

Ene Reactions of Allylic Derivatives of Silicon, Germanium, Tin and Lead with *N*-Phenyltriazolinedione: the Effect of Varying the Metal

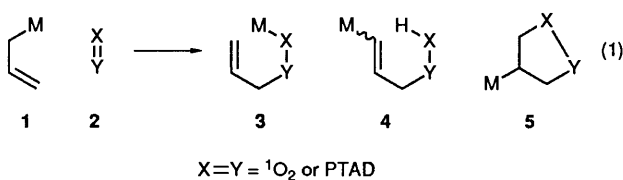
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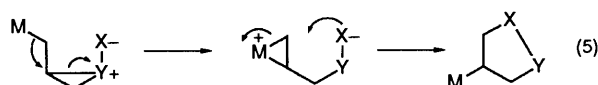
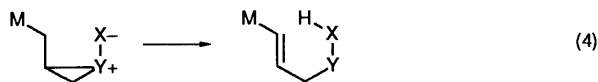
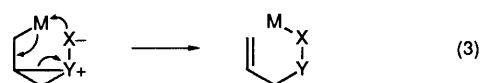
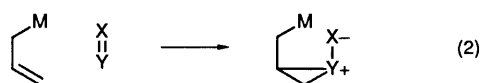
The compounds $\text{Ph}_3\text{MCH}_2\text{CH}=\text{CH}_2$ and $\text{Ph}_3\text{MCHCH}=\text{CH}(\text{CH}_2)_3$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ or Pb) have been treated with 4-phenyl-1,2,4-triazoline-3,5-dione, and the relative yields of the products of the M-ene reaction, of the H-ene reaction, and of the reaction involving cycloaddition with shift of the organometallic substituent, have been determined. The silicon compounds react principally by the H-ene process. The cycloaddition process is at a maximum (50% or 70%) with the germanium compounds, and the tin compounds show mainly the M-ene reaction, with some cycloaddition but no H-ene reaction. Triphenylprop-2-enylplumbane [and di(prop-2-enyl)mercury and phenyl(prop-2-enyl)mercury] show only the M-ene reaction.

In trimethyl(1,1-dimethylprop-2-enyl)silane, in which the H-ene reaction is blocked, only cycloaddition with shift of the silyl group is observed.

The use of a metal as a hydrogen-equivalent in ene reactions is important in organic synthesis because it provides the possibility of modulating the reactivity by varying the metal and its ligands.¹ Allylic derivatives of metals (**1**) have been shown to react with singlet oxygen²⁻⁵ or with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD)³⁻⁷ (**2**)* to give the products of M-ene reaction (**3**), of H-ene reaction (**4**), or of cycloaddition with shift of the metal (**5**) [eqn. (1)].



It has been suggested³ that these reactions proceed by mechanisms analogous to that which is broadly accepted for the ene reaction of hydrocarbons.⁸ The ene and enophile form a complex [eqn. (2)] which can then undergo pericyclic transfer of the metal [eqn. (3)], or of hydrogen [eqn. (4)] or a [1,2] shift of the metal with accompanying ring closure [eqn. (5)].²⁻⁶



We have investigated the effect of varying the ligands about the metal in the reaction of allylic tin(IV) compounds with singlet oxygen and with PTAD,⁴ and we found that as the tin

centre became more electropositive, the proportion of the M-ene reaction [reaction (3)] increased, and, with a suitable choice of ligands, this could be caused to be the exclusive reaction.

We now report a study of the effect of varying the metal within Group 14 (Si, Ge, Sn and Pb), keeping the non-ene ligands on the metal constant, as Ph_3 . So that the whole series could be studied with the same enophile, we have chosen to use PTAD rather than singlet oxygen, because the reactivity of the prop-2-enyl-silanes and -germanes towards singlet oxygen is often inconveniently low.

Results and Discussion

Triphenyl(prop-2-enyl)-silane (**6a**), -germane (**6b**), -stannane (**6c**), and -plumbane (**6d**) were prepared by treating a solution of prop-2-enyl bromide and the triphenylmetal chloride or bromide in THF with magnesium, and cyclohex-2-enyltriphenylsilane (**6e**), -germane (**6f**), and -stannane (**6g**) by metallating cyclohexene with $\text{BuLi}/\text{Bu}^+\text{OK}/\text{TMEDA}$ then treating the product with the appropriate triphenylmetal chloride. Despite a number of attempts, we were unable to prepare cyclohex-2-enyltriphenylplumbane by this method.

The propenyl- and cyclohexenyl-metallic compounds **6**, were mixed with an equimolar amount of PTAD in chloroform at room temperature, and the time needed for discharge of the red colour of the PTAD was noted. The products of the M-ene reaction (**7**), of the H-ene reaction (**8**), and of the cycloaddition process (**9**) [eqn. (6)] were identified in solution by ${}^1\text{H}$ NMR spectroscopy, on the basis of the data established in our study of the reaction of allylic tin compounds with PTAD and ${}^1\text{O}_2$.²⁻⁴ The products were then separated by column chromatography and characterised; the N-M group in the M-ene adducts **7** underwent hydrolysis during chromatography, and the corresponding 1-alkenyl-4-phenyl-1,2,4-triazolidine-3,5-dione was isolated. The rates of the reactions and the yields (NMR spectroscopy) of the three types of product are shown in Table 1 associated with eqn. (6).

The propenyl and cyclohexenyl derivatives of the same metal show a similar reactivity. When cyclohexene itself is mixed with PTAD, the colour persists for *ca.* 30 min, and the only detectable product is the 1-cyclohex-2-enyl-1,2,4-triazolidine-3,5-dione.

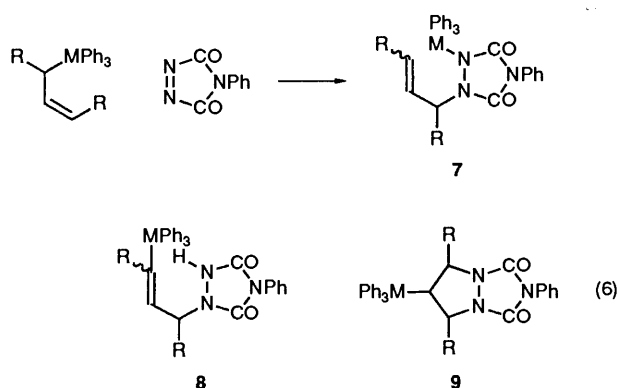
The presence of the triphenylsilyl group thus has little effect on the rates of these H-ene reactions, but the other metal substituents accelerate the reaction, and this reactivity increases in the series $\text{M} = \text{H} \approx \text{Si} < \text{Ge} < \text{Sn} < \text{Pb}$. This may be the

* IUPAC name: 4-phenyl-4*H*-1,2,4-triazole-3,5-dione.

Table 1 Products of the reaction of PTAD with allyl- and cyclohexenyl-metallic compounds in CHCl_3

Reactant	Reactant			Time/min	Products (%) ^a		
	M	R	R		M-ene 7	H-ene 8	Cycloaddition 9
At room temperature							
6a	Si	H	H	40	—	8a 100	—
6b	Ge	H	H	25	7b 20	8b 30	9b 50
6c	Sn	H	H	10	7c 55	—	9c 45
6d	Pb	H	H	1	7d 100	—	—
6e	Si	—	—	40	—	8e 90	9e 10
6f	Ge	—	—	25	7f 5	8f 25	9f 70
6g	Sn	—	—	10	7g 63	—	9g 37 ^b
At -40 °C							
6b	Ge	H	H		7b 10	8b 10	9b 80
6f	Ge	—	—		7f 0	8f 15	9f 85

^a By NMR spectroscopy. ^b In CH_2Cl_2 ; data from ref. 3.



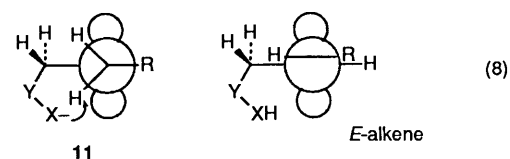
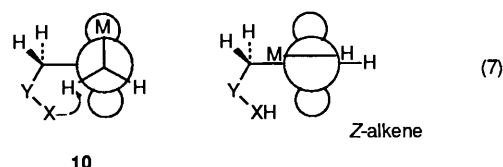
result of π - σ^* conjugation between the $\text{C}=\text{C}$ double bond and the $\text{C}-\text{M}$ bond, which enhances the reactivity of the double bond towards the electrophilic enophile [eqn. (2)].³ It is also likely that there is some interaction between the nucleophilic end of the enophile and the metal in the reaction intermediate which lowers the energy of the transition state through which it is formed.³

Triphenyl(prop-2-enyl)silane (**6a**) showed only the H-ene reaction to give the triazolidinedione **8a**. With the germane **6b**, the reaction is faster and the H-ene product **8b** drops to 30%; 20% of the total reaction gives the M-ene product **7b**, but the major product (50%) is **9b** from the cycloaddition reaction.

These H-ene reactions might in principal give either *E*- or *Z*-vinylmetallic compounds which can be distinguished by the magnitude of the NMR coupling constant between the *trans* or *cis* pair of vinylic protons. Trimethyl(prop-2-enyl)silane reacts with PTAD by the H-ene reaction to give only the *Z*-alkene (**6**) and with singlet oxygen to give 78% of *Z*- and 22% of *E*-alkene.⁹ Similarly we found that trimethyl(prop-2-enyl)stannane with PTAD or with singlet oxygen gave only the *Z*-alkene.³ In the present work, we find that triphenyl(prop-2-enyl)silane (**6a**) and triphenyl(prop-2-enyl)germane (**6b**) with PTAD again give the *Z*-alkenes **8a** and **8b**. In contrast, simple hydrocarbon enes usually give *E*-alkenes.⁹

As Shimizu has pointed out,⁹ this stereoselectivity can be accommodated within the model for the mechanism for the H-ene reaction which is illustrated in eqns. (2) and (4), though the importance of an intermediate is open to question.^{9,10} The $\text{C}-\text{M}$ bond, because of carbon-metal bond hyperconjugation, will tend to eclipse the *p*-orbital on C-2 in the open-chain canonical

form of the intermediate [which in the limit can lead to migration of the metal as in reaction (5)]; this imposes on the transition state the conformation shown in structure **10**, which leads to the *Z*-alkene. If an alkyl group rather than an organometallic group is present, the conformation of the transition state will be dictated by steric considerations as shown in structure **11**, and hydrogen transfer will lead to the *E*-alkene. If the ene has a more complex structure, interaction of these two effects may change this stereoselectivity.^{9,10}



Moving down the group to tin, the reaction is faster still. The yield of the H-ene product drops to zero; the M-ene product is now the major component, and the cycloaddition reaction is reduced to 45% of the whole. Finally, with triphenyl(prop-2-enyl)plumbane, the reaction is essentially instantaneous, and only the M-ene product is formed.

We showed previously⁴ that diprop-2-enylmercury and prop-2-enylmercury chloride reacted with singlet oxygen by only the M-ene route [reaction (3)]; similarly phenyl(prop-2-enyl)mercury and diprop-2-enylmercury reacted with PTAD immediately on mixing, to give only the Hg-ene product.

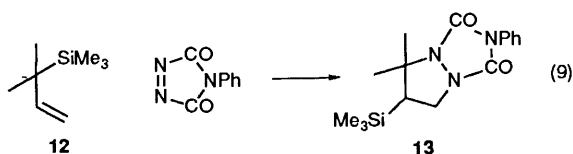
The cyclohex-2-enyltriphenylmetallic compounds **6e-g** show a similar general pattern of chemoselectivity to that of the triphenyl(propenyl)metallic compounds **6a-d**: as we progress down the group from silicon to tin, the yield of the M-ene product rises, the yield of the H-ene product falls, and the yield of the cycloadduct is at a maximum with germanium.

We investigated briefly the effect of temperature on the chemoselectivity of the reaction of triphenyl(prop-2-enyl)germane and cyclohex-2-enyltriphenylgermane with PTAD, and the results are included in Table 1. When the temperature is reduced from ambient to -40 °C, the proportion of the cycloaddition reaction increases at the expense of the M-ene

and H-ene reactions, and 80–85% yields of the cycloadducts can be obtained. We observed a similar pattern of behaviour previously in the reactions of tributyl(cyclohex-2-enyl)stannane with singlet oxygen and with PTAD.³

The general conclusion then is similar to that which we reached by studying the effect of varying the ligands about tin:⁴ within the Group 14 metals, as the metal centre is made more electropositive, the reaction becomes faster and the M-ene process dominates and can be caused to occur to the exclusion of the H-ene and the cycloaddition processes.

None of the systems which we have investigated here, or previously, where the enophile is ¹O₂ or PTAD, has shown an Si-ene reaction [eqn. (3), M = R₃Si]: the H-ene or cycloaddition reactions operate exclusively. It appeared likely then that if the α -CH₂ group were completely methylated, so that the H-ene reaction could not occur, the cycloaddition with shift of the silyl group exclusively would be observed. Indeed, this does in practice occur: when (1,1-dimethylprop-2-enyl)trimethylsilane (**12**) was treated with PTAD, 6,6-dimethyl-3-phenyl-7-trimethylsilyl-1,3,5-triazabicyclo[3.3.0]octane-2,4-dione (**13**) was obtained as the only product [eqn. (9)].



It might be expected that with suitable enes and enophiles it might be possible to observe cycloadditions with shift of hydrogen, analogous to the shift of the metal in reaction (5), but we cannot locate any such example in the literature and we have not yet been able to design a system which shows this behaviour.

Experimental

¹H and ¹³C NMR spectra were recorded on solutions in CDCl₃ on a Varian VXR-400 spectrometer; chemical shifts were measured relative to the solvent using δ_{H} 7.24 and δ_{C} 77.00. Coupling constants are given in Hz. IR spectra were recorded on a Perkin-Elmer PE983 instrument. Column chromatography was carried out on Merck silica gel 60 (70–230 mesh).

Triphenyl(prop-2-enyl)metallic compounds 6a–d. General Method.—A solution of allyl bromide (3 g, 25 mmol) in tetrahydrofuran (THF) (30–50 cm³) and the triphenylmetallic chloride (bromide for germanium) (5 mmol) in THF (5 cm³) at a rate such as to maintain gentle refluxing. After work-up, the crude product was chromatographed with light petroleum (b.p. 30–40 °C) as eluent, to give the triphenyl(prop-2-enyl)metallic compound in 70–90% yield. The properties of the products were as follows.

Triphenyl(prop-2-enyl)silane (6a). M.p. 91–92 °C (lit.¹¹ 91–92 °C); δ_{H} 2.39 (2 H, d, *J* 7.87, CH₂), 4.88 (1 H, dd, *J* 1.83 and 8.57, H-3), 4.95 (1 H, dd, *J* 1.63 and 15.13, H-3'), 5.84 (1 H, ddt, H-2), 7.39 (9 H, m, Ph), 7.51 (6 H, m, Ph).

Triphenyl(prop-2-enyl)germane (6b). M.p. 89–91 °C (lit.¹² 90–91.5 °C); δ_{H} 2.48 (2 H, d, *J* 8.00, CH₂), 4.86 (1 H, dd, H-3), 4.96 (1 H, dd, *J* 1.97 and 16.9, H-3'), 5.91 (1 H, ddt, H-2), 7.39 (9 H, m, Ph), 7.52 (6 H, m, Ph).

Triphenyl(prop-2-enyl)stannane (6c). M.p. 74–75 °C (lit.¹³ 72–74 °C); δ_{H} 2.45 (2 H, d, *J* 8.39, CH₂), 4.80 (1 H, dd, *J* 2.05 and 10.89, H-3), 4.97 (1 H, dd, *J* 1.47 and 16.85, H-3'), 6.07 (1 H, ddt, H-2), 7.39 (9 H, m, Ph), 7.55 (6 H, m, Ph).

Triphenyl(prop-2-enyl)plumbane (6d). M.p. 75–76 °C (lit.¹⁴ 76–77 °C); δ_{H} 2.97 (2 H, d, *J* 8.25, *J*²⁰⁷Pb 87.60, CH₂), 4.76 (1 H,

dd, *J* 9.90 and 1.31, H-3), 4.97 (1 H, dd, *J* 16.82 and 1.48, H-3'), 6.21 (1 H, ddt, *J* 9.91, 1.45 and 16.82, H-2), 7.42 (9 H, m, Ph), 7.58 (6 H, m, Ph).

Triphenyl(cyclohex-2-enyl)metallic Compounds 6e–g. General Method.—Butyllithium (10 mmol) in hexane was syringed into a mixture of potassium *tert*-butoxide (12 mmol) and cyclohexene (20 cm³) at –75 °C under nitrogen. Tetramethylethylenediamine (12 mmol) was then added, and the mixture was allowed to warm to room temperature and stirred for 5 h.

A solution of Ph₃SiCl, Ph₃GeBr, or Ph₃SnCl (10 mmol) in THF (10 cm³) was then added dropwise at –30 °C. The mixture was stirred at room temperature for 2 h, then hydrolysed with 5% aqueous ammonium chloride. The product was extracted into diethyl ether or dichloromethane, and washed with water. The solvent was removed and the product was isolated in 80–95% yield by chromatography.

Triphenyl(cyclohex-2-enyl)silane (6e). M.p. 130–132 °C (lit.¹⁵ 130–132 °C); δ_{H} 1.49 (1 H, m), 1.73 (2 H, m), 2.01 (3 H, m), 2.51 (1 H, m, SiCH), 5.72 (1 H, m, =CH=), 5.84 (1 H, dd, =CH–), 7.37 (9 H, m, Ph), 7.57 (6 H, m, Ph); δ_{C} 22.90, 24.11, 24.33, 25.08, 127.06, 127.69, 127.82, 129.42, 134.38, 136.16 (Found: C, 84.7; H, 7.4. C₂₄H₂₄Si requires C, 84.65; H, 7.10%).

Triphenyl(cyclohex-2-enyl)germane (6f). M.p. 113–114 °C; δ_{H} 1.51–2.15 (6 H, m), 2.76 (1 H, m, GeCH), 5.7 (1 H, m, =CH=), 5.88 (1 H, m, =CH–), 7.41 (9 H, m, Ph), 7.53 (6 H, m, Ph) (Found: C, 74.6; H, 6.3. C₂₄H₂₄Ge requires C, 74.87; H, 6.28%).

Triphenyl(cyclohex-2-enyl)stannane (**6g**) is described in ref. 2.

Reactions with PTAD. General Procedure.—An equivalent of the allylic metallic compounds was added to a solution of PTAD (0.25 g, 1.45 mmol) in CHCl₃ (20 cm³). When the red colour of the PTAD had been discharged, any insoluble metallic compound was filtered off and washed with solvent. The soluble component was chromatographed using light petroleum (b.p. 30–40 °C)–diethyl ether (1:1 v:v) as eluent, and the products were purified by recrystallisation from benzene–hexane, or by further chromatography. The *N*-metallotriazolidines **7b–d**, **f**, **g** underwent hydrolysis on the column to give the corresponding protic compounds. The characteristics of the products were as follows.

1-(Prop-2-enyl)-4-phenyl-1,2,4-triazolidine-3,5-dione. (From the 2-triphenylmetallic compounds **7b–d**.) M.p. 115–116 °C (lit.¹⁶ 116.5–117.5 °C); δ_{H} 4.17 (2 H, ddd, *J* 6.30, 1.10 and 0.50, NCH₂), 5.30 (1 H, ddd, *J* 10.15, 2.53 and 0.50, H-3), 5.34 (1 H, ddd, *J* 17.10, 2.53 and 1.10, H-3'), 5.83 (1 H, ddd, *J* 17.10, 10.15 and 6.30, H-2), 7.34 (1 H, m, Ph), 7.47 (4 H, m, Ph), 8.62 (1 H, br, NH).

(Z)-1-(3-Triphenylsilylprop-2-enyl)-4-phenyl-1,2,4-triazolidine-3,5-dione (8a). M.p. 168–169 °C; δ_{H} 4.01 (2 H, dd, *J* 6.74 and 1.06, NCH₂), 6.51 (1 H, d, *J* 14.10, H-3), 6.65 (2 H, dt, *J* 6.71 and 14.19, NH and =CH–), 7.34 (1 H, m, Ph), 7.40 (13 H, m, Ph), 7.58 (6 H, m, Ph); δ_{C} 48.49, 125.42, 128.30, 129.12, 130.07, 131.03, 131.06, 134.06, 135.68, 143.84, 143.87, 152.70 (CO), 153.16 (CO); ν_{max} (Nujol)/cm^{–1} 3145.5, 1771.6, 1694.9, 1604.7, 1591.4, 1494.6, 1134.4 (Found: C, 73.0; H, 5.25; N, 8.8. C₂₉H₂₅N₃O₂Si requires C, 73.23; H, 5.30; N, 8.83%).

(Z)-1-(3-Triphenylgermylprop-2-enyl)-4-phenyl-1,2,4-triazolidine-3,5-dione (8b). M.p. 167–168 °C; δ_{H} 4.07 (2 H, dd, *J* 6.71 and 1.03), 6.22 (1 H, br s, NH), 6.54 (1 H, d, *J* 12.91), 6.65 (1 H, dt, *J* 12.88 and 6.68), 7.32 (1 H, m), 7.41 (13 H, m), 7.56 (6 H, m); δ_{C} 48.82, 125.39, 128.20, 128.68, 129.10, 129.57, 131.08, 132.33, 134.74, 136.17, 141.53, 152.81, 153.00; ν_{max} (Nujol)/cm^{–1} 3158.5, 1771.6, 1698.2, 1608.1, 1594.7, 1497.9, 1130.7, 1090.7 (Found: C, 66.75; H, 4.75; N, 8.0. C₂₉H₂₅GeN₃O₂ requires C, 66.97; H, 4.84; N, 8.08%).

3-Phenyl-7-triphenylgermyl-1,3,5-triazabicyclo[3.3.0]octane-2,4-dione (9b). M.p. 130–132 °C; δ_{H} 2.80 (1 H, tt, *J* 12.17 and

7.66, GeCH), 3.56 (2 H, dd, *J* 11.72), 4.37 (2 H, dd, *J* 11.44 and 7.63), 7.44 (20 H, m, Ph); δ_C 29.52, 48.95, 125.39, 128.06, 128.84, 129.07, 129.96, 131.73, 133.15, 134.89, 154.75; ν_{\max} (Nujol)/cm⁻¹ 1765.0, 1714.9, 1698.2, 1427.8, 1404.5, 1294.3 (Found: C, 66.7; H, 4.6; N, 7.9. C₂₉H₂₅GeN₃O₂ requires C, 66.97; H, 4.84; N, 8.08%).

3-Phenyl-7-triphenylstannyl-1,3,5-triazabicyclo[3.3.0]octane-2,4-dione (**9c**). M.p. 172–173.5 °C; δ_H 2.53 (1 H, tt, *J* 7.48 and 12.81, *J*¹¹⁷Sn 34.24, *J*¹¹⁹Sn 35.44, SnCH), 3.64 (2 H, dd, *J* 12.88 and 11.60), 4.41 (2 H, dd, *J* 11.60 and 7.48), 7.34 (1 H, m, Ph), 7.44 (13 H, m, Ph), 7.54 (6 H, m, Ph); δ_C 27.48, 50.41, 125.40, 128.07, 129.08, 129.15, 129.89, 131.73, 135.00, 136.93, 155.30; ν_{\max} (Nujol)/cm⁻¹ 1775.0, 1704.9, 1594.7, 1494.6, 1244.2, 1120.7 (Found: C, 61.4; H, 4.55; N, 7.4. C₂₉H₂₅N₃O₂Sn requires C, 61.52; H, 4.45; N, 7.42%).

1-(Cyclohex-2-enyl)-4-phenyl-1,2,4-triazolidine-3,5-dione. (From the 2-triphenylmetalloyl compounds **7f–g**.) M.p. 168–171 °C (lit.¹⁶ 171–172 °C); δ_H 1.65 (1 H, m), 1.80 (2 H, m), 1.95 (1 H, m), 2.02 (2 H, m), 4.80 (1 H, m, NCH), 5.57 (1 H, dm, *J* 10.05 and 2.24, =CH–), 6.02 (1 H, dm, *J* 10.05 and 2.37, –CH=), 7.35 (1 H, m, Ph), 7.48 (4 H, m, Ph), 8.50 (1 H, br, NH).

1-(3-Triphenylsilylcyclohex-2-enyl)-4-phenyl-1,2,4-triazolidine-3,4-dione (**8e**). M.p. 175–176 °C; δ_H 1.74 (1 H, m), 1.89 (2 H, m), 2.06 (1 H, m), 2.22 (2 H, m), 4.91 (1 H, m, NCH), 5.99 (1 H, d, *J* 1.44, =CH–), 7.38 (14 H, m, Ph), 7.5 (6 H, m, Ph), 7.70 (1 H, br, NH); δ_C 21.40, 25.69, 27.74, 54.34, 125.59, 127.98, 128.26, 129.12, 129.76, 131.01, 132.94, 136.17, 138.04, 143.04, 152.92 (CO), 154.07 (CO); ν_{\max} (Nujol)/cm⁻¹ 1771.6, 1691.5, 1618.1, 1598.1, 1494.6, 1437.8, 776.9 (Found: C, 74.4; H, 5.6; N, 8.3. C₃₂H₂₉N₃O₂Si requires C, 74.53; H, 5.67; N, 8.15%).

1-(3-Triphenylgermylcyclohex-2-enyl)-4-phenyl-1,2,4-triazolidine-3,5-dione (**8f**). M.p. 170.5–171.5 °C; δ_H 1.76 (1 H, m), 1.89 (2 H, m), 2.05 (1 H, m), 2.27 (2 H, m), 4.93 (1 H, m, NCH), 5.91 (1 H, d, *J* 1.68, =CH–), 7.35 (14 H, m, Ph), 7.48 (6 H, m, Ph); δ_C 21.44, 25.89, 28.52, 54.12, 125.61, 128.20, 128.31, 129.07, 129.19, 131.00, 135.00, 135.14, 135.25, 144.40, 152.67 (CO), 154.14 (CO); ν_{\max} (Nujol)/cm⁻¹ 1775.0, 1691.5, 1598.1, 1497.9, 1481.2, 1437.8, 1087.3, 1020.6 (Found: C, 68.4; H, 4.95; N, 7.4. C₃₂H₂₉GeN₃O₂ requires C, 68.61; H, 5.22; N, 7.50%).

11-Triphenylgermyl-4-phenyl-2,4,6-triazatricyclo[5.3.1.0^{2,6}]-undecane-3,5-dione (**9f**). M.p. 231–232 °C; δ_H 1.60–1.80 (4 H, m), 1.84 (2 H, m), 2.50 (1 H, m, GeCH), 4.95 (2 H, m, NCH), 7.44 (14 H, m), 7.51 (6 H, m); δ_C 18.10, 27.10, 40.71 (40.77), 60.32 (60.44), 125.46, 128.09, 129.81, 129.10, 129.70, 131.77, 134.911, 135.07, 155.79 (CO); ν_{\max} (Nujol)/cm⁻¹ 1765.0, 1711.5, 1681.5, 1594.7, 1494.6, 1397.8, 907.1 (Found: C, 68.2; H, 5.25; N, 7.5. C₃₂H₂₉GeN₃O₂ requires C, 68.61; H, 5.22; N, 7.50%).

Trimethyl(1,1-dimethylprop-2-enyl)silane (**12**). This was prepared from 1,1-dimethylprop-2-ynol according to the following route.¹⁷ $\text{HC}\equiv\text{CCMe}_2\text{OH} \xrightarrow{\text{i,ii}} \text{Me}_3\text{SiC}\equiv\text{CCMe}_2\text{OH} \xrightarrow{\text{iii}} \text{Me}_3\text{Si-C}\equiv\text{CCMe}_2\text{Cl} \xrightarrow{\text{iv}} \text{Me}_3\text{SiC}\equiv\text{CCMe}_2\text{MgCl} \xrightarrow{\text{v}} \text{Me}_3\text{SiC}\equiv\text{CC-Me}_2\text{SiMe}_3 \xrightarrow{\text{vi,vii}} \text{HC}\equiv\text{CCMe}_2\text{SiMe}_3 \xrightarrow{\text{viii}} \text{H}_2\text{C}=\text{CHMe}_2\text{SiCMe}_3$. [Reagents: i, EtMgBr; ii, Me₃SiCl;¹⁸ iii, conc. HCl;¹⁹ iv, Mg/THF at 0 °C; v, Me₃SiCl;¹⁷ vi, AgNO₃/EtOH; vii, KCN;²⁰ viii, H₂/Pd–BaSO₄–quinoline/pentane at room temp.²⁰]. The Grignard reagent was prepared from

the propargyl chloride at 0 °C, when the disilyl compound was isolated in 75% yield; if the reaction was carried out at room temperature, the yield was much smaller. The silane **12** showed the following properties: δ_H 0.05 (9 H, s, Me₃Si), 0.99 (6 H, s, Me₂), 4.72 (1 H, dd, *J* 1.59 and 17.21, H-3), 4.86 (1 H, dd, *J* 1.59 and 10.55, H-3'), 5.85 (1 H, dd, *J* 10.80 and 17.46, H-2).

Reaction with PTAD gave 3-phenyl-6,6-dimethyl-7-trimethylsilyl-1,3,5-triazabicyclo[3.3.0]octane-2,4-dione (**13**). M.p. 132–134 °C; δ_H 0.17 (9 H, s, Me₃Si), 1.40 (3 H, s, Me), 1.71 (3 H, s, Me), 2.00 (1 H, dd, *J* 7.90 and 12.82, SiCH), 3.63 (1 H, dd, *J* 10.08 and 12.82, H-8), 3.95 (1 H, dd, *J* 7.93 and 10.07, H-8'), 7.32 (1 H, tt, *J* 7.36 and 1.22, Ar *p*-H), 7.43 (2 H, dd, *J* 8.17 and 7.70, Ar *m*-H), 7.50 (2 H, dd, *J* 1.46 and 8.26, Ar *o*-H); δ_C 21.81, 27.04, 43.08, 44.79, 65.72; 125.40, 127.73, 128.93, 131.88 (Ar); 150.51, 150.82 (CO); ν_{\max} (Nujol)/cm⁻¹ 2918.5, 2851.7, 1758.3, 1698.2, 1454.5, 1404.5, 1374.4, 1254.2, 1117.4, 890.4, 843.7, 756.9, 686.8 (Found: C, 60.4; H, 7.55; N, 13.2. C₁₆H₂₃N₃O₂Si requires C, 60.54; H, 7.30; N, 13.24%).

Acknowledgements

We thank the Royal Society and the Chinese Academy of Sciences for the award of a Royal Scholarship to J. C.

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Paper 2/03287B

Received 23rd June 1992

Accepted 16th July 1992