aqueous and alcoholic solutions that are typically ~5 M or 40% in KOH. The half-life for decomposition of (*E*)-methanediazoate according to the mechanism of Scheme I under these conditions would likely be several to many hours at least. Unlikely alternative mechanisms for diazomethane generation are the onset of a new mechanism for decomposition of the (*E*)-methanediazoate in strongly basic aqueous solution or mechanisms for decomposition of the nitroso compounds that do not involve diazoates. It seems most likely that the diazomethane is formed from the intermediacy of the considerably more reactive (*Z*)-methanediazoate that instantly decomposes the diazomethane in alcoholic and basic aqueous media.[4,9,32]

Summary. This study establishes a semiquantitative picture of methyl group transfer in aqueous solution from one of the two simplest alkanediazoates to the product methanol. The decomposition chemistry of higher homologues of both **1** and its syn isomer is known to involve more complexity, likely including the intermediacy of carbocations.[4,33,34] We are currently investigating these and other aspects of diazoate chemistry.

Acknowledgment. We wish to thank Prof. Tina Aymes at the Department of Chemistry, University of Kentucky, for quantitating the amount of deuterium incorporation into methanol by 500 MHz ^{1}H NMR (Table III) and Prof. N. Ganapathisubramanian at the Department of Chemistry, Wake Forest University, for helpful discussions. We are particularly grateful to Prof. A. J. Kresge, University of Toronto, who pointed out an inconsistency in our initial interpretations concerning diazomethane hydrolysis that stimulated further investigation.

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Enolates of α-Allenyl Ketones: Formation and Aldol Reactions of Cumulenolates

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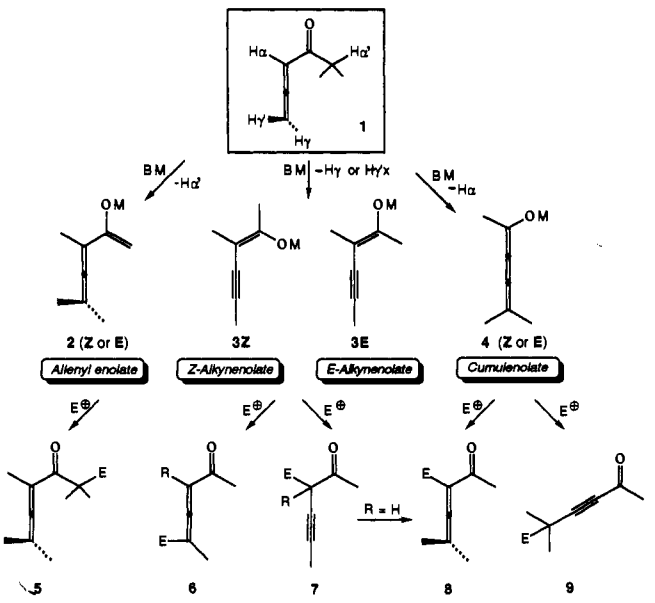
Abstract: Enolization of α-allenyl ketones under kinetic conditions, followed by reactions with aldehydes and ketones, affords aldol products that suggest the intermediacy of cumulenolates, formed via the abstraction of a vinylic α-hydrogen. The origin for this marked difference with α-alkenyl ketones is attributed to the enhanced acidity of allenic hydrogens, to the predominance of the s-trans conformation, and to lithium complexation with both the carbonyl and the allene moieties. The relative stability of these enolates was examined with the use of semiempirical (MNDO) calculations which indicated that the lowest energy isomers are the (*Z*)-alkynolates. Both experimental and computational evidence suggest that the kinetic intermediate is the cumulenolate, while the thermodynamic enolate is the (*Z*)-alkynenolate.

Introduction

The α-allenyl ketone (α-allenic ketone, α-oxoallene) moiety is characterized by unique chemical reactivity resulting from the mutual activation of two of the most versatile functional groups in organic chemistry.[1] Although they are not common in target molecules, α-allenyl ketones do exist in nature[2] and have been used effectively in suicide enzyme inhibitors.[3] Despite the development of many synthetic routes to α-allenyl ketones,[1,4] their rich reactivity has not been fully exploited. Among the processes that have been studied[1] are their reactions with nucleophiles,[5] dienophiles,[6] and oxidizing agents,[7] as well as their thermal[8] and Lewis acid-catalyzed isomerizations.[9] During the exploration of a new synthetic strategy for the synthesis of eight-membered rings,[10] we had an

Scheme I



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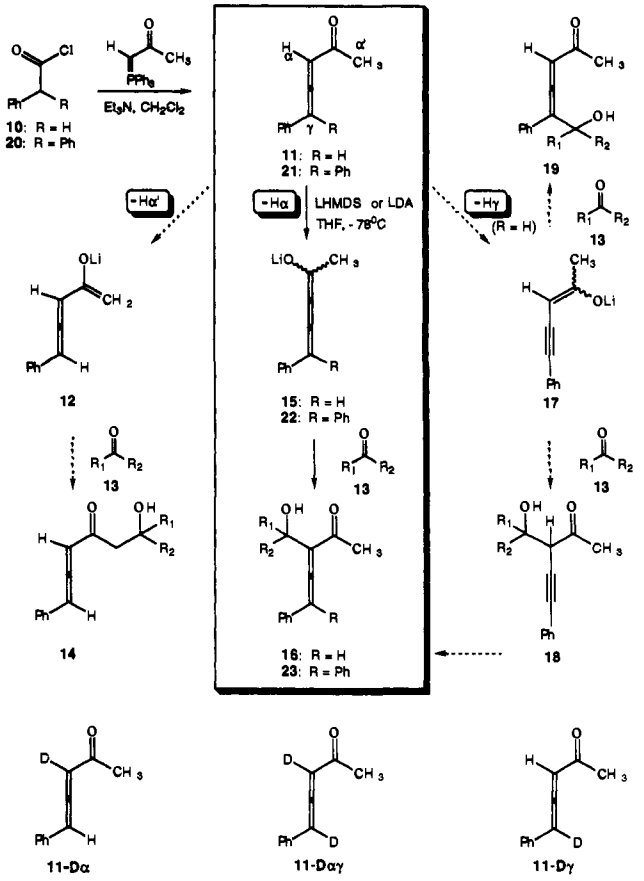
Scheme II



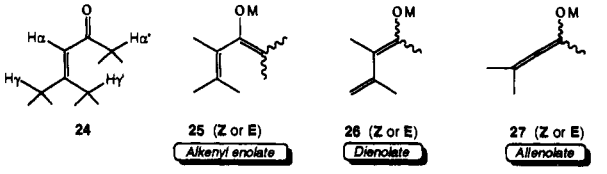
opportunity to investigate the use of α-allenyl ketones as enolate precursors in the aldol reaction. This work has led to the present study of the enolization of this carbonyl system, which to our knowledge has not been previously investigated.

Conversion of carbonyl compounds to their enolates,[11] followed by alkylation[12] or aldol reaction,[13] is one of the most synthetically useful methods for the formation of carbon–carbon bonds.[14] The development of procedures for the regio-[15] and stereocontrolled[16] formation of various types of enolates[17] under kinetic or thermodynamic conditions has played a key role in the widespread use of these processes. Also, recent advances on the structures of enolates[18] and dialkylamide bases,[19] combined with the evolution of theoretical approaches[20] and new developments regarding the principle of stereoelectronic control,[21] have provided further mechanistic insights.

Table I. Aldol Reactions of the Enolates of **11** and **21** with Carbonyl Compounds **13**

allenyl ketone	R	carbonyl compd	R_1	R_2	aldol product	yield, %
11	H	**13a**	CH_2=C(Me)	H	**16a**	63
11	H	**13b**	Me_2CH	H	**16b**	62
11	H	**13c**	Me_3C	H	**16c**	47
11	H	**13d**	Ph	H	**16d**	51
11	H	**13e**	$-(CH_2)_5-$		**16e**	18
21	Ph	**13a**	CH_2=C(Me)	H	**23a**	64
21	Ph	**13b**	Me_2CH	H	**23b**	60
21	Ph	**13d**	Ph	H	**23d**	50
21	Ph	**13f**	Ph	Me	**23f**	35

Scheme III



While the lithiation of simple or heterosubstituted allenes with alkyllithium reagents is well-known,[22] a similar deprotonation of α-allenyl ketones (**1**) is not possible, due to the propensity of the conjugated carbonyl system to undergo 1,2- or 1,4-addition. In this case abstraction of a hydrogen with a suitable base (BM) can take place in one of several ways (Scheme I). Removal of Hα′ would afford the *allenyl enolate* (1,3,4-trien-2-olate, **2**); abstraction of Hγ or Hγ′ would lead to the *alkynenolate* (1-en-3-yn-1-olate, **3**), while abstraction of Hα would allow the formation of the *cumulenolate* (1,2,3-trien-1-olate, **4**). Subsequent reaction of enolates **2–4** with electrophiles would result in the formation of a variety of products **5–9** (Scheme **I**).

We report herein that α-allenyl ketones having α-hydrogens do not follow the usual regioselectivity for enolization of α-alkenyl ketones (enones). *Under the usual kinetic conditions their enolization takes place preferably at the vinylic α-position, forming a cumulenolate* (*4*).

Results

Deprotonation and Aldol Reactions of α-Allenyl Ketones. The first allenyl ketone that we examined was the phenyl-substituted derivative **11**, readily prepared by the reaction of phenylacetyl chloride (**10**) with 1-(triphenylphosphoranylidene)-2-propanone in the presence of triethylamine.[23] Compound **11** was treated with a bulky lithium amide base [$(Me_3Si)_2NLi$ (LHMDS) or $(Me_2CH)_2NLi$ (LDA)] under the usual conditions of kinetic control (THF, −78 °C), and the resulting lithium enolate was reacted with various carbonyl compounds **13**. We anticipated that,

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(21) For a review, see: Pollack, R. M. *Tetrahedron* **1989**, *45*, 4913.
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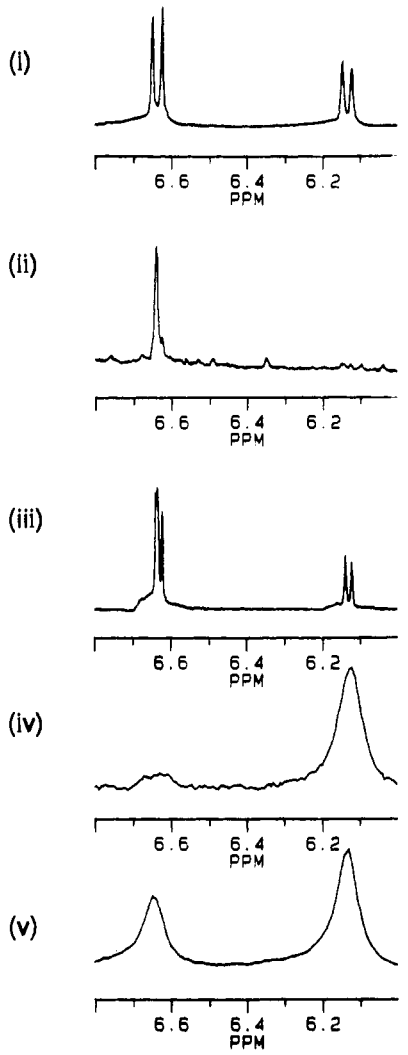


Figure 1. Olefinic region of (i) 360-MHz ^{1}H NMR spectrum of allenyl ketone **11**; (ii) ^{1}H NMR spectrum of recovered allenyl ketone **11-Dα** after enolization with LHMDS and THF at −78 °C followed by slow addition of the enolate to a mixture of D_2O/AcCl; and (iii) ^{1}H NMR spectrum of a mixture of **11**, **11-Dα**, and **11-Dαγ**, obtained by addition of D_2O/AcCl to the enolate [note that while there is a singlet at δ 6.63 (Hγ of **11-Dα**), there is no singlet at δ 6.13 (Hα of **11-Dγ**)]; (iv) ^{2}H NMR spectrum of **11-Dα**; (v) ^{2}H NMR spectrum of the mixture of **11-Dα** and **11-Dαγ**.

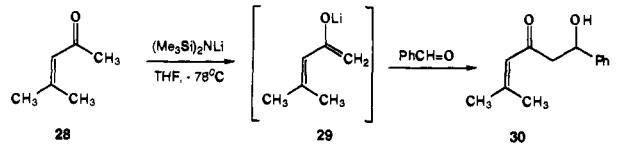
similarly to the enolization of enones, the kinetic enolate in this case might be the allenyl enolate (**12**), which would react with **13** to give aldols **14** (Scheme II). We found, however, the only isolated products were the α-aldol derivatives **16**,[24] as indicated by the presence of the α′-methyl group and the γ-hydrogen in their NMR spectra. Although compounds **16** may be formed directly from the cumulenolate **15**, they can also be derived via the alkyne to allene isomerization of aldol product **18** obtained from the alkynenolate **17**. The γ-aldol products **19**, also obtainable from **15** or **17**, were not detected.

Several attempts to identify the type of enolate formed under these conditions via the corresponding silyl enol ethers were unsuccessful. However, slow addition of the enolate to a mixture of D_2O and acetyl chloride[25] gave **11-Dα** almost exclusively, indicating the intermediacy of **15**. Furthermore, fast addition of the enolate or addition of D_2O/AcCl to the enolate resulted in the formation of a mixture of **11**, **11-Dα**, and **11-Dαγ**, but not **11-Dγ**. These structural assignments were based on the ^{1}H NMR

(24) While aldol products **16** exist as diastereomers, due to the stereogenicity of the allenyl moiety, these isomers could not be separated or identified spectroscopically.

(25) We thank Professor M. E. Jung of the University of California at Los Angeles for helpful suggestions regarding this reaction.

Scheme IV



28 **29** **30**

spectra (i–iii) and the ^{2}H NMR spectra (iv,v) shown in Figure 1. These results can be explained by an equilibration of the cumulenolate (**15**) with **11-Dα** to give the more stable α-deuterated alkynenolate, which leads to **11-Dαγ** upon quenching. The absence of **11-Dγ** indicates that enolate **17** was not formed during the initial kinetic deprotonation. From these experiments we can conclude that the kinetic enolate derived from **11** is the cumulenolate (**15**), while the thermodynamic enolate is the alkynenolate (**17**).

Further evidence for the likely intermediacy of **15** was obtained when allenyl ketone **21**, lacking a γ-hydrogen, was subjected to similar conditions. Once again, compound **21**, prepared similarly from **20**, afforded aldol products **23** (presumably via **22**) and thus confirmed the preferential abstraction of Hα over Hα′. Table I lists the results of this type of aldol reaction of **11** and **21** with several carbonyl compounds. Not surprisingly, aldehydes gave higher yields of products than did ketones.

Discussion

Comparison with α-Alkenyl Ketones. The reluctance of α-allenyl ketones (**1**) to be converted to the allenyl enolates (**2**) contrasts the behavior of α-alkenyl ketones (**24**) under similar conditions. The kinetic intermediate in this case is usually the cross-conjugated *alkenyl enolate*[26,27] (1,3-dien-2-olate, **25**), involving abstraction of Hα′, while the thermodynamic enolate is the more conjugated *dienolate*[28] (1,3-dien-1-olate, **26**), involving abstraction of Hγ or Hγ′ (Scheme III). Abstraction of the vinylic hydrogen (Hα) from **24** to give the *allenolate* (1,2-dien-1-olate, **27**) is rare,[29] although this type of enolate has been generated from other precursors[30] including α-alkynyl ketones,[31] acyl silanes,[32] acyl lithium,[33] and propargylic sulfoxides.[34]

Since the direct removal of the α-vinylic hydrogen of α,β-unsaturated carbonyl compounds is generally not possible under the usual strongly basic conditions, a number of alternative methods were developed involving masked carbonyl derivatives[35] or conjugate addition–elimination sequences.[36] Also, the corresponding aldol products can be obtained via the Baylis–Hillman process,[37]

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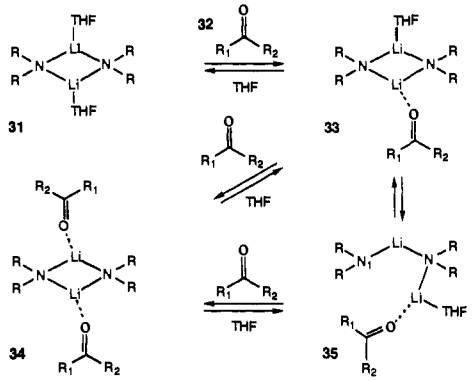
Scheme V



involving prolonged reactions with certain tertiary amines such as 1,4-diazabicyclo[2.2.2]octane (DABCO)[38] and 3-hydroxyquinuclidine.[39]

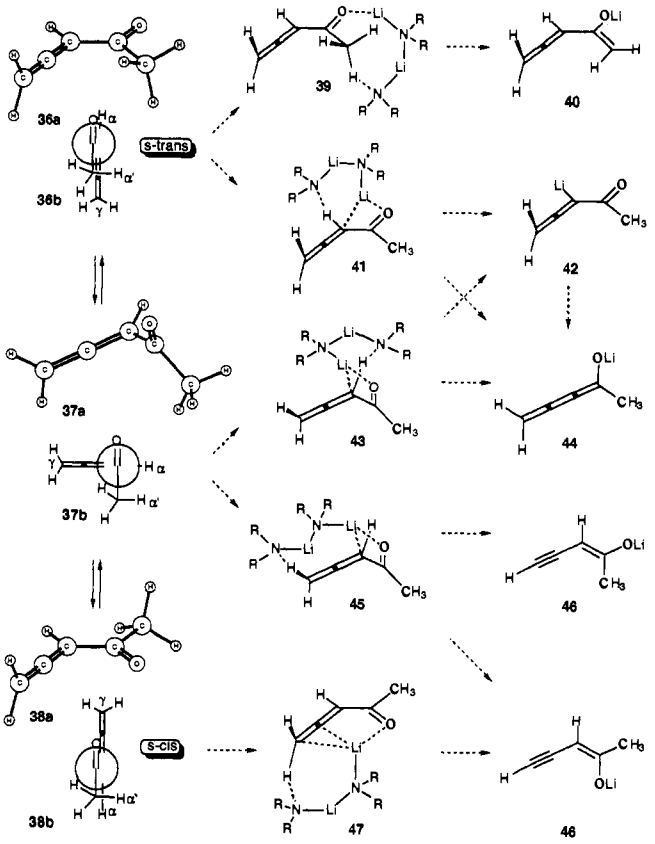
To directly compare the aldol reactions of α-alkenyl[25] and α-allenyl ketones, we subjected mesityl oxide (**28**) to the same conditions used for **11** and **21**. As expected, kinetic deprotonation with LHMDS followed by reaction with benzaldehyde gave exclusively the α'-aldol product (30), presumably via dienolate **29** (Scheme IV).

Transition-State Models for the Deprotonation of α-Allenyl Ketones. As indicated from the results reported herein, the preferred deprotonation pathway for α-allenyl ketones is the removal of a vinylic hydrogen (Hα). At first, the preferred abstraction of Hα may be attributed to thermodynamic reasons, since this hydrogen not only is located next to a carbonyl but is also allylic in respect to Cβ=Cγ. Although the metallation of simple allenes is possible with alkyllithiums, the conditions used herein involve milder and bulkier bases and very low temperatures, which are more likely to involve kinetically controlled deprotonations. Therefore, the observed enolization of α-allenyl ketones should be analyzed in the context of recent spectroscopic,[40] crystallographic,[41] and computational studies[42] on the aggregation state and complexing ability of dialkylamide bases.

It has been established[43] that in THF solutions lithium dialkylamides exist primarily as solvated cyclic dimers (**31**) which can form several types of complexes with carbonyl substrates (**32**) such as **33**–**35** (Scheme V). A crystal structure of type **34** was recently reported by Williard,[41b] while the solvated open dimer **35** was postulated by Collum[42] as an intermediate in the Lewis acidic activation of carbonyl compounds. Subsequent coordination of the basic N-atom (N_1) to an acidic hydrogen of the carbonyl substrate leads to deprotonation.

The deprotonation preference may be directly correlated to the conformation of the carbonyl substrate[44] and its lithium complex,

Scheme VI



which generally prefers the s-trans form. Using ab initio calculations, Houk[45] has recently shown that all of the lithium complexes of acrolein, acrylic acid, and methyl acrylate favor the s-trans form, despite differences in the lithium-free conformations. For α-allenyl carbonyl derivatives the conjugated s-trans geometry is normally the most favored conformation, even prior to lithium complexation.[46] In the case of the parent α-allenyl ketone, semiempirical (AM1)[47] calculations with MOPAC[48] showed that the s-trans conformer (**36**) is 0.23 kcal/mol more stable than the s-cis conformer (**38**) and 1.38 kcal/mol more stable than the perpendicular conformation (**37**) (Scheme VI).

For stereoelectronic reasons[21] it is expected that a hydrogen that has a perpendicular orientation toward the carbonyl plane would be preferentially abstracted, and that this preference would be limited by the rate of interconversion among the conformations involved. Inspection of the Newman projections **36b**, **37b**, and **38b** shows that Hα' can always adopt this conformation due to the free rotation of the methyl group. The vinylic hydrogen Hα, however, in both the conjugated s-trans (**36**) and s-cis (**38**) conformations has an eclipsed relationship to the carbonyl and adopts the perpendicular orientation only in the higher energy, nonconjugated conformation (**37**). The reverse relationship exists with the vinylic hydrogens Hγ, which have a perpendicular arrangement in both the s-trans and s-cis conformations.

The abstraction of Hα' to give the allenyl enolate (**40**) is presumably not favored. This type of kinetic enolization could have taken place via a cyclic transition state, such as **39**, which invokes an open dimer for the base (solvent molecules not represented). This type of cyclic TS model, originally proposed by Ireland,[49] has been used widely to rationalize the *Z*/*E* selectively

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Table II. Energies and Selected Bond Lengths and Bond Angles from MNDO Calculations

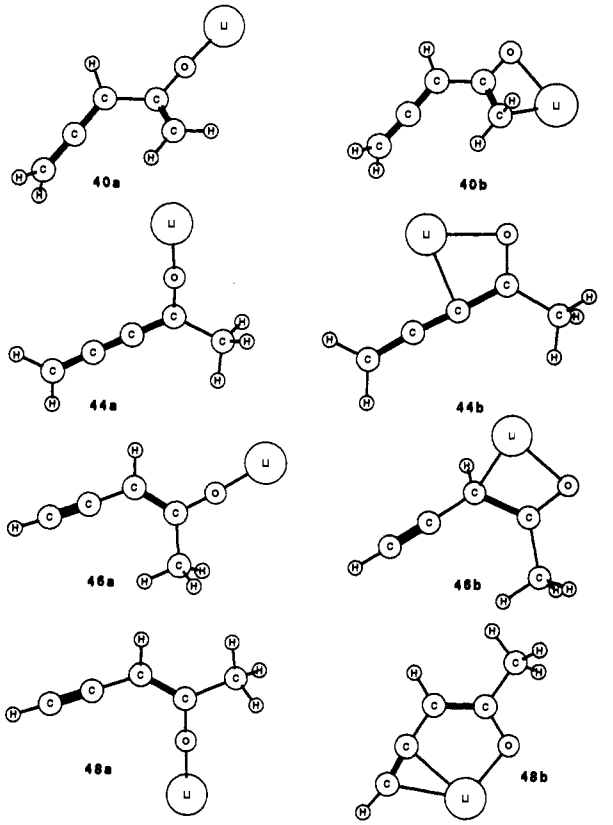
	structure							
	40a	**44a**	**46a**	**48a**	**40b**	**44b**	**46b**	**48b**
heat of formation, (kcal/mol)	7.18	6.53	2.37	1.47	−1.01	−4.86	−5.58	−23.57
relative energy, kcal/mol	30.75	30.10	25.94	25.04	22.56	18.71	17.99	0.00
bond lengths, Å								
C(1)–C(2)	1.368	1.525	1.527	1.526	1.378	1.522	1.485	1.525
C(2)–C(3)	1.496	1.346	1.381	1.381	1.385	1.393	1.450	1.414
C(2)–O	1.318	1.305	1.310	1.306	1.176	1.288	1.235	1.289
C(3)–C(4)	1.313	1.260	1.409	1.410	1.218	1.296	1.389	1.409
C(4)–C(5)	1.305	1.315	1.200	1.200	1.202	1.324	1.170	1.228
C(1)–Li					1.800			
C(3)–Li						2.088	1.913	
C(4)–Li								2.200
C(5)–Li								2.191
O–Li	1.700	1.721	1.712	1.714	1.972	2.045	2.069	1.948
bond angle, deg								
C(2)–O–Li	176.84	175.45	175.98	177.72	79.78	89.381	81.616	112.34

during the kinetic enolization of carbonyl derivatives. A number of modifications to this model were suggested to account for the stereoelectronic effect,[50] the conformational preferences of the carbonyl substrate,[51] and the aggregation state of the base.[52]

Abstraction of Hα may be rationalized with a similar cyclic TS (**41**). To our knowledge, this would constitute the first use of this model for the direct abstraction of a vinylic α-hydrogen from a carbonyl compound. While in TS **41** the C—Hα bond is not oriented perpendicularly to the C=O π-system, this type of TS-stabilizing arrangement exists with the Cβ=Cγ bond, due to the allene geometry. In this TS model the C=O does not participate in the resonance stabilization of the emerging anion. This pathway, therefore, may initially lead to the allenyl lithium species (**42**), which is expected to be rapidly converted to the cumulenolate (**44**), as previously shown for lithium allenolates.[53] An alternate TS model (**43**) leading directly to the cumulenolate (**44**) involves conformation **37**, which has a perpendicular arrangement among the C=O and C=C=C moieties. Although the conjugation among the C=O and C=C=C groups is lost in this TS, it may be compensated by the simultaneous stabilization of the incipient anion by both the Cβ=Cγ and C=O bonds. A late product-like TS would be favored in this case. Similarly to **39**, model **43** also represents the lithium dialkylamide base as an open dimer and allows one of the two basic N-atoms to line up favorably with Hα while one of the two Li atoms is coordinated with the carbonyl oxygen and possibly with Cα. *This additional coordination of the lithium atom with an allenic carbon, shown in TS models 41, 43, 45, and 47, may play a key role in the preferential abstraction of Hα/Hγ over Hα′.*

Similar TS models can be postulated for the abstraction of Hγ to form the (*E*)- (**46**) or (*Z*)-alkynenolate (**48**). This type of remote deprotonation is another example of *complex-induced proximity effect.*[54,55] In this case the TS would have the C=O and C=C=C groups perpendicular (**45**) or s-cis coplanar (**47**). The latter would afford the (*Z*)-enolate (**48**) selectively, while **45** may lead to either enolate geometry. *The observed preference for the abstraction of Hα instead of Hγ can be attributed to a higher energy for the initial lithium complex in the s-cis form.*

Scheme VII



Relative Stabilities of Enolates Derived from α-Allenyl Ketones. To obtain some insight on the geometries and relative thermodynamic stabilities of lithium enolates **40**, **44**, **46**, and **48**, we carried out semiempirical calculations (MNDO)[56] with MOPAC.[48] Despite a tendency to overestimate the lithium–carbon interaction, the MNDO approach has been used widely for the study of organolithium compounds, including lithium enolates. For example, McKee[20b] has shown that while MNDO incorrectly predicted that the global minimum has the lithium atom bonded to both the oxygen and the α-carbon, it did identify the correct geometry found by higher level ab initio calculations, which is characterized by an almost linear alignment of the C–O–Li angle.

We have also found such low-energy distorted geometries (**40b**, **44b**, **46b**, **48b**) for the enolates studied herein (Scheme VII). Interestingly, the lowest energy isomer was the (*Z*)-alkynenolate (**48b**), which contains bonds between the lithium atom and both alkynyl C-atoms similar to those postulated in TS **47**. While

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lithium solvation may prevent the existence in solution of structures having additional C–Li bonds (e.g., **40b**, **44b**, **46b**, **48b**), the existence of these structures as energy minima provides support for the coordination of lithium to the allene moiety, invoked in TS **41**, **43**, **45**, and **47**. The same order of relative stabilities was also observed with the more realistic enolate structures (**40a**, **44a**, **46a**, **48a**) and should be the same even with further Li solvation. These structures are characterized by a C–O–Li angle of about 176° (Table II), which is close to those calculated at higher levels of theory for other lithium enolates.[20b,57]

On the basis of these calculations, the lowest energy enolate form (*thermodynamic enolate*) is predicted to be the (*Z*)-alkynenolate (**48**), followed by its *E* isomer (**46**), while the cumulenolate (**44**) and allenyl enolate (**40**) are higher in energy. The extended conjugation present in **44**, **46**, and **48** is obviously responsible for the increased stability of these systems in comparison to **40**, which is conjugated in a crossed manner.

Conclusion

We have found an unusual reactivity of α-allenyl ketones when they are subjected to aldol reaction conditions. Deprotonation of these compounds under kinetic conditions appears to proceed with the preferential abstraction of Hα to form the cumulenolate, which, therefore, is the *kinetic enolate*. The abstraction of Hγ to generate the most stable (*Z*)-alkynenolate (*thermodynamic enolate*) is less preferred, while the abstraction of Hα′ is the least favored. The preference for Hα abstraction may be the result of the predominance of the s-trans conformation, which does not allow the abstraction of Hγ, while the s-cis conformation could allow the abstraction of Hγ via a complex-induced proximity effect. A possible coordination of lithium to an allenic carbon may also play a directing role. Semiempirical MNDO calculations showed the enolates that would lead to the observed products, namely the (*Z*)-alkynenolate and the cumulenolate, to be more stable than the allenyl enolate. Due to the increasing synthetic utility of allene derivatives, used of this new chemistry could lead quickly to highly functionalized systems. A number of synthetic applications are currently under way in our laboratories.

Experimental Section

All starting materials were purchased from Aldrich Chemical Co. and used without further purification. Reactions were typically run in flame-dried flasks equipped with a stirring bar and filled with predried argon from a three-way stopcock with attached argon-filled balloon. Methylene chloride and triethylamine were distilled from CaH_2 and THF from sodium benzophenone. ^1H NMR spectra were recorded on a Bruker 250- or 360-MHz NMR spectrometer, and ^{13}C spectra were recorded at 63 or 90 MHz on the same instruments. Solution samples were made in $CDCl_3$. Mass spectral data were obtained on a Hewlett-Packard 7070 spectrometer. All IR spectra were recorded on a Perkin-Elmer 281 instrument. TLC analysis was done using Merck precoated silica gel 60 F_{254}, 0.25-mm thickness. Products were purified by flash column chromatography using Kieselgel 60 (230–400 mesh) silica gel.

5-Phenyl-3,4-pentadien-2-one (11). To an ice-cooled (0 °C) solution of 1-(triphenylphosphoranylidene)-2-propanone (4.12 g, 13.49 mmol) and triethylamine (1.32 g, 1.8 mL, 13.49 mmol) in CH_2Cl_2 (40 mL) stirred under argon was added dropwise a solution of phenylacetyl chloride (2 g, 13.49 mmol) in CH_2Cl_2 (13 mL). The reaction mixture turned bright yellow, and TLC (15% Et_2O/petroleum ether) showed complete reaction immediately. Approximately half of the solvent was removed on a rotary evaporator, and diethyl ether was added to precipitate the Ph_3PO. After filtration, silica gel was added to adsorb the reaction products and the solvent was evaporated in vacuo. Purification by flash column chromatography yielded **11** (1.17 g, 7.4 mmol, 55%) as a light yellow oil: IR ($CDCl_3$) 1940, 1676, 1361, 1233, 910, 730 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.37–7.25 (m, 5 H), 6.63 (d, 1 H), 6.13 (s, 1 H), 2.25 (s, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 213.4, 198.0, 131.0, 129.0, 128.2, 127.3, 101.1, 98.5, 26.8; EIMS *m/e* (relative intensity) 158 (M^+, 37), 115 (26), 91 (43), 77 (23), 58 (38), 43 (100); HRMS exact mass calcd for $C_{11}H_{10}O$ (M^+) 158.0732, found 158.0726.

General Procedure for Aldol Reactions. To a stirred THF solution of lithium hexamethyldisilazide (1.00 mL of 1.0 M, 1.00 mmol), cooled to −78 °C (dry ice/acetone bath) under argon, was added dropwise a solution of the allenyl ketone (1 mmol) in THF (2 mL). Stirring of the resulting orange-yellow solution continued for 30 min, and then a solution of the carbonyl compound (1 mmol) in THF (1 mL) was added dropwise, turning the reaction mixture into a ruby red color. TLC analysis (30% Et_2O/petroleum ether) showed complete reaction immediately. The reaction mixture was quenched at −78 °C with a solution of saturated ammonium chloride. The layers were separated, and the aqueous layer was extracted three times with Et_2O. The combined organic layers were then washed with water and saturated sodium chloride and then dried over anhydrous magnesium sulfate. The product was purified by flash column chromatography (30% Et_2O/petroleum ether).

Aldol product 16a was prepared from **11** and methacrolein (**13a**) in 63% yield: IR ($CDCl_3$) 3400, 2915, 2840, 1925, 1670, 1485, 1445, 1370 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.37–7.25 (m, 5 H), 6.71 (s, 1 H), 5.09 (m, 2 H), 4.91 (d, 1 H), 3.23 (d, 1 H), 2.31 (s, 3 H), 1.71 (s, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 214.0, 199.4, 144.3, 131.0, 129.1, 128.4, 127.3, 113.7, 112.0, 100.3, 72.7, 27.8, 18.8; CIMS *m/e* (relative intensity) 229 (MH^+, 53), 228 (82), 211 (100), 158 (63), 115 (18); HRMS exact mass calcd for $C_{15}H_{17}O_2$ (MH^+) 229.1229, found 229.1241.

Aldol product 16b was prepared from **11** and isobutyraldehyde (**13b**) in 62% yield: IR ($CDCl_3$) 3390, 2940, 2920, 2840, 1923, 1665, 1460, 1350, 1233 cm^{-}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.35–7.25 (m, 5 H), 6.70 (s, 1 H), 4.22 (br, 1 H), 2.94 (d, 1 H), 2.30 (s, 3 H), 1.93 (m, 1 H), 0.97 (d, 3 H), 0.92 (d, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 213.9, 199.6, 131.3, 129.1, 128.3, 127.3, 114.2, 100.0, 75.1, 33.0, 27.8, 19.7, 18.0; CIMS *m/e* (relative intensity) 231 (MH^+, 51), 213 (100), 158 (33), 115 (14); HRMS exact mass calcd for $C_{15}H_{19}O_2$ (MH^+) 231.1385, found 231.1381.

Aldol product 16c was prepared from **11** and pivaldehyde (**13c**) in 47% yield: IR ($CDCl_3$) 3400, 2940, 2920, 2840, 1925, 1660, 1460, 1350, 1230 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ δ 7.36–7.24 (m, 5 H), 6.71 (s, 1 H), 4.36 (s, 1 H), 3.15 (br, 1 H), 2.31 (s, 3 H), 0.91 (s, 9 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 214.7, 199.4, 131.3, 129.1, 128.3, 127.4, 112.9, 100.0, 75.0, 36.5, 27.7, 25.9.

Aldol product 16d was prepared from **11** and benzaldehyde (**13d**) in 50% yield: IR ($CDCl_3$) 3400, 1930, 1674, 1490, 1450, 1352, 905, 730, 690 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.4–7.1 (m, 5 H), 6.62 (s, 1 H), 5.73 (d, 1 H), 3.47 (d, 1 H), 2.29 (s, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 214.4, 199.8, 130.8, 129.7, 129.0, 128.3, 128.2, 127.7, 127.2, 126.0, 116.4, 100.8, 71.5, 27.8; CIMS *m/e* (relative intensity) 265 (MH^+, 15), 248 (100), 158 (51), 115 (15); HRMS exact mass calcd for $C_{18}H_{17}O_2$ (MH^+) 265.1228, found 265.1232.

Aldol product 16e was prepared from **11** and cyclohexanone (**13e**) in 18% yield: IR ($CDCl_3$) 3450, 2925, 2840, 1922, 1660, 1485, 1440, 1350, 1240 cm^{-}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.40–7.25 (m, 5 H), 6.68 (s, 1 H), 4.33 (s, 1 H), 2.31 (s, 3 H), 2.0–1.1 (m, 10 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 213.7, 201.4, 131.3, 129.1, 128.2, 127.0, 118.3, 99.9, 73.0, 41.9, 37.4, 37.2, 28.6, 27.0, 25.6, 24.9, 21.8, 21.7; CIMS *m/e* (relative intensity) 257 (M^+, 15), 239 (100), 158 (16); HRMS exact mass calcd for $C_{17}H_{21}O_2$ (MH^+) 257.1542, found 257.1555.

5,5-Diphenyl-3,4-pentadien-2-one (21). Diphenylacetyl chloride (**20**) was prepared from diphenylacetic acid (2 g, 9.4 mmol) and $SOCl_2$ (3.4 mL, 5.59 g, 47 mmol) by refluxing in toluene (6 mL) under argon for 3–4 h. After removal of the excess $SOCl_2$ and the solvent in vacuo, the crude material (2.2 g, 9.4 mmol) was dissolved in CH_2Cl_2 (9 mL). This solution was added dropwise to a solution of 1-(triphenylphosphoranylidene)-2-propanone (2.9 g, 9.4 mmol) and triethylamine (0.958 g, 1.8 mL, 9.4 mmol) in CH_2Cl_2 (27 mL) and stirred at 0 °C under argon. The reaction mixture turned bright yellow, and TLC analysis (10% Et_2O/petroleum ether) showed complete reaction immediately. Approximately half of the solvent was removed on a rotary evaporator, and diethyl ether was added to precipitate the Ph_3PO. After filtration, silica gel was added to adsorb the reaction products and all of the solvent was removed. Purification via flash column chromatography (10% Et_2O/petroleum ether) yielded **21** (1.83 g, 7.8 mmol, 83%) as a light yellow oil: IR (neat) 1935, 1689, 1600, 1500, 1454, 1368, 1236, 762, 698 cm^{-}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.40–7.17 (m, 10 H), 6.24 (s, 1 H), 2.34 (s, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 215.2, 198.1, 134.0, 128.8, 128.5, 128.4, 113.7, 100.1, 27.1; EIMS *m/e* (relative intensity) 234 (M^+, 93), 191 (100), 165 (21), 43 (42); HRMS exact mass calcd for $C_{17}H_{14}O$ (M^+) 234.1045, found 234.1037.

Aldol product 23a was prepared from **21** and methacrolein (**13a**) in 64% yield: IR ($CDCl_3$) 3450, 1920, 1670, 1590, 1448, 1350, 1240, 1225 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.4–7.3 (m, 10 H), 5.16 (br, 2 H), 4.95 (s, 1 H), 3.39 (br, 1 H), 2.28 (s, 3 H), 1.58 (s, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 213.5, 199.4, 144.5, 133.9, 128.8, 128.4, 128.3, 115.4, 112.0, 72.9, 27.9, 18.7; CIMS *m/e* (relative intensity) 305 (MH^+, 7), 287 (100), 235 (25); HRMS exact mass calcd for $C_{21}H_{21}O_2$ (MH^+) 305.1542, found 305.1542.

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Aldol product 23b was prepared from **21** and isobutyraldehyde (**13b**) in 60% yield: IR ($CDCl_3$) 3450, 3045, 3020, 2955, 1920, 1665, 1595, 1490, 1450, 1352, 1230 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.43-7.26 (m, 10 H), 4.31 (t, 1 H), 2.92 (d, 1 H), 2.39 (s, 3 H), 1.97 (m, 1 H), 0.88 (dd, 6 H); ^{13}C NMR (360 MHz, $CDCl_3$) δ 213.4, 199.7, 134.1, 128.8, 128.4, 128.3, 113.2, 103.0, 75.4, 32.9, 28.0, 19.7, 17.9; CIMS *m/e* (relative intensity) 307 (MH^+, 20), 289 (100), 23 4 (31), 191 (18); HRMS exact mass calcd for $C_{21}H_{23}O_2$ (MH^+) 307.1698, found 307.1712.

Aldol product 23d was prepared from **21** and benzaldehyde (**13d**) in 50% yield: IR ($CDCl_3$) 3390, 3040, 3018, 2960, 2900, 1920, 1660, 1590, 1485, 1445, 1235 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.35-7.01 (m, 15 H), 5.80 (s, 1 H), 3.62 (br, 1 H), 2.37 (s, 3 H); ^{13}C NMR (360 MHz, $CDCl_3$) δ 213.7, 199.4, 141.3, 133.9, 128.7, 128.6, 128.3, 128.3, 128.21, 128.18, 128.0, 127.6, 126.4, 115.6, 115.0, 71.8, 27.9; CIMS *m/e* (relative intensity) 341 (MH^+, 6), 323 (100), 235 (94), 191 (36), 105 (16); HRMS exact mass calcd for $C_{24}H_{21}O_2$ (MH^+ 341.1542, found 341.1534.

Aldol product 23f was prepared from **21** and acetophenone (**13f**) in 35% yield: IR ($CDCl_3$) 3460, 3040, 3020, 2920, 1920, 1662, 1593, 1490, 1448, 1355, 1260, 1245 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 7.45-7.21 (m, 15 H), 5.08 (s, 1 H), 2.35 (s, 3 H), 1.67 (s, 3 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 212.8, 201.0, 147.4, 129.0, 128.9, 128.5, 128.5, 128.4, 128.1, 128.1, 126.8, 124.5, 116.3, 115.1, 76.6, 30.5, 28.6; FAB *m/e* (relative intensity) 355 (MH^+, 8), 319 (12), 295 (24), 234 (100), 191 (23), 121 (27); HRMS exact mass calcd for $C_{25}H_{23}O_2$ (MH^+) 355.1698, found 355.1696.

Acknowledgment. Support by the donors of the Petroleum Research Fund of the American Chemical Society (20838-G1, 23475-AC), by the American Cancer Society (CH 525), and by the National Institutes of Health (RO1-GM 45970) is gratefully acknowledged.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of compounds **11**, **16a**, **16b**, **16c**, **16d**, **16e**, **23a**, **23b**, **23d**, and **23f** (10 pages). Ordering information is given on any current masthead page.

$Ni_{23}Se_{12}(PEt_3)_{13}$. An Intramolecular Intergrowth of NiSe and Ni

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Contribution from the AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974. *Received January 9, 1992*

Abstract: The reaction of $Ni(COD)_2$ (COD = cyclooctadiene) with Et_3PSe at elevated temperature gives a mixture of Ni_3Se_2 and elemental Ni. When the same reagents are combined at lower temperature the cluster compound $Ni_{23}Se_{12}(PEt_3)_{13}$ is formed and can be isolated as a crystalline solid. We have determined the structure of this compound crystallographically (trigonal space group *R3c*, a = 17.577 (1) Å, c = 75.191 (6) Å, V = 20118 Å^3, Z = 6). The crystallography shows the cluster to be a fusion of distorted fragments of NiSe (NiAs structure type) and hexagonally close packed elemental Ni. This cluster can be converted thermally to the same solid products (Ni_3Se_2 and Ni) as those resulting from the combination of Ni^0 and Se^0 under the more forcing conditions. This shows that the cluster is allowable as an intermediate in the molecules-to-solids conversion.

Introduction

We report that bis(cyclooctadiene)Ni, $Ni(COD)_2$, reacts with triethylphosphine selenide, Et_3PSe, in refluxing toluene to give a mixture of extended solids, Ni_3Se_2 and elemental Ni. We also report the synthesis, structure, and thermal behavior of $Ni_{23}Se_{12}(PEt_3)_{13}$, **1**, a molecular cluster compound we have been able to isolate from the reaction of the two zerovalent[1] precursor molecules. We analyze the structure of **1** in relation to extended solid-state compounds and see that it can be viewed as a fusion of a molecular fragment of NiSe and a molecular fragment of Ni. In this way we show that the title compound is a molecular example of a solid-state intergrowth compound.

We have shown previously that inorganic solid-state tellurides can result from the reaction of low-valent transition-metal complexes with trialkylphosphine tellurides[2] and have seen that such reactions can be arrested at the molecular stage. In the particular case of nickel telluride[2c] we found that two cluster intermediates can be isolated, $Ni_9Te_6(PEt_3)_8$ and $Ni_{20}Te_{18}(PEt_3)_{12}$, and that each cluster can be identified with a fragment of the NiTe structure. We suggested that in such simple solid-forming reactions the structure of the solid is mimicked very early on in the growth process. To test this hypothesis we examined the reaction of Ni^0 with triethylphosphine selenide.

Experimental Section

Unless noted to the contrary all operations were conducted under an inert atmosphere using standard drybox and Schlenk techniques. All solvents were anhydrous grade, used as purchased from Aldrich. Bis(cyclooctadiene)nickel was either prepared using literature methods[3] or purchased from Strem Chemicals and used as received. Triethylphosphine (Aldrich) and selenium (Alfa) were used as received. Triethylphosphine selenide was prepared by the action of triethylphosphine on selenium. Powder X-ray diffraction patterns were recorded on a Rigaku Miniflex diffractometer (Cu Kα).

Preparation of Ni- and Se-Containing Solid-State Compounds. $Ni(COD)_2$ (0.28 g, 1.0 mmol) was dissolved in 15 mL of toluene and Et_3PSe (0.20 g, 1.0 mmol) was dissolved in 5 mL of toluene. The Se-containing solution was added to the Ni-containing solution, and the resulting mixture was heated at reflux 17 h. The mixture was cooled and filtered to give a black solid (90.0 mg). This solid did not diffract X-rays. A portion of this solid (53 mg) was heated at 270 °C for 18 h. This gave a shiny black solid (45 mg). Powder X-ray diffraction showed this to be Ni_3Se_2 with small interferences due to elemental Ni.

Preparation of $Ni_{23}Se_{12}(PEt_3)_{13}$. $Ni(COD)_2$ (2.46 g, 9.0 mmol) was suspended in toluene (50 mL) to which PEt_3 (0.2 mL, 1.7 mmol) had been added. In a separate vessel Et_3PSe (6.71 g, 34.1 mmol) was dissolved in toluene (100 mL). The solution of Et_3PSe was diluted with heptane (100 mL), taking care that the phosphine selenide remained in

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0002-7863/92/1514-10334$03.00/0