(d, J = 6 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 13.39 (q), 17.34 (t), 23.76 (t), 25.99 (t), 29.31 (q), 31.19 (q), 32.07 (t), 32.76 (s), 33.30 (d), 37.25 (q), 38.58 (d), 41.60 (t), 42.39 (t), 47.59 (d), 73.19 (s), 73.58 (t); mass spectrum m/e (relative intensity) 300 (M^+ - 18, 6), 285 (11), 205 (17), 189 (30), 163 (22), 137 (44), 121 (24), 109 (22), 95 (60), 81 (100); calcd for $C_{16}H_{28}O_3S$ (M^+ - 18) m/e 300.1759, found m/e 300.1748.

37: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.70-2.20 (m, 16 H), 0.88 (s, 3 H), 0.94 (m, 3 H), 1.26 (s, 3 H), 3.29 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 17.26 (t), 17.66 (q), 18.66 (t), 23.95 (t), 25.61 (t), 29.14 (q), 31.30 (q), 31.87 (t), 32.52 (s), 37.08 (d), 39.98 (d), 41.48 (t), 42.08 (t), 47.46 (d), 73.17 (s); mass spectrum m/e (relative intensity) 332 (M^+ - 18, 13), 317 (10), 205 (42), 163 (100), 135 (15), 123 (24), 109 (72), 95 (47), 81 (88), 71 (83); calcd for $C_{15}H_{25}I$ (M^+ - 18) m/e 332.1001, found 332.0984.

(+)-**9**: $[\alpha]_D$ = +17.7 ± 0.1°, $[\alpha]_{365}$ = +60.3 ± 0.1° (c = 1.2, $CHCl_3$) (lit.[4] $[\alpha]_{365}$ = +8° ($CHCl_3$)). The spectroscopic data of (+)-**9** were identical with those of (±)-**9**.

Acknowledgment. We would like to thank A. van Veldhuizen for recording ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra, and C. J. Teunis and H. Jongejan for mass spectral data and elemental analyses.

Abbreviations: NDC, nicotinium dichromate; Oxone, a mixture of $KHSO_5$, $KHSO_4$, and K_2SO_4 in the ratio of 2:1:1, respectively.

Registry No. (±)-**1**, 58844-48-7; (±)-**2**, 136391-44-1; (±)-**3**, 136391-49-6; (±)-**4**, 136391-47-4; (±)-**5**, 136734-22-0; (±)-**6**, 136777-50-9; (±)-**7**, 122674-22-0; (±)-**8**, 136734-23-1; (±)-**9**, 136734-24-2; (+)-**9**, 83378-02-3; (±)-**10**, 136734-25-3; (±)-**11**, 136734-26-4; (+)-**11**, 136734-27-5; (±)-**12**, 136734-28-6; (±)-**13**, 136631-02-2; (±)-**14**, 136631-03-3; (±)-**15**, 136631-04-4; (±)-**16**, 136631-05-5; (±)-(*E*)-**17a**, 136658-51-0; (±)-(*Z*)-**17a**, 136631-06-6; (±)-(*E*)-**17b**, 136631-07-7; (±)-(*Z*)-**17b**, 136631-08-8; (±)-**18a**, 136734-29-7; (±)-**18b**, 136734-30-0; (±)-**19a**, 136734-31-1; (±)-**19b**, 136734-32-2; (±)-(*E*)-**20**, 136631-09-9; (±)-(*Z*)-**20**, 136631-10-2; (±)-**21** (isomer 1), 136631-11-3; (±)-**21** (isomer 2), 136631-12-4; (±)-**22**, 136631-13-5; (±)-**23**, 136734-33-3; (±)-**24**, 136734-34-4; (±)-**25**, 136734-35-5; (±)-(*E*)-**26**, 136631-14-6; (±)-(*Z*)-**26**, 136631-15-7; (±)-**27**, 136734-36-6; (±)-**28**, 136734-37-7; **29**, 3466-64-6; **30**, 18172-87-7; **31**, 122421-95-8; **31** (epoxide, isomer 1), 136631-22-6; **31** (epoxide, isomer 2), 136734-39-9; **32**, 136631-16-8; **33**, 136631-17-9; **34**, 136631-18-0; **35**, 136631-19-1; **36**, 136631-20-4; **37**, 136631-21-5; (-)-α-santonin, 481-06-1.

Supplementary Material Available: NMR spectra (^{1}H and ^{13}C) for **5-12** and **25** (18 pages). Ordering information is given on any current masthead page.

E/Z Isomerization, Solvolysis, Addition, and Cycloaddition Reactions of (*E*)-*tert*-Butylketene Methyl *tert*-Butyldimethylsilyl Acetal

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In the presence of catalytic amounts of CF_3COCH_3 or CF_3COCF_3, the silyl ketene acetal *E*-**1** was isomerized into its *Z* isomer (*Z*/*E* ratio 90:10). For this novel *E*/*Z* isomerization a mechanism is proposed, in which addition and reelimination of the fluoro ketone, through a 1,4-dipolar intermediate operates. With the protic nucleophiles CH_3OH, CF_3CH_2OH, or PhOH, the ketene acetal *E*-**1** afforded the ortho esters **2** as addition products, while CH_3CO_2H, CF_3CO_2H, or H_2O led to methyl pivalate as the solvolysis product. This chemistry is readily explained through protonation of the ketene acetal *E*-**1** to generate the corresponding carbenium ion. At low temperature the reaction with TCNE gave the silylketene imine **3** as labile cycloadduct, which underwent on workup desilylation to give the TCNE-incorporated ester **6**; the latter eliminated hydrogen cyanide at room temperature to give the ene ester **7**. With MTAD the labile silyl ene product **4** was obtained initially, which underwent silyl migration to give N-silylated urazole **8**; final desilylation led to the stable urazole **9**. Also for the ene reactions of TCNE and MTAD with the silyl ketene acetal *E*-**1**, a 1,4-dipolar intermediate is proposed to intervene.

Introduction

The cycloaddition chemistry of electron-rich olefins, particularly enol ethers, has been extensively investigated, mainly with the cyclophile tetracyanoethylene (TCNE)[2] but to some extent also with 1,2,4-triazoline-3,5-diones (TAD).[3] In a recent series of papers Huisgen and Brückner[4] employed 2,2-bis(trifluoromethyl)ethylene-1,1-dicarbonitrile (BTF) as enophile and confirmed earlier studies with TCNE[5] that the [2 + 2] cycloadducts are produced in a stepwise mechanism with a 1,4-dipole as a bona fide intermediate. Kinetics, solvent effect, and trapping experiments were used as mechanistic tools to establish rigorously the intervention of such dipolar species in these cycloaddition reactions.

Silyl ketene acetals, which, because of their high reactivity, serve as valuable building blocks in organic synthesis,[6] have received comparatively little attention as cycloaddition partners with such reactive cyclophiles. For example, we showed[7] that such ketene acetals afford with singlet oxygen α-silylperoxy esters. In this photooxygenation, at low temperature first the labile dioxetanes were produced exclusively and stereoselectively. Subsequently, on warming the dioxetanes opened up to the corresponding 1,4-dipole, and silatropic migration afforded the α-silylperoxy ester as a final product. This sequence

(1) This work was assisted by Nana Novak as undergraduate research participant in the IAESTE program (Jugoslavia).

(2) Fatiadi, A. J. *Synthesis* **1986**, *4*, 249; **1987**, *9*, 749; **1987**, *11*, 959.

(3) (a) Cookson, R. C.; Gupe, S. S.; Stevens, I. D.; Watts, C. T. *Org. Synth.* **1971**, *51*, 121. (b) Adam, W.; DeLucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762.

(4) (a) Huisgen, R.; Brückner, R. *Tetrahedron Lett.* **1990**, *31*, 2553. (b) Brückner, R.; Huisgen, R. *Tetrahedron Lett.* **1990**, *31*, 2557, 2561.

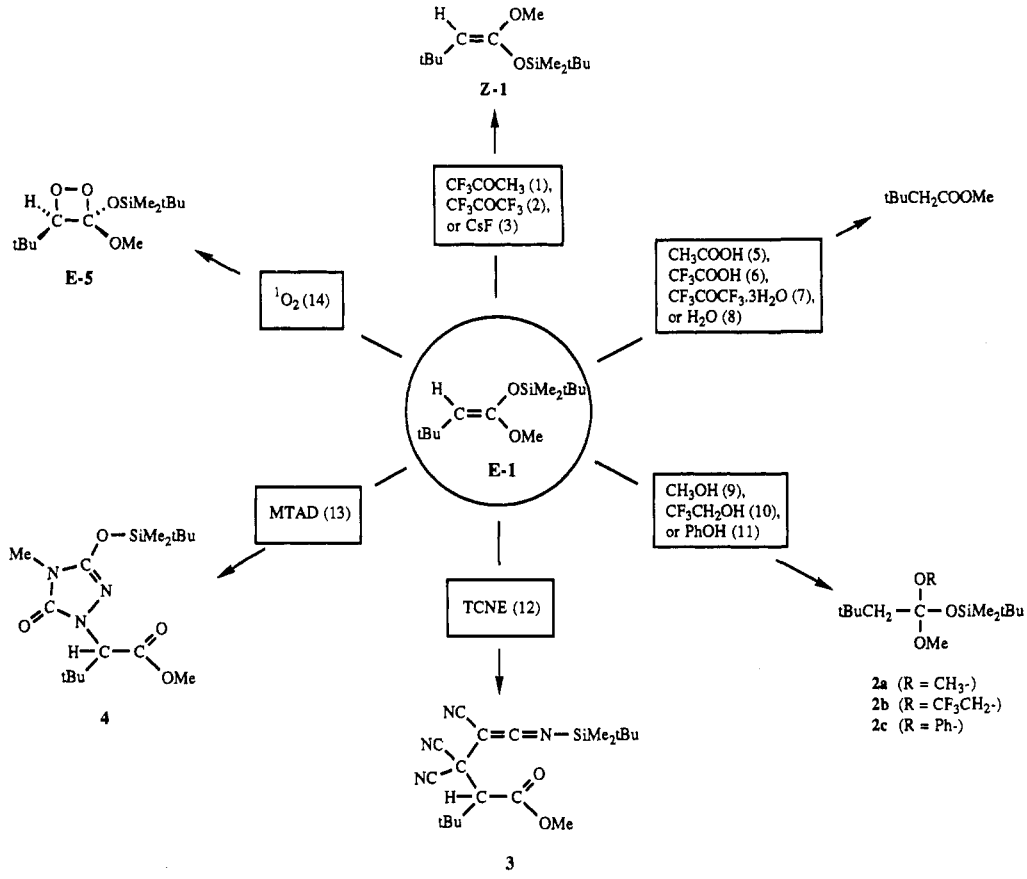
(5) (a) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117, 199. (b) Huisgen, R.; Steiner, G. *J. Am. Chem. Soc.* **1973**, *95*, 5054, 5055. (c) Steiner, G.; Huisgen, R. *J. Am. Chem. Soc.* **1973**, *95*, 5056. (d) Huisgen, R.; Schug, R. *J. Chem. Soc., Chem. Commun.* **1975**, 59. (e) Schug, R.; Huisgen, R. *J. Chem. Soc., Chem. Commun.* **1975**, 60.

(6) Brownbridge, P. *Synthesis* **1983**, 1.

(7) (a) Adam, W.; del Fierro, J.; Quiroz, F.; Yany, F. *J. Am. Chem. Soc.* **1980**, *102*, 2127. (b) Wang, X.-H. Dissertation, University of Würzburg, 1990. (c) Adam, W.; Wang, X.-H. *J. Org. Chem.* **1991**, *56*, 4737.

0022-3263/91/1956-7244$02.50/0

Scheme I. Reactions of (*E*)-*tert*-Butylketene Methyl *tert*-Butyldimethylsilyl Acetal (*E*-1)[a]



[a] Numbers in parentheses refer to entries in Table I.

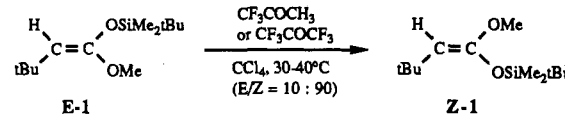
of events is contrary to TCNE and BTF as cyclophiles, in which first the 1,4-dipole is generated, followed by collapse into the observed cycloadduct.

In view of this mechanistic dichotomy in the cycloaddition behavior of $^1O_2$ versus TCNE and TAD toward electron-rich olefins, it was of interest to investigate the reaction of silyl ketene acetals with the TCNE and TAD cyclophiles. To confirm whether 1,4-dipoles intervene, the fluoro ketones CF_3COCH_3 and CF_3COCF_3 were employed as trapping agents. Thereby we uncovered an unprecedented *E*/*Z* isomerization of the silyl ketene acetal, namely (*E*)-*tert*-butylketene methyl *tert*-butyldimethylsilyl acetal (*E*-1). The preliminary results of the novel isomerization have already been reported;[7c] herewith we present the details of our study.

Results

As shown in the rosette (Scheme I) the (*E*)-*tert*-butylketene methyl *tert*-butyldimethylsilyl acetal (*E*-1) undergoes a number of unusual reactions, which include isomerizations (entries 1–3), solvolyses (entries 5–8), additions (entries 9–11), and cycloadditions (entries 12–14). The detailed results for the individual cases are given in Table I.

Isomerizations (Table I; entries 1–3). For this purpose the silyl ketene acetal *E*-1 was prepared from $tBuCH_2COOMe$ by using LDA to generate the enolate, followed by treatment with $ClSiMe_2tBu$ to give *E*-1 as the sole isomer. On exposure to catalytic amounts of CF_3COCH_3 (Table I, entry 1) or CF_3COCF_3 (Table I, entry 2) at 35 °C in CCl_4, the silyl ketene acetal *E*-1 was readily isomerized into its *Z* isomer. By ^1H NMR analysis of the reaction mixture a 90:10 mixture of the *Z* and *E* isomers was established (eq 1). Unfortunately, column chromatography on silica gel or Florisil and fractional distillation failed to separate the isomers. Their configurations were established by NOE experiments.[7b,c]

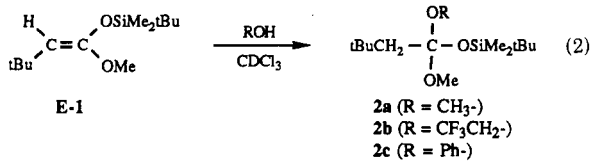


(1)

While catalytic amounts of CF_3COCH_3 and CF_3COCF_3 were effective in isomerizing *E*-1 into *Z*-1, acetone (Table I, entry 4) caused no isomerization even in 5 molar excess in CCl_4 at 35 °C for 48 h. The only other reagent that induced the *E*-1 into *Z*-1 interconversion was CsF (Table I, entry 3). Thus, when a solution of *E*-1 was treated with catalytic amounts (20 mol %) of CsF in $CDCl_3$/acetone-d_6 or $CDCl_3$/THF at 20 °C for 24 h, 75% of *E*-1 was converted into its *Z*-1 isomer.

Solvolyses (Table I; entries 5–8). A solution of *E*-1 in CCl_4 at 20 °C was allowed to react with catalytic amounts of CH_3COOH (20 mol %) and the *E*-1 was transformed immediately and completely to the corresponding methyl pivalate (Table I, entry 5). Similarly, catalytic amounts of CF_3COOH (Table I, entry 6) or $CF_3COCF_3·3H_2O$ (Table I, entry 7) gave complete hydrolysis. Also, a 5 molar excess of H_2O (Table I, entry 8) at 20 °C hydrolyzed the *E*-1 into the corresponding methyl pivalate within 48 h. In CD_3OD hydrolysis was complete in 3–4 h for *E*-1 and in 20 min for *Z*-1 (results not shown in Table I).

Additions (Table I; entries 9–11). The reaction of silyl ketene acetal *E*-1 with CH_3OH (200 mol %) in $CDCl_3$ at 50 °C led to the ortho ester **2a** (eq 2) in 70 % yield (Table I, entry 9). With CF_3CH_2OH in $CDCl_3$ at 35 °C the ortho ester **2b** (eq 2) was produced quantitatively (Table I, entry 10). Using a 0.5 molar excess of CF_3CH_2OH, the reaction



rate was increased substantially; within 6 h the addition was complete. Analogously, ***E*-1** reacted with phenol to give quantitatively the ortho ester product **2c** (eq 2) at –20 °C in $CDCl_3$ already within 5 min (Table I, entry 11). Since the ortho ester carbon is a chirality center, as expected, the NMR spectra of both addition products **2b,c** revealed the CH_2 group as an AB pattern (^1H NMR) and the two methyl groups of the $SiMe_2$ group possess different chemical shifts (^1H and ^{13}C NMR).

Cycloadditions (Table I; entries 12–14). The chemistry of ***E*-1** with TCNE (Table I, entry 12) is summarized in Scheme II. The initial product that was observed by ^1H NMR monitoring of the reaction mixture at –60 °C in $CDCl_3$ was the silylketene imine **3** (85% yield); also some 15% of unidentified product was obtained. In the ^{13}C NMR spectrum, the signal at δ 169.3 was assigned to the carbonyl carbon of the ester group and that at δ 146.8 to the ketene imine carbon. At elevated temperatures (in $CDCl_3$ at 20 °C within 3 d), **3** was converted into the desilylated hydrolysis product **6**. After recrystallization, the ester **6** was obtained in 59% yield. The structure of the ester **6** was determined by ^1H and ^{13}C NMR, IR, and elemental analysis. Attempted purification of ketene imine **3** by silica gel chromatography gave quantitatively the unsaturated ester **7** by HCN elimination. Ene ester **7** was fully characterized by ^1H and ^{13}C NMR, IR, and elemental analysis.

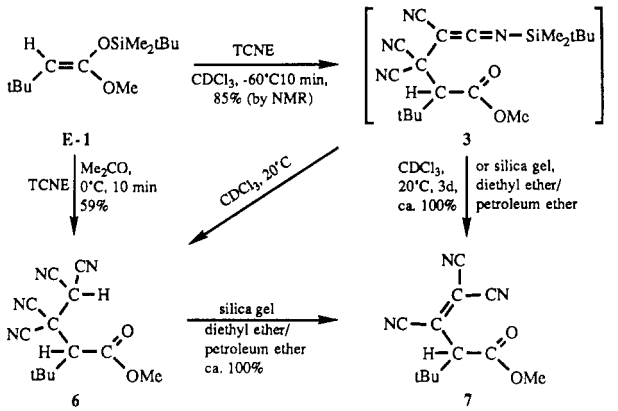
The transformations of the silyl ketene acetal ***E*-1** with MTAD (Table I, entry 13) are presented in Scheme III. At –60 °C in $CDCl_3$ immediate ^1H NMR analysis showed that as initial product the O-silylated urazole derivative **4** was formed. The ^{13}C NMR spectrum of **4** exhibits signals at δ 170.0 for the ester group and δ 156.8 and 159.2 for the C=N and C=O groups of the O-silylated urazole ring. On warmup to 20 °C, **4** underwent silyl migration to give the N-silylated urazole **8**, which reveals in the ^{13}C NMR its ester carbonyl carbon at δ 169.3 and the urazole carbonyl carbons at δ 148.1 and 153.4. The ^1H NMR spectrum of the O-silylated urazole **4** displays signals at δ 0.34 and 0.38 for the two methyl substituents of $SiMe_2$ group and δ 3.87 for the methinyl hydrogen atom, while for the N-silylated urazole **8** these signals are located at δ 0.31, 0.33, and 4.60.

The urazole **8** was desilylated into **9** by chromatography on silica gel. When CH_2Cl_2 was used as solvent for the reaction of ***E*-1** with MTAD at –60 °C, the urazole **9** was obtained as sole product after workup at 0 °C; complete characterization rested on ^1H and ^{13}C NMR, IR, MS, and elemental analysis. In the ^1H NMR spectra the CH group (δ 4.76) of **9** is close to that of **8** (δ 4.60), but quite different from that of **4** (δ 3.87).

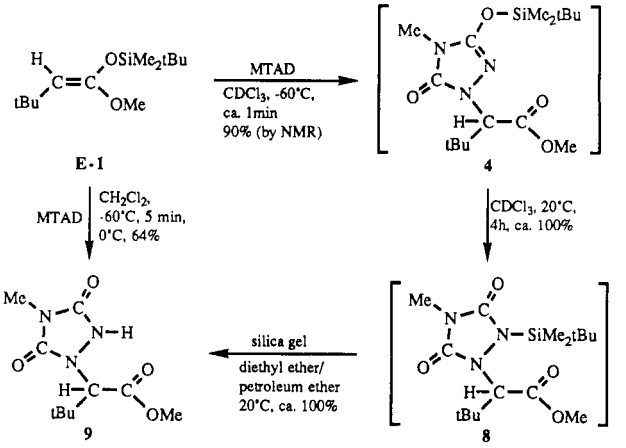
Cycloaddition of the silyl ketene acetals ***E*-1** or ***Z*-1** (as 90:10 *E*/*Z* mixture) with singlet oxygen (Table I, entry 14), generated by photosensitization with TPP at –20 °C in $CDCl_3$, gave quantitatively the dioxetanes ***E*-5** or ***Z*-5** with complete retention of the initial ketene acetal stereochemistry (eq 3).[7c] On warming to 20 °C, both dioxetanes ***E*-5** and ***Z*-5** gave essentially quantitatively the α-silylperoxy ester by silyl migration.[7c]

Miscellaneous Reactions (Table I, entries 15–19). When a catalytic amount of $HgBr_2/Me_3SiBr$ (30 mol %) was added to a solution of ***E*-1** in CCl_4 at 20 °C, after 24 h $tBuCH_2COOCH_3$ (30%) and unidentified products

Scheme II. Reactions of *E*-1 with TCNE



Scheme III. Reactions of *E*-1 with MTAD



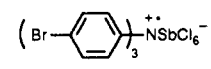
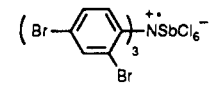
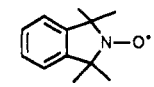
(70%) were detected, but no ***E*-1** into ***Z*-1** isomerization (Table I, entry 15) was observed. Treatment of a solution of ***E*-1** in CCl_4 with catalytic or equimolar amounts of $(n\text{-}Bu)_4N^+F^-$ at 0 °C caused complete consumption of ***E*-1** within 20 h, but only unidentified products were found (Table I, entry 16). Similarly, the triarylaminium radical cations [tris(4-bromophenyl)ammoniumyl]hexachloroantimonate (Magic Blue) and [tris(2,4-dibromophenyl)ammoniumyl]hexachloroantimonate (Magic Green) (Table I, entries 17 and 18) at 35 °C in CCl_4 led to complete consumption of ***E*-1** within 0.5 h, but besides 40% of methyl pivalate, only unidentified products (60%) were detected. The silyl ketene acetal ***E*-1** was inert to the nitroxyl radical 1,1,3,3-tetramethyl-1,3-dihydroisoindolin-2-yloxyl even at 35 °C for 24 h (Table I, entry 19).

Discussion

An unusual set of transformations has been observed for the silyl ketene acetal ***E*-1**, which includes *E*/*Z* isomerizations, solvolyses, additions, and ene type and [2 + 2] cycloadditions (Scheme I). Of these, the solvolyses and addition reactions can be readily reconciled in terms of straightforward carbenium ion chemistry (Scheme IV). Protonation of the ketene acetal ***E*-1** generates the cation **10**, which either is desilylated by the counterion A^- to produce methyl pivalate or is combined with the counterion A^- to afford the ortho esters **2**. As expected, water and the stronger acids, $CF_3COCF_3 \cdot 3H_2O$, CH_3CO_2H, and CF_3CO_2H, lead to hydrolysis by desilylation, while for the weaker acids, phenol, CF_3CH_2OH, and methanol, addition is preferred.

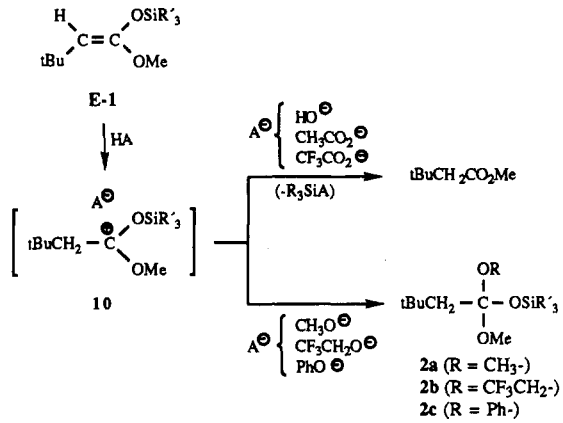
For the remaining reactions (ene type and [2 + 2] cycloadditions, isomerizations), despite the observed diversity

Table I. Reactions of (*E*)-*tert*-Butylketene Methyl *tert*-Butyldimethylsilyl Acetal (*E*-1)

		reaction conditions					
entry	reagent	ratio[a]	solvent	temp (°C)	time (h)	product(s)	yield[b] (%)
1	CF_3COCH_3	0.2	CCl_4 or $CDCl_3$	30–40	3–4	*Z*-1	90[c]
2	CF_3COCF_3	0.2	CCl_4 or $CDCl_3$	30–40	3–4	*Z*-1	90[c]
3	CsF	0.2	$CDCl_3$/acetone-d_6 or $CDCl_3$/THF	20	24	*Z*-1	75[c]
4	CH_3COCH_3	5.0	CCl_4	35	48	no reaction	*d*
5	CH_3COOH	0.2	CCl_4	20	<0.1	$tBuCH_2COOMe$	100
6	CF_3COOH	0.2	CCl_4	20	<0.1	$tBuCH_2COOMe$	100
7	$CF_3COCF_3 \cdot 3H_2O$	0.2	CCl_4	20	<0.1	$tBuCH_2COOMe$	100
8	H_2O	5.0	CCl_4	20	48	$tBuCH_2COOMe$	100
9	CH_3OH	2.0	$CDCl_3$	50	8	**2a** $tBuCH_2COOMe$	70 30
10	CF_3CH_2OH	1.5	$CDCl_3$	35	6	**2b**	97
11	C_6H_5OH	1.0	$CDCl_3$	−20	<0.1	**2c**	97
12	TCNE	1.0	$CDCl_3$	−60	0.2	**3**	85
13	MTAD	1.0	$CDCl_3$	−60	<0.1	**4**	90
14	$^1O_2$	*e*	CH_2Cl_2	−80	1	*E*-5	100
15	$HgBr_2/Me_3SiBr$	0.3	THF	20	24	$tBuCH_2COOMe$ unidentified products	30 70
16	$(n\text{-}Bu)_4N^+F^-$	0.2–1.0	CCl_4	0	20	unidentified products	90
17		0.2–1.0	CCl_4	20	0.5	$tBuCH_2COOMe$ unidentified products	40 60
18		0.2–1.0	CCl_4	20	0.5	$tBuCH_2COOMe$ unidentified products	40 60
19		0.2–1.0	CCl_4	35	24	no reaction	*d*

[a] Molar ratio of reagent to substrate *E*-1; ca. 0.2 mmol of *E*-1 was used. [b] Product yields (by ^1H NMR) refer to crude reaction mixtures; when several products were observed, the relative yields normalized to 100% are reported; error ca. 5% of the stated values; consumption of *E*-1 was in most cases complete. [c] *Z*/*E* ratio is 90:10 for entries 1 and 2 and 75:25 for entry 3. [d] *E*-1 quantitatively recovered. [e] Excess $^1O_2$ produced by tetraphenylporphine photosensitization.

Scheme IV. Mechanism of the Hydrolysis and Addition Reactions of *E*-1 with Protic Reagents

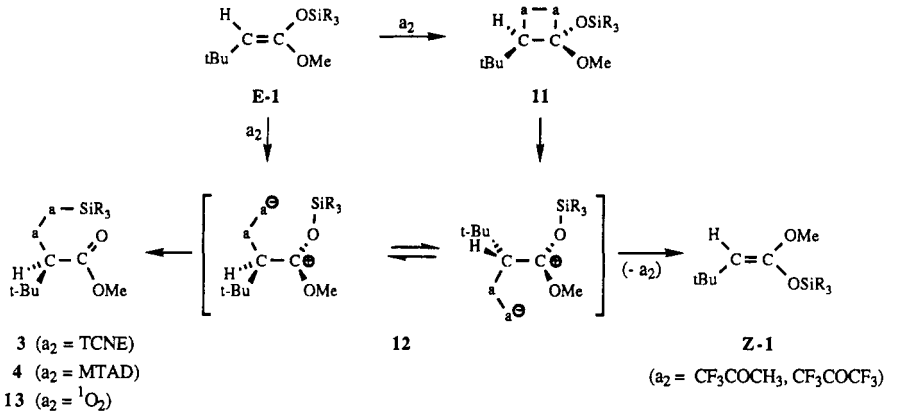


in chemical behavior, we propose that one common mechanism operates to rationalize these transformations, namely the intervention of 1,4-dipolar intermediates **12** (Scheme V). Depending on the enophile, the 1,4-dipole **12** may be formed directly (TCNE, MTAD)[4,5] from the ketene acetal *E*-1 or the [2 + 2] cycloadduct **11** ($^1O_2$) serves as precursor. For $^1O_2$ we have previously[7b,c] detected by NMR spectroscopy the 1,2-dioxetane *E*-5 as the exclusive product at −80 °C and shown that at the elevated temperature (20 °C) it rearranged into the α-silylperoxy ester **13**. In the presence of acetaldehyde during the rearrangement of the dioxetane *E*-5 into peroxy ester **13**, the 1,4-dipol **12** could be trapped in the form of the expected 1,2,4-trioxane; but such trapping was not observed during the cycloaddition between *E*-1 and $^1O_2$ to give the dioxetane **5**. Thus, for $^1O_2$ as enophile the sequence of events is *E*-1 → *E*-5 → **12** and not *E*-1 → **12** → *E*-5 (Scheme V).

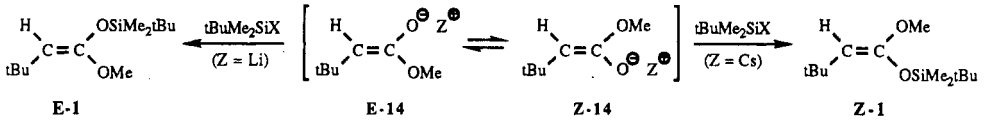
Although it was established[4,5] that for enol ethers the reaction with TCNE led to the [2 + 2] cycloadduct through a 1,4-dipole (trapping by methanol), for the ketene acetal *E*-1 neither with TCNE nor MTAD could we detect such [2 + 2] cycloaddition products by NMR monitoring even at −60 °C; only the ene products **3** and **4** were observed. Presumably silyl group migration is more facile than cyclization. Attempts to trap the 1,4-dipole **12** derived from TCNE and *E*-1 with methanol led exclusively to the methyl pivalate, although the silyl ketene acetal *E*-1 is stable toward methanolysis under the employed reaction conditions. TCNE and methanol afford the addition product 2-methoxy-1,1,2,2-tetracyanoethane, a strong carbon acid,[4b] which hydrolyses the acid-labile *E*-1 to the methyl pivalate. Unfortunately, buffering by amines (DABCO, dimethylaniline or pyridine) to avoid these complications in the trapping experiment was not possible because TCNE reacts instantly with these bases to give highly colored solutions.

Analogous to the enol ether and TCNE cycloaddition, we postulate that the 1,4-dipole **12** is also formed directly in the reaction of the enophiles TCNE and MTAD with ketene acetal *E*-1, but silyl migration to the ene products **3** and **4** dominates over cyclization to the corresponding [2 + 2] adducts **12** (Scheme V). Preferred migration of the silyl group to the nitrogen versus carbon center in 1,4-dipole **12** for TCNE by generating initially the silyl ketene imine **3** is expected for the harder R_3Si electrophile (Scheme II). Desilylation into **6** and loss of hydrogen cyanide to give **7** are logical subsequent reactions on workup and silica gel chromatography. Similarly, for MTAD the oxygen versus nitrogen site is selected by leading initially to product **4** (Scheme V). Chromato-

Scheme V. Mechanism of the Cycloaddition Reactions of *E*-1 with Enophiles



Scheme VI. Stereoselectivity in the Silylation of Enolates *E*/*Z*-14



graphic workup generates the silylurazole 8 and subsequently the desilylated urazole 9.

Novel and surprising, however, is the *E* to *Z* isomerization of the silyl ketene acetal 1 by catalytic amounts of CF_3COCH_3 or CF_3COCF_3; with dry acetone, even as solvent, no reaction was observed. Again, as shown in Scheme V, we propose that the 1,4-dipole 12 intervenes, the latter with the negative charge localized on the oxygen atom of the fluoro ketone enophile. Rotation about the carbon–carbon bond in the 1,4-dipole 12 and ejection of the fluoro ketone regenerates the silyl ketene acetal, but as its *Z* diastereomer.

There exists no precedent in the literature for such a fluoro ketone catalyzed *E*/*Z* isomerization. What comes closest to this process is the report[8] that catalytic amounts of $HgBr_2/Me_3SiBr$ effect such isomerizations. In our case, this reagent gave with ketene acetal ***E*-1** ca. 30% methyl pivalate, and 70% unidentified products, but no ***Z*-1** isomer (Table I). Furthermore, that electron transfer as possible mode for *E*/*Z* isomerization was not responsible was demonstrated by the fact that the aminium radical cations Magic Blue and Green[9] caused predominant formation of intractable products and some methyl pivalate, but again no ***Z*-1** isomer (Table I, entries 17 and 18). Also free-radical chemistry appears not to be involved in the *E*/*Z* isomerization as illustrated by the fact that the silyl ketene acetal ***E*-1** was inert toward the nitroxyl radical in Table I (Table I, entry 19).

At first sight it is surprising that the fluoro ketones effect the isomerization of ***E*-1** to ***Z*-1** to generate finally a 10:90 *E*/*Z* mixture. On steric grounds the opposite would have been expected. To establish whether this ratio represents the equilibrium mixture would require pure ***Z*-1**. Unfortunately, all attempts to obtain the latter pure by distillation or silica gel chromatography failed.

In regard to this stereochemical preference, i.e. 100% ***E*-1** to be isomerized to a 10:90 mixture of ***E*-1** and ***Z*-1**, most revealing was the observation that catalytic amounts of cesium fluoride in $CDCl_3$/THF or $CDCl_3$/acetone-d_6 also caused isomerization (Table I). In fact, CsF under these conditions was the only other effective catalyst for *E*/*Z* isomerization besides the fluoro ketones. The question presents itself, why in the preparation of the ketene acetal 1 by silylation of the lithium enolate exclusively the *E* isomer was formed (an X-ray structure determination of a related silyl ketene acetal confirms this[10]), while in the CsF-catalyzed isomerization predominantly the *Z* isomer was produced? Both reactions must involve an enolate (Scheme VI), but the state of aggregation of the enolate/metal cation species 14, i.e. lithium versus cesium, presumably dictates the steric preference of the *tert*-butyl group toward the methoxy versus enolate oxygen site. Since lithium enolates are extensively aggregated,[11] while cesium enolates are relatively naked,[12] the equilibrium for the *E*/*Z* enolates lies for Li^+ exclusively on the side of the *E* isomer and for Cs^+ predominantly toward the *Z* isomer. This enolate equilibrium mixture is so to speak "frozen in" on silylation to give the ketene acetal ***E*-1** for the Li^+ and predominantly its ***Z*-1** isomer for the Cs^+ counterions.

Also the presence of HMPA (hexamethylphosphoramide) can express such *E*/*Z* preference. For example, the lithium enolate of methyl phenylacetate afforded on silylation with $tBuMe_2SiCl$ in THF (no HMPA) an *E*/*Z* ratio of 91:9 but in THF (23% HMPA) 16:84.[13] In this case the ethyl substituent does not interact sterically with the enolate oxygen site as effectively as the *tert*-butyl substituent in our lithium enolate 14, so that even in the presence of ca.2% HMPA on silylation exclusively ***E*-1** is produced.

In summary, we provide experimental evidence that the cycloaddition chemistry observed here in the reactions of the enophiles $^1O_2$, TCNE, MTAD, and CF_3COR with the silyl ketene acetal ***E*-1** proceeds through the 1,4-dipole 12 as common intermediate (Scheme V). Thus, either the ene products **3** (a_2 = TCNE), **4** (a_2 = MTAD), and **13** ($a_2 = {}^1O_2$) or the isomerized ketene acetal ***Z*-1** ($a_2 = CF_3COR$) is obtained (Scheme V). However, only for $^1O_2$ was also the [2 + 2] cycloadduct produced; in fact, at low temperature

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the dioxetane ***E*-5** was formed exclusively and completely stereoselectively.[7c] Thus, while for TCNE, MTAD, and CF_3COR the 1,4-dipoles **12** are produced directly,[4,5] for $^1O_2$ the dioxetane serves as precursor. This dichotomy in the behavior of enophiles toward silyl ketene acetals is undoubtedly of mechanistic interest, but the fact that such acetals can be conveniently *E*/*Z* isomerized by fluoro ketones is unprecedented and deserves further exploration for synthetic applications.

Experimental Section

Infrared (IR) spectra were measured on a Perkin-Elmer 1420 spectrometer. ^1H NMR spectra were obtained on a Hitachi-Perkin-Elmer R-24B (60 MHz) or a Bruker AC 200 (200 MHz) or AC 250 (250 MHz), and ^{13}C NMR spectra were obtained on a Bruker AC 200 (50 MHz) or AC 250 (63 MHz) spectrometer. Mass spectra were obtained with a Varian MAT CH 7 or with a Finnegan S 200 mass spectrometer. The elemental analysis were carried out by the Microanalytical Laboratory of the University of Würzburg.

(*Z*)-*tert*-Butylketene Methyl *tert*-Butyldimethylsilyl Acetal (*Z*-1). A solution of silyl ketene acetal ***E*-1** (2.20 g, 9.00 mmol), prepared as previously described,[7c] and CF_3COCH_3 (0.202 g, 1.80 mmol) in CCl_4 (10 mL) was heated at 35 °C, and the reaction progress was monitored by ^1H NMR. After about 3 h, 90% of ***E*-1** had been converted into the *Z* isomer, and the isomer composition did not change on further standing. Rota-evaporation (20 °C, 17 Torr) of the solvent and the CF_3COCH_3 gave a 10:90 mixture of ***E*/*Z*-1** isomers. Attempts to separate the isomers failed, since they decomposed during silica gel as well as Florisil column chromatography and fractional distillation. IR (CaF_2): ν 2966, 2910, 2870, 1670, 1474, 1360, 1238, 1160, 1100, 977, 952, 915 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 0.16 (s, 6 H, $SiMe_2$), 0.94 (s, 9 H, SitBu), 1.08 (s, 9 H, CtBu), 3.35 (s, 1 H, CH), 3.43 (s, 3 H, OMe). ^{13}C NMR (50 MHz, $CDCl_3$): δ −3.8 (q, $SiMe_2$), 18.2 (s, SitBu), 26.0 (q, SitBu), 29.5 (s, CtBu), 31.3 (q, CtBu), 54.5 (q, OMe), 85.1 (d, C-2), 155.9 (s, C-1).

When ***E*-1** (0.245 g, 1.00 mmol) was treated with hexafluoroacetone (0.0332 g, 0.200 mmol) in 2 mL of CCl_4 or $CDCl_3$ at 35 °C also a 10:90 mixture of ***E*/*Z*-1** was obtained. Treatment of ***E*-1** (0.0490 g, 0.200 mmol) with CsF (0.006 08 g, 0.0400 mmol) in a mixture of $CDCl_3$ and acetone-d_6 or $CDCl_3$ and THF (0.5 mL, 4:1) at 20 °C for 24 h led to a 25:75 mixture of ***E*/*Z*-1**. However, no isomerization of ***E*-1** (0.0490 g, 0.200 mmol) was observed with acetone (0.0580 g, 1.00 mmol) in 0.5 mL of CCl_4 at 35 °C.

1,1-Dimethoxy-1-[dimethyl(1,1-dimethylethyl)siloxy]-3,3-dimethylbutane (2a). A sample of silyl ketene acetal ***E*-1** (0.0730 g, 0.300 mmol) and methanol (0.0190 g, 0.600 mmol) in $CDCl_3$ (0.5 mL) was heated at 50 °C. The reaction progress was monitored by ^1H NMR. After ca. 8 h all ***E*-1** was consumed and the reaction mixture was submitted to spectral analysis. Ortho ester **2a** (ca. 70%) and methyl pivalate (ca. 30%) were characterized by their ^1H and ^{13}C NMR, IR and MS. On attempted purification by column chromatography the ortho ester **2a** decomposed. IR ($CDCl_3$): ν 3020, 2920, 2280, 1770, 1495, 1390, 1380, 1335, 1270, 1230, 1200, 1100, 1036, 995, 857 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 0.13 (s, 6 H, $SiMe_2$), 0.89 (s, 9 H, SitBu), 0.97 (s, 9 H, CtBu), 1.59 (s, 2 H, CH_2), 3.17 (s, 6 H, 2 OCH_3). ^{13}C NMR (63 MHz, $CDCl_3$): δ −2.5 (q, $SiMe_2$), 18.4 (s, SitBu), 26.3 (q, SitBu), 29.8 (s, CtBu), 31.0 (q, CtBu), 47.9 (t, CH_2), 48.6 (q, OCH_3), 114.5 (s, CO_3). MS (70 eV): *m*/*z* (rel intensity) 248 (1) [M^+], 245 (20), 219 (17), 205 (51), 145 (35), 99 (100), 89 (55), 83 (23), 75 (19), 73 (65), 59 (24), 57 (81).

1-(2,2,2-Trifluoroethoxy)-1-methoxy-1-[dimethyl(1,1-dimethylethyl)siloxy]-3,3-dimethylbutane (2b). A sample of silyl ketene acetal ***E*-1** (0.0490 g, 0.200 mmol) and CF_3CH_2OH (0.0300 g, 0.300 mmol) in CCl_4 (0.5 mL) was monitored by ^1H NMR on a Hitachi-Perkin-Elmer R-24B (60 MHz) spectrometer at ca. 35 °C. After 6 h all ***E*-1** was consumed and the reaction mixture was submitted to spectral analysis. Ortho ester **2b** (ca. 97%) was characterized by its ^1H and ^{13}C NMR, IR, and MS. On attempted purification by column chromatography, the orther ester **2b** decomposed. IR (CCl_4): ν 2958, 2900, 2860, 1461, 1409, 1361, 1280, 1245, 1165, 1090, 940 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 0.16 (s, 6 H, $SiMe_2$), 0.90 (s, 9 H, SitBu), 0.99 (s, 9 H, CtBu), 1.56 and 1.71 (AB, J = 17.5 Hz, 2 H, CH_2), 3.23 (s, 3 H, OCH_3), 3.79 (m, 2 H, CH_2CF_3). ^{13}C NMR (63 MHz, $CDCl_3$): δ −3.2 and −3.0 (2 q, $SiMe_2$), 18.3 (s, SitBu), 26.1 (q, SitBu), 29.9 (s, CtBu), 30.9 (q, CtBu), 48.2 (t, CH_2), 48.9 (q, OCH_3), 59.5 (q, J = 37.8 Hz, CH_2CF_3), 114.8 (s, CO_3), 124.3 (q, J = 277.2 Hz, CF_3). MS (70 eV): *m*/*z* (rel intensity) = 344 (1) [M^+], 329 (1) [$M^+ - CH_3$], 313 (7), 287 (16), 273 (29), 99 (59), 89 (42), 77 (27), 73 (76), 57 (100), 43 (17).

1-Methoxy-1-[dimethyl(1,1-dimethylethyl)siloxy]-1-phenoxy-3,3-dimethylbutane (2c). A solution of silyl ketene acetal ***E*-1** (0.0490 g, 0.200 mmol) and phenol (0.0190 g, 0.200 mmol) in $CDCl_3$ (0.5 mL) was monitored by ^1H (200 MHz) and ^{13}C (50 MHz) NMR directly in a Bruker AC 200 spectrometer at −20 °C. After ca. 5 min all ***E*-1** was consumed and ortho ester **2c** (ca. 97% yield) was detected. On attempted purification by column chromatography the orthoester **2c** decomposed. IR (CCl_4): ν 2960, 2860, 1740, 1595, 1492, 1364, 1353, 1313, 1230, 1090, 1020, 960, 930 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 0.21 (s, 3 H, SiMe), 0.25 (s, 3 H, SiMe), 0.93 (s, 9 H, SitBu), 1.01 (s, 9 H, CtBu), 1.54 and 1.95 (AB, J = 14 Hz, 2 H, CH_2), 3.35 (s, 3 H, OMe), 6.80–7.30 (m, 5 H, Ph). ^{13}C NMR (50 MHz, $CDCl_3$): δ −3.3 (q, SiMe), −2.3 (q, SiMe), 18.4 (s, SitBu), 26.2 (q, SitBu), 29.6 (s, CtBu), 31.0 (q, CtBu), 48.2 (t, CH_2), 49.0 (q, OCH_3), 115.4–129.1 (m, Ph), 154.0 (s, CO_3). MS (70 eV): *m*/*z* (rel intensity) 339 (1) [M^+], 324 (2) [$M^+ - CH_3$], 273 (21), 245 (29), 213 (18), 173 (16), 157 (26), 93 (70), 77 (76), 57 (100).

***N*-[Dimethyl(1,1-dimethylethyl)silyl]-2,3,3-tricyano-4-carbomethoxy-5,5-dimethylhex-1-enimine (3).** Under a nitrogen gas atmosphere a solution of TCNE (0.0380 g, 0.300 mmol) in dry $CDCl_3$ (0.5 mL) was introduced into a NMR tube and cooled to −60 °C with a dry ice bath. The consumption of the silyl ketene acetal ***E*-1** (0.0730 g, 0.300 mmol) was added and the reaction was monitored by ^1H NMR at −40 °C. After 10 min all ***E*-1** was consumed and the ketene imine **3** (85%) was detected by ^1H and ^{13}C NMR and IR spectra. Attempted purification of the ketene imine **3** by column chromatography led to decomposition. IR ($CDCl_3$): ν 2960, 2860, 2220, 2152, 1730, 1465, 1435, 1360, 1255, 1214, 1160, 850 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 0.41 (s, 6 H, $SiMe_2$), 0.99 (s, 9 H, SitBu), 1.23 (s, 9 H, CtBu), 3.00 (s, 1 H, CH), 3.76 (s, 3 H, OMe). ^{13}C NMR (50 MHz, $CDCl_3$): δ −5.0 (q, $SiMe_2$), 17.5 (s, SitBu), 24.8 (q, SitBu), 28.9 (q, CtBu), 33.8 [s, $C(CN)_2$], 34.3 (s, CtBu), 52.5 (d, CH), 60.3 (q, OMe), 111.9 (s, CCN), 113.8 (s, 2 CN), 114.2 (s, CN), 146.8 (s, C=N), 169.3 (s, C=O).

3,3,4,4-Tetracyano-2-(1,1-dimethylethyl)butanoic Acid Methyl Ester (6). A 100-mL, three-necked, round-bottomed flask, equipped with a magnetic stirring bar and a pressure-equalizing dropping funnel, was flushed with dry nitrogen gas. Under a nitrogen gas atmosphere a solution of the silyl ketene acetal ***E*-1** (0.489 g, 2.00 mmol) in dry acetone (2 mL) was introduced, and the flask was cooled with ice bath to 0 °C. A solution of TCNE (0.256 g, 2.00 mmol) in dry acetone (3 mL) was added dropwise, and the reaction mixture was stirred for 5–10 min. The solvent was removed by rotaevaporation (0–5 °C, 15 Torr), and the crude product was crystallized from $CHCl_3$ to give 0.305 g (59%) of ester **6**, colorless prisms, mp 98–100 °C. IR ($CDCl_3$): ν 2980, 2926, 2250, 1730, 1470, 1435, 1360, 1300, 1220, 1166 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.32 (s, 9 H, tBu), 3.13 (s, 1 H, CH), 3.85 (s, 3 H, OMe), 5.00 (s, 1 H, CH). ^{13}C NMR (50 MHz, $CDCl_3$): δ 28.9 (q, tBu), 32.9 (d, CH), 35.4 [s, $C(CN)_2$], 38.2 (s, tBu), 53.3 (d, CH), 57.5 (q, OMe), 107.0 (s, CN), 107.6 (s, CN), 109.8 (s, CN), 111.3 (s, CN), 168.7 (s, C=O). Anal. Calcd for $C_{13}H_{14}N_4O_2$(258.3): C, 60.45; H, 5.46; N, 21.70. Found: C, 60.58; H, 5.43; N, 21.69.

3,4,4-Tricyano-2-(1,1-dimethylethyl)-3-butenoic Acid Methyl Ester (7). The crude product **7** (0.101 g) was chromatographed on silica gel, by eluting with a 1:1 mixture of petroleum ether (bp 30–50 °C) and diethyl ether to give 0.0490 g (78%) of ene–ester **7**, colorless prisms, mp 89–91 °C (from $CHCl_3$). On standing at ca. 20 °C for 6 d, a sample of ketene imine **3** in $CDCl_3$ was converted quantitatively into ene–ester **7**. IR ($CDCl_3$): ν 2960, 2930, 2860, 2240, 2220, 1750, 1470, 1433, 1374, 1210, 1150, 1007 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.20 (s, 9 H, tBu), 3.77 (s, 1 H, CH), 3.83 (s, 3 H, OMe). ^{13}C NMR (50 MHz, $CDCl_3$): δ 28.2 (q, tBu), 37.9 (s, tBu), 53.2 (d, CH), 60.1 (q, OMe), 102.1 [s, $C(CN)_2$], 109.3 (s, CN), 109.4 (s, CN), 113.1 (s, CN), 144.0 [s,

C(CN)], 166.4 (s, C=O). Anal. Calcd for $C_{12}H_{13}N_3O_2$(231.3): C, 62.33; H, 5.67; N, 18.17. Found: C, 62.86; H, 5.82; N, 18.38.

2-[4-Methyl-3-[dimethyl(1,1-dimethylethyl)siloxy]-4,5-dihydro-5-oxo-1,2,4-triazol-1-yl]-3,3-dimethylbutanoic Acid Methyl Ester (4). Under a nitrogen gas atmosphere a solution of MTAD (0.0230 g, 0.200 mmol) in dry $CDCl_3$ (ca. 1 mL) was introduced into a dry NMR tube and cooled with a dry ice bath to −60 °C. Silyl ketene acetal ***E*-1** (0.0490 g, 0.200 mmol) was added, and the reaction progress was monitored by ^1H and ^{13}C NMR. After ca. 5 min all of ***E*-1** was converted into adduct **4** (ca. 90%), as determined by its ^1H and ^{13}C NMR and IR spectra. Attempted purification by silica gel chromatography led to decomposition. IR ($CDCl_3$): ν 2960, 2860, 2246, 1770, 1740, 1700, 1610, 1470, 1400, 1370, 1260, 1210, 850 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 0.34 (s, 3 H, SiMe), 0.38 (s, 3 H, SiMe), 0.89 (s, 9 H, SitBu), 1.21 (s, 9 H, CtBu), 3.04 (s, 3 H, NMe), 3.69 (s, 3 H, OMe), 3.87 (s, 1 H, CH). ^{13}C NMR (50 MHz, $CDCl_3$): δ −5.1 (q, SiMe), −3.6 (q, SiMe), 18.5 (s, SitBu), 25.3 (q, NMe), 26.0 (q, SitBu), 28.9 (q, CtBu), 34.7 (s, CtBu), 52.5 (q, OMe), 74.2 (d, CH), 156.8 (s, C=O), 159.2 (s, C=O), 170.0 (s, COO).

2-[4-Methyl-2-[dimethyl(1,1-dimethylethyl)silyl]-3,5-dioxo-1,2,4-triazolidin-1-yl]-3,3-dimethylbutanoic Acid Methyl Ester (8). A sample of adduct **4** was allowed to stand at 20 °C for 4 h. All of product **4** was converted into silylurazole **8**, which was characterized by ^1H and ^{13}C NMR and IR spectra. IR ($CDCl_3$): ν 2960, 2860, 2246, 1740, 1710, 1630, 1510, 1470, 1260, 1240, 900 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 0.31 (s, 3 H, SiMe), 0.33 (s, 3 H, SiMe), 0.96 (s, 9 H, SitBu), 1.10 (s, 9 H, CtBu), 3.09 (s, 3 H, NMe), 3.64 (s, 3 H, OMe), 4.60 (s, 1 H, CH). ^{13}C NMR (63 MHz, $CDCl_3$): δ −5.0 (q, SiMe), −4.9 (q, SiMe), 18.0 (s, SitBu), 25.5 (q, SitBu), 26.1 (q, NMe), 27.4 (q, tBu), 35.1 (s, tBu), 51.7 (q, OMe), 63.4 (d, CH), 148.1 (s, C=O), 153.4 (s, C=O), 169.3 (s, COO). On attempted purification by silica gel chromatography urazole **8** was desilylated into the urazole **9**. The spectral data of urazole **9** are given below.

2-(4-Methyl-3,5-dioxo-1,2,4-triazolidin-1-yl)-3,3-dimethylbutanoic Acid Methyl Ester (9). A 100-mL, three-necked, round-bottomed flask, equipped with a magnetic stirring bar and a pressure-equalizing dropping funnel, was flushed with dry nitrogen gas. Under a nitrogen gas atmosphere a solution of MTAD (0.228 g, 2.00 mmol) in CH_2Cl_2 (3 mL) was introduced, and the contents were cooled by means of a dry ice bath to −60 °C. A solution of silyl ketene acetal ***E*-1** (0.489 g, 2.00 mmol) in CH_2Cl_2 (2 mL) was added dropwise. After complete addition, a few minutes later the solvent was removed by rotaevaporation (0 °C, 15 Torr), and the residue was recrystallized from a 1:1 mixture of THF and petroleum ether (bp 30–50 °C) to result in 0.311 g (64%) of the desilylated urazole **9** as colorless needles, mp 146–148 °C. IR ($CDCl_3$): 3340, 2960, 2260, 2240, 1775, 1710, 1475, 1395, 1370, 1250, 1130 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 1.06 (s, 9 H, tBu), 3.08 (s, 3 H, NMe), 3.80 (s, 3 H, OMe), 4.76 (s, 1 H, CH), 8.04 (s, 1 H, NH). ^{13}C NMR (63 MHz, $CDCl_3$): δ 25.2 (q, NMe), 27.3 (q, tBu), 36.4 (s, tBu), 52.3 (q, OMe), 64.2 (d, CH), 152.7 (s, C=O), 154.9 (s, C=O), 170.3 (s, COO): MS (70 eV): *m/z* (rel intensity) 243 (16) [M^+], 187 (77), 155 (100), 128 (25), 116 (22), 101 (12), 85 (12), 69 (13), 57 (92), 41 (34). Anal. Calcd for $C_{10}H_{17}N_3O_4$(243.3): C, 49.37; H, 7.04; N, 17.27. Found: C, 49.27; H, 7.32; N, 17.56.

General Procedure for the Solvolysis and Miscellaneous Reactions of (*E*)-Butylketene Methyl *tert*-Butyldimethylsilyl Acetal (*E*-1). A solution of silyl ketene acetal ***E*-1** (0.20 mmol) and the reagent (0.04–0.20 mmol) in CCl_4 or $CDCl_3$ (0.5 mL) was introduced into a NMR tube, and the reaction progress was monitored by ^1H NMR.

***E*-1** (0.0490 g, 0.200 mmol) was treated with CH_3COOH (0.00240 g, 0.0400 mmol), CF_3COOH (0.00456 g, 0.0400 mmol), or $CF_3COCF_3 \cdot 3H_2O$ (0.00880 g, 0.0400 mmol) at 20 °C for 5 min, and $tBuCH_2COOMe$ was formed quantitatively.

When ***E*-1** (0.0490 g, 0.200 mmol) was treated with H_2O (0.0180 g, 1.00 mmol) at 20 °C, after 48 h the $tBuCH_2COOMe$ was detected in ca. 100% yield.

When ***E*-1** (0.0490 g, 0.200 mmol) was treated with CD_3OD (0.5 mL, as solvent) at 20 °C, after 3–4 h tBuCHDCOOMe was detected in ca. 100% yield.

A solution of ***E*-1** (0.0490 g, 0.200 mmol) in THF (0.5 mL) was treated with $HgBr_2$ (0.0216 g, 0.0600 mmol) and Me_3SiBr (0.009 20 g, 0.0600 mmol) at 20 °C for 24 h. Methyl pivalate (30%) and unidentified products (70%) were detected.

When ***E*-1** (0.0490 g, 0.200 mmol) was treated with $(n\text{-}Bu)_4N^+F^-$ (0.0522 g, 0.200 mmol) at 0 °C for 20 h, 90% of it was converted into unidentified products.

When ***E*-1** (0.049 g, 0.200 mmol) was treated with Magic Blue (0.0326 g, 0.0400 mmol) or Magic Green (0.042 g, 0.0400 mmol) at 20 °C, immediately the methyl pivalate (40%) and unidentified products (60%) were formed (Table I, entries 17 and 18).

When ***E*-1** (0.0490 g, 0.200 mmol) was treated with 1,1,3,3-tetramethyl-1,3-dihydroisoindolin-2-yloxyl (0.0380 g, 0.200 mmol) at 35 °C for 24 h no reaction was observed (Table I, entry 19).

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Registry No. (*E*)-**1**, 58367-56-9; (*Z*)-**1**, 58367-61-6; **2a**, 136947-00-7; **2b**, 136911-61-0; **2c**, 136911-62-1; **3**, 136911-63-2; **4**, 136911-66-5; **6**, 136911-64-3; **7**, 136911-65-4; **8**, 136911-67-6; **9**, 136911-68-7; TCNE, 670-54-2; MTAD, 13274-43-6; CF_3CH_2OH, 75-89-8; $tBuCH_2COOMe$, 10250-48-3; tBuCHDCOOMe, 136911-69-8; CF_3COMe, 421-50-1; CF_3COCF_3, 684-16-2; CsF, 13400-13-0; $(4\text{-}BrC_6H_4)_3N^{\bullet+}SbCl_6^-$, 24964-91-8; $(2,4\text{-}Br_2C_6H_3)_3N^{\bullet+}SbCl_6^-$, 58047-17-9; Me_2CO, 67-64-1; $MeCO_2H$, 64-19-7; CF_3CO_2H, 76-05-1; MeOH, 67-56-1; phenol, 108-95-2; methyl pivalate, 598-98-1; 1,1,3,3-tetramethyl-1,3-dihydroisoindolin-2-yloxyl, 80037-90-7.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of the compounds **2a**, **2b**, **2c**, **3**, **4**, and **8** (14 pages). Ordering information is given on any current masthead page.