and Mn_2Ge cores)[3,9] so is the Cr_3Se anion of **2** isoelectronic with the neutral Mn_3Ge compound **4** (Chart I).

The central selenium atom provides formally all available valence electrons for bonding to the three $(\eta^5\text{-}C_5H_5)Cr(CO)_2$ fragments ($d^5\text{-}ML_5$); the latter are isolobal with CH and CH_2^+ fragments, so that a structural relationship with *exo*-methylenecyclopropane exists for the anion of **2** as well as for the neutral compound **4** on account of the isolobal mapping Se $\leftarrow\!\circ\!\rightarrow$ C^{2-} $\leftarrow\!\circ\!\rightarrow$ CH^- (for **2**) and Ge $\leftarrow\!\circ\!\rightarrow$ C as well as $(\eta^5\text{-}C_5H_5)Mn(CO)_2$ $\leftarrow\!\circ\!\rightarrow$ CH_2 (for **4**).[10]

The ^1H NMR spectra of the Cr_3Se complex **2** shows that the molecule is fluxional in solution. At −80 °C three well-resolved C_5H_5 signals appear, two of which broaden as the temperature is raised and form a single resonance at −40 °C. This observation is in agreement with a cis/trans isomerization of the dinuclear fragment $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2$. The appearance of *one* sharp signal for the exocyclic $(\eta^5\text{-}C_5H_5)Cr(CO)_2$ moiety within the entire temperature range and at exactly the same chemical shift indicates that free rotation of this fragment occurs about the associated CrSe bond on the NMR time scale, which indicates the presence of triple bond contributions to this entity.[9]

Compound **2** is extremely sensitive to oxygen. Thus, upon exposure to air the starting material **1** is rapidly produced, albeit not quantitatively. The complex is stable in solution only at temperatures well below ambient but rapidly decomposes at room temperature to give the selenium-free salt $[Co(\eta^5\text{-}C_5H_5)_2]^+[(\eta^5\text{-}C_5H_5)Cr(CO)_3]^-$ [11a] and the cubane-type cluster compound $(C_5H_5)_4Cr_4Se_4$ [11b] (X-ray structure analyses).

The formation of the diamagnetic polynuclear anion of the ionic complex **2** from a one-electron reduction of a diamagnetic starting material is a special case of what may turn out to be a new area for synthetic endeavor: the study of the secondary reactions of the initially formed radical anions.

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(9) Cf.: Kostic, N. M.; Fenske, R. F. *J. Organomet. Chem.* **1982**, *233*, 337.

(10) Review: Hoffmann, R. *Angew. Chem.* **1982**, *94*, 725; *Angew. Chem. Int. Ed. Engl.* **1983**, *21*, 711.

(11) (a) Herrmann, W. A.; Rohrmann, J.; Herdtweck, E.; Riede, F.; Ziegler, M. L.; Sergeson, G. *Chem. Ber.*, in press. (b) Black crystals, insoluble in all common organic solvents. IR (cm^{-1}, KBr) 3102 w, 1872 m, 1431 m, 1005 m, 802 vs.

γ-Silicon Stabilization of Carbonium Ions

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Received November 25, 1985

Silyl substitution on the γ-carbon has recently been shown experimentally to have large effects on the stability of carbocation intermediates.[1] Further, these effects are strongly orientation dependent. In this paper, we offer an explanation of these results based on theoretical calculations on some model compounds.

Extensive theoretical and experimental results[2,3] have shown that the stabilization of H^- exchange between carbocations

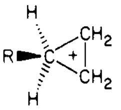
$$RCH_2^+ + HCH_3 \rightarrow RCH_3 + HCH_2^+$$

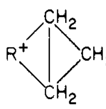
caused by silyl in the α-position is more effective than hydrogen by about 17 kcal/mol but less effective than methyl by about the same amount. Because α-silyl destabilizes an alcohol by about 7 kcal/mol, silyl is less stabilizing than methyl by 6–8 kcal/mol for OH^- exchange between cations. These α effects are regarded as inductive and hyperconjugative.

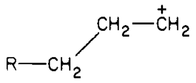
Wierschke et al.[2] have recently published a theoretical study of β-silyl. They concluded that the inductive effect was about equivalent to that of methyl but that the SiC bond was much more effective at hyperconjugative stabilization of the adjacent $\text{-}CH_2^+$ than was a CC bond. This was deduced from the strong orientation dependence of the stabilization energy which was maximum for a coplanar arrangement of the empty p orbital on the $\text{-}CH_2^+$ and the SiC bond.

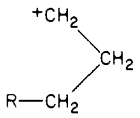
In γ-substituted compounds, one is always comparing hyperconjugation with a CC bond vs. hyperconjugation with CH bonds, so a strong dependence of the hyperconjugation on substituent is unexpected. Also, a γ substituent seems too far removed from the α site to exert much of an inductive effect. Nevertheless the experimental data show a large orientational dependence for γ-trimethylsilyl stabilization.

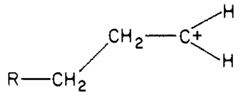
We have calculated RHF energies with various basis sets and symmetry-constrained geometry optimization. The symmetry constraints allow us to examine model conformations typical of the more constrained molecules studied experimentally. We have considered H, CH_3, SiH_3, and Li γ substitution of the propyl carbocation and alcohol. The alcohol was in a planar, all trans configuration with respect to RCCCOH. Several configurations were considered for each cation. The labels in Table I correspond to


cor (C_s)


edg (C_s)


tra-per (C_s)


cis-per (C_s)


tra-pla (C_s)

Here -per refers to a terminal CH_2^+ group perpendicular to the C–C–C mirror plane while -pla refers to a terminal CH_2^+ group lying in the C–C–C mirror plane. A few of the most critical optimized angles and bond lengths are included in Table I.

The stabilization energies (SE) in Table I for the different propyl cations were computed relative to the trans-perpendicular conformation. In the process of doing this calculation, we found that the 3-21G geometry, reported in The Carnegie-Mellon Archive,[4] was not fully optimized. The 1-propyl cation potential surface is unusually flat, so large geometry changes are possible with little change in energy. This is apparent in the small energy change in going from the trans-perpendicular structure, through the corner-protonated form, to the cis-perpendicular structure.[5] Because the surface is so flat, the results are also very basis set dependent with corner protonated lowest for 3-21G, trans perpendicular lowest for 6-31G, and cis perpendicular lowest for 6-31G*. In the latter case no trans-perpendicular stationary energy could be found. The flatness of the energy surface makes one anticipate that chemical substitution will also produce large changes in geometry.

For the other compounds in Table I, the stabilization energy is defined as the RHF energy for OH^- exchange with the *corresponding* conformation of propyl.

$$R(CH_2)_3^+ + H(CH_2)_3OH \rightarrow R(CH_2)_3OH + H(CH_2)_3^+$$

Cis-perpendicular silyl and trans- and cis-perpendicular lithium

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(1) Shiner, V. J., Jr.; Ensinger, M. W.; Kriz, G. S. *J. Am. Chem. Soc.* **1986**, *108*, 842.

(2) Wierschke, S. C.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496.

(3) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806.

(4) Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. *Carnegie-Mellon Quantum Chemistry Archive*, 2nd ed.; 1981. Starting with the geometry reported there, we reproduced their energy and gradient. Further optimization with a tighter criteria for convergence led to the structure reported here. The main change was that the C_α–C_γ distance increased from 2.05 to 2.12 Å while the maximum gradient component decreased from 0.000288 to 0.000117.

(5) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649.

0002-7863/86/1508-3135$01.50/0

Table I. Stabilization Energies of Various Conformations

R	shape	basis	SE[a]	C_α–C_γ[c]	C_α–C_β[c]	C_β–C_γ[c]	H–C_β–H[b]	H–C_β[c]	–*E*[d]
H	cor	6-31	–0.7	1.88	1.38	1.88	117	1.07	117.3069
H	edg	6-31	–10.3	1.81	1.49	1.49	118	1.07	117.2915
H	tra-per	6-31	0.0	2.25	1.41	1.66	113	1.08	117.3080
H	cis-per	6-31	–0.1	2.04	1.39	1.71	115	1.07	117.3078
H	tra-pla	6-31	–2.2	2.54	1.44	1.53	100	1.10	117.3045
H	2-propyl	6-31	17.3	2.59	1.45	1.45		1.08	117.3356
H	hydroxy	6-31		2.53	1.52	1.53	107	1.08	193.0320
H	propane	6-31		2.54	1.53	1.53	108	1.09	118.2162
H	cor	3-21	0.0	1.93	1.37	1.93	118	1.07	116.7053
H	tra-per	3-21	0.0	2.12	1.38	1.78	117	1.07	116.7053
H	cis-per	3-21	–0.0	2.01	1.38	1.84	117	1.07	116.7053
H	cor	6-31*		1.82	1.37	1.82	117	1.07	117.3592
H	cis-per	6-31*		1.89	1.38	1.74	118	1.08	117.3594
CH_3	cor	6-31	2.3	1.93	1.37	1.93	117	1.07	156.3289
CH_3	tra-per	6-31	3.1	2.30	1.40	1.69	114	1.08	156.3312
CH_3	cis-per	6-31	–2.8	2.40	1.40	1.74	114	1.08	156.3216
CH_3	tra-pla	6-31	1.4	2.54	1.44	1.53	100	1.10	156.3251
CH_3	edg	6-31	–17.6	1.86	1.48	1.48	117	1.07	156.2817
CH_3	hydroxy	6-31		2.54	1.52	1.53	107	1.09	232.0503
CH_3	propane	6-31		2.55	1.53	1.53	106	1.09	157.2347
CH_3	tra-pla	6-31*		2.54	1.44	1.53	100	1.10	156.3882
CH_3	tra-per	6-31*		2.11	1.38	1.71	116	1.08	156.3954
SiH_3	cor	6-31	4.4	1.90	1.37	1.90	117	1.07	407.3384
SiH_3	tra-per	6-31	10.0	1.82	1.40	1.67	115	1.07	407.3484
SiH_3	tra-pla	6-31	–0.1	2.54	1.44	1.53	100	1.10	407.3288
SiH_3	edg	6-31	13.5	1.68	1.49	1.49	117	1.07	407.3375
SiH_3	hydroxy	6-31		2.53	1.52	1.54	107	1.09	483.0565
SiH_3	propane	6-31		2.56	1.53	1.54	106	1.09	408.2405
SiH_3	tra-per	6-31*		1.75	1.39	1.67	116	1.07	407.4488
SiH_3	tra-pla	6-31*		2.55	1.44	1.53	100	1.10	407.4248
Li	cor	6-31	42.2	2.13	1.35	2.13	117	1.07	124.1933
Li	edg	6-31	94.5	1.57	1.49	1.49	115	1.08	124.2778
Li	tra-pla	6-31	23.0	2.57	1.45	1.52	99	1.10	124.1638
Li	hydroxy	6-31		2.58	1.52	1.54	106	1.09	199.8511

[a] kcal/mol relative to tra-per 1-propyl for propyl cations, relative to corresponding 1-propyl conformation for other cations. [b] Bond angle in degrees. [c] Bond length in Å. [d] RHF energy in hartrees. Other relevant 6-31G RHF energies: CH_4 –40.1806; CH_3^+ –39.2162; OH^- –75.3118; $SiH_3CH_2CH_3$ –369.2217; $SiH_3CH_2CH_2^+$ –368.3477; $CH_3CH_2CH_3$ –118.2162; SiH_3CH_3 –330.2073; CH_3CH_3 –79.1976; $HCH_3CH_3^+$ –79.4068; $CH_3CH_3CH_3^+$ –369.4958; $CH_3CH_2^+$ –78.2807.

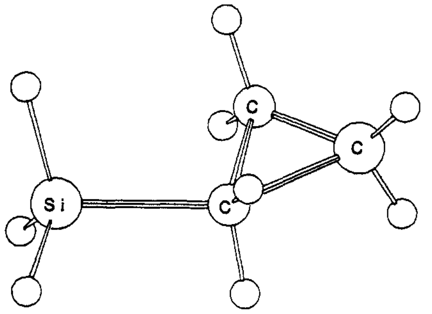

Figure 1. 6-31G* SCF optimized structure for the trans-perpendicular 3-silylpropyl cation.

are missing because they spontaneously changed to another structure upon optimization. All basis sets used were from Pople and co-workers[6] except that the 6-31G silicon basis of Gordon was used.[7,8] Correlation and zero-point corrections would change these results somewhat, but the principle trends are already visible.[9,10]

Table II. Mulliken Charges on Molecular Fragments

R	shape	basis	R	$C_\gamma H_2$	$C_\beta H_2$	$C_\alpha H_2$	OH
H	cor	6-31	0.29	–0.01	0.36	0.36	
H	edg	6-31	0.30	0.18	0.28	0.18	
H	tra-per	6-31	0.30	–0.04	0.11	0.64	
H	cis-per	6-31	0.27	0.02	0.21	0.51	
H	tra-pla	6-31	0.24	–0.05	0.09	0.73	
H	hydroxy	6-31	0.16	–0.17	0.04	0.32	–0.36
H	cor	3-21	0.34	–0.01	0.34	0.34	
H	tra-per	3-21	0.36	–0.05	0.15	0.54	
H	cis-per	3-21	0.33	0.00	0.24	0.43	
H	cor	6-31*	0.30	–0.01	0.36	0.36	
H	cis-per	6-31*	0.30	–0.01	0.29	0.42	
CH_3	cor	6-31	0.20	0.13	0.34	0.34	
CH_3	tra-per	6-31	0.21	0.09	0.10	0.60	
CH_3	cis-per	6-31	0.19	0.20	0.07	0.60	
CH_3	tra-pla	6-31	0.15	0.08	0.08	0.71	
CH_3	hydroxy	6-31	0.00	–0.02	0.05	0.32	–0.36
CH_3	edg	6-31	0.29	0.25	0.22	0.25	
CH_3	tra-pla	6-31*	0.10	0.08	0.12	0.69	
CH_3	tra-per	6-31*	0.20	0.08	0.20	0.52	
SiH_3	cor	6-31	0.52	–0.22	0.35	0.35	
SiH_3	tra-per	6-31	0.61	–0.30	0.29	0.41	
SiH_3	tra-pla	6-31	0.45	–0.25	0.10	0.71	
SiH_3	hydroxy	6-31	0.28	–0.34	0.08	0.33	–0.36
SiH_3	edg	6-31	0.68	0.04	0.24	0.04	
SiH_3	tra-per	6-31*	0.53	–0.18	0.29	0.36	
SiH_3	tra-pla	6-31*	0.35	–0.16	0.12	0.69	
Li	cor	6-31	0.75	–0.16	0.21	0.21	
Li	edg	6-31	0.85	–0.02	0.21	–0.02	
Li	tra-pla	6-31	0.64	–0.35	0.04	0.66	
Li	hydroxy	6-31	0.51	–0.44	0.02	0.30	–0.38

Methyl can be seen to exert a weak inductive stabilization on all the structures except cis perpendicular. Silyl, on the other hand,

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(6) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; Defrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(7) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

(8) The Pople 6-31G basis for Si gave -407.3500 for tra-per $SiH_3C_3H_6^+$ at the geometry obtained with the Gordon basis.

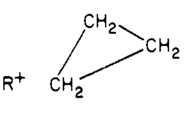
(9) Relative to SE defined by H^- exchange with methane, the 6-31G basis RHF energies show β-silyl to be 57 kcal/mol stabilizing compared to 35 kcal/mol for methyl. This definition gives 45 kcal/mol as the stabilization energy of $SiH_3–(CH_2)_3^+$ and 38 kcal/mol for $CH_3–(CH_2)_3^+$. Of more relevance, relative to SE defined by H^- exchange with ethane, β-silyl is 26 kcal/mol stabilizing compared to 5.5 kcal/mol for methyl. Relative to SE defined by H^- exchange with propane, γ-silyl is 10.1 kcal/mol stabilizing compared to 2.9 kcal/mol for methyl. These latter numbers can be compared with the OH^- exchange SE of Table I for the tra-per orientation.

strongly favors the trans-perpendicular structure. Judging from the CC bond lengths, this is not because of improved hyperconjugation. Rather, the C_α–C_γ distance is greatly shortened compared to CH_3, because of an enhanced tendency toward ring closing with SiH_3. Thus, the silyl group causes a new resonance structure to become important. Figure 1 shows the trans-perpendicular silyl structure resulting from the 6-31G* calculation.

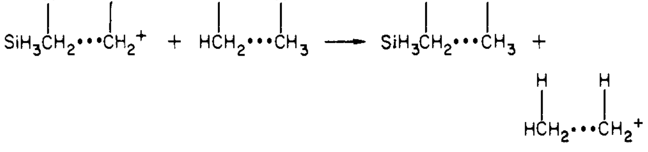
Inspection of the Mulliken charges on the CH_2 groups in Table II clarifies what is happening. The silyl group exerts a large inductive effect on the adjacent CH_2. In the trans-perpendicular conformation this negative CH_2 is able to bond directly to the positive cation carbon to form a closed cyclopropane-like structure. Thus in addition to the usual hyperconjugation resonance structures,

$$R{-}CH_2{-}CH_2{-}CH_2^+ \leftrightarrow R{-}CH_2^+{\cdots}CH_2{=}CH_2$$

one must also consider the ionic structure



For Li this latter structure completely dominates, and geometry optimization leads to edge-lithiated cyclopropane with a huge, orientation-specific stabilization energy. Because of the electropositive nature of SiH_3, the edge-silylated structure is also considerably stabilized relative to edge-protonated or edge-methylated cyclopropane. This resonance structure will continue to exert a strong effect even for very long intervening chains provided the carbon adjacent to silicon can get close to C_α. Since connection by a long intervening chain is equivalent to no connection at all, a hint of the asymptotic limit can be seen from the fact that $SiH_3CH_3{\cdots}CH_3^+$ is stabilized relative to H^- exchange with $HCH_3{\cdots}CH_3^+$



$$\overset{H}{\overset{|}{SiH_3CH_2}}{\cdots}\overset{H}{\overset{|}{CH_2^+}} + \overset{H}{\overset{|}{HCH_2}}{\cdots}\overset{H}{\overset{|}{CH_3}} \longrightarrow \overset{H}{\overset{|}{SiH_3CH_2}}{\cdots}\overset{H}{\overset{|}{CH_3}} + \overset{H}{\overset{|}{HCH_2}}{\cdots}\overset{H}{\overset{|}{CH_2^+}}$$

by 39.1 kcal/mol while $CH_3CH_3{\cdots}CH_3^+$ is stabilized by only 1.5 kcal/mol in this comparison.

These model calculations have provided a straightforward theoretical explanation of the otherwise surprising experimental results. They characterize for the first time a general intramolecular mode of electronic interaction whereby electropositive substituents in the γ-position can stabilize carbonium ions.

Acknowledgment. This work was partially supported by NSF Grant CHE-84-13552 and used VAX11-780 and FPS 164 computers whose purchase was partially funded by NSF Grants CHE-83-09446 and CHE-84-05851.

Registry No. $(CH_2)_3{\cdot}H^+$, 17806-70-1; $CH_3CH^+CH_3$, 19252-53-0; $CH_3CH_2CH_2^+$, 19252-52-9; $CH_3CH_2CH_2OH$, 71-23-8; $CH_3CH_2CH_2$, 74-98-6; $(CH_2)_2CH(CH_3){\cdot}H^+$, 27733-92-2; $CH_3CH_2CH_2CH_2^+$, 25453-90-1; $CH_3CH_2CH_2CH_2OH$, 71-36-3; $CH_3CH_2CH_2CH_3$, 106-97-8; $(CH_2)_2CH(SiH_3){\cdot}H^+$, 101932-92-7; $SiH_3CH_2CH_2CH_2^+$, 101932-93-8; $SiH_3CH_2CH_2CH_2OH$, 75967-15-6; $SiH_3CH_2CH_2CH_3$, 13154-66-0; $LiCH_2CH_2CH_2^+$, 101932-94-9; $LiCH_2CH_2CH_2OH$, 101932-95-0.

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(10) The effect of polarization basis functions and electron correlation have been considered for the four critical structures—silyl and methyl, tra-per and tra-pla. For methyl the trans-perpendicular structure is 3.8 kcal/mol below the trans planar at the 6-31G RHF level. This increases to 4.5 kcal/mol at the 6-31G* RHF level and increases further to 8.1 kcal/mol when electron correlation is included (with the 6-31G* basis set). For silyl the perpendicular form is 12.3 kcal/mol more stable with 6-31G RHF, 15.0 kcal/mol more stable with 6-31G* RHF, and 25.1 kcal/mol more stable when electron correlation is included. This larger correlation effect is associated with the increased resonance between the Si^+ and C^+ structures. The electron correlation in these examples was computed by using our standard MRSD-CI method with perturbation extrapolation to the basis set limit.

Liquid-Crystalline Solvents as Mechanistic Probes. 22. The Influence of Smectic Order of *n*-Butyl Stearate and Lyotropic Gels on the Diastereomeric Ratio of Cyclobutanols from the Norrish II Reactions of Aliphatic, Linear Ketones[1]

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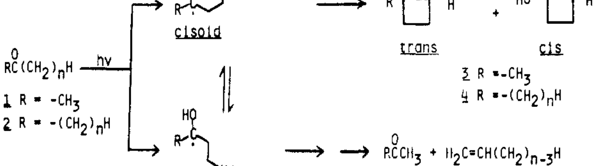
Received January 16, 1986

Recently, we demonstrated that liquid-crystalline solvents are capable of mediating the dynamics of 1,4-biradicals generated during the Norrish II reactions of ketones.[1,2] In this work, we examine the Norrish II reaction (eq 1) of a series of 2- and *sym-n*-alkanones (**1** and **2**) in the smectic B phase of *n*-butyl stearate (BS) and in the smectic B-like 50% aqueous gel phases of potassium stearate (KS), potassium palmitate (KP), and an equimolar mixture of potassium stearate/1-octadecanol (KSO).[3a,4]



Alkanones with chains longer than 12 carbons exhibit Norrish II quantum efficiencies which are relatively insensitive to temperature and solvent viscosity; their singlet and triplet reaction components maintain a nearly constant ratio.[5] For ketones like **1** and **2**, available evidence indicates that the cyclization products **3** and **4** emanate from cisoid 1,4-biradicals, and elimination products arise primarily from transoid 1,4-biradicals.[2a,6] The ratio of cyclobutanol diastereomers is controlled by a combination of intramolecular steric effects and intermolecular medium influences.

The use of lyotropic gels as a new type of ordered medium for investigating solute reactivity offers a well-characterized bridge between nonaqueous liquid crystals and more disordered lyotropic systems (lipid bilayers, vesicles, and micelles). Even within the gels, gradations of order are apparent from measures of Norrish II reactivity of the solutes. In fact, we find that the trans/cis ratio of diastereomeric cyclization products[7] (**3** or **4**) depends much

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(1) For Part 21, see: Zimmermann, R. G.; Liu, J. H.; Weiss, R. G., submitted for publication in *J. Am. Chem. Soc.*

(2) (a) Hrovat, D. A.; Liu, J. H.; Turro, N. J.; Weiss, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7033. (b) Nerbonne, J. M.; Weiss, R. G. *Isr. J. Chem.* **1979**, *18*, 266.

(3) (a) Krishnamurti, D.; Krishnamurthy, K. S.; Shashidar, R. *Mol. Cryst. Liq. Cryst.* **1969**, *8*, 339. (b) Fischer, E. W.; Strobl, G. R.; Detenmaier, M.; Stamm, M.; Steidle, N. *Discuss. Faraday Soc.* **1979**, *68*, 26. (c) Krishnamurthy, K. S.; Krishnamurti, D. *Mol. Cryst. Liq. Cryst.* **1970**, *6*, 407. (d) Krishnamurthy, K. S. *Ibid.* **1986**, *132*, 255.

(4) Vincent, J. M.; Skoulios, A. *Acta Crystallogr.* **1966**, *20*, 432, 441, 447.

(5) (a) Hartley, G. H.; Guillet, J. E. *Macromolecules* **1968**, *1*, 413. (b) Encina, M. V.; Lissi, E. A. *J. Photochem.* **1976**, *5*, 287. (c) Encina, M. V.; Lissi, E. A. *Ibid.* **1975**, *4*, 321.

(6) Caldwell, R. A.; Dhawan, S. N.; Majima, T. *J. Am. Chem. Soc.* **1984**, *106*, 6454.

(7) Samples of **1** or **2** in N_2-saturated KS, KP, or KSO (sealed in 1.5–1.8 mm o.d. Kimax capillary tubes) and solutions of **2** in BS (sealed under vacuum in 0.8 mm i.d. Pyrex cells) were irradiated in a thermostated water bath with a quartz-filtered 450-W medium-pressure Hg Hanovia lamp. Conversions of the ketones were approximately 10–15%. The ketones and products were extracted from the gels with ether prior to analyses. Extractions and analyses of gels, doped with known proportions of ketones and products, were conducted to ensure the validity of the procedures. The extracts and the BS samples were analyzed by gas chromatography. The assignments of *trans*- and *cis*-cyclobutanols is based upon both the relative retention times and the relative yields of the two diastereomers (as obtained in isotropic solvents). (a) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506. (b) Casal, H. L.; de Mayo, P.; Miranda, J. F.; Scaiano, J. C. *Ibid.* **1983**, *104*, 6959. (c) Ariel, S.; Ramamurthy, V.; Scheffer, J. R.; Trotter, J. *Ibid.* **1983**, *105*, 6959. (d) Turro, N. J.; Liu, K.-C.; Chow, M.-F. *Photochem. Photobiol.* **1977**, *26*, 413.

0002-7863/86/1508-3137$01.50/0