

Table I. Yields of Monochloropermethylpolysilanes

<i>n</i>	% Me(SiMe ₂) _{<i>n</i>} Cl	% Me(SiMe ₂) _{<i>n</i>} Me
2	58	19
3	67	16
4	82	8
6	90	5

Table II. Nmr Chemical Shifts^a

Compound	-SiMe ₂ Cl	-SiMe ₂ -	-SiMe ₃
Me(SiMe ₂) ₂ Cl	0.432		0.147
Cl(SiMe ₂) ₂ Cl	0.532		
Me(SiMe ₂) ₃ Cl	0.478	0.163	0.129
Cl(SiMe ₂) ₃ Cl	0.520	0.258	
Me(SiMe ₂) ₄ Cl	0.447	0.138, 0.165	0.092
Cl(SiMe ₂) ₄ Cl	0.498	0.245	
Me(SiMe ₂) ₆ Cl	0.427	0.225, 0.204, 0.197, 0.123	0.070
Cl(SiMe ₂) ₆ Cl	0.484	0.243, 0.269	

^a All shifts are expressed in ppm downfield from TMS and were obtained from 60-MHz spectra of dilute ethyl ether solutions at 30° with cyclohexane as the internal standard.

At least three conceivable explanations for the observed high yields must be considered. (1) The dichloropolysilane may form a chelate intermediate with magnesium in the Grignard reagent. (2) The monochloropolysilane and dichloropolysilane may differ significantly in reactivity toward methylmagnesium iodide. This would involve an electronic effect being transmitted through the silicon chain causing the dichloropolysilane to be more reactive toward the methylmagnesium iodide. (3) A catalytic redistribution of Cl(SiMe₂)_{*n*}Cl and Me(SiMe₂)_{*n*}Me to give Me(SiMe₂)_{*n*}Cl may take place in the presence of MgX₂ or MeMgX. A similar redistribution occurs for the disilanes in the presence of AlCl₃.⁹ Reid and Wilkins¹⁰ and Corriu and Henner¹¹ have discussed the role of intermediates in the reaction of Grignard reagents with haloorganosilanes.

Successive portions of methylmagnesium iodide were added to a solution of 1,4-dichlorooctamethyltetrasilane at -20°. No methylmagnesium iodide was detected by nmr until a stoichiometric amount had been added. Further addition resulted in the methylmagnesium iodide remaining for several minutes indicating that the monochlorotetrasilane reacts much more slowly with methylmagnesium iodide than does the dichlorotetrasilane. Similar results were obtained with 1,6-dichloropermethyloctasilane, but the reaction was slower and as a result was studied at 10°. No spectral feature resulted which could be attributed to a long-lived intermediate species. These results tend to support the transmission of an electronic effect through the silicon chain but cannot rule out completely either of the other two possibilities.

A mixture of Me(SiMe₂)₆Me and Cl(SiMe₂)₆Cl in ethyl ether containing anhydrous MgCl₂, MgI₂, or MeMgI did not react during 2 days to form any Me(SiMe₂)₆Cl. Thus, the high yields are not due to catalytic redistributions.

For the determination of the relative importance of the transmission of electronic effects and the formation

(9) H. Sakurai, K. Tominaga, and M. Kumada, *Bull. Chem. Soc. Jap.*, **39**, 1820 (1966).

(10) A. F. Reid and C. J. Wilkins, *J. Chem. Soc.*, 4029 (1955).

(11) R. J. P. Corriu and B. J. L. Henner, *J. Chem. Soc., Chem. Commun.*, 116 (1973).

of a chelate intermediate, ClMe₂Si(CH₂)₄SiMe₂Cl¹² was treated with methylmagnesium iodide. The resulting yields were 26% for Me₃Si(CH₂)₄SiMe₃¹⁴ and 47% for Me₃Si(CH₂)₄SiMe₂Cl¹⁶ and correspond approximately to a statistical distribution of products. Therefore, the dominating effect for the above reactions of polysilanes appears to be the transmission of electronic effects through the silicon chain.

The above results are consistent with the high yields of monochloropolysilanes being a consequence of a considerable difference in reactivity of the monochloro- and dichloropolysilanes toward methylmagnesium iodide. The trend in yields may be attributable to the chlorines being more strongly bound in the longer chains. This trend may reflect increased back-donation of electrons from the chlorine into a vacant polysilane orbital with increasing chain length. The greater reactivity of the dichloropolysilanes can be explained by the transmission of the effect of the second chlorine through the silicon chain *via* molecular orbitals.

The nmr data in Table II, as well as the above chemical evidence, are consistent with the transmission of electronic effects through silicon chains. In each case, the proton resonance of the -SiMe₂Cl group occurs at a higher field for Me(SiMe₂)_{*n*}Cl than for the corresponding Cl(SiMe₂)_{*n*}Cl. No variation of δ_{-SiMe₂Cl} was observed in the Me₃Si(CH₂)₄SiMe₃, Me₃Si(CH₂)₄SiMe₂Cl, ClMe₂Si(CH₂)₄SiMe₂Cl series (δ_{-SiMe₃} 0.025, δ_{-SiMe₂Cl} 0.390).

This study has shown that the Grignard method can be readily used to prepare 1-chloro permethylated polysilanes as a result of the transmission of electronic effects through silicon chains. For the tetra- and hexasilanes, the Grignard reaction is particularly advantageous since other convenient methods give side reactions.

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(12) Prepared by addition of BrMg(CH₂)₄MgBr in tetrahydrofuran to excess Me₂SiCl₂ at 0°: bp 50-52° (1 mm) (lit.¹³ 70-72° (4 mm)); yield 61%. *Anal.* Calcd for C₈H₂₀Si₂Cl₂: Cl, 29.14. Found: Cl, 29.08.

(13) M. Ishikawa, M. Kumada, and H. Sakurai, *J. Organometal. Chem.*, **23**, 63 (1970).

(14) Bp 30° (1 mm) (lit. 193° (732 mm)); *n*_D²⁰ 1.4259 (lit.¹⁵ 1.4260).

(15) L. H. Sommer and G. R. Ansul, *J. Amer. Chem. Soc.*, **77**, 2482 (1955).

(16) *Anal.* Calcd for C₈H₂₀Si₂Cl: Cl, 15.90. Found: Cl, 15.91.

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A Novel Cyclization of Diallenic Sulfones

Sir:

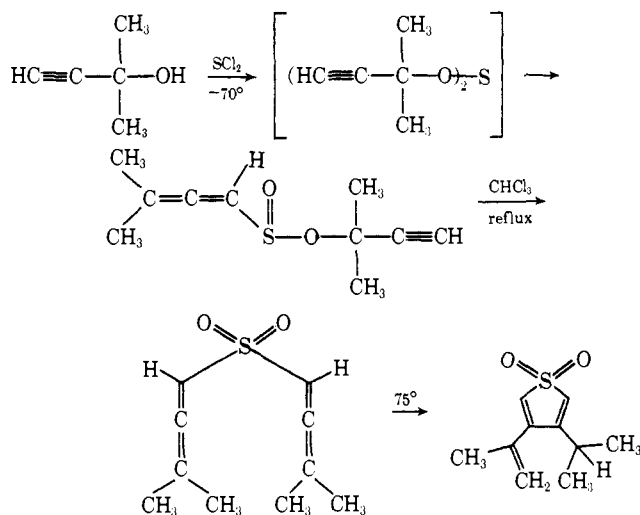
In view of the vast amount of interesting work performed so far on intermolecular reactions of monoallenic systems,¹ it is quite surprising that the study of intramolecular reactions of diallenic systems has received relatively little attention in the past. The Cope-type

(1) For reviews on this subject see (a) J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 1 (1962); (b) K. Griesbaum, *Angew. Chem., Int. Ed. Engl.*, **5**, 933 (1966); (c) D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967); (d) J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Forsch.*, **15**, 281 (1970); (e) T. Okamoto, *Bull. Inst. Chem. Res., Kyoto Univ.*, **50**, 450 (1972).

rearrangement of 1,2,6,7-cyclodecatetraene to 2,3-divinyl-1,3-cyclohexadiene at 300° has been reported by Skattebøl^{2a} and by Harris.^{2b} Somewhat analogous behavior has been reported for the rearrangement of 1,2,6,7-octatetraene^{2a,c,d} and of *o*-dipropadienylbenzene.^{2e} Conjugated diallenes undergo thermal cyclization to derivatives of 3,4-dimethylenecyclobutenes^{2a,f,g} and have been suggested as intermediates in the rearrangement of 1,5-hexadiynes to the same type of products.^{2h,i}

The lack of considerable activity on diallenic systems may be a consequence of the difficulty to synthesize such compounds by simple methods. Prompted by our success to obtain diallenic sulfones by a very convenient method involving a double [2,3]sigmatropic rearrangement of propargylic sulfoxylates³ (Scheme I),

Scheme I



we have recently decided to undertake an investigation of the thermal behavior of these compounds. We have found that the tetramethyldiallenyl sulfone shown in Scheme I (mp 62°)⁴ undergoes facile cyclization on heating at 75° to the thiophene 1,1-dioxide derivative (mp 68–69°),⁴ in quantitative yield. This transformation is most easily detected by inspection of the change in the nmr (CDCl₃, 100 MHz) from a two signal spectrum, δ 1.82 (d, 12 H), 6.0 (septet, 2 H), for the reactant to a six signal spectrum for the product, δ 1.12 (d, 6 H, $J = 7$ Hz), 1.98 (d, 3 H, $J = 1$ Hz), 2.73 (septet, 1 H, $J = 6.5$ Hz), 5.12 (d, 1 H, $J = 1$ Hz), 5.28 (m, 1 H), 6.30 (sharp m, 2 ring protons).⁵

(2) (a) L. Skattebøl and S. Solomon, *J. Amer. Chem. Soc.*, **87**, 4506 (1965); (b) J. F. Harris, Jr., *Tetrahedron Lett.*, 1359 (1965); (c) W. R. Roth, M. Heiber, and G. Erker, *Angew. Chem., Int. Ed. Engl.*, **12**, 504 (1973); (d) W. Grimme and H. J. Rother, *ibid.*, **12**, 505 (1973); (e) C. M. Bowes, D. F. Montecalvo, and F. Sondheimer, *Tetrahedron Lett.*, 3181 (1973); (f) F. Toda, H. Ishihara, and K. Akagi, *ibid.*, 2531 (1969); (g) H. Hopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 732 (1970); (h) W. D. Huntsman and H. J. Wristers, *J. Amer. Chem. Soc.*, **89**, 342 (1967); (i) T. J. Henry and R. G. Bergman, *ibid.*, **94**, 5103 (1972).

(3) This synthesis is based on previous work on [2,3]sigmatropic rearrangements of propargylic and allylic sulfoxylates and sulfoxylates. See S. Braverman and H. Mechoulam, *Isr. J. Chem.*, **5**, 71 (1967); S. Braverman and Y. Stabinsky, *Chem. Commun.*, 270 (1967); *Isr. J. Chem.*, **5**, 125 (1967); S. Braverman, *Int. J. Sulfur Chem.*, **C**, 6, 149 (1971), and references cited therein; R. Tang and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 2100 (1970), and references cited therein; G. Smith and C. J. M. Stirling, *J. Chem. Soc. C*, 1530 (1971); Q. E. Thompson, *J. Org. Chem.*, **30**, 2703 (1965).

(4) All new compounds gave satisfactory elemental analysis, as well as nmr, ir, and mass spectral data in accord with the assigned structures.

Starting with γ -deuterio-, and γ -bromo- α,α -dimethyl-propargyl alcohols, the corresponding 2,5-dideuterio- and 2,5-dibromothiophene 1,1-dioxides were obtained.⁴ The nmr spectra of these products were very similar to that of the original one, except for the absence of the peak at δ 6.30 as expected.

A kinetic study of this novel cyclization in various solvents indicated that the rate of rearrangement was practically insensitive to the change in ionizing power of the solvent (see Table I). This result rules out the op-

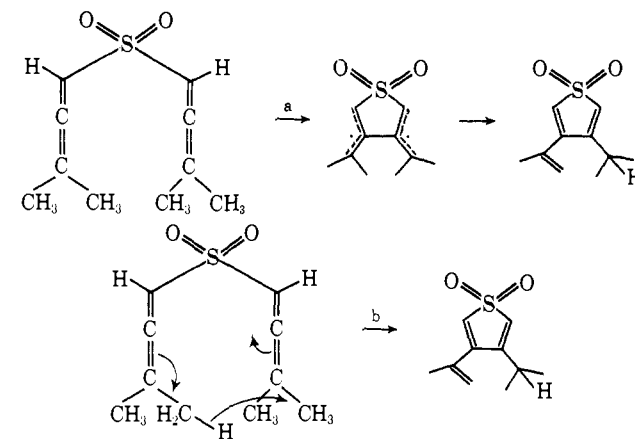
Table I. Rate Constants^a for the Rearrangement of Bis- γ,γ -dimethylallyl Sulfone^b to 3-Isopropenyl-4-isopropylthiophene 1,1-Dioxide at 75.0°

Solvent	10 ⁵ k, sec ⁻¹	Solvent	10 ⁵ k, sec ⁻¹
Chloroform	7.48 ± 0.17	Acetonitrile	8.15 ± 0.22
Ethyl acetate	7.97 ± 0.30	Methanol	8.11 ± 0.56
Acetone	6.14 ± 0.33		

^a Determined by nmr. ^b [Sulfone] = 0.05 M.

eration of an ionic mechanism and is reminiscent of the results obtained by Kiefer⁷ on the allene-olefin cycloaddition. There seem to be two possible mechanisms which are consistent with the observed solvent effect (Scheme II).

Scheme II



The first possible mechanism (a) is a two-step process involving intramolecular formation of a 2,2'-bisallyl-type diradical intermediate in the first, rate determining stage, followed by a fast intramolecular hydrogen abstraction and formation of the new double bond. Obviously, this interpretation parallels that advanced for allene dimerizations^{1,8} only with respect to the first stage of the reaction. The occurrence of hydrogen transfer instead of ring closure of the diradical in the second stage can be explained tentatively by steric effects. The second possible mechanism (b) is based on the assumption that the reaction is essentially an intra-

(5) Further support for the assigned structure of the cyclization product was obtained through its reduction with zinc, acetic acid, and hydrochloric acid⁶ to 3,4-diisopropylthiophene: nmr (CDCl₃, 100 MHz) δ 6.86 (s, 2 aromatic protons), 2.95 (septet, 2 H, $J = 7$ Hz), 1.21 (d, 12 H, $J = 6$ Hz).

(6) F. G. Bordwell and W. H. McKellin, *J. Amer. Chem. Soc.*, **73**, 2251 (1951).

(7) E. F. Kiefer and M. Y. Akamura, *J. Amer. Chem. Soc.*, **90**, 4187 (1968).

(8) T. L. Jacobs and R. C. Kammerer, *J. Amer. Chem. Soc.*, **94**, 7190 (1972).

molecular ene reaction,^{9,10} or alternatively it can also be regarded as a variant of the symmetry-allowed 1,5-hydrogen shift.¹¹ Obviously, further work is required before a final conclusion can be reached with regard to the exact mechanism.

Besides the mechanistic aspects of this unique cyclization, we are presently engaged on an examination of its synthetic utility¹² and on an exploration of its scope by a study of other diallenic and related systems.

Acknowledgment. The authors are grateful to Professor M. Sprecher for stimulating comments and discussions.

(9) H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969); for recent reports on ene reactions of alkylallenes with various enophiles see ref 10.

(10) H. H. Wasserman and L. S. Keller, *Chem. Commun.*, 1483 (1970); D. C. England and C. G. Krespan, *J. Org. Chem.*, **35**, 3322 (1970); J. C. Martin, P. L. Carter, and J. L. Chitwood, *ibid.*, **36**, 2225 (1971); H. A. Chia, B. E. Kirk, and D. R. Taylor, *Chem. Commun.*, 1144 (1971); H. Gotthardt, *Tetrahedron Lett.*, 2343 (1971); D. R. Taylor and D. B. Wright, *J. Chem. Soc., Perkin Trans. 1*, 956 (1973).

(11) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(12) It is of interest to note that while it is quite difficult to obtain thiophene 1,1-dioxides by oxidation of thiophenes,¹³ the present method may afford an easy route for their synthesis. Subsequent reduction can also afford variously substituted thiophenes.

(13) L. A. Paquette, "Principles of Modern Heterocyclic Chemistry," W. A. Benjamin, New York, N. Y., 1968, p 106; C. D. Hurd, *Quart. Rep. Sulfur Chem.*, **4**, 90 (1969).

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Photodecarbonylation of 3-Cyclopentenones. Triplet Pericyclic Reactions¹

Sir:

An interesting mechanistic feature of the pericyclic fragmentations of 3-cyclopentenones (e.g., **1a** and **1b**) results from the prediction of orbital symmetry^{2a} theory that both linear sigmasymmetric or nonlinear axisymmetric decarbonylation are "allowed" in ground state. To the best of our knowledge, no experimental test of these ideas has been reported for any simple member of the 3-cyclopentenone family of structures **1**.³ However, in other pertinent cases, Lemal has reported that diazines such as **2** (which are isoelectronic with 3-cyclopentenones) lose nitrogen by a *sigmasymmetric* pathway.⁴ In the *closest* example related to the work to be reported here, Saltiel⁵ has found that benzene sensitized decomposition of the sulfones, **3**, exhibit preferential *axisymmetric* reactivity. These results can be interpreted in terms of the expected reversal of stereospecificity of a *linear* cycloreversion as one proceeds from a thermal fragmentation to a (π, π^*) photochemical fragmentation.^{2a}

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(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

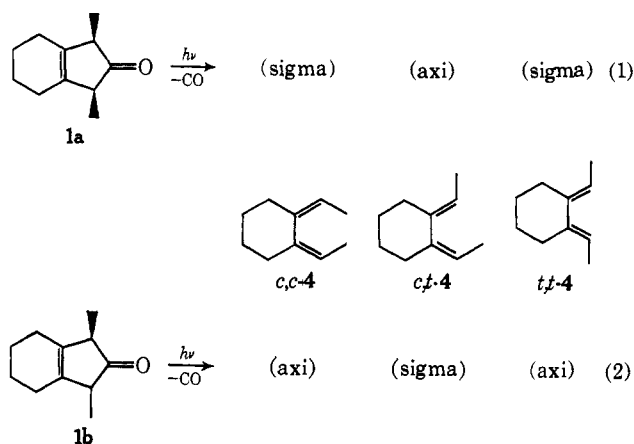
(3) Quinkert observed decarbonylation and subsequent 1,4 closure of the initial photoproducts during the irradiation of 2,5-diphenyl-3,4-benzocyclopentanone: *Angew. Chem., Int. Ed. Engl.*, **10**, 196 (1971).

(4) (a) S. D. McGregor and F. M. Lemal, *J. Amer. Chem. Soc.*, **88**, 1335 (1966); (b) J. E. Baldwin, *Can. J. Chem.*, **44**, 2051 (1966).

(5) J. Saltiel and L. Metts, *J. Amer. Chem. Soc.*, **89**, 2232 (1967).

On the other hand, it appears that the orbital correlation of the n, π^* state of cyclopentenone may not establish favorable preservation or orbital symmetry during fragmentation. Some question exists if such an example falls under the jurisdiction of conventional orbital symmetry rules. Lemal^{4a} has suggested that 3-cyclopentenones might decarbonylate in a sigmasymmetric fashion not only in the ground state but in a n, π^* state as well. Baldwin^{4b} has pointed out that simple MO correlation diagrams do not give a direct prediction of allowedness for n, π^* decarbonylations. So far, no specific predictions relevant to the effect of spin multiplicity have been made in the literature. We report here our results on the photochemistry on the 3-cyclopentenones **1a** and **1b** and show that our data can be interpreted in support of a *dual linear and nonlinear concerted pathway for decomposition via a 3-cyclopentenone triplet*.

Irradiation of **1a** and **1b** in benzene at room temperature results (eq 1 and 2) in efficient loss of carbon



monoxide and quantitative formation of the 1,3-dienes *c,c*-**4**, *t,c*-**4**, and *t,t*-**4**. The yields of 1,3-dienes listed in Table I are extrapolated values which refer to zero con-

Table I

Ketone	ϕ^a	$k_q\tau^b$	Relative % yields ^c		
			<i>c,c</i> - 4	<i>t,c</i> - 4	<i>t,t</i> - 4
1a	0.49	4.3	0.18	0.22	0.60
1b	0.50	2.3	<0.04	0.48	0.52

^a The quantum yields were measured at 313 nm in benzene for the total diene production. ^b The values were obtained for 1,3-pentadiene quenching in benzene at 25°. ^c Extrapolated to 0% conversion, see text.

version as an appropriate correction for sensitized dienes isomerization. Stern-Volmer quenching of reactions 1 and 2 by 1,3-pentadienes occurs but results in *no change* in the relative diene yields of *c,c*-**4**, *c,t*-**4**, and *t,t*-**4**. Stern-Volmer plots were linear to 0.2 M quencher concentration which yield $k_q\tau$ values equal to 4.3 and 2.3 M⁻¹ for **1a** and **1b**, respectively. Comparable 1,3-pentadiene quenching has been reported for cyclopentenone **1c**.⁶

In an effort to determine the role of the singlet state in these reactions, the fluorescence lifetimes of **1b** and the tetramethyl ketone **5** were determined (Table II).

(6) P. S. Engel and H. Ziffer, *Tetrahedron Lett.*, 5181 (1969).