J. Org. Chem. **1993,** *58,* 6377–6389 **6377**

Experimental and Theoretical Investigations on the Structure and Reactivity of α-Lithiomethoxyallene and Its Grignard Analog

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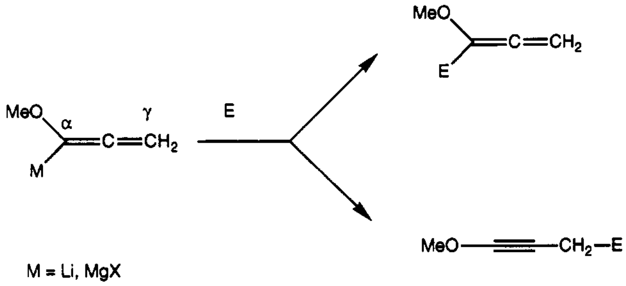
Received May 4, 1993[•]

^{13}C NMR, ^{6}Li,^{1}H-HOESY-NMR, and IR spectroscopy of α-lithiomethoxyallene (7) and 1-lithio-1-ethoxy-3-*tert*-butylallene (8) as well as *ab initio* model calculations on monomeric and dimeric α-lithio*hydroxy*allene prove 7 and 8 to be dimeric in THF (7 forms a tetramer in diethyl ether) with a nonclassically 1,3-bridged structure. Alternative oxygen-coordinated structures could be excluded definitely. *Ab initio* calculations indicate that the methoxyallene α-Grignard derivative either has a classic allenic structure or an O-coordinated allenic form (or is a mixture of both) in solution. An alternative propargylic-type isomer is unfavorable energetically. Model computed reactions with hydrogen as the electrophile indicate that the regiospecific α-substitution of α-lithiomethoxyallene is favored kinetically over the γ-substitution. In contrast, the reaction of the classic (α-hydroxyallenyl)-magnesium hydride with an electrophile leads to the formation of an alkyne (by γ-substitution) while that of the O-coordinated isomer yields the corresponding allene (by α-substitution).

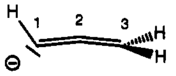
Introduction

In synthesis, α-metalated methoxyallene serves as an α,β-unsaturated acyl anion equivalent.[1] While the lithium derivative reacts with electrophiles exclusively at the α-C atom to give α-substituted methoxyallenes, the Grignard reagent yields mixtures of allenic and (by γ-substitution) of alkynic derivatives (Scheme I).[1,2] We used NMR and IR techniques to elucidate the structure of α-lithiomethoxyallene in solution and performed *ab initio* calculations on lithium and Grignard model compounds to investigate the regioselectivity of the substitution reaction.

Scheme I



Due to their unusual structural and electronic features as well as the ambident nucleophilicity, allenic anions have been the topic of many experimental[3] and theoretical[4] studies. The parent H_2CCCH^- anion *in principle* could adopt two different forms (besides cyclopropenyl anion and propynyl anion which is the global minimum structure[4e]): the allenic anion 1 and the propargylic isomer **2a**. It is now well established by photoelectron spectroscopy[5] and by *ab initio* calculations[4g] that the allenic-type structure 1 is the only minimum structure of H_2CCCH^- in the gas phase.



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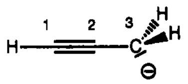
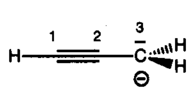


2a



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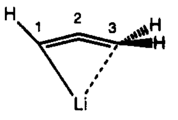

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However, the structure of H_2CCCH^- might be quite different in solution and in the solid state where contact ion pairs are present. *Ab initio* calculations predicted for

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• Abstract published in *Advance ACS Abstracts,* October 1, 1993.

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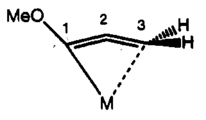
allenyllithium a nonclassically 1,3-bridged arrangement 3.[4b,e] A conventional allenic structure with the lithium cation located in the direction of the deprotonated hydrogen atom could not be found. Indeed, the bridged type was observed in the crystal structures of the lithium salt of 2,2,5,8,8-pentamethyl-3,6-nonadiyne[4d,6,8] as well as in the lithium salt of 2,2,8,8-tetramethylnon-3-yne-5,6-diene.[4d,6,8] In contrast, the sodium salt of 2,2,5,8,8-pentamethyl-3,6-nonadiyne[7] shows a more classic nonbridged arrangement.

The ^{13}C NMR spectrum of allenyllithium in THF also is in agreement with the allenic type structure: the chemical shift of C2 (196.4 ppm)[9] resembles that of neutral allene (212.6 ppm), rather than C2 of propyne (82.4 ppm). In addition, the IR spectra of allenyllithium and some other lithiated allenic derivatives show asymmetric valence vibrations around 1880 cm^{-1}.[10] Although these frequencies are lowered considerably compared to neutral allene derivatives (1930–1970 cm^{-1}),[11] they were interpreted in terms of allenic type structures of the organometallic compounds.[10a,12] In contrast, CC-triple bond vibrations of neutral alkynes are observed in the 2100–2250 cm^{-1} region.[11] Although these facts show that allenyllithiums favor allenic rather than propargylic type structures, reactions with electrophiles can give alkyne as well as allene products (or often mixtures of both) depending on the nature of the substituents and the electrophiles.[12]

The structures of the allenic Grignard compounds are less unambiguous than those of the lithium derivatives. The reactions of magnesium either with propargyl bromide or with allenyl bromide both resulted in the formation of allenylmagnesium bromide[13] with an IR absorption band at 1885 cm^{-1}.[14] However, various other Grignard reagents derived from substituted propargyl bromides show both an allenic valence vibration at ca. 1890–1910 cm^{-1} *and* an acetylenic band at 2160–2210 cm^{-1}.[15] Thus, allenic Grignards are involved in allenic and propargylic equilibria.[12] Again, reactions with electrophiles give allenes or alkynes or mixtures of both.[2]

The α-metalated methoxyallene is a very useful acyl anion synthon.[1] Besides the 1,3-bridged allenic form 4 and the propargylic isomer 5, a third oxygen-coordinated form 6 is conceivable. In this paper we investigate the structure of α-lithiomethoxyallene (7) and of 1-lithio-1-ethoxy-3-*tert*-butylallene (8) experimentally in etheral solutions using IR and NMR methods. Compound 8 was synthesized to avoid problems with the rearrangement of 7 into the acetylenic isomer 9 (which proceeds very rapidly at temperatures above −20 °C).[1a] *Ab initio* calculations on monomeric and dimeric lithium model compounds (metalated *hydroxy*allenes) help to clarify the structures. In addition, we reinvestigated the structure of various monomeric and dimeric allenyllithium species[4b,e] as well as Grignard derivatives computationally. Furthermore, we examined the reaction of monomeric α-lithiated *hydroxy*allene (as a model compound) and of the analogous Grignard reagents with hydrogen as the simplest model electrophile to probe the regiospecificity of the electrophilic substitution.



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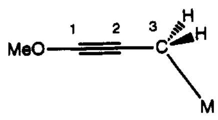

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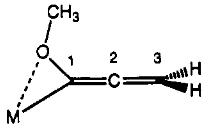

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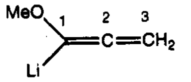

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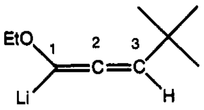

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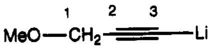

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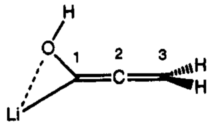

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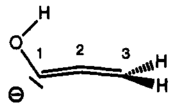

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Experimental Section

1-^{6}Lithio-1-ethoxy-3-*tert*-butylallene (8). 1-Ethoxy-3-*tert*-butylallene[16] (587 mg, 4.2 mmol) was dissolved in 3 mL of hexane. To this solution was added 3.15 mL of a 1.33 M solution of *n*-Bu-^{6}Li in hexane[17] (1 equiv) at −50 °C. After stirring for 10 min, 1 equiv (0.63 mL) TMEDA was added. During the addition, a precipitate formed which dissolved after adding the complete amount of TMEDA. After stirring at 0 °C for ca. 0.5 h the resulting solution was filtered and the filtrate cooled to −78 °C. After 1 d, colorless crystals ($8 \cdot TMEDA_{0.5}$ by integration of an ^{1}H NMR spectrum) formed which were recrystallized from hexane.

NMR Spectra. ^{13}C NMR spectra were recorded with a JEOL GX400 NMR spectrometer at 100.6 MHz and ^{1}H NMR spectra at 400 MHz. d_8-THF was used as the solvent or diethyl ether with an external d_6-acetone standard. The samples were prepared by weighing ca. 3 mmol of methoxyallene[1a] or 1-ethoxy-3-*tert*-butylallene[16] under argon in a 10-mm NMR tube which was sealed with a rubber septum. Ca. 1.5 mL of the solvent was added via a syringe. To this solution, 1 equiv of ^{6}Li-labeled *n*-BuLi[17] (the original hexane solvent was replaced by ca. 1.5 mL of THF or diethyl ether) was added via a syringe at ca. −78 °C for methoxyallene and ca. −20 °C for 1-ethoxy-3-*tert*-butylallene. The final concentration was ca. 1 M. The NMR spectra were

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Table I. *Ab initio* Calculated Selected Geometrical Parameters (Å, deg), HF-Natural Charges ρ (au), C=C=C Valence Vibration Frequencies (cm^{-1}), and Relative Energies ΔE (kcal/mol) of Monomeric (3) and Dimeric (10) Allenyl- and Propargyllithium (11) and the Free Allenyl Anion 1 as Well as the Free Propargyl Anions 2a and 2b at the MP2(FU)/6-31G*//MP2(FU)/6-31G* + ΔZPE Level^a

	1:^{b} C_s	2a:^{b} C_s (NIMAG = 1)	2b:^{b} C_{2v} (NIMAG = 2)	3: C_s	10: C_{2h}	11: C_{2h}
C1–C2	1.280 (1.276)	1.248 (1.223)	1.249 (1.224)	1.276 (1.269)	1.296 (1.284)	1.248 (1.214)
C2–C3	1.366 (1.346)	1.397 (1.386)	1.388 (1.384)	1.373 (1.344)	1.345 (1.327)	1.410 (1.402)
C1–Li				2.057 (2.015)	2.265 (2.303)	
C3–Li						2.454 (2.562)
C1′–Li					2.133 (2.139)	
C3′–Li						2.151 (2.159)
H1–C1–C2	128.18 (118.47)	179.54 (178.99)	180.00 (180.00)	135.71 (127.94)	119.59 (116.51)	152.78 (160.05)
C1–C2–C3	172.83 (175.73)	176.96 (178.93)	180.00 (180.00)	156.53 (160.88)	164.75 (168.23)	163.96 (168.10)
Li–C1–C2				68.55 (71.49)	64.55 (65.29)	
Li–C3–C2						58.03 (56.55)
ΣC3^c	359.59 (359.98)	351.34 (357.99)	360.00 (360.00)	355.84 (357.37)	358.29 (359.03)	336.55 (333.43)
ρ_{C1}^{d}	−0.497	−0.424	−0.433	−0.457	−0.573	−0.291
ρ_{C2}	−0.029	+0.043	+0.035	−0.059	−0.035	+0.021
ρ_{C3}^{d}	−0.474	−0.619	−0.602	−0.403	−0.257	−0.594
ρ_{Li}				+0.918	+0.864	+0.863
ν^f	1885 (1817)			1900 (1868)	1894^e (1894)^e	1987 (2050)
ΔE	–	–	–	–	0.00	1.33
ΔE	0.00	3.74	3.60	–	–	–

^{a} Values in parentheses are from HF/6-31G* optimized geometries. ^{b} 6-31+G* basis set. ^{c} Angle sum at C3. ^{d} Charges of the hydrogen atoms are summed to the heavy atom. ^{e} Experimental reference values.[10a] ^{f} MP2 (HF) frequencies scaled by 0.966 (0.922).

recorded at ca. −90 °C (for the conditions, see Table III). Resolution inhancement (Gaussian window) was applied to the ^{13}C signal for which ^{6}Li,^{13}C coupling was expected.

The ^{6}Li,^{1}H-HOESY spectra were determined on an in situ generated solution of ^{6}Li-labeled lithiomethoxyallene in d_8-THF and a solution of crystals of 1-lithio-1-ethoxy-3-*tert*-butylallene·TMEDA$_{0.5}$ (8·TMEDA$_{0.5}$) in d_8-THF. The mixing times were 2.0 s. A 1 M aqueous solution of LiBr was used as a standard for the ^{6}Li spectra.

IR Spectra. Precooled solutions of 1-lithio-1-ethoxy-3-*tert*-butylallene (8) in THF, diethyl ether, and hexane + 7% THF as well as α-lithiomethoxyallene (7) in THF (prepared similarly to the NMR samples) were transferred via syringes into a liquid cell with KBr windows. IR spectra were recorded in the 2400–1700 cm^{-1} region at ambient temperature using a Beckman AccuLab 3 IR spectrometer (even a lithiomethoxyallene solution proved to be stable at rt the few minutes needed for the measurement).

Computational Methods

Optimizations were carried out at the HF level using the gradient optimization techniques implemented in the GAUSSIAN 90[18] and 92[19] program packages. Comparison between the HF/6-31G* and the MP2(FU)/6-31G* optimized monomeric and dimeric allenyl and propargyllithium derivatives showed that the influence of electron correlation on the geometries is negligible (see Table I). Thus, HF geometries were used. While the 6-31G* basis set was applied for the larger dimeric allenyl and propargyllithium species, as well as for their hydroxy derivatives, the 6-31+G* basis set was used for all other lithiated and neutral parent compounds. A truncated 6-31(+)G* basis set (diffuse functions only on carbon and oxygen) was employed for all magnesium compounds.[20] This truncated basis set was used since severe SCF convergence problems were experienced with the 6-31+G* basis set. Electron correlation was taken into account with MP2(FC) single point calculations with the 6-31+G** and the 6-31(+)G** basis sets on the HF optimized geometries of the lithium and magnesium compounds, respectively. MP2(FC)/6-311(+)G*//HF/6-31G* single point calculations were performed on the dimeric (hydroxyallenyl)- and -propargyl)lithium species in order to minimize the basis set superposition error.[21] All species were shown to be either minima (number of imaginary frequencies (NIMAG) = 0) or transition structures (TS) (NIMAG = 1) by diagonalization of the force constant matrix. Except otherwise noted, all species mentioned in this article are minimum structures. The relative energies were corrected for zero point vibration (ZPE) (scaled by 0.89 for the HF and by 0.94 for the MP2 frequencies).[20] Population analyses were carried out using the *natural bond orbital* (NBO) program of Weinhold and Reed.[22]

Results and Discussion

A. Structure of Allenyllithium. The allenyl anion 1 was optimized at MP2(FU)/6-31+G* for comparison. The two C–C distances of the slightly bent anion (α(CCC) = 173°) are quite different (1.280 and 1.366 Å, see Table I) in agreement with previous calculations by Li.[4g] The negative charge is localized mainly at C1 (−0.497) and at C3 (−0.474). The propargylic anion structure **2a** is not a minimum, but rather the transition structure for the inversion of 1 at C1. The charge is mainly concentrated at the pyramidalized C3 atom (−0.619). In contrast to the results at lower HF level by Li[4g], the C_{2v} structure **2b** is *not* the TS for the inversion at C1, but exhibits *two*

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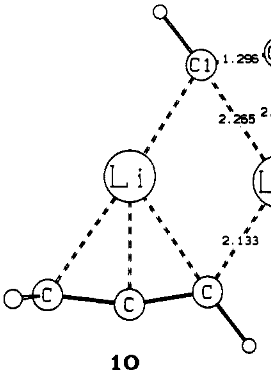
Chart I



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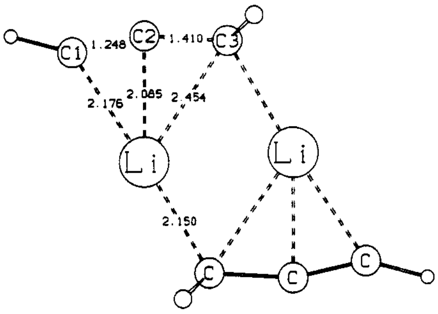
MP2(FU)/6-31G*



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MP2(FU)/6-31G*

imaginary frequencies at higher HF/6-31G* and HF/6-31+G* levels as well as at the MP2(FU)/6-31+G* level.[23]

The only monomeric minimum energy structure of allenyllithium is the 1,3-bridged form **3** at the MP2(FU)/6-31G* level[25] (see Table I). The CC distances are essentially the same as in the free anion. However, the anionic moiety is bent to a higher degree (157° in **3** vs 173° in **1**). As in the free anion, the charge in **3** is mainly localized at C1 (−0.457) and at C3 (−0.403). Due to the charge localizing influence of the lithium gegenion,[24] the charge is shifted somewhat toward C1. Compared to vinyllithium, the C1–C2 separation is shortened considerably (1.276 Å in **3** vs 1.354 Å in vinyllithium at MP2(FU)/6-31G*[25]) and the Li-C1-C2 angle is narrowed (68.6° vs 116.5°). Both effects in **3** are due to the stabilizing interaction (148.8 kcal/mol, from the NBO second-order perturbation analysis[22] at HF/6-31G*//MP2(FU)/6-31G*[26]) of the anionic lone pair orbital at C1 with the antibonding π^* orbital of the C2–C3 bond.

A dimeric allenyllithium aggregate **10** is formed by connecting two monomers **3** via a Li-C1-Li′-C1′ four-membered ring. As in the monomer **3**, the allenyl anion moieties of the dimer are bent significantly and the C3 atom is pyramidalized (the angle sum is 358.29°, see Table I). The C–C distances are almost the same in the dimer as in the monomer but differ from those in neutral allene (1.311 Å at MP2(FU)/6-31G*[25]). In contrast to the monomeric allenyllithium we were able to find a second dimeric structure **11** which could be conceived as a propargyllithium dimer (note the strong pyramidalization at C3). The C1–C2 bond (1.248 Å) is somewhat longer than the triple bond in propyne (1.218 Å at MP2(FU)/6-31G*[25]) and the C2–C3 bond (1.410 Å) is shorter than in propyne (1.461 Å at MP2(FU)/6-31G*[25]) due to conjugation of the anionic C3-lone pair orbital into the antibonding C2–C1 π^* orbital. In contrast to allenyllithium **10**, the negative charge in **11** is localized at C3 due to the contact to *two* lithium cations (−0.594 in **11** vs −0.257 in **10**). Therefore, the increased electrostatic Li-C3 interaction is responsible for the stability of a *dimeric* propargyllithium. Indeed, the X-ray structure of the dimeric lithium salt of 2,2,8,8-tetramethyl-2,5-trimethylsilyl-3,6-nonadiyne shows a propargyllithium moiety.[4d,6]

Table II. ***Ab initio* Calculated Selected Geometrical Parameters (Å, deg), HF-Natural Charges ρ (au), C=C=C Valence Vibration Frequencies (cm^{-1}), and Relative Energies ΔE (kcal/mol) of Monomeric (12, 14) and Dimeric (13, 15) (Hydroxyallenyl)lithium and Dimeric (Hydroxypropargyl)lithium (16) and the Free Hydroxyallenyl Anion 22 at the MP2(FC)/6-31+G**//HF/6-31+G* + ΔZPE Level for the Monomers and MP2(FC)/6-311(+)G*//HF/6-31G* + ΔZPE Level for the Dimers**

	22: C_s	12: C_s	13: C_i	14: C_s	15: C_{2h}	16: C_{2h}
C1–C2	1.302	1.299	1.307	1.296	1.299	1.205
C2–C3	1.329	1.329	1.316	1.309	1.306	1.441
C1–O	1.403	1.358	1.374	1.455	1.434	1.319
C1–Li		1.970	2.226	1.913	2.089	
C3–Li						2.355
C1′–Li			2.163		2.441	
C3′–Li						2.166
O–C1–C2	117.71	123.31	118.30	116.99	116.57	168.13
C1–C2–C3	176.68	161.85	168.33	177.94	177.08	167.46
Li–C1–C2		74.56	69.78	179.69	122.25	
Li–C3–C2						54.05
ΣC3^a	359.98	359.19	359.67	360.00	360.00	330.37
$\rho_O{}^b$	−0.381	−0.282	−0.289	−0.420	−0.391	−0.216
$\rho_{C1}{}^b$	−0.061	−0.199	−0.264	−0.267	−0.273	+0.155
ρ_{C2}	−0.230	−0.230	−0.173	−0.147	−0.141	−0.146
$\rho_{C3}{}^b$	−0.329	−0.221	−0.153	−0.102	−0.095	−0.669
ρ_{Li}		+0.921	+0.936	+0.878	+0.899	+0.877
ν^c	1820	1855	1906	1979	1987	2250
ΔE		0.00	–	2.37	–	–
ΔE		–	12.14	–	0.00	21.27

^{a} Angle sum at C3. ^{b} Charges of the hydrogen atoms summed to the heavy atom. ^{c} Computed C=C=C valence vibration frequencies scaled by 0.922 (see text).

It is known that frequencies calculated for C=C=C and C≡C bond vibrations of positively charged allenyl and propargyl species at HF and MP2 levels tend to be rather inaccurate.[27] Nevertheless, the agreement is fairly good between the experimental frequency of allenyllithium (1894 cm^{-1})[10a] and the calculated MP2 frequencies (scaled by 0.94) of **3** (1849 cm^{-1}) and of **10** (1844 cm^{-1}). The calculated frequency of **11** (1934 cm^{-1}) is much higher. The relative energies also favor **10** (0.0 kcal/mol) over **11** (+1.3 kcal/mol). Hence, C_3H_3Li has an allenic rather than a propargylic-type structure. For the correction of further

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(23) Although structure **2b** has two imaginary frequencies, it is 0.14 kcal/mol more stable than **2a** due to its smaller zero-point energy. The relative energies (kcal/mol) without ZPE correction are: 1 (0.00), **2a** (4.83), **2b** (5.08). The similar energies of **2a** and **2b** indicate that the hypersurface is quite shallow at these points. Higher theoretical levels will be necessary to access the true transition structure for the inversion at C1.

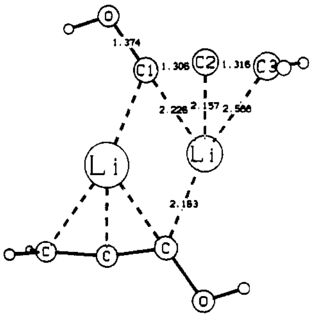
(24) For the charge-localizing influence of the gegenion, see ref 7 and Lambert, C.; Wu, Y.-D.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1993**, *255*, and literature cited therein.

(25) Quantum chemical archive of the Friedrich-Alexander Universität Erlangen-Nürnberg, unpublished.

(26) We stress that an interaction energy of this magnitude derived from a second-order perturbation analysis is by no means quantitative but only qualitative.

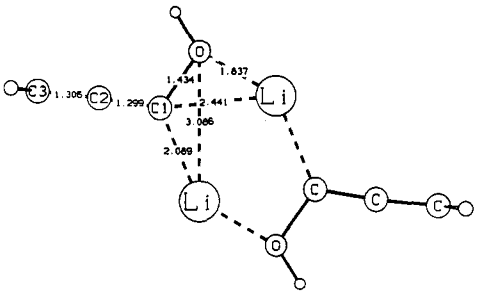
(27) Vancik, H.; Percac, K.; Buzek, P.; Schleyer, P. v. R., to be published.

Chart II



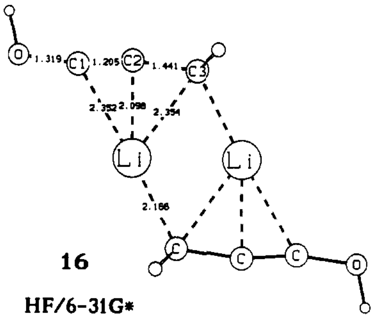
13

HF/6-31G*



15

HF/6-31G*



16

HF/6-31G*

frequency calculations we assumed that the error based on the HF and MP2 calculated frequencies vs the experimentally observed C=C=C valence vibration is proportional for all metalated allenyl and propargyl species. Therefore we calibrated the HF and MP2 calculated C=C=C frequencies using the dimer **10** as a reference for which the experimental C=C=C valence vibration (1894 cm^{-1}) is known. The new scaling factors are: HF = 0.922 and MP2 = 0.966 for the calculations of C=C=C valence vibrations.

B. Structure of α-Lithiomethoxyallene. Hydroxyallene was used as a model for methoxyallene for all *ab initio* calculations to minimize computational cost. The geometrical parameters of the monomeric (**12**) (for depictions of **12**, **17–21**, see reactions 1–9) and dimeric (**13**) 1,3-bridged forms of α-lithiohydroxyallene (see Table II) are similar to those of allenyllithium. However, **13** has C_i symmetry whereas **10** has C_{2h} symmetry. In contrast to **10**, the C3 arrangement is essentially planar in **13** and the anion moiety is less bent. The differences in the C1–C2 and C2–C3 separations also are less pronounced in the hydroxy derivatives **12** and **13** as well as in the free hydroxyallenyl anion **22** than in **3** or **10**. The smaller CC differences are due to the lower interaction energy of the C1-lone pair orbital in **12** with the C2–C3 antibonding π^* orbital (60.0 kcal/mol, from a NBO second-order perturbation analysis[22] at HF/6-31+G**//HF/6-31+G*[26]).

Both the oxygen-coordinated monomer **14** and the dimer **15** are minima on the hypersurface. C3 has a planar coordination sphere and the C–C distances are quite similar. The rather long C1–O separations in the lithium derivatives (1.455 Å in the monomer and 1.434 Å in the dimer) compared to the neutral hydroxyallene (1.357 Å) indicate some vinylidene carbenoid character. A similar C–O elongation was observed in the oxygen-coordinated isomer of lithiomethanol $LiCH_2OH$ (1.523 Å at MP2/6-311++G**[28]) vs methanol (1.421 Å at MP2/6-311++G**[28]). As in the case of the dimeric C_3H_3Li we also found a dimeric structure of (hydroxypropargyl)lithium **16**. The C1–C2 and C2–C3 distances (1.205 and 1.441 Å, respectively) resemble those of 1-propynol (1.185 and 1.472 Å, respectively). Again, the arrangement at C3 is strongly pyramidalized. A monomeric propargyllithium structure (corresponding to **5**) could not be located.

The oxygen-coordinated isomer **14** is 2.4 kcal/mol less stable than the 1,3-bridged form **12**. The order is reversed in the dimers: **15** is 6.1 kcal/mol (per monomer) lower in energy than **13**. We assume this to be due to the better coordination of the lithium cations by the oxygen atoms in the dimer **15** vs the monomer **14**. This stabilization should be reduced or even inverted by external solvation of the lithium cations. Despite several attempts to model a 1,3-bridged solvated dimeric lithiohydroxyallene, we were not able to find a useful minimum structure since hydrogen bonding between the hydroxy groups and the solvent model molecules (H_2O or HF) distorted the molecular geometry.

To establish the real structure of α-lithiomethoxyallene, we determined the NMR spectra in THF and diethyl ether as well as the IR spectra. Due to its tendency to rearrange into an alkynyllithium derivative at temperatures above −20 °C, lithiomethoxyallene had to be synthesized at ca. −78 °C in THF or diethyl ether and measured *in situ* without isolation of the metalated product. The NMR data are given in Table III.

In **7**, the ^{13}C signal of C1 is shifted ca. 30 ppm downfield and the C3 signal is ca. 20 ppm moved upfield vs the parent compound. The essentially unchanged C2 signal at ca. 195 ppm proves **7** to have an allenic structure both in THF and in diethyl ether. The C1 ^{13}C signal of a ^6Li-labeled lithiomethoxyallene exhibits scalar ^{13}C–^6Li coupling:[29] a quintuplet ($^1J_{^{13}C,^6Li} = 6.0$ Hz) at −100 °C in THF indicates a dimer, and a septuplet ($^1J_{^{13}C,^6Li} = 4.5$ Hz) at −93 °C in diethyl ether indicates a tetrameric aggregate (see Figure 1, parts a and b). In addition, the C3-H

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(28) (a) Boche, G.; Opel, A.; Marsch, M.; Harms, K.; Haller, F.; Lohrenz, J. C. W.; Thümmler, C.; Koch, W. *Chem. Ber.* **1992**, *125*, 2265. (b) Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467.

Table III. NMR Data of α-Lithiomethoxyallene and 1-Lithio-1-ethoxy-3-*tert*-butylallene as Well as the Neutral Parent Compounds (chemical shift in ppm)

		C1	C2	C3	C4	C5	OCH_2/OCH_3	OCH_2CH_3
methoxyallene	^1H NMR (26 °C, $CDCl_3$)	6.77 (t, 6.1 Hz)		5.48 (d, 6.1 Hz)			3.41 (s)	
methoxyallene	^{13}C NMR (26 °C, $CDCl_3$)	122.8	201.1	91.2			55.8	
7	^1H NMR (−86 °C, 0.71 M in d_8-THF)			3.81 (s)			3.31 (s)	
7	^{13}C NMR (−100 °C, 0.82 M in d_8-THF)	154.1	194.1	67.0			57.7	
7	^{13}C NMR (−93 °C, 1.26 M in diethyl ether)	150.4	195.4	69.8			56.7	
1-ethoxy-3-*tert*-butylallene	^1H NMR (25 °C, $CDCl_3$)	6.7 (d, 6 Hz)		5.8 (d, 6 Hz)		1.1 (s)	3.6 (q, 6 Hz)	1.3 (t, 6 Hz)
1-ethoxy-3-*tert*-butylallene	^{13}C NMR (25 °C, d_6-acetone)	122.5	190.1	117.1	32.9	29.2	63.4	14.3
$8\cdot TMEDA_{0.5}$	^1H NMR (−30 °C, 0.44 M in d_8-THF)			4.34 (s)		0.95 (s)	3.59 (q, 6.0 Hz)	1.14 (t, 6.0 Hz)
$8\cdot TMEDA_{0.5}$	^{13}C NMR (−30 °C, 0.44 M in d_8-THF)	159.3	188.1	96.8	32.7	31.6	64.6	16.1
8	^{13}C NMR (−92 °C, 1.20 M in THF, ext d_6-acetone)	157.9/158.0	186.5/186.4	95.4	31.8	30.5	63.7/63.6	14.6

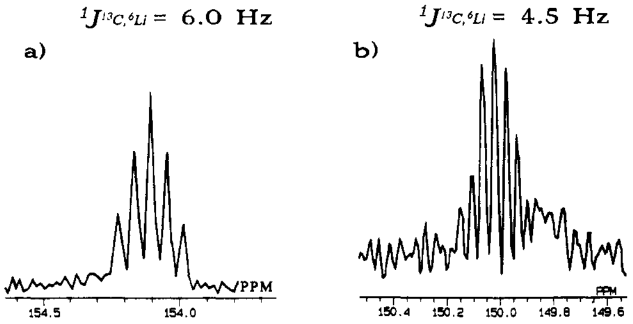

Figure 1. C1 ^{13}C NMR signal of ^6Li-labeled α-lithiomethoxyallene (7) (a) in d_8-THF at −100 °C and (b) in diethyl ether at −93 °C.

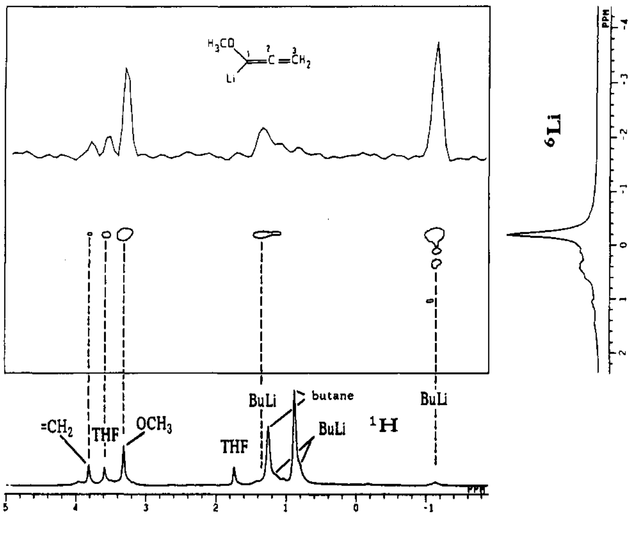

Figure 2. $^6Li,^1H$-HOESY spectrum of ^6Li-labeled α-lithiomethoxyallene (7) (0.71 M) in d_8-THF at 6 °C. Mixing time 2.0 s.[32]

coupling constant (from a gated decoupling NMR experiment) of 161.8 Hz in 7 compared with 162 Hz in allenyllithium[9] vs 167.5 Hz in methoxyallene[30] and 168 Hz in allene[9] also is in agreement with an allenic structure. However, neither the C–H coupling constant nor the NMR chemical shifts decide whether 7 has a nonclassically 1,3-bridged (4) or an O-coordinated allenic geometry (6).

Thus, we applied the $^6Li,^1H$-HOESY NMR technique (HOESY: heteronuclear Overhauser effect spectroscopy) which can be used to detect close proximities (ca. <3.5 Å) between ^1H and ^6Li nuclei.[29b,31] The HOESY spectrum of α-lithiomethoxyallene in THF solution (in which 7 is dimeric) is shown in Figure 2. Besides cross peaks between the Li signal and the protons of excessive *n*-BuLi and of THF,[32] there are two cross peaks involving the lithioallene: one to the methoxy protons at 3.31 ppm and one to the CH_2 protons of the allenic moiety at 3.81 ppm. From the *ab initio* calculations of dimeric lithiohydroxyallenes 13 and 15, Li–$C3H_2$ distances of 2.82 Å in the 1,3-bridged form 13 and of 4.69 Å in the O-coordinated form 15 result. The latter distance clearly is too long to cause a detectable Overhauser effect. Hence, the cross peak between the lithium signal and the $C3H_2$ protons rules out an O-coordinated isomer 15. In addition, the observation of a quintuplet for the C1 ^{13}C signal of 7 shows that C1 is coordinated by *two* lithium cations. However, in the hypothetical O-coordinated dimer 15 one Li–C separation only is 2.44 Å. This is probably too long to result in Li–C coupling. The scaled calculated C=C=C valence vibration frequency (1906 cm^{-1}) of 13 also is in good agreement with that observed in THF solution (1870 cm^{-1}). In contrast, we calculated a frequency at 1987 cm^{-1} for the O-coordinated dimer 15.

For comparison, we also investigated the structure of 1-lithio-1-ethoxy-3-*tert*-butylallene 8 in THF. Unlike α-lithiomethoxyallene, the 3-substituted lithium compound cannot rearrange into an alkynyllithium derivative and therefore is stable for a short period at ambient temperature. Although we were able to crystallize a complex of 8 with 0.5 equiv of TMEDA from hexane, the crystals unfortunately proved to be unsuitable for X-ray analysis.

In analogy to 7, significant changes in the ^{13}C NMR spectrum of 8 in THF only are observed for C1 and C3 compared to the neutral parent compound. The C1 ^{13}C signal of a ^6Li-labeled compound 8 is split into a six-line multiplet (see Figure 3). This is interpreted as the

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(29) For the relation of $^6Li,^{13}C$ couplings with the chemical structure, see e.g. (a) ref 17 and (b) Bauer, W.; Schleyer, P. v. R. *Adv. Carbanion Chem.* **1992**, *1*, 89.

(30) Runge, W. *Z. Naturforsch.* **1979**, *34b*, 118.

(31) (a) Bauer, W.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 970. (b) Bauer, W.; Schleyer, P. v. R. *Magn. Reson. Chem.* **1988**, *26*, 827.

(32) Due to fast chemical exchange even at −86 °C, there is only one ^6Li signal at −0.2 ppm observable both for lithiomethoxyallene *and* excess (ca. 20%) *n*-BuLi dimer. The HOESY cross peaks of the ^6Li signal with the α-protons at −1.1 ppm and the β-protons at 1.35 ppm of *n*-BuLi are very intense due to the small Li–H distances. The other Li signals between 1.1 and 0.1 ppm are due to small amounts of other *n*-BuLi aggregations (see ref 31a).

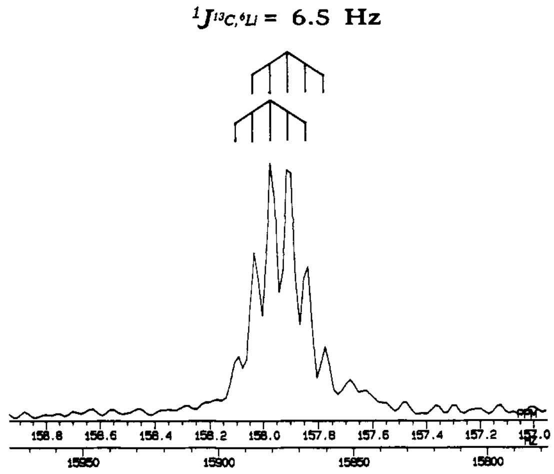

Figure 3. C1 ^{13}C NMR signal of ^6Li-labeled 1-lithio-1-ethoxy-3-*tert*-butylallene (8) in THF at −92 °C.

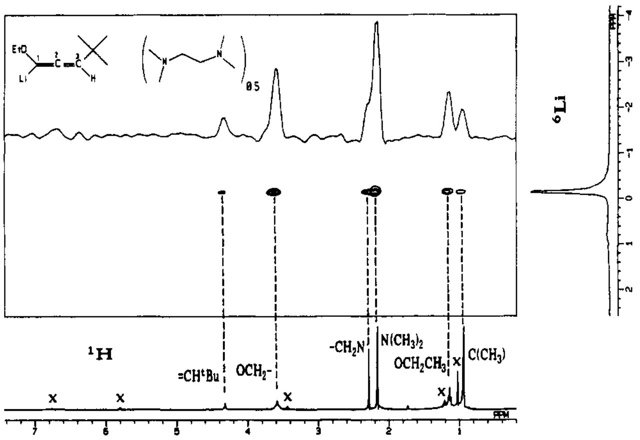

Figure 4. $^6Li,^1H$-HOESY spectrum of ^6Li-labeled 1-lithio-1-ethoxy-*tert*-butylallene·TMEDA$_{0.5}$ in d_8-THF at −60 °C. X denotes signals of the educt allene. Mixing time 2.0 s.

superposition of two quintuplets ($^1J_{^{13}C,^6Li}$ = 6.5 Hz) which are separated by ca. 6.5 Hz. Since 8 is chiral, the two quintuplets are assigned to a pair of enantiomeric dimers (*RR*-dimer and *SS*-dimer) and to the diastereomeric meso form of a dimer (*RS*-dimer). Since both diastereomeric dimers of 8 are formed in approximately equal amounts and the difference in the chemical shift of C1 of both diastereomers is approximately equal to the coupling constant, a six-line multiplet results. In addition, two equally intense singlets are observed for each, the C2 and the OCH$_2$ carbon atoms of the two diastereomers. A $^6Li,^1H$-HOESY spectrum of 8·TMEDA$_{0.5}$ in THF (Figure 4) shows ^6Li cross peaks to all protons of the lithioallene and the TMEDA molecule.[33] Again, the cross peak due to the H3 proton at 4.34 ppm indicates a 1,3-bridged structure for 8. In addition, the C=C=C vibrations of 8 in THF (1875 cm^{-1}), in diethyl ether (1880 cm^{-1}), and in hexane (1885 cm^{-1}) are very similar to that observed for 7 and also are in agreement with a dimeric 1,3-bridged allenic form.

Table IV. ***Ab initio* Calculated Selected Geometrical Parameters (Å, deg), HF-Natural Charges ρ (au) and Relative Energies ΔE (kcal/mol) of Allenyl- (17), Propargyl- (17), (Hydroxyallenyl)- (19, 20), and (Hydroxypropargyl)- (21) magnesium Hydride at the MP2(FC)/6-31(+)G**//HF/6-31(+)G* + ΔZPE Level**

	17: C_s	18: C_s	19: C_s	20: C_s	21: C_s
C1–C2	1.299	1.205	1.304	1.294	1.192
C2–C3	1.309	1.449	1.309	1.305	1.466
C1–Mg	2.086		2.100	2.076	
C3–Mg		2.145			2.122
Mg–C1–C2	113.08		114.51	170.38	
Mg–C3–C2		79.93			101.03
C1–C2–C3	176.53	165.02	175.83	177.77	175.67
H–C1–C2/ O–C1–C2	116.83	170.94	122.71	119.38	179.05
$\sum$C3^a	359.98	335.79	360.00	360.00	329.27
$\rho_O{}^b$			−0.305	−0.400	−0.210
$\rho_{C1}{}^b$	−0.741	−0.140	−0.300	−0.319	+0.272
ρ_{C2}	+0.053	−0.071	−0.153	−0.113	−0.188
$\rho_{C3}{}^b$	−0.144	−0.649	−0.063	−0.035	−0.684
$\rho_{Mg}{}^b$	+0.831	+0.860	+0.820	+0.867	+0.811
ΔE	0.00	1.66	–	–	–
ΔE	–	–	0.00	0.72	9.97

^{a} Angle sum at C3. ^{b} Charges of the hydrogen atoms summed to the heavy atom.

C. Structure of Allenylmagnesium Hydride. We computed monomeric allenylmagnesium hydride to model an allenic Grignard reagent. We assume the influence of the halogen atom to be negligible.[34] The allenic form 17 of C$_3$H$_3$MgH only is bent slightly (177°, see Table IV) compared to allenyllithium 3 (157°). The charge in 17 mainly is localized at C1 (−0.741 vs −0.144 at C3) due to the contact to the highly positive charged magnesium "dication" (charge +1.494 at HF/6-31(+)G**//HF/6-31(+)G*). The M–C1–C2 angle (113°) also is significantly wider than that of allenyllithium 3 (69°) and the C1–C2 and C2–C3 bond lengths (1.299 and 1.309 Å) in 17 are very similar. Allenylmagnesium hydride adopts a more classic allenyl structure due to the somewhat higher degree of covalency in the Mg–C1 bond (83% ionic) vs Li–C1 in 3 (92% ionic). Similar behavior was observed in allylic Grignard compounds[34a,35] which favor a classic monohapto structure rather than a symmetrically bridged geometry like the alkali-metal allyl compounds.[36]

Although only the allenic structure 17 could be observed experimentally,[13] we found a second *monomeric* minimum 18. This propargylic geometry is 1.7 kcal/mol less stable than 17 and has a strongly pyramidalized C3 atom environment. Interestingly, the C–C–C unit is bent more in 18 (165°) and the Mg–C3–C2 angle is smaller (80°) than in the allenic form 17. The charge in 18 is localized predominantly at C3 (−0.649) due to the gegenion contact. Again, the strong electrostatic stabilization is reponsible for the stability of a propargyl-M compound. While the bonding to a highly charged magnesium "dication" is enough to stabilize a *monomeric* propargylmagnesium

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[33] The HOESY cross peaks of the ethoxy and *tert*-butyl protons of 8 as well as of the methoxy protons of 7 can be explained by close Li–H proximities (ca. 2.5 to 3.0 Å) in the 1,3-bridged arrangements. The Li–OCH$_3$ distances can be estimated from a HF/6-31G* optimized dimer of 7 to be 2.84 Å (for a picture, see supplementary material).

[34] Magnesium hydride derivatives have been used frequently as models for Grignard reagents, see e.g. (a) Clark, T.; Rohde, C.; Schleyer, P. v. R. *Organometallics* **1983**, *2*, 1344. (b) Kaneti, J.; Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Andrade, J. G.; Moffat, J. B. *J. Am. Chem. Soc.* **1986**, *108*, 1481.

[35] Marsch, M.; Harms, K.; Massa, W.; Boche, G. *Angew. Chem.* **1987**, *26*, 696.

[36] (a) Boche, G.; Etzrodt, H.; Marsch, M.; Massa, W.; Baum, G.; Dietrich, H.; Mahdi, M. *Angew. Chem.* **1986**, *98*, 84. (b) Schümann, U.; Weiss, E.; Dietrich, H.; Mahdi, W. *J. Organomet. Chem.* **1987**, *322*, 299. (c) Seebach, D.; Maetzke, T.; Haynes, R. K.; Paddon-Row, M. N.; Wong, S. S. *Helv. Chim. Acta* **1988**, *71*, 299. (d) Corbelin, S.; Kopf, J.; Lorenzen, N. P.; Weiss, E. *Angew. Chem.* **1991**, *103*, 875. (e) Hommes, N. J. R. v. E.; Bühl, M.; Schleyer, P. v. R.; Wu, Y.-D. *J. Organomet. Chem.* **1991**, *409*, 307.

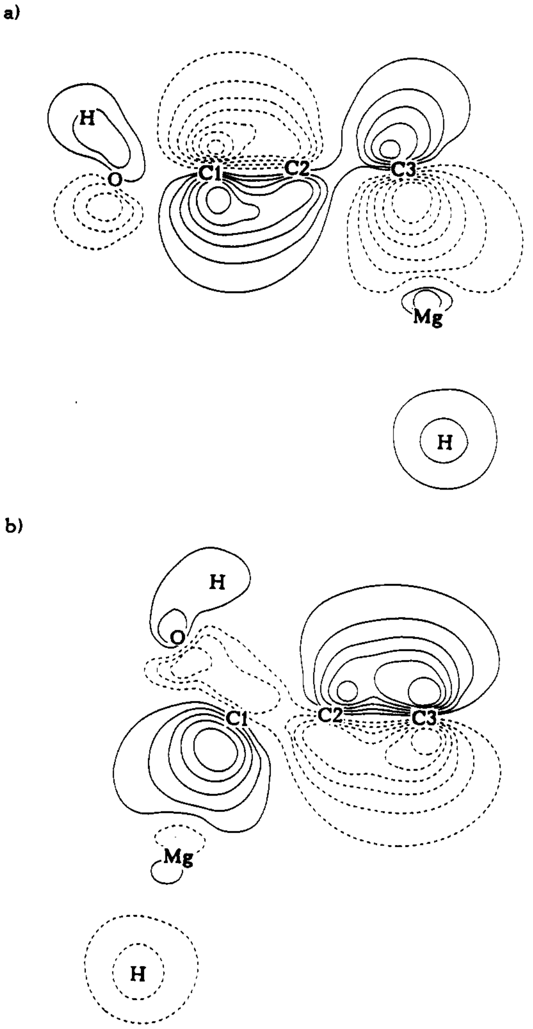

Figure 5. (a) Butadienyl-dianion-like π-HOMO (−0.31589 eV) of (hydroxypropargyl)magnesium hydride (**21**) at HF/6-31(+)-G**//6-31(+)G* level. (b) Allyl anion-like π-HOMO (−0.34545 eV) of (hydroxyallenyl)magnesium hydride (**19**) at the HF/6-31(+)G**//HF/6-31(+)G* level.

hydride, the contact to *two* lithium cations is needed to form a stable *dimeric* propargyllithium.

D. Structure of (α-Hydroxyallenyl)magnesium Hydride. The α-metalated hydroxyallene **19** has essentially the same geometry as the allenylmagnesium hydride **17** (see Table IV). In contrast to the allenylmagnesium hydride **17** and the propargylmagnesium hydride **18** which differ by only 1.7 kcal/mol in energy, the propargylic form **21** is 10.0 kcal/mol less stable than the allenic isomer **19**. The **21** and **18** geometries also differ: the C–C–C moiety is less bent in **21** (176° vs 165°) and the Mg–C3–C2 angle is wider (101° vs 80°). The differences in energies and geometries can be rationalized by a simplified MO scheme: the O–C1–C2–C3 system of **21** is almost linear. An oxygen lone pair orbital, C1 and C2 p-orbitals, and the anionic lone pair orbital of C3 (all lying in the C_s-plane of the molecule) form a butadienyl-dianion-like system.[37] The π-HOMO (see Figure 5a) is occupied with two electrons and is *antibonding* (two nodal planes). The molecule seeks to avoid this destabilizing interaction by bending away the anionic C3-lone pair. A wide C2–C3–Mg angle results. In contrast, the allenic isomer **19** forms an allyl-anion-like system. The π-HOMO (see Figure 5b) also is occupied with two electrons but is *nonbonding* (one nodal plane) and not destabilizing. The oxygen is not involved in the π-system of allenic type molecules, and similar structures for **17** and **19** result. However, in compounds with a propargylic geometry the interaction of the oxygen lone pair with the propargylic π-system is destabilizing. For this reason the dimeric forms of propargyllithium **11** and allenyllithium **10** are similar in energy but the propargylic hydroxy derivative **21** and **16** are 10.0 and 9.1 kcal/mol, respectively, less stable than the allenic species **19** and **13**.

In addition, there is a second allenic isomer **20** in which the magnesium is coordinated by the oxygen of the hydroxy group. This form only is 0.72 kcal/mol less stable than **19**. Since no experimental geometries or spectroscopic data of methoxyallene Grignard reagents are available, we cannot exclude that the α-metalated methoxyallene is an equilibrium mixture of both forms **19** and **20** in solution. However, the propargylic form **21** can be excluded due to its higher energy.

E. Reactivity of Allenyllithium and α-Lithiohydroxyallene. Insight into the regiospecificity of the electrophilic substitution of α-lithiomethoxyallene was gained by computing the reaction between monomeric α-lithio*hydroxy*allene and hydrogen (the simplest electrophile). We assume that the relative reaction barrier heights will govern the reaction course (kinetic control) since low temperatures normally are employed.

The hydrogenolysis of nonsubstituted allenyllithium **3** was calculated (reactions 1 and 2 in Charts III and IV, respectively) for comparison. Starting from the 1,3-bridged allenyllithium **3**, two reaction pathways are feasible: first, attack of H_2 (as the electrophile) at C1 can give allene (reaction 1) and second, attack at C3 gives propyne (reaction 2). While reaction 1 proceeds with an activation barrier of 18.7 kcal/mol via an C1–Li–H–H "four center" *allenic* type transition structure (similar CC bond lengths), reaction 2 has an activation energy of 17.4 kcal/mol and a C3–Li–H–H "four center" transition structure which has more *propargylic* character (quite different CC bond lengths). Both reactions lead to π-complexes of LiH and allene or of LiH and propyne. Dissociation leads to the free hydrocarbons and free LiH.

Although the overall thermodynamics of the hydrogenolysis reactions are endothermic, the relative activation barriers are comparable in a qualitative sense for all calculated systems and we can deduce the regiospecificity from these barriers. The quite similar activation barriers for the C1 and C3 attack (reaction 1 vs reaction 2) lead one to assume that the nature of the electrophiles or allene substituents may totally alter the regiospecificity of the substitution by changing the relative activation barriers for C1 vs C3 attack slightly. In fact, different blends of allenes and alkynes were observed as the products of the reaction of allenyllithium with various electrophiles.[10a]

The reaction of the 1,3-bridged form of α-lithiohydroxyallene with hydrogen at C1 (reaction 3 in Chart V) is very similar to that of lithioallene (reaction 1). Again, an allenic type transition state lies 17.8 kcal/mol above the educt energies. The hydroxy substituent influences neither the energy nor the structure of the transition state. In contrast, the attack at C3 (reaction 4) has a considerably higher activation barrier (22.9 kcal/mol)! Although the geometry of the transition state is very similar to that of the C3 attack of allenyllithium (propargylic TS, reaction

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[37] Fleming, I. *Grenzorbitale und Reaktionen organischer Verbindungen*; VCH: Weinheim, 1979; p 144.

Chart III

Reaction 1 (MP2(FC)/6-31+G**//6-31+G* + ΔZPE)

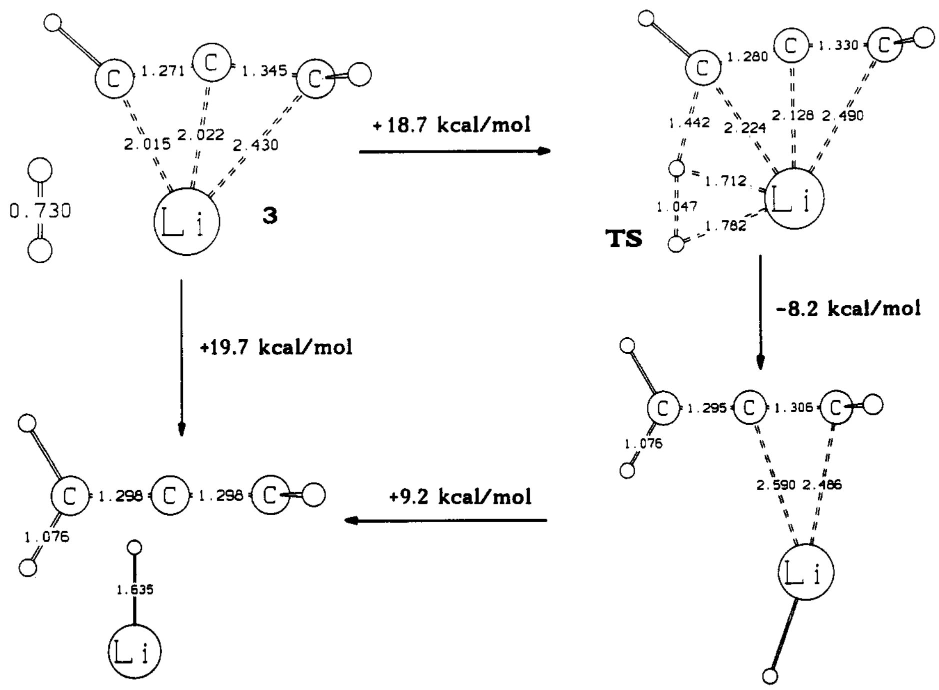
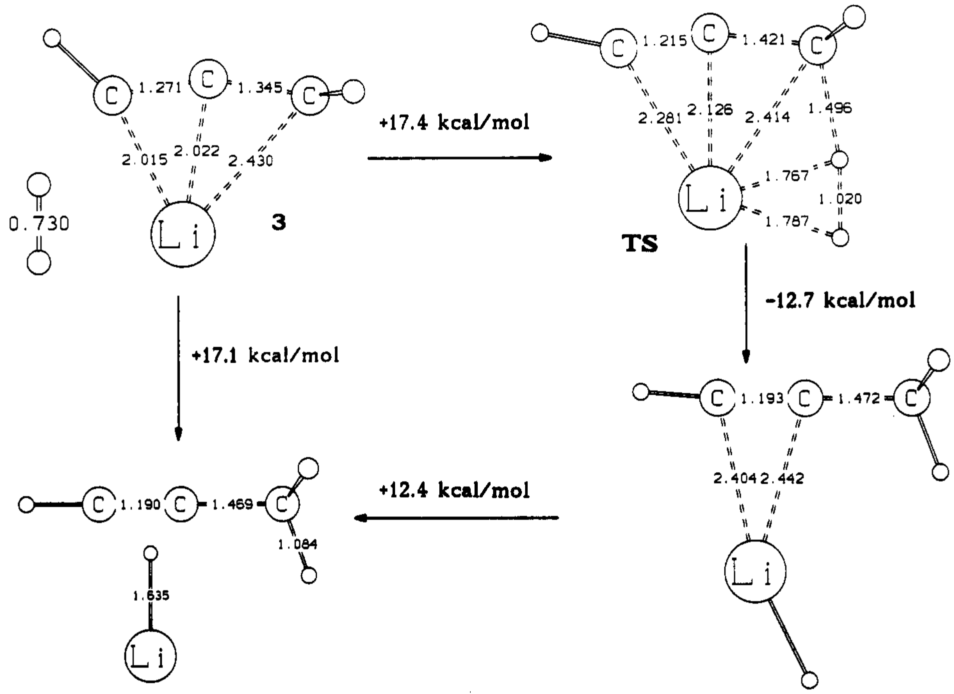


Chart IV

Reaction 2 (MP2(FC)/6-31+G**//6-31+G* + ΔZPE)



2), the TS in reaction 4 (Chart VI) is *destabilized* relative to the educts vs the TS of reaction 2. The destabilization is due to the butadienyl-dianion-like O–C1–C2–C3 system of the transition state. Like 21, the HOMO of the TS has two nodal planes and is (formally) antibonding and destabilizing. After the hydrogen transfer, an O-coordinated LiH complex is formed due to the somewhat better electrostatic interaction of Li^+ to oxygen vs a π-complexation.

While the activation barriers for the C1 and C3 attack of allenyllithium 3 are quite similar, C1 attack at α-lithiohydroxyallene 12 (α-substitution) is clearly favored over C3 attack (γ-substitution) due to the lower activation barrier. Our calculations demonstrate that the *destabilizing* influence of the hydroxy group in the propargylic TS (reaction 4) is responsible for the experimental observation that α-lithiomethoxyallene is substituted regiospecifically at C1, regardless of the nature of the

Chart V

Reaction 3 (MP2(FC)/6-31+G**//6-31+G* • ΔZPE)

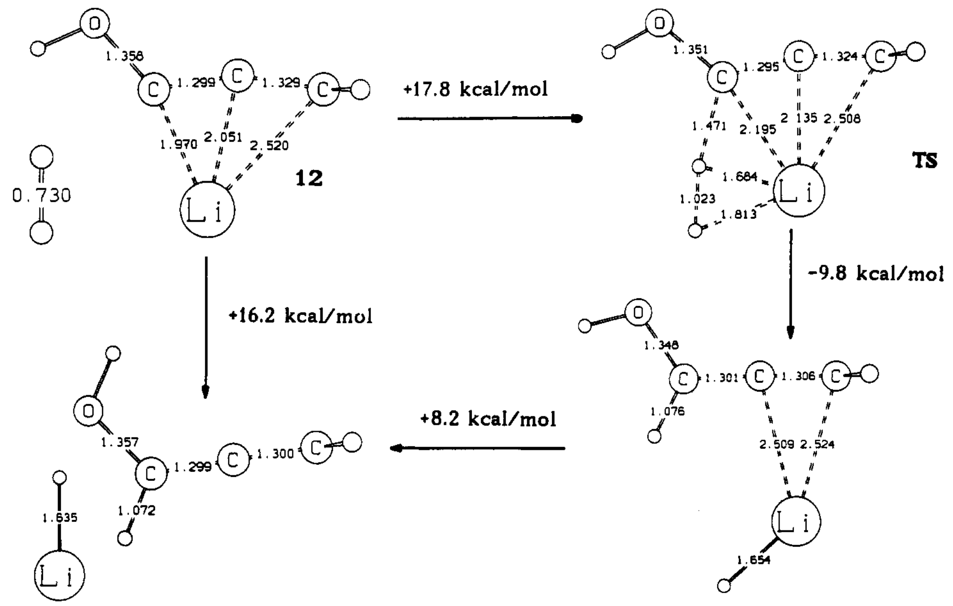
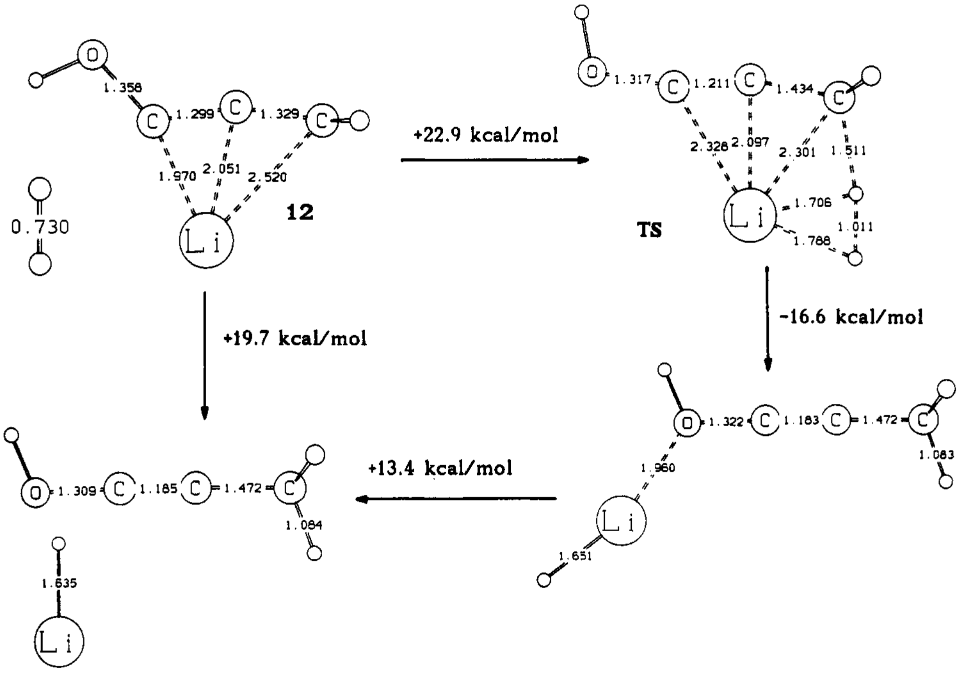


Chart VI

Reaction 4 (MP2(FC)/6-31+G**//6-31+G* + ΔZPE)



electrophile. In addition, the thermodynamics also slightly favor the formation of hydroxyallene over propynol (reaction 3 is 3.5 kcal/mol less endothermic than reaction 4).

F. Reactivity of Allenylmagnesium Hydride, Propargylmagnesium Hydride, and Their Hydroxy Derivatives. The reaction of allenylmagnesium hydride 17 with hydrogen (reaction 5 in Chart VII) takes a totally different course than the reaction of H_2 with allenyllithium 3. Since allenylmagnesium hydride has a more classic structure, the hydrogen molecule can only attack at C3 yielding the propargylic instead of the allenic product (as in the lithium case, reaction 1). The geometry of the "six center" transition structure comprises the features of the allenic educt and of the propargylic product. Such a "six center" S_E2' mechanism has been proposed earlier.[13] The activation barrier, 17.3 kcal/mol, is similar to that in the lithium case (17.4 kcal/mol, reaction 2). No "four center" reaction path with hydrogen attack at C1 of allenylmagnesium hydride, which would lead to the allenic product, could be located.

A similar S_E2' mechanism was calculated for the substitution of propargylmagnesium hydride 18 (which is only 1.7 kcal/mol less stable than allenylmagnesium hydride 17) with hydrogen (reaction 6 in Chart VIII). Again, attack does not occur at the metalated carbon atom

Chart VII

Reaction 5 (MP2(FC)/6-31(+)G**//6-31(+)G* + ΔZPE)

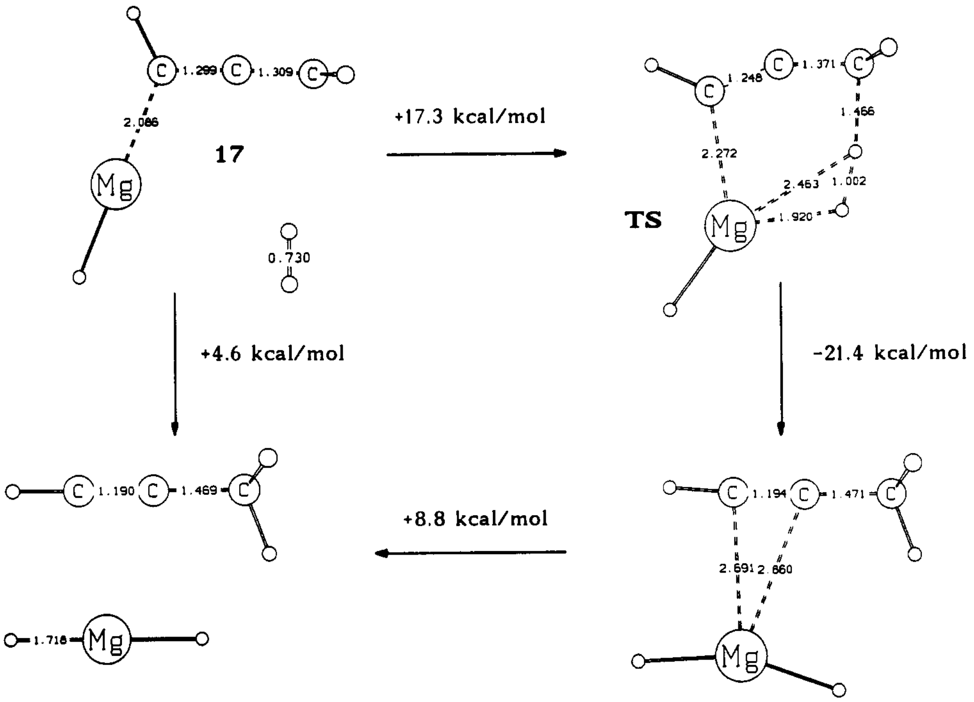
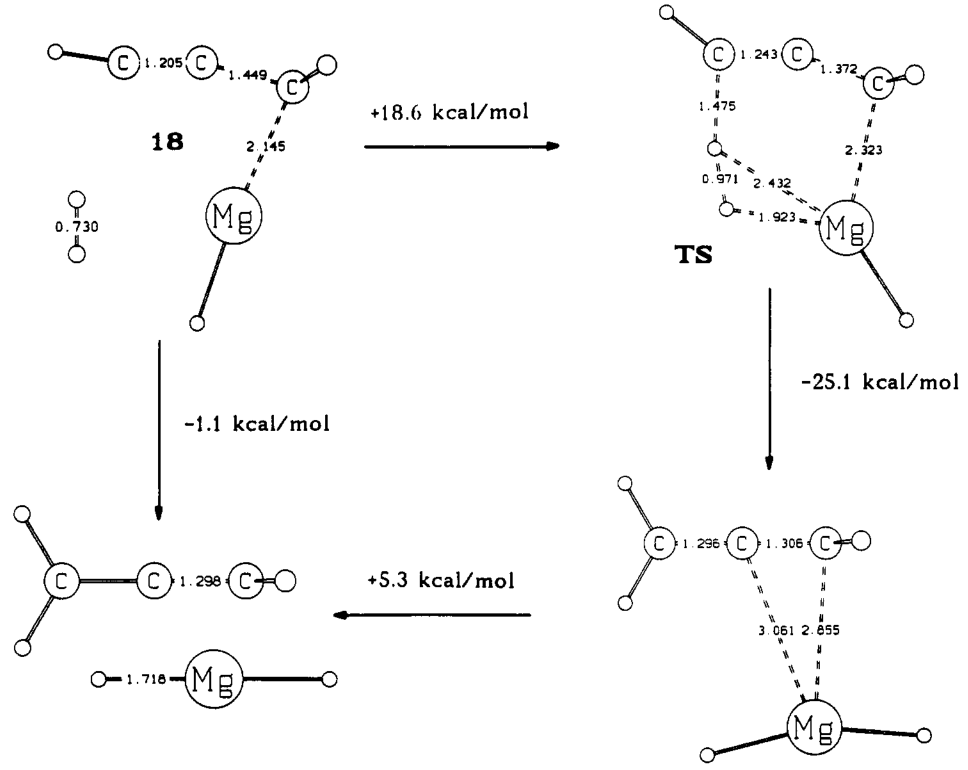


Chart VIII

Reaction 6 (MP2(FC)/6-31(+)G**//6-31(+)G* + ΔZPE)



C3 but rather at C1 to give the allenic product. The transition state geometry also is intermediate between those of the educt and the product. The hydrogenolysis activation barrier (18.6 kcal/mol) is only slightly higher than for the C3 attack of allenylmagnesium hydride 17 (reaction 5).

In view of the similar activation barriers computed for reactions 5 and 6, the relative amounts of the allenic vs the propargylic forms of the Grignard reagent will determine the ratio of the alkynic and allenic products (under kinetic, low-temperature reaction conditions) resulting from electrophilic attack. Since C_3H_3MgBr has the allenic form exclusively in solution, alkynic products should predominate from reaction with electrophiles. Experimental observations agree.[13]

The reaction of (hydroxyallenyl)magnesium hydride 19 with hydrogen (reaction 7 in Chart IX) is similar to that of the nonsubstituted allenylmagnesium hydride 17 (re-

Chart IX

Reaction 7 (MP2(FC)/6-31(+)G**//6-31(+)G* + ΔZPE)

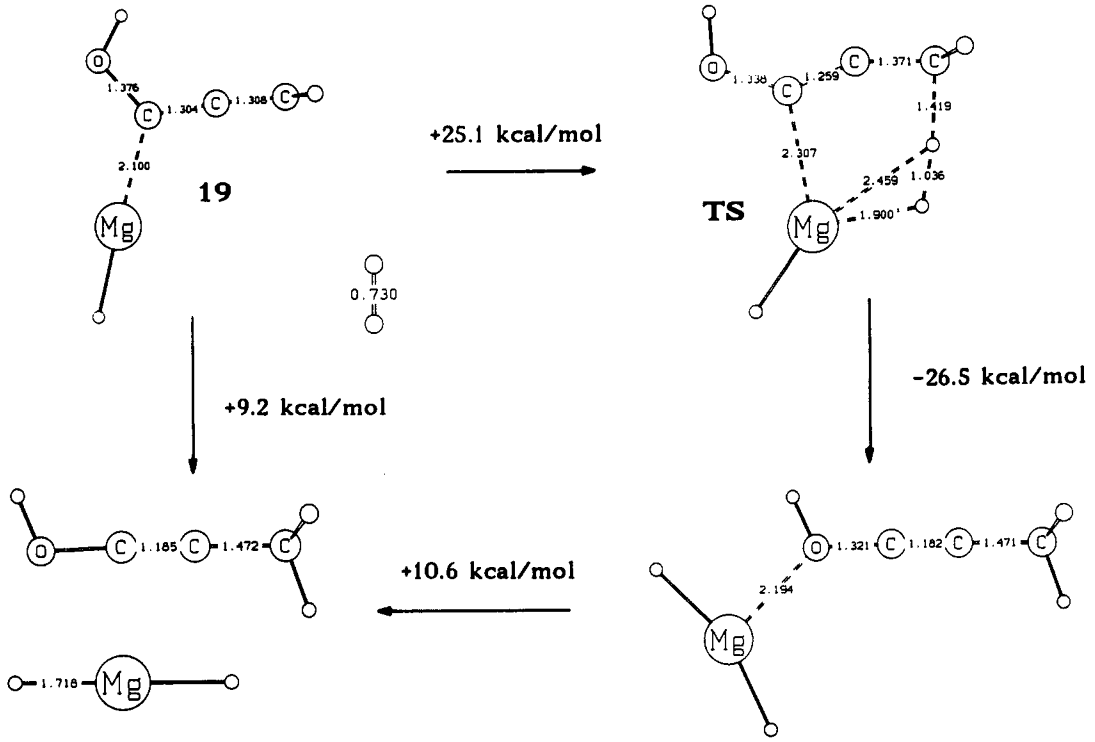
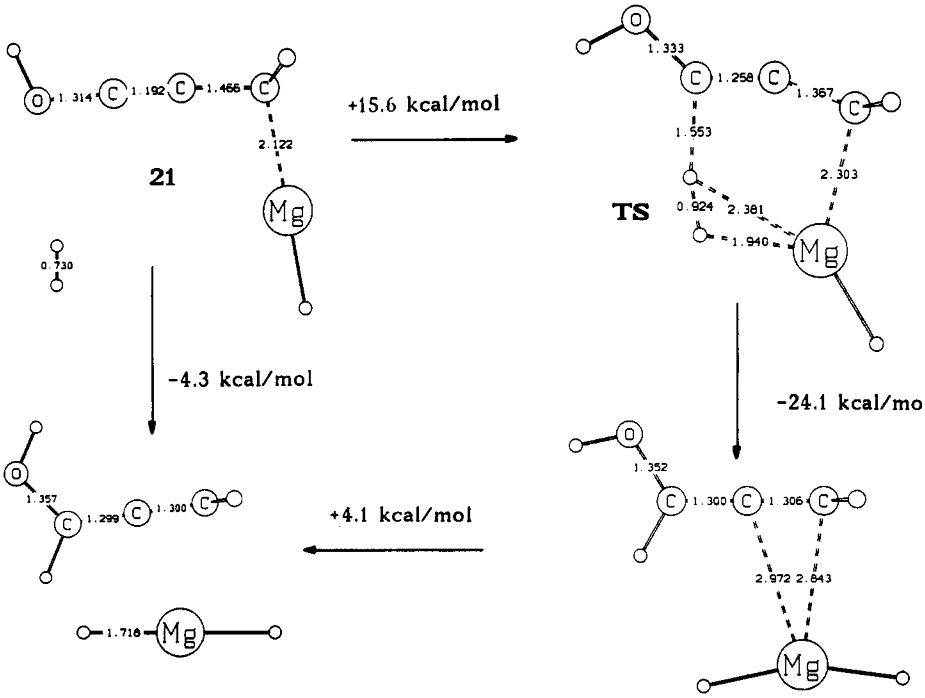


Chart X

Reaction 8 (MP2(FC)/6-31(+)G**//6-31(+)G* + ΔZPE)

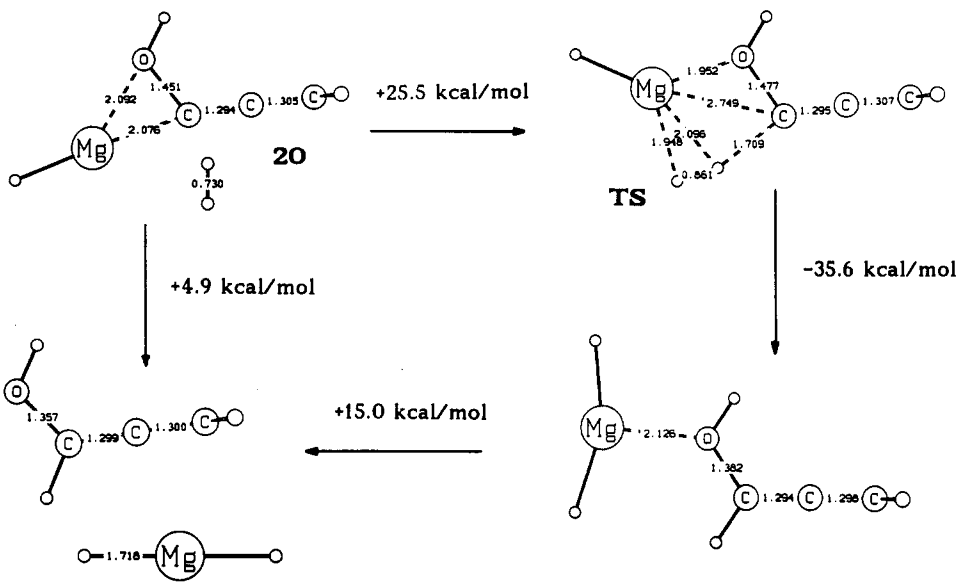


action 5). Again, the metalated allene **19** has a more classic structure and the S_E2' attack of the electrophile occurs at C3 to give the alkynic alcohol. The reaction barrier is rather high (25.1 kcal/mol) due to the destabilized transition state. This has some butadienyl dianion character. In contrast, the propargylic educt **21** (reaction 8 in Chart X) is 10.0 kcal/mol less stable than the allenic form **19** (reaction 7) and thus the activation barrier for attack at C1 is lower in **21** (15.6 kcal/mol, reaction 8). This is due to the less pronounced, destabilizing butadienyl dianion character of the slightly s-shaped transition state of reaction 8 than of the almost linear O–C1–C2–C3 arrangement of **21**. The S_E2' mechanism results in hydroxyallene product formation in reaction 8.

However reaction 8 should not occur in solution to a significant extent. The (hydroxypropargyl)magnesium

Chart XI

Reaction 9 (MP2(FC)/6-31(+)G**//6-31(+)G* + ΔZPE)



hydride **21** is too unstable thermodynamically to be present in equilibrium with (hydroxyallenyl)magnesium hydride. Instead, we propose a third reaction mechanism which could occur in solution (reaction 9 in Chart XI). The O-coordinated **20** only is 0.7 kcal/mol less stable than the allenic isomer **19** and such form might be present in an equilibrium in solution. An S_E2' reaction with an electrophile (reaction 9) could proceed at the metalated carbon atom, C1, due to the wide Mg–C1–C2 angle (170°). This would result in the formation of the allenic product. Indeed, the activation barrier (25.5 kcal/mol) is of comparable magnitude as that of reaction 7. The blend of alkynic and allenic products should depend on the ratios of **19** and **20** in solution. Actually, mixtures of both types of products were found experimentally for the reaction of acetone with (methoxyallenyl)magnesium bromide, but (*tert*-butoxyallenyl)magnesium bromide gave mainly the alkynic product.[2]

Conclusions

Using ^{13}C NMR, $^{6}Li,^{1}H$-HOESY NMR techniques, and IR spectra in combination with *ab initio* calculations, we demonstrated that α-lithiomethoxyallene **7** is a nonclassically 1,3-bridged dimeric aggregate in THF and a tetrameric aggregate in diethyl ether. O-Coordinated, as well as propargylic isomers, could be excluded. No experimental data are available on the structure of the Grignard derivative of methoxyallene. However, *ab initio* calculations indicate that the Grignard compound has a classic allenic or an O-coordinated allenic form (or is a mixture of both forms). In addition, the calculations show that hydroxypropargyl metal compounds (**16**, **21**) (disregarding the nature of the metal) are unstable compared to allenic isomers (**13**, **15**, **19**, **20**) since a destabilized butadienyl-dianion-like system is formed in the propargylic derivatives. Calculated model reactions of α-lithiohydroxyallene **12** with hydrogen indicate that the experimentally observed exclusive α-substitution is kinetically preferred over the γ-substitution. The "four center" transition state geometry has allenic character. The influence of the hydroxy group hinders the γ-substitution since the transition state is destabilized due to the butadienyl-dianion-like arrangement.

In contrast, the substitution of the hydroxyallenyl Grignard reagent **19** proceeds via a "six center" transition state and results in the formation of the alkynic product (γ-substitution). The formation of the allenic product via α-substitution of the hydroxypropargylic Grignard **21** should be favored kinetically. However, the hydroxypropargylic Grignard educt **21** is thermodynamically too unstable vs the allenic isomer **19** to be present in an equilibrium to a significant extent. However, the α-substitution reaction of the alternative O-coordinated isomer **20** gives the allenic product.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie (scholarship to C.L.). We thank Professor Dr. H.-U. Reissig for suggesting this study and for a sample of methoxyallene. In particular, we are grateful to Dr. W. Bauer for the measurement of the HOESY spectra.

Supplementary Material Available: Computational data for all compounds and the structure of 7 (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.