$(SiMe_3)_2$,[13] which has the corresponding structural parameters of 125.5 (1.8)° and 1.735 (12) Å.

Treatment of **1** (1.06 g, 2 mmol) in THF (20 mL) with *n*-BuLi (1.3 mL of a 1.6 M solution in hexane) afforded, after 30 min of stirring, a THF solution of $LiN(SiPh_3)_2$. Then 12-crown-4 (0.7 mL, ~4 mmol) was added by syringe and the resultant solution was stirred for 10 min. Filtration, followed by a reduction in volume under reduced pressure to incipient crystallization and overnight cooling in a −20 °C freezer, gave **2** as colorless crystals. Yield 1.1 g, 58%; mp 178–182 °C. The crystal structure of **2**[12] (Figure 2) shows that separation of the cation and anion is achieved to give the first example of a well-characterized free disubstituted amide (NR_2^-)[14] ion. This occurrence is interesting since 12-crown-4 failed in this respect with both $LiN(SiMe_3)_2$[15] and $LiNPh_2$[16] giving instead the adduct [12-crown-4·$LiNR_2$] (R = $SiMe_3$ or Ph). Success in the case of **2** is probably due to the larger size of the $SiPh_3$ substituent and the more electron withdrawing effect of the $SiPh_3$ (in comparison with $SiMe_3$), which reduces the strength of the Li–N bond. More subtle considerations probably involve a better size match between cation and anion, which affords a greater lattice energy and heat of formation for **2** over the corresponding species with either a $[N(SiMe_3)_2]^-$ or $[NPh_2]^-$ anion.

The most interesting structural parameters for the anion of **2** involve the Si–N–Si angle, 154.9 (3)°, and the Si–N distances, 1.633 (4) and 1.634 (4) Å. The angle is considerably (~19°) wider and the bonds considerably (~0.09 Å) shorter than those of the precursor. These changes are in accord with a greater availability of both nitrogen lone pairs in the absence of the Li^+ ion. The increasing angle at N also implies more p-like orbitals for the lone pairs and a greater p–d (N–Si) interaction, which in turn gives a shorter Si–N bond. As already mentioned $[Ph_3SiNSiPh_3]^-$ is isoelectronic with $[Ph_3PNPPh_3]^+$.[17] It is notable that since the latter species may adopt a large range (ca. 135–180°)[18] of angles at N it is quite probable that the corresponding angle in **2** will be equally variable and may, with the appropriate cation, afford a linear $[Ph_3Si–N–SiPh_3]^-$ array as seen in the isoelectronic species $Ph_3SiOSiPh_3$.[19] This should result in a further decrease in the Si–N bond length probably nearer to the value of 1.568 (3) Å seen for the SiN double bond in the compound $t\text{-}Bu_2Si{=}N{-}Si\text{-}t\text{-}Bu_3$ (**3**).[20] The almost linear structure of this compound also suggests a considerable amount of nitrogen lone pair involvement indicated by $t\text{-}Bu_2Si{=}\overset{\frown}{\ddot{N}}{-}Si\text{-}t\text{-}Bu_3$. This N–Si distance is also shortened having a value of 1.695 (3) Å. Thus the average N–Si length in **2** is almost exactly equal to the mean of the N–Si bond lengths, 1.632 (3) Å, observed in **3**.

Acknowledgment. We thank the National Science Foundation (CHE-8618739) for financial support and Dr. Marilyn Olmstead for useful discussions.

Supplementary Material Available: Tables of data collection and refinement, atom coordinates, thermal parameters, bond distances and angles, and hydrogen coordinates (19 pages). Ordering information is given on any current masthead page.

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Regioselective Photoisomerization of Fluoro Aryl Dienes. Role of Dipolar Intermediates of Excited Dienes[†]

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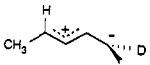
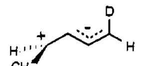
Recently, Squillacote and Semple[1] reported regioselective isomerization of 1-deuterio-*trans*-1,3-pentadiene at the less substituted 1,2-center. The result was attributed to preferential formation of the orthogonal allyl (cation)–methylene (anion) (**1a**) intermediate. This suggestion was thought to be consistent with the calculated results[2] of such a dipolar structure being more stable than the oppositely polarized structure (**1b**), the latter first postulated by Dauben following the observation of a stereoselective cyclization of ethylidenecyclooctene.[3] However, the result is also consistent with the reaction being directed by differences in mass or in reaction volume.[4] Now we report cases of regioselective isomerization of substituted dienes where the results are more likely to be dominated by the polar substituents and are consistent with selective formation of the Dauben intermediate.

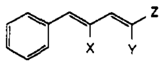


1a



1b

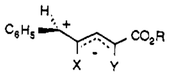
Compounds prepared for this study are aryl diene esters (**2**, **4**, **5**, and **6**) and aldehyde (**3**) with or without fluorine substituents.



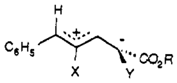
2: X=Y=H, Z=CO_2R
3: X=Y=H, Z=CHO
4: X=H, Y=F, Z=CO_2R
5: X=F, Y=H, Z=CO_2R
6: X=Y=F, Z=CO_2R

In most cases the all-trans and the monocis geometric isomers were isolated from synthetic mixtures or photomixtures, and the dicis isomer was isolated from reaction of C_2-fluorophosphonate[5] with *cis*-cinnamaldehyde. The structures of the isomers were deduced from their ^1H and ^{19}F NMR spectra (data presented in the supplementary material). The all-trans isomers were then irradiated, with the progress of the reaction followed by HPLC or F NMR. With the exception of compound **2**, all isomerization reactions are highly regioselective, favoring formation of the 4-cis isomer. Selected data are listed in Table I. We might add that because of the minute amount of the minor product for compounds **3**–**6**, it was necessary to reach close to 20% conversion before it was possible to measure the product distribution.

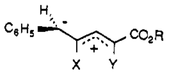
Of the four possible zwitterionic intermediates (**7a**–**d**) it is clear that only structures **7a** and **7c** could lead to selective isomerization at the 4,5-bond. However, the nature of the substituents in these



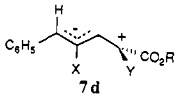
7a



7b



7c



7d

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Table I. Photoisomerization of Aryl Dienes (**2–6**) in Hexane[a,b]

compd	% conv[c]	% product dist	
		2-cis	4-cis
2	5[d,e]	70	30
3	22[d]	3	97
4	24[d,f]	5	95
5	26[d,f]	<2	>98
6	15[d]	6	94

[a] Degassed solutions of all-trans isomers of aryl dienes in hexane (~0.01 M) were irradiated in Pyrex tubes for 3–25 min with a Hanovia 550-W medium-pressure Hg lamp. [b] For compound **3**, a 0–54 Corning glass filter was used. [c] Higher conversions reported for accurate determination of minor components. [d] Analyzed by HPLC on an Altex 5-μm silica gel column. An HP-1040A diode array detector system was connected in conjunction with a single-wavelength detector. Data corrected for absorbance at detecting wavelength. [e] At higher conversions comparable amounts of dicis isomer are produced. [f] Analysis by ^{19}F NMR.

compounds (i.e., Z being highly electron withdrawing) could safely rule out participation of structure **7c**. Hence, for compound **2** the ester group has apparently added sufficient stabilization to the transition state going to the Dauben intermediate **7a**, making its formation competitive with that of **7b**, which is otherwise thought to be more favored, e.g., in the hydrocarbon series.[1] But, with the addition of highly electron withdrawing fluorine substituent at either or both termini of the allyl anion (**4–6**) or the replacement of the ester group by the more electropositive aldehyde group (**3**),[6] formation of the Dauben intermediate apparently becomes competitively the dominant one.

We stress in the above discussion the importance of *relative ease of formation of the zwitterionic intermediates* and *not* the relative stability of the intermediates in determining product distributions. The difference is nontrivial when one considers that the direction of photoisomerization is determined by competitive twisting of double bonds of the Franck–Condon species while relative stability of the zwitterionic species is a thermodynamic parameter which may or may not have a significant effect on a nonreversible kinetic process cascading down the excited singlet potential surface. The polar effect being detected in this work must be a manifestation of the developing polar character[2b] of the structure corresponding to the barriers of twisting the planar excited diene. Taking this into consideration, it is then not surprising that other effects such as steric and medium effects could readily become a more dominant kinetic factor in determining the direction of twisting of the planar diene structure as revealed by an earlier study of the polyenes from this laboratory.[4] Consistent with this explanation is our added observation that a methyl substituent at the β-carbon (3-methyl-**4**) reverses the regioselectivity, making isomerization at the α,β center 4 times more favored than at the γ,δ center. For the nonpolar pentadiene system,[1] the regioselective chemistry could simply be reflecting the different masses at the two reaction centers.

We might add that the current proposal of selective formation of the Dauben intermediate in photoisomerization of negatively substituted dienes appears to be consistent with other examples of regioselective isomerization of polyenes in the literature. Hence, it was reported that removal of the 13-methyl group (hence absence of steric repulsion) in retinal results in elimination of the 13-cis isomer in photoisomerization of the all-trans isomer[7] (hence selective formation of the allyl (anion)–heptatrienyl (cation) intermediates while the same isomer is the major product in the parent retinal.[8] Also, consistent with the involvement of such intermediates is the observation that fluorine substituents in the retinal analogues appear to cause a noticeable preference for isomerization at a site adjacent to the substituted double bond.[9]

In summary, we believe that the current systems involving more polar substituents more convincingly reveal the fact that the polar character of the excited state plays a significant role in directing position of isomerization. Selective formation of the two possible intermediates is also dependent on the nature of the substituent on the chromophore. Furthermore, it should be noted that photocyclization is a different reaction where symmetry restriction could forbid possible reaction from one, but not the other, zwitterionic intermediate. Hence, detection of a specific reaction does not ensure that the corresponding intermediate is lower in energy. No such restrictions are present in the geometric isomerization reaction. Therefore, one must be cautious in applying any interpretation derived from the isomerization reaction to the more restricted cyclization process.

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Supplementary Material Available: ^{1}H and ^{19}F NMR data of isomers of compounds **2–6** (1 page). Ordering information is given on any current masthead page.

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Water Suppression in Two-Dimensional Spin-Locked Nuclear Magnetic Resonance Experiments Using a Novel Phase-Cycling Procedure

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A prerequisite for the determination of three-dimensional structures of proteins by NMR is the sequential assignment of proton resonances by means of two-dimensional techniques that rely on through-bond and through-space connectivities.[1] For through-bond connectivity, the power of the recently introduced homonuclear Hartmann–Hahn (HOHAHA) techniques[2-6] has been clearly demonstrated.[7-11] Because all the NOE's used for assignment purposes involve the NH protons[1] (with the exception of $C^{\alpha}H(i)$–$C^{\beta}H(i + 3)$ NOE's), it is essential to correlate the NH

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