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Intramolecular Photocyclization of 1-(Trimethylsilyl)-1,5-Hexadien-3-ones

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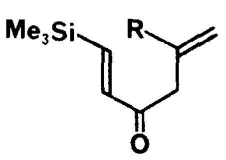
Dedicated to Professor Harry H. Wasserman on the occasion
of his sixty-fifth birthday.

Abstract: An influence upon the regiochemistry of cyclization due to a 1-trimethylsilyl substituent is indicated upon comparison of the photochemistry of 4a,b and their carbon analogs 5a,b.

In previous studies we have demonstrated the importance of structural features in controlling the regiochemistry of intramolecular photochemical cyclization of 1,5-hexadien-3-ones.[1] The parent system (1, see Table) undergoes 1,5-cyclization and subsequent closure to give bicyclo[2.1.1]hexan-2-one following the familiar "rule of five";[2] however, if the dienone is substituted with an alkyl group at C(5) (as in 2) or the conjugated double bond is incorporated in a five- or six-membered ring (3), 1,6-closure becomes competitive. We now report that a trimethylsilyl (TMS) group at C(1) has an effect upon the cyclization of these dienones and that this is not a steric effect. The only relevant previous report[3] known to us concerned a different sort of regiochemical effect of the trialkylsilyl group in intermolecular photocycloadditions.

We examined ketones 4a,b and 5a,b. These were readily prepared from E-3-trimethylsilyl-2-propenal[4] and E-4,4-dimethyl-2-pentenal[5] by addition of allyl- or methallylmagnesium chloride and oxidation of the carbinol.[6,7] Dilute solutions of the dienones were irradiated through an uranium glass filter (λ>340 nm) containing ~6% of methanol or t-butanol. A photostationary mixture of the E and Z isomers of 4 and 5 was rapidly established,[8] followed by



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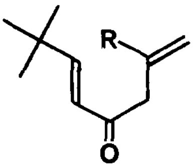
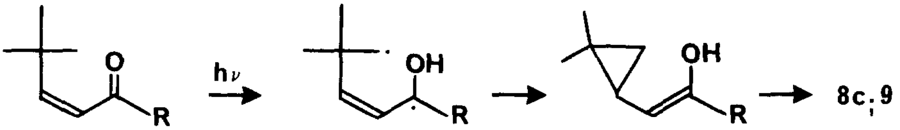
a. R=H
b. R=CH$_3$



5

slow formation of the products (1-6 days for complete conversion). The results of these irradiations are collected in the Table.

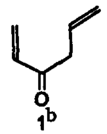
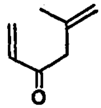
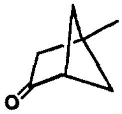
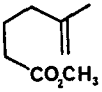
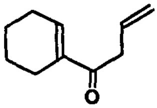
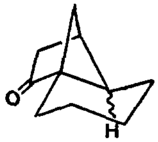
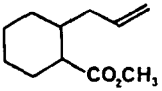
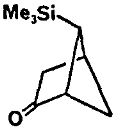
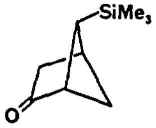
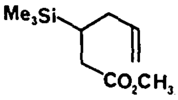
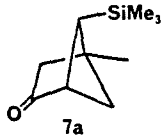
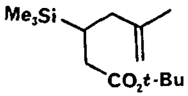
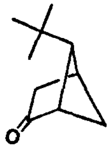
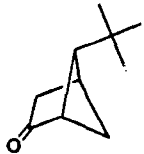
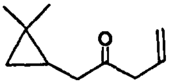
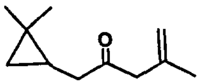
Photolysis of **4a** yielded the expected[1] bicyclic ketones **6a,b**[9] and a small amount of 1,6 closure product **6c**. Irradiation of **4b** afforded largely ester **7b**.[11] The C(5) substituent and ring effects noted above are roughly additive, and in molecules containing both, highly regioselective 1,6 closure can occur.[1] Apparently the C(1) TMS group also acts synergistically when a C(5) methyl group is present. Irradiation of *t*-butyl dienones **5a,b** gave no 1,6-closure products and thus no unusual[12] steric effect appears to be operating in the formation of **6c** and **7b**. There is precedent for the formation of cyclopropyl ketones from *t*-butyl enones;[13] a reasonable mechanism is shown below.



$R = CH_2CH{=}CH_2;\ CH_2C(CH_3){=}CH_2$

The mechanism whereby the TMS group influences the cyclization of **4** is not yet clear. Although nothing is known about the influence of silyl substitution on excited states of enones, its influence on carbon-centered radicals is well established. β-Silyl substitution imparts particular stability to radicals,[14] and this fact can explain the regioselectivity observed in [2+2] photocycloaddition of olefins to 2- and 3-trialkylsilyl-2-cyclopenten-1-ones.[3] Furthermore, α-silyl substitution is also known to alter radical reactivity.[15] There is good evidence that isomerization of hexadienones to bicyclo[2.1.1]-hexanones involves initial 1,5, rather than 2,6, bonding,[1] so that our present results suggest that the C(1) TMS group somehow favors 1,6 over 1,5 closure. The magnitude of this effect is about the same as that resulting from incorporation of the conjugated double bond in a six-membered ring, so that one interesting mechanistic speculation is that the geometric requirement for β-silyl stabilization in the transition state leading to bonding at C(1) limits torsion about the C(1)-C(2) bond roughly to the extent possible in a cyclohexene. Investigations are now underway to explore this possibility.[16]

Table. Products of Photolysis of 1,5-Hexadien-3-ones

Dienone	Ratio 1,5/1,6 Closure	Products[a]				
		1,5 closure		1,6 closure	Other
 1[b]	only 1,5				
 2[c]	61:39				
 3[d]	93:7				
4a	94:6	 6a	 6b	 6c	
4b	13:87	 7a		 7b	
5a	only 1,5	 8a	 8b		 8c
5b	–				 9

[a] Ketene photoproducts isolated as methyl or t-butyl esters; yields 70-90%. [b] Bond, F. T.; Jones H. C.; Scerbo, C. Tetrahedron Lett. **1965**, 4685 and ref. 1; [c] Smith, A. B., III; Agosta, W. C. J. Am. Chem. Soc. **1973**, 95, 1961 and references cited therein; [d] ref. 1.

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4. Jung, M. E.; Gaede, B. *Tetrahedron* **1979**, *35*, 621; see also Denmark, S. E.; Jones, T. K. *J. Org. Chem*. **1982**, *47*, 4595.
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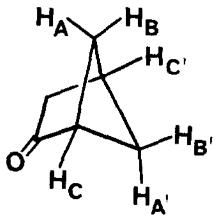
6. Corey, E. J.; Suggs, J. W. *Tetrahedron Lett*. **1975**, 2647.
7. The dienones and their products (all new compounds) were purified by VPC and gave satisfactory ^1H NMR (60- or 300-MHz), IR, and high resolution mass spectra (EI or CI) and/or elemental analyses.
8. The *Z* isomer formed in the photolysis of **4b** was isolated and characterized.
9. The stereochemistry of the C(5) substituent can be assigned upon examination of the 300-MHz ^1H NMR of these compounds. For endo isomers **6a** and **8a** (H_A absent), $H_{A'}$ is observed at high field as a doublet of doublets coupled to $H_{B'}$ and H_C (or $H_{C'}$). For **6a**: $H_{A'}$, δ 1.62, $J_{A'C} = 0.7$, $J_{A'B'} = 6.6$ Hz; for **8a**: $H_{A'}$, δ 1.37, $J_{A'C} = 0.6$, $J_{A'B'} = 6.9$ Hz. Exo isomers **6b**, **7a**, and **8b** all have two high field signals (H_A, $H_{A'}$) having the expected splitting.[10] For **6b**: δ 1.50, $H_{A'}$, $J_{AA'} = 8.5$, $J_{A'B'} = 7.9$ Hz; 1.15, H_A, $J_{AA'} = 8.6$ Hz; for **7a**: δ 1.54, $H_{A'}$, $J_{AA'} = J_{A'B'} = 7.7$ Hz; 1.19, H_A, $J_{AA'} = 8.2$ Hz; for **8b**: δ 1.75, H_A, $J_{AA'} = 6.5$ Hz; 1.52, $H_{A'}$, $J_{AA'} = 6.7$, $J_{A'B'} = 8.2$ Hz.



10. Wolff, S.; Agosta, W. C. *J. Org. Chem*. **1980**, *45*, 1332 and references cited therein.
11. The stereospecific formation of **7a** will be discussed in our full paper.
12. No 1,6 closure products are observed in the photolysis of 1,1-dimethyl-1,5-hexadien-3-one.[1]
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