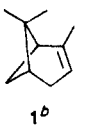
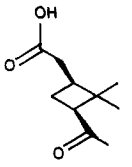
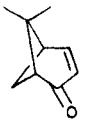
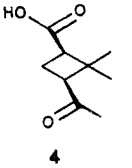
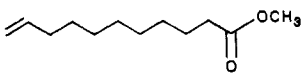
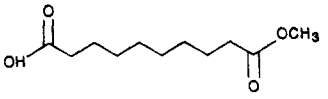
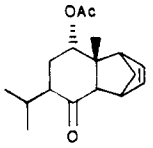
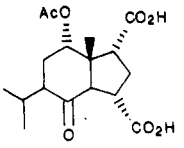
Table I. Carbon-Carbon Double Bond Cleavage by Silica Gel/$KMnO_4$

entry	compound	product	yield, %[a]
1	 1[b]	 2	84 (63)[c]
2	 3	 4	79
3	cyclohexene (5)	adipic acid (6)	74
4	cinnamyc acid (7)	benzoic acid (8)	73
5	cinnamyl acetate (9)	benzoic acid (8)	87
6	 10	 11	85
7	methyl oleate (12)	azelaic monomethyl acid (13) + nonanoic acid[d] (14)	79
8	 15	 16	62

[a] Yields refers to isolated product. [b] When optically active (+)-α-pinene was used the (+)-pinonic was obtained. [c] After column chromatography. [d] The two products were not separated; after extensive methylation with diazomethane, the mixture was analyzed by GC.

Experimental Section

General. ^1H NMR spectra were recorded on a Varian FT-80A or Perkin-Elmer Hitachi R-24A spectrometer. Mass spectra were obtained on a Hewlett-Packard 5995 GC-MS with a ionizing voltage of 70 eV. Optical rotations were obtained on a Bellinghan + Stanley polarimeter. Gas chomatographic analyses were performed on a CG-2527 or Varian-3700 instrument. Melting points were determined on a Kofler apparatus and are uncorrected.

Preparation of the Silica Gel/$KMnO_4$ Reagent. Silica gel (15 g) was added to a 6×10^{-2} M of aqueous potassium permanganate (375 mL), and the resulting slurry was evaporated in a rotary evaporator (70–80 °C) to give a free flowing solid.

Cleavage of Carbon–Carbon Double Bond: a Typical Procedure. Sebacic Acid Monomethyl Ester (11). To 15.0 g of silica gel supported $KMnO_4$ in a chromatographic column (25 mm i.d.) was added methyl undecenoate (**10**) (269 mg, 1.36 mmol) dissolved in benzene (80 mL). After all the solution was percolated, more solvent (30 mL) was added, and pressure was applied on top of the column. After evaporation of the solvent, 16 mg of the starting material was recovered. Then, water was added (150 mL) and eluted under pressure. The aqueous phase was acidified (HCl), treated with solid ($NaHSO_3$), and extracted with ethyl ether (3 × 50 mL). After drying with anhydrous Na_2SO_4 the solvent was removed at reduced pressure, affording **11** (249 mg, 85% yield): ^1H NMR δ 1.31 (br s, 8 H), 1.5–1.8 (m, 4 H), 2.1–2.4 (m, 4 H), 3.66 (s, 3 H), 8.25 (br s, 1 OH); IR (film) 3600–2600 (OH), 1740 (COOMe), 1720 (COOH) cm^{-1}.

Adipic Acid (6). Cyclohexene (112 mg, 1.36 mmol) was cleaved by using the above procedure. When the aqueous phase was extracted with ether only a small quantity of adipic acid was recovered. Continuous extraction of the aqueous phase with the same solvent gave an additional amount of the desired product. Combination of both fractions afforded (147 mg, yield 74%) of adipic acid, mp 151–154 °C (acetone/petroleum ether), (lit.[14] mp 151–153 °C).

Acknowledgment. We thank Conselho de Desenvolvimento Cientifico e Tecnológico (CNPq) and Fundação de Amparo a Pesquisas do Estado de São Paulo (FAPESP) for financial support. One of us (W.O.C.) thankfully acknowledges FAPESP for an undergraduate fellowship.

Registry No. **1**, 80-56-8; **2**, 61826-55-9; **3**, 1123-46-2; **4**, 28587-41-9; **5**, 110-83-8; **6**, 124-04-9; **7**, 621-82-9; **8**, 65-85-0; **9**, 103-54-8; **10**, 111-81-9; **11**, 818-88-2; **12**, 112-62-9; **13**, 1732-10-1; **14**, 112-05-0; **15**, 108817-94-3; **16**, 108817-95-4.

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Sodium Metal Promoted Condensations of Carbamates

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The well-known acyloin condensation[1] of esters has been used widely for the synthesis of both carbocycles and heterocycles. It has been used with acid chlorides,[2] anhydrides,[3] half-ester amides,[4] and other nitrogen-containing

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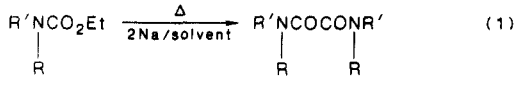
Table I. Summary of Carbamate Reduction Reactions



(1)

1 2

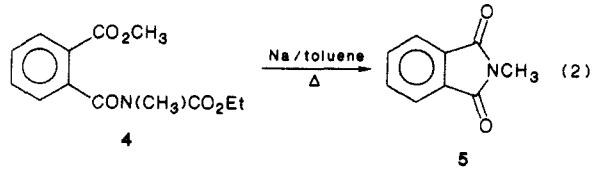
start mat.	R + R'	reactn cond[a]	% diamide	% start mat.	other
1a	$(CH_2)_4$	2.8/1 xylene/4 h	25.5	62.5	
1b	$(CH_2)_5$	3.0/1 xylene/24 h	29.5	13.1	24.4 mg[b]
1c	CH_3 CH_2Ph	2.0/1 xylene/9 h	14.0	26.7	
1d	CH_3 Ph	2.6/1 benzene/1 h	58	0	
1e	Ph Ph	2.0/1 benzene/1 h	49	0	
1f	$(CH_2)_3C_6H_4$	3.5/1 heptane/2.5 h	27	74	
1g	CH_3 o-C_6H_4-E[c]	4.1/1 xylene/6 h	0	8	32[d]

[a] Ratio sodium/starting material solvent/total reaction time. [b] Unidentified. [c] E = CO_2CH_3. [d] Compounds **3a** and **3b**.

systems,[5] but simple amides were unreactive.[6] The half-ester amides reacted at the ester end,[4] and there are two reports of carbamates that were unreactive while a diester cyclization took place.[7] We wondered why no work had been reported on carbamates and began a study to examine their reactivity.[8]

We report a new reaction of carbamates **1a–f** with sodium under acyloin conditions to give substituted oxalate diamide **2** condensation products. The yields, structures, and reaction conditions are shown in Table I. While the simple alkyl cases **1a–c** were slow, required stringent conditions, and gave fairly low yields of product, the phenyl-substituted systems gave about 50% yields in 1 h at 80 °C. The reduction of the conformationally constrained **1f** gave 27% of **2f** in 2.5 h[9] at 92 °C. Reactions of **1g** under a variety of conditions gave the cleavage product methyl *N*-methylanthranilate (**3a**) along with recovered **1g** and some cleavage product that had been transesterified to ethyl *N*-methylanthranilate (**3b**).

Reaction of **4** with sodium for 2 h at toluene reflux gave 93% yield of N-methylphthalimide (**5**). Longer reaction



(2)

4 5

times gave reduced yields of **5**. When silylcarbamate **6** was added directly via syringe to a highly dispersed sodium sample in benzene, no condensation was observed, and only desilylated **7** was recovered. A series of adipamates produced neither intermolecular oxalates nor intramolecular acyloin-like cyclizations between the ester and carbamate groups.

$$\underset{\mathbf{6}}{CH_3CH_2CH_2CH_2N(Si(CH_3)_3)CO_2Et} \xrightarrow[Na/PhH]{\Delta} \underset{\mathbf{7}}{n\text{-}BuNHCO_2Et} \quad (3)$$

The usual acyloin mechanism[1] can satisfactorily explain the relative reactivity of the carbamates and the observation of the oxalate diamide products. The oxalate diamides are not further reduced both because of the low reactivity of simple amides with reducing metals and the steric problems associated with forming planar radical anions in tetrasubstituted oxalate diamides.[10]

In summary, carbamates can be reduced by sodium metal under acyloin conditions to give oxalate diamide products, and phenyl-substituted cases produced the best yields in the cases examined.

Experimental Section[11]

Materials. Compounds **1a–f**, **2b–e**, **3a,b**, **5**, and **7** were all prepared by their literature procedures. Compound **6** was prepared by the saccharin procedure.[12]

General Reaction Conditions for Acyloin-Type Reactions. After all glassware had been oven-dried overnight, a 0.25 to 1 L Morton flask was equipped with a heating mantle, a Hershberg stirrer,[13] constant pressure addition funnel, and condenser with a nitrogen inlet. Approximately 100–450 mL of solvent followed by freshly cut metallic sodium were added,[14] the system was flushed with nitrogen, and heating was begun until a few milliliters of solvent distilled out of the empty condenser. The condenser cooling water was then started and the stirrer run at 1500–2000 rpm for 10 min to disperse the sodium. The carbamate (5–20 mmol/50 mL of solvent) was added dropwise (0.5–3 h) and refluxed for the specified time. After cooling in an ice bath, an excess of glacial acetic acid diluted with solvent was added dropwise with stirring. After removing the sodium acetate by filtration and the solvent in vacuo, the crude product was analyzed by NMR and TLC before pumping on a vacuum pump. The crude was reexamined before chromatographing on Florisil columns with slowly increasing eluent polarity from hexane through ether, acetone, and methanol. Product identities were confirmed by comparison with authentic samples.

Methyl *N*-Methyl-*N*-carbethoxyanthranilate (1g). A 16.3-g (78.8 mmol) sample of *N*-methyl-*N*-carbethoxyanthranilic acid[15] was esterified with distilled ethereal diazomethane. After workup, concentration afforded 16.8 g (97%) of a clear oil: n^{23} 1.517; IR 1740, 1695 cm^{-1}; NMR δ 7.2–7.8 (4 H, br, Ar H), 4.1 (2 H, q, CH_2O), 3.9 (3 H, s, OCH_3), 3.3 (3 H, s, NCH_3), 1.2 (3 H, t, CH_3). Anal. Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.38. Found: C, 60.38; H, 6.51.

Oxalyl Dipyrrolidide (2a). The procedure for the preparation of **2b**[16] was used. Crystallization from ether afforded 4.8 g (90%)

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(9) The temperature effect was marked as no reaction occurred in 4 h in refluxing benzene, and cleavage to give tetrahydroquinoline was the exclusive product in 30 min in refluxing toluene.
(10) (a) Voss, J. *Tetrahedron* **1972**, *28*, 2627. (b) Voss, J. *Liebigs Ann. Chem.* **1974**, 1231. (c) Siddall, T. H., III.; Good, M. L. *J. Inorg. Nucl. Chem.* **1967**, *29*, 149.
(11) ^1H NMR spectra were recorded at 60 MHz in deuteriochloroform. Solvents were dried and distilled under nitrogen before use. Detailed experimental and references are available.
(12) Bruynes, C. A.; Jurriens, T. K. *J. Org. Chem.* **1982**, *47*, 3966.
(13) Hershberg, E. B. *Ind. Eng. Chem. Anal. Ed.* **1936**, *8*, 313.
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(15) Ettinger, L. *Chem. Ber.* **1909**, *42*, 3193.
(16) Schotten, C. *Chem. Ber.* **1882**, *15*, 425.

of white crystals: mp 77-78 °C; IR ($CDCl_3$) 1640 cm^{-1}; NMR δ 3.5 (8 H, m, CH_2N), 1.9 (8 H, m, CH_2). Anal. Calcd for $C_{10}H_{16}N_2O_2$: C, 61.22; H, 8.16. Found: C, 61.34; H, 8.15.

Oxalyl Bis(tetrahydroquinolinide) (2f). A 1.5-g (11 mmol) sample of tetrahydroquinoline was acylated with oxalyl chloride in benzene–pyridine. After workup, crystallization afforded 1.54 g (43.7%) of white crystals: mp 138-140 °C; IR 1660 cm^{-1}; NMR δ 7.13 (8 H, m, Ar H), 3.6 (4 H, m, CH_2N), 1.63 (8 H, m, CH_2). Anal. Calcd for $C_{20}H_{20}N_2O_2$: C, 74.97; H, 6.29. Found: C, 75.00; H, 6.40.

Methyl *N*-Methyl-*N*-carbethoxyphthalamate (4). A 2.4-g (10 mmol) sample of *N*-carbethoxyphthalamic acid[17] was methylated with an excess of sodium hydride and methyl iodide in DMF to give 2.2 g (83%) of **4** as an oil, which was chromatographed: IR 1720, 1700, 1670 cm^{-1}; NMR δ 7.90 (1 H, dd, Ar H, ortho to CON), 7.33 (3 H, m, Ar H), 3.90 (2 H, q, CH_2O), 3.73 (3 H, s, CH_3O), 3.33 (3 H, s, CH_3N), 0.87 (3 H, t, CH_3). Anal. Calcd for $C_{13}H_{15}NO_5$: C, 58.86; H, 5.66; N, 5.28. Found: C, 58.74; H, 5.66; N, 5.11.

(17) Peron, Y. G.; Minor, W. F.; Crast, L. B. *J. Med. Chem.* **1962**, *5*, 1016.

Acknowledgment. We thank the Research Corporation for partial support of this work, Dr. Woodfin V. Ligon of GE Corporate R & D for high resolution mass spectra, and Micro-Tech of Skokie, IL, for elemental analyses.

Registry No. **1a**, 5470-26-8; **1b**, 5325-94-0; **1c**, 59325-17-6; **1d**, 2621-79-6; **1e**, 603-52-1; **1f**, 54915-68-3; **1g**, 33923-02-3; **2a**, 85802-71-7; **2b**, 17506-94-4; **2c**, 14288-21-2; **2d**, 14288-22-3; **2e**, 109124-48-3; **2f**, 109124-49-4; **3a**, 85-91-6; **3b**, 35472-56-1; **4**, 109124-50-7; **5**, 550-44-7; $EtO_2CN(Me)$-2-$C_6H_4CO_2H$, 79228-33-4; $Cl_2(CO)_2$, 79-37-8; HO_2C-2-$C_6H_4CONHCO_2Et$, 49599-18-0; tetrahydroquinoline, 25448-04-8.

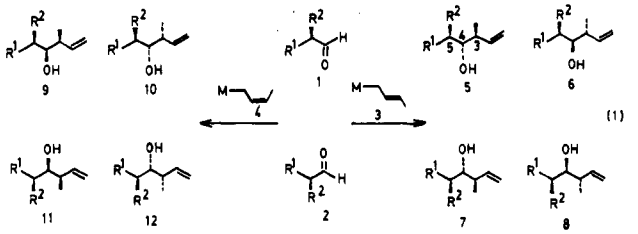
Communications

A Highly Diastereoselective Addition of (*E*)- and (*Z*)-Crotyldiisopinocampheylboranes to α-Substituted Aldehydes

Summary: (*E*)- and (*Z*)-Crotyldiisopinocampheylboranes **13-16** were used for diastereofacial selectivity in their reaction with α-substituted chiral aldehydes (*S*)-2-methylbutyraldehyde (**17**) and (*S*)-2-(benzyloxy)propionaldehyde (**18**).

Sir: The reaction of certain allylmetal and crotylmetal reagents with chiral carbonyl compounds constitutes a powerful method for control of acyclic stereochemistry and their value as biosynthetic intermediates has been amply demonstrated.[2-5] A variety of crotylmetal compounds with high stereochemical purity are now available. Many of the crotylmetals, especially crotyl boron compounds, undergo reaction with aldehydes in which the olefin geometry is transmitted predictably via cyclic transition states to either a syn (from *Z*) or anti (from *E*) relationship around the newly formed C–C bond in the product alcohols.[6] An as yet unsolved problem involves control of facial selectivity in reactions of crotylmetals with α-substituted chiral aldehydes.

Like enolates, crotyl organometallic reagents react with α-substituted chiral aldehydes to furnish diastereomeric mixtures of (3,4- and 4,5)-anti,anti (**5** and **7**), -anti,syn (**6** and **8**), -syn,anti (**10** and **12**), and -syn,syn (**9** and **11**) adducts (eq 1).[3e,4a] Enantiomeric homoallyl alcohol units (R_1 = CH_3; R_2 = C_2H_5, OBz) constitute a characteristic structural feature of numerous macrolide and polyether antibiotics.[7] The major problem in stereocontrol concerns the selectivity in the relative configuration of the newly formed C–C bond to the configuration present in the aldehydes. Although considerable effort has been devoted to the elucidation of the stereochemistry of the reaction of crotylmetal compounds with α-substituted chiral aldehydes, relatively little information is available regarding such reactions. Hence, the development of new crotyl organometallic reagents possessing high stereoselectivities remains a desirable goal.



(1)

We recently described the stereochemistry of the reactions of allyldiisopinocampheylboranes [derived from (+)- and (−)-α-pinene] with α-substituted chiral aldehydes.[8] In general, these reactions are highly stereoselective, with high

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