oxidation with *m*-chloroperbenzoic acid according to the usual manner: bp 70–71 °C (1 mmHg); mp 18–19 °C; NMR ($CDCl_3$) δ 2.8 (s, 3 H), 1.9 (m, 14 H). Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.49; H, 9.74; N, 7.80.

Reaction of 2-Methylspiro[oxaziridine-3,2′-tricyclo-[3.3.1.1^{3,7}]decane] (3) with Nucleophilic Reagents. 3 (0.15 mmol) and 0.3 mmol of nucleophilic reagent were dissolved in 0.4 mL of freshly distilled deuteriochloroform and allowed to react at the appropriate temperature. Formation of products 4 and 6 in $CDCl_3$ solution was followed by monitoring IR absorptions at 1701 and 1665 cm^{-1}, respectively (the characteristic absorption bands of C═O and C═N). Starting material in the reaction solution was checked by NMR, using diphenylmethane as an internal standard.

Reaction of *cis*- and *trans*-2-Methyl-3-phenyloxaziridines (*cis*- and *trans*-7) with Nucleophilic Reagents. Reactions were carrried out as for **3**. *p*-Nitrobenzaldehyde (0.4 mmol) was added before the reaction began and the products, *N*-(*p*-nitrobenzylidene)methylamine (**9**) and *N*-benzylidenemethylamine (**6**), were measured by GC analysis, using *n*-$C_{16}H_{34}$ and *n*-$C_{12}H_{26}$ as internal standards.

Reaction of *cis*- and *trans*-2-Alkyl-3-phenyloxaziridines (*cis*- and *trans*-10) with Triphenylphosphine. The reaction procedure and product analysis were similar to the above description. *n*-$C_{13}H_{28}$ was used as internal standard for GC analysis of *N*-benzylidenebutylamine.

Reaction of 2-*tert*-Butyloxaziridine (13) with Nucleophilic Reagents. The reaction procedure was similar to that described for the reactions of *cis*- or *trans*-7 with nucleophilic reagents. The yield of *N*-methylenebutylamine was determined by NMR, using diphenylmethane as internal standard.

Acknowledgment. We wish to thank Dr. K. Fujimori for helpful discussions and a supply of phenylseleniums.

Registry No. 3, 54530-08-4; **4**, 700-58-3; **6**, 54530-06-2; *cis*-**7**, 39245-63-1; *trans*-**7**, 40264-03-7; **8**, 622-29-7; **9**, 877-80-5; *cis*-**10** (R = Et), 57527-56-7; *trans*-**10** (R = Et), 57527-57-8; *cis*-**10** (R = *i*-Pr), 72257-44-4; *trans*-**10** (R = I-Pr), 57527-58-9; *cis*-**10** (R = cyclohexyl), 75780-72-2; *trans*-**10** (R = cyclohexyl), 75768-08-0; *trans*-**10** (R = *t*-Bu), 3585-81-7; **11** (R = Et), 25105-58-2; **11** (R = *i*-Pr), 25105-60-6; **11** (R = cyclohexyl), 42974-61-8; **12** (R = Et), 6852-54-6; **12** (R = *i*-Pr), 6852-56-8; **12** (R = cyclohexyl), 2211-66-7; **12** (R = *t*-Bu), 6852-58-0; **13**, 16479-80-4; **14**, 13987-61-6; *p*-nitrobenzaldehyde, 555-16-8; Ph_3N, 603-34-9; Ph_3P, 603-35-0; Ph_3As, 603-32-7; Ph_2O, 101-84-8; Ph_2S, 139-66-2; Ph_2Se, 1132-39-4; PhSH, 108-98-5; PhSeH, 645-96-5; Et_2NH, 109-89-7; CH_3SCH_3, 75-18-3.

Reactions of Allylsilanes with 4-Substituted 1,2,4-Triazoline-3,5-diones

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The reaction between allyltrimethylsilane (1) and 4-phenyl-1,2,4-triazoline-3,5-dione (2) was studied, and the structures of three products were determined by using ^1H NMR, ^{13}C NMR, and mass spectra. The effects of solvent and temperature on the relative yields of products were studied, and a reaction mechanism involving an ionic intermediate was suggested. The mechanism of the reaction between diallyldimethylsilane (3) with triazolinediones was found to be quite similar to that of 1.

We have previously reported that triazolinediones undergo a variety of interesting reactions with alkenes. For example, 4-phenyl-1,2,4-triazoline-3,5-dione (**2**) reacts rapidly with enol ethers to generate a dipolar species, the existence of which was proven by its interception with alkyl ketones.[1] Compound **2** also reacts rapidly at 0 °C with styrene on a 2:1 molar basis, the reaction sequence being an initial Diels–Alder reaction followed by an ene reaction.[2]

Enol esters undergo reaction with **2** to generate an intermediate dipolar species, which disappears rapidly via an unusual dipolar rearrangement.[3] The existence and participation of the dipole was confirmed via an extensive kinetic study.[4]

β-Dicarbonyl compounds undergo rapid reaction with **2**, yielding both 1:1 and 1:2 adducts.[5] Kinetic studies support a reaction mechanism that involves a 1,4-dipolar intermediate, generated via reaction of **2** and the enol of the β-dicarbonyl compound.

Thus, the rapid reactions of **2** with a variety of structures opens up many potential uses of such compounds in synthesis. Kinetic investigations[6] have shown **2** to be one of the most powerful dienophiles known, being 10^3 times more reactive than tetracyanoethylene. It was first investigated as an enophile (eq 1) by Pasto and Chen.[7] More recent investigations of the ene reaction of **2** have shown it to be 3 × 10^4 times more reactive than conventional azo dicarboxylates.[8] We have recently reported on the structure and properties[9] of the ene reaction of **2** with a variety of substituted alkenes, as well as a systematic kinetic study

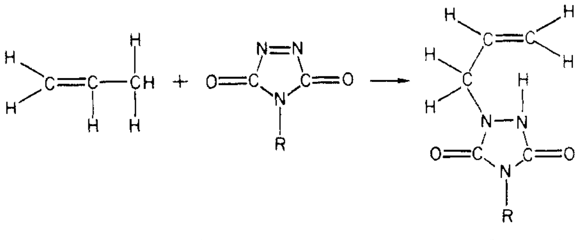

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Table I. ^{1}H NMR Data for Products of Reaction of 1 and 2

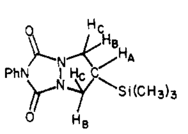
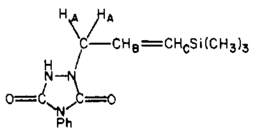
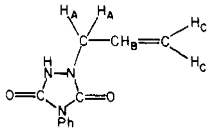
	chemical shift, ($CDCl_3$), δ		
			
proton	**4**	**5**	**6**
$SiCH_3$	0.10 (s, 9)	0.15 (s, 9)	
H_A	1.84 (tt, 1)	4.23 (d, 2)	4.17 (d, 2)
H_B	4.10 (dd, 2)	5.86 (dt, 1)	5.89 (ddt, 1)
H_C	3.41 (dd, 2)	6.24 (dt, 1)	5.27 (d, 2)
C_6H_5	7.46 (m, 5)	7.48 (s, 5)	7.47 (s, 5)
>NH		8.65 (br s, 1)	8.65 (br s, 1)
$J(H_A\text{-}H_B)$, Hz	7.7	6.0	
$J(H_A\text{-}H_C)$, Hz	10.9	1.5-2	
$J(H_B\text{-}H_C)$, Hz	11.3	14.5	

Table II. ^{13}C NMR Data for Products of Reaction of 1 and 2

	chemical shift, ppm		
carbon	4	5	6
>C=O	154.8	153.7, 152.3	153.4, 152.2
C=CSi		138.5	
C=CSi		136.4	
C=C			129.9
Ph >C—N	131.8	131.0	131.0
o-C—N	128.8	128.9	128.9
p-C—N	127.7	128.0	128.1
m-C—N	125.1	125.3	125.4
C=C			120.4
CN<	48.0	48.1	48.8
SiC<	30.1		
SiC	−3.4	−0.2	

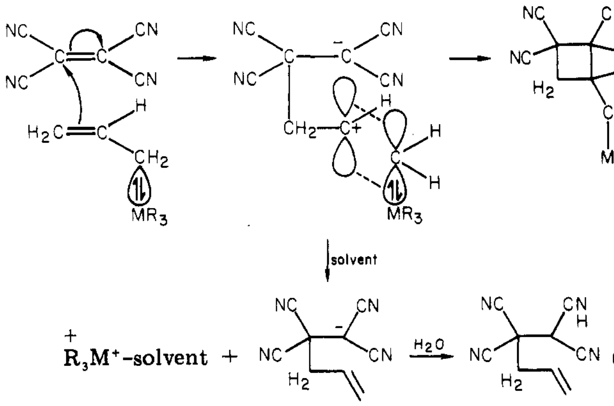
and effects of substituents on this rapid ene reaction.[10]

In the course of an attempt[11] to synthesize polymers by using the ene reaction[12] (eq 1) between bis(triazolinediones) and diallyl compounds, we found that reactions of $(CH_3)_3SiCH_2CH{=}CH_2$ (1) and $(CH_3)_2Si(CH_2CH{=}CH_2)_2$ (3) with triazolinediones gave products different from those expected from the usual ene reaction. In this study, we have isolated the reaction products and determined their structures. Furthermore, we have examined the effects of solvent and temperature on the reaction and proposed a mechanism for the reaction.

The high degree of reactivity of allyl–X bonds has been recognized for many years. Examples include halogens in S_N2' and S_N1 processes[13] and the ene reaction,[12] where X = H, which reflects the low bond-dissociation energy of the allylic hydrogen atom and resonance stabilization of the incipient allylic intermediate.[14]

An unusual reduction of an allylic C–N bond by phenylborane was observed by Butler and Statton.[15] More recent studies of this reaction, utilizing dideuteriophenylborane,[16] provided evidence in support of a concerted, facile elimination of propene, in which transposition of the allyl moiety occurred.

Following these early studies, the labile nature of the allyl–X bond for many examples of X have been reported. Hartman and Traylor[17] have shown that allyltriphenylstannane and 1 as well as other similar molecules undergo reaction with tetracyanoethylene to yield 4,4,5,5-tetracyano-1-pentene, a product in which MR_3 has been displaced (M = metal atom). These authors concluded that rates of reaction were roughly in agreement with σ^+ values of Y in $YCH{=}CH_2$ and suggested that the mechanism of the reaction involved σ–π conjugation, first proposed by Eaborn and Parker,[18] of the carbon–metal bonds; thus, their results showed that this conjugation is similar to η–π conjugation of lone-pair electrons, e.g., RO, NH_2, and NR_2, in both its magnitude and electrical effects. The course for the reaction was proposed (eq 2).



(2)

Schweig, Weidner, and Manuel[19] have considered the σ(Si–C)–π conjugation concept and have shown that the destabilization of the π MOs in allyl and benzyl compounds of element M of group 4B can be quantitatively predicted on the basis of the hyperconjugation M–C/π interaction model. The results of their quantitative analysis provide a definitive interpretation of M–C (M = C, Si, Ge, Sn) hyperconjugation which has recently been intensively studied.

Calas, Dunogues, Pillot, Biran, Pisciotti, and Arreguy[20] have shown that 1 undergoes reaction with acyl halides in presence of Lewis acids to generate allyl alkyl ketones, thus eliminating the Me_3Si moeity.

Hosima and Sakurai[21] have shown that 1 undergoes reaction with alkyl ketones in presence of $TiCl_4$ to yield

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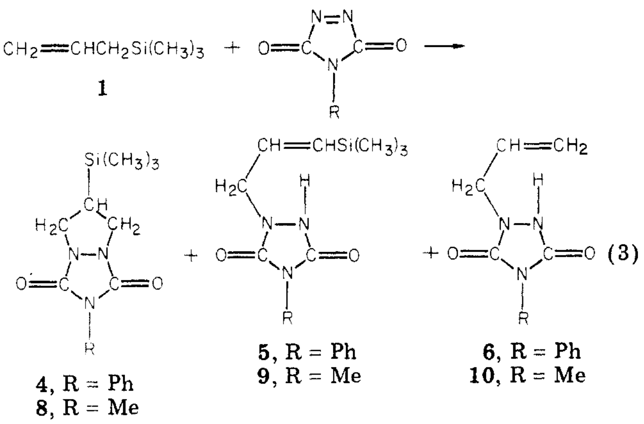
the corresponding allyldialkylcarbinols in which regiospecific transposition occurred in the allyl moeity.

Thus, some of the unusual structures obtained in this study are accounted for on the basis of these reports.

Results and Discussion

Structures of Products. Compound 1 was permitted to react with 2 in 1,2-dichloroethane. After removal of solvent, the ^{1}H NMR spectrum of the product was determined. Peaks which would not be expected from a usual ene reaction were observed at δ 3.4 and 5.3. The latter peak appeared to be assignable to vinyl protons. Thin-layer chromatography also suggested the presence of at least three different reaction products. Separation of the reaction products was effected by column chromatography (silica gel). Elution with chloroform containing 3–5% of methanol gave three products (4–6, eq 3). ^{1}H NMR data



1

4, R = Ph
8, R = Me

5, R = Ph
9, R = Me

6, R = Ph
10, R = Me

(3)

for these compounds are shown in Table I. The NMR spectrum of the crude mixture was a superimposition of the NMR spectra of 4–6, and the relative yields of 4–6 were found to be 11%, 71%, and 17%, respectively.

The NMR spectrum of 5 agreed with the structure expected from the usual ene reaction. On the other hand, 6 showed no SiCH$_3$ protons, and its melting point and NMR spectrum agreed completely with those of the ene product obtained by the reaction between propylene and 2.

Determination of the structure of 4 was most difficult. This compound, a 1:1 adduct, was eluted first in column chromatography and was insoluble in alkaline solution, suggesting that the compound has no NH proton on the urazole ring, which is known to be acidic.[9]

In the ^{13}C NMR spectrum of 4 (Table II), only one kind of carbonyl carbon was observed, while two peaks were observed in the cases of 5 and 6. Furthermore, 4 had only one carbon at relatively high field (30.1 ppm). The mass spectrum of 4 was very simple, and major peaks were those from $^+$Si(CH$_3$)$_3$ (m/e 73) and phenyl isocyanate (m/e 119). These results strongly support the five-membered-ring structure for 4.

Effect of Solvent and Temperature. As we have already reported,[9,10] the reaction of alkenes with triazolinediones invariably gave products which would be expected from the usual ene reaction. Solvent effects were small, and we concluded that the reaction proceeds via a concerted mechanism which is usual for such reactions.

However, the results of the reaction between 1 and 2 suggested a different reaction mechanism. That is, the reaction seems to be more ionic, and so stronger solvent effects would be expected.

The reaction of 1 and 2 was carried out in several solvents of different polarity, and the relative yields of 4–6 were determined by using ^{1}H NMR (Table III).

Table III. Solvent Effect on Relative Yields of Products in the Reaction[a] between 1 and 2

solvent	relative yield, % 4	5	6
benzene	18	73	9
1,2-dichloroethane	11	71	17
dichloromethane	10	72	18
ethyl acetate	9	71	20
acetone	7	44	48
acetone + H$_2$O[b]	6	21	73
acetonitrile	6	28	67
acetonitrile + H$_2$O[b]	4	12	84

[a] [2] = 0.11 mol/L; [1] = 0.12 mol/L; reaction temperature 25 °C. [b] 3.3 vol %.

Table IV. Solvent Effect on Relative Yields of Products in the Reaction[a] between 1 and 7

solvent	relative yield, % 8	9	10
benzene	8	89	3
1,2-dichloroethane	6	83	11
acetonitrile	4	52	44

[a] [4] = 0.11 mol/L; [1] = 0.12 mol/L; reaction temperature 25 °C.

Table V. Effect of Temperature on Relative Yields of Products in the Reaction[a] between 1 and 2

solvent	temp, °C	relative yield, % 4	5	6
benzene	25	18	73	9
	65	10	86	5
1,2-dichloroethane	−25[b]	24	36	40
	0	22	45	32
	25	11	71	17
acetonitrile	−25[b]	<2	13	85
	0[b]	4	17	79
	25	6	28	67
	65	7	41	51

[a] [2] = 0.11 mol/L; [1] = 0.12 mol/L. [b] [2] = 0.11 mol/L; [1] = 0.24 mol/L.

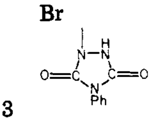
As expected, a remarkable solvent effect on the relative yields was observed. In the least polar solvent, benzene, the relative yields of 5 and 6 were 73% and 9%, respectively; while in the most polar solvent, acetonitrile, they were 28% and 67%. Solvents also affected the yield of 4 slightly. Addition of small amounts of water to polar solvents such as acetone or acetonitrile further increased the yield of 6.

In the case of 4-methyl-1,2,4-triazoline-3,5-dione (7), the relative yield of 9 was much higher than that in the case of 2. The relative yield of 9 in benzene was as high as 89%, and even in acetonitrile it was 52% (Table IV). However, the tendency of the solvent effect was similar to that observed for 2.

The effect of temperature on the relative yields of products was also observed (Table V). An increase in temperature resulted in an increase in the relative ratio of the normal ene reaction product. Even in acetonitrile, almost half of the reaction products were the normal ene product. On the other hand, the effect of temperature on the relative yield of 4 was different in polar solvents from that in nonpolar solvents. In nonpolar solvents, the yield of 4 increased obviously, while it decreased in acetonitrile.

Proposed Reaction Mechanism. In order to get further information regarding the reaction mechanism, the

Table VI. Relative Reactivity of Allyl Compounds[a] in the Reaction with 2

Y	rel reactivity[b]	Y	rel reactivity[b]
$Si(CH_3)_3$ (1)	1	Br	<0.003
$CH_2CH_2CH_3$	0.05		<0.003
$OCH_2CH_2CH_3$	0.01		
$OOCCH_3$	0.01		
CN	<0.003		
		Ph	0.02

[a] $YCH_2CH=CH_2$. [b] Based on reactivity of 1 for 1.

relative reactivity of several allyl compounds with 2 was compared by measuring the time required for the complete discharge of the 2 color (Table VI).

As shown in Table VI, the reactivity of 1 is much higher than that of the other allyl compounds. The reactivity of 1 is almost as high as that of 2-methyl-1-pentene, of which the second-order rate constant was found to be 0.2 L/mol/s.[10] Neither an electron-donating group (OC_3H_7) nor an electron-withdrawing group (CN) accelerates the reaction as much as the trimethylsilyl group.

On consideration of these results and the existence of vacant 3d orbitals of the silicon atom[22] and/or the σ(Si–C)π conjugation postulated earlier,[18] it seems quite reasonable to assume an interaction between silicon and nitrogen (11). Such an interaction would facilitate attack of the terminal carbon atom of 1 on the nitrogen atom of 2 and probably make the formation of a 1,4-dipole (12) possible. Once 12 is formed, the $^+Si(CH_3)_3$ group could easily move to nitrogen to form 13. As the Si–N bond is known to be very sensitive to moisture,[23] it can readily be explained why 6 is obtained instead of 13 (Scheme I).

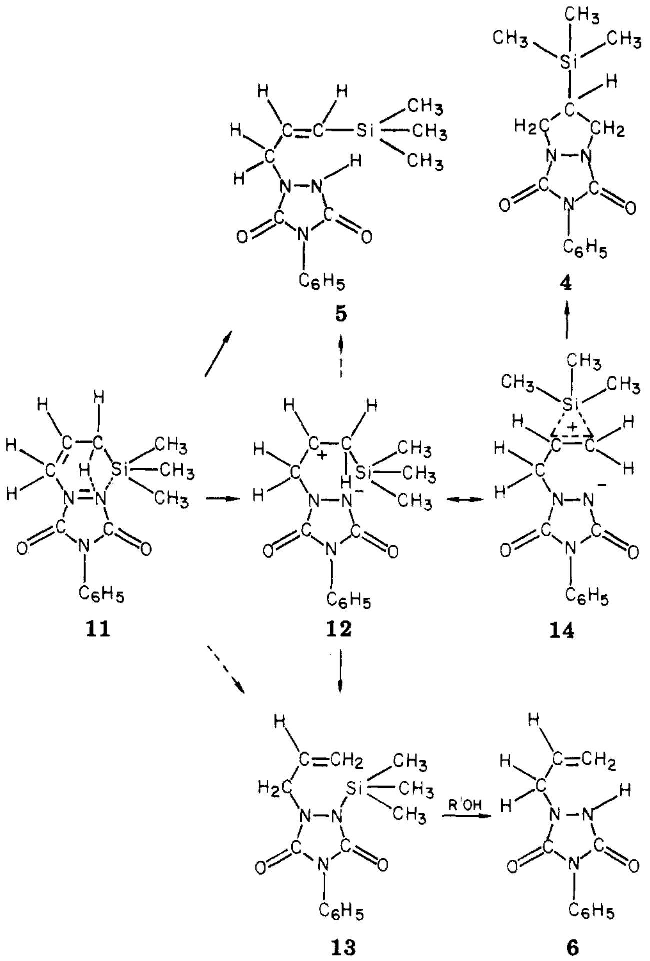
The formation of 4 also seems to relate to the ionic intermediate 12. However, direct transformation of 12 to 4 appears to be rather difficult, since it includes transformation of a secondary carbonium ion to a primary one. If we hypothesize a three-membered-ring intermediate (14), a cocontributor to the resonance hybrid along with 12, the formation of 4 from 12 ↔ 14 may be more readily explained.

In polar solvents, the ionic intermediate would be more stable and so formed more easily. At higher temperatures, this intermediate would be less stable, and the relative yields of 4 or 6 would therefore decrease. An intermediate like 12 ↔ 14 would be expected to be more stable at lower temperature, especially in nonpolar solvents. As a result, the relative yield of 4 increased about twice in dichloroethane by decreasing the temperature from +25 to −25 °C. Compound 5 might be formed via intermediate 12 ↔ 14, but direct formation from 11 seems to be more plausible.

Detection of 13 in the Reaction Mixture. In the earlier discussion, it was suggested that 6 was obtained as the result of hydrolysis of 13. In order to prove this point, we synthesized 13 by reaction of chlorotrimethylsilane with the ene product obtained from 2 and propylene. Compound 13 was dissolved in acetonitrile-d_3, and the ^{1}H NMR spectra were observed for this compound before and after addition of methanol-d_1. After the treatment by methanol-d_1, the NMR spectrum agreed with that of 6 except for the disappearance of the $SiCH_3$ protons attributed to 13 and appearance of $SiCH_3$ protons of Me_3SiOMe.

In order to observe the ^{1}H NMR spectrum of the products just after completion of the reaction, we mixed 2 dissolved in acetonitrile-d_3 and 1 in an NMR tube, and the NMR spectrum was measured. The spectrum appeared as a superimposition of 5 and 13. Furthermore, the spectrum after the addition of methanol-d_1 showed that 13 had completely changed to 6.

Scheme I



From these data, it is apparent that 13 was obtained as the initial reaction product which was then hydrolyzed during purification to give 6.

Reaction of 3 with 2. On the basis of the results described above, it is apparent that the proposed mechanism for the reaction between 2 and 1 is strongly supported by the results. However, at this point, it was not clear whether this mechanism would also apply to the reaction between bis(triazolinediones) and 3; the latter compound has two allyl groups and would be a useful comonomer in a copolymerization reaction with bis(triazolinediones).

In order to simplify the system, the 1:1 reaction between 3 and 7 was carried out in benzene, a solvent which had been shown to give the lowest yield of products such as 10. Actually, the products corresponding to 8 and 10 were formed in very low yields, and the usual 1:1 (15) and 1:2 (16) ene products were obtained as major products at a molar ratio of 2:1 (eq 4). This mixture was easily purified by column chromatography and pure 1:1 ene product 15 was obtained. Then, further reaction of 15 with an equimolar amount of 2 was undertaken in acetonitrile.

If the reaction analogous to that observed for 1 applies to this reaction, 18, 19, and 6 should be obtained as the major products after alcoholysis with methanol (eq 5 and 6). Indeed, 6 was isolated from the reaction mixture, although 19 was not obtained; however, its dimer was identified (see Experimental Section).

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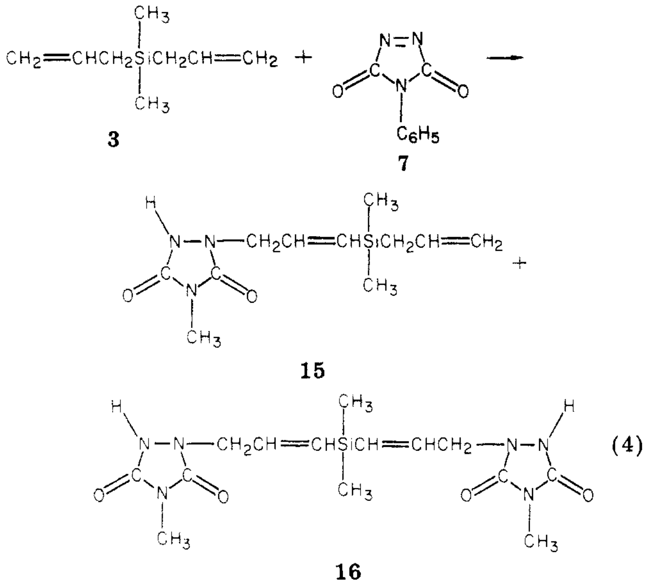

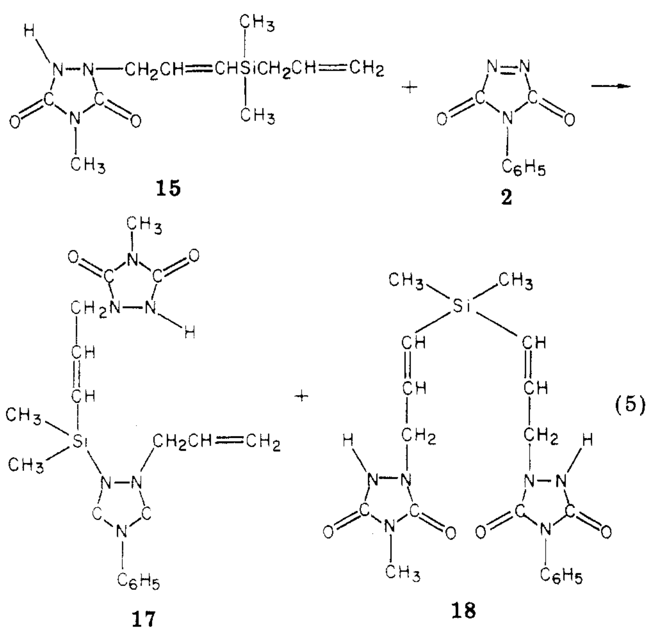

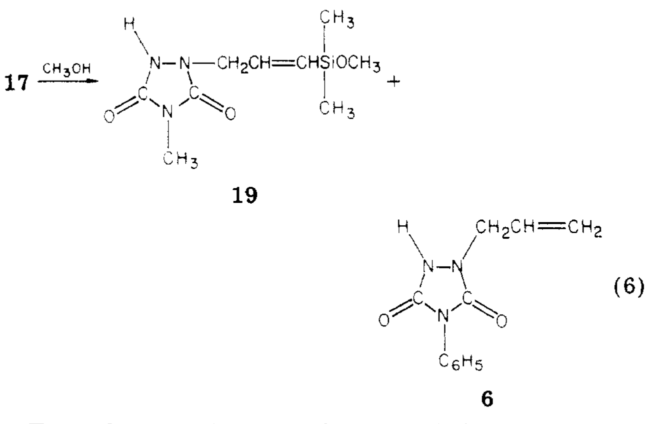

From these results, it can be concluded that the mechanism of the reaction between **3** and triazolinediones is quite similar to that of **1** and that it should be possible to synthesize high molecular weight polymers from **3** and bis(triazolinediones) if appropriate solvents and temperature ranges are chosen.

Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H NMR spectra were taken on a Varian A-60 spectrometer and ^{13}C NMR spectra on a Varian XL-100 FT spectrometer at 25.16 Hz. Mass spectral data were obtained by using a Hitachi Perkin-Elmer RMU mass spectrometer. Microanalyses were performed by Atlantic Microlab, Inc.

Allyltrimethylsilane (**1**) and diallyldimethylsilane (**3**) were purchased from PCR Inc.

Compounds **2** and **4** were prepared according to the method previously described.[9]

Reaction between 1 and 2. To 2.71 g (23.7 mmol) of **1** in 20 mL of 1,2-dichloroethane was added 3.50 g (20.0 mmol) of **2** in 75 mL of 1,2-dichloroethane dropwise in 1 h. The red color of **2** was completely discharged after 1 h, and a slightly yellow solution was obtained. Solvent and excess **1** were removed on a rotary evaporator to give a slightly yellow oil. The oil was dissolved in chloroform and purified by column chromatography (silica gel; eluents were chloroform and 3–5% methanol in chloroform). After the chromatography procedure was repeated, three pure compounds (**4**–**6**) were obtained. After recrystallization from benzene–hexanes, 0.57 g of **4**, 2.09 g of **5**, and 1.20 g of **6** were obtained. ^{1}H and ^{13}C NMR for these compounds are shown in Tables I and II.

Data for **4**: mp 126–127 °C; mass spectrum, *m/e* (relative intensity) 289 (M$^+$, 31), 119 (14), 91 (6), 73 (100), 59 (6), 45 (9), 43 (6), 32 (15), 28 (<5). Anal. Calcd for $C_{14}H_{19}O_2N_3Si$: C, 58.10; H, 6.62; N, 14.52. Found: C, 58.08; H, 6.62; N, 14.50.

Data for **5**: mp 81–82 °C; mass spectrum, *m/e* (relative intensity) 289 (M$^+$, 35), 274 (17), 234 (53), 127 (10), 119 (21), 113 (11), 100 (12), 91 (15), 85 (39), 83 (12), 73 (98), 64 (11), 59 (100), 45 (24), 43 (25), 28 (21). Anal. Calcd for $C_{14}H_{19}O_2N_3Si$: C, 58.10; H, 6.62; N, 14.52. Found: C, 58.17; H, 6.62; N, 14.51.

Data for **6**: mp 114–115 °C; mass spectrum, *m/e* (relative intensity) 217 (M$^+$, 63), 160 (12), 132 (14), 119 (30), 91 (15), 77 (15), 41 (100), 39 (16), 32 (14), 28 (98).

Effect of Solvent and Temperature. To **2** (1.71 mmol) dissolved in 15 mL of solvent kept at a constant temperature was added 0.30 mL (1.86 mmol) of **1** with stirring. After complete discharge of the color, the solvent and other volatile compounds were removed on a rotary evaporator. The residue was dissolved in methanol in order to hydrolyze **13** completely to **6**, and then the methanol was removed. The residue was dried in vacuo and dissolved in chloroform-*d* to observe the ^{1}H NMR. The relative yields of **4**–**6** were calculated by integrating the peaks at δ 3.4, 5.3, and 5.9.

1-(2-Propenyl)-2-(trimethylsilyl)-4-phenyl-1,2,4-triazoline-3,5-dione (13). To 0.46 g of 1-(2-propenyl)-4-phenyl-1,2,4-triazoline-3,5-dione (**6**), which was prepared by the reaction[9] between propylene and **2**, dissolved in 10 mL of benzene, were added 0.56 mL of triethylamine and 2.54 mL of chlorotrimethylsilane in a dry box. After 1.5 h, triethylamine hydrochloride was removed by filtration. Benzene was removed by the freeze–dry method. The residue was dissolved in benzene again, and a small amount of insoluble solids was removed. Benzene was removed by the same method to give a white solid residue. The solid residue was dissolved in acetonitrile-d_3, and the ^{1}H NMR of the solution was measured. To the solution, 30 μL of methanol-D$_1$ was added, and ^{1}H NMR was observed again. The results support the earlier conclusions (see Results and Discussion).

Reaction in Acetonitrile-d_3. A 60-mg sample of **2** was weighed into a NMR tube and dissolved in 0.6 mL of acetonitrile-d_3. A 48-μL sample of **1** was added to the solution, and the ^{1}H NMR was observed. A 30-μL sample of methanol-d_1 was added to the solution, and the NMR was observed again. The results support the conclusions outlined in the Results and Discussion.

1-[3-(Allyldimethylsilyl)prop-2-enyl]-4-methyl-1,2,4-triazoline-3,5-dione (15). To 1.63 g (14.4 mmol) of **7** in 100 mL benzene, 2.08 g (14.8 mmol) of **3** was added at once. After 30 min, the color of **7** was discharged completely, and benzene was removed on a rotary evaporator. The residue was dissolved in methanol, after which the methanol was removed to give a colorless oil. ^{1}H NMR of the oil showed that the main products were **15** and **16** (**15**/**16** ratio 2:1). After purification by column chromatography (silica gel; 3.3% ethanol in chloroform as eluent), pure **15** was obtained as a colorless oil: ^{1}H NMR (acetonitrile-d_3) δ 0.16 (s, 6), 1.73 (d, 2), 2.94 (5.3), 4.11 (d, 2), 4.85 (m, 2), 5.48 ~6.58 (m, 3), 7.97 (br s, 1). Anal. Calcd for $C_{11}H_{19}O_2N_3Si$: C, 52.14;

H, 7.56; N, 16.58. Found: C, 51.91; H, 7.63; N. 16.51.

Reaction of 15 with 2. Compound **15** (2.08 g, 8.2 mmol) and 1.43 g (8.2 mmol) of **2** were dissolved in 70 mL of acetonitrile. After 2 h, the red color disappeared, and 10 mL of methanol was added. Volatile compounds were removed on a rotary evaporator, and the residual solids were purified by column chromatography (silica gel; 3.3% ethanol in chloroform as eluent). Compound **6** (826 mg, 46% yield) was isolated as pure crystals. The residue was found to contain **18** and dimer of **19** by NMR analysis, both NCH_3 and NC_6H_5 proton signals being observed in **18** and the NC_6H_5 proton signals being absent in the disiloxane derived via hydrolysis of **19**.

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Registry No. 1, 762-72-1; **2**, 4233-33-4; **3**, 1113-12-8; **4**, 75782-33-1; **5**, 58263-25-5; **6**, 73970-92-0; **7**, 13274-43-6; **8**, 75782-34-2; **9**, 75782-35-3; **10**, 75782-36-4; **13**, 75782-37-5; **15**, 75782-38-6; **16**, 75782-39-7; **18**, 75790-44-2; **19**, 75781-13-4; propylene, 115-07-1.

Molecular Organization by Hydrogen Bonding: Juxtaposition of Remote Double Bonds for Photocyclization in a 2-Pyridone Dimer

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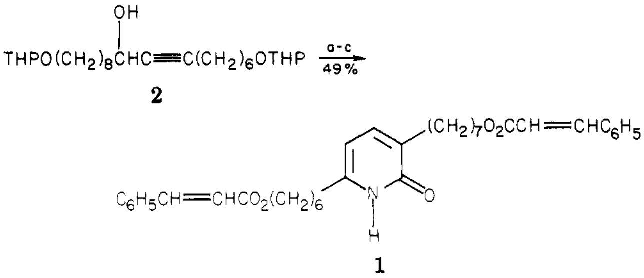
Irradiation of the hydrogen bonded dimer of 3-[7-(cinnamoyloxy)heptyl]-6-[6-(cinnamoyloxy)hexyl]-2-pyridone (**1**) provides the δ-truxinic acid ester **3** and the β-truxinic acid ester **4**, respectively. The photocyclization occurs via a 25-membered ring in yields which are significantly greater than those achieved in the absence of dimerization as shown by photolysis of a monomeric model system.

Study of hydrogen bonded substrates which have pendant groups suitably disposed for subsequent reaction is of interest because of the advantages which this facile entropic activation could provide over conventional methodology.[1,2] Ten years ago Breslow and Scholl used this approach to achieve 87.5% functionalization at the C-10 to C-15 positions in a hexadecyl chain by photolysis of *n*-hexadecyl hemisuccinate in the presence of benzophenone-4-carboxylic acid.[2] Our recent studies, which have shown that hydrogen-bonding associations of pyridones dramatically perturb the hydroxypyridine–pyridone equilibria in a variety of solvents,[3] suggest that the dimerization of 2-pyridones could provide an anchor which would bring otherwise distant groups into juxtaposition for reaction. In a severe test of this proposition we have investigated the photocyclization of the cinnamate moieties of 3-[7-(cinnamoyloxy)heptyl]-6-[6-(cinnamoyloxy)hexyl]-2-pyridone (**1**). Our results show that the δ- and β-truxinic acid esters, expected for interaction between double bonds which are separated by 25 atoms, are formed in the hydrogen bonded dimer of **1** in yields which are significantly greater than those expected from the corresponding monomer.[4]

Results

The elegant methodology of Overman and co-workers[5] was used to prepare **1** from 1,17-bis(2-tetrahydropyranyloxy)heptadec-7-yn-9-ol (**2**). A highly convergent synthesis of **2** from methyl 9-hydroxynonanoate and 8-(2-tetrahydropyranyloxy)-1-octyne is detailed in the Experimental Section. Vapor-pressure osmometry of **1** in benzene establishes that this material is completely dimerized at a 0.00516 M concentration in benzene. At the same concentration in chloroform, **1** is 35% dimerized, consistent with previous observations on related systems.[3]



$THPO(CH_2)_8CH(OH)C{\equiv}C(CH_2)_6OTHP \xrightarrow[49\%]{a-c}$

2

1

a, (1) NaH, Et_2O, (2) 1-cyanopyrrolidine, Et_2O; b, (1) xylene, 137 °C, (2) CH_3OH, $TsOH{\cdot}H_2O$; c, (1) $C_6H_5CH{=}CHCOCl$, pyridine, Δ, (2) H_2O, pyridine, Δ

Irradiation of 0.005 M **1** in benzene with light from a sunlamp for 36 h provides material which could be seen by ^1H NMR to be a mixture of **1** bearing (*Z*)- and (*E*)-

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[6] Efforts to prepare the more suitable *N*-methyl-2-pyridone model compound were not successful. Investigation of the ultraviolet spectrum of 3-(7-acetoxyheptyl)-6-(6-acetoxyhexyl)-2-pyridone prepared from **20** established the pyridone form to be the only detectable protomer.

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