

**Figure 1.** Schematic view of the orbitals involved in the hyperconjugative stabilization of transition states of addition to trigonal carbon.



since face selection occurs at both termini. Two of the four are boat-shaped; these are ruled out by Evans' experiments.<sup>13</sup> The other two are chairs that differ in that one (A) has the phenyl group axial and the other (B) has it equatorial (Scheme I; this arbitrarily shows the R isomer).

The same synthetic sequence beginning with 1-O-F gives a 50/50 mixture of two diastereomers 6 and 7, with configurations RR,SS and RS,SR, respectively; they were quantitatively separated by means of column chromatography. Note that 6 and 7 differ from 4 by a fluoro sub-



(13) Evans, D. A.; Nelson, J. V. J. Am. Chem. Soc. 1980, 102, 774.

stituent at  $C_5$  and  $C_7$ , respectively. If one follows Scheme I through with this in mind, it can be seen that **6A** and **7B** give *E*-8, whereas **7A** and **6B** produce *Z*-8. In one of



the diastereomers, the steric and electronic effects operate in opposition, in the other, they act in unison. The configurations of the two products E- and Z-8 were determined easily be means of the effects of the fluorine atom and of the added shift reagent Eu(fod)<sub>3</sub> on the <sup>13</sup>C NMR spectra; quantitative analysis of the mixtures showed that one diastereomer gave rise to an E/Z ratio of 81/19, the other of 36/64. The electronic factor clearly favors syn approach as predicted. With no assumption except that the difference in energy between A and B is unaffected by whether the fluorine is located at  $C_5$  or  $C_7$ , we calculate that the predilection for syn approach amounts to a factor of 1.4, and the steric difference between A and B causes a rate ratio of 2.6 between the two approaches. As a result, a 50/50 mixture of 6 and 7 would show a net preference for bonding at the fluoro side of nearly 60%.

The secondary question whether **A** or **B** is the sterically preferred transition state is one we can at present not answer definitively, although our extensive <sup>13</sup>C NMR studies of **6** and 7 suggest that the one giving the most syn approach is 7 (RS,SR; equatorial phenyl). This evidence will be discussed in the full paper; the important conclusion for now is that in this sigmatropic shift, the face selected is that antiperiplanar to the most electron-rich bond. In that regard, the oxy-Cope rearrangement now joins all other additions to trigonal carbon examined to date.

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## An Unprecedented Intramolecular Migration of Carbon Groups from Aluminum to an Adjacent Vinylic Center and Its Application to the Synthesis of Stereodefined Olefins

Summary: Hydroalumination of 1-chloro-1-alkynes by sodium trialkylaluminum hydrides furnishes stereo- and regioselectively the respective (E)-1-chloro-1-alkenylalanates, which, in the presence of NaOMe, undergo a novel 1,2-migration of a carbon group from Al to the adjacent vinylic center to generate a useful synthesis of diand trisubstituted olefins of defined geometry.

Sir: Migratory insertion reactions are ubiquitous in organoboron chemistry, representing the most common method for synthesizing carbon-carbon bonds by using boron.<sup>2,3b</sup> On the other hand, this type of 1,2-migration reaction has rarely been observed for the corresponding organoaluminums.<sup>3</sup> Until recently, in fact, the only reported examples of organoaluminums that appear to have undergone migratory insertion are the reaction of organoalanes with diazomethane to yield the homologous alanes<sup>4</sup> and the reaction of lithium chloropropargylide with

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<sup>(2)</sup> Brown, H. C. Organic Synthesis via Boranes; Wiley-Interscience: New York, 1975. Negishi, E. In Comprehensive Organometallic Chemistry; Wilkinson, G., Stone, F. G. A., Abel, F. W., Eds.; Pergammon Press: Oxford, 1982; Vol. 7, pp 255–363. Negishi, E.; Idacavage, M. J. Org. React. 1985, 33, 1–246.

<sup>(3) (</sup>a) Mole, J.; Jeffrey, E. A. Organoaluminum Compounds; Elsevier: Amsterdam, 1972.
(b) Negishi, E. Organometallics in Organic Synthesis; Wiley-Interscience: New York, 1980; Vol. 1, Chapter 5.
(c) Zweifel, G.; Miller, J. A. Org. React. 1984, 32, 375-517.

 $(n-\text{Hex})_3$ Al to produce a mixture of the respective propargylic and allenic alanes.<sup>5</sup> Negishi,<sup>6</sup> however, has now demonstrated that organoaluminums and a variety of other main group organometallics in addition to boranes readily participate in these 1,2-migration reactions. This work has prompted us to report our results concerning a new migratory insertion reaction of organoaluminums, which involves the transfer of a carbon group from Al to the adjacent vinylic center in sodium (1-chloro-1-alkenyl)trialkylalanates 1. This rearrangement represents an aluminum counterpart to the well-known 1,2-migration reaction observed for the corresponding 1-halo-1-alkenylborates in the Zweifel trans-olefin synthesis.<sup>7</sup>

In a manner analogous to the known trans-hydroalumination of 1-chloro-1-alkynes by LiAlH<sub>4</sub>,<sup>8</sup> treatment of a diglyme solution of sodium trimethylaluminum hydride<sup>3a,9a</sup> (1.5 equiv) at 0 °C with 1-chloro-1-octyne<sup>10</sup> produced stereo- and regioselectively the sodium [(Z)-1chloro-1-octenvl]trimethylalanate (1a) in 89% yield as evidenced from <sup>1</sup>H NMR (the vinylic proton was present as a triplet, J = 8 Hz, at 5.88 ppm) and GC analyses of the trans-1-chloro-1-octene (2) obtained upon protonolysis. None of the corresponding cis-1-chloro-1-octene was present based on GC comparison with an authentic sample.<sup>11</sup> In addition, 11% of 1-octyne had formed. Allowing the reaction mixture to warm to room temperature resulted after protonolysis in the formation of cis-2-nonene (3a) (17%), 1-octyne (19%), and, interestingly, the diene 5 (12%), with no trans-1-chloro-1-octene remaining as determined by GC analysis. The formation of **3a** shows that the desired migratory insertion of a methyl group from Al to the  $\alpha$ -vinylic carbon in the alanate 1a did indeed occur, albeit in low yield. The diene 5 may be derived from an



initial redistribution reaction between the nucleophilic vinylalanate 1a and the electrophilic vinylalane that is produced from it upon 1,2-migration. Migratory insertion

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(11) An authentic sample of cis-1-chloro-1-octene was prepared from 1-chloro-1-octyne via hydroboration with disiamylborane (THF, 25 °C, 4 h) followed by protonolysis using acetic acid (50 °C, 12 h).<sup>5</sup>

Table I. Yields of Alkenes 3 and Alkenyl Iodides 4 Prepared from 1-Chloro-1-alkynes and Sodium Trialkylaluminum Hydrides (eq 1)

			% yield <sup>a</sup> GC (isolated)		
entry	R	R′	3	4	
а	n-C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub>	69	(63)	
b	$n - C_6 H_{13}$	$C_2 H_5^b$	74°	(67)	
с	$n - C_{10} H_{21}$	$CH_3$	69		
d	$n - C_{10}H_{21}$	$C_2 H_5^b$	68		

<sup>a</sup> Spectral and analytical data were consistent with the assigned structure. <sup>b</sup>Sodium triethylaluminum hydride was prepared by heating a slight excess of NaH with Et<sub>3</sub>Al in diglyme at 50 °C for 2 h. The unreacted NaH was then removed by filtration. 'None of the trans isomer was detected by GC comparison with authentic samples of cis- and trans-3-decene (Wiley Organics).

of the resultant mixed divinylalanate followed by hydrolysis would afford the observed diene 5. In order to



circumvent the undesired redistribution reaction, the presence or generation of trigonal aluminum species must be avoided. Accordingly, addition of NaOMe (1.5 equiv) to the reaction solution prior to the warming of 1a, followed by heating at 50 °C for 18 h, produced by <sup>1</sup>H NMR a triplet of quartets (J = 7, 2 Hz) at 5.37 ppm for the vinylic proton in the methoxyalanate 6a,12 and upon hydrolysis and GC analysis only the desired cis-2-nonene (3a) (69%) and byproduct 1-octyne (31%). No trace of the diene 5 was detected. Moreover, the reaction was highly stereoselective since the ratio of cis-:trans-2-nonene obtained was ≥99.5:0.5.14

The intermediate methoxyalanate 6 also undergoes stereospecific iodination. For example, treatment of 6a with I<sub>2</sub> (1.25 equiv,  $-78 \rightarrow 25$  °C) afforded the corresponding (*E*)-vinyl iodide 4a in 63% isolated yield.<sup>15,16</sup>

<sup>(12)</sup> The structural assignments for the alkenylalanates 1a and 6a are supported by the fact that the <sup>1</sup>H NMR chemical shifts of their vinylic protons closely resemble those of known structure 7 and 8, respectively. Thus, the 1-chloro-1-alkenylalanate 7 (prepared from treatment of 1-chloro-1-octyne with 1.25 equiv of LiAlH<sub>4</sub> in diglyme<sup>8</sup>) exhibits a pair of triplets<sup>13</sup> (J = 8 Hz) at 5.98 and 6.01 ppm for the vinylic proton, while the methoxyvinylalanate 8 (derived from hydroalumination of 5-decyne with *i*-Bu<sub>2</sub>AlH,<sup>3c</sup> followed by treatment with NaOMe in diglyme) exhibits a triplet (J = 7 Hz) at 5.44 ppm. These chemical shift similarities, we believe, support the intermediacy of 1a and 6a in the reaction.



(13) The presence of two separate triplets (in ca. equal proportion) may be due to the formation of a mixture of the monoalkenylalanate 7 and the corresponding dialkenylalanate species 9.



(14) By GC comparison with authentic samples of cis- and trans-2nonene obtained from Wiley Organics. (15) Oda, H.; Morizawa, Y.; Oshima, K.; Nozaki, H. Tetrahedron Lett.

1984, 25, 3221. Hara, S.; Takinami, S.; Hyuga, S.; Suzuki, A. Chem. Lett. 1984, 345. The E stereochemistry assigned to 4a was additionally supported by the fact that its lithium-halogen exchange with t-BuLi (2.0 equiv, THF, -78 °C) formed upon protonolysis a ratio of cis-:trans-2nonene<sup>14</sup> of  $\geq$ 99.0:1.0.

<sup>(4)</sup> Hoberg, H. Ann. Chem. 1962, 656, 1; 1966, 695, 1; Angew. Chem., Int. Ed. Engl. 1966, 5, 513.

<sup>(5)</sup> Zweifel, G. In Aspects of Mechanism and Organometallic Chemistry; Brewster, J. H., Ed.; Plenum Press: New York, 1978; pp 229-249. (6) Negishi, E.; Akiyoshi, K. J. Am. Chem. Soc. 1988, 110, 646.

This iodination reaction and the fact that alkenylaluminums are known to react stereospecifically with a wide variety of both organic and inorganic electrophiles<sup>3</sup> should make this new methodology useful for not only the synthesis of disubstituted olefins, but stereodefined trisubstituted alkenes as well. As shown in Table I, the reaction also proceeds equally well with sodium triethylaluminum hydride<sup>9</sup> to provide the respective ethylated olefins.

(16) A detailed procedure for the preparation of 4a is as follows. To a mixture of 0.24 g (8.0 mmol) of 80% NaH and 8 mL of dry diglyme was added under argon at 0 °C 3.75 mL (7.50 mmol) of 2.0 M Me<sub>3</sub>Al in hexane. The reaction mixture was warmed to room temperature, stirred for 2 h, and then filtered under argon through a medium glass frit. The hexane contained in the filtrate was removed under reduced pressure (25 °C, 30 Torr), and the clear solution of sodium trimethylaluminum hydride obtained was treated at 0 °C with 0.72 g (5.0 mmol) of 1-chloro-1-octyne. The solution was stirred for 1 h at 0 °C and to it was added 0.40 g (7.5 mmol) of NaOMe. The mixture was then warmed to 50 °C and stirred overnight. The reaction was cooled to -78 °C and treated with a solution of 1.59 g (6.25 mmol) of I<sub>2</sub> in 5 mL of diglyme. After the mixture was warmed to 25 °C, GC examination of an aliquot showed complete iodination had occurred, as no residual cis-2-nonene (3a) was present after hydrolysis. However, due to the formation of some 1-iodo-1-octyne, the reaction solution was additionally treated with 1.0 mL (2.0 mmol) of 2.0 M Me<sub>3</sub>Al in hexane, which after 24 h at room temperature had converted all 1-iodo-1-octyne into 1-octyne (after protonolysis), thereby simplifying the isolation procedure. The reaction mixture was slowly poured into a mixture of 3 N HCl and pentane. The aqueous layer was extracted with pentane, and the combined organic phase was washed sequentially with 3 N HCl, saturated NaHCO<sub>3</sub>, 20% Na<sub>2</sub>SO<sub>3</sub>, and saturated NaCl. Concentration and short-path distillation provided 0.79 g (63%) of 4a:15 bp 45 °C (0.1 Torr); IR (neat) 3020 (w), 2950 (s), 2920 (s), 2850 (s), 1638 (m), 1465 (m), 1455 (m), 1385 (m), 1135 (m), 1060 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS)  $\delta$  0.90 (t, 3 H), 1.2-1.5 (br s, 8 H), 2.05 (m, 2 H), 2.35 (d, J = 1.5 Hz, 3 H), 6.15 (tq, J = 7.2, 1.5 Hz, 1 H).

Unlike the corresponding 1-halo-1-alkenylborates, which undergo facile migratory insertion,<sup>7</sup> the 1-chloro-1-alkenylalanates 1 are stable in diglyme at temperatures up to 0 °C. As a result, we were able to carry out crossover experiments to verify the intramolecular nature of this rearrangement. Thus, to a mixture of NaOMe in diglyme were sequentially added at 0 °C equimolar amounts of the 1-chloro-1-alkenylalanates 1a and 1d. The reaction mixture was heated at 50 °C for 18 h, and, following protonolysis, GC analysis showed the presence of only the alkenes 3a and 3d. Neither of the crossover products 3b and 3c was detected. Likewise, the similar reaction of a mixture of 1b and 1c produced only 3b and 3c. It may, therefore, be concluded on the basis of these experiments that the carbon-group migration from Al to the adjacent vinylic center in 1 is an intramolecular process. Furthermore, this study appears to represent the first example of crossover experiments being used to conclusively demonstrate the intramolecular nature of a migratory insertion process involving a main-group organometallic.<sup>17</sup>

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Articles

## Selective Transport of Polyfunctional Cations through Bulk Liquid Membranes Assisted by Macrocyclic Polyethers

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Imidazolium perchlorate is transferred from the aqueous to a chloroform phase containing (di)benzo crown ethers with a ring size varying between 24 and 33 ring atoms. X-ray analysis of the crystalline 1:1 complex of imidazolium perchlorate and benzo-30-crown-10 proved that imidazolium is completely encapsulated and coordinated to the host molecule via hydrogen bonding. In transport experiments through chloroform bulk liquid membranes, the highest flux of imidazolium thiocyanate was observed with benzo-30-crown-10 as the carrier molecule. In competition experiments guanidinium thiocyanate exhibited a higher flux than the imidazolium salt. A selectivity coefficient of more than 100 was obtained with benzo-27-crown-9 as the carrier, due to an almost complete discrimination between the guanidinium and the imidazolium cations.

## Introduction

Selectivity in separation processes can be achieved when a synthetic macrocyclic receptor is used that has the ability to complex a specific guest selectively compared with other guests. The large synthetic macrocycles with at least 27 ring atoms have not received much attention in complexation experiments both with centrosymmetrical and with polyfunctional cations, although we have recently shown that these macrocycles exhibit a remarkably high K<sup>+</sup>/Na<sup>+</sup> selectivity similar to the antibiotic valinomycin, a structurally related 36-membered macrocycle.<sup>1</sup>

<sup>(17)</sup> Subsequent to the preparation of this manuscript, a related reaction was published describing the 1,2-migration of alkyl groups in 1-bromo-1-alkenylzincates: Harada, T.; Hara, D.; Hattori, K.; Oku, A. *Tetrahedron Lett.* 1988, 29, 3821.

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