characterization of two intermediates: the clusters $Ni_9Te_6(PEt_3)_8$ and $Ni_{20}Te_{18}(PEt_3)_{12}$.

$Ni(COD)_2$, $Et_3P$, and $Et_3PTe$ were combined in toluene at room temperature to give a black, optically very dense solution. This solution was homogeneous and quite stable at room temperature (see below), but when heated to reflux for several hours, the solution became colorless and polycrystalline nickel telluride precipitated in quantitative yield. Powder X-ray diffraction measurements confirm that polycrystalline NiTe was formed at low temperature. This should be compared to the ceramic route in which the elements are combined[5] at 400–600 °C for several days to several weeks.

It is clear from this experiment not only that NiTe can be made by using molecular equivalents of the zerovalent elements but also that Ni–Te bonds are formed quickly and that the intermediate Ni–Te complexes are stable at room temperature. Fenske and co-workers[6] have shown that a variety of nickel chalcogenide clusters are stable under similar conditions, so we set out to characterize the molecular species that formed initially in this reaction.

$Ni(COD)_2$, $Et_3PTe$, and $Et_3P$ were combined in toluene at room temperature in the relative molar ratio of 1:1:1, and a black, apparently homogeneous solution resulted. Pentane was added to this mixture, and large crystals of a black solid, **1**, grew during the next several days (yield: 26%). The structure of this compound, whose stoichiometry is $Ni_{20}Te_{18}(PEt_3)_{12}$, was determined crystallographically, and a drawing of that structure is shown in Figure 1.

The evaluation of the entire structure in terms of its constituent parts shows that there is a great deal of local symmetry. Covering the surface of the cluster molecule are the 12 phosphine ligands, each attached to a surface Ni atom ($Ni_a$ in Figure 1). Each of these Ni atoms is also bonded to four Te atoms such that each

---

[1] Brennan, J. G.; Siegrist, T.; Carroll, P. J.; Stuczynski, S. M.; Brus, L. E.; Steigerwald, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 4141.

[2] (a) Steigerwald, M. L.; Sprinkle, C. R. *Organometallics* **1988**, *7*, 245. (b) Steigerwald, M. L.; Rice, C. R. *J. Am. Chem. Soc.* **1988**, *110*, 4228. (c) Steigerwald, M. L. *Chem. Mater.* **1989**, *1*, 52.

[3] Zingaro, R. A.; Stevens, B. H.; Irgolic, K. *J. Organomet. Chem.* **1965**, *4*, 320.

[4] Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic Press: New York, 1974; Chapter 5.

[5] Barstad, J.; Gronvold, F.; Rose, E.; Vestersjo, E. *Acta Chem. Scand.* **1966**, *20*, 2865.

[6] (a) Fenske, D.; Basoglu, R.; Hachgenei, J.; Rogel, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 160. (b) Fenske, D.; Ohmer, J.; Hachgenei, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 522. (c) Fenske, D.; Ohmer, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 148. (d) Fenske, D.; Hollnagel, A.; Merzweiler, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 965. (e) Fenske, D.; Ohmer, J.; Hachgenei, J.; Mertzweiler, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1277.

0002-7863/89/1511-9240$01.50/0