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The Stereochemistry of Allenic Enol Tautomerism – Independent Generation and Reactivity of the Enolates[‡]

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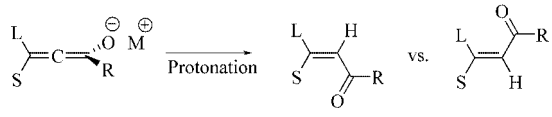
A priori, allenic enolates as reaction intermediates may be protonated to afford (*Z*)- or (*E*)-α,β-unsaturated carbonyl products. The allenic enolates are tautomeric with α-vinylcarbanions. The literature on the behavior of these species on protonation is highly varied both in stereochemical outcome and in mechanistic interpretation. The current study has provided an independent mode of generation of the allenic enolates and has investigated the reaction stereochemistry of protonation to afford the stereoisomeric α,β-unsaturated carbonyl products. Under kinetic conditions, these highly reactive species are protonated in the α,β-π plane with preference (*E*) to the larger β group. Under thermodynamic conditions, addition/elimination equilibrates the two product stereoisomers. The kinetic protonation stereochemistry is a function of solvent, proton donor, and donor concentration. Computations serve to clarify the reaction mechanism. It was found that the stereochemistry of ketonization of allenic enolates follows the reaction course suggested as possible some decades earlier and common to less unique enolates. Additionally, the linear versus the bent enolate structure proves to depend on the countercation.

Introduction

Our interest in the mechanism of protonation of mesomeric anions began decades earlier.[2] One unique system that had not received our experimental attention was the behavior of allenic enols and enolates. Nevertheless, at the time it was suggested that these are intermediates in the Michael addition to acetylenic ketones and esters.[2] It was noted that the allenic enolate species have two orthogonal π systems, and it was proposed that under kinetic conditions, the preferred protonation would be in the α,β plane, which leads to the thermodynamically less stable α,β-unsaturated carbonyl product.

Thus, our original 1955 suggestion[2] considered that the transition state for protonation of the allenic enolate had an α-carbon atom that should be close to sp-hybridized as a result of the considerable exothermicity of the reaction. The proposal further suggested that protonation would occur from the less-hindered face, having group S, with the consequence that the higher-energy product would predominate (see Scheme 1).

Since that time a large amount of research has involved reactions that must proceed either by way of the allenic enolates or via their tautomeric vinyl carbanions in which an α,β-enone has lost its α-hydrogen atom.



Scheme 1. Two alternative stereochemistries of kinetic protonation of allenic enolates (L = larger group, S = smaller group).

Background

In literature studies the stereochemical conclusions in the case of the Michael addition to ethynylcarbonyl compounds have been remarkably varied. The literature falls into two categories: (a) the addition of anionic nucleophiles lacking copper,[3] and (b) the addition of cuprates to the β-carbon atom of the ethynyl system.[4]

In the basic reaction both vinyl carbanions and allenic enolates have been considered as intermediates. In the Michael addition to ethynyl esters and ethynyl ketones, varied stereochemistries have been observed.[3a] The alkynones were reported reasonably consistently to afford the (*Z*) adducts while the alkynyl esters largely afforded (*E*) adducts. Nevertheless, product equilibration was noted to be a factor. In another investigation,[3b] the esters were reported to lead to (*Z*) products while with acetamidomalonate as the

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nucleophile, Michael addition to *tert*-butyl propargylate, the (*E*) stereoisomeric product was reported.[3c]

Very early in the investigations of cuprate addition to ethynyl systems were the pioneering studies by Corey,[4a] Siddall,[4b] and Klein.[4c,4d] The Corey study assumed stereospecific formation of a vinylcopper intermediate at low temperatures which isomerized to the (*E*) counterpart at higher temperatures. Siddall considered two alternative reaction intermediates, the vinylcopper and the copper allenolate, without a preference; however, at low temperature (*Z*) addition was again observed. The most definitive mechanistic studies were by Klein who provided evidence for a vinylcopper intermediate using infrared spectroscopy at low temperatures. The formation and reaction of the vinylcopper species was shown to be stereospecific. But at higher temperatures, the initial (*Z*)-vinylcopper species isomerized to the (*E*) species. Additionally, Klein considered the copper allenolate as the intermediate permitting the isomerization. Interestingly, treatment of the vinylcopper species with methyllithium led to a new species assumed to be the allenolate. This gave a varied stereochemistry which was rationalized utilizing our less-hindered protonation mechanism.[2] Much more recently Krause[4e] utilized NMR analysis and concluded that two copper allenolates are the species resulting from Michael addition with the copper coordinating differently but intramolecularly with the allenic system. Subsequently, Ullenius and Krause[4f] have suggested that both vinylcopper and copper allenolates are accessible depending on the reagents used. It was suggested that protonation of allenolates proceeded unselectively in the cases studied. Finally, a theoretical study by Nakamura and Morokuma has indicated that the vinylcopper species is of lower energy than the allenolate which is involved only as an intermediate permitting equilibration between (*Z*) and (*E*) stereoisomers.[4g]

Hence, we were left with a rather confusing situation relative to the matter of protonation of allenolates. The present study primarily addresses the stereochemistry of the allenic enolate when it is clearly present. The relative stability of the linear allenic enolate and the vinyl carbanion tautomer is also considered. Computational results provide evidence on the relative stability of the linear allenic enolate vs. the vinyl carbanion as a function of the counter cation.

Results

Syntheses of Reactants

At the outset, it was the intention of the present research to prepare an isolable precursor to a typical allenic enolate, generate the enolate under controlled conditions, and determine the stereochemistry of the protonation reaction. For this purpose the allenyl ether **4** was chosen.

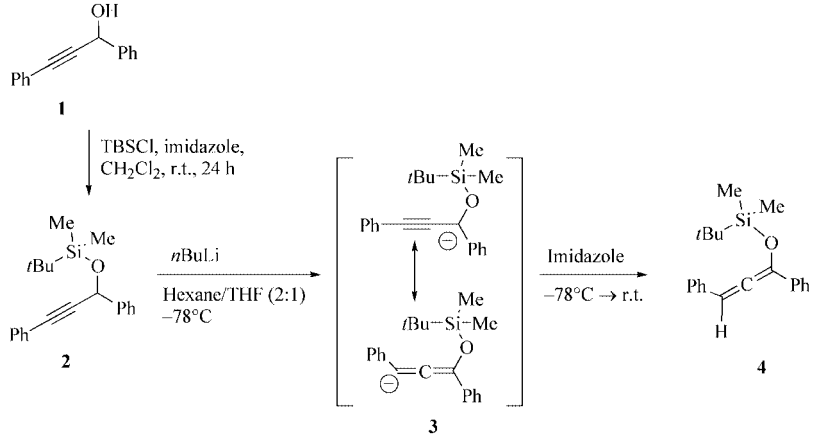
A series of allenyl silyl ethers has been reported in an elegant study by Reich[5] which made use of the Brook rearrangement.[6] Additionally, allenyl silyl ethers have been obtained by a variety of approaches.[7]

Our synthesis, as outlined in Scheme 2, proved particularly suitable for the system of interest. This began with phenyl(phenylethynyl)methanol (**1**). On silylation with the *tert*-butyldimethylsilyl chloride/imidazole combination, the silyl ether **2** was obtained. With trial and error variation of the reaction conditions, using *n*-butyllithium in hexane it proved possible to generate anion **3**. This anion was protonated with imidazole to give the desired allenyl silyl ether **4**.

During the imidazole protonation the lithium imidazole salt precipitated and could readily be removed. The structure of allenyl silyl ether **4** was confirmed by ^{1}H and ^{13}C NMR spectroscopy and its high-resolution mass spectrum. Our general approach was inspired by reports[5,8] of anions such as **3** reacting on silylation to afford allenyl silyl ethers. However, those reported modes of generation and protonation, applied to our anion **3**, were unsuccessful.

Kinetic Protonation Studies

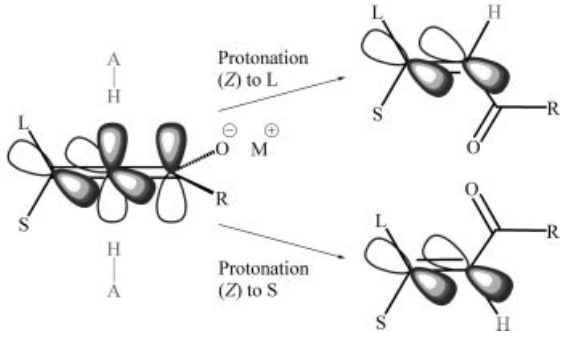
Allenyl ether **4** proved stable at room temperature and began to dimerize only after several days. The allenolate **5** was generated by an addition of a soluble fluoride salt to a solution of the siloxyallene **4** and the corresponding proton donor; see Scheme 3. In all cases these runs were monitored



Scheme 2. Synthesis of *tert*-butyldimethylsilyl ether **4**.

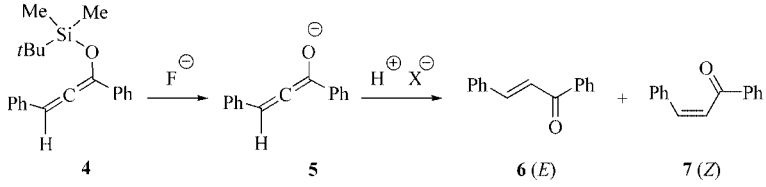
vs. time to assure kinetic control of the stereoselectivity. The results of the protonation with different donors, solvents and concentrations are summarized in Tables 1, 2 and 3. It is seen that there is a general preference for the formation of the (*Z*) stereoisomer **7**. The maximum stereoselectivity observed was with diisopropylammonium as the proton donor in dichloromethane. A plausible rationale is an increasing intervention by aggregate donors, somewhat analogous to the acetic acid effect noted in Table 3 and discussed below.

The high stereoselectivity with diisopropylammonium as the proton donor led us to consider the effect of its concentration (Scheme 4). Table 2 summarizes our findings which revealed that the stereoselectivity increased with the concentration of the amine hydrochloride. With 0.15 M hydrochloride the selectivity reached 85%. In the case of acetic acid as the proton donor, a similar increase in selectivity was encountered as the acetic acid concentration was increased. This reached 84% as noted in Table 3.



Scheme 4. Preferred protonation (*E*) to the larger β substituent (L); L is the larger and S is the smaller β substituent.

A particularly puzzling aspect of the literature reports was the variation in stereoselectivity encountered in the various studies involving Michael addition of nucleophiles to propargyl reactants. This led us to check the behavior of (*Z*)-chalcone in the presence of nucleophiles. The sodium



Scheme 3. Generation and kinetic protonation of 1,3-diphenylallenolate **5**.

Table 1. Stereoselectivity with a variety of proton donors.

Proton source	(*Z*)/(*E*) ratio [normalized to (*E*) isomer]				
	THF (TBAF)	CH_2Cl_2 (TBAF)	MeOH (TBAF)	MeOH (KF)	*i*PrOH (TBAF)
None added	0.07	–	–	1.7	1.85
AcOH	2.5	2.3	2.3	1.88	2.6
PivOH	2.5	2.8	–	–	2.5
o-*t*Bu-phenol[a]	2.7	2.8	2.8	2.0	2.15
Tetramethyl-piperidinium[b]	–[c]	–	–	–	3.2
iPr_2NH_2Cl	–[c]	4.2	2.7	2.7	3.2

[a] 2,6-Di-*tert*-butyl-4-methylphenol. [b] 2,2,6,6-Tetramethyl-4-propoxypiperidinium chloride. [c] Proton donor insufficiently soluble.

Table 2. Results of the protonation of allenolate **5** by diisopropylammonium chloride in *i*PrOH with increasing concentrations of the proton donor.

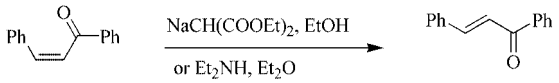
Proton donor concentration [M]	Relative donor concentration	(*Z*)/(*E*) ratio [normalized to (*E*) isomer]
0.03	2	2.9
0.05	4	3.2
0.15	8	4.6
0.15	16	5.5

Table 3. Protonation of allenolate **5** in THF with increasing acetic acid concentrations.

Proton donor concentration [M]	Relative donor concentration	(*Z*)/(*E*) ratio [normalized to (*E*) isomer]
0.04	2	0.67
0.08	4	2.5
0.12	8	4.2
0.20	12	4.5
0.22	16	5.1
0.39	32	5.1

conjugate base of diethyl malonate was typically used as the base in the Michael addition of diethyl malonate to ethynyl phenyl ketones.

In the present study with 0.09 M sodium malonate and (*Z*)-chalcone in ethanol at room temperature, an 80% (*Z*) → (*E*) conversion resulted in 2 h. A similar isomerization was observed with diethylamine in diethyl ether. In 3 h at room temperature a 1:1 (*Z*)/(*E*) mixture resulted and the conversion approached 80% in 20 h [note Equation (1)].



(1)

7 (*Z*) **6** (*E*)

Discussion of Results and Conclusions

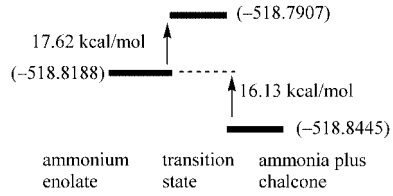
The first general conclusion is that on kinetic protonation the typical allenic enolate studied does so by preferential attack from the less hindered side of the nearly linear enolate moiety as suggested in our first publication on enolate chemistry.[2] Thus, protonation occurs (*E*) to the large β-phenyl group under most conditions. This then leads to the thermodynamically less stable stereoisomer, namely (*Z*)-chalcone (**7**).

Inspection of Table 1 reveals relatively little variation in stereoselectivity with proton donors differing in steric bulk. 2,6-Di-*tert*-butyl-4-methylphenol does not show an enhanced selectivity compared with the smaller acetic and pivalic acid proton donors (note Table 1) in agreement with an early transition state. Additionally, it is clear that there are two modes of protonation – directly by the proton donor utilized and indirectly by the solvent. At lower proton donor concentrations the selectivity diminishes as solvent protonation becomes dominant (note, for example, Table 1). With methanol as a solvent, the selectivity is low and one may conclude that it is methanol which delivers the proton.

Table 3 also reveals another point of interest, namely the increasing (*Z*)/(*E*) stereoselectivity as a function of increasing acetic acid concentration in THF, a solvent which alone cannot serve as a proton donor. This suggests that protonation here is more than unimolecular, perhaps by the more acidic acetic acid dimer. A similar effect has been seen in our previous protonation studies (see ref.[1] and papers cited therein).

Computational Aspects

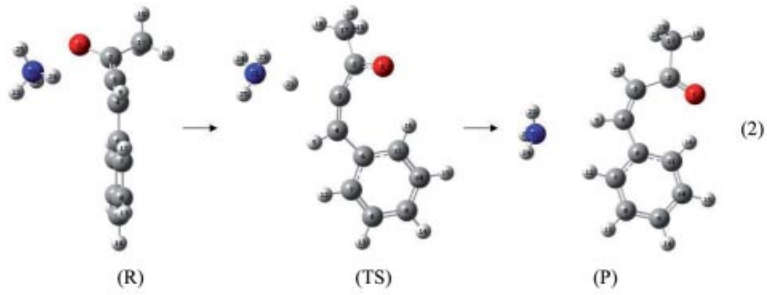
A complementary computational approach seemed of interest. In this, ammonia replaced an amine. Using QST2 and QST3 in the Gaussian03 group of programs,[9] the reaction course depicted in Equation (2) resulted. The QST2 method required prior geometry optimizations of the reactant R (an ammonium enolate) and the product P (chalcone plus an ammonia molecule). This was followed by the search for the reaction transition state (TS). Once a transition state was obtained, this was used for a QST3 computation. For the initial geometry optimizations RHF/3-21g* was used, followed by density functional B3LYP/3-21g* and then B3LYP/6-31g*. Frequency computations revealed one imaginary eigenvalue for the transition structure (TS) obtained. Our selection of computational methodology was based on practicality in order to give quantitatively meaningful but approximate results. Thus, the approach is approximate in not utilizing explicit solvent but simulation of a dielectric medium. In the QST3/B3LYP/6-31g* transition state the hydrogen atom was found to be 1.086 Å from the nitrogen atom and 1.865 Å from the allenic α-carbon atom. Scheme 5 gives the density functional B3LYP/6-31g* energies obtained for the reaction. These, are "pseudo gas phase" ones and too large for a solution process. They do, however, illustrate semiquantitatively the reaction energetics. Computational details are given in the Supporting Information.



Scheme 5. B3LYP computations (energies in parentheses are in Hartrees).

Additionally, the geometries of the initial enolates as a function of the counter cation were studied with the same B3LYP/6-31G* methodology. Geometry optimization of the enolates with sodium, lithium and copper as the counter cations was carried out. In all the cases a high dielectric medium was used to simulate solvent and the R groups were simulated by hydrogen (see the Supporting Information for computational details). The energies and angularities are listed in Table 4. Interestingly, with sodium and lithium as the counter cations, an essentially linear allenic enolate was preferred (Table 4, Entries 2–4). In the lithium case (Entry 4), the lithium–oxygen pair distance (1.72 Å) was longer than expected for covalency. With sodium as the counter cation (Entries 2 and 3), the geometry again was linear and independent of the distance between the sodium cation and the negative oxygen atom. But for lithium by searching, there was found a local minimum of higher energy and with a bent, vinyl structure (Entry 5). With copper the (bent) vinyl carbanion structure resulted as a global minimum on geometry optimization (Table 4, Entries 6 and 8). However, again, a local minimum of higher energy, now with a linear structure was found computationally (Entries 7 and 9).

In comparing the lithium and copper equilibria of the global minima with the higher energy local minima, it is seen that the preferred linear lithium species is lower in energy than the vinyl one by 7.5 kcal/mol [Equation (3)] while, in contrast, the vinylcopper minimum is lower in energy than the linear counterpart by 13.8 kcal/mol [note Equation (4)].



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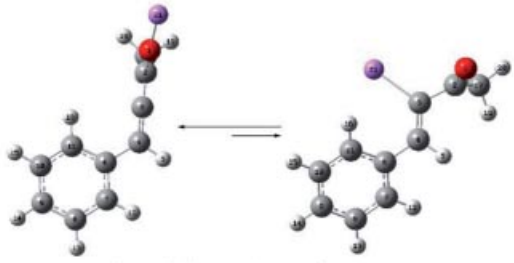
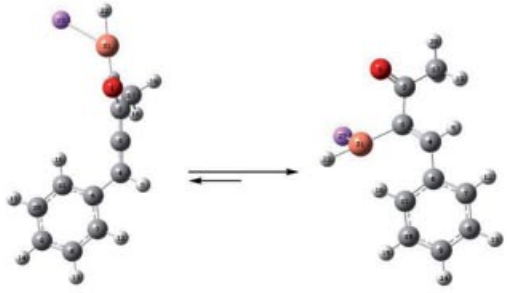


(3)

linear lithium enolate preferred



(4)

vinylcopper anion preferred

Table 4. Computational results on linearity vs. environment.

Entry	Enolate	Angle 2–3–4 [°]	M–O bond length [Å]	Energy [Hartrees]	Comments
1	gas phase	137.764	n. a.	–461.67390	no cation, minimum
2	Na	179.593	2.09	–624.02296	Na–O not fixed, minimum
3	Na	179.467	4.12	–624.02299	Na–O fixed at 4.12 Å, minimum
4	Li	179.137	1.72	–469.27035	global minimum
5	Li	115.806	1.24	–469.25869	local minimum
6	Cu	121.165	1.89	–2103.14748	single copper
7	CuR_2	178.521	1.178	–2103.11993	local minimum
8	CuRLi(1)	116.736	1.87	–2110.16989	global minimum
9	CuRLi(2)	179.382	1.08	–2110.14836	local minimum

Thus, much of the literature discrepancies now become understandable. The copper species, indeed, is a vinyl species with a nonlinear enone structure as originally proposed by Klein. However, a local minimum of linear structure and higher energy was found computationally (note Entries 6 and 8). We can surmise that this linear copper enolate is the intermediate permitting (*Z*)- and (*E*)-vinyl carbanions to equilibrate at higher temperatures.

The role of the cation is seen to be considerable. With no cation or solvent present, the preferred gas-phase species is the (bent) vinyl carbanion (note Entry 1 in Table 4). The general preference of linearity with the lithium and sodium counter cations may be ascribed to the inability of these to form covalent bonds to the α-carbon atom and the preference for a high electron density at the oxygen atom. The result is the formation of the linear allenic enolate studied experimentally in this investigation.

Conclusions

It is seen that the original 1955 speculation,[2] and that of some subsequent literature (vide supra), of allenic enols with their two orthogonal π systems protonating to give the less stable of two α,β-unsaturated carbonyl products is confirmed experimentally and computationally. However,

the preference for the linear allenolate extends only for polar media and with alkali metal cations. In contrast, ab initio computations find a preference for the vinyl carbanion geometry along with a higher energy local minimum with linearity in the absence of solvent and in the case of copper.

Experimental Section

General Procedures: Nuclear magnetic resonance spectra (^{1}H and ^{13}C, 300 MHz and 75 MHz, respectively) were obtained in $CDCl_3$ with TMS as an internal standard. Isomer ratios were determined by ^{1}H NMR spectral integrals. These were collected with a relaxation delay of 17.0 s. Melting points were determined in open capillaries and a heating block. Column chromatography (CC) was performed on a column slurry-packed with 60–200 mesh silica gel. All solvents were freshly distilled from appropriate drying agents under nitrogen before use.

Synthesis of 1,3-Diphenylprop-2-yn-1-ol (1): The method employed by Spee et al.[10] afforded a yield of 9.7 g (91%), b.p. 127–129 °C/1 Torr. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.61 (d, J = 6.25 Hz, 1 H), 5.67 (d, J = 6.25 Hz, 1 H), 7.22–7.49 (m, 8 H), 7.56 (m, 2 H) ppm.

Synthesis of 1-(*tert*-Butyldimethylsiloxy)-1,3-diphenylprop-2-yne (2): To a stirred solution of 1,3-diphenylprop-2-yn-1-ol (**1**, 3.5 g, 16.8 mmol) and imidazole (1.3 g, 18.5 mmol) in 30 mL of dichloromethane a solution of tBuMe$_2$SiCl (2.8 g, 18.5 mmol) in 20 mL of dichloromethane was added at once. The reaction mixture was stirred at room temp. for 24 h. Then the solution was washed with water and with aqueous Na_2CO_3 (10%). The organic phase was dried with sodium sulfate and concentrated in vacuo. The residue was flash-filtered with hexane through a short silica gel column. Concentration in vacuo afforded the product as a colorless oil, which became yellow after exposure to air and light. Yield 5.34 g (98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.23 (s, 3 H), 0.26 (s, 3 H), 0.99 (s, 9 H), 5.77 (s, 1 H), 7.3–7.47 (m, 8 H), 7.58–7.62 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –4.8, –4.3, 18.4, 25.9, 65.3, 85.7, 90.1, 126.2, 127.7, 128.2, 128.3, 131.6, 141.7 ppm. EI-HRMS: calcd. for $C_{17}H_{17}OSi^{\cdot}$ 265.1049 $[M-t\text{Bu}]^{\cdot+}$, found 265.1047.

Proton Transfer in 1-(*tert*-Butyldimethylsiloxy)-1,3-diphenylprop-2-yne (2) to Afford 1-(*tert*-Butyldimethylsiloxy)-1,3-diphenylpropa-1,2-diene (4): To a stirred solution of 1-(*tert*-butyldimethylsiloxy)-1,3-diphenylprop-2-yne (**2**, 1.0 g, 3.1 mmol) in hexane/THF (10 mL/5 mL) a solution of nBuLi (1.53 mL, 2.48 N in hexane) at –78 °C was slowly added. The mixture turned dark red. The reaction mixture was stirred at –78 °C for 30 min and then a solution of imidazole (0.26 g, 3.8 mmol) in THF (5.0 mL) was added in one portion to the vigorously stirred solution at –78 °C. The color changed to pale orange and a lithium imidazole salt precipitated. After further stirring at –78 °C for 20 min, the solution was diluted with 30 mL of dry hexane and stirred until room temp. was reached, followed by filtration and concentration in vacuo of the filtrate. The residue was partitioned between 25 mL of dry acetonitrile and 75 mL of hexane. The hexane layer was filtered and concentrated in vacuo to give the product as a yellow oil; yield 0.87 g (87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.14 (s, 3 H), 0.20 (s, 3 H), 1.0 (s, 9 H), 6.95 (s, 1 H), 7.22–7.42 (m, 8 H), 7.54–7.57 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –4.7, –4.5, 18.5, 26.1, 107.6, 125.2, 127.8, 128.0, 128.4, 128.9, 134.6, 135.3, 200.6 ppm. EI-HRMS: calcd. for $C_{21}H_{26}OSi$ 322.1753 $[M]^{\cdot+}$, found 322.1756.

General Procedure for Kinetic Protonation of 1-(*tert*-Butyldimethylsiloxy)-1,3-diphenylpropa-1,2-diene (4) with Acetic Acid in THF To Afford Chalcone Isomers 6 and 7: To a stirred solution of siloxyallene **4** (0.20 g, 0.64 mol) in10 mL of THF 1.3 mL of a 2.0 M THF solution of glacial acetic acid was added followed by 1.3 mL of a 1.0 M THF solution of tetrabutylammonium fluoride. The reaction mixture was stirred at room temperature and samples of the reaction solution were taken to monitor the process by HPLC. After 2 h of stirring, the reaction mixture was partitioned between water (100 mL) and hexane (30 mL), the organic phase dried with magnesium sulfate and concentrated in vacuo at room temperature. The residual mixture contained (*Z*)- and (*E*)-chalcone in a ratio of 2.4:1 as measured by ^{1}H NMR analysis; the corresponding characteristic peaks of (*Z*)- and (*E*)-chalcone were identified by comparison with pure isomers. After column separation (SiO_2//hexane/dichloromethane, 4:1) three major fractions were collected. **(a):** 5.0 mg of a monosilated dimer of the reactant allene **8**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.19 (s, 3 H), 0.48 (s, 3 H), 0.79 (s, 9 H), 4.76 (dd, J = 9.6, J = 2.7 Hz, 1 H), 4.87 (d, J = 9.6 Hz, 1 H), 6.39 (d, J = 2.1 Hz, 1 H), 6.79 (m, 2 H), 7.02 (m, 3 H), 7.09 (m, 3 H), 7.16–7.26 (m, 5 H), 7.4 (dq, J = 8.4 Hz, 2 H), 7.55 (tt, J = 7.8 Hz, 2 H), 7.64 (tt, J = 7.2 Hz, 1 H), 8.12 (dt, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.8, –1.3, 18.5, 26.1, 49.3, 52.9, 86.1, 126.3, 127.1, 127.2, 127.4, 127.6, 127.9, 128.1, 128.4, 128.9, 129.2, 129.6, 133.5, 134.9, 137.4, 138.0, 141.3, 143.8, 195.9 ppm. EI-HRMS: calcd. for $C_{32}H_{29}O_2Si^{\cdot}$ 473.1937 $[M-t\text{Bu}]^{\cdot+}$, found 473.1923. **(b):** (*Z*)-Chalcone **7**, 49 mg. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.62 (d, J = 12.9 Hz, 1 H), 7.02 (d, J = 12.9 Hz, 1 H), 7.20–7.26 (m, 3 H), 7.37–7.43 (m, 4 H), 7.52 (tt, J = 7.2, J = 1.4 Hz, 1 H), 7.97 (dm, J = 7.2 Hz, 2 H) ppm. **(c):** (*E*)-Chalcone **6**, 22 mg. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.44 (m, 3 H), 7.47–7.68 (m, 6 H), 7.82 (J = 15.6 Hz, 1 H), 8.03 (dm, J = 7.0 Hz, 2 H) ppm. This gives a (*Z*)/(*E*) ratio of 2.23:1, slightly different from the one measured by NMR spectroscopy, apparently due to isomerization on silica gel.

General Procedure for Kinetic Protonation of 1-(*tert*-Butyldimethylsiloxy)-1,3-diphenylpropa-1,2-diene (4) with Varying Solvents and Proton Donors: To a stirred solution of allene **4** (0.050 g, 0.16 mmol) in 10 mL of the selected solvent (THF, MeOH, CH_2Cl_2, or iPrOH) a calculated amount of a studied proton donor was added followed by crystalline tetrabutylammonium fluoride (0.11 g, 0.32 mmol). The reaction mixture was stirred at room temperature for 2 h. Then the reaction mixture was partitioned between water (100 mL) and hexane (30 mL), the organic phase was dried with magnesium sulfate and concentrated in vacuo at room temperature. The ratio of (*Z*)/(*E*) isomers in the residual mixture was determined by ^{1}H NMR analysis.

General Procedure for Kinetic Protonation of 1-(*tert*-Butyldimethylsiloxy)-1,3-diphenylpropa-1,2-diene (4) in Methanol with KF: To a stirred solution of allene **4** (50 mg, 0.16 mmol) in 10 mL of MeOH a calculated amount of the selected proton donor was added followed by 0.32 mL of a 1.0 M MeOH solution of potassium fluoride. The solution was stirred at room temperature for 2 h. Then the reaction mixture was partitioned between water (100 mL) and hexane (30 mL), the organic phase was dried with magnesium sulfate and concentrated in vacuo at room temperature. The ratio of (*Z*)/(*E*) isomers in the residual mixture was measured by ^{1}H NMR analysis.

Preparation of an Analytical Sample of (*Z*)-Chalcone (7) by UV Irradiation of (*E*)-Chalcone (6): After irradiating a solution of (*E*)-chalcone (**6**, 25 g) in acetonitrile (250 mL) with a 100-W mercury lamp with circulated 0.2 M aqueous $CuSO_4$ as a UV filter for 12 h,

a mixture (1:1) of the isomers was obtained. The solvent was removed and the residual yellow oil was separated in portions. The (*Z*)/(*E*) mixture (5.0 g) was chromatographed on an activated carbon (Barnebey-Cheney) column (25 mm × 400 mm). Following elution with 500 mL of hexane, the (*Z*) isomer was eluted with 300 mL of benzene. After the first 50 mL of eluent, 2.1 g of essentially pure (*Z*)-chalcone (**7**) was eluted as a yellow oil. The oil was recrystallized from methanol at –25 °C to give 1.6 g of yellow crystals of (*Z*)-chalcone (**7**), m.p. 44–45 °C.

Susceptibility of (*Z*)-Chalcone (7) to Epimerization with Diethylamine: To a stirred solution of (*Z*)-chalcone (**7**, 0.10 g, 0.48 mmol) in 5.0 mL of diethyl ether 0.050 mL of diethylamine was added. The mixture was stirred at room temp. for 40 min and an aliquot was concentrated in vacuo and the residue analyzed by ^{1}H NMR spectroscopy. The mixture consisted of (*Z*)- and (*E*)-chalcone in a ratio of 1.4:1. No traces of signals of an amine adduct were detected. After 3 h of reaction, the (*Z*)/(*E*) ratio was 1:1. After 20 h, the (*Z*)/(*E*) ratio was 0.17:1. After 44 h, the (*Z*)/(*E*) ratio was less than 0.03:1.

Epimerization of (*Z*)-Chalcone (7) by Sodium Diethyl Malonate: To a stirred solution of diethyl malonate (0.015 g, 0. 09 mmol) in absolute ethanol (5 mL) sodium hydride (0.004 g, 0.1 mmol, 60% dispersion in mineral oil) was added. The mixture was stirred for 5 min and (*Z*)-chalcone (**7**, 0.1 g, 0.48 mmol) was added. The mixture was stirred at room temp. for 2 h and the first sample was analyzed. The sample was concentrated in vacuo to dryness at room temp. and the residue was analyzed by ^{1}H NMR spectroscopy. The mixture consisted of (*Z*)-/(*E*)-chalcone in a ratio of 0.17:1 along with a corresponding amount of the Michael reaction product.

Supporting Information (see footnote on the first page of this article): NMR spectra and computational deatils.

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