(Trialkylsilyl)vinylketenes: Synthesis and Application as Diene Components in Diels−Alder Cycloadditions

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New strategies for the synthesis of (trialkylsilyl)vinylketenes ("TAS-vinylketenes") are described based on the photochemical Wolff rearrangement of α′-silyl-α′-diazo-α,β-unsaturated ketones and the 4π electrocyclic ring opening of cyclobutenones. These remarkably robust vinylketenes undergo highly regioselective [4 + 2] cycloadditions with reactive olefinic and acetylenic dienophiles to produce highly substituted cyclohexenones and phenols in which the ketene carbonyl dominates in controlling the regiochemical course of the reaction. The stereochemical course of these cycloadditions follows the Alder endo rule, as illustrated in the reaction of nitropropene with TAS-vinylketene **22**.

Introduction

The utility of ketenes in organic synthesis is well-established.[1] *Vinylketenes* (α,β-unsaturated alkenylketenes) have the capacity to function as exceptionally versatile four-carbon building blocks for the assembly of a variety of carbocyclic systems. [2 + 2] Cycloadditions of vinylketenes with alkenes and alkynes are especially valuable transformations which provide efficient access to 2-vinylcyclobutanone and cyclobutenone derivatives. Prior work in our laboratory has demonstrated that these cycloadditions can serve as triggering steps for pericyclic cascades leading to the formation of six-[2] and eight-membered[3] carbocyclic compounds (Figure 1). In these reactions, vinylketenes function in their "normal mode" of reactivity: as electron-deficient 2π components for [2 + 2] cycloadditions. It occurred to us that intriguing new synthetic transformations might be possible if this normal reaction pathway could be suppressed, allowing vinylketenes to express their underlying reactivity as electron-rich conjugated dienes. In this case, vinylketenes might participate as four-carbon components in Diels−Alder and related cycloadditions, opening up new avenues for the synthesis of six-membered carbocyclic and heterocyclic compounds.

The extension of the Diels−Alder reaction to include highly functionalized dienes has greatly expanded the utility of this important synthetic method.[4] An objective of continuing interest in this area has been the development of vinylketene *equivalents* capable of participating as diene components in Diels−Alder cycloadditions. The tendency of vinylketenes to form only [2 + 2] cycloadducts with alkenes and the intrinsic instability of these ketenes

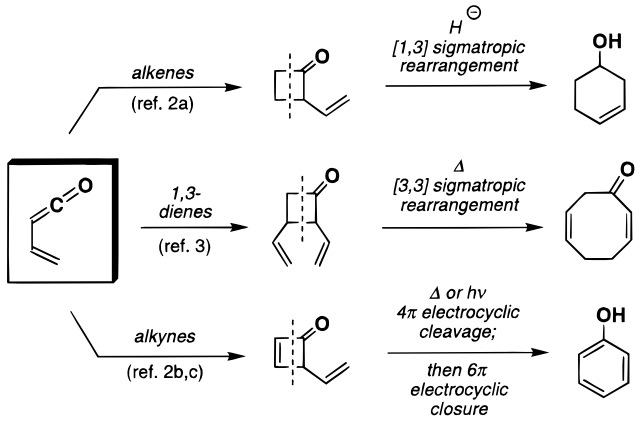

Figure 1. Annulation methods based on pericyclic cascades triggered by [2 + 2] cycloadditions of vinylketenes.

generally precludes their direct use as [4 + 2] enophiles.[5] Vinylketene *acetals* have found use as vinylketene surrogates; however, the scope of this methodology is somewhat limited because of the sensitivity of these compounds and the fact that the *s*-cis conformation required for cycloaddition is usually disfavored in these *Z*-substituted dienes.[4c,6]

The remarkable ability of silyl substituents to stabilize ketenes and suppress their tendency to dimerize is well-documented and has been attributed to a combination of σ donation by the electropositive silyl group and hyperconjugative σ−π interactions.[7] Several years ago, we reported the synthesis and isolation of (trimethylsilyl)vinylketene (**2**), a moderately stable, fully characterizable compound which can be stored for several weeks at

(1) (a) Tidwell, T. T. *Ketenes*; Wiley: New York, 1991. (b) Schaumann, E.; Scheiblich, S. In *Methoden der Organischen Chemie (Houben-Weyl)*; Kropf, E., Schaumann, E., Eds.; Thieme: Stuttgart, Germany, 1993; Vol. E15, Parts 2, 3.

(2) (a) Danheiser, R. L.; Martinez-Davila, C.; Sard, H. *Tetrahedron* **1981**, *37*, 3943. (b) Danheiser, R. L.; Gee, S. K. *J. Org. Chem.* **1984**, *49*, 1672. (c) Danheiser, R. L.; Brisbois, R. G.; Kowalczyk, J. J.; Miller, R. F. *J. Am. Chem. Soc.* **1990**, *112*, 3093.

(3) Danheiser, R. L.; Gee, S. K.; Sard, H. *J. Am. Chem. Soc.* **1982**, *104*, 7670.

(4) (a) Fringuelli, F.; Taticchi, A. *Dienes in the Diels-Alder Reaction*; Wiley: New York, 1990. (b) Petrzilka, M.; Grayson, J. I. *Synthesis* **1981**, 753. (c) Danishefsky, S. *Acc. Chem. Res.* **1981**, *14*, 400.

(5) Only a few cases of vinylketenes participating in [4 + 2] cycloadditions have been reported. For examples, see: (a) Day, A. C.; McDonald, A. N.; Anderson, B. F.; Bartczak, T. J.; Hodder, O. J. R. *J. Chem. Soc., Chem. Commun.* **1973**, 247. (b) Berge, J. M.; Rey, M.; Dreiding, A. S. *Helv. Chim. Acta* **1982**, *65*, 2230. (c) Collomb, D.; Doutheau, A. *Tetrahedron Lett.* **1997**, *38*, 1397.

(6) 1-Methoxy-1-(trimethylsiloxy)-1,3-butadienes undergo Diels−Alder reactions in poor yield unless the diene is substituted with additional electron-donating substituents. For example, see: Savard, J.; Brassard, P. *Tetrahedron* **1984**, *40*, 3455.

(7) For a discussion, see ref 1a and the following: Gong, L.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1991**, *113*, 6021.

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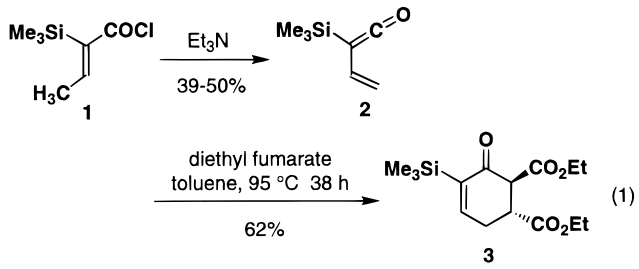
Published on Web 10/21/1998

0 °C in solution.[8,9] As predicted, **2** fails to enter into typical ketene [2 + 2] cycloadditions and instead participates as a diene component in [4 + 2] cycloadditions with electron-deficient alkenes and alkynes (e.g., eq 1). Unfortunately, the scope of these reactions is restricted by the limited thermal stability of this vinylketene, which must be handled and stored in solution. In addition, although **2** is conveniently prepared by dehydrohalogenation of the α,β-unsaturated acyl chloride **1**, we were not able to extend this approach to the efficient synthesis of more highly substituted vinylketene derivatives.

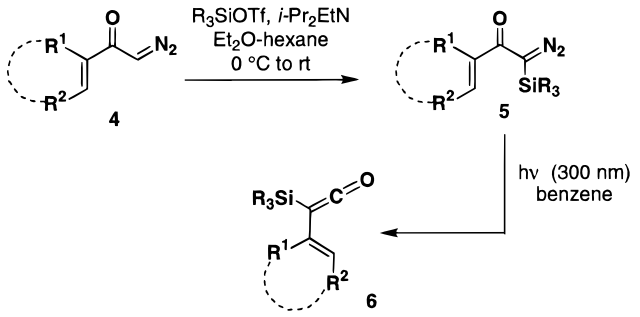


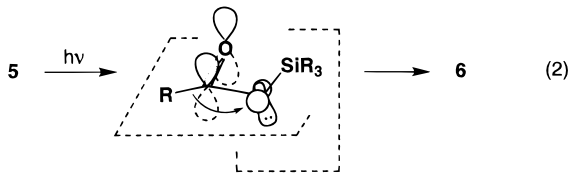
In this paper we report two new strategies for the synthesis of substituted (trialkylsilyl)vinylketenes ("TAS-vinylketenes") based on (a) the photochemical Wolff rearrangement of α′-silyl-α′-diazo-α,β-unsaturated ketones and (b) the 4π electrocyclic ring opening of cyclobutenones. Access to a variety of substituted TAS-vinylketenes via these methods has permitted a systematic investigation of their Diels−Alder reactions with alkene and alkyne dienophiles, the details of which are disclosed herein.

Results and Discussion

Although dehydrohalogenation provides convenient access to (trimethylsilyl)vinylketene (**2**), this strategy is not well-suited for the synthesis of more highly substituted TAS-vinylketenes. In some cases the requisite precursors are not readily available, and regiochemical ambiguities can arise in dehydrohalogenation (1,4-elimination) reactions involving β,β-disubstituted-α,β-unsaturated carboxylic acid derivatives. Recently, we have demonstrated that the photochemical Wolff rearrangement provides an efficient method for the synthesis of vinylketenes.[2c,10] In these transformations, the vinylketene is not isolated, but is trapped in situ with an alkyne, initiating a cascade of pericyclic reactions leading ultimately to the formation of a highly substituted aromatic system.[11] The efficiency of this process suggested that the rearrangement of α′-silyl-α′-diazo-α,β-unsaturated ketones (**5**) might provide the basis for a new route to TAS-vinylketenes (Scheme 1). We recognized, however, that the Wolff rearrangement of α-substituted-α-diazo ketones such as **5** might not prove to be a straightforward process. The photochemical Wolff rearrangement is generally thought to proceed via the singlet excited state of the diazo ketone by way of a concerted rearrangement of the migrating group with backside displacement of nitrogen.[10] This mechanism is possible only from the conformation in which the migrating bond and C−N bond have an antiperiplanar relationship. The requisite conformation of **5** (depicted in Scheme 1) is expected to be disfavored due to steric repulsion between the bulky trialkylsilyl group and the vinyl moiety, suggesting that concerted rearrangement of **5** might not be an efficient process. Fortunately, however, Maas and co-workers have shown that saturated alkyl(TAS)ketenes can be generated by means of the Wolff rearrangement,[12] suggesting that alternative mechanisms for this transformation may be possible. For example, dissociation of nitrogen might produce an acylcarbene that could rearrange to the desired ketene via the conformation depicted in eq 2.

Scheme 1





Synthesis of TAS-vinylketenes by Photochemical Wolff Rearrangement. The α-diazo ketones required for our study were all prepared using the "detrifluoroacetylative" diazo transfer strategy previously developed in our laboratory.[13] Thus, the methyl ketone precursor to **4** is treated with 1.1 equiv of lithium hexamethyldisilazide in THF at −78 °C to produce the lithium enolate, which is acylated by exposure to 1.2 equiv of trifluoroethyl trifluoroacetate at −78 °C for 5−10 min. Treatment of the resulting α-trifluoroacetyl ketone with 1.5 equiv of MsN_3 in the presence of 1.0 equiv of water and 1.5 equiv of Et_3N in acetonitrile (25 °C, 4 h) then affords the desired diazo ketones in good to excellent yield after chromatographic purification. It should be noted that α′-diazo-α,β-unsaturated ketones generally cannot be prepared by addition of diazomethane to acyl chlorides because of competing side reactions involving dipolar cycloadditions to the conjugated double bond.[14]

(8) Danheiser, R. L.; Sard, H. *J. Org. Chem.* **1980**, *45*, 4810.
(9) For Diels−Alder reactions of (silyl)vinylketenimines, see: Differding, E.; Vandevelde, O.; Roekens, B.; Van, T. T.; Ghosez, L. *Tetrahedron Lett.* **1987**, *28*, 397.
(10) For reviews of the photo Wolff rearrangement, see: (a) Regitz, M.; Maas, G. *Diazo Compounds—Properties and Synthesis*; Academic Press: New York, 1986. (b) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; Wiley: New York, 1998. (c) Zollinger, H. *Diazo Chemistry II: Aliphatic, Inorganic, and Organometallic Compounds*; VCH: New York, 1995.
(11) For applications of this aromatic annulation strategy in the total synthesis of natural products, see: (a) Danheiser, R. L.; Casebier, D. S.; Loebach, J. L. *Tetrahedron Lett.* **1992**, *33*, 1149. (b) Danheiser, R. L.; Casebier, D. S.; Huboux, A. H. *J. Org. Chem.* **1994**, *59*, 4844. (c) Danheiser, R. L.; Helgason, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 9471. (d) Danheiser, R. L.; Trova, M. P. *Synlett* **1995**, 573. (e) Danheiser, R. L.; Casebier, D. S.; Firooznia, F. *J. Org. Chem.* **1995**, *60*, 8341.
(12) (a) Maas, G.; Brückmann, R. *J. Org. Chem.* **1985**, *50*, 2801. (b) Brückmann, R.; Schneider, K.; Maas, G. *Tetrahedron* **1989**, *45*, 5517.
(13) (a) Danheiser, R. L.; Miller, R. F.; Brisbois, R. G.; Park, S. Z. *J. Org. Chem.* **1990**, *55*, 1959. (b) Danheiser, R. L.; Miller, R. F.; Brisbois, R. G. *Org. Synth.* **1995**, *73*, 134.

Silylation of the diazo ketones was accomplished using a modification of the method of Maas and co-workers.[15] As reported by Maas, the silylated α-diazo ketones have a tendency to undergo protodesilylation during their preparation and isolation caused by the presence of acidic trialkylammonium triflate byproducts. We found that this problem can be minimized by employing a solvent system consisting of equal parts Et_2O and hexane. The ammonium salts have reduced solubility in this medium, and the desired silylation products are obtained in 10−30% higher yield as compared to reaction in Et_2O alone. A variety of α′-trialkylsilyl-α′-diazo-α,β-enones can be prepared in good yield by employing this protocol (Table 1). Diazo ketones **14**−**21** were isolated as yellow to orange oils that can be stored in solution at 0 °C for several days without significant decomposition. In the case of several of the less substituted substrates (entries 4−7), byproducts were obtained that appear to be the result of a 1,3-(C→O) silyl shift to form a diazo alkene which then undergoes dipolar cycloadditions with the α,β-unsaturated carbonyl compounds. This side reaction can be suppressed by carrying out the reaction at lower concentration (0.02 instead of 0.1 M) and by employing an inverse addition protocol in which the base and diazo ketone are added to a solution of the trialkylsilyl triflate.

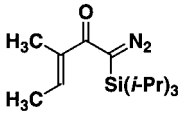
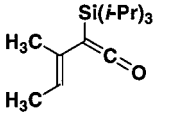
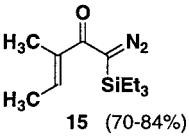
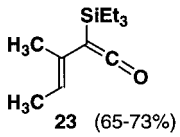
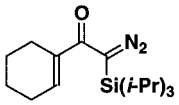
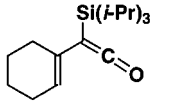
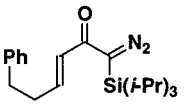
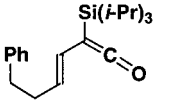
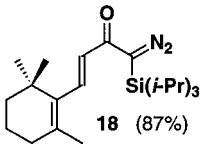
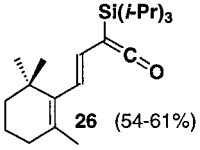
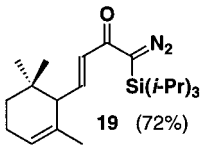
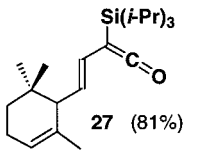
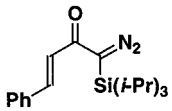
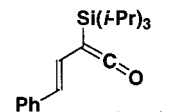
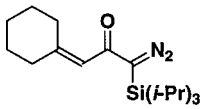
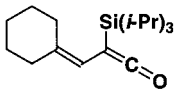
Table 1 summarizes the results of our investigation of the photochemical Wolff rearrangement of these α′-silyl-α′-diazo-α,β-enones. Best results were obtained by irradiation of the diazo compound in degassed benzene at 300 nm using a Rayonet RPR-100 photochemical reactor. It is important that the internal temperature of the reactor chamber be maintained at 30−35 °C by use of a cooling fan. In addition to benzene, 1,2-dichloroethane, hexane, and toluene are all suitable solvents for the reaction. As indicated in Table 1, better yields are obtained in the synthesis of more highly substituted vinylketenes, possibly because of the greater stability of the diazo ketones in these cases. In addition, irradiation of **21** produced none of the desired ketene; in this case, an unidentifiable product was isolated in low yield.

As anticipated, these TAS-vinylketenes are remarkably robust substances, in dramatic contrast to typical vinylketenes. The triisopropylsilyl derivatives **22**, **24**, and **26** were recovered unchanged after heating in C_6D_6 at 80 °C for 4 days, although some decomposition of the (triethylsilyl)vinylketene **23** was observed after heating at this temperature for 10 h. Also notable is the observation that these ketenes can be purified by conventional silica gel chromatography without any detectable decomposition!

TAS-vinylketenes exhibit a number of interesting spectral characteristics. The IR spectra of the TAS-vinylketenes show the expected strong diagnostic stretch near 2100 cm^{-1} resulting from the symmetric stretching modes of the ketene backbone (C═C═O). The ^{13}C NMR spectrum has two notable features. As expected, the C-1 (C═*C*═O) carbons of TAS-vinylketenes are extensively deshielded and give a low field signal near 180 ppm, while the C-2 carbon (*C*═C═O) exhibits an unusually high field signal near 20 ppm.

Synthesis of TAS-vinylketenes by Electrocyclic Cleavage of Cyclobutenones. In our previous studies on the application of vinylketenes in annulation routes to six-[2] and eight-membered[3] rings, we have shown that the electrocyclic ring opening of cyclobutenones provides an especially attractive method for the generation of these reactive species.[16] It therefore appeared likely that

Table 1. Synthesis of TAS-vinylketenes via Photochemical Wolff Rearrangement

entry	diazo ketone[a]	silylation[b] product (yield)[d]	Wolff rearrangement[c] product (yield)[d]
1	**7**	 **14** (86-89%)	 **22** (79-80%)
2	**7**	 **15** (70-84%)	 **23** (65-73%)
3	**8**	 **16** (75%)	 **24** (89%)
4	**9**	 **17** (34-38%)	 **25** (41%)
5	**10**	 **18** (87%)	 **26** (54-61%)
6	**11**	 **19** (72%)	 **27** (81%)
7	**12**	 **20** (39%)	 **28** (35%)
8	**13**	 **21** (93-100%)	 **29** (0%)

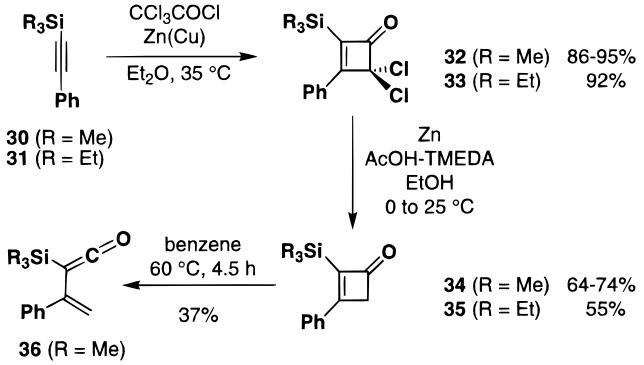
[a] For preparation of **7**, **8**, and **12**, see ref 13. The following diazo ketones were prepared by the method described in ref 13: **9** (74−86%), **10** (80−97%), **11** (85−94%), and **13** (62−66%). [b] The diazo ketone is treated with 1.0 equiv of the trialkylsilyl triflate and 1.0 equiv of *i*-Pr_2EtN in 1:1 Et_2O−hexane at 0−25 °C for 15 min to 4 h. [c] The diazo ketone is irradiated at 300 nm in benzene at 30−35 °C for 2−4 h. [d] Isolated yield.

(14) See references cited in ref 13a.

(15) See ref 12 and the following: Brückmann, R.; Maas, G. *Chem. Ber.* **1987**, *120*, 635.

(16) For reviews on the chemistry of cyclobutenones, see: (a) Bellus, D.; Ernst, B. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 797. (b) Wong, H. N. C.; Lau, K.-L.; Tam, K.-F. *Top. Curr. Chem.* **1986**, *133*, 83. (c) Moore, H. W.; Yerxa, B. R. In *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; Jai Press: London, 1995; pp 81−162.

Scheme 2



2-trialkylsilylcyclobutenones might afford TAS-vinylketenes in good yield upon heating. In fact, Tidwell has recently shown that silylated bisketenes can be generated in a similar fashion by the thermal or photochemical ring opening of cyclobutenediones.[17] Scheme 2 outlines the application of this strategy to the synthesis of TAS-vinylketene **36**. Addition of dichloroketene to (trialkylsilyl)acetylenes **30** and **31** according to our previously reported procedure[18] provides the desired dichlorocyclobutenones **32** and **33** in high yield. As previously noted, the phenyl group dominates in directing the regiochemical course of the [2 + 2] cycloaddition, whereas in the case of (trialkylsilyl)acetylenes with *alkyl* substituents, mixtures of regioisomeric cycloadducts are generally obtained. Dechlorination of 4,4-dichlorocyclobutenones does not proceed smoothly under conventional conditions, but can be accomplished in good yield by employing the protocol developed independently in our laboratory[18b,c] and that of Dreiding.[19] Upon heating in benzene at 60 °C for 4.5 h, **34** undergoes smooth conversion to the desired TAS-vinylketene **36**. As expected, this (trimethylsilyl)vinylketene proved less stable to chromatography than the triethyl- and triisopropylsilyl derivatives **22**−**28** and could only be obtained in 37% yield after purification on Florisil. For this reason, it ultimately proved advantageous to generate **36** in situ for [4 + 2] cycloadditions rather than to subject this sensitive compound to prior isolation and purification.

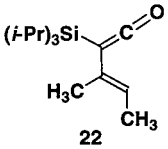
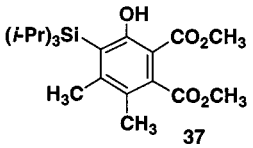
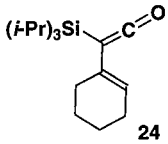
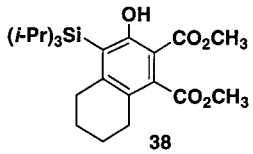
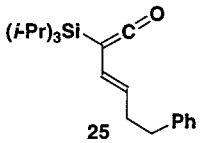
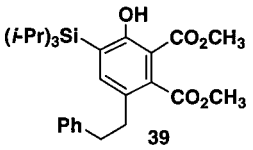
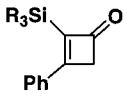
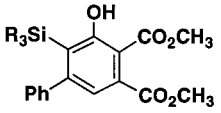
[4 + 2] Cycloadditions of TAS-vinylketenes. Previous work in our laboratory had established the ability of (trimethylsilyl)vinylketene to function as a diene component in Diels−Alder reactions, although the scope of this process is somewhat limited by the thermal instability of the vinylketene. Preliminary experiments indicated that substituted TAS-vinylketenes, especially triisopropylsilyl derivatives, are more robust compounds, and we consequently expected that these derivatives would engage in [4 + 2] cycloadditions with a broader range of substrates, providing a useful synthetic route to highly substituted cyclohexenones and phenols. We therefore undertook a systematic investigation of Diels−Alder reactions of these TAS-vinylketenes, focusing on the scope, regiochemistry, and stereochemical course of the process.

(17) Allen, A. D.; Lai, W.-Y.; Ma, J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1994**, *116*, 2625. Zhao, D.-C.; Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1993**, *115*, 10097.

(18) (a) Danheiser, R. L.; Sard, H. *Tetrahedron Lett.* **1983**, *24*, 23. (b) Danheiser, R. L.; Savariar, S. *Tetrahedron Lett.* **1987**, *28*, 3299. (c) Danheiser, R. L.; Savariar, S.; Cha, D. D. *Organic Syntheses*; Wiley: New York, 1993; Collect. Vol. VIII, pp 82−86.

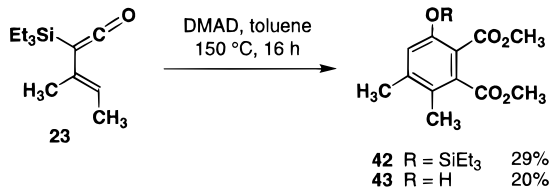
(19) Ammann, A. A.; Rey, M.; Dreiding, A. S. *Helv. Chim. Acta* **1987**, *70*, 321.

Table 2. Cycloadditions of TAS-vinylketenes with DMAD[a]

entry	vinylketene (or precursor)	cycloadduct	yield (%)[b]
1	 **22**	 **37**	95
2	 **24**	 **38**	73
3	 **25**	 **39**	61
4	 **34** (R = Me)	 **40**	63
5	**35** (R = Et)	**41**	55

[a] Cycloadditions were conducted in degassed toluene at 150 °C for 3−22 h (entries 1−3); or at 110 °C for 42−55 h (entries 4 and 5). [b] Isolated yield.

The relative reactivity of different TAS-vinylketenes was explored initially by examining their cycloadditions with dimethylacetylene dicarboxylate (DMAD) (Table 2). In a typical reaction, a degassed toluene solution of TAS-vinylketene **22** and 1.0 equiv of DMAD was heated at 150 °C for 16 h in a threaded Pyrex tube sealed with a Teflon cap. Concentration and purification by chromatography on silica gel provided the expected phenol **37** in nearly quantitative yield. Protodesilylation of this cycloadduct was achieved readily (80% yield) by exposure to 20 equiv of TFA in dichloromethane at 25 °C for 2 h. Interestingly, cycloaddition with the corresponding triethylsilyl derivative **23** afforded a mixture of products tentatively assigned as the silyl ether **42** and phenol **43** (eq 3). In this case, the acidity of the phenolic product



(3)

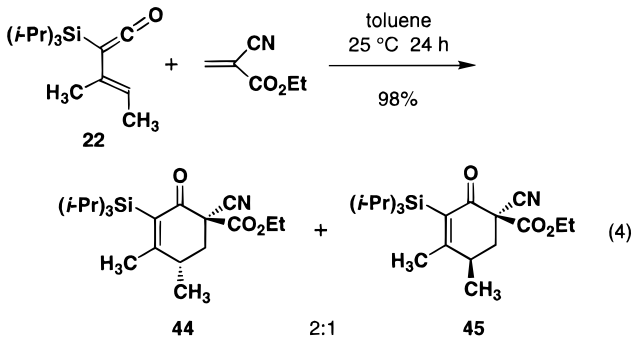
apparently promotes desilylation of the cycloadduct at the elevated reaction temperature. This process is not as facile in the case of the triisopropylsilyl derivative **37** because of the steric bulk of the silyl group.

As illustrated in entries 4 and 5, heating 2-silylcyclobutenones **34** and **35** in toluene at reflux in the presence of DMAD affords phenols **40** and **41** in good yield, presumably via the in situ electrocyclic ring open-

ing of **34** and **35** to generate TAS-vinylketenes which then undergo [4 + 2] cycloaddition. Lower yields of the desired phenols were obtained when the reactions were conducted at higher temperatures and butenolide side products were isolated.[20]

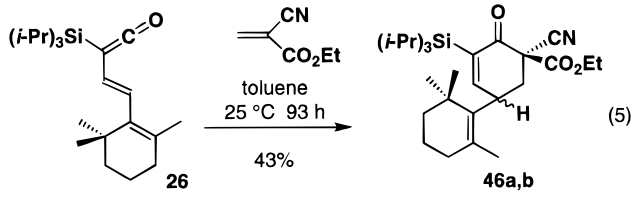
Regiochemical Course of TAS-vinylketene Cycloadditions. Prior studies with (trimethylsilyl)vinylketene[8] had confirmed our expectation that [4 + 2] cycloadditions with this vinylketene would be highly regioselective. The carbonyl oxygen of the vinylketene is predicted to function as an electron donor substituent, while trialkylsilyl groups are known to exert only a weak directing effect on the regiochemical course of the Diels–Alder reaction of silyl-substituted dienes.[21]

The regiochemical course of Diels–Alder reactions with substituted TAS-vinylketenes was initially probed by examining the reaction of **22** with ethyl cyanoacrylate. As outlined in eq 4, this cycloaddition proceeds readily



(4)

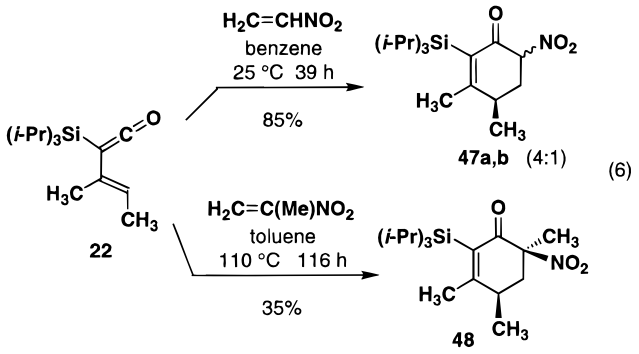
at room temperature to afford a 2:1 mixture of two cycloadducts in nearly quantitative yield. ^{1}H NMR analysis clearly indicates that both products have the predicted regiochemistry, and analysis of coupling constant data suggests that the major adduct (**44**) has the cyano group cis to the methyl group on the new six-membered ring.[22] TAS-vinylketene **26** reacts with ethyl cyanoacrylate at room temperature in a similar fashion, albeit more slowly, to afford an inseparable 4:1 mixture of cycloadducts **46a** and **46b** (eq 5). In this case the



(5)

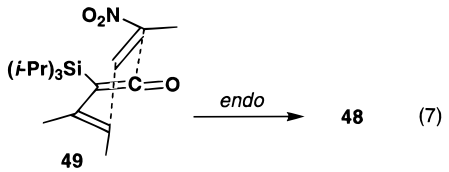
stereochemistry of the major isomer could not be unambiguously identified.

Stereochemical Course of TAS-vinylketene Cycloadditions. Since ethyl cyanoacrylate bears two electron-withdrawing groups, the cycloadditions of this dienophile were not informative with regard to the stereochemical course of the Diels–Alder reactions of TAS-vinylketenes. Simple acrylate derivatives proved insufficiently reactive (vide infra), so we turned our attention to reactions of nitroalkenes. As shown in eq 6,



(6)

TAS-vinylketene **22** combines with nitroethylene[23] and 2-nitropropene[24] in regioselective Diels–Alder reactions to produce **47** and **48**, respectively. Because of the high acidity of the doubly activated α′ proton in **47a** and **47b**, these products are expected to undergo equilibration, so that the identity of the major product does not necessarily provide insight into the stereochemical course of the cycloaddition step. No such ambiguity is associated with the reaction of 2-nitropropene, and indeed this cycloaddition produces a single cycloadduct whose structure was established as **48** by analysis of ^{1}H NMR coupling constant data and an NOE study. This result indicates that, as in other Diels–Alder reactions, cycloadditions involving TAS-vinylketenes follow the Alder endo rule and prefer transition states in which the dienophile activating group adopts an endo orientation (**49**) relative to the diene system (eq 7).



(7)

Scope of TAS-vinylketene Cycloadditions. Disappointingly, vinylketene **22** failed to react with less reactive dienophiles such as *N*-phenylmaleimide and chloroacrylonitrile; in each case, complex mixtures of products were obtained. However, monoactivated allenyl dienophiles proved excellent partners for the reaction, providing access to phenolic products that could otherwise be produced only by cycloadditions with less reactive acetylene dienophiles. The reaction outlined in Scheme 3 is representative. Thus, addition of cyanoallene[25] to TAS-vinylketene **22** in toluene at 150 °C gave a single product in good yield, which NOE studies revealed to be

(20) The butenolide byproducts most likely result from reaction of the TAS-vinylketene with oxygen. For a related reaction, see: Zhao, D.-C.; Tidwell, T. T. *J. Am. Chem. Soc.* **1992**, *114*, 10980.

(21) (a) Fleming, I.; Percival, A. *J. Chem. Soc., Chem. Commun.* **1976**, 681. (b) Fleming, I.; Percival, A. *J. Chem. Soc., Chem. Commun.* **1978**, 178. (c) Jung, M. E.; Gaede, B. *Tetrahedron* **1979**, *35*, 621. (d) Batt, D. G.; Ganem, B. *Tetrahedron Lett.* **1978**, 3323. (e) For a review on the application of silyl-substituted conjugated dienes in synthesis, see: Luh, T.-Y.; Wong, K.-T. *Synthesis* **1993**, 349.

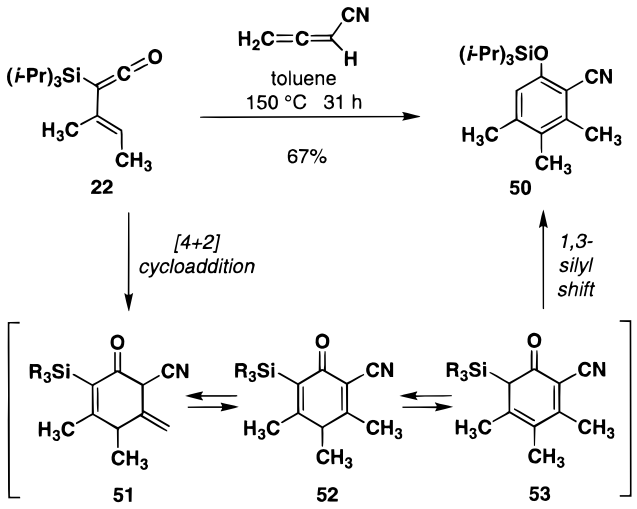
(22) The ^{1}H NMR spectrum for the major diastereomer **44** exhibits a large geminal coupling constant (J_{ab} = 13.9 Hz) between the protons H_a and H_b at C-5, and H_a and H_b couple to the C-4 proton H_c with coupling constant values of similar magnitude (J_{ac} = 6.4 Hz and J_{bc} = 6.0 Hz). These values are consistent with typical equatorial–equatorial and equatorial–axial values. For the minor diastereomer **45**, the ^{1}H NMR spectrum shows a large geminal coupling constant (J_{ab} = 14.2 Hz) between H_a and H_b; H_b is coupled to H_c with J_{bc} = 5.4 Hz, and a large axial–axial coupling constant (J_{ac} = 10.7 Hz) is observed between protons H_a and H_c.

(23) Ranganathan, D.; Rao, C. B.; Ranganathan, S.; Mehrotra, A. K.; Iyengar, R. *J. Org. Chem.* **1980**, *45*, 1185.

(24) Miyashita, M.; Yanami, T.; Yoshikoshi, A. *Organic Syntheses*; Wiley: New York, 1990; Collect. Vol. VII, pp 396–397.

(25) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes, and Cumulenes*; Elsevier: New York, 1981; pp 173–175.

Scheme 3



not the expected *o*-(triisopropylsilyl)phenol but rather the isomeric silyl ether **50**. As shown in Scheme 3, isomerization of the presumed initial cycloadduct **51** to **50** may proceed via the intermediacy of the α-silyl ketone **53**. 1,3-Silyl shifts of α-silyl ketones to form silyl enol ethers are well-known processes.[26]

In an attempt to expand the scope of the [4 + 2] cycloadditions of TAS-vinylketenes to include dienophiles of low reactivity, the application of Lewis acids as catalysts for the reaction was examined. It should be noted that Lewis acids have found considerable use as catalysts for [2 + 2] cycloadditions of TAS-ketenes with aldehydes.[27] Unfortunately, attempts to promote the cycloaddition of vinylketene **22** with methyl acrylate using either Me_2AlCl or $BF_3{\cdot}OEt_2$ under a variety of conditions proved unsuccessful. In all cases, extensive decomposition of the **22** was observed and none of the desired cycloadduct was detected.

Conclusions

The photochemical Wolff rearrangement of α′-silyl-α′-diazo-α,β-unsaturated ketones and the 4π electrocyclic ring opening of 2-silylcyclobutenones provide useful methods for the preparation of a variety of substituted TAS-vinylketenes. These remarkably robust vinylketenes undergo highly regioselective [4 + 2] cycloadditions with reactive olefinic and acetylenic dienophiles to produce highly substituted cyclohexenones and phenols in which the ketene carbonyl dominates in controlling the regiochemical course of the reaction. The stereochemical course of these cycloadditions follows the Alder endo rule, as illustrated in the reaction of nitropropene with vinylketene **22**. Studies are currently underway in our laboratory to develop routes to TAS-vinylketenes bearing electron-donating substituents; these derivatives are expected to exhibit increased reactivity, expanding the scope of this methodology to include less activated dienophiles. The extension of this chemistry to include the syntheses of oxygen and nitrogen heterocycles via hetero Diels−Alder reactions of TAS-vinylketenes is also under investigation.

Experimental Section

Materials. Commercial grade reagents and solvents were used without further purification, except as indicated below. Benzene, diethyl ether, DME, DMSO, and THF were distilled from sodium benzophenone ketyl or dianion. Acetonitrile, dibromomethane, dichloroethane, dichloromethane, diisopropylamine, diisopropylethylamine, DMAD, HMDS, toluene, triethylamine, triisopropylsilyl chloride, and triethylsilyl trifluoromethanesulfonate were distilled from calcium hydride. 1-Acetyl-1-cyclohexene, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one, 4-(2,6,6-trimethyl-1-cyclohexen-2-yl)-3-buten-2-one, and *trans*-3-penten-2-one were purified by distillation. Alkyllithium reagents were titrated in THF or hexane at 0 °C with *sec*-butanol, using 1,10-phenanthroline as an indicator.[28]

General Procedures. All reactions were performed in flame-dried glassware under a positive pressure of argon and stirred magnetically unless otherwise indicated. Air- and moisture-sensitive liquids and solutions were transferred via syringe or cannula and were introduced into reaction vessels through rubber septa. Reaction product solutions were concentrated by using a Büchi rotary evaporator at 15−20 mmHg. Column chromatography was performed on EM Science silica gel 60 (35−75 μm). Photochemical Wolff reactions were carried out in a Rayonet photochemical reactor model RPR-100 containing 16 300-nm, low-pressure mercury vapor bulbs (Southern New England Ultraviolet Company).

General Procedure for Diazo Transfer. (*E*)-1-Diazo-6-phenyl-3-hexen-2-one (9). A 50-mL, three-necked, round-bottomed flask equipped with a rubber septum, argon inlet adapter, and glass stopper was charged with HMDS (1.00 mL, 0.760 g, 4.33 mmol) in 16 mL of THF and then cooled at 0 °C while *n*-BuLi (2.53 M in hexane, 1.70 mL, 4.33 mmol) was added rapidly dropwise over 2 min. After 10 min, the solution was cooled at −78 °C while a solution of *trans*-6-phenyl-3-hexen-2-one[29] (0.687 g, 3.94 mmol) in 12 mL of THF was added dropwise over 5 min. The reaction mixture was stirred at −78 °C for 30 min, and then 2,2,2-trifluoroethyl trifluoroacetate (TFETFA, 0.63 mL, 0.922 g, 4.70 mmol) was added in one portion. After 10 min, the reaction mixture was poured into a separatory funnel containing 20 mL of 5% aqueous HCl solution and 25 mL of Et_2O. The aqueous phase was extracted with two 15-mL portions of Et_2O, and the combined organic phases were then washed with 20 mL of saturated NaCl solution, dried over Na_2SO_4, filtered, and concentrated to give a yellow-orange oil, which was immediately dissolved in 14 mL of CH_3CN and transferred to a 50-mL, three-necked, round-bottomed flask equipped with a rubber septum, argon inlet adapter, and glass stopper. Water (0.071 mL, 0.071 g, 3.94 mmol), Et_3N (0.82 mL, 0.600 g, 5.91 mmol), and methanesulfonyl azide (MsN_3, 0.75 mL, 0.782 g, 6.45 mmol) were added rapidly dropwise in that order. The resulting solution was stirred at room temperature for 2.5 h, then diluted with 50 mL of Et_2O and extracted with three 15-mL portions of 10% aqueous NaOH solution, three 15-mL portions of water, and 20 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated to afford 1.43 g of an orange oil. Column chromatography on 50 g of silica gel (gradient elution with 0−20% EtOAc−hexane) provided 0.680 g (86%) of diazo ketone **9** as a yellow oil: IR (CCl_4) 3024, 2924, 2099, and 1655 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.26−7.32 (m, 2H), 7.16−7.23 (m, 3H), 6.84 (dt, J = 15.4, 6.8 Hz, 1H), 5.99 (d, J = 15.5 Hz, 1H), 5.27 (s, 1H), 2.77 (t, J = 7.6 Hz, 2H), 2.52 (dt, J = 7.1, 7.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.6, 143.9, 140.8, 128.5, 128.4, 127.7, 126.2, 55.2, 34.5, and 34.0; UV (hexane) λ_{max}, nm (ε) 247 (5700). Anal. Calcd for $C_{12}H_{12}ON_2$: C, 71.97; H, 6.04; N, 13.99. Found: C, 71.72; H, 5.85; N, 13.85.

(26) See: Munschauer, R.; Maas, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 306 and references therein.

(27) For examples, see: (a) Brady, W. T.; Saidi, K. *J. Org. Chem.* **1979**, *44*, 733. (b) Maruoka, K.; Concepcion, A. B.; Yamamoto, H. *Synlett* **1992**, 31.

(28) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

(29) Liedtke, R. J.; Gerrard, A. F.; Diekman, J.; Djerassi, C. *J. Org. Chem.* **1972**, *37*, 776.

1-Diazo-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (10). Reaction of 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (2.1 mL, 2.00 g, 10.4 mmol) with LiHMDS (11.4 mmol) and TFETFA (1.7 mL, 2.45 g, 12.5 mmol) in 50 mL of THF according to the general procedure provided a yellow-orange oil, which was then treated with H_2O (0.19 mL, 0.187 g, 10.4 mmol), Et_3N (2.2 mL, 1.58 g, 15.6 mmol), and MsN_3 (1.8 mL, 1.89 g, 15.6 mmol) in 36 mL of CH_3CN at 25 °C for 3 h to yield 3.96 g of an orange oil. Column chromatography on 50 g of silica gel (gradient elution with 0−10% EtOAc−hexane) provided 2.18 g (97%) of diazo ketone **10** as a yellow-orange oil.

1-Diazo-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one (11). Reaction of 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one (2.2 mL, 2.00 g, 10.4 mmol) with LiHMDS (11.4 mmol) and TFETFA (1.7 mL, 2.45 g, 12.5 mmol) in 30 mL of THF according to the general procedure provided a yellow-orange oil, which was then treated with H_2O (0.19 mL, 0.190 g, 10.4 mmol), Et_3N (2.2 mL, 1.57 g, 15.6 mmol), and MsN_3 (1.8 mL, 1.89 g, 15.6 mmol) in 36 mL of CH_3CN at 25 °C for 4.5 h to yield 3.32 g of a yellow-orange oil. Column chromatography on 80 g of silica gel (gradient elution with 0−10% EtOAc−hexane) provided 2.17 g (94%) of diazo ketone **11** as a yellow-orange oil.

3-Cyclohexylidene-1-diazopropan-2-one (13). Reaction of 1-cyclohexylidenepropan-2-one[30] (0.216 g, 1.56 mmol) with LiHMDS (1.75 mmol) and TFETFA (0.26 mL, 0.381 g, 1.91 mmol) in 5 mL of THF according to the general procedure provided a yellow oil, which was then treated with H_2O (0.029 mL, 0.029 g, 1.59 mmol), Et_3N (0.33 mL, 0.240 g, 2.39 mmol), and MsN_3 (0.28 mL, 0.292 g, 2.39 mmol) in 6.5 mL of CH_3CN at room temperature for 2 h to yield 0.280 g of a yellow oil. Column chromatography on 10 g of silica gel (gradient elution with 0−10% EtOAc−hexane) provided 0.170 g (66%) of diazo ketone (**13**) as a yellow oil.

General Procedure for Silylation of Diazo Ketones: Method A. 1-Diazo-3-methyl-1-(triisopropylsilyl)-3-penten-2-one (14). A 100-mL, three-necked, round-bottomed flask equipped with a rubber septum and argon inlet adapter was charged with diazo ketone **7** (0.854 g, 6.87 mmol) in 40 mL of a 1:1 solution of Et_2O−hexane and then cooled at 0 °C using an ice−water bath while *i*-Pr_2EtN (1.2 mL, 0.890 g, 6.87 mmol) was added dropwise over 1 min. After 5 min, TIPSOTf (1.8 mL, 2.05 g, 6.70 mmol) was added dropwise over 1 min, and the resulting solution was stirred for 2.5 h while the ice−water bath warmed to 25 °C. The reaction mixture was filtered through Celite with the aid of 10 mL of Et_2O, and the filtrate was concentrated to afford 2.09 g of an orange oil. Column chromatography on 25 g of silica gel (elution with 5% EtOAc−hexane) provided 1.71 g (89%) of diazo ketone **14** as a yellow oil: IR (CCl_4) δ 2940, 2860, 2065, and 1610 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.13 (q, $J = 6.6$ Hz, 1H), 1.83 (s, 3H), 1.78 (d, $J = 6.8$ Hz, 3H), 1.37 (sept, $J = 6.7$ Hz, 3H), and 1.10 (d, $J = 7.9$ Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.9, 136.3, 129.9, 49.8, 18.4, 13.6, 13.1, and 11.5; UV (CH_3CN) λ_{max}, nm (ϵ) 292 (3000), 238 (6200), and 221 (6300); HRMS *m/z* calcd for $C_{15}H_{28}ON_2Si$ 280.1971, found 280.1963.

1-Diazo-3-methyl-1-(triethylsilyl)-3-penten-2-one (15). Reaction of diazo ketone **7** (0.201 g, 1.62 mmol), *i*-Pr_2EtN (0.28 mL, 0.208 g, 1.61 mmol), and TESOTf (0.36 mL, 0.430 g, 1.61 mmol) in 8 mL of Et_2O−hexane at 0−25 °C for 3 h according to the general procedure (method A) gave an orange oil. Column chromatography on 10 g of silica gel (gradient elution with 0−5% EtOAc−hexane) provided 0.326 g (84%) of diazo ketone **15** as a yellow oil.

1-Diazo-2-(1-cyclohexenyl)-1-(triisopropylsilyl)-2-ethenone (16). Reaction of diazo ketone **8** (0.403 g, 2.69 mmol), *i*-Pr_2EtN (0.47 mL, 0.349 g, 2.70 mmol), and TIPSOTf (0.72 mL, 0.820 g, 2.69 mmol) in 20 mL of Et_2O−hexane at 0−25 °C for 4 h according to the general procedure (method A) gave a yellow oil. Column chromatography on 10 g of silica gel (gradient elution with 0−2% EtOAc−hexane) provided 0.620 g (75%) of diazo ketone **16** as a yellow oil.

General Procedure for Silylation of Diazo Ketones: Method B. (*E*)-1-Diazo-6-phenyl-1-(triisopropylsilyl)-3-hexen-2-one (17). A 250-mL, three-necked, round-bottomed flask equipped with a rubber septum, magnetic stir bar, glass stopper, and argon inlet adapter was charged with TIPSOTf (0.67 mL, 0.760 g, 2.48 mmol) in 90 mL of a 1:1 solution of Et_2O−hexane and then cooled at 0 °C in an ice−water bath. A 50-mL, two-necked, round-bottomed flask equipped with a rubber septum, magnetic stir bar, and argon inlet adapter was charged with diazo ketone **9** (0.496 g, 2.48 mmol) in 20 mL of ether and cooled at 0 °C in an ice−water bath while *i*-Pr_2EtN (0.43 mL, 0.320 g, 2.48 mmol) was added dropwise over 10 s. The diazo ketone solution was then transferred dropwise via cannula over 5 min to the triflate solution. The resulting mixture was stirred for 1.5 h while the ice−water bath was allowed to warm to room temperature and then filtered through Celite with the aid of 5 mL of Et_2O. Concentration of the filtrate afforded 2.80 g of an orange oil. Column chromatography on silica gel (gradient elution with 0−50% benzene-hexane) provided 0.340 g (38%) of diazo ketone **17** as an orange oil.

1-Diazo-1-(triisopropylsilyl)-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (18). Reaction of TIPSOTf (0.19 mL, 0.217 g, 0.707 mmol) with diazo ketone **10** (0.150 g, 0.687 mmol) and *i*-Pr_2EtN (0.12 mL, 0.088 g, 0.689 mmol) in 35 mL of Et_2O−hexane at 0−25 °C for 1.5 h according to the general procedure (method B) gave 0.270 g of an orange oil. Column chromatography on 10 g of silica gel (gradient elution with 0−3% EtOAc−hexane) provided 0.230 g (87%) of diazo ketone **18** as an orange oil.

1-Diazo-1-(triisopropylsilyl)-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one (19). Reaction of diazo ketone **11** (0.152 g, 0.690 mmol), *i*-Pr_2EtN (0.12 mL, 0.089 g, 0.69 mmol), and TIPSOTf (0.19 mL, 0.217 g, 0.707 mmol) in 3 mL of Et_2O−hexane at 0−25 °C for 1 h according to the general procedure (method A) gave 0.280 g of an orange oil. Column chromatography on 10 g of silica gel (gradient elution with 0−2% EtOAc−hexane) provided 0.190 g (72%) of diazo ketone **19** as a yellow oil.

(*E*)-1-Diazo-4-phenyl-1-(triisopropylsilyl)-3-buten-2-one (20). Reaction of TIPSOTf (0.78 mL, 0.889 g, 2.90 mmol), diazo ketone **12** (0.509 g, 2.90 mmol), and *i*-Pr_2EtN (0.51 mL, 0.380 g, 2.90 mmol) in 130 mL of Et_2O−hexane at 0−25 °C for 15 min according to the general procedure (method B) gave 1.08 g of a red-orange oil. Column chromatography on 40 g silica gel (gradient elution with 0−5% EtOAc−hexane) provided 0.370 g (39%) of diazo ketone **20** as an orange oil.

3-Cyclohexylidene-1-diazo-1-(triisopropylsilyl)propan-2-one (21). Reaction of diazo ketone **13** (0.110 g, 0.670 mmol), *i*-Pr_2EtN (0.11 mL, 0.0816 g, 0.632 mmol), and TIPSOTf (0.18 mL, 0.200 g, 0.660 mmol) in 6 mL of Et_2O−hexane at 0−25 °C for 2 h according to the general procedure (method A) gave 0.330 g of a yellow oil. Column chromatography on 10 g of silica gel (gradient elution with 0−5% EtOAc−hexane) provided 0.200 g (93%) of diazo ketone **21** as a yellow oil.

General Procedure for Photochemical Wolff Rearrangement. (*E*)-2-(1-Methyl-1-propenyl)-2-(triisopropylsilyl)ketene (22). A solution of diazo ketone **14** (0.760 g, 2.71 mmol) in 27 mL of benzene was distributed evenly between two 25-cm Vycor tubes fitted with rubber septa. A second rubber septum (inverted) was secured with wire to each tube to ensure a good seal, and the reaction mixtures were degassed (three freeze−pump−thaw cycles at −196 °C, <0.5 mmHg) and then irradiated with 300-nm light for 4 h in a Rayonet reactor. The resulting solutions were combined and concentrated to afford 0.710 g of a yellow oil. Column chromatography on 30 g of silica gel (elution with hexane) provided 0.550 g (80%) of ketene **22** as a viscous yellow oil: IR (film) 2941, 2881, and 2081 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.18 (q, $J = 6.7$ Hz, 1H), 1.81 (s, 3H), 1.62 (d, $J = 6.7$ Hz, 3H), 1.15−1.27 (m, 3H), 1.10 (d, $J = 6.4$ Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.7, 123.9, 119.5, 22.4, 18.8, 18.6, 14.0, and 12.5; UV (hexane) λ_{max},

(30) Normant, H.; Sturtz, G. *C. R. Hebd. Seances Acad. Sci.* **1963**, *256*, 1800.

nm (ϵ) 229 (9000); HRMS *m/z* calcd for $C_{15}H_{28}OSi$ 252.1909, found 252.1907.

(*E*)-2-(1-Methyl-1-propenyl)-2-(triethylsilyl)ketene (23). Reaction of diazo ketone **15** (0.419 g, 1.76 mmol) in 18 mL of benzene for 4 h according to the general procedure gave a yellow-orange oil. Column chromatography on 10 g of silica gel (elution with hexane) provided 0.270 g (73%) of ketene **23** as a viscous yellow oil.

2-(1-Cyclohexenyl)-2-(triisopropylsilyl)ketene (24). Reaction of diazo ketone **16** (1.16 g, 3.78 mmol) in 38 mL of benzene for 4 h according to the general procedure gave 2.20 g of an orange-brown oil. Column chromatography on 15 g of silica gel (elution with hexane) provided 0.940 g (89%) of ketene **24** as a viscous yellow oil.

(*E*)-2-(4-Phenyl-1-butenyl)-2-(triisopropylsilyl)-ketene (25). Reaction of diazo ketone **17** (0.290 g, 0.81 mmol) in 8 mL of benzene for 2 h according to the general procedure gave 0.300 g of a red oil. Column chromatography on 10 g of silica gel (elution with hexane) provided 0.110 g (41%) of ketene **25** as a viscous yellow oil.

(*E*)-2-(2-(2,6,6-Trimethyl-1-cyclohexenyl)ethenyl)-2-(triisopropylsilyl)ketene (26). Reaction of diazo ketone **18** (0.230 g, 0.630 mmol) in 6 mL of benzene for 2 h according to the general procedure gave 0.210 g of a yellow-brown oil. Column chromatography on 10 g of silica gel (elution with hexane) provided 0.130 g (61%) of ketene **26** as a viscous yellow oil.

(*E*)-2-(2-(2,6,6-Trimethyl-2-cyclohexenyl)ethenyl)-2-(triisopropylsilyl)ketene (27). Reaction of diazo ketone **19** (0.160 g, 0.430 mmol) in 4 mL of benzene for 2.5 h according to the general procedure gave 0.160 g of a red oil. Column chromatography on 10 g of silica gel (elution with hexane) provided 0.120 g (81%) of ketene **27** as a viscous yellow oil.

(*E*)-2-(2-Phenylethenyl)-2-(triisopropylsilyl)ketene (28). Reaction of diazo ketone **20** (0.370 g, 1.13 mmol) in 12 mL of benzene for 3 h according to the general procedure gave 0.250 g of a red oil. Column chromatography on 10 g of silica gel (elution with hexane) provided 0.120 g (35%) of ketene **28** as a viscous yellow oil.

4,4-Dichloro-3-phenyl-2-(triethylsilyl)-2-cyclobutenone (33). A 500-mL, three-necked, round-bottomed flask equipped with a rubber septum, reflux condenser, and pressure-equalizing addition funnel was charged with activated zinc[31] (7.26 g, 111 mmol) and a solution of (triethylsilyl)-phenylacetylene[32] (4.01 g, 37.0 mmol) in 80 mL of ether. The resulting solution was heated at reflux while a solution of trichloroacetyl chloride (4.2 mL, 37.0 mmol) in 125 mL of ether was added dropwise over 3 h. The reaction mixture was heated at reflux for 14 h and then allowed to cool to room temperature and filtered. The filtrate was extracted with two 100-mL portions of saturated $NaHCO_3$, two 100-mL portions of water, and two 100-mL portions of saturated NaCl, dried over $MgSO_4$, filtered, and concentrated to give 6.67 g of a red-brown liquid. Column chromatography on 40 g of silica gel (elution with 0−2% ether−pentane) provided 5.55 g (92%) of cyclobutenone **33** as a yellow oil: IR (film) 2950 and 1770 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.91−7.94 (m, 2H), 7.57−7.60 (m, 3H), and 0.85−1.00 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.4, 181.9, 149.8, 133.1, 129.9, 129.7, 129.2, 91.0, 7.2, and 3.1.

General Procedure for Reductive Dechlorination. 3-Phenyl-2-(trimethylsilyl)-2-cyclobutenone (34). A 50-mL, three-necked, round-bottomed flask equipped with a rubber septum, 25-mL pressure-equalizing addition funnel, and argon inlet adapter was charged with zinc dust (0.626 g, 9.53 mmol), TMEDA (1.44 mL, 9.53 mmol), and 8 mL of ethanol and then cooled at 0 °C using an ice−water bath. Acetic acid (0.55 mL, 9.53 mmol) was added over 2 min, and then a solution of cyclobutenone **32** (0.463 g, 1.64 mmol) in 5 mL of ethanol was added dropwise via the addition funnel over 12 min. The reaction mixture was stirred for 15 min, and then the ice−bath was removed and the reaction mixture was stirred for 3 h at 25 °C. The resulting mixture was filtered through Celite with the aid of 80 mL of 1:1 Et_2O−pentane. The filtrate was extracted with 100 mL of 1 M aqueous HCl solution, 100 mL of water, 80 mL of saturated $NaHCO_3$, and 80 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated to give 0.409 g of a yellow liquid. Column chromatography on 20 g of silica gel (gradient elution with 0−4% EtOAc−hexane) provided 0.257 g (74%) of **34** as a yellow oil: IR (film) 2950 and 1785 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.59−7.61 (m, 2H), 7.50−7.51 (m, 3H), 3.71 (s, 2H), and 0.32 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.0, 176.7, 131.4, 129.2, 128.7, 128.6, 126.4, 54.6, and −1.2; HRMS *m/z* calcd for $C_{13}H_{16}OSi$ 216.0970, found 216.0970.

3-Phenyl-2-(triethylsilyl)-2-cyclobutenone (35). Reaction of zinc dust (1.14 g, 17.5 mmol), TMEDA (2.6 mL, 17.5 mmol), acetic acid (1.00 mL, 17.5 mmol), and cyclobutenone **33** (0.99 g, 3.0 mmol) in 29 mL of ethanol at 0−25 °C for 4.5 h according to the general procedure gave 0.848 g of a yellow liquid. Column chromatography on 25 g of silica gel (gradient elution with 0−10% ether−pentane) provided 0.428 g (55%) of **35** as a yellow oil: IR (film) 2070 and 1740 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.63−7.66 (m, 2H), 7.51−7.54 (m, 3H), 3.75 (s, 2H), 0.99 (t, J = 6.8 Hz, 9H), and 0.86 (q, J = 6.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.5, 178.1, 147.2, 133.6, 131.4, 129.0, 128.7, 52.1, 7.4, and 3.4; HRMS *m/z* calcd for $C_{16}H_{22}OSi$ 258.1440, found 258.1441.

2-(1-Phenylethenyl)-2-(trimethylsilyl)ketene (36). A 25-mL, two-necked, round-bottomed flask equipped with a glass stopper and reflux condenser was charged with cyclobutenone **34** (0.106 g, 0.497 mmol) in 18 mL of benzene and then heated at 60 °C for 4.5 h. The resulting mixture was allowed to cool to room temperature and then concentrated to give 0.113 g of a yellow oil. Column chromatography (twice) on 2.0 g of Florisil (elution with hexane) provided 0.039 g (37%) of ketene **36** as a pale yellow oil: IR (film) 2080 and 1740 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41−7.43 (m, 2H), 7.30−7.40 (m, 3H), 4.98 (s, 2H), and 0.28 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.9, 142.7, 139.4, 128.3, 128.0, 126.8, 110.9, 26.0, and −0.6; HRMS *m/z* calcd for $C_{13}H_{16}OSi$ 216.0970, found 216.0970.

General Procedure for Diels−Alder Reaction with DMAD. Dimethyl 5,6-Dimethyl-3-hydroxy-4-(triisopropylsilyl)phthalate (37). A threaded Pyrex tube (20 mm o.d.; 16 mm i.d.) was charged with a solution of vinylketene **22** (0.092 g, 0.370 mmol) and DMAD (0.052 g, 0.370 mmol) in 0.4 mL of toluene. The reaction mixture was degassed (three freeze−pump−thaw cycles at −196 °C, <0.5 mmHg), and then the tube was sealed with a threaded Teflon cap. The reaction mixture was heated at 150 °C for 24 h and then allowed to cool to room temperature and concentrated to give 0.200 g of an orange oil. Column chromatography on 10 g of silica gel (gradient elution with 0−70% benzene−hexane) provided 0.140 g (95%) of **37** as white crystals: mp 73−73.5 °C; IR (CCl_4) 2950, 2870, 1740, and 1670 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.57 (s, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 2.37 (s, 3H), 2.10 (s, 3H), 1.58 (sept, J = 7.5 Hz, 3H), and 1.08 (d, J = 7.2 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 170.2, 165.7, 135.2, 128.3, 126.5, 124.5, 104.9, 52.6, 52.2, 22.1, 19.3, 16.9, and 13.6; UV (CH_3CN) λ_{max}, nm (ϵ) 322 (9700), 257 (9900), and 220 (32 000). Anal. Calcd for $C_{21}H_{34}O_5Si$: C, 63.92; H, 8.69. Found: C, 63.88; H, 8.67.

Dimethyl 5,6-Dimethyl-3-hydroxyphthalate (43). A 10-mL, two-necked, round-bottomed flask equipped with a rubber septum and argon inlet adapter was charged with a solution of phthalate **37** (0.200 g, 0.507 mmol) and 0.6 mL of dichloromethane. Trifluoroacetic acid (0.78 mL, 1.16 g, 10.1 mmol) was added dropwise to the reaction mixture over 1 min, and the resulting solution was stirred at room temperature for 2 h. The reaction mixture was concentrated to afford 0.290 g of a brown oil. Column chromatography on 15 g of silica gel (gradient elution with 0−10% EtOAc−hexane) provided 0.092 g (76%) of phthalate **43** as a colorless oil: IR ($CHCl_3$) 3700, 3640, 3040, 2990, 1730, and 1660 cm^{-1}; ^1H NMR (300 MHz,

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(32) Jun, C.-H.; Crabtree, R. H. *J. Organomet. Chem.* **1993**, *447*, 177.

$CDCl_3$) δ 10.76 (s, 1H), 6.84 (s, 1H), 3.88 (s, 6H), 2.25 (s, 3H), and 2.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 169.3, 159.7, 146.2, 134.6, 124.7, 119.7, 106.7, 52.8, 52.3, 20.8, and 15.6.

Dimethyl 3-Hydroxy-5,6,7,8-tetrahydro-4-(triisopropylsilyl)naphthalene-1,2-dicarboxylate (38). Reaction of ketene **24** (0.154 g, 0.550 mmol) and DMAD (0.076 g, 0.540 mmol) in 0.4 mL of toluene at 150 °C for 22 h according to the general procedure gave 0.290 g of a brown oil. Column chromatography on 10 g of silica gel (gradient elution with 0−80% benzene−hexane) afforded 0.170 g (73%) of phenol **38** as a pale yellow oil: IR (CCl_4) 2950, 2870, 1740, and 1670 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.45 (s, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 2.86 (t, J = 5.9 Hz, 2H), 2.59 (t, J = 6.4 Hz, 2H), 1.60−1.71 (m, 4H), 1.54 (sept, J = 7.3 Hz, 3H), and 1.06 (d, J = 7.3 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 169.9, 165.0, 155.1, 135.7, 125.6, 125.3, 105.1, 52.8, 52.3, 31.8, 26.3, 22.1, 21.7, 19.5, and 13.8.

Dimethyl 6-(2-Phenylethyl)-3-hydroxy-4-(triisopropylsilyl)phthalate (39). Reaction of ketene **25** (0.090 g, 0.270 mmol) and DMAD (0.058 g, 0.410 mmol) in 0.3 mL of toluene at 150 °C for 3 h according to the general procedure gave 0.120 g of a brown oil. Column chromatography on 10 g of silica gel (elution with 50% dichloromethane−petroleum ether) provided 0.079 g (61%) of phenol **39** as a white solid: mp 77.5−79.0 °C; IR (CCl_4) 2943, 2860, 1740, and 1670 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.19 (s, 1H), 7.12−7.29 (m, 6H), 3.91 (s, 3H), 3.90 (s, 3H), 2.79−2.85 (m, 4H), 1.43 (sept, J = 7.6 Hz, 3H), and 1.04 (d, J = 7.6 Hz, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 169.6, 165.0, 144.6, 141.1, 134.9, 128.5, 128.5, 128.4, 126.3, 126.0, 107.7, 52.8, 52.3, 37.7, 35.0, 18.8, and 11.5; UV (CH_3CN) λ_{max}, nm (ϵ) 317 (7500), 310 (5900), and 219 (32 000). Anal. Calcd for $C_{27}H_{38}O_5Si$: C, 68.90; H, 8.14. Found: C, 68.80; H, 8.17.

General Procedure for Diels−Alder Reaction with Cyclobutenones. Dimethyl 3-Hydroxy-5-phenyl-4-(trimethylsilyl)phthalate (40). A 25-mL, two-necked, round-bottomed flask equipped with a glass stopper and reflux condenser was charged with a solution of cyclobutenone **34** (0.109 g, 0.511 mmol), DMAD (0.063 mL, 0.511 mmol), and 7 mL of toluene. The resulting solution was heated at 110 °C for 42 h and then allowed to cool to room temperature. Concentration of the resulting mixture afforded 0.260 g of an orange oil. Column chromatography on 26 g of silica gel (elution with 20% EtOAc−hexane) provided 0.116 g (63%) of phenol **40** as a white solid: mp 51−52 °C; IR (CCl_4) 1740 and 1660 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.21 (s, 1H), 7.33−7.35 (m, 3H), 7.22−7.24 (m, 2H), 6.79 (s, 1H), 3.91 (s, 3H), 3.85 (s, 3H), and −0.04 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 169.4, 166.5, 156.0, 143.0, 135.1, 129.3, 128.7, 127.9, 127.8, 121.1, 106.9, 52.8, 52.5, and 0.8; HRMS *m*/*z* calcd for $C_{19}H_{22}O_5Si$ 358.1236, found 358.1235.

Dimethyl 3-Hydroxy-5-phenyl-4-(triethylsilyl)phthalate (41). Reaction of cyclobutenone **35** (0.111 g, 0.429 mmol) and DMAD (0.053 mL, 0.429 mmol) in 7 mL of toluene at 110 °C for 55 h according to the general procedure gave 0.167 g of an orange oil. Column chromatography on 10 g of silica gel (gradient elution with 0−70% benzene−hexane) afforded 0.095 g (55%) of phenol **41** as a white solid: mp 61−61.5 °C; IR (CCl_4) 1730 and 1660 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.28 (s, 1H), 7.32−7.36 (m, 5H), 6.79 (s, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 0.78 (t, J = 7.8 Hz, 9H), and 0.48 (q, J = 7.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 169.5, 166.8, 157.2, 143.1, 135.0, 128.7, 127.8, 127.7, 127.0, 121.3, 106.6, 52.8, 52.5, 7.8, and 4.2; HRMS *m*/*z* calcd for $C_{22}H_{28}O_5Si$ 400.1706, found 400.1707.

6-Cyano-3,4-dimethyl-6-(ethoxycarbonyl)-2-(triisopropylsilyl)-2-cyclohexen-1-one (44, 45). A 10-mL, two-necked, round-bottomed flask equipped with a rubber septum and argon inlet adapter was charged with a solution of ketene **22** (0.201 g, 0.800 mmol) and ethyl cyanoacrylate (0.120 g, 0.960 mmol) in 0.8 mL of toluene. The reaction mixture was stirred for 24 h and then concentrated to give 0.390 g of a pale yellow oil. Column chromatography on 10 g of silica gel (gradient elution with 0−20% EtOAc−hexane) provided 0.113 g (38%) of **44** (mp 81.5−82 °C), 0.625 g (20%) of **45** (mp 65−66.5 °C), and 0.120 g (40%) of a mixture of **44** and **45** as white solids (total yield, 98%). For the major diastereomer **44**: IR (CCl_4) 2940, 2870, 2240, 1750, and 1690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.29 (dq, J = 10.8, 7.1 Hz, 1H), 4.18 (dq, J = 10.7, 7.1 Hz, 1H), 2.89 (dd, J = 13.9, 6.0 Hz, 1H), 2.72 (app q, J = 6.7 Hz, 1H), 2.15 (dd, J = 13.9, 6.4 Hz, 1H), 2.08 (s, 3H), 1.44 (sept, J = 7.5 Hz, 3H), 1.35 (d, J = 7.1 Hz, 3H), 1.31 (t, J = 7.1 Hz, 3H), 1.06 (d, J = 7.5 Hz, 12H), and 1.04 (d, J = 7.4 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.7, 174.6, 165.0, 132.1, 117.4, 63.9, 55.1, 37.3, 35.9, 24.6, 21.0, 19.4, 19.3, 14.2, 13.1, and 13.0. Anal. Calcd for $C_{21}H_{35}O_3NSi$: C, 66.79; H, 9.34; N, 3.71. Found: C, 66.57; H, 9.42; N, 3.62. For the minor diastereomer **45**: IR (CCl_4) 2950, 2870, 1755, and 1695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.39 (dq, J = 10.8, 7.2 Hz, 1H), 4.30 (dq, J = 12.0, 7.2 Hz, 1H), 2.81 (ddq, J = 5.4, 10.7, 7.0 Hz, 1H), 2.52 (dd, J = 14.2, 5.4 Hz, 1H), 2.25 (dd, J = 14.2, 10.7 Hz, 1H), 2.10 (s, 3H), 1.43 (sept, J = 7.5 Hz, 3H), 1.34 (t, J = 7.1 Hz, 3H), 1.27 (d, J = 7.0 Hz, 3H), and 1.08 (app t, J = 7.5 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.0, 172.5, 164.9, 132.3, 115.9, 63.1, 55.0, 37.1, 36.0, 23.4, 20.2, 19.1, 18.9, 14.0, and 12.7. Anal. Calcd for $C_{21}H_{35}O_3NSi$: C, 66.79; H, 9.34; N, 3.71. Found: C, 66.86; H, 9.41; N, 3.62.

6-Cyano-6-(ethoxycarbonyl)-2-(triisopropylsilyl)-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-cyclohexen-1-one (46a,b). A 10-mL, two-necked, round-bottomed flask equipped with a rubber septum and argon inlet adapter was charged with a solution of ketene **18** (0.209 g, 0.600 mmol) and ethyl cyanoacrylate (0.118 g, 0.940 mmol) in 2.2 mL of toluene. Five additional portions of ethyl cyanoacrylate (0.054 g, 0.430 mmol) were added at intervals of ca. 15 h. After 93 h, the reaction mixture was concentrated to afford 0.750 g of a pale yellow oil. Column chromatography on 10 g of silica gel (gradient elution with 0−3% EtOAc−hexane) provided 0.120 g (43%) of a 4:1 mixture of diastereomers **46a** and **46b** as a yellow oil. For the mixture of diastereomers: IR (CCl_4) 2940, 2860, 1740, and 1680 cm^{-1}. For the major diastereomer: ^1H NMR (300 MHz, $CDCl_3$) δ 7.07 (s, 1H), 4.29 (dq, J = 9.0, 7.1 Hz, 1H), 4.26 (dq, J = 10.8, 7.2 Hz, 1H), 3.53 (dd, J = 11.2, 3.1 Hz, 1H), 2.84 (dd, J = 14.0, 5.0 Hz, 1H), 2.66 (dd, J = 14.0, 11.7 Hz, 1H), 1.89−1.96 (m, 2H), 1.57 (s, 3H), 1.43−1.65 (m, 4H), 1.26−1.41 (m, 3H), 1.33 (t, J = 7.1 Hz, 3H), 1.05 (s, 6H), and 1.04 (d, J = 7.5 Hz, 18H); HRMS *m*/*z* calcd for $C_{28}H_{45}O_3NSi$ 471.3169, found 471.3164.

***cis*-6-Nitro-3,4-trimethyl-2-(triisopropylsilyl)-2-cyclohexen-1-one (47a) and *trans*-6-Nitro-3,4-trimethyl-2-(triisopropylsilyl)-2-cyclohexen-1-one (47b).** A 10-mL, two-necked, round-bottomed flask equipped with a rubber septum and argon inlet adapter was charged with a solution of ketene **22** (0.208 g, 0.822 mmol), two crystals of BHT, and 0.8 mL of benzene. A solution of nitroethylene[23] (0.99 M in benzene, 0.83 mL, 0.820 mmol) was added, and the resulting mixture was stirred at room temperature. Two additional portions of nitroethylene solution were added (0.83 mL, 0.820 mmol) after 12 and 20 h. The reaction mixture was stirred for a total of 39 h and then concentrated to give 0.290 g of a pale yellow oil. Column chromatography on 30 g of silica gel (gradient elution with 0−10% EtOAc−hexane) provided 0.230 g (85%) of a 2:1 mixture of diastereomers **47a** and **47b** as a yellow oil. For the mixture of diastereomers: IR (CCl_4) 2930, 2850, 1735, and 1670 cm^{-1}. For the major diastereomer: ^1H NMR (300 MHz, $CDCl_3$) δ 5.42 (dd, J = 4.2, 12.5 Hz, 1H), 2.88 (dd, J = 5.7, 13.1 Hz, 1H), 2.53−2.75 (m, 1H), 2.27−2.41 (m, 1H), 2.13 (s, 3H), 1.43 (sept, J = 7.6 Hz, 3H), 1.34 (d, J = 7.2 Hz, 3H), and 1.05 (d, J = 7.4 Hz, 18H). For the minor diastereomer: ^1H NMR (300 MHz, $CDCl_3$) δ 5.37 (dd, J = 4.7, 12.4 Hz, 1H), 2.80 (dd, J = 6.0, 13.7 Hz, 1H), 2.53−2.73 (m, 1H), 2.27−2.41 (m, 1H), 2.08 (s, 3H), 1.54 (sept, J = 7.5 Hz, 3H), 1.29 (d, J = 6.9 Hz, 3H), and 1.08 (d, J = 7.4 Hz, 18H). For the mixture of diastereomers: ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.9, 191.6, 174.6, 172.7, 132.6, 132.1, 88.9, 86.5, 37.6, 37.5, 34.3, 33.6, 24.5, 23.3, 20.9, 19.1, 19.0, 18.9, 18.5, 12.6, 12.5, and 11.4.

6-Nitro-3,4,6-trimethyl-2-(triisopropylsilyl)-2-cyclohexen-1-one (48). A threaded Pyrex tube was charged with a solution of ketene **22** (0.154 g, 0.610 mmol), nitropropene[24] (0.104 g, 1.20 mmol), and one crystal of BHT in 0.6 mL of

toluene. The reaction mixture was degassed (three freeze−pump−thaw cycles at −196 °C, <0.5 mmHg) and tightly sealed with a threaded Teflon cap. The reaction mixture was heated at 110 °C for 16 h and then concentrated to give 0.230 g of a brown oil. Column chromatography on 15 g of silica gel (gradient elution with 0−10% EtOAc−hexane) provided 0.073 g (35%) of **48** as a white solid: mp 82−84 °C; IR (CCl_4) 2930, 2860, and 1670 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.71 (dd, J = 13.5, 9.8 Hz, 1H), 2.52 (m, 1H), 2.27 (dd, J = 13.5, 5.8 Hz, 1H), 2.08 (s, 3H), 1.78 (s, 3H), 1.43 (sept, J = 7.4 Hz, 3H), 1.28 (d, J = 7.1 Hz, 3H), and 1.04 (app t, J = 7.6 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.9, 171.8, 132.2, 93.1, 40.4, 37.0, 23.4, 20.9, 20.4, 19.1, 19.0, 12.7, and 12.5.

2-[(Triisopropylsilyl)oxy]-4,5,6-trimethylbenzonitrile (50). A threaded Pyrex tube was charged with a solution of ketene **22** (0.153 g, 0.605 mmol) and cyanoallene (0.132 g, 2.03 mmol) in 0.6 mL of toluene. The reaction mixture was degassed (three freeze−pump−thaw cycles at −196 °C, <0.5 mmHg) and tightly sealed with a threaded Teflon cap. The reaction mixture was heated at 150 °C for 31 h and concentrated to provide a brown oil. Column chromatography on 10 g of silica gel (gradient elution with 0−45% dichloromethane−petroleum ether) provided 0.130 g (67%) of **50** as white crystals: mp 58−59 °C; IR (CCl_4) 2950, 2870, 2225, and 1730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.55 (s, 1H), 2.43 (s, 3H), 2.26 (s, 3H), 2.11 (s, 3H), 1.32 (sept, J = 6.9 Hz, 3H), and 1.13 (d, J = 7.0 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 142.5, 140.7, 127.9, 117.7, 117.0, 103.5, 21.6, 18.9, 18.0, 15.1, and 13.0; UV (CH_3CN) λ_{max}, nm (ϵ) 222 (470); HRMS m/z calcd for $C_{19}H_{31}ONSi$ 317.2175, found 317.2165.

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Supporting Information Available: Characterization data for compounds **10**, **11**, **13**, **15**−**21**, and **23**−**28** and ^1H NMR spectra for all new compounds (39 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.

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