Allenylketenes: Versatile Substrates in Nucleophilic, Electrophilic, and Cycloaddition Reactions

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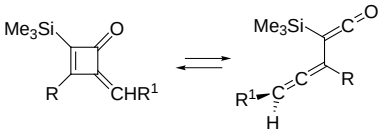
Abstract: 4-Methylene-2-trimethylsilyl-3-phenylcyclobutenones **3** are obtained from the corresponding cyclobutenedione **7** by Tebbe and Peterson methylenation reactions, and upon photolysis give 3-phenyl substituted allenylketenes $R^1CH=C=C(Ph)C(SiMe_3)=C=O$ **4**. These are more reactive in ring closure back to **3** than are the 3-trimethylsilyl analogs **1**, as predicted on the basis of molecular orbital calculations. Reactions of allenylketenes **1** and **4** include addition of H_2O followed by cyclization to form butenolides **13**, addition of aniline to give allenyl carboxamide **14** and lactam **15**, addition of CF_3CO_2H to form allenyl carboxylic acid **17**, addition of Br_2 in a 1,4-fashion to give penta-2,4-dienoic acid derivatives **18**, and reaction with *m*-chloroperbenzoic acid to give the unique allenyl acylsilane **23**. [4+1]-Cycloaddition reactions of **1** and **4** with Me_3SiCHN_2 give methylenecyclopentenones **24** and **25** while acetaldehyde undergoes BF_3•OEt_2 catalyzed [2+2] cycloadditions forming β-lactones. [4+2] Cycloadditions occur with benzaldehyde to form the highly crowded exomethylene pentenolactone **29**, and with TCNE forming methylenecyclohexenones **31**.

Key words: allenes, ketenes, cyclobutenones, cycloaddition, silyl substituents, addition reactions, olefination reactions

1 Introduction

We have reported the formation of stabilized and persistent allenylketenes **1** from photolysis of 2,3-bis(trimethylsilyl)-substituted methylenecyclobutenones **2** (Eq. 1).[1a] The allenylketenes were isolated as long-lived species at room temperature, but at thermal equilibrium both **1** and **2** were present in significant amounts. The stabilization of these ketenes by silyl substituents is a manifestation of the β-silicon effect, and arises from σ-π hyperconjugative electron donation of the Si−C bond to the electron-deficient p-orbital of the ketene carbonyl. This stabilization has been quantified using ab initio molecular orbital calculations, and for different substituents is correlated with group electronegativities, so that the less electronegative groups are the more stabilizing.[1b,c] Stabilization parameters *SE* for substituents on ketenes[1b,c] and allenes[1c] relative to hydrogen were derived from ab initio molecular orbital calculations and isodesmic reactions (Eq 2) and together with the calculated relative energies of the parent compounds give accurate predictions of the relative amounts of **1** and **2** present at thermal equilibrium.[1a] The predicted preference for the depicted *anti*-planar geometry of **1a** (R^1 = Ph) has been confirmed by X-ray crystallography.[1a]

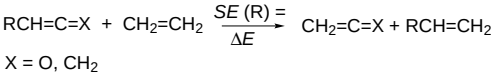
Allenylketenes **1** were shown to react with nucleophilic water to form lactones (Eq. 3)[1a] and with nitroxyl radicals with oxygen atom transfer, to give butenolides (Eq. 4),[1d]



2 (R = Me_3Si) **1** (R = Me_3Si)
3 (R = Ph) **4** (R = Ph)

a, R^1 = Ph; **b**, R^1 = H; **c**, R^1 = CO_2Et

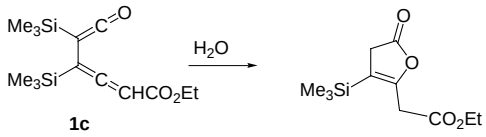
Equation 1



X = O, CH_2

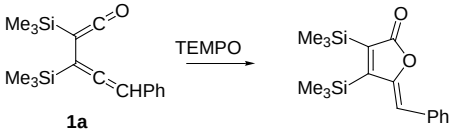
Equation 2

and have considerable promise as synthetic reagents. The related 1,2-bis(ketenes),[2] vinylallenes,[3] and 1,2-bis(allenes)[4] have also attracted a great deal of recent attention in synthetic and mechanistic study.



1c

Equation 3

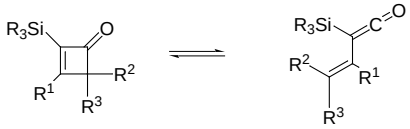


1a

Equation 4

Danheiser and co-workers[5] have prepared α-silylalkenylketenes **5** by Wolff rearrangements, by dehydrochlorinations, and by cyclobutenone ring opening (Eq. 5). Unsubstituted vinylketene is calculated to be of approximately equal stability to cyclobutenone, so the α-silyl derivatives **5** are significantly favored relative to their ring closed forms due to the ketene stabilizing ability of silicon (Eq. 5). These vinylketenes are however quite

reactive, and with electron deficient alkynes and alkenes give phenols[5b] and cyclohexenones,[5b] respectively, and with allenes form *O*-silylated phenols.[5b] Reactions with carbenoid reagents give cyclopentenones,[5c] while [4+2] cycloaddition reactions occur on the oxo group of $(EtO_2C)_2C{=}O$, and on the C=N bond of imines.[5d]



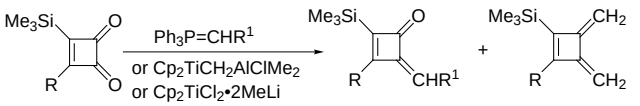
5

Equation 5

The current report deals with the extension of our studies to the preparation of allenylketenes bearing activating phenyl groups, and to the examination of some nucleophilic, electrophilic, and cycloaddition reactions of these species.

2 Synthesis and Stabilization of Allenylketenes

Previously we prepared methylenecyclobutenones **2** from cyclobutenediones **6** by reaction with Wittig, Tebbe, or Petasis[6a,b] reagents (Eq. 6). Reactions of **6** with one equivalent of Wittig reagent were highly selective, giving 32 to 90% of purified products **2** ($R^1 = CO_2Et$, Ph, $SiMe_3$) of monoalkylidenation, with no observed bis(alkylidenation) (Eq. 6). However the Wittig reaction of **6** gave none of **2b** (R^1 = H), but a 54% yield of this product was successfully obtained from reaction of **6** with 0.5 equivalent of Tebbe



6 (R = Me_3Si)
7 (R = Ph)

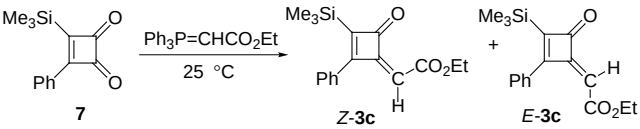
2 (R = Me_3Si)
3 (R = Ph)

8 (R = Me_3Si)
9 (R = Ph)

Equation 6

reagent, along with 17% of the product **8** of bis(methylenation).[1a] Further study now reveals that Nysted reagent $[(CH_2ZnBr)_2Zn{\bullet}THF]$[6c,d] gives comparable results to the Tebbe reagent, while Peterson olefination (Me_3SiCH_2Li followed by HF/MeCN)[6e] gives **2b** in 79% yield, with none of **8** (Table 1).

To further explore the reactivity of allenylketenes, and, as a further test of the efficacy of the calculated substituent stabilizing parameters for predicting equilibrium constants for methylenecyclobutenone/allenylketene equilibrations (see Appendix), we have now also examined the phenyl-substituted derivatives **3**. Reaction of 3-phenyl-2-trimethylsilylcyclobutene-1,2-dione (**7**)[2f] with one equivalent of $Ph_3P{=}CHCO_2Et$ gave after chromatography a 90% yield of a 3:2 mixture of (*Z*)-**3c** and (*E*)-**3c** (Eq. 7). The stereochemistry was assigned based on the deshielding of the vinyl proton in (*E*)-**3c** due to the effect on the *syn*-H of the carbonyl group.



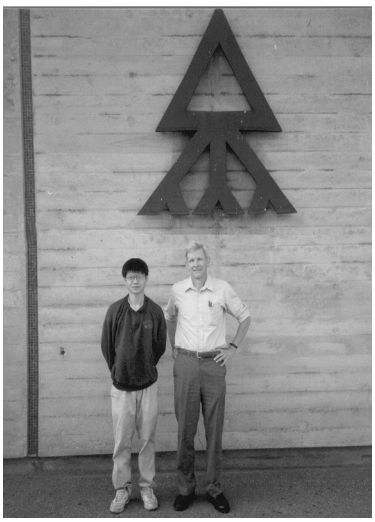
7

Z-**3c**

E-**3c**

Equation 7

Biographical Sketches



The authors are standing beneath the alchemical symbol for tartaric acid displayed on the wall of the Lash Miller Chemical Laboratory

Tom Tidwell received his Ph. D. at Harvard with Professor P. D. Bartlett in 1964 for work on steric crowding, and carried out postdoctoral work with Teddy Traylor at the University of California, San Diego, and with Alan Katritzky at the University of East Anglia in the UK. Since 1972 he has been at the University of Toronto, and has pursued synthetic, mechanistic, and computational studies of reactive intermediates, including ketenes, carbocations, carbanions, and free radicals. He has served IUPAC as Chair of the Commission on Physical Organic Chemistry and is currently Vice President of the Organic Division. For recreation he enjoys playing tennis and the history of organic chemistry.

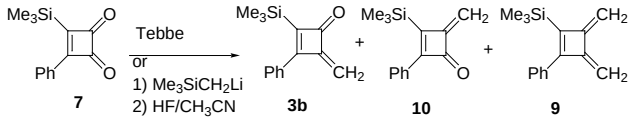
Wen-wei Huang received his undergraduate education in China the JiNan University, and an M.Sc. degree in polymer chemistry from Laurentian University, in Sudbury, Ontario. In 1999 he received the Ph. D. from the University of Toronto for studies on allenylketenes, and is now a postdoctoral fellow at Emory University, Atlanta, Georgia, in the laboratory of Professor Lanny Liebeskind. His main research interest is in organic synthesis.

Table 1 Products of Olefination of Cyclobutenediones **6** and **7**

Reactant	Reagent	Products	Yield (%)
6 (R = Me_3Si)	$Ph_3P{=}CH_2$[a]	**2b**	0
	Tebbe (1 equiv)[a,b]	**2b**	10
		+ **8**	20[c]
	Tebbe (0.5 equiv)[a,b]	**2b**	54
		+ **8**	17[c]
	Nysted[d]	**2b**	50
		+ **8**	10[c]
	Peterson[e]	**2b**	79
	$Ph_3P{=}CHCO_2Et$	**2c**	91
7 (R = Ph)	Tebbe[b]	**3b**	40
		+ **9**	10
		+ **10**	21[c]
	Peterson[e]	**3b**	33
		10	32

[a] Ref 1a.
[b] $Cp_2TiCH_2AlClMe_2$.
[c] Yields based on **6** or **7**.
[d] $(CH_2ZnBr)_2Zn{\cdot}THF$.
[e] Me_3SiCH_2Li, then HF.

Reaction between **7** and Tebbe reagent yielded **3b**, **9**, and **10** in a ratio of 4:1:2 (Eq. 8). When methylenation of dione **7** was done by the Peterson method, **3b** and **10** were obtained in almost equal amounts. The structures of **3b** and **10** were distinguished based on an NOE study of **3b**, in which irradiation of the higher field vinyl proton of **3b** gave 5.5% enhancement of the phenyl group. Thus both of these reagents are much less selective than is $Ph_3P{=}CHCO_2Et$ for reaction at a particular carbonyl group in **7**.



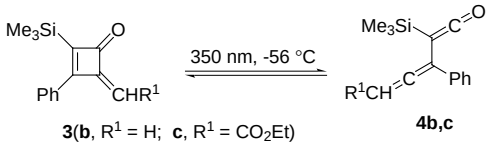
Equation 8

Photolyses of **3b** and of **3c** in $CDCl_3$ at −56 °C with 350 nm light gave solutions of the allenylketenes **4b** and **4c**, respectively (Eq. 9). Evidence for the structures of **4b** and **4c** includes the presence of ketene bands at ν = 2093 and 2094 cm^{-1}, and allene bands at ν = 1935 and 1941 cm^{-1}, respectively, in the IR spectra. The ^1H NMR spectra of **4b** and **4c** showed peaks at δ = 0.26 and 0.25 due to the TMS groups, 5.20 and 5.99 due to the allene hydrogens, and 7.20−7.50 due to the phenyl hydrogens, respectively. However, unlike the bis(trimethylsilyl)allenylketenes **1**, the phenyl analogs **4b** and **4c** were unstable at room temperature, and slowly reverted back to the methylenecyclobutenones **3b** and **3c**, respectively, as observed by ^1H NMR or UV spectra.

Table 2 Summary of Rate Constants in Isooctane for Ring Closure of Allenylketenes **4b** and **4c** to Cyclobutenones **3b** and **3c**

Product	T(°C)	k_{obs} (s^{-1})
4b	25.1	5.23×10^{-5}[a]
4c	25.0	1.02×10^{-3}[b]

[a] E_a = 22.0 ± 0.1 kcal/mol, $\Delta H^{\ddagger}$ = 21.4 ± 0.1 kcal/mol, $\Delta S^{\ddagger}$ = –6.4 ± 0.4 cal K^{-1} mol^{-1}.
[b] E_a = 18.5 ± 0.2 kcal/mol, $\Delta H^{\ddagger}$ = 17.9 ± 0.2 kcal/mol, $\Delta S^{\ddagger}$ = –11.6 ± 0.5 cal K^{-1} mol^{-1}.

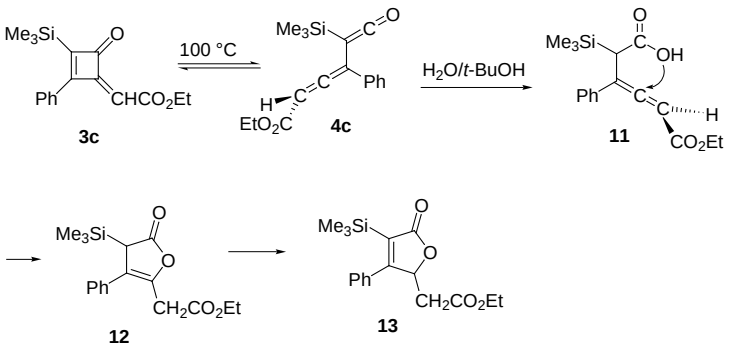


Equation 9

The kinetics of the ring-closure reactions in isooctane were measured by monitoring the appearance of the UV of **3b** at λ = 240 nm and the disappearance of **4c** at λ = 217 nm, respectively, and the results are summarized in Table 2. There is remarkable agreement in the experimental barrier for ring closure of the phenyl-substituted allenylketene **4b** which is 4.2 kcal/mol less than that of the Me_3Si substituted analog, as compared to the estimate (see Appendix) of 4.3 kcal/mol lower stabilizing effect of Ph in **4b** relative to the Me_3Si in **1b**.

Photolysis of **10** with 350 nm light gave no ring opening to an allenylketene that could be detected by conventional IR or NMR spectroscopy. This is not unexpected, as the possible allenylketene product does not have a silyl-stabilized ketenyl moiety, and is predicted to be 10.3 kcal/mol less stable than **10** based on the stabilizing effect of the substituents, so that facile ring closure back to **10** could occur (see Appendix).

Ring closure of allenylketene **4c** in $CDCl_3$ at room temperature gave (*Z*)-**3c** and (*E*)-**3c** in a ratio near 1:1, thus showing little torquoselectivity[7a] in this ring closure process, in contrast to results for the ring closure of vinylallenes.[3] On heating (*E*)-**3c** or (*Z*)-**3c** in $CDCl_3$ at 100°C, an equilibrium was established between (*E*)-**3c** and (*Z*)-**3c** with a 3.6:1 ratio in favor of the *Z*-isomer.

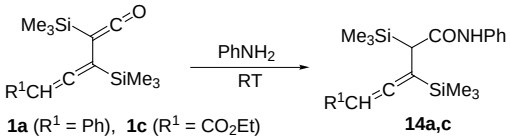


Scheme

3 Nucleophilic Additions

Heating (*E*)-**3c** in a mixture of H_2O/*t*-BuOH (1/9) in a sealed vial at 100 °C for 24 hours gave lactone **13** in 86% yield after chromatography (Scheme). The reaction is believed to proceed through the allenylketene **4c**, followed by trapping with water to give acid **11** and then cyclization to lactone **12**, which isomerizes to **13**. The conjugative stabilization of **13** may facilitate its formation without the desilylation noted in Eq. 3.[1a]

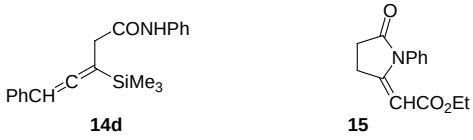
Reactions of **1a** and **1c** with aniline gave amides **14a** and **14c**, respectively, as mixtures of diastereomers in ratios of 1.2:1 and 4.8:1, respectively, as determined by the ^{1}H NMR spectra of the product mixtures (Eq. 10). The greater selectivity for formation of one of the diastereomers in the formation of **14c** is evidently not a steric effect, and may indicate some assistance by the CO_2Et group in the product forming delivery of the proton to C_β of the intermediate enol amide. Related types of intramolecular participation have been proposed in additions to bisketenes.[2e]



1a (R^1 = Ph), **1c** (R^1 = CO_2Et) **14a,c**

Equation 10

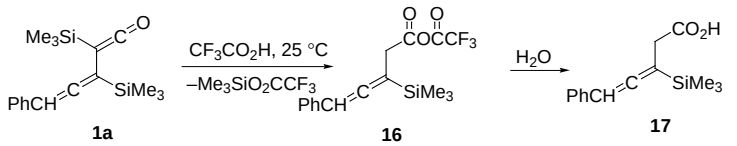
Treatment of **14a** with Al_2O_3 in pentane gave the desilylated product **14d** in overall 71% yield, while similar treatment of **14c** gave 64% of the known[7b] lactam **15**. Formation of **15** presumably occurs by a process related to that shown in the Scheme.



4 Electrophilic Additions

The reactions of **1b** with CF_3CO_2H in an NMR tube gave an intermediate, presumably the desilylated mixed anhydride **16**, identified by the ^{1}H NMR spectrum of the reaction mixture. Hydrolysis led to the isolated acid **17** (Eq. 11).

Reaction of **1a** with Br_2 gave the dienylacyl bromide **18a**, which with MeOH gave 92% of the ester **18b**. Reaction of **1a** with NBS at −56 °C followed by stirring at 25 °C for 2 h gave **18c** (Eq. 12), whose structure was confirmed by X-ray crystallography (Figure 1). The reaction with Br_2 occurs with 1,4-addition, which is the same result observed for the bisketene **20** (R = Me_3Si), which at −78 °C gave **21** (Eq. 13), which rearranged at higher temperature.[2d] When the reaction of NBS with **1a** was carried out at −23 °C with immediate measurement of the spectra a transient intermediate was detected which by ^{1}H NMR showed two non-equivalent Me_3Si groups, and two two-proton multiplets at δ = 2.80 and 3.25, while the IR spectrum showed a band at 1580 cm^{-1}. These spectral features disappeared with time, and were replaced by those of **18c**. The structure of the transient intermediate is assigned as the acyl imidate **18d**. The alkylation of succinate salts occurs partially on oxygen to give analogous alkyl imidates with the



Equation 11

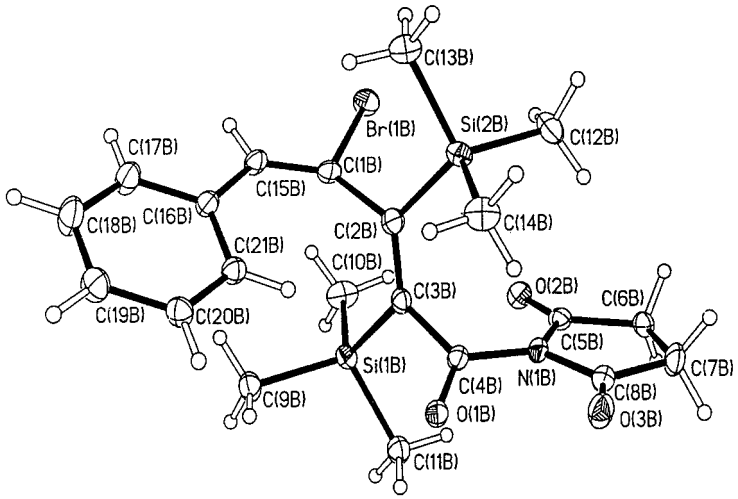
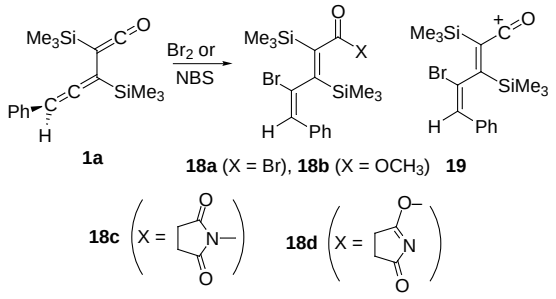
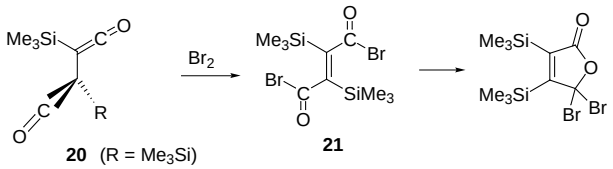


Figure 1 X-ray crystal structure of **18c**

succinyl protons as two two-proton multiplets at δ = 1.6 and 2.7, respectively,[8a] and IR bands at ν = 1565-1570 cm^{-1} for the C=N absorption.[8b]



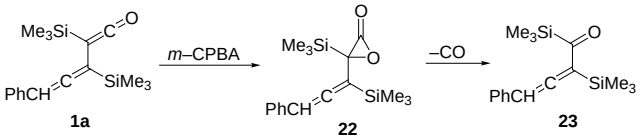
Equation 12



Equation 13

The formation of **18c** with NBS indicates initial electrophilic attack by Br^+ occurs on the central carbon of the allene group from the side opposite the phenyl, leading to the observed geometry. The cationic intermediate **19** could be formed, with a highly conjugated dienylacylium ion structure.

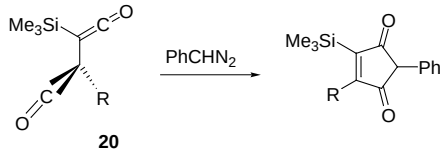
Reaction of **1a** with *m*-chloroperbenzoic acid gave 58% of the allenylketone **23**, possibly through the α-lactone **22** (Eq. 14). This reaction represents a unique synthesis of an acylsilane, a family of significant interest.[9] The formation of α-lactones in ketene oxidations with peracids has been observed,[10] and in some instances these react by decarbonylation, perhaps with assistance by nucleophilic attack on the α-lactone.



Equation 14

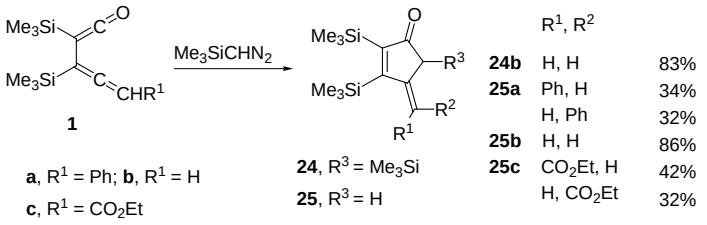
5 Cycloaddition Reactions

In studies of 1,2-bisketenes **20** [4+1] cycloaddition reactions with diazoalkanes forming cyclopentene-1,4-diones as illustrated in Eq. 15 were observed.[2c] Reactions of **20** with aldehydes and with alkynes led to a variety of other cycloaddition products.[2c] We have now examined comparable reactions of the allenylketenes **1**.



Equation 15[2c]

Allenylketenes **1** generated photochemically[1a] from methylenecyclobutenones **2** were added to Me_3SiCHN_2 at room temperature. After evaporation of the solvent, the trimethylsilylmethylenecyclopentenone **24a** could be detected by ^1H NMR, but only **24b** could be chromato-



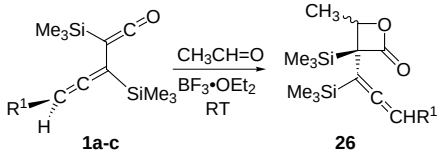
a, R^1 = Ph; **b**, R^1 = H
c, R^1 = CO_2Et

Equation 16

graphed without desilylation. Therefore **24a** and **24c** were treated with MeOH and SiO_2 followed by chromatography on silica gel to give the separated (*E*)- and (*Z*)-**25a** and **25c** as shown (Eq. 16). Similar desilylation of **24b** gave **25b**.

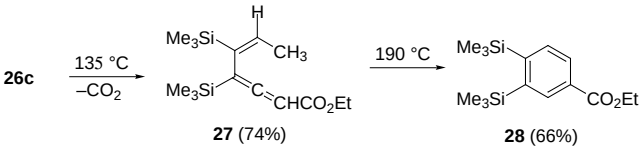
The *E*/*Z*-stereochemistries of **25a** and **25c** were assigned by the higher field shift of the vinyl protons in the *E*-isomers due to the deshielding effect of the endocyclic double bond and the larger allylic couplings of the vinyl protons in the *E*-isomers to the CH_2 grouping. These assignments were confirmed by NOE experiments for (*E*)- and (*Z*)-**25c**, in which irradiation of the CH_2 group resulted in 15% enhancement of the vinyl proton for (*Z*)-**25c**, while no enhancement was seen in (*E*)-**25c**.

For the further elucidation of the cycloaddition reactions of allenylketenes the reactions with acetaldehyde catalyzed with BF_3•OEt_2 were first examined, and led to the formation of mixed *cis*/*trans* β-lactones (2-oxetanones) **26** as shown in Eq. 17. The products **26** from substituted allenes **1a** and **1c** also occurred as diastereomers due to the chirality of the allenyl groups. The major isomer of **26b** was established as *trans* by an NOE experiment. Previously[2c] the reaction of bisketene **20** (R = Me_3Si) was also found to favor formation of *trans*-lactone, and by analogy **26a** and **26c** are also believed to favor this configuration. Pyrolysis of **26c** (90% *trans*) gave **27** in 74% yield after chromatography, assigned the *E*-stereochemistry at the alkenyl group, as decarboxylation of β-lactones occurs with retention of configuration (Eq. 18).[11] Further pyrolysis of **27** gave cyclization to **28** (eq 18), presumably by a [1,5]-sigmatropic hydrogen shift followed by electrocyclic ring closure.



a, R^1 = Ph; **b**, R^1 = H; **c**, R^1 = CO_2Et

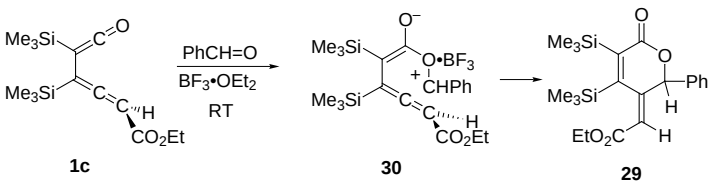
Equation 17



Equation 18

The recent observation of a vinylketene acting as a diene in [4+2] cycloaddition to a carbonyl group is noted above,[5d] and the startling finding has appeared that the net [2+2] cycloaddition of diphenylketene to cyclopentadiene, first reported in 1920, involves initial [4+2] cycloaddition of cyclopentadiene to the C=O of Ph_2C=C=O.[5e] It was of interest to examine the behavior of allenylketenes. The reaction of **1c** with benzaldehyde catalyzed by BF_3•OEt_2 gave the α-pyrone **29** (Eq. 19), whose structure was proven by X-ray crystallography (Figure 2).

The ^{1}H NMR spectrum of **29** showed a remarkable temperature dependence, as illustrated in Figure 3, and this may be attributed to freezing out of bond rotations in the molecule, as has been previously observed in other crowded vinylsilanes.[12] The formation of this crowded product may be rationalized by formation of the zwitterionic intermediate **30**, which undergoes ring closure with rotation of the CO_2Et group outward away from the phenyl (Eq. 19). Alternatively initial C–C bond formation



Equation 19

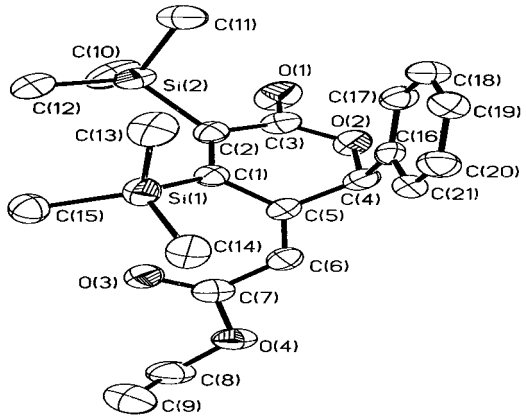
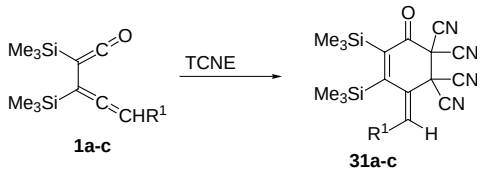


Figure 2 X-ray crystal structure of α-pyrone **29**

may occur, or even a concerted reaction, with the same stereochemical consequences. Theoretical study of BF_3 promoted [2+2] cycloaddition of CH_2=O with CH_2=C=O favors a mechanism with BF_3 coordination to the oxygen of CH_2=O, and a quasi-concerted but asynchronous cycloaddition with priority to C−C bond formation.[13]

As further examples of [4+2] cycloadditions of allenylketenes participating as dienes the reactions of **1** with tetracyanoethylene (TCNE) were examined, and each readily participated in this process at room temperature (Eq. 20). Complete conversion of **1** to **31a−c** as the only observable products were observed when the reactions were monitored by ^{1}H NMR spectroscopy. The *Z*-configuration shown at the exomethylene group was confirmed for **31a** (R^1 = Ph) by X-ray (Figure 4), and is expected for approach of TCNE opposite the Ph or CO_2Et groups in the transition states.



1a-c **31a-c**

Equation 20

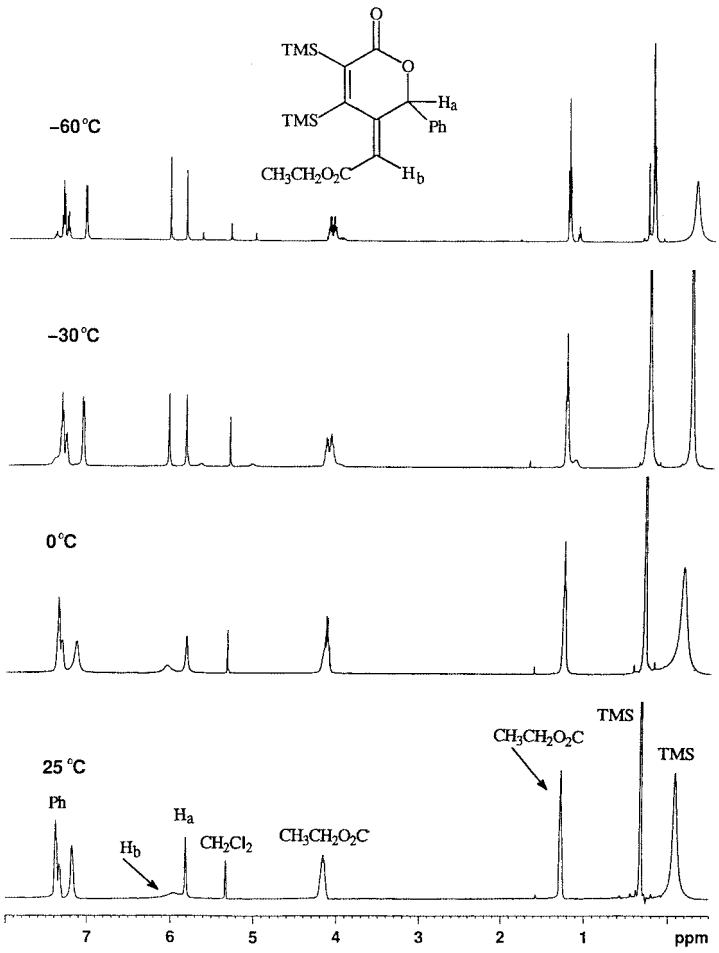


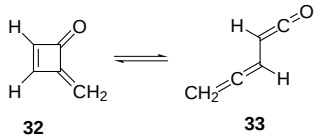
Figure 3 Temperature dependent ^{1}H NMR spectra of **29**

Conclusion

The stability of allenylketenes are accurately predicted by ab initio molecular orbital calculations, and a variety of compounds are readily prepared and enter into a diverse array of reactions with the different classes of organic reagents. Opportunities beckon for the discovery of further reactions of these versatile intermediates, and for further transformations of the products.

Appendix

The stabilities of allenylketenes derived from **3b**, **3c** and **10** may be estimated by the methods we have used previously.[1a] Thus the parent methylenecyclobutenone **32** was calculated to be 10.7 kcal/mol more stable than its isomeric allenylketene **33** (Eq. 21).[1a] Compared to hydrogen, the calculated stabilizing effects of the SiH_3 group on a ketene and on an allene relative to the effect on an alkene are 7.6 kcal/mol and 3.0 kcal/mol respectively, and assuming additivity of substituent effects and equating the stabilizing effect of Me_3Si and SiH_3 the 10.6 kcal/mol substituent stabilization of allenylketene **1b** (R^1 = H) predicts 0.1 kcal/mol greater stability for the methylenecyclobutenone **2b**, compared to the experimentally determined value of 3.0 kcal/mol at 25 °C. On the assumption that the effect of the phenyl group on an allene relative to the effect on an alkene is similar to that of the $CH{=}CH_2$ group, which is destabilizing by 1.3 kcal/mol compared to hydrogen,[1c] the phenyl-substituted allenylketene **4b** (R^1 = H) would be about 4.3 kcal/mol less stabilized compared to the isomeric methylenecyclobutenone **3b** than is the bis(trimethylsilyl)allenylketene **1b** (Eq. 1). The theoretically calculated[1a] energy barrier (E_a) for ring closure of allenylketene **33** was 23.0 kcal/mol and the experimental energy barriers (E_a) for ring closure of allenylketene **1b**[1a] and **4b** are 26.2 and 22.0 kcal/mol, respectively.



32 **33**

Equation 21

IR spectra were recorded on a Nicolet FTIR-8210E spectrometer or a Bomem Michelson 100 FT-IR spectrophotometer. NMR spectra were recorded on Varian VXR-200 or Varian Unity-400 instruments using TMS as internal standard. UV spectra and kinetics were measured using a Perkin Elmer Lambda 12 spectrometer. UV irradiation was carried out in a Rayonet photochemical reactor at 5°C. Tebbe reagent (0.5 M in toluene) was purchased from Fluka Co. Me_3SiCH_2Li (1.0 M solution in pentane), Nysted reagent (20% in THF), and Me_3SiCHN_2 were purchased from Aldrich. Radial chromatography was carried out on a silica gel plate using a Chromatotron from Harrison Research.

(*E*)- and (*Z*)- 4-(Ethoxycarbonylmethylene)-3-phenyl-2-trimethylsilylcyclobuten-1-ones [(*E*)- and (*Z*)-(3c)]

A solution of $Ph_3P{=}CHCO_2Et$ (0.310 g, 0.89 mmol) and cyclobutenedione **7** (0.205 g, 0.89 mmol) in $CHCl_3$ (50 mL) was stirred for 24 h under N_2 at 25 °C. The solvent was evaporated, and the viscous product was separated by column chromatography to give (*Z*)-**3c** (0.145 g, 54%) and (*E*)-**3c** (96 mg, 36%).

(*Z*)-**3c**

IR (neat): ν = 1769 (C=O), 1707 cm^{-1} (CO_2Et).

^1H NMR ($CDCl_3$): δ = 0.30 [s, 9 H, $(CH_3)_3Si$], 1.34 (t, 3 H, *J* = 7.1 Hz, CH_3), 4.26 (q, 2 H, *J* = 7.1 Hz, CH_2), 5.69 (s, 1 H, C=CH), 7.53 (br s, 5 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = −1.4, 14.2, 60.7, 104.2, 128.0, 128.9, 131.1, 131.7, 164.8, 166.2, 175.5, 184.5, 184.9.

UV (cyclohexane): λ_{max} (ε) = 217 (16 000), 261 (25 000) nm.

EI-MS: *m*/*z* = 300 (M^+, 29), 285 ($M^+ - CH_3$, 11), 271 ($M^+ - C_2H_5$, 51), 227 ($M^+ - Me_3Si$, 49), 73 (Me_3Si^+, 100);

HRMS: *m*/*z* calcd for $C_{17}H_{20}O_3Si$ 300.1182, found 300.1176.

(*E*)-**3c**

IR (neat): ν = 1766 (C=O), 1715 cm^{-1} (CO_2Et).

^1H NMR ($CDCl_3$): δ = 0.21 [s, 9 H, $(CH_3)_3Si$], 0.95 (t, 3 H, *J* = 7.1 Hz, CH_3), 3.94 (q, 2 H, *J* = 7.1 Hz, CH_2), 5.84 (s, 1 H, C=CH), 7.40−7.48 (m, 5 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = −1.4, 13.8, 60.3, 101.3, 127.7, 128.2, 130.4, 133.2, 162.9, 164.9, 177.7, 188.2, 188.6 (one C not seen).

UV (cyclohexane): λ_{max} (ε) = 218 (16 000), 259 (22 000) nm.

EI-MS: *m*/*z* 300 (M^+, 26), 285 ($M^+ - CH_3$, 10), 271 ($M^+ - C_2H_5$, 42), 227 ($M^+ - Me_3Si$, 49), 73 (Me_3Si^+, 100).

HRMS: *m*/*z* calcd for $C_{17}H_{20}O_3Si$ 300.1182, found 300.1177.

Heating (*E*)-**3c** (15 mg, 0.050 mmol) in degassed $CDCl_3$ (0.8 mL) in a sealed NMR tube at 100 °C for 4 h gave a mixture of (*Z*)-**3c** and (*E*)-**3c** in a ratio of 3.6:1, as measured by ^1H NMR spectroscopy. This ratio did not change on further heating.

Reaction Between Dione 7 and Tebbe Reagent

A solution of dione **7** (0.121 g, 0.53 mmol) in anhyd THF (8 mL) at −78°C and Tebbe reagent[6a] (1.1 mL, 0.5 M in toluene, 0.55 mmol)

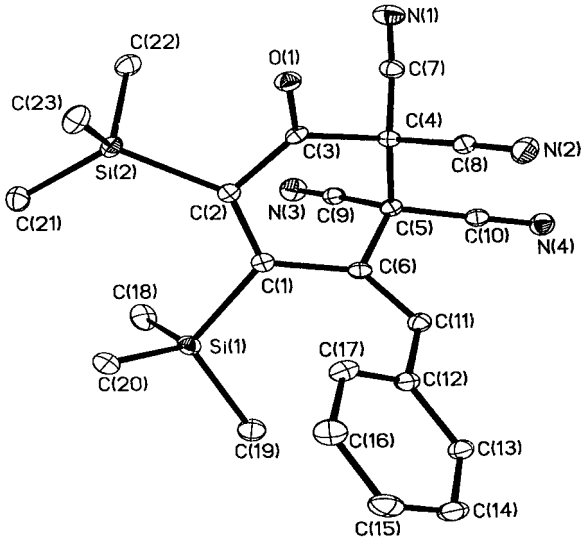


Figure 4 X-ray crystal structure of **31a**

was stirred 6 h at −15 °C and then the reaction mixture was poured into pentane (50 mL) and filtered. The filtrate was concentrated and chromatographed (5% EtOAc/hexanes) to give 4-methylene-3-phenyl-2-trimethylsilylcyclobutene-1-one (**3b**) (0.048 g, 40%) 4-methylene-2-phenyl-3-trimethylsilylcyclobuten-1-one (**10**) (0.026 g, 21%), and 3,4-bis(methylene)-1-phenyl-2-trimethylsilylcyclobutene (**9**) (0.011 g, 10%).

3b

IR ($CDCl_3$): ν = 1756, 1602 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.31 [s, 9 H, $(CH_3)_3Si$], 4.93 (d, 1 H, *J* = 1.8 Hz, C=CH), 5.17 (d, 1 H, *J* = 1.8 Hz, C=CH), 7.50−7.64 (m, 5 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = −1.2, 95.0, 128.5, 128.8, 131.5, 132.2, 158.6, 165.9, 185.5, 191.2.

EI-MS: *m*/*z* = 228 (M^+, 73), 213 ($M^+ - CH_3$, 44), 200 (M^+ − CO, 47), 185 (100), 73 (Me_3Si^+, 68).

HRMS: *m*/*z* calcd for $C_{14}H_{16}OSi$ 228.0970, found 228.0968.

10

IR ($CDCl_3$): ν = 1764, 1602 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.41 [s, 9 H, $(CH_3)_3Si$], 4.82 (d, 1 H, *J* = 1.4 Hz, C=CH), 5.11 (d, 1 H, *J* = 1.4 Hz, C=CH), 7.40−7.72 (m, 5 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = −1.4, 96.2, 128.1, 128.6, 130.0, 130.4, 161.6, 169.6, 183.9, 189.1.

EI MS: *m*/*z* = 228 (M^+, 35), 213 ($M^+ - CH_3$, 10), 200 (M^+ − CO, 49), 185 (40), 159 (60), 73 (Me_3Si^+, 100).

HRMS: *m*/*z* calcd for $C_{14}H_{16}OSi$ 228.0970, found 228.0972.

9

IR ($CDCl_3$): ν = 1602 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.28 [s, 9 H, $(CH_3)_3Si$], 4.79 (s, 1 H, C=CH), 4.84 (s, m 1 H, C=CH), 4.86 (s, 1 H, C=CH), 4.91 (s, 1 H, C=CH), 7.37−7.48 (m, 5 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = −0.7, 92.6, 93.9, 127.6, 128.3, 128.7, 133.8, 150.1, 152.0, 157.2, 164.1.

EI-MS: *m*/*z* = 226 (M^+, 100), 211 ($M^+ - CH_3$, 73), 159 (91), 111 (57), 73 (Me_3Si^+, 89).

HRMS: *m*/*z* calcd for $C_{15}H_{18}Si$ 226.1178, found 226.1186.

Methylenation of Dione 7 by Peterson Method

To a stirred solution of dione **7** (0.154 g, 0.67 mmol) in anhyd Et_2O (15 mL) and anhyd THF (15 mL) at −78 °C was added Me_3SiCH_2Li (0.7 mL, 1.0 M in pentane, 0.7 mmol) dropwise. The solution was stirred for 1 h at −78 °C, allowed to warm to 0 °C, and was poured into aq sat. NH_4Cl (30 mL) and extracted with Et_2O, which was dried and evaporated. The residue was dissolved in MeCN (20 mL), cooled in an ice bath, and HF/MeCN solution (4 drops 50% HF aqueous solution in 8 mL MeCN) was added dropwise with monitoring by TLC and once the starting material had disappeared the reaction mixture was poured into aq sat. $NaHCO_3$ (20 mL) and extracted with pentane, which was dried and evaporated. Chromatography gave **3b** (50 mg, 33%) and **10** (49 mg, 32%).

NOE Study of 3b

When the vinyl proton at δ = 4.93 was saturated a 5.5% increase was observed for the 7.2 ppm phenyl protons and an 33% increase was observed at the 5.17 ppm vinyl proton.

3-Phenyl-2-(trimethylsilyl)penta-1,3,4-trien-1-one (4b)

A solution of **3b** (15 mg, 0.66 mmol) in $CDCl_3$ (0. 8 mL) in an NMR tube was irradiated with 350 nm light for 3 h at −56 °C to give **4b**.

IR ($CDCl_3$): ν = 2093 (C=C=O), 1935 cm^{-1} (C=C=C).

^1H NMR ($CDCl_3$): δ = 0.26 [s, 9 H, $(CH_3)_3Si$], 5.20 (s, 2 H, $C=CH_2$), 7.20−7.50 (m, 5 H, C_6H_5).

5-Ethoxycarbonyl-3-phenyl-2-trimethylsilylpenta-1,3,4-trien-1-one (4c)

A solution of (*E*)-**3c** (15 mg, 0.5 mmol) in $CDCl_3$ (0.8 mL) in a NMR tube was iradiated with 350 nm light 3 h at −56 °C to give **4c**.

IR ($CDCl_3$): ν = 2094 (C=C=O), 1941 (C=C=C), 1725 cm^{-1} (CO_2Et).

^1H NMR ($CDCl_3$): δ = 0.25 [s, 9 H, $(CH_3)_3Si$], 1.29 (t, 3 H, *J* = 7.2 Hz, CH_3), 4.22 (m, 2 H, CH_2), 5.99 (s, 1 H, C=CH), 7.30−7.45 (m, 5 H, C_6H_5).

Kinetics of Ring Closure of Allenylketene 4b

Samples of **4b** were prepared by irradiating methylenecyclobutenone **3b** in isooctane with 350 nm light for 5 min. The rates of conversion to **3b** were then measured by monitoring the increase of the aborption at 240 nm.

Kinetics of Ring Closure of Allenylketene 4c

Samples of **4c** were prepared by irradiating methylenecyclobutenone (*Z*)-**3c** in isooctane with 350 nm light for 5 min. The rates of conversion to **3c** were then measured by monitoring the decrease of the absorption at 217 nm. A solution of (*Z*)-**3c** (15 mg, 0.5 mmol) in degassed $CDCl_3$ (1.0 mL) was irradiated with 350 nm light at −56 °C for 3 h. The low temperature (−20 °C) ^1H NMR showed that (*Z*)-**3c** completely converted to allenylketene **3c**. Then, the NMR tube with the solution of allenylketene **4c** was left standing at 25 °C overnight. The ^1H NMR spectrum showed that allenyleketene **3c** converted back to (*Z*)-**3c** and (*E*)-**3c** in a 1:1 ratio. Heating (*Z*)-**3c** (15 mg, 0.5 mmol) in degassed $CDCl_3$ (0.8 mL) in a sealed NMR tube at 100 °C for 4 h gave a mixture of (*Z*)-**3c** and (*E*)-**3c** in a ratio of 3.6:1 as measured by ^1H NMR. This ratio did not change on further heating.

Hydration of Allenylketene 4c to 13

A solution of (*E*)-**3c** (35.2 mg, 0.12 mmol) in H_2O (0.1 g), and *t*-BuOH (0.9 g) in a sealed vial was heated for 24 h at 100 °C. Then EtOAc (20 mL) was added and the solution was dried ($MgSO_4$), evaporated and chromatographed (5% EtOAc in hexane) to give lactone **13** (32 mg, 86%) as an oil.

IR ($CDCl_3$): ν = 1740 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.10 [s, 9 H, $(CH_3)_3Si$], 1.19 (t, 3 H, *J* = 7.2 Hz, CH_3), 2.42 (dd, 1 H, *J* = 16.2, 8.6 Hz C*H*H), 2.58 (dd, 1 H, *J* = 16.2, 3.9 Hz, CH*H*), 4.06 (q, 1 H, *J* = 7.2 Hz, CH), 4.07 (q, 1 H, *J* = 7.2, CH), 5.56 (dd, 1 H, *J* = 8.6, 4.0 Hz), 7.19−7.45 (m, 5 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = −1.1, 14.0, 37.7, 61.1, 80.6, 127.6, 128.6, 129.4, 129.8, 132.9, 169.2, 175.2, 176.0.

EI-MS: *m*/*z* 318 (M^+, 53), 303 ($M^+ - CH_3$, 100), 257 (29), 245 ($M^+ - Me_3Si$, 62), 231 (37), 213 (43), 159 (26), 75 (56), 73 (Me_3Si^+, 44).

HRMS: *m*/*z* calcd for $C_{17}H_{22}O_4Si$ 318.1287, found 318.1301.

2,3-Bis(trimethylsilyl)-*N*,5-diphenylpenta-3,4-dienamide (14a)

To a solution of allenylketene **1a** (83 mg, 0.28 mmol) in CH_2Cl_2 (10 mL) was added aniline (0.52 g, 5.6 mmol) and the mixture was stirred overnight at r.t. Then Et_2O (50 mL) was added, the mixture was washed with 5% HCl (3 × 20 mL) and H_2O (2 × 20 mL). The organic layer was dried ($MgSO_4$). Filtration and evaporation gave **14a** (106 mg, 98%) as a gum. ^1H NMR analysis showed that **14a** was a mixture of two diastereomers in 1.2:1 ratio.

IR ($CDCl_3$): ν = 3397 (NH), 1910 (C=C=C), 1662 cm^{-1} (CONH).

Major isomer: ^{1}H NMR ($CDCl_3$): δ = 0.18 [s, 9 H, $(CH_3)_3Si$], 0.21 [s, 9 H, $(CH_3)_3Si$], 2.70 (br s, 1 H, Me_3SiCH), 6.22 (br s, 1 H, C=CH), 6.96−7.86 (m, 11 H, NH, 2 × C_6H_5).

Minor isomer: ^{1}H NMR ($CDCl_3$): δ = 0.15 [s, 9 H, $(CH_3)_3Si$], 0.20 [s, 9 H, $(CH_3)_3Si$], 2.69 (br s, 1 H, Me_3CH), 6.23 (br s, 1 H, C=CH), 6.96−7.86 (m, 11 H, NH, 2 × C_6H_5).

3-Trimethylsilyl-*N*,5-diphenylpenta-3,4-dienamide (14d); Typical Desilylation Procedure

To **14a** (21 mg, 0.05 mmol) in pentane (5 mL) was added Al_2O_3 (0.5 g) and the mixture was stirred at 25 °C for 4 h and filtered. The Al_2O_3 was washed with EtOAc (10 mL), the solvent evaporated, and the residue was purified by chromatography to give **14d** (12 mg, 71%) as a gum.

IR ($CDCl_3$): ν = 1921 (C=C=C), 1682 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$): δ = 0.23 [s, 9 H, $(CH_3)_3Si$], 3.20 (dd, 1 H, *J* = 2.2, 5.7 Hz, C*H*H), 3.26 (dd, 1 H, *J* = 2.2, 5.7 Hz, CH*H*), 6.11 (t, 1 H, *J* = 2.2 Hz, C=CH), 7.06−7.38 (m, 10 H, 2 × C_6H_5), 7.59 (br s, 1 H, NH).

^{13}C NMR ($CDCl_3$): δ = −1.4, 39.0, 90.7, 96.2, 119.7, 124.2, 126.1, 126.7, 128.9, 134.3, 137.6, 168.5, 207.6.

EI-MS: *m*/*z* = 321 (M^+, 18), 244 (42), 84 (100), 73 (Me_3Si^+, 31).

HRMS: *m*/*z* calcd for $C_{20}H_{23}NOSi$ 321.1549, found 321.1538.

5-(Ethoxycarbonyl)-2,3-bis(trimethylsilyl)-*N*-phenylpenta-3,4-dienamide (14c)

A solution of allenylketene **1c** (64 mg, 0.22 mmol) in CH_2Cl_2 (10 mL) and aniline (200 mg, 2.1 mmol) was stirred overnight at 25 °C. After the addition of Et_2O (50 mL), the organic layer was washed with 5% HCl (3 × 20 mL) and H_2O (2 × 20 mL), dried ($MgSO_4$) and evaporated to give **14c** (80 mg, 94%) as a yellow oil. ^{1}H NMR analysis showed that **14c** was a mixture of two diastereomers in a ratio of 4.8:1.

Major isomer: ^{1}H NMR ($CDCl_3$): δ = 0.20 [s, 9 H, $(CH_3)_3Si$], 0.23 [s, 9 H, $(CH_3)_3Si$], 1.28 (t, 3 H, *J* = 7.1 Hz, CH_3), 2.60 (s, 1 H, Me_3SiCH), 4.21 (q, 2 H, *J* = 7.1 Hz, OCH_2), 5.58 (s, 1 H, C=CH), 7.08−7.65 (m, 6 H, NH, C_6H_5).

Minor isomer: ^{1}H NMR ($CDCl_3$): δ = 0.18 [s, 9 H, $(CH_3)_3Si$], 0.19 [s, 9 H, $(CH_3)_3Si$], 1.26 (t, 3 H, *J* = 7.2 Hz, CH_3), 2.66 (d, 1 H, *J* = 1.2 Hz, Me_3SiCH), 4.16−4.33 (m, 2 H, OCH_2), 5.48 (d, 1 H, *J* = 0.8 Hz, C=CH), 7.06−7.70 (m, 5 H, C_6H_5), 8.94 (br s, 1 H, NH).

4-(Carbethoxymethylene)-*N*-phenylbutyrolactam (15)

Desilylation of **14c** (19 mg, 0.05 mmol) as for **14a** (see above) gave after chromatography **15**[7b] (10 mg, 64%) as a white solid, mp 139−141 °C.

IR ($CDCl_3$): ν = 1738, 1700, 1628 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.23 (t, 3 H, *J* = 7.1 Hz, CH_3), 2.74−2.78 (m, 2 H, CH_2), 3.30−3.44 (m, 2 H, CH_2), 4.14 (q, 2 H, *J* = 7.1 Hz, OCH_2), 5.00 (t, 1 H, *J* = 2.0 Hz, C=CH).

^{13}C NMR ($CDCl_3$): δ = 14.4, 25.0, 28.5, 59.6, 93.4, 127.6, 129.1, 129.9, 134.1, 161.1, 167.3, 176.6.

Addition of Trifluoroacetic Acid to Allenylketene 1a; 3-Trimethylsilyl-5-phenylpenta-3,4-dienoic Acid (17)

To a solution of allenylketene **1a** (16 mg, 0.052 mmol) in $CDCl_3$ (1.0 mL) in an NMR tube was added CF_3CO_2H (40 μL, 0.52 mmol) in one portion at 25 °C. The ^{1}H NMR spectrum showed the presence of CF_3CO_2H, $CF_3CO_2SiMe_3$, and **16**.

^{1}H NMR ($CDCl_3$): δ = 0.21 [s, 9 H, $(CH_3)_3Si$], 3.39 (d, 2 H, *J* = 2.4 Hz, CH_2), 6.08 (t, 1 H, *J* = 2.4 Hz, C=CH), 7.21−7.40 (m, 5 H, C_6H_5).

Then Et_2O (10 mL) was added and the mixture was washed with H_2O (4 × 5 mL). The organic layer was dried and evaporated to give the acid **17** as a gum.

IR ($CDCl_3$): ν = 1927 (C=C=C), 1709 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$): δ = 0.17 [s, 9 H, $(CH_3)_3Si$], 3.17 (d, 2 H, *J* = 2.4 Hz, CH_2), 5.99 (t, 1 H, *J* = 2.2 Hz, C=CH), 7.15−7.30 (m, 5 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = −1.4, 35.5, 90.5, 94.2, 126.2, 126.3, 128.6, 134.7, 177.4, 208.1.

EI-MS: *m*/*z* = 246 (M^+, 16), 231 ($M^+ - CH_3$, 22), 218 (M^+ − TMS, 56), 128 (41), 73 (Me_3Si^+, 100).

HRMS: *m*/*z* calcd for $C_{14}H_{18}O_2Si$ 246.1076, found 246.1067.

2,3-Bis(trimethylsilyl)-4-bromo-5-phenylpenta-2,4-dienoyl Bromide (18a)

Allenylketene **1a** (39 mg, 0.13 mmol) in $CDCl_3$ (0.8 mL) was cooled to −23 °C and Br_2 (21 mg, 0.13 mmol) in $CDCl_3$ (0.5 mL) was added with rapid loss of the Br_2 color. The spectra showed only the presence of **18a**.

IR ($CDCl_3$): ν = 1796 cm^{-1} (COBr).

^{1}H NMR ($CDCl_3$): δ = 0.11 [s, 9 H, $(CH_3)_3Si$], 0.28 [s, 9 H, $(CH_3)_3Si$], 6.78 (s, 1 H, C=CH), 7.20−7.32 (m, 5 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = −0.7, 0.22, 125.6, 127.7, 128.5, 128.52, 130.5, 135.8, 150.9, 161.6, 178.1.

Methyl 2,3-Bis(trimethylsilyl)-4-bromo-5-phenylpenta-2,4-dienoate (18b)

A solution of allenylketene **1a** (53 mg, 0.18 mmol) in CH_2Cl_2 (1.0 mL) was cooled in −23 °C (dry ice/CCl_4), and Br_2 (28 mg, 0.18 mmol) in CH_2Cl_2 (0.5 mL) was added. The mixture was cooled to −78°C and MeOH (4 mL) was added slowly. The mixture was then warmed to r.t., and the solvent was evaporated to give after chromatography **18b** (67 mg, 92%) as a gum.

IR ($CDCl_3$): ν = 1709 cm^{-1} (ester C=O).

^{1}H NMR ($CDCl_3$): δ = 0.07 [s, 9 H, $(CH_3)_3Si$], 0.22 (s, 9 H, $[CH_3)_3Si$], 3.75 (s, 3 H, OCH_3), 6.77 (s, 1 H, C=CH), 7.20−7.34 (m, 5 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = −0.68, -0.03, 51.3, 126.0, 127.6, 128.4, 128.5, 130.4, 135.9, 152.0, 160.9, 172.0.

EI-MS: *m*/*z* = 412 (M^+, 1), 410 (M^+, 1), 397 ($M^+ - CH_3$, 11), 395 ($M^+ - CH_3$, 10), 227 (M^+ − Br, 98), 183 (61), 97 (64), 89 (46), 73 (Me_3Si^+, 100).

HRMS: *m*/*z* calcd for $C_{18}H_{27}O_2Si_2{}^{81}Br$ 412.0712, found 412.0702; calcd for $C_{18}H_{27}O_2Si_2{}^{79}Br$ 410.0733, found 410.0721.

***N*-2,3-Bis(trimethylsilyl)-4-bromo-5-phenylpenta-2,4-dienoylsuccinimide (18c)**

To a suspension of NBS (39 mg, 0.22 mmol) in CH_2Cl_2 (1.0 mL) was added allenylketene **1a** (65 mg, 0.22 mmol) in CH_2Cl_2 (1.0 mL) at −56 °C (octane/CO_2). The mixture was allowed to warm to r.t. and stirred for 2 h. Evaporation of the solvent and chromatography gave **18c** (76 mg, 74%)[14] as a white solid; mp 165−167°C.

IR ($CDCl_3$): ν = 1749 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$): δ = 0.08 [s, 9 H, $(CH_3)_3Si$], 0.18 [s, 9 H, $(CH_3)_3Si$], 2.83 (s, 4 H, 2 CH_2), 6.83 (s, 1 H, C=CH), 7.24−7.43 (m, 5 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = −0.05, 0.48, 28.5, 124.8, 127.8, 128.4, 128.9, 131.3, 135.7, 154.2, 160.1, 170.1, 173.6.

EI-MS: *m*/*z* = 479 (M^+, 1), 477 (M^+, 1), 464 ($M^+ - CH_3$, 3), 462 ($M^+ - CH_3$, 3), 398 ($M^+ - Br$, 34), 310 (16), 244 (28), 227 (100), 183 (31), 156 (28), 97 (29), 73 (Me_3Si^+, 74).

HRMS: *m*/*z* calcd for $C_{21}H_{28}NO_3Si_2{}^{79}Br$ 477.0791, found 477.0795.

Acyl Imidate 18d

To a suspension of NBS (14 mg, 0.078 mmol) in $CDCl_3$ (0.8 mL) was added allenylketene **1a** (23 mg, 0.078 mmol) in $CDCl_3$ (0.5 mL) at −23 °C. The mixture was stirred 0.5 h at −23 °C and was transferred to an NMR tube. The ^1H NMR spectrum was measured immediately at r.t., and showed one major product assigned as the acyl imidate **18d**.

^1H NMR ($CDCl_3$): δ = 0.14 [s, 9 H, $(CH_3)_3Si$], 0.29 [s, 9 H, $(CH_3)_3Si$], 2.80 (m, 2 H, CH_2), 3.25 (m, 2 H, CH_2), 6.81 (s, 1 H, C=CH), 7.24−7.43 (m, 5 H, C_6H_5).

IR ($CDCl_3$): ν = 1585 cm^{-1}.

The signals assigned to **18d** were completely converted to those of (*E*)-**18c** within 1 h.

1,2-Bis(trimethylsilyl)-4-phenylbuta-2,3-dien-1-one (23)

To a solution of allenylketene **1a** (105 mg, 0.35 mmol) in CH_2Cl_2 (10 mL) was added *m*-CPBA (72 mg, 0.36 mmol) in one portion at 0 °C. The mixture was allowed to warm to r.t. and the stirring was continued for 3 h. The solvent was evaporated and chromatographed on silica gel (5% EtOAc in hexanes) to give allenyl silyl ketone **23** (58 mg, 58%) as a yellow solid; mp 116−117 °C.

IR ($CDCl_3$): ν = 1908 (C=C=C), 1591 cm^{-1} (C=O).

^1H NMR ($CDCl_3$): δ = 0.17 [s, 9 H, $(CH_3)_3Si$], 0.19 [s, 9 H, $(CH_3)_3Si$], 6.30 (s, 1 H, C=CH), 7.20−7.36 (m, 5 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = −1.9, −0.9, 93.0, 111.8, 126.5, 127.0, 128.9, 132.7, 219.2, 236.8.

EI-MS: *m*/*z* 288 (M^+, 21), 260 ($M^+ - CO$, 15), 172 (51), 155 (36), 73 (Me_3Si^+, 100).

HRMS: *m*/*z* calcd $C_{16}H_{24}OSi_2$ 288.1366, found, 288.1376.

2,3,5-Tris(trimethylsilyl)-4-methylenecyclopent-2-en-1-one (24b)

To a stirred solution of allenylketene **1b** (0.080 g, 0.36 mmol) in Et_2O (5 mL) at r.t. was added Me_3SiCHN_2 (0.25 mL, 2.0 M in hexanes, 0.5 mmol), and the mixture was stirred overnight. Evaporation of the solvent and radial chromatography (5% EtOAc/hexanes) gave 0.092 g (83%) **24b** as a light yellow oil.

IR (neat): ν = 1675 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.02 (s, 9 H), 0.27 (s, 9 H), 0.35 (s, 9 H), 2.80 (t, 1 H, *J* = 1.0, 0.9 Hz, CH), 5.03 (d, 1 H, *J* = 0.7 Hz, C=CH), 5.04 (d, 1 H, *J* = 1 Hz, C=CH).

^{13}C NMR ($CDCl_3$): δ = −2.8, 1.2, 2.3, 49.7, 109.3, 153.7, 159.4, 178.5, 210.3.

EI-MS: *m*/*z* 310 (M^+, 54), 295 ($M^+ - CH_3$, 33), 207 (75), 73 (Me_3Si^+, 100).

HRMS m/z calcd for $C_{15}H_{30}OSi_3$ 310.1604, found 310.1607.

(*E*) and (*Z*)-2,3-Bis(trimethylsilyl)-4-(phenylmethylene)cyclopent-2-en-1-one [(*E*)- and (*Z*)-25a]

To a stirred solution of allenylketene **1a** (0.151 g, 0.50 mmol) in Et_2O (5 mL) at r.t. was added Me_3SiCHN_2 (0.6 mL, 2.0 M in hexanes, 1.2 mmol), and the mixture was stirred for 24 h at r.t. The solvent was evaporated and the crude product was dissolved in MeOH (10 mL), and silica gel (0.5 g) was added and the mixture stirred for 24 h, filtered, concentrated, and chromatographed (5% EtOAC/hexanes) to give (*E*)-**25a** (0.050 g, 32%), and (*Z*)-**25a** (0.053 g, 34%).

(*E*)-**25a**

IR (neat): ν = 1681 cm^{-1} (C=O).

^1H NMR ($CDCl_3$): δ = 0.32 [s, 9 H, $(CH_3)_3Si$], 0.46 [s, 9 H, $(CH_3)_3Si$], 3.18 (d, 2 H, *J* = 1.9 Hz, CH_2), 6.79 (t, 1 H, *J* = 1.6 Hz, C=CH), 7.26−7.39 (m, 5 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = 1.20, 2.40, 40.3, 127.5, 127.7, 128.6, 129.0, 137.0, 144.2, 156.2, 184.8, 210.2.

EI-MS: *m*/*z* = 314 (M^+, 68), 299 ($M^+ - CH_3$, 86), 198 (47), 73 (Me_3Si^+, 100).

HRMS: *m*/*z* calcd 314.1522, found 314.1537.

(*Z*)-**25a**

IR (neat): ν = 1679 cm^{-1} (C=O).

^1H NMR ($CDCl_3$): δ = −0.05 [s, 9 H, $(CH_3)_3Si$], 0.32 [s, 9 H, $(CH_3)_3Si$], 3.14 (d, 2 H, *J* = 1.1 Hz, CH_2), 6.63 (br s, 1 H, C=CH), 7.1−7.3 (m, 5 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = 0.7, 2.33, 45.8, 124.4, 127.6, 128.5, 129.6, 138.7, 144.7, 163.6, 184.8, 208.3.

EI-MS: *m*/*z* = 314 (M^+, 64), 299 ($M^+ - CH_3$, 82), 198 (37), 73 (Me_3Si^+, 100).

HRMS: *m*/*z* calcd for $C_{18}H_{26}OSi_2$ 314.1522, found 314.1520.

2,3-Bis(trimethylsilyl)-4-methylenecyclopent-2-en-1-one (25b)

A solution of **24b** (0.051 g, 0.16 mmol) in MeOH (10 mL) was stirred 24 h at 25°C with silica gel (0.5 g), filtered, evaporated, and chromatographed (10% EtOAc/hexanes) to give **25b** (33 mg, 86%).

IR (neat): ν = 1700 cm^{-1} (C=O).

^1H NMR ($CDCl_3$): δ = 0.28 (s, 9 H, $(CH_3)_3Si$), 0.37 [s, 9 H, $(CH_3)_3Si$], 2.90 (t, 1 H, *J* = 1.2, 1.5 Hz, CH), 5.25 (d, 1 H, *J* = 1.2 Hz, C=CH), 5.42 (d, 1 H, *J* = 1.6 Hz, C=CH).

^{13}C NMR ($CDCl_3$): δ = 1.1, 2.1, 41.1, 111.5, 150.1, 159.4, 181.8, 210.4.

EIMS: *m*/*z* = 238 (M^+, 15), 223 ($M^+ - CH_3$, 100), 195 (23), 155 (37), 122 (25), 73 (Me_3Si^+, 65).

HRMS: *m*/*z* calcd for $C_{12}H_{22}OSi_2$ 238.1209, found 238.1210.

(*E*)- and (*Z*)-2,3-Bis(trimethylsilyl)-4-(ethoxycarbonylmethylene)cyclopent-2-en-1-one [(*E*) and (*Z*)-25c]

Reaction of allenylketene **1c** (0.104 g, 0.35 mmol) with Me_3SiCHN_2 (0.2 mL, 2.0 M in hexanes, 0.4 mmol) as for **1a** gave after chromatography (7% EtOAc/hexanes) (*Z*)-**25c** (0.046 g, 42%) and (*E*)-**25c** (0.035 g, 32%).

(*Z*)-**25c**

IR (neat): ν = 1701 cm^{-1} (C=O).

^1H NMR ($CDCl_3$): δ = 0.28 [s, 9 H, $(CH_3)_3Si$], 0.30 [s, 9 H, $(CH_3)_3Si$], 1.30 (t, 3 H, *J* = 7.1 Hz, CH_3), 3.03 (d, 2 H, *J* = 1.3 Hz, CH_2), 4.19 (q, 2 H, *J* = 7.1 Hz, CH_2), 5.82 (t, 1 H, *J* = 1.3 Hz, C=CH).

^{13}C NMR ($CDCl_3$): δ = 0.18, 2.31, 14.3, 44.9, 60.4, 112.3, 158.5, 166.3, 167.2, 184.3, 205.6.

EI-MS: *m*/*z* 310 (M^+, 10), 295 ($M^+ - CH_3$, 38), 281 ($M^+ - C_2H_5$, 98), 267 (36), 193 (39), 73 (Me_3Si^+, 100).

HRMS: *m*/*z* calcd for $C_{15}H_{26}O_3Si_2$ 310.1421, found 310.1412.

(*E*)-**25c**

IR (neat): ν = 1700 cm^{-1} (C=O).

^1H NMR ($CDCl_3$): δ = 0.30 [s, 9 H, $(CH_3)_3Si$], 0.40 [s, 9 H, $(CH_3)_3Si$], 1.30 (t, 3 H, *J* = 7.1 Hz, CH_3), 3.32 (d, 2 H, *J* = 1.8 Hz,

CH_2), 4.20 (q, 2 H, J = 7.1 Hz, CH_2), 6.05 (t, 1 H, J = 1.8 Hz, C=CH).

^{13}C NMR ($CDCl_3$): δ = 0.83, 1.86, 14.3, 40.0, 60.3, 114.9, 158.8, 164.7, 166.4, 180.8, 209.1. EI-MS: m/z = 310 (M^+, 25), 295 ($M^+ - CH_3$, 38), 281 ($M^+ - C_2H_5$, 100), 267 (17), 193 (26), 73 (Me_3Si^+, 96).

HRMS: m/z calcd for $C_{15}H_{26}O_3Si_2$ 310.1421, found 310.1409.

NOE Study of Compound 25c

When the CH_2 protons of (*Z*)-**25c** at δ =3.03 were saturated a 15% increase was observed at the 5.82 ppm proton. When the CH_2 protons of (*E*)-**25c** at δ = 3.32 were saturated no NOE of the vinyl proton was observed.

Lactone 26a from Allenylketene 1a and Acetaldehyde

To allenylketene **1a** (60 mg, 0.20 mmol) and freshly distilled acetaldehyde (60 μL, 47 mg, 1.1 mmol) in CH_2Cl_2 (1 mL) was added BF_3•OEt_2 (10 μL, 12 mg, 0.08 mmol) and the mixture was stirred 1 h at 25 °C. Then Et_2O (10 mL) was added and the solution was washed with H_2O (3 × 5 mL), dried, and evaporated to give the allenyl β-lactone 2**6a** (62 mg, 89%) as a gum. ^{1}H NMR analysis showed that **26a** was a mixture of four diastereomers, assigned as two *cis* and two *trans* products in a ratio of 1:1:9:9.

IR ($CDCl_3$): ν = 1912 (C=C=O), 1796 cm^{-1} (β-lactone).

Major (*trans*) isomers: ^{1}H NMR ($CDCl_3$): δ = 0.14 [s, 9 H, $(CH_3)_3Si$], 0.21 [s, 9 H, $(CH_3)_3Si$], 0.26 [s, 9 H, $(CH_3)_3Si$], 0.28 [s, 9 H, $(CH_3)_3Si$], 1.41 (d, 3 H, J = 6.0 Hz, CH_3), 1.50 (d, 3 H, J = 6.4 Hz, CH_3), 4.51 (q, 1 H, J = 6.4 Hz, OCH), 4.54 (q, 1 H, J = 6.0 Hz, OCH), 5.99 (s, 2 H, 2 × C=CH), 7.15−7.33 (m, 10 H, 2 × C_6H_5).

Minor isomers (*cis* products): ^{1}H NMR ($CDCl_3$): δ = 0.23 [s, 9 H, $(CH_3)_3Si$], 0.24 [s, 9 H, $(CH_3)_3Si$], 0.25 [s, 9 H, $(CH_3)_3Si$], 0.27 [s, 9 H, $(CH_3)_3Si$], 1.56 (d, 3 H, J = 6.8 Hz, CH_3), 1.61 (d, 3 H, J = 6.8 Hz, CH_3), 4.62 (q, 1 H, J = 6.8 Hz, OCH), 4.67 (q, 1 H, J = 6.8 Hz, OCH), 6.04 (s, 2 H, 2 × C=CH), 7.15−7.33 (m, 10, 2 × C_6H_5).

Lactone 26b from Allenylketene 1b and Acetaldehyde

Allenylketene **1b** (55 mg, 0.24 mmol) reacted with acetaldehyde (60 μL, 47 mg, 1.1 mmol) as for **1a** to give allenyl β-lactone **26b** (58 mg, 88%) as a light yellow oil. ^{1}H NMR analysis showed that **26b** was a mixture of *cis* and *trans* products in a ratio of 1:10.6.

IR ($CDCl_3$): ν = 1920 (C=C=C), 1796 cm^{-1} (β-lactone).

Major (*trans*) isomer: ^{1}H NMR ($CDCl_3$): δ = 0.18 [s, 9 H, $(CH_3)_3Si$], 0.21 [s, 9 H, $(CH_3)_3Si$], 1.44 (d, 3 H, J = 6.0 Hz, CH_3), 4.49 (d, 1 H, J = 11.4 Hz, C=CH), 4.45 (d, 1 H, J = 11.5 Hz, C=CH), 4.55 (q, 1 H, J = 6.0 Hz, OCH).

^{13}C NMR ($CDCl_3$): δ = −3.05, -0.25, 18.6, 55.4, 71.5, 74.3, 91.1, 172.1, 209.1.

Minor (*cis*) isomer: ^{1}H NMR ($CDCl_3$): δ = 0.19 [s, 9 H, $(CH_3)_3Si$], 0.25 [s, 9 H, $(CH_3)_3Si$], 1.61 (d, 3 H, J = 6.6 Hz, CH_3), allenic proton and methine group are covered by the signals of the major isomer.

^{13}C NMR ($CDCl_3$): δ = −0.96, −0.21, 18.3, 55.6, 71.6, 79.2, 94.2, 209.2, carbonyl carbon is covered by the carbonyl signal of the major isomer.

NOE Study of 26b

When the lactone Me_3Si group of (*E*)-**26b** was saturated, an 18% increase was observed at the ring CH proton. When the allenyl Me_3Si group of (*E*)-**26b** was saturated, no NOE of the methyl proton or ring CH proton was observed.

Lactone 26c from Allenylketene 1c and Acetaldehyde

Allenylketene **1c** (68 mg, 0.23 mmol), acetaldehyde (60 μL, 47 mg, 1.1 mmol), and BF_3•OEt_2 (10 μL, 12 mg, 0.08 mmol) were stirred for 1 h in CH_2Cl_2 (1 mL) similar to **1a**. Workup gave allenyl β-lactone **26c** (74 mg, 94%) as an oil. ^{1}H NMR analysis showed that **26c** was a mixture of four diastereomeric isomers, assigned as two *cis* and two *trans* isomers in an approximate ratio of 1:1:9:9. The ratio is approximate due to the interference of impurities.

IR ($CDCl_3$): ν = 1924 (C=C=C), 1803 (β-lactone), 1711 cm^{-1} (CO_2Et).

^{1}H NMR *trans* products: ($CDCl_3$): δ = 0.20 [s, 9 H, $(CH_3)_3Si$], 0.23 [s, 9 H, $(CH_3)_3Si$], 0.27 [s, 9 H, $(CH_3)_3Si$], 0.28 [s, 9 H, $(CH_3)_3Si$], 1.27 (2 t, 6 H, CH_3), 1.43 (d, 3 H, J = 6.2 Hz, CH_3), 1.56 (d, 3 H, J = 6.3 Hz, CH_3), 4.18 (m, 4 H, OCH_2), 4.57 (m, 2 H, OCH), 5.36 (s, 1 H, C=CH), 5.37 (s, 1 H, C=CH).

Ethyl (*Z*)-4,5-Bis(trimethylsilyl)hepta-2,3,5-trienoate [(*Z*)-27]

A solution of the mixed isomers of **26c** (24 mg, 0.07 mmol) in xylene (5 mL) was heated in an oil bath at 140 °C for 12 h. The solvent was evaporated and the residue was chromatographed on silica gel to afford **27** (16 mg, 74%) as an oil.

IR (neat): ν = 1920 (C=C=C), 1695 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$): δ = 0.08 [s, 9 H, $(CH_3)_3Si$], 0.17 [s, 9 H, $(CH_3)_3Si$], 1.25 (t, 3 H, CH_3, J = 7.2 Hz), 1.73 (d, 3 H, J = 6.6 Hz, CH_3), 4.15 (m, 2 H, CH_2), 5.21 (s, 1 H, C=CH), 5.87 (q, 1 H, J = 6.6 Hz, C=CH).

^{13}C NMR ($CDCl_3$): δ = −1.35, −0.69, 14.3, 17.2, 60.2, 80.7, 102.3, 134.2, 136.6, 168.1, 205.2.

EI-MS: m/z = 296 (M^+, 34), 178 (59), 147 (25), 105 (38), 73 (Me_3Si^+, 100).

HRMS. m/z calcd for $C_{15}H_{28}O_2Si_2$ 296.1628, found 296.1638.

Ethyl 3,4-Bis(trimethylsilyl)benzoate (28)

A solution of **26c** (43 mg, 0.13 mmol) in decahydronaphthalene (2 mL) was heated in an oil bath at 190 °C for 4 h. The reaction mixture was purified by chromatography on silica gel giving **28** (24 mg, 66%) as an oil.

IR (neat): ν = 1720 cm^{-1} (C = O).

^{1}H NMR ($CDCl_3$): δ = 0.38 [s, 9 H , $(CH_3)_3Si$), 0.39 (s, 9 H, TMS), 1.39 (t, 3 H, J = 7.0 Hz, CH_3), 4.38 (q, 2 H, J = 7.1 Hz, CH_2), 7.74 (d, 1 H, J = 7.7 Hz, C_6H_5), 7.94 (dd, 1 H, J = 1.8, 7.9 Hz, C_6H_5), 8.32 (d, 1 H, J = 1.8 Hz, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = 1.84, 1.88, 14.4, 60.9, 128.1, 129.1, 135.0, 135.4, 146.4, 152.2, 166.9. EI-MS: m/z 294 (M^+, 26), 279 (M+-CH_3, 33), 263 (29), 249 (32), 235 (22), 221 (M+- TMS, 25), 191 (26), 161 (47), 148 (43), 133 (44), 73 (Me_3Si^+, 100).

HRMS: m/z calcd for $C_{15}H_{26}O_2Si_2$ 294.1471, found 294.1475.

Pyrone 29 from Allenylketene 1c and Benzaldehyde

A solution of allenylketene **1c** (198 mg, 0.67 mmol) in CH_2Cl_2 (5 mL) with distilled benzaldehyde (70 μL, 73 mg, 0.69 mmol) and BF_3•OEt_2 (40 μL, 48 mg, 0.32 mmol) was stirred for 1 h at r.t. After the addition of Et_2O (50 mL), the solution was washed with H_2O (3 × 20 mL) and the organic layer was dried ($MgSO_4$), evaporated, and chromatographed to give **29** (117 mg, 43%)[14] as a white solid; mp 89−90°C.

IR ($CDCl_3$): ν = 1710 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$): δ = −0.08 [br s, 9 H, $(CH_3)_3Si$], 0.34 [s, 9 H, $(CH_3)_3Si$], 1.29 (t, 3 H, J = 7.2, CH_3), 4.19 (m, 2 H, OCH_2), 5.78 (s, 1 H, OCH), 5.87 (br s, 1 H, C=CH), 7.10−7.40 (m, 5 H, C6H5).

^{13}C NMR ($CDCl_3$): δ = 1.7, 2.0, 14.2, 60.7, 81.4, 119.0, 125.5, 128.2, 128.5, 135.7, 145.9, 153.0, 164.0, 165.5.

EI-MS: m/z = 402 (M^+, 4), 387 ($M^+ - CH_3$, 16), 373 ($M^+ - C_2H_5$, 47), 147 (31), 105 (24), 73 (Me_3Si^+, 100).

HRMS: *m/z* calcd for $C_{21}H_{30}O_4Si_2$ 402.1683, found 402.1672.

4-(Benzylidene)-2,3-bis(trimethylsilyl)-5,5,6,6-tetracyanocyclohex-2-en-1-one [(*Z*)-31a]

Allenylketene **1a** (101 mg, 0.34 mmol) was reacted with TCNE (52 mg, 0.41 mmol) as for **1c** (see below) to afford (*Z*)-**31a** (132 mg, 92%)[14] as a solid; mp 122−124 °C.

IR ($CDCl_3$): ν = 2250 (CN), 1693 cm^{-1} (C=O).

^1H NMR ($CDCl_3$): δ = 0.03 [s, 9 H, $(CH_3)_3Si$], 0.41 [s, 9 H, $(CH_3)_3Si$], 7.26−7.46 (m, 6 H, C=CH and C_6H_5).

^{13}C NMR ($CDCl_3$): δ = 1.12, 1.86, 48.6, 53.3, 106.9, 108.0, 108.3, 109.6, 124.2, 129.3, 130.6, 130.9, 133.3, 135.4, 155.4, 176.2, 179.2.

EI-MS: *m/z* = 428 (M^+, 7), 413 ($M^+ - CH_3$, 19) 385 (12), 246 (20), 227 (23), 147 (15), 73 (Me_3Si^+, 100).

HRMS: *m/z* calcd for $C_{23}H_{24}N_4OSi_2$ 428.1489, found 428.1484.

2,3-Bis(trimethylsilyl)-4-methylidene-5,5,6,6-tetracyanocyclohex-2-en-1-one (31b)

Allenylketene **1b** (70 mg, 0.31 mmol) reacted with TCNE (48 mg, 0.37 mmol) as for **1c** (see below) to give **31b** (116 mg, 95%) as a gum.

^1H NMR ($CDCl_3$): δ = 0.35 [s, 9 H, $(CH_3)_3Si$], 0.44 [s, 9 H, $(CH_3)_3Si$], 5.87 (d, 1 H, C=CH, *J* = 2.8 Hz), 5.33 (d, 1 H, C=CH, *J* = 2.7 Hz).

^{13}C NMR ($CDCl_3$): δ = 1.17, 2.02, 48.4, 51.6, 106.9, 108.4, 125.5, 132.2, 153.1, 172.6, 175.9.

EI-MS: *m/z* 352 (M^+, 2), 337 ($M^+ - CH_3$, 49) 385 (12), 246 (20), 227 (23), 147 (15), 73 (Me_3Si^+, 100).

HRMS: *m/z* calcd for $C_{17}H_{20}N_4OSi_2$ 352.1176, found 352.1161.

2,3-Bis(trimethylsilyl)-4-(ethoxycarbonylmethylidene)-5,5,6,6-tetracyanocyclohex-2-en-1-one [(*Z*)-31c]

A solution of allenylketene **1c** (64 mg, 0.22 mmol) in CH_2Cl_2 (10 mL) with TCNE (33.3 mg, 0.26 mmol) was stirred at r.t. for 8 h. The solvent was evaporated and the product was chromatographed to give (*Z*)-**31c** (80 mg, 87%) as a gum.

IR ($CDCl_3$): ν = 2265 (CN), 1720 cm^{-1} (C=O).

^1H NMR ($CDCl_3$): δ = 0.37 [s, 9 H, $(CH_3)_3Si$], 0.40 [s, 9 H, $(CH_3)_3Si$], 1.34 (t, 3 H, CH_3, *J* = 7.1 Hz), 3.45 (m, 2 H, OCH_2), 6.48 (s, 1 H, C=CH).

^{13}C NMR ($CDCl_3$): δ = 0.97, 2.06, 14.0, 47.1, 51.5, 62.4, 107.1, 107.6, 107.8, 109.2, 122.5, 139.9, 152.8, 163.3, 175.0, 177.4.

EI-MS: *m/z* = 424 (M^+, 2), 409 ($M^+ - CH_3$, 13) 381 (11), 353 (12), 296 (10), 165 (10), 73 (Me_3Si^+, 100).

HRMS: *m/z* calcd for $C_{20}H_{24}N_4O_3Si_2$ 424.1387, found 424.1399.

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