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Stereoselective and Regioselective Thermal and Photochemical Preparation of Siloxy Dienes[1,2]

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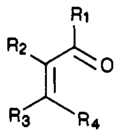
It is shown that (*Z*)-2-hydroxy 2,4-dienes (*Z*-dienols), formed by photoenolization of the β-alkyl-α,β-unsaturated ketones **1a–e**, can be trapped by a silylating reagent to give the (*Z*)-2-trimethylsiloxy 2,4-dienes **2a–e**. This corresponds to stereoselective and regioselective production of just one of the three isomeric silyl dienol ethers which can be formed from each of these ketones. In contrast, silylation of the same ketones under thermal conditions generally gives the 2-trimethylsiloxy 1,3-dienes **4**. Uniquely among the siloxy dienes examined, **3d** apparently undergoes a rearrangement to **4d** via a 1,5-hydrogen shift.

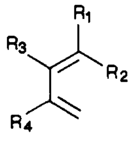
Silyl enol ethers have found many applications in synthetic organic chemistry.[3] They have served as enolate precursors and as substrates for ring formation reactions involving cycloaddition, and their reactions with electrophiles under Lewis acid catalysis have been used as an alternative to base-catalyzed enolate routes for carbon–carbon bond formation.[3] Procedures have been developed for regioselective formation of silyl enol ethers from nonsymmetrical ketones[3] and methods have been developed for stereoselective preparation of *E* and *Z* isomers in cases where the enol ethers can exhibit geometrical isomerism.[4]

Silyl dienol ethers (siloxy dienes) have also been prepared and their reactions studied, although in less detail.[3d] Siloxy dienes can serve as precursors to dienolates which react with electrophiles to give α-substituted-β,γ-unsaturated carbonyl compounds[3d]; alternatively, they can react with electrophiles under Lewis acid catalyzed conditions to give γ-alkylated-α,β-unsaturated ketones.[5] They have also been used widely as Diels–Alder dienes.[6]

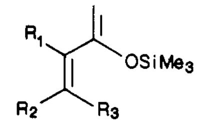
Chart I



	R_1	R_2	R_3	R_4
1a	CH_3	H	CH_3	CH_3
1b	CH_3	H	H	H
1c	CH_3	CH_3	CH_3	H
1d	CH_3	CH_3	CH_3	CH_3

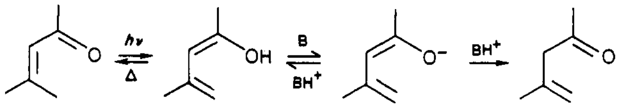


	R_1	R_2	R_3	R_4
2a	CH_3	$OSiMe_3$	H	CH_3
2b	CH_3	$OSiMe_3$	H	H
2c	CH_3	$OSiMe_3$	CH_3	H
2d	CH_3	$OSiMe_3$	CH_3	CH_3
2g	H	OCH_3	H	H
3a	$OSiMe_3$	CH_3	H	CH_3
3b	$OSiMe_3$	CH_3	H	H
3c	$OSiMe_3$	CH_3	CH_3	H
3d	$OSiMe_3$	CH_3	CH_3	CH_3
3g	OCH_3	H	H	H



	R_1	R_2	R_3
4a	H	CH_3	CH_3
(*E*)**4b**	H	CH_3	H
(*Z*)**4b**	H	H	CH_3
(*E*)**4c**	CH_3	CH_3	H
4d	CH_3	CH_3	CH_3

Scheme I



1 **5** **6** **7**

A serious limitation on the use of siloxy dienes is that their preparation from the most convenient precursors, α,β-unsaturated ketones, leads to mixtures of isomers. For example, 4-methyl-3-penten-2-one, **1a**, can, in principle, give three different dienolates on deprotonation, yielding three possible siloxy dienes, **2a**–**4a**, following quenching of the dienolate with a silylating reagent such as chlorotrimethylsilane. Generally, an α,β-unsaturated ketone such as **1a** is deprotonated at C-1 (the α' position) by strong base as this position is the kinetically, although not normally the thermodynamically, more acidic site.[7] Silylation of the dienolate than yields the kinetic isomer, e.g., **4a**, a 2-siloxy-1,3-butadiene.[7] Under equilibrating conditions (e.g., heating with chlorotrimethylsilane in DMF in the presence of triethylamine) the equilibrium isomers, e.g., **2a** and **3a**, which are 2-siloxy-2,4-butadienes, can, in

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(2) Financial assistance from the Natural Sciences and Engineering Research Council, Canada, and Imperial Oil Ltd. is gratefully acknowledged.

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principle, be obtained,[5,7a] although this is not general, the kinetic dienes being formed instead under these conditions in some cases.[7b] The equilibrium isomers can also be prepared by reaction of β,γ-unsaturated ketones with strong base followed by treatment with chlorotrimethylsilane,[5,8] but the starting ketones can be difficult to obtain, although they can be made photochemically by interception of photoenols with base.[9]

Table I. Yields for the Thermal and Photochemical Preparation of Siloxy Dienes

ketone	products % yields			procedure
1a	**2a**	**3a**	**4a**	
	51	5	0	A[a]
	17	5	0	A[b]
	25	3	38	B[c]
	11	1	65	C[d]
	5		4	C[e]
	9[f]	*f*	53	C[d,g]
	0	0	96[h]	D[i,j]
	87[f]	*f*		E[k]
1b	**2b**	**3b**	**4b**	
	17	2	0	A[a]
	12	2	0	A[b]
	2	0	27	B[c]
	12	0	70	C[d]
	11[f]		60	C[d,g]
			l	D[e]
1c	**2c**	**3c**	**4c**	
	63	10	0	A[a]
	26	2	0	A[b]
	2	0	34	B[c]
1d	**2d**	**3d**	**4d**	
	68	0	0	A[a]
	22	0		A[b]
	13	0	72	B[c]
	0	0	>90	D[e]
1e	**2e**	**3e**		
	45	43		A[a]
	70	1		B[c]
1f	**2f**		**4f**	
	85		1	A[a]
	13		61	B[c]

[a] Procedure A: small-scale photochemical preparation; 10 mL of 0.1 M enone in DMF containing 10 equiv of imidazole and 5 equiv of chlorotrimethylsilane irradiated by using a medium pressure mercury lamp filtered through water and Pyrex. Reactions were given an aqueous workup and yields were calculated from the ^1H NMR of the reaction mixture following addition of an internal standard (benzene). The product ratios were checked by GC. [b] Procedure A but on a large scale (300 mL of solution were irradiated and the products isolated following an aqueous workup and distillation). The yields are of isolated product following distillation. [c] Procedure B: silylation in hot DMF containing triethylamine and chlorotrimethylsilane. Yields calculated from ^1H NMR and GC of the reaction mixture following addition of an internal standard. [d] Procedure C: silylation with chlorotrimethylsilane, triethylamine, and a Lewis acid (zinc chloride) in benzene. Yield calculated from the ^1H NMR and GC of the reaction mixture following addition of an internal standard. [e] From ref 17. Titanium tetrachloride was used as the Lewis acid catalyst instead of zinc chloride. [f] The geometry of the double bond was not determined: this compound could be the *E* isomer **3** or a mixture of **2** and **3**. [g] From ref 16. [h] From ref 7e. [i] Procedure D: quantitative formation of the dienolate of the ketone using lithium diisopropylamide followed by trapping with chlorotrimethylsilane. [j] However, ref 17 reports that these conditions gave **2a** and **4a** in the ratio 1:2. [k] Procedure E: treatment of the ketone with KH followed by chlorotrimethylsilane. From ref 5a. [l] No yield given: ref 6k and 7i.

Selective synthetic routes to the kinetic and equilibrium siloxy dienes are desirable as the reactivities of the isomers are different; for example, the 2-siloxy 1,3-dienes react with electrophiles under Lewis acid catalysis at the 1-position[3d] to give 1-substituted 3-alken-2-ones, whereas the 2-siloxy 2,4-dienes can react at the γ-position[5] to give 4-substituted-3-alken-2-ones. The latter is in contrast to the reactivity of the corresponding dienolate which is attacked by electrophiles at the α-position[10] to give 3-substituted-4-alken-2-ones. Furthermore, if the double-bond geometry of the 2-siloxy 2,4-dienes could be controlled, then this might be of use in the Diels–Alder applications of these compounds.

Recently we have been studying the photochemical enolization reactions of β-alkyl-α,β-unsaturated carbonyl compounds.[9] We have found that these compounds react from the singlet excited state by hydrogen transfer from the β-alkyl group syn to the carbonyl function to yield a *Z*-dienol (a (*Z*)-2-hydroxy-2,4-butadiene; structure **5** in Scheme I).[9a,g] The *Z*-dienol can reketonize by a thermal hydrogen transfer (a 1,5-sigmatropic hydrogen shift proceeding suprafacially) to give back the conjugated ketone.[9b,f] Alternatively, the dienol can be intercepted by base to give the dienolate **6** which can then reketonize, normally by a α-protonation,[9h] to give[9b,g] the β,γ-unsaturated carbonyl compound **7**. We have observed that the dienolate can also be trapped as its silyl dienol ether if a silylating agent is present.[9a,g] This suggested that the photoenolization and trapping reaction sequence could be useful for the generation of the *Z* isomers of equilibrium siloxy dienes and allow a stereo- and regioselective route for their preparation complementary to the routes available for preparation of the kinetic isomers. Described here are the results of a study in which we examined the photoenolization–trapping sequence as a procedure for the stereo- and regioselective preparation of (*Z*)-2-siloxy 2,4-dienes and compared it with procedures for preparation of siloxy dienes thermally under both equilibrating and kinetic conditions.

Results

Trapping of Photochemically Produced Dienols. Irradiation of 0.1 M solutions of the β-alkyl-α,β-unsaturated ketones **1a–f** in dimethylformamide (DMF) with Pyrex and water filtered ultraviolet light from a medium pressure mercury lamp[11] produced no observable reaction apart from *E–Z* isomerization arround the double bond in the cases of **1b**, **1c**, and **1e**. Under these conditions most of the excitation energy is lost by twisting of the enone double bond,[12] and some is lost by photoenolization followed by reketonization back to the parent conjugated ketone[9h] (reketonization occurs intramolecularly by an uncatalyzed 1,5-hydrogen shift mechanism[9h]). However, when the solutions of ketones **1a–f** contained 5 equiv of chlorotrimethylsilane and 10 equiv of imidazole, irradiation resulted in the disappearance of the enones and in each case formation of a major product identified as the Z-2-siloxy-2,4-pentadienes **2a–f**. The siloxy dienes were sep-

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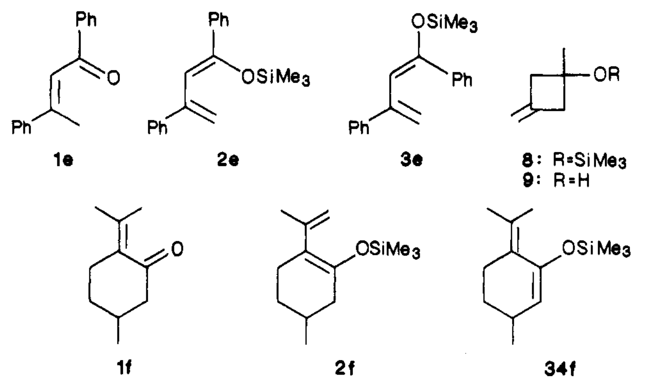
(11) Under these conditions the $n \rightarrow \pi^*$ absorption band of the ketone is excited. The Pyrex filter ensures that the siloxy diene products do not absorb light and so avoids their secondary photolysis, while the water filter absorbs infrared light and reduces heating of the solution which would accelerate thermal silylation reactions.

(12) Morrison, H.; Rodriguez, O. *J. Photochem.* **1974/5**, *3*, 471.

Chart II



arated from the reaction mixture by means of an aqueous workup and were purified by preparative gas chromatography in small-scale reactions and by distillation in larger scale reactions. The results are summarized in Table I (procedure A). The yields are generally only fair but in view of the ready availability of the ketones this does not represent a major disadvantage, especially since the products are easily separated by distillation in the larger scale reactions. The low yields are in part due to the competing deconjugation reaction of the ketones;[9] however, the β,γ-unsaturated ketones which are produced undergo fragmentation by efficient secondary photochemistry to give readily removable volatile products.[9g]

In the case of 4-methyl-3-penten-2-one, **1a**, the major product, (*Z*)-4-methyl-2-(trimethylsiloxy)-2,4-pentadiene, **2a**, was accompanied by small amounts of 4-methyl-4-penten-2-one, **7**. The latter compound arises from interception of the photochemically produced dienol by imidazole followed by reketonization by α-protonation[9] and represents a failure to trap the dienolate with the silylating reagent; this can be minimized by using high concentrations of silylating reagent. At high conversions (*E*)-4-(trimethylsiloxy)-2-methyl-1,3-pentadiene, **3a**, and the cyclobutane silyl ether **8** also appeared in small amounts. In view of its late appearance **8** is probably a secondary irradiation product arising from **7**. This has precendent; Yang[13] has shown that irradiation of **7** yields the methylenecyclobutanol **9** via Norrish type II hydrogen abstraction followed by ring closure of the intermediate biradical. In the reaction described here **9** would be silylated under the reaction conditions to give **8**.

The formation of **3a** is presumed to arise from sensitized formation of triplet excited state of the primary product **2a**. The primary product **2a** can act as a classical diene quencher and intercept the triplet excited states of **1a** or **7**. The formation of **3a** only at later reaction times, when its concentration has built up to a sufficient level for it to act as a triplet quencher, supports this. The amount of **3a** formed increased if the mixture was over irradiated (i.e., if the irradiation was continued beyond the point that most of the ketone had been converted. Thus in preparative irradiations the yields of **2a** and **3a** at optimum conversion were 51% and 5%, respectively; the ratio **2a**:**3a** rose to 70:30 with no substantial increase in their combined yield if the irradiation time was doubled.

Only very small amounts of the *E* isomers **3** were formed at high conversions in the cases of ketones **1b–d**. In the case of ketone **1e**, however, considerable quantities of the *E* isomer were formed as a secondary product from the initially formed *Z* isomer. This could arise if the ketone has a longer lived triplet state than the others examined, making it more able to sensitize the primary product **2e**, or alternatively it could arise from the fact that the siloxy diene absorbs to longer wavelength than the others studied and so undergoes *E–Z* isomerization as a result of direct irradiation. The latter is probably the case as repetition of the reaction in the presence of triplet quenchers did not reduce the amount of the *E* isomer **3e** formed. The course of the reaction for **1e** is illustrated in Figure 1; it can be seen that the *Z* isomer is the primary product with the *E* isomer appearing after an initial induction period. The observation of an induction period indicates that the *E* isomer is indeed formed from the *Z* isomer and rules out the possibility that the ketone is also photoenolizing to give both *E* and *Z* photodienols directly, as is the case with ortho alkyl aromatic ketones.[14]

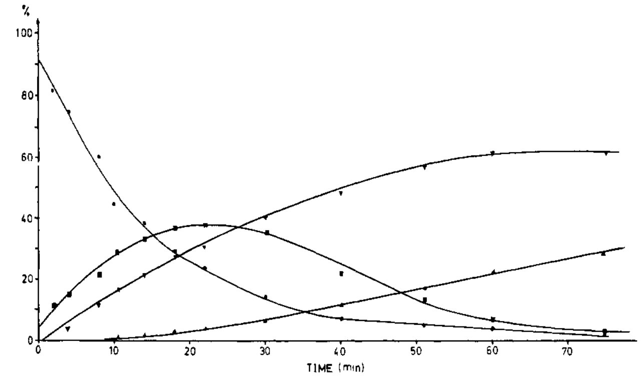


Figure 1. Plot of reaction mixture composition (as determined by GC) against irradiation time for the irradiation of dypnone, **1e**, in DMF containing $ClSiMe_3$ and imidazole: (●) (*E*)-**1e**; (■) (*Z*)-**1e**; (▼) **2e**; (▲) **3e**.

A very slow dark reaction was also observed with all the ketones studied; for example, dissolution of 4-methyl-3-penten-2-one, **1a**, in DMF containing imidazole and chlorotrimethylsilane in the same proportions as the photochemical experiment resulted in the slow formation of **4a** only. Its rate of formation was sufficiently slow, however, that negligible quantities of **4a** were formed in the photochemical experiment.

The structures of the siloxy dienes obtained were deduced by comparison of the ^{1}H NMR spectra of the major photochemical products (the *Z* isomers **2**) with the structural isomers **4** and the *E* isomers **3**. Samples of **4** for comparison were prepared thermally as described in the next section, while samples of the *E* isomers for comparison were prepared by photosensitized *E–Z* isomerization of the photochemical products (the *Z* isomers), except in the cases of **1a** and **1e** where sufficient quantities of the *E* isomers **3a** and **3e** were formed in the photochemical preparation of **2a** and **2e**. For all the ketones examined the structural isomers **4** (the 2-siloxy-1,3-pentadienes) can readily be distinguished from the equilibrium isomers **2** and **3** (2-siloxy-2,4-pentadienes) by comparison of the observed chemical shifts for the olefinic hydrogens with those which can be calculated for the siloxy dienes using additive chemical shift correlations.[15] This comparison is shown in Table II. For the *E* and *Z* siloxy dienes **2a** and **2b**, and **3a** and **3b**, calculated chemical shifts predict that the proton present at position 3 (H_a in Table II) should appear at up to 0.5 ppm to lower field in the *E* isomer **3** as compared with the *Z* isomer **2**. That this is indeed so has been shown for 1-alkoxy-1,3-butadienes such as **2g** and **3g** (see

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(13) Yang, N. C.; Thing, D.-M. *Tetrahedron Lett.* **1966**, 3671.

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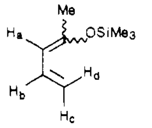
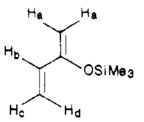
Table II. ^{1}H NMR Chemical Shifts for Olefinic Hydrogens of Siloxy Dienes 2, 3, and 4





	H_a	H_b	H_c	H_d	
2a	4.82		4.80	4.88	calcd[a]
	4.88		4.59	4.81	$CDCl_3$
	5.00		4.90	5.00	$C_6D_5CD_3$[b]
	5.08		4.84	5.04	$C_6D_5CD_3$
3a	4.90		4.80	4.88	calcd[a]
	5.21		4.65	4.80	$CDCl_3$
4a	3.95, 3.95	5.75			calcd[a]
	4.10, 4.19	5.51			$CDCl_3$[d]
	4.26, 4.38	5.68			C_6D_6
	4.10, 4.20	5.47			$CDCl_3$
2b	4.82	6.25	5.02	5.16	calcd[a]
	5.25	6.56	4.78	4.96	$CDCl_3$
	5.33	6.92	4.96	5.12	C_6D_6
3b	4.90	6.25	5.02	5.16	calcd[a]
	5.25	6.37			$CDCl_3$
	5.67	6.40	4.90	5.08	C_6D_6
(*E*)-**4b**	3.95	6.03		5.61	calcd[a]
	4.18	5.86		5.96	$CDCl_3$
	4.23, 4.29	5.88		6.12	C_6D_6
(*Z*)-**4b**	3.95	5.97		5.47	calcd[a]
	4.23, 4.29	5.80	6.25		C_6D_6
2c		6.25	5.02	5.16	calcd[a]
		6.91	4.85	4.93	$CDCl_3$
		7.28	5.00	5.06	C_6D_6
3c		6.25	5.02	5.16	calcd[a]
		6.69	4.97	5.11	C_6D_6
(*E*)-**4c**	3.95			5.33	calcd[a]
	4.12, 4.29			5.93	$CDCl_3$
2d			4.80	4.88	calcd[a]
			4.78	4.86	$CDCl_3$
4d	3.95				calcd[a]
	4.49, 4.21				C_6D_6
2e	5.64		5.56	5.20	calcd[a]
	5.88		5.45[c]	5.64[c]	$CDCl_3$
3e	5.49		5.56	5.20	calcd[a]
	5.69[c]		5.19[c]	4.88[c]	$CDCl_3$
2f			4.80	4.88	calcd[a]
			4.72[c]	4.75[c]	$CDCl_3$
4f	4.40				calcd[a]
	4.76				$CDCl_3$
2g	5.04	6.25	5.02	5.16	calcd[a]
	5.04	6.69	4.83	4.99	$CDCl_3$[d]
3g	5.18	6.25	5.02	5.16	calcd[a]
	5.49	6.13	4.73	4.96	$CDCl_3$[d]

[a] Calculated chemical shifts were derived by using additive chemical shift correlations from ref 15. [b] Data from ref 17. [c] Values may be interchanged. [d] Data from ref 16.

Table II) derived from α,β-unsaturated aldehydes[16a] and evidence has been presented to show that the same correlation holds for the corresponding trimethylsiloxy dienes.[16b] Comparison of the chemical shifts of the protons in the 3 position of the *E* and *Z* siloxy dienes **2** and **3** derived from ketones **1a** and **1b** reveals that in the major photochemical product this proton appears at lower chemical shift, indicating that it has structure **2** and so has the *Z* stereochemistry.

For the siloxy dienes derived from ketones **1b** and **1c**, the photochemical product can be assigned the *Z* stereochemistry by examination of the chemical shift of the proton in the 4-position (H_b in Table II). Additive chemical shift correlations do not predict any change in chemical shift of this proton with changing stereochemistry about the 2,3-double bond;[15] however, an effect might be expected since in the *Z* isomer this proton may be exposed to a shielding influence from the oxygen function, depending upon the conformation of the diene. That this is so has been demonstrated[16a] for the alkoxy dienes **2g** and **3g**, and it has also been argued for the siloxy analogues.[16b] The data are given in Table II and reveal that the proton at position 3 appears at up to 0.5 ppm to lower field in the *Z* isomer **2g** as compared with the *E* isomer **3g**. Comparison of the chemical shifts of the corresponding protons in the *E* and *Z* isomers **2** and **3** derived from ketones **1b** and **1c** again indicates that the major photochemical product is the *Z* isomer **2**.

The validity of the assignments for siloxy dienes **2a** and **3a** was corroborated by the observation of a nuclear Overhauser effect; irradiation of the methyl protons at position 1 of **2a** resulted in an NOE enhancement of the vinyl proton at position 3 of 32%, whereas no NOE was observed in **3a** when the same experiment was performed. Also, the ^{1}H NMR spectrum of **2a** in toluene-*8*-*d* is identical with that already reported elsewhere[17] for a sample of **2a** prepared by a different route (see Table II).

In the case of siloxy dienes **2d** and **3d** the stereochemistries could not be assigned by using chemical shift arguments because both the 2 and 3 positions of the dienes are substituted by methyl groups. Furthermore, no NOE effect between the methyl groups could be observed in either isomer, presumably because of rapid spin relaxation within the methyl groups. It was anticipated that the double-bond geometries in **2d** and **3d** could be confirmed by preparing the *E* isomer from the *Z* isomer by photochemical sensitization of the major product of the photoenolization/trapping reaction of **1d** (the presumed *Z* isomer **2d**) and examining their NMR spectra in the presence of lanthanide shift reagents. However, when the presumed *Z* isomer was irradiated in benzene under conditions where the benzene absorbed all of the light so that only the triplet excited state of **2d** could be formed, it was found that the product obtained was not the *E* isomer **3d** but instead the structural isomer **4d**. The structure of **4d** followed unambiguously from the ^{1}H NMR spectrum which was identical with that obtained from the sample of **4d** prepared thermally as described in the next section. The formation of **4d** from **2d** upon sensitized irradiation can be understood in terms of initial *E*–*Z* isomerisation to give the *E* isomer **3d** followed by a thermal 1,5-hydrogen shift in **3d** to give **4d** and serves to confirm the stereochemistry of **2d**. If this mechanism is correct, then the thermal 1,5-hydrogen shift must be rapid since the *E* isomer did not build up to concentrations observable by NMR when the sensitization experiment was performed in an NMR tube. Also, since the concentration of *E* isomer remains too low for it to be detected, it follows that the hydrogen shift leading to **4d** must be thermal rather than photochemical since the concentration of **3d** never becomes high enough to absorb any light or to be sensitized by the sensitizer.

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The possibility that the rearrangement of **3d** to **4d** might occur for the other siloxy dienes prepared was examined. Dienes **3a**, **3b**, and **3c** were apparently stable and survived preparative GC and prolonged heating in benzene-*6-d*. In addition, the reaction did not procede in reverse: heating dienes **4a** and (*Z*)-**4b** under the same conditions did not result in formation of **3a** and **3b**, respectively. Dienes **3b**, **3c**, and (*Z*)-**4b** were prepared by sensitized photochemical *E*–*Z* isomerization of **2b**, **2c**, and (*E*)-**4b**; (*E*)-**4b** was prepared thermally as described below.

The structures of the *E* and *Z* siloxy diene isomers **2e** and **3e** derived from dypnone, **1e**, cannot be assigned from their ^{1}H NMR spectra; the assignment of the *Z* geometry to the first formed isomer is based upon analogy with the other compounds studied. The assignment is supported by the observation that formation of the siloxy dienes under equilibrating thermal conditions (described below) produces exclusively the siloxy diene first formed in the photochemical experiment and assigned the *Z* stereochemistry. Inspection of the dienes **2e** and **3e** suggests that the *Z* diene should be the more stable as in this geometry the 1-phenyl substituent is more able to adopt the planar conformation necessary for conjugation with the diene system.

Thermal Preparation of Siloxy Dienes. The procedures which have been reported for thermal preparation of siloxy dienes from α,β-unsaturated ketones include heating with chlorotrimethylsilane in DMF in the presence of triethylamine[5a,b,7a,b,h] (procedure B), treatment with chlorotrimethylsilane in benzene in the presence of a Lewis acid catalyst[16,17] (procedure C), and treatment with a strong base (e.g., lithium diisopropylamide) followed by chlorotrimethylsilane[5a,b,7a–k] (procedure D). The literature reports suggest that with few exceptions (see ref 17 and footnote k in Table I) procedure D produces 2-siloxy 1,3-dienes derived from the kinetic dienolate resulting from deprotonation of the α' position of the unsaturated ketone. Similarly, the major products from procedure C are the "kinetic" siloxy dienes. Procedure B is less predictable; in some cases the dienes derived from the kinetic dienolate are produced,[7b] while in others those from the equilibrium dienolates are obtained.[5a,b,7a] An alternative to procedure C ("procedure E") for the production and trapping of equilibrium dienolates has been reported for one ketone (**1a**) which involves treatment of the ketone with potassium hydride followed by chlorotrimethylsilane.[5a] The only reported product was the siloxy diene **2a** or **3a** (the stereochemistry was not described). This procedure does not appear to have been systematically investigated for other unsaturated ketones.

In order to determine whether the general conclusions concerning the procedures A–D reached above were applicable to the ketones **1a–f**, the products derived from these ketones by some of these procedures were examined; the results are summarized in Table I along with the relevant literature reports for these compounds.

The results given in Table I indicate that, for the ketones examined, conditions B, C, and D all give the siloxy diene derived from the kinetic dienolate as the major product and this selectivity is greatest for procedure D. The exceptions are ketone **1a**, which gives substantial amounts of siloxy diene **2a** along with **4a** when subjected to procedure B, and ketone **1e** which cannot form a kinetic dienolate.

It has been reported[25] that the thermodynamically more stable enol ether of 2-methylcyclohexanone is formed regioselectively when cyclohexanone is treated with the magnesium salt of diisopropylamine and chlorotrimethylsilane. This procedure was also examined for the enone **1a** to determine if any regioselectivity of siloxy diene formation could be obtained. However, the reaction did not yield siloxy dienes; the major products were recovered ketone and polymeric material.

Conclusions

The results reported here indicate that trapping of dienols produced photochemically from simple β-alkyl-α,β-unsaturated ketones results in the regioselective formation of (*Z*)-2-siloxy 2,4-dienes with a high degree of stereoselectivity and allows their isolation in useful yields on the gram scale. The procedure complements the thermal reactivity of these ketones which can be converted to 2-siloxy 1,3-dienes under a variety of conditions, the best of which is quantitative formation of the kinetic dienolate with strong base followed by trapping with chlorotrimethylsilane.

Experimental Section

General Methods. DMF was dried over activated molecular sieves; THF was distilled from sodium benzophenone ketyl immediately prior to use. Care was taken to exclude moisture from all reactions. GC was performed on SE30 stationary phases. Polar column packings were found to hydrolyze the siloxy dienes. Chlorotrimethylsilane and triethylamine were distilled before use as were all the ketones. Ketones **1a** and **1c** were commercial samples; ketone **1b** was prepared by acid-catalyzed condensation of acetone with paraldehyde[20] (this procedure was found to yield a mixture of **1b** and **1a**) and also by treatment of (*E*)-2-butenoic acid with 2 equiv of methyllithium.[21] Ketone **1d** was prepared by dehydrohalogenation of 4-chloro-3,4-dimethyl-2-pentanone in quinoline[22] and **1e** was prepared by condensation of acetophenone.[23] Ketone **1f** was a commercial sample of the natural product and was purified by the literature method.[24] ^{1}H NMR spectra were routinely recorded at 60 MHz and characterization samples were recorded at 100 MHz or 200 MHz as noted. Mass spectra were recorded at 70 eV.

Irradiations (Procedure A in Table I). Large-Scale Irradiations. To a rapidly stirred solution of ketone **1c** (300 mmol) and imidazole (20 g) in DMF (300 mL) was added chlorotrimethylsilane (22 mL). A 450-W medium pressure mercury lamp (Hanovia) housed in a Pyrex sleeve inside a water-cooled quartz well was immersed in the solution. The solution was irradiated for 18 h and during this time the progress of the reaction was followed by GC of worked up aliquots. When the starting ketone had been consumed the solution was transferred to a dropping funnel and was added dropwise to a vigorously stirred ice cold suspension of $NaHCO_3$ (27 g) in saturated aqueous $NaHCO_3$ (250 mL) over a period of 15 min. The resulting mixture was immediately extracted with pentane (3 × 150 mL); the combined pentane extracts were washed with saturated aqueous $NaHCO_3$ (75 mL) and dried over $MgSO_4$ containing a small quantity of $NaHCO_3$. Following filtration the solvent was removed by distillation and the residue was distilled under reduced pressure to give a major fraction: bp 54–64 °C/20 mmHg; yield 1.46 g (28%). ^{1}H NMR analysis of the product indicated that it contained **2c** and **3c** in the ratio 93:7. Spectral data for the products below are given below.

This procedure was also carried out for ketones **1a**, **1b**, and **1d**. The yields of products obtained are given in Table I, and the spectral characterization data are given below. The products from ketones **1a**, **1b**, and **1d** distilled at 68–72 °C/30mm, 57–75 °C/23mm, and 59–76 °C/13mm, respectively.

Small-Scale Irradiations. Imidazole (1.75 g, 0.0257 mol) was weighed into a dry flask and DMF (25 mL), ketone **1a** (0.3 mL, 0.25 g, 0.0026 mol), and $ClSiMe_3$ (1.6 mL, 1.36 g, 0.013 mol) were added. A portion (10 mL) of the solution obtained was placed in a dry Pyrex tube and held in front of a medium pressure mercury lamp (Hanovia, 450 W) supported inside a quartz water

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jacket. The reaction progress was followed by gc of worked up aliquots. After 20-h irradiation the reaction mixture was added dropwise to a vigorously stirred suspension of $NaHCO_3$ (11 g) in cold water (100 mL) and immediately extracted into pentane (2 × 50 mL) and the combined extracts were dried ($MgSO_4$). GC analysis indicated a mixture of **2a**, **3a**, and **4a** in the ratio 94:4:2, respectively. Irradiation for longer periods of time resulted in higher yields and an increased proportion of isomer **3a**. The presence of the cyclobutanol derivative **8** was also indicated in 4% yield, and this yield also increased at longer irradiation times. Following filtration and evaporation of the organic extract, the residue was dissolved in $CDCl_3$ and a known weight of benzene was added. From the ^1H NMR spectrum the absolute yield of the major product **2a** was determined as 40%; in an experiment where the reaction was taken to higher conversion the yield of **2a** was raised to 51% but 5% of **3a** was also formed (i.e. **2a**:**3a** = 91:9. In a small-scale irradiation where absolute yields were not determined but the variation in the proportion of **2a**:**3a**:**8** was determined with time, after 16-h irradiation the ratio was 71:14:15 and had become 52:21:27 after a further 8-h irradiation. A sample of the product was purified by preparative GC to give **2a**, **3a**, and **8**.

For **2a**: ^1H NMR ($CDCl_3$, 200 MHz) 4.88 (1 H, pentuplet, J = 0.8), 4.81 (1 H, ddq, J = 0.5, 0.8, 2.7), 4.59 (1 H, dq, J = 0.8, 2.7), 1.81 (3 H, dt, J = 0.8, 0.5), 1.73 (3 H, s), 0.11 (9 H, s); ^1H NMR toluene-*8-d*, 100 MHz) 5.08 (1 H, m), 5.04 (1 H, m), 4.84 (1 H, m), 2.04 (3 H, broadened singlet), 1.66 (3 H, broadened singlet), 0.11 (9 H, s); MS, *m/e* 170 (relative intensity) (M^+, 19), 155 (74), 75 (54), 73 (100); M^+ found 170.1124, $C_9H_{18}OSi$ requires 170.1127.

For **3a**: ^1H NMR (100 MHz, $CDCl_3$) 5.21 (1 H, br s), 4.80 (1 H, br s), 4.65 (1 H, br s), 4.65 (1 H, br s), 1.90 (3 H, br s), 1.79 (3 H, br s), 0.18 (9 H, s) [irradiation of the methyl groups resulted in the signal at 5.21 ppm becoming a doublet (J = 1.2 Hz), that at 4.8 ppm became a doublet (J = 2.4 Hz), and that at 4.65 became a double doublet (J = 1.2, 2.4 Hz). The methyl at 1.90 ppm was sharpened when the vinyl H at 5.21 ppm was irradiated and the methyl at 1.79 was sharpened when the vinyl protons at 4.80 and 4.65 were irradiated together.]; MS, *m/e* (relative intensity) 170 (M^+, 24), 155 (80), 75 (52), 73 (100); M^+, found 170.1125, $CH_{18}OSi$ requires 170.1127.

For **8**: ^1H NMR (100 MHz, $CDCl_3$) 4.76 (2 H, m), 2.85 (2 H, br A of AB, J = 16 Hz), 2.55 (2 H, br B of AB, J = 16 Hz), 1.32 (3 H, s), 0.05 (9 H, s); MS, *m/e* (relative intensity) 169 (M^+ −1, 7), 155 (62), 75 (52), 73 (100); highest mass ion, found 169.1043, $C_9H_{17}OSi$ requires 169.1049.

The ketones **1b–f** were irradiated under the above conditions and on similar scales to yield **2b–f** and **3e** following separation by preparative GC.

2b: ^1H NMR (200 MHz, $CDCl_3$) 6.56 (1 H, dt, J = 17.3, 10.5 Hz), 5.25 (1 H, double sextet, J = 10.5, 0.7 Hz), 4.96 (1 H, double doublet of pentuplets, J = 17.3, 2.2, 0.7 Hz), 4.78 (1 H, double doublet of pentuplets, J = 10.5, 2.2, 0.7 Hz), 1.84 (3 H, q, J = 0.7 Hz), 0.22 (9 H, s); ^1H NMR (200 MHz, C_6D_6) 6.92 (1 H, dt, J = 17, 10 Hz), 5.33 (1 H, double sextet, J = 10, 0.8 Hz), 5.12 (1 H, double doublet of pentuplets, J = 17, 2.2, 0.7 Hz), 4.96 (1 H, double doublet of pentuplets, J = 10, 2.2, 0.7 Hz), 1.68 (3 H, q, J = 0.7 Hz).

2c: ^1H NMR (200 MHz, $CDCl_3$) 6.91 (1 H, X of ABX, J = 11, 17.5 Hz), 4.93 (1 H, ddq B of ABX allylically coupled to CH_3, J = 17.5, 1.7, 0.7 Hz), 4.85 (1 H, ddq, A of ABX allylically coupled to CH_3, J = 11, 1.7, 0.7 Hz), 1.86 (3 H, br s), 1.64 (3 H, s), 0.13 (9 H, s); ^1H NMR (200 MHz, C_6D_6) 7.28 (1 H, X of ABX, J = 11, 17.5 Hz), 5.06 (1 H, B of ABX, J = 17.5, 1.7 Hz), 5.00 (1 H, A of ABX, J = 11, 1.7 Hz), 1.71 (3 H, s), 1.65 (3 H, s), 0.10 (9 H, s); MS, *m/e* (relative intensity) 170 (M^+, 32), 155 (42), 75 (45), 73 (100), M^+ found, 170.1125, $C_9H_{18}OSi$ requires 170.1127; IR ν_{max} (neat) 3100 (w), 2970 (m), 1640 (s), 1255 (s), 1200 (s), 1010 (s), 950 (s), 850 (s), 760 (m) cm^{-1}.

2d: ^1H NMR (200 MHz, $CDCl_3$) 4.76 (1 H, m), 4.68 (1 H, m), 1.77 (3 H, br s), 1.72 (3 H, br s), 1.58 (3 H, br s); MS, *m/e* (relative intensity) 184 (M^+, 45), 179 (75), 75 (56), 73 (100), M^+ found, 184.1285, $C_{10}H_{20}OSi$ requires 184.1283; IR ν_{max} (neat) 3070 (w), 2960 (s), 1660 (m), 1630 (sh), 1250 (s), 1215 (s), 1005 (s), 890 (s), 835 (s), 745 (s) cm^{-1}.

2e: ^1H NMR (200 MHz, $CDCl_3$) 7.52–7.0 (10 H, m), 5.88 (1 H, d, J = 1 Hz), 5.64 (1 H, dd, J = 1.2 Hz), 5.45 (1 H, d, J = 2 Hz), 0.31 (9 H, s).

3e: ^1H NMR (200 MHz, $CDCl_3$) 7.5–7.0 (10 H, m), 5.69 (1 H, dd, J = 1, 1.5 Hz), 5.19 (1 H, dd, J = 1, 1.5 Hz), 4.88 (1 H, t, J = 1.5 Hz).

2f: ^1H NMR (200 MHz, $CDCl_3$) 4.65 (1 H, A of ABX_3, J = 2.4, 1.4 Hz), 4.62 (1 H, B of ABX_3, J = 2.4, 0.8 Hz), 2.3–1.5 nm), 1.4–0.9 (m), −0.03 (9 H, s); MS, *m/e* (relative intensity) 224 (M^+, 65), 209 (91), 75 (37), 73 (100), M^+ found 224.1596, $C_{13}H_{24}OSi$ requires 224.1596; IR ν_{max} (neat) 3070 (w), 2950 (S), 2910 (s), 2870 (s), 2830 (s), 1650 (m), 1625 (m), 1250 (s), 1195 (s), 1140 (s), 850 (s), 750 (m).

General Procedure for Thermal Preparations of Siloxy Dienes. Three thermal procedures were used: procedure B (treatment of the ketone with $ClSiMe_3$ in DMF at 80 °C in the presence of Et_3N), procedure C (treatment of the ketone with $ClSiMe_3$ in C_6H_6 in the presence of Et_3N and $ZnCl_2$), and procedure D (addition of a THF solution of the ketone to a THF solution of lithium diisopropylamide followed by addition of $ClSiMe_3$.

Procedures B. The procedure is from that described by Jung and McCombs for the conversion of methyl vinyl ketone to 2-(trimethylsiloxy)-1,3-butadiene.[18] Et_3N (1.7 mL, 1.23 g, 0.0122 mol), and DMF (8 mL) were placed in a dry reaction flask and maintained under an atmosphere of dry nitrogen. 4-Methyl-3-penten-2-one, **1a**, (0.58 mL) in DMF (2 mL) was added to the reaction flask followed by $ClSiMe_3$ (1.30 mL) in DMF (2 mL). The mixture was heated in an oil bath maintained at a temperature of 80 °C for 15 h. The cooled reaction mixture was filtered through a plug of glass wool into a dropping funnel and then added dropwise to a vigorously stirred suspension of $NaHCO_3$ (1.5 g) in ice cold water (20 mL). When the addition was complete the mixture was immediately extracted with pentane (3 × 20 mL). The combined pentane extracts were washed with aqueous $NaHCO_3$ (20 mL) and dried ($MgSO_4$ and a pinch of $NaHCO_3$). Following filtration and removal of the pentane by distillation at atmospheric pressure a brown oil was obtained (1.68 g) which GC analysis indicated contained a mixture of siloxy dienes **2a**, **3a**, and **4a** in the ratio 39:4:57. The ^1H NMR speectrum of a weighed sample of the mixture in the presence of a known amount of added C_6H_6 indicated that the absolute yields of **2a**, **3a**, and **4a** were 25%, 2.5%, and 38%, respectively. The relative yields of the three products varied with the time of reaction and temperature of heating; 20 h at 90 °C gave **2a**, **3a**, and **4a** in the ratio 40:10:50, and at 120 °C the ratios after 1 h and 24 h were 47:7:46 and 52:15:33, respectively. Samples of the three isomeric siloxy dienes were separated by preparative GC.

For **4a**: ^1H NMR (100 MHz, $CDCl_3$) 5.47 (1 H, br s), 4.15 (1 H, s), 4.06 (1 H, s), 1.80 (3 H, br s), 1.66 (3 H, br s), 0.11 (9 H, s); ^1H NMR (200 MHz, C_6D_6) 5.68 (1 H, s), 4.38 (1 H, s), 4.26 (1 H, s), 1.92 (1 H, s), 1.62 (1 H, s), 0.18 (9 H, s); MS, *m/e* (relative intensity) 170 (M^+, 28), 155 (100), 75 (95), 73 (91), M^+ found, 170.1122, $C_9H_{18}OSi$ requires 170.1127; IR ν_{max} (CCl_4) 3100 (w), 2980 (m), 2920 (m), 1640 (m), 1255 (s), 1025 (s), 855 (s) cm^{-1}.

The procedure was also carried out for ketones **1b–f**. The yields of the products are given in Table I.

For **4b**: ^1H NMR (200 MHz, $CDCl_3$) 5.96 (1 H, dq, J = 15, 5 Hz), 5.86 (1 H, d, J = 15 Hz), 4.18 (2 H, s), 1.74 (3 H, d, J = 5 Hz), 0.20 (9 H, s); ^1H NMR (200 MHz, C_6D_6) 6.12 (1 H, dq, J = 15, 7 Hz), 5.88 (1 H, dq, J = 15, 1.5 Hz), 4.29 (1 H, q, J = 0.5 Hz), 4.23 (1 H, q, J = 0.5 Hz), 1.58 (3 H, ddt, J = 7, 1.5, 0.5 Hz), 0.17 (9 H, s).

For **4c**: ^1H NMR (200 MHz, $CDCl_3$) 5.93 (1 H, q, J = 7 Hz), 4.29 (1 H, s), 4.12 (1 H, s), 1.63 (3 H, s), 1.60 (3 H, d, J = 7 Hz), 0.10 (9 H, s); ^{13}C NMR ($CDCl_3$) 157.2 (4°), 131.7 (4°), 122.7 (CH), 90.8 (CH_2), 13.82 (CH_3), 12.80 (CH_3), 0.062 (CH_3); MS, *m/e* (relative intensity) 170 (M^+, 15), 155 (100), 75 (45), 73 (30), M^+ found 170.1131, $C_9H_{18}OSi$ requires 170.1127; IR ν_{max} (neat) 3120 (w), 2950 (s), 1595 (s), 1295 (s), 1255 (s), 1150 (s), 1025 (s), 850 (s) cm^{-1}; UV λ_{max} (pentane) 233 nm (log ϵ 3.91).

For **4d**: ^1H NMR (200 MHz, $CDCl_3$) 4.24 (1 H, br s), 3.97 (1 H, br s), 1.73 (3 H, s), 1.64 (3 H, br s), 1.58 (3 H, s), 0.094 (9 H, s); ^1H NMR (200 MHz, C_6D_6) 4.49 (1 H, s), 4.21 (1 H, s), 1.85 (3 H, s), 1.83 (3 H, s), 1.53 (3 H, s), 0.18 (9 H, s); ^{13}C NMR ($CDCl_3$) 158.0 (4°), 129.7 (4°), 127.9 (4°), 93.8 (CH_2), 22.5 (CH_3), 20.6 (CH_3), 17.0 (CH_3), 0.16 (CH_3); MS, *m/e* 184 (M^+), 169, 75, 73 (base), M^+ found 184.1280, $C_{10}H_{20}OSi$ requires 184.1283; IR ν_{max} (neat) 3100 (w), 2950 (s), 1620 (s), 1300 (s), 1250 (s), 1225 (s), 1130 (m), 1100 (s), 1010 (s), 840 (s), 745 (m).

For **4f**: ^1H NMR (100 MHz, $CDCl_3$) 4.76 (1 H, d, *J* = 4 Hz), 2.6–1.8 (4 H, m), 1.92 (3 H, s), 1.65 (3 H, s), 1.35–1.1 (1 H, m), 0.92 (3 H, d, *J* = 7 Hz), 0.11 (9 H, s); MS, *m/e* (relative intensity) 224 (M^+, 23), 209 (100), 75 (9), 73 (24), M^+ found 224.1584, $C_{13}H_{24}OSi$ requires 224.1596.

Procedure C was performed for the ketones **1a** and **1b** using a method derived from that described by Danishefsky.[19]

Procedure C. In a dried flask was placed $ZnCl_2$ (anhydrous, 0.026 g) and Et_3N (2.0 mL). The mixture was stirred under a dry nitrogen atmosphere for 1 h before 3-penten-2-one, **1b**, (0.517 g) in C_6H_6 (1 mL) was added followed by $ClSiMe_3$ (1.60 mL). The mixture was stirred for 2 h and then heated in an oil bath maintained at a temperature of 80 °C for 9 h. The cooled reaction mixture was filtered through a plug of glass wool into a dropping funnel and worked up as described under procedure B to give a mixture of **2b**, **3b**, and **4b** in the ratio 9:7:84 as determined by ^1H NMR. The reaction was performed similarly for ketone **1a**, except that the mixture was not heated, to give **2a**, **3a**, and **4a** in the ratio 14:1:85.

Procedure D was performed on ketone **1d** only.

Procedure D. In a dried flask, under an atmosphere of dry nitrogen, were placed dry THF (4 mL) and a crystal of 2,2′-bipyridyl indicator. The solution was cooled in an ice bath and diisopropylamine (0.62 mL) was added followed by a hexane solution of butyllithium (5.5 mL of a 0.73 M solution). After 5 min, 3,5-dimethyl-3-penten-2-one, **1d**, (0.54 mL) in dry THF (2 mL) was added dropwise to the well-stirred purple solution. Excess $ClSiMe_3$ (2.0 mL) was then added to the reaction mixture, and after 30 min of further stirring the reaction mixture was worked up as described for procedure B to give 1.24 g of a yellow oil. The GC of the product indicated that the yield was in excess of 90%. A sample of the product was purified by preparative GC to give **4d** identical with a sample prepared by procedure C.

***E–Z* Isomerization of Siloxy Dienes. *E–Z* Isomerization of 2c.** The siloxy diene **2c** (0.12 g) was dissolved in benzene (10 mL) in a quartz tube and irradiated with a low pressure mercury lamp (254-nm light). The reaction was followed by GC and after 2 h approximately half of **2c** had been converted to the geometrical isomer **3c**. The benzene was evaporated and the residue purified by GC to give a mixture of **2c** and **3c**. The ^1H NMR of the mixture in C_6D_6 indicated similar quantities of **2c** and **3c**. For **3c**: ^1H NMR (C_6D_6) 6.69 (1 H, X of ABX, *J* = 17, 11 Hz), 5.11, 4.97 (2 H, AB of ABX, *J* = 17, 11, 1.5 Hz), 1.86 (3 H, s), 1.75 (3 H, s), 0.07 (9 H, s).

***E–Z* Isomerization of 2b.** The siloxy diene **2b** (0.0112 g) was dissolved in C_6D_6 (ca. $^1/_3$ mL) in a quartz NMR tube containing biphenyl (0.1105 g) and the tube was suspended adjacent to a low pressure mercury lamp. Under these conditions the lamp emits mainly at 254 nm and the biphenyl absorbs all the light. The progress of the reaction was followed by ^1H NMR which indicated that after 4 h **2b** and **3b** were present in the ratio 9:8. The mixture of isomers was stable in the absence of light (i.e., their ratio remained unchanged) over a period of 380 h at room temperature and they survived preparative GC at 80 °C. For **2c**: ^1H NMR (200 MHz, C_6D_6) 6.40 (1 H, ddd, *J* = 17.3, 10.9, 10.3 Hz), 6.67 (1 H, double sextuplet, *J* = 10.9, 0.7), 5.08 (1 H, dd, *J* = 17.3, 2.2 Hz), 4.90 (1 H, double doublet of sextuplets, *J* = 10.3, 2.2, 0.7 Hz), 1.75 (3 H, t, *J* = 0.7 Hz).

***E–Z* Isomerization of (*E*)-4b.** The (*E*)-siloxy diene **4b** (0.0195 g) was dissolved in C_6D_6 (ca. $^1/_3$ mL) in a quartz NMR tube and irradiated with a low pressure mercury lamp for 5 h as described for **2b**. In this reaction the solvent served as the sensitiser. The 200-MHz ^1H NMR spectrum of the mixture of (*E*)- and (*Z*)-**4b** indicated that they were present in the ratio 70:30, respectively. The mixture of *E* and *Z* isomers was stable (i.e., their ratio remained unchanged) over a period of 22 h at 80 °C (the NMR tube was suspended in the vapors of boiling benzene and the ^1H NMR spectrum rerecorded). For (*Z*)-**4b**: ^1H NMR (200 MHz, $CDCl_3$) 6.25 (1 H, dq, *J* = 16, 7 Hz), 5.80 (1 H, dq, *J* = 16, 1.5 Hz), 4.29 (1 H, s), 4.23 (1 H, s), 1.29 (3 H, dd, *J* = 7, 1.5 Hz).

Registry No. **1a**, 141-79-7; **1b**, 78-94-4; **1c**, 1567-73-3; **1d**, 684-94-6; **1e**, 22573-24-6; **1f**, 15932-80-6; **2a**, 76915-32-7; **2b**, 103322-97-0; **2c**, 103322-98-1; **2d**, 103322-99-2; **2e**, 103323-00-8; **2f**, 76430-27-8; **3a**, 99884-75-0; **3b**, 103323-05-3; **3c**, 103323-01-9; **3e**, 103323-02-0; **4a**, 6651-46-3; (*E*)-**4b**, 81802-34-8; (*Z*)-**4b**, 103323-06-4; (*E*)-**4c**, 103323-03-1; **4d**, 103323-04-2; **4f**, 58898-35-4; **8**, 81459-09-8.

Synthesis of Phosphinamides in the 5,6-Oxaphosphabicyclo[2.2.2]octene Series as Possible Precursors of Metaphosphoramidates[1]

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The readily dimerizable 1-aminophosphole oxides were found to function as dienes in the Diels–Alder reaction with *N*-phenylmaleimide, thereby providing phosphinamides with the 7-phosphanorbornene structure. The dimers also possess this structural feature, which has been subjected to the oxygen-insertion reaction with *m*-chloroperbenzoic acid. The Diels–Alder adducts react cleanly to provide the insertion product at the P–C bond, providing the 5,6-oxaphosphabicyclo[2.2.2]octene ring system; the dimers undergo reaction first at the phosphinamide nitrogen of the 2-phospholene ring and then at the 7-phosphanorbornene P–C bond. Stereochemical features of an aminophosphole oxide dimer and of the O-insertion product of a Diels–Alder adduct were unequivocally established by X-ray crystal structure analyses. The O-insertion occurred with retention of the configuration at phosphorus. ^{31}P and ^{13}C NMR spectra were also of value in structure assignments. The 5,6-oxaphosphabicyclo[2.2.2]octene prepared from the Diels–Alder adduct was completely decomposed by loss of the bridging phosphorus on heating in toluene at 100 °C for 30 h. On the assumption that the fragment may be a metaphosphoramidate, trapping experiments with cyclohexanol and benzylamine were attempted. Only the latter gave a phosphorylation product, but since it greatly increased the rate of phosphorus debridging, it must be directly involved in a process that causes the ejection of the bridge. Intermediates in this process were detected by ^{31}P NMR.

Ring strain in the 7-phosphanorbornene (7-PNB) system is of such magnitude that special chemical properties, not found in simpler systems, can arise. Among these properties is the insertion of oxygen by peracids into a C–P bond, a process reminiscent of the Baeyer–Villiger reaction with ketones. This reaction was first demonstrated with phosphine oxides[2,3] in the 7-PNB system and then with

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[2] Kashman, V.; Awerbouch, O. *Tetrahedron Lett.* **1975**, *31*, 53.