benzylide was generated by using sodium amide, a predominance of diene product was observed.

In summary, reactions of a semistabilized arsonium ylide were studied. Deprotonation of allyltriphenylarsonium tetrafluoroborate with either LiHMDS or KHMDS, followed by treatment with aldehydes, results in virtually exclusive epoxide or olefin formation, respectively. This appears to be the first case where the choice of the counterion of the base used for arsonium allylide generation is solely responsible for the observed product selectivity.

Experimental Section

General Procedures. Reactions were carried out under an atmosphere of dry nitrogen. Tetrahydrofuran was freshly distilled from sodium and benzophenone. Hexamethyldisilazane was distilled from calcium hydride and stored over potassium hydroxide pellets. Potassium hydride (35% dispersion in oil) and *n*-butyllithium (solution in hexane) were purchased from Aldrich. Flash column chromatography was carried out by using the method of Still.[15] Chromatography of the epoxides was carried out by using silica gel columns loaded as a slurry in hexane/EtOAc/triethylamine (10:5:1) and flushed with hexane. Lithium hexamethyldisilazide (LiHMDS) and potassium hexamethyldisilazide (KHMDS) were generated immediately prior to use.

(*E*)-1-(2,6-Bis(methoxymethoxy)phenyl)-1,3-butadiene (3). Into a 250-mL round-bottomed flask was placed 1 (1.813 g, 4.18 mmol) in 50 mL of THF at −60 °C. To this was added KHMDS (7.58 mmol) in 10.0 mL of THF via cannula. The resulting orange solution was warmed to −50 °C over 45 min and then cooled down to −65 °C. Aldehyde 2 (0.999 g, 4.42 mmol) in 10.0 mL of THF was then added. The solution immediately became lighter in color and was allowed to warm to 25 °C over 3 h. The solution was stirred for 17 h at 25 °C and then quenched with 25 mL of H_2O. After removal of the solvent in vacuo, the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organics were dried through Na_2SO_4 and concentrated in vacuo to give a brown oil. Chromatography (hexanes/EtOAc, 9:1) of the crude product gave 3 (0.840 g, 76%) as a white solid: mp 53.0–54.0 °C; ^{1}H NMr (300 MHz, $CDCl_3$) δ 3.499 (6 H, s), 5.134 (1 H, d, J = 10.2 Hz), 5.226 (4 H, s), 5.290 (1 H, d, J = 17.8 Hz), 6.538 (1 H, dt, J = 10.2, 10.3, 16.8 Hz), 6.794 (2 H, d, J = 8.3 Hz), 6.889 (1 H, d, J = 16.1 Hz), 7.092 (1 H, t, J = 8.3 Hz), 7.233 (1 H, dd, J = 10.4, 16.1 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 56.2 (q), 95.1 (t), 108.9 (d), 116.3 (t), 117.0 (s), 124.1 (d), 128.1 (d), 134.4 (d), 139.5 (d), 156.2 (s) ppm; IR ($CHCl_3$) 3019 (m), 2976 (w), 2935 (w), 1592 (w), 1577 (w), 1471 (w), 1215 (s), 1153 (m), 1098 (w), 1082 (w), 1043 (s), 1011 (w), 923 (w), 770–758 (s), 669 (s) cm^{-1}; high-resolution MS calcd for $C_{14}H_{18}O_4$ 250.1205, found 250.1205. Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.17; H, 7.26. Found: C, 67.06; H, 7.17.

***trans*-2-(2,6-Bis(methoxymethoxy)phenyl)-3-vinyloxirane (4).** Into a 50-mL round-bottomed flask was placed 1 (0.280 g, 0.65 mmol) in 10 mL of THF at −60 °C. To this was added LiHMDS (0.71 mmol) in 2.0 mL of THF via cannula. The resulting orange solution was warmed to −55 °C over 45 min and then cooled down to −65 °C. Aldehyde 2 (0.1061 g, 0.47 mmol) in 1 mL of THF was then added. The solution immediately became lighter in color and was allowed to warm to 25 °C over 3 h. The solution was stirred for 24 h at 25 °C and then quenched with 5 mL of H_2O. After removal of the solvent in vacuo, the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organics were dried through Na_2SO_4 and concentrated in vacuo to give an orange oil. Chromatography (hexanes/EtOAc, 9:1) of the crude product gave 4 (0.101 g, 81%) as faint yellow crystals. Recrystallization from cold hexanes gave faint yellow crystals: mp 45.0–45.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.503 (6 H, s), 3.818 (1 H, dd, J = 2.4, 7.5 Hz), 3.917 (1 H, d, J = 2.4 Hz), 5.207 (4 H, s), 5.352 (1 H, d, J = 10.2 Hz), 5.577 (1 H, d, J = 17.2 Hz), 5.781 (1 H, ddd, J = 7.4, 10.2, 17.2 Hz), 6.781 (2 H, d, J = 8.4 Hz), 7.191 (1 H, t, J = 8.3 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 54.4 (d), 56.1 (q), 58.9 (d), 94.9 (t), 108.7 (d), 115.2 (s), 118.7 (t), 129.6 (d), 136.3 (d), 157.2 (s) ppm; IR ($CHCl_3$) 3019 (s), 2976 (w), 1600 (w), 1473 (w), 1215 (s), 1155 (w), 1044 (w), 927 (w), 770–756 (s), 669 (s) cm^{-1}; high-resolution MS calcd for $C_{14}H_{18}O_5$ 266.1154, found 266.1140. Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.14; H, 6.83. Found: C, 62.81; H, 6.82.

Acknowledgment. We are grateful to the National Institutes of Health (ES-02851) for the support of this work.

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Single-Pot Reductive Conversion of Amino Acids to Their Respective 2-Oxazolidinones Employing Trichloromethyl Chloroformate as the Acylating Agent: A Multigram Synthesis

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Received January 10, 1989

The emergence of the oxazolidinone ring system as the chiral auxiliary of choice in stereodifferentiating reactions owes its genesis principally to the pioneering work of the Evan's laboratory.[2] This amino acid based ring system has been so extensively exploited in recent years that it has been the subject of several reviews,[3,4] which all enumerate its capabilities in determining final product stereochemistry.

In continuing our research efforts in chiral Darzen's chemistry, wherein we utilized 2-oxazolidinones as our chiral auxiliary, we required large quantities of (4*S*)-4-phenyl-2-oxazolidinone (**5c**).[5] Existing synthesis methodologies for this very important class of compounds generally start with expensive optically active α-amino alcohols and use either diethyl carbonate or phosgene as the acylating agent. The Evan's diethyl carbonate procedure[2d] gave inconsistent results in our hands, and the alternative use of phosgene for large-scale preparations was not practical in this laboratory.

To circumvent using the expensive α-amino alcohol as a starting point, we simply needed to find efficient conditions for reducing α-amino acids. Our initial attempts at using the BF_3/borane methyl sulfide complex in refluxing THF as originally reported by Lane,[6] and later by

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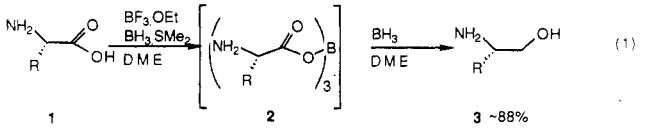
Table I. Synthesis of 2-Oxazolidinone Chiral Auxiliaries via Borane Methyl Sulfide Reduction of Trichloromethyl Chloroformate Amino Alcohol Acylation

compound 5	% yield[a]	$[\alpha]^{25}_D$, deg [lit. value]	mp, °C (lit. value)
a, $CH(CH_3)_2$	70	−16.65 (*c* 1.02, EtOH) [−16.6 (*c* 5.81, EtOH)[2d]]	70–71.5 (71.5)[16]
b, CH_2Ph	78	+4.38 (*c* 1.00, $CHCl_3$) [+14.8 (*c* 7.0, $CHCl_3$)[2e]]	
		−62 (*c* 1.00, $CHCl_3$)[b] [+4.9 (*c* 1.10, EtOH)[2f]]	85–87 (87–88.5)[2f]
c, Ph	80	+59 (*c* 1.00, $CHCl_3$)[b] [+49.5 (*c* 2.1, $CHCl_3$)[17]]	129.5–130 (132–133)[17]

[a] Isolated recrystallized yield. All three compounds gave satisfactory combustion analyses (±0.3%). [b] Chiral purity was checked directly on a Chiralcel OC HPLC column. The rotations for the 4*R* enantiomers of **5b** and **5c** are +64° (*c* 1.00, $CHCl_3$) and −57.7° (*c* 1.00, $CHCl_3$), respectively.

Evans[2d,f] and Gawley,[7] proved to be very dangerous on scales larger than 0.5–1.0 mol. The insidious induction periods followed by violent expulsions of solvent presented too great a hazard for use as a routine large-scale laboratory prep.

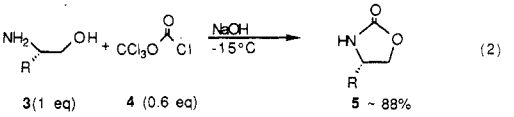
The mechanism of borane reduction of carboxylic acids has recently been delineated[8f] and was shown to involve principally a mono(acyloxy)borane. Such an (acyloxy)-borane is activated toward borane reduction to the alcohol but is probably accompanied in solution by bis- and tris-(acyloxy)boranes, both of which are also reducable, but at different rates. In any event, we surmised that if the rate of formation of these intermediates are faster than their subsequent reduction, one can expect a violent reaction (disproportionation or reduction) when a critical mass of this material has accumulated. We were able to minimize this problem simply by using the higher boiling solvent dimethoxyethane (DME)[9] to expedite the reduction step and by carefully regulating the rate of borane addition. The rate of this addition is crucial in that it has to be large enough to maintain a vigorous reflux but not so great as to result in an uncontrollable exotherm. We found a 1.0–2.5-h addition time at ≃2.5–6.0 mL/min to be sufficient on a 5-L scale for **1a–c** (Table I). The conditions reported herein have been shown to be reliable and the results reproducible up through 12-L size.



(1)

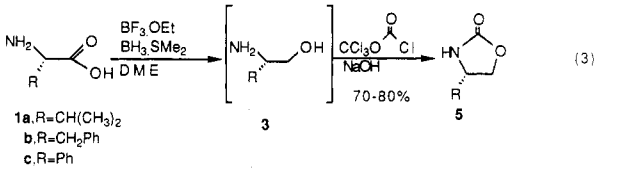
The acylation step was accomplished very nicely by using trichloromethyl chloroformate (TCF or "diphosgene")[10] as the acylating agent. Although TCF has been known since 1887 and has been used in the synthesis of carbonates,[11] isocyanates,[12b] diisocyanides,[13] *N*-carboxy anhydrides,[14] isocyanato acid chlorides,[12] and isocyanato chloroformates,[12b] we did not find where this reagent was used to prepare oxazolidinones from α-amino alcohols.

As shown in eq 2, with excess base, only about 0.5 equiv of TCF is required since both carbons of **4** are at the same oxidation level and are capable of being incorporated as the carbonyl carbon in **5**. Since base hydrolysis is required



(2)

in workup of step one, *we found it very expedient at this point to carry out the reduction and acylation (eq 1 and 2) in the same vessel without isolation of the intermediate amino alcohol (eq 3).* Isolated (recrystallized) overall yields of 2-oxazolidinones **5a–c** were generally excellent (70–80%) (Table I).



(3)

Evidence of racemization during these transformations has never been detected by us. Earlier studies on **5a** have already been devoted to that question and have shown the stereochemical integrity to remain intact.[15] Nevertheless, we determined the chiral purity of **5b** and **5c** by synthesizing their respective optical isomers from the parent *d*-amino acids and using a Chiracel OC HPLC column. We thus found >99% ee, indicating that racemization had not occurred.

This single-pot procedure for conversion of a chiral amino acid to its 2-oxazolidinone derivative without isolation of any intermediates will allow even further access to this valuable asymmetric tool. Furthermore, since both enantiomers of phenylalanine and phenylglycine are comparable in cost and readily available, one now has equal access to both optical isomers of their respective 2-oxazolidinone derivatives.

Experimental Section

Optical rotations were measured on a Perkin-Elmer 241 MC polarimeter. Melting points were measured on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Ethylene glycol dimethyl ether (DME) was stored over 4-Å molecular sieves prior to use. Borane methyl sulfide complex (10.0 M), boron trifluoride etherate, and DME were purchased from Aldrich Chemical Co. Trichloromethyl chloroformate was purchased in bulk quantities from Alfa.

Routine HPLC analyzes were performed on a Series 4 Perkin-Elmer gradient instrument with a Kratos GM 970 variable-wavelength detector using a Waters 19 mm (i.d.) × 2.5 cm μ-Bondapak reverse-phase C_{18} column. The mobile phase for **5c**

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was 10/90 acetonitrile/sodium perchlorate (0.10 M) adjusted to pH 2.5 with perchloric acid; flow rate 1 mL/min; λ = 211 nm. The above solvent ratio for **5b** was 20/80; flow rate 2 mL/min; λ = 211 nm.

Chiral HPLC determinations were done on a 0.46 cm (i.d.) × 2.5 cm Chiracel OC column from J. T. Baker Chemical Co. using hexanes/2-propanol (65/35) at 1 mL/min; λ = 211 nm.

General Procedure for Synthesis of 4-Substituted 2-Oxazolidinones from Their Respective Amino Acids. A 5-L, three-necked, round-bottomed flask was equipped with the following: a mechanical stirrer, a heating mantle, a claisen adapter containing a 500-mL addition funnel with a nitrogen inlet on top, and a take-off claisen adapter with thermometer and a "Therm-O-Watch"[18] attached. On top of the take-off claisen was a 16-cm flood trap, two 25-cm condensers connected in series, and a nitrogen outlet bubbler. The flask was swept with nitrogen and filled with 2.65 mol of the amino acid and 2.5 L of ethylene glycol dimethyl ether (DME) and warmed to ≃67 °C. The addition funnel was charged with 397 mL (3.23 mol) of boron trifluoride etherate and added to the flask at ≃67 °C over 1 h under nitrogen. After the addition, the yellow homogeneous solution was allowed to stir at 67 °C for an additional 1 h and the *nitrogen flow was stopped* to reduce the volume of out-flowing gases.

The reaction solution was then heated to a solution temperature of 80 °C at which time 424 mL (4.24 mol) of borane methyl sulfide complex (10.0 M) was added very carefully over a 1.0–2.5-h period (a 1.0-h addition time was satisfactory for only phenylglycine). The usual rate of addition was 2.5–6.0 mL/min. The reaction solution temperature has to be maintained within the 80–86 °C range. ***Note**: Caution has to be exercised when adding the borane methyl sulfide complex, especially for **5a** and **5b**. The rate of addition should be such that the first condenser shows a vigorous reflux and the solution temperature should never be allowed to drop much less than 80 °C with the flask being externally heated during the addition. A faster rate of addition than that recommended above will result in a lowering of the solution temperature, which may result in a violent expulsion of gases and solvent.* If such an exotherm occurs it may be controlled by stopping the addition and removing the nitrogen inlet to equalize the pressure within the reaction apparatus. The stirring may also be stopped if necessary. After the borane addition, the solution was heated under reflux for 4 h and then allowed to cool to ambient temperature. The reaction mixture was checked for starting material by HPLC for **5b** and **5c** or by TLC for **5a** (10 mL:10 mL:1 mL; chloroform–methanol–concentrated ammonium hydroxide with ninhydrin as detector, R_f = 0.31). If starting material is found to be present, add at ambient temperature 5–10% more borane methyl sulfide and heat the reaction solution to reflux 1 h more.

Methanol (400 mL) was added carefully to the reaction mixture initially at ambient temperature. The solution was then heated to a solution temperature of ≃85 °C. Solvent was removed via the take-off claisen until the reaction solution was half to one-third its original volume (1.5–2.0 L of solvent was removed). Aqueous NaOH (6 N, 1440 mL) was added to the hot (≃80 °C) reaction mixture, and the solution was heated to 85 °C for 0.5 h. The flask was cooled to ambient temperature, and 1 L of methylene chloride was added.[19] The flask was then cooled to −15 to −20 °C using a dry ice/acetonitrile bath. The addition funnel was charged with 193 mL (1.60 mol) of trichloromethyl chloroformate (TCF) in 250 mL of methylene chloride. This solution was added to the cooled reaction flask with stirring at a temperature not warmer than −10 °C and kept within a pH range of 9.0–11.0 by adding 50% NaOH simultaneously via the claisen adapter as needed (usually ≃205 mL). The addition of TCF was done over 1–1.5 h. After the addition, the reaction mixture was stirred for 1 h at ambient temperature where the final pH should be within the 9.25–9.5 range.

The contents of the reaction vessel were poured into a 12-L separatory funnel and 5-L of water was added. The bottom organic layer was removed, and the aqueous layer was washed with methylene chloride (3 × 1 L). The combined organic layer was washed with 1 L each of water and brine and then dried ($MgSO_4$). The dried solution was filtered and then concentrated under vacuum to near dryness. The crystalline mass was triturated with 400 mL of hexanes/ethyl acetate (4:1, v/v) cooled to ≃6 °C, treated with 400 mL more of hexanes, and allowed to stand overnight at ≃6 °C. The crystals were collected by filtration then recrystallized by dissolving in 0–4 L of methylene chloride, which was removed by distillation and replaced with about 500 mL of hexanes/ethyl acetate (4/1, v/v). The crystals that formed after standing overnight at ≃6 °C were collected by vacuum filtration and dried under vacuum.

Registry No. **1a**, 72-18-4; **1b**, 63-91-2; **1c**, 2935-35-5; **5a**, 17016-83-0; **5b**, 90719-32-7; **5c**, 99395-88-7; TCF, 503-38-8.

(18) Purchased from Instruments for Research and Industry (I^2R), Cheltenham, PA 19012.

(19) If desired, the amino alcohol may be isolated by methylene chloride extraction at this point.

Convenient Synthesis of Nickel [5,7,12,14,19,21,26,28-$^{13}C_8$]Phthalocyanine

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Received December 30, 1988

Metallophthalocyanines are convenient precursors for diverse low-dimensional electrical conductors. Recently we wished to prepare large quantities of nickel [5,7,12,14,19,21,26,28-$^{13}C_8$]phthalocyanine (**4**) with high isotopic enrichment. Previously macrocycle **4** had been prepared at five times natural abundance by the cyclization of 1,2-dicyanobenzene (**3**).[1] The partially labeled 1,2-dicyanobenzene (**3**) in turn was prepared from ^{13}C-enriched potassium cyanide through the use of copper(I) cyanide. However, we were reluctant to employ this methodology to achieve greater enrichment because of the high cost of 99% potassium [^{13}C]cyanide and low overall yield of the process. Herein we report an efficient method to prepare **4** using (arene)tricarbonylchromium chemistry.[2]

(1,2-Dichlorobenzene)tricarbonylchromium (**1**) was readily prepared from 1,2-dichlorobenzene and chromium hexacarbonyl.[3] The reaction of **1** with potassium [^{13}C]-cyanide and 18-crown-6[4] in DMSO solution smoothly provided the (1,2-di[^{13}C]cyanobenzene)tricarbonylchromium (**2**). This material was not isolated but was directly air-oxidized under photolytic conditions[5] to produce 1,2-di[^{13}C]cyanobenzene (**3**) (63%). The nucleophilic displacement reaction of **1** to produce **3** is notable on three counts. Firstly, excess cyanide is not required to ensure good conversion; the reaction is stoichiometric. Secondly, the yield in the reaction is easily reproducible. In our hands the conversion of 1,2-dihalobenzenes into phthalonitrile using copper(I) cyanide was capricious and depended critically on the copper reagent. Thirdly, the product **3** was not contaminated by 2-chlorobenzonitrile. Phthalonitrile prepared by using copper(I) cyanide fre-

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