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INTRAMOLECULAR METAL—DOUBLE BOND INTERACTIONS

VII. INTRAMOLECULAR CYCLIZATION OF ALKENYL DERIVATIVES OF LITHIUM, ALUMINUM, GALLIUM AND INDIUM

T.W. DOLZINE and J.P. OLIVER*
Department of Chemistry, Wayne State University, Detroit, Michigan 48202 (U.S.A.)
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Summary

The intramolecular cyclization reactions of tri-1-hex-5-enyl Group III derivatives and of 1-hex-5-enyllithium have been investigated and it is proposed that the reactions may be depicted as internal addition across the terminal double bonds of the alkenyl species. The cyclization reaction proceeds more readily for the 1-hex-5-enyl derivatives than for any other chain length and is dependent on temperature, concentration and solvent. ^{1}H NMR data and cryoscopic molecular weight data are presented for several diisobutylalkenyl- and diisobutylalkyl-aluminum derivatives. These data have been interpreted in terms of a direct intramolecular interaction between the metal center and the π-electron system of the olefinic site. The intramolecular cyclization reactions for the 1-hept-6-enyl, 1-oct-7-enyl- and 1-undec-10-enylaluminum derivatives also were investigated and it was found that cyclization occurred only for the 1-hept-6-enyl derivative.

Introduction

Intramolecular cyclization of organometallic compounds are presently known for 1-hex-5-enylaluminum derivatives [1—3], 1-hex-5-enyllithium [4] and for Grignard reagents [5]. In the former case cyclization takes place on the addition of an aluminum hydride to 1,5-hexadiene and in the latter, cyclization or cyclic intermediates have been reported for 1-but-3-enyl, 1-pent-4-enyl and 1-hex-5-enyl derivatives. Hata and Miyaki [2] prepared several diisobutylalkenylaluminum derivatives from the addition of diisobutylaluminum hydride to α,ω-dienes and found that in the alkenyl groups the addition of the aluminum—carbon bond to the terminal olefin occurred intramolecularly to give cyclic

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* For correspondence.

products. They postulated a complex existing between the aluminum atom and the olefin before addition occurs. They reported that quantitative cyclization had occurred for the 1-hex-5-enyl derivative, 8.5% for the 1-hept-6-enyl derivative and that cyclic products were not observed for the longer chain diisobutylalkenylaluminum derivatives.

In this paper we report the synthesis and a study of the intramolecular cyclization of 1-hex-5-enyllithium and of the tri-1-hex-5-enyl Group III metal derivatives. Our studies of Group III species include the investigation of trialkenylaluminum, gallium and indium derivatives. We also report ^{1}H NMR parameters and cryoscopic molecular weight data for several diisobutylalkenyl- and diisobutylalkyl-aluminum derivatives. These data establish the existence of an aluminum-π-electron interaction in several of the hex-5-enyl derivatives and for hept-6-enylaluminum species. A study of the intramolecular cyclization reactions of the diisobutylalkenylaluminum derivatives indicates that the reactions proceed through an internal aluminum—carbon bond addition to the terminal olefin with the yield of cyclic product dependent on temperature, solvent and concentration in the reaction system. A preliminary account of this work has appeared previously [6].

Experimental

Experimental conditions and reagents

All manipulations were performed using high vacuum techniques or in a dry box (Ar or N_2 atmosphere) scavenged with sodium—potassium alloy with all necessary precautions taken to insure oxygen- and water-free conditions.

All solvents were dried over sodium—potassium alloy, then degassed and stored on a high vacuum line. 1-Chloro-5-hexene was obtained from Chemical Samples Company and dried over molecular sieves. 1-Hex-5-enylmercuric chloride was prepared from the respective Grignard and mercuric chloride. The di-1-hex-5-enylmercury derivative was prepared by disproportionation of 1-hex-5-enylmercuric chloride with sodium stannite by the method of Nesmeyanov [7]. Di-1-hex-5-enylmercury was purified by high vacuum distillations (10^{-6} mm) and analyzed by NMR and mass spectroscopy. The latter gave rise to a parent ion of $[CH_2{=}CH(CH_2)_3CH_2]_2Hg^+$ with *m/e* 368 based on ^{202}Hg isotope. All subsequent handling was performed in a sodium—potassium scavenged inert atmosphere box. All α-alkenes and α,ω-dienes were obtained from Chemical Samples Company, dried over molecular sieves and stored in a high vacuum line until needed. Diisobutylaluminum hydride was obtained from Texas Alkyls, Inc. and stored in an inert atmosphere box.

Cryoscopic molecular weight measurements

The molecular weights were determined cryoscopically in cyclohexane (K_f = 20.0) using a modified Beckmann [8] apparatus for air-sensitive compounds and a Beckmann thermometer. An error estimate was obtained by the determination of the molecular weight of $Al_2(CH_3)_6$ in cyclohexane (experimental molecular weight = 141.7, calculated value = 144.0, error = 1.6%). The freezing points of the pure solvent and the solutions were determined graphically by plotting temperature vs. time.

Nuclear magnetic resonance techniques

NMR spectra were recorded on a Varian A60-A spectrometer. Line positions were calibrated by use of audio frequency side bands of the internal standards, cyclopentane or benzene, and were corrected to TMS = 0 by addition of 1.50 or 7.24 ppm, respectively, to the observed values. A minimum of two spectra were calibrated for each sample. All parameters reported are based on first order analyses of the spectra. The values obtained are reliable to approximately ± 0.01 ppm for the chemical shifts and ± 0.3 Hz for the coupling constants as shown by comparison with spectra of similar systems analyzed by computer simulation methods [9].

Tris(cyclopentylmethyl)aluminum, gallium and indium derivatives

Tris(cyclopentylmethyl)aluminum, $Al[CH_2(cyclo\text{-}C_5H_9)]_3$, was prepared from aluminum dust and di-1-hex-5-enylmercury in an evacuated sealed pyrex tube at 10^{-6} mm. The gallium and indium derivatives were similarly prepared from the respective metal and di-1-hex-5-enylmercury. The conditions for preparation and NMR parameters for all the Group III cyclopentylmethyl derivatives are listed in Tables 1 and 2 respectively. The purity and completeness of the reaction were determined from the NMR spectra of the samples. All cyclopentylmethyl derivatives formed 1/1 complexes when mixed with trimethylamine. The Group III derivatives produced methylcyclopentane when hydrolyzed with a 10% v/v HCl/H_2O mixture. The hydrolysis mixture was extracted with diethyl ether and dried over anhydrous magnesium sulfate. The product was identified by comparison of its retention times with an authentic sample on a 30% SE-30 gas chromatograph column and only one product was detected in the hydrolysis mixture. The pyrolysis of tris(cyclopentylmethyl)aluminum at 100° eliminated methylenecyclopentane, $H_2C{=}(cyclo\text{-}C_5H_8)$. The gallium and indium derivatives were thermally stable at this temperature.

Cyclopentylmethyllithium

Cyclopentylmethyllithium, $LiCH_2(cyclo\text{-}C_5H_9)$, also was prepared from the di-1-hex-5-enylmercury and lithium metal. Tables 1 and 2 list the reaction con-

TABLE 1

EXPERIMENTAL CONDITIONS FOR CYCLIZATION REACTIONS OF 1-HEX-5-ENYL METAL DERIVATIVES OBTAINED BY EXCHANGE OF DI-HEX-5-ENYLMERCURY AND METAL

Metal	Time for complete cyclization [a]	Temp. (°C)	Solvent
Li	8 days	25	C_5H_{10}
Li	96 h	25	C_6H_6
Li	<1 h	25	$(C_2H_5)_2O$
Al	48 h	40	Neat
Al	48 h	25	C_5H_{10}
Ga	3 weeks	95	Neat
In	3 weeks	110	Neat

[a] The time for complete reaction in each case was determined by following its progress by the changes observed in the NMR spectrum of the reaction mixture. In all cases, except for aluminum, the reaction mixture showed resonances which could be associated with unreacted mercury derivative, uncyclized metal derivative and cyclic product. For aluminum reactions only starting material and the cyclic product were observed.

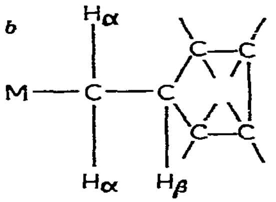
TABLE 2

NMR PARAMETERS FOR SEVERAL METAL CYCLOPENTYLMETHYL DERIVATIVES [a]

	δ_α [b]	δ_m	δ_n	$J_{\alpha\beta}$
$Al[CH_2(cyclo\text{-}C_5H_9)]_3$	0.47	1.65 1.72 1.75		6.6
$(CH_3)_3NAl[CH_2(cyclo\text{-}C_5H_9)]_3$	0.06	1.63 1.74	2.09	6.5
$Ga[CH_2(cyclo\text{-}C_5H_9)]_3$	0.91	1.67 1.76 2.02		6.9
$(CH_3)_3NGa[CH_2(cyclo\text{-}C_5H_9)]_3$	0.50	1.70 1.78 1.81	1.96	6.6
$In[CH_2(cyclo\text{-}C_5H_9)]_3$	0.94	1.65 1.69 1.75		6.8
$(CH_3)_3NIn[CH_2(cyclo\text{-}C_5H_9)]_3$	0.77	1.75 1.86	1.93	6.8
$Hg[CH_2(cyclo\text{-}C_5H_9)]_2$	1.20	$[\delta(^{199}Hg—H)$ 95.72 Hz]		6.5
$Li[CH_2(cyclo\text{-}C_5H_9)]_n$ [c]	—0.60	1.68 1.71 1.83		6.3

[a] Chemical shifts and coupling constants were obtained from spectra taken on a Varian A60-A. Line positions were calibrated by use of audio frequency side band techniques. All spectra were obtained on benzene solutions with benzene used as the internal standard. The chemical shifts were corrected to TMS by addition of 7.24 ppm to the observed value. *J* values are given in Hz.

[b]



δ_m = multiplet of cyclopentyl ring protons; δ_n = methyl proton chemical shift of $(CH_3)_3N$. [c] Degree of aggregation not determined.

ditions and NMR parameters respectively. The reaction of lithium metal with di-1-hex-5-enylmercury at room temperature was contaminated with bis(cyclopentylmethyl)mercury which was identified from its mass spectrum, which gave a parent ion of $Hg[CH_2(cyclo\text{-}C_5H_9)]_2^+$ at *m/e* 368 based on ^{202}Hg isotope, and from the NMR spectrum (Table 2). If the reaction mixture was stirred for one week at 8° the product was not contaminated with the cyclic mercury derivative, but gave a quantitative yield of cyclopentylmethyllithium. Cyclopentylmethyllithium on hydrolysis with 10% v/v HCl/H_2O mixture gave methylcyclopentane and was pyrolyzed at 100° to give methylenecyclopentane.

Reaction of diisobutylaluminum hydride with 1,5-hexadiene in various solvents

The reaction of diisobutylaluminum hydride with 1,5-hexadiene was carried out in a pyrex tube adapted with a side arm with septum and a reflux condenser. The condenser was adapted with a standard joint (14/20) thus allowing complete evacuation of the vessel. In each experiment 10 ml (0.08 mol) of 1,5-hexadiene was vacuum distilled into the vessel after it had been dried over molecular sieves.

TABLE 3

REACTION OF DIISOBUTYLALUMINUM HYDRIDE WITH 1,5-HEXADIENE IN VARIOUS SOLVENTS

Solvent	Temp. (°C)	Time (h)	Hydrolysis product, yield ^{a} (%)		
			CH_3(cyclo-C_5H_9)	$CH_3(CH_2)_4$-CH_3	$CH_3(CH_2)_3$-$CH=CH_2$
THF	60	12	0.0	2.5	97.5
THF	70	12	62.9	37.1	0.0
Et_2O	60	12	4.9	19.0	76.1
$(C_6H_5)_2O$	60	12	95.3	4.2	0.5
C_5H_{10} ^{a}	70	12	100.0	0.0	0.0
Neat ^{a}	25	12	100.0	0.0	0.0

^{a} Relative yields.

The solvents were dried over sodium—potassium alloy, and then distilled (10 ml) directly into the reaction vessel. The vessel was then pressurized with N_2 gas and connected to a mercury bubbler. Diisobutylaluminum hydride, 2 ml, was added to the ether mixture via the septum using a 5 ml syringe. The mixture was heated with an oil bath at 60° for 12 h. The excess ether and 1,5-hexadiene were vacuum distilled leaving a viscous liquid. The organoaluminum compound was hydrolyzed with 10% v/v HCl/H_2O. The hydrolysis product was extracted with diethyl ether and dried over anhydrous magnesium sulfate. The products were identified by comparison of retention time with authentic samples on a 30% SE-30 gas chromatograph column. The chromatogram was then integrated to determine the relative percent of each component in the hydrolysis mixture. The results of this experiment are listed in Table 3. The solvents used in this experiment were THF, diethyl ether and diphenyl ether.

Diisobutyl(1-hept-6-enyl)aluminum

Diisobutyl(1-hept-6-enyl)aluminum, $(i\text{-}C_4H_9)_2Al[CH_2(CH_2)_4CH=CH_2]$, was prepared by the addition of diisobutylaluminum hydride to 1,6-heptadiene. The reaction vessel was similar to that described in the above synthesis. A mixture of 0.005 mol of diisobutylaluminum hydride and 0.015 mol of 1,6-heptadiene was heated for 16 h at 60°. The excess diene was then removed by a high vacuum distillation. Anhydrous cyclopentane was added to the reaction mixture which was heated for 4 days at 50°. Following hydrolysis with 10% v/v HCl/H_2O, 44.2% of methylcyclohexane and 55.8% of n-heptane were recovered. The original product was the desired diisobutyl(1-hept-6-enyl)aluminum compound as evidenced by the NMR spectrum. Diisobutyl(1-hept-6-enyl)aluminum formed a 1/1 trimethylamine adduct when mixed at room temperature with excess amine. The NMR parameters of diisobutyl(1-hept-6-enyl)aluminum and the diisobutyl-(1-hept-6-enyl)aluminum—trimethylamine adduct are listed in Table 4. Cryoscopic molecular weight measurements indicated that diisobutyl(1-hept-6-enyl)aluminum is slightly associated with a molecular weight of 273.3 (R_2AlR' calcd. 236.0).

Other reactions were preformed on this system using similar techniques. In these experiments temperature and the mole ratio of the reactants were varied (Table 5).

Diisobutyl(n-heptyl)aluminum

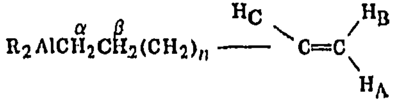
Diisobutyl(n-heptyl)aluminum, $(i\text{-}C_4H_9)_2Al[CH_2)_6CH_3]$, was prepared by

TABLE 4

NMR PARAMETERS FOR SEVERAL DIISOBUTYLALKYL- AND DIISOBUTYLALKENYL-ALUMINUM DERIVATIVES[a,b]

Compound	δ_A	δ_B	δ_C	δ_α	J_{AB}	J_{AC}	J_{AD}	J_{BC}	J_{BD}	J_{CD}	$J_{\alpha\beta}$
$Al(R)_2[CH_2(CH_2)_4CH{=}CH_2]$ [c]	4.92^{1}	4.87^{1}	5.78^{7}	0.30^{1}	2.51	17.50	1.28	9.43	1.03	6.28	6.85
$B\cdot Al(R)_2[CH_2(CH_2)_4CH{=}CH_2]$ [c,d]	4.89^{4}	4.82^{1}	5.78^{5}	-0.11^{1}	2.66	17.29	1.32	9.64	1.04	6.28	6.80
				-0.08^{8}							6.77
$Al(R)_2[(CH_2)_6CH_3]$ [c]				0.28^{5}							6.53
$B\cdot Al(R)_2[(CH_2)_6CH_3]$ [c,d]				-0.10^{9}							6.58
				-0.08^{6}							6.57
$Al(R)_2[CH_2(CH_2)_5CH{=}CH_2]$ [c]	4.92^{4}	4.87^{7}	5.79^{0}	0.26^{9}	2.56	17.55	1.32	9.42	1.05	6.30	6.85
$B\cdot Al(R)_2[CH_2(CH_2)_5CH{=}CH_2]$ [c,d]	4.89^{8}	4.82^{6}	5.77^{7}	-0.10^{9}	2.64	17.36	1.36	9.61	1.10	6.30	6.85
				-0.08^{5}							6.83
$Al(R)_2[(CH_2)_7CH_3]$ [c]				0.25^{8}							6.87
$B\cdot Al(R)_2[(CH_2)_7CH_3]$ [c,d]				0.11^{5}							6.85
				-0.09^{1}							6.80
$Al(R)_2[CH_2(CH_2)_8CH{=}CH_2]$ [c]	4.91^{1}	4.85^{7}	5.77^{5}	0.26^{7}	2.59	17.48	1.32	9.43	1.10	6.26	6.87
$B\cdot Al(R)_2[CH_2(CH_2)_8CH{=}CH_2]$ [c,d]	4.90^{4}	4.84^{6}	5.76^{8}	-0.10^{6}	2.60	17.38	1.35	9.53	1.11	6.36	6.84
				-0.08^{2}							6.78

[a] Chemical shifts and coupling constants were derived from first order analysis and are reliable to ± 0.01 ppm and ± 0.3 Hz respectively. Line positions were calibrated by use of audio frequency side band techniques on a Varian A60-A. All spectra were obtained on cyclopentane solutions with cyclopentane as the internal standard. The chemical shifts were corrected to TMS by addition of 1.50 ppm to the observed value. J values are given in Hz.

[b] 

$$R_2Al\overset{\alpha}{C}H_2\overset{\beta}{C}H_2(CH_2)_n\text{——}C(H_C){=}C(H_B)(H_A)$$

. [c] $R = i\text{-}C_4H_9$. [d] $B = N(CH_3)_3$.

TABLE 5

REACTION CONDITIONS FOR THE REACTION OF α,ω-DIENES WITH DIISOBUTYLALUMINUM HYDRIDE

α,ω-Diene	Mole	$[(i\text{-}Bu)_2AlH]$ (mole)	Temp. (°C)	Time (h)	Hydrolysis products [a]		
					n-Alkane (%)	n-Alkene (%)	Methylcycloalkane (%)
1,5-Hexadiene [b]	0.02	0.042	70	12	n-Hexane (0.9)		Methylcyclopentane (99.1)
1,6-Heptadiene [b]	0.02	0.042	70	12	n-Heptane (97.6)		Methylcyclohexane (2.4)
1,6-Heptadiene [b]	0.02	0.042	125	13	n-Heptane (91.5)		Methylcyclohexane (8.5)
1,6-Heptadiene	0.03	0.005	130	16	n-Heptane (22.6)	n-Heptene (10.6)	Methylcyclohexane (66.7)
1,6-Heptadiene [c]	0.03	0.01	60	16	n-Heptane (55.8)		Methylcyclohexane (44.2)
1,7-Octadiene	0.03	0.005	130	16	n-Octane (11.7)	n-Octene (88.3)	

[a] Relative yields. [b] Ref. 2. [c] After initial reaction excess diene was removed and cyclopentane added. Mixture was then heated for four days at 50°.

the addition of diisobutylaluminum hydride to 1-heptene. The mixture was heated at 70° for 16 h. The product formed a 1/1 trimethylamine adduct when mixed with an excess of the amine. The NMR parameters of diisobutyl(n-heptyl)-aluminum and the diisobutyl(n-heptyl)aluminum—trimethylamine adduct are listed in Table 4. Cryoscopic molecular weight measurements indicated a molecular weight of 434.2 (R_2AlR' calcd. 252.0).

Diisobutyl(1-oct-7-enyl)aluminum

Diisobutyl(1-oct-7-enyl)aluminum, $(i\text{-}C_4H_9)_2Al[CH_2(CH_2)_5CH{=}CH_2]$, was prepared by the addition of diisobutylaluminum hydride to 1,7-octadiene. The reaction mixture was heated at 70° for 16 h. The reaction vessel was similar to that used in the above reactions. The desired product formed a 1/1 trimethylamine when mixed with an excess of the amine. The NMR spectra of diisobutyl(1-oct-7-enyl)aluminum and diisobutyl(1-oct-7-enyl)aluminum—trimethylamine adduct are listed in Table 4. Cryscopic molecular weight measurements indicated a molecular weight of 400.07 (R_2AlR' calcd. 252.0).

The synthesis of this compound was attempted again using different reaction conditions (Table 5). The mixture was heated at 130° for 16 h at which time the excess diene was removed and the remaining organoaluminum compound hydrolyzed with 10% v/v HCl/H_2O mixture. The mixture was then extracted with diethyl ether and dried over anhydrous magnesium sulfate. The products were identified by comparison of retention times with authentic samples on a 30% SE-30 gas chromatography column. The results of this experiment are listed in Table 5.

Diisobutyl(n-octyl)aluminum

Diisobutyl(n-octyl)aluminum, $(i\text{-}C_4H_9)_2Al[(CH_2)_7CH_3]$ was prepared by the reaction of diisobutylaluminum hydride with 1-octene. The reaction mixture was heated at 70° for 16 h. The product formed a 1/1 adduct when mixed with trimethylamine at room temperature. The NMR parameters of diisobutyl(n-octyl)-aluminum and the diisobutyl(n-octyl)aluminum—trimethylamine adduct are listed in Table 4. Cryoscopic molecular weight measurements indicated a molecular weight of 412.3 (R_2AlR' calcd. 254.0).

Diisobutyl(1-undec-10-enyl)aluminum

Diisobutyl(1-undec-10-enyl)aluminum, $(i\text{-}C_4H_9)_2Al[CH_2(CH_2)_8CH{=}CH_2]$, was prepared by the addition of diisobutylaluminum hydride with 1,10-undecadiene. The reaction mixture was heated at 70° for 16 h. The product diisobutyl-(1-undec-10-enyl)aluminum formed a 1/1 adduct when mixed with trimethylamine at room temperature. The NMR parameters of diisobutyl(1-undec-10-enyl)-aluminum and diisobutyl(1-undec-10-enyl)aluminum—trimethylamine adduct are listed in Table 4. Cryoscopic molecular weight measurements indicated the molecular weight to be 305.8 (R_2AlR' calcd. 294.0).

Results and discussion

The studies on the reaction of 1-hex-5-enyl metal derivatives of lithium, aluminum, gallium, and indium have shown that complete cyclization occurs when reaction between di-1-hex-5-enylmercury and the appropriate metal is carried out under the conditions described in Table 1.

NMR spectra taken at intervals less than required for complete reaction gave rise to complex patterns resulting from mixtures which contained unreacted di-hex-1-enylmercury, alkenylmetal derivatives, and cyclized products for all reactions except those involving aluminum in a non-coordinating solvent. In the latter case, only unreacted starting material and cyclized product were observed.

These data and subsequent studies outlined below lead to the proposed reaction scheme shown in eqns. 1 and 2 in which initial metal exchange occurred, followed by cyclization. The reaction may be further complicated by additional exchange steps such as those shown in eqns. 3 and 4 which lead to the formation of the cyclic mercury derivative $Hg[CH_2(cyclo\text{-}C_5H_9)]_2$. This situation pertains for M = Li, but was not observed for any of the other metals studied under the conditions used. The route for the formation of the $Hg[CH_2(cyclo\text{-}C_5H_9)]_2$ was confirmed by separate experiments in which neat samples or solutions of $Hg[(CH_2)_4CH{=}CH_2]_2$ in the absence of a second metal were heated for extended periods of time. The products obtained from these reactions were mercury, unreacted starting material, and a variety of pyrolysis products. No detectable amounts of $Hg[CH_2(cyclo\text{-}C_5H_9)]_2$ were present. An interesting qualitative observation made on the lithium/$Hg[(CH_2)_4CH{=}CH_2]_2$ system was that near the end of the reaction time used essentially all of the starting mercury compound had been cleaved by the lithium while significant amounts of $Hg[CH_2(cyclo\text{-}C_5H_9)]_2$ remained. This leads immediately to the conclusion that the cleavage of the cyclic mercury compound is significantly slower than the cleavage of the straight chain derivative.

$$\frac{n}{2}Hg[(CH_2)_4CH{=}CH_2]_2 + mM \rightarrow mM[(CH_2)_4CH{=}CH_2]_n + \frac{n}{2}Hg \qquad (1)$$

$$mM[(CH_2)_4CH{=}CH_2]_n \rightarrow mM[CH_2(cyclo\text{-}C_5H_9)]_n \qquad (2)$$

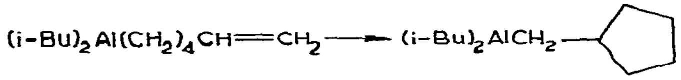
$$M[CH_2(cyclo\text{-}C_5H_9)]_n + Hg[(CH_2)_4CH{=}CH_2]_2 \rightleftharpoons \{M[CH_2(cyclo\text{-}C_5H_9)]_{n-1}\text{-}[(CH_2)_4CH{=}CH_2] + Hg[CH_2(cyclo\text{-}C_5H_9)][(CH_2)_4CH{=}CH_2]\} \qquad (3)$$

$$M[CH_2(cyclo\text{-}C_5H_9)]_n + Hg[CH_2(cyclo\text{-}C_5H_9][(CH_2)_4CH{=}CH_2] \rightleftharpoons Hg[CH_2(cyclo\text{-}C_5H_9)]_2 + M[CH_2cyclo\text{-}C_5H_9)]_{n-1}[(CH_2)_4CH{=}CH_2] \qquad (4)$$

In subsequent studies the effect of solvent on the cyclization was investigated both for the lithium reaction and for the reaction of diisobutylaluminum hydride with 1,5-hexadiene. For the solvent effects on the lithium exchange followed by cyclization, the results are collected in Table 1. These data show that the time required for complete exchange and cyclization is solvent-dependent and follows the order cyclopentane $<$ benzene $\lll$ diethylether with reaction times of 8 days, 96 h and < 1 h, respectively. These times are significant when the reaction is used for synthetic purposes, but are of limited value for kinetic interpretation since the overall reaction involved is sequential with the first step the metal exchange indicated in eqn. 1 followed by cyclization as shown in eqn. 2. No studies have been made which show the specific rates for the cyclization step under the various conditions.

In the second reaction, the reaction of diisobutylaluminum hydride with 1,5-hexadiene, a two step reaction, occurs as shown in eqns. 5 and 6. Again the

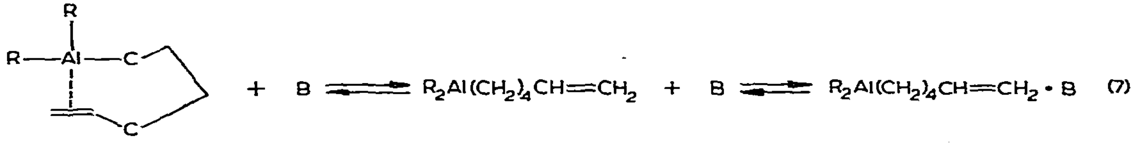
$$(i\text{-Bu})_2AlH + H_2C{=}CH(CH_2)_2CH{=}CH_2 \longrightarrow (i\text{-Bu})_2Al(CH_2)_4CH{=}CH_2 \qquad (5)$$


(6)

solvent affects the reaction markedly. In hydrocarbon solvents no unsaturated aluminum derivative could be isolated, while in coordinating solvents species containing an unsaturated moiety could be observed. It was found that in THF no cyclopentylmethyl derivative was formed, but under identical conditions, except for the change in solvent to diethyl ether and to diphenyl ether, 4.9% and 95% of the cyclopentylmethyl derivative were formed, respectively (see Table 3).

These solvent effects may be interpreted in terms of the interaction of the solvent on the species present in solution and the role these species play in the cyclization process. For the lithium derivative, the increase in solvent polarity increases both the rate of the metal exchange and the rate of the cyclization process. These changes are in accord with the known behavior of metal exchange for lithium derivatives and the enhanced reactivity of organolithium species in basic media in which the lithium aggregate size is decreased [10]. For the reaction involving the aluminum species, the opposite trend is observed; i.e., in the more basic solvents, the cyclization reaction is reduced or stopped.

This clearly is a reflection of the fact that the reactive aluminum species is a monomer which contains a vacant orbital available for interaction with the double bond. The effect of the basic solvent is clearly shown in eqn. 7. The

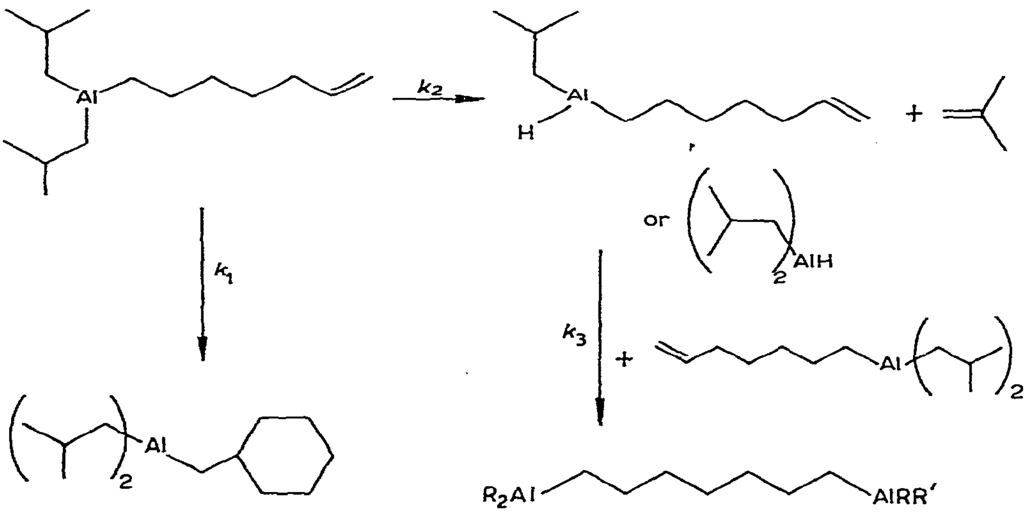

(7)

base B interacts with the vacant oribtal on the aluminum monomer, thus removing it from the reaction system. The relative stability of the aluminum—base adduct will determine the rate of cyclization, therefore, since this will determine the concentration of the monomer and of the reactive species. This is clearly illustrated by the data given in Table 3.

Preliminary studies by Hata and Miyaki [2] established that diisobutyl-(1-hept-6-enyl)aluminum yields 1% cyclohexylmethyl derivative under their normal reaction conditions (70°) and that on increasing the temperature to 125° a small increase in the cyclic product (to 8.5%) was observed along with extensive coupling reactions. In view of these results and our success at formation of the cyclopentyl derivatives, we concluded that variation of reaction conditions might result in improved yields of cyclic product and might further provide a route to larger ring systems.

We observed that if after the synthesis of diisobutyl(1-hept-6-enyl)aluminum the excess diene was removed and cyclopentane solvent added and the cyclization then carried out by maintaining the reaction mixture at 50°, a 44.2% yield of methylcyclohexane was recovered on hydrolysis of the reaction mixture. Various reaction conditions are shown in Table 5. The best yield obtained was 66.7% after workup when the reaction was carried out at 130°. The reaction path is obviously complex and the products obtained will depend on the relative rates of several competing paths, some of which are illustrated in Scheme 1. The best yields of cyclic products will result from optimization of both kinetic and thermodynamic considerations for these systems. Similar studies were also made on diisobutyl-1-oct-7-enylaluminum in an attempt to cyclize the 1-oct-7-enyl group to a cycloheptylmethyl derivative. The conditions for one of the reactions are listed in Table 5 and show no formation of cycloheptyl product.

SCHEME 1



To further characterize the systems under investigation and to provide additional information about the effects of chain length on the intramolecular interaction between the metal and the double bonds in these derivatives, studies were carried out to determine the average molecular weight in solution. The molecular weights were determined cryoscopically for a series of diisobutylalkenyl- and diisobutylalkyl-aluminum derivatives and are given in Table 6. These data show that for saturated derivatives there is a shift in the equilibrium toward monomer with increasing chain length and/or bulkiness of the organic groups. This is in full accord with other data in the literature which shows that dissociation of alkylaluminum species increases with increasing steric hindrance of the organic moieties [11—13].

Examination of the data for the unsaturated species shows a quite different pattern with the butenyl-, pentenyl- and heptenyl-aluminum derivatives primarily monomeric, a shift toward dimer for the octenyl species and finally a decrease again to monomer for diisobutylundecenylaluminum. Further, a direct comparison between the related pairs of aluminum species given in Table 6 shows that for the butenyl—butyl, pentenyl—pentyl and diisobutyl(heptenyl)—diisobutyl(n-heptyl) pairs the equilibrium is shifted far toward monomer for the unsatur-

TABLE 6

THE AVERAGE DEGREE OF AGGREGATION OF SEVERAL ALKYL- AND ALKENYL-ALUMINUM DERIVATIVES DETERMINED CRYOSCOPICALLY IN CYCLOHEXANE SOLUTION

Compound	M [a]	n [b]
$Al(CH_3)_3$ [c]	0.22	1.97
$Al[(CH_2)_3CH_3]_3$ [c,d]	0.081	1.96
$Al[(CH_2)_2CH{=}CH_2]_3$ [c]	0.042	0.98
$Al[(CH_2)_4CH_3]_3$ [c]	0.057	1.80
$Al[(CH_2)_3CH{=}CH_2]_3$ [c]	0.057	0.99
$Al(C_6H_{13})_3$ [d]		1.89
$Al(i\text{-}C_4H_9)_2[(CH_2)_6CH_3]$	0.055	1.81
$Al(i\text{-}C_4H_9)_2[(CH_2)_5CH{=}CH_2]$	0.043	1.15
$Al(n\text{-}C_8H_{17})_3$ [d]		1.77
$Al(i\text{-}C_4H_9)_2[(CH_2)_7CH_3]$	0.061	1.62
$Al(i\text{-}C_4H_9)_2[(CH_2)_6CH{=}CH_2]$	0.062	1.58
$Al(i\text{-}C_4H_9)_2[(CH_2)_9CH{=}CH_2]$	0.026	1.04
$Al(neo\text{-}C_5H_{11})_3$ [d]		1.02
$Al[CH_2(C_2H_5)CH(CH_2)_3CH_3]_3$ [d]		0.93

[a] M = molality. [b] $n = K_fM/\Delta t$. [c] Ref. 13. [d] Ref. 12.

ated species; but when one attains a chain length of 8 carbons in the octenyl—octyl pair, there is no experimentally significant difference between the molecular weights of the saturated and unsaturated species. This observation indicates that the metal—multiple bond interaction is no longer sufficient to perturb the equilibrium to a measurable extent for the octenyl derivative.

The observed monomeric nature of diisobutylundecenylaluminum is most likely due to the general trend toward monomer with increasing chain length [12] and in part is a result of the lower concentrations used which will also favor monomer. There are not sufficient data available, however, to fully evaluate the factors involved.

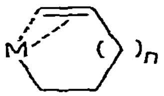
It has been shown that NMR parameters of unsaturated organoaluminum species may provide information regarding possible metal—double bond interactions [13]. The NMR parameters for the aluminum derivatives reported in this paper are given in Table 4. The compounds studied are diisobutyl(1-hept-6-enyl)diisobutyl(n-heptyl)-, diisobutyl(1-oct-7-enyl)-, diisobutyl(n-octyl)-, diisobutyl(1-undec-10-enyl)aluminum and their trimethyl adducts. Examination of both the chemical shifts and the coupling constants of the various derivatives shows that little perturbation of the NMR parameters occurs, unlike the changes noted elsewhere for the pentenylaluminum species [13], and therefore this approach does not provide additional information concerning the interaction.

Conclusions

It is clear from the studies described in this work that 1-hex-5-enyl derivatives of lithium and of Group III metals may be cyclized to cyclopentylmethyl species under a variety of experimental conditions with a high yield of the cyclic product. This product may be hydrolyzed, pyrolyzed to the methylenecyclopentane, or could be used in subsequent reaction steps. Similarly, although less efficiently, diisobutyl(1-hept-6-enyl)aluminum may be cyclized to the methylcyclohexane derivative.

The ease of these reactions makes them potentially useful for synthesis of compounds containing 5- and 6-membered rings.

The study of reaction times, solvent effects, and physical measurements of the unsaturated organometallic species all lead to the conclusion that the cyclization reaction proceeds via a complex reaction path with initial formation of the alkenylmetal derivative. The cyclization then occurs with prior formation of a metal—double bond complex as suggested both for intra- and inter-molecular processes involving metal—carbon bond addition to olefins [13—16]. The complex critical to the cyclization step is illustrated in I.



(I)

The rate of formation of the final cyclic product will depend on a variety of factors and may be controlled in any of several steps. This has clearly been shown for the reactions of aluminum derivatives in which the rate controlling step for formation of $Al[CH_2(cyclo\text{-}C_5H_9)]_3$ is the formation of the unsaturated aluminum derivative indicated in eqn. 1 while cyclization of the diisobutyl(1-hept-6-enyl)aluminum appears to be controlled by formation of the metal—double bond complex shown in I.

Additional studies on the factors governing the rates of reaction and stereochemistry of the products are currently under investigation and will be provided at a later date.

Acknowledgement

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