lipid structure, to the temperature of the vesicles relative to their phase transition,[17] and to the thermal history of the vesicles.[7] We have also observed that the reaction is sensitive to the size of the lipid bilayer structure. Small sonicated vesicles of lipid diacetylenes are less sensitive to light than vesicles of larger radius or extended bilayers of lipid diacetylene. Since the reaction is very sensitive to the lipid chain order, these preliminary observations suggest that the lipid chains in small sonicated vesicles of lipid diacetylenes are more disordered and support the interpretation of the NMR spectra of sonicated lipid vesicles, which suggest that lipid chain disorder is increased as a result of the increased surface curvature of the vesicles.[15]

Registry No. 1, 75898-24-7; **2** (X = Cl), 80028-58-6; **3**, 80028-59-7.

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Measurement of Relative Rates of Type I Photolysis by Chemically Induced Dynamic Nuclear Polarization[1]

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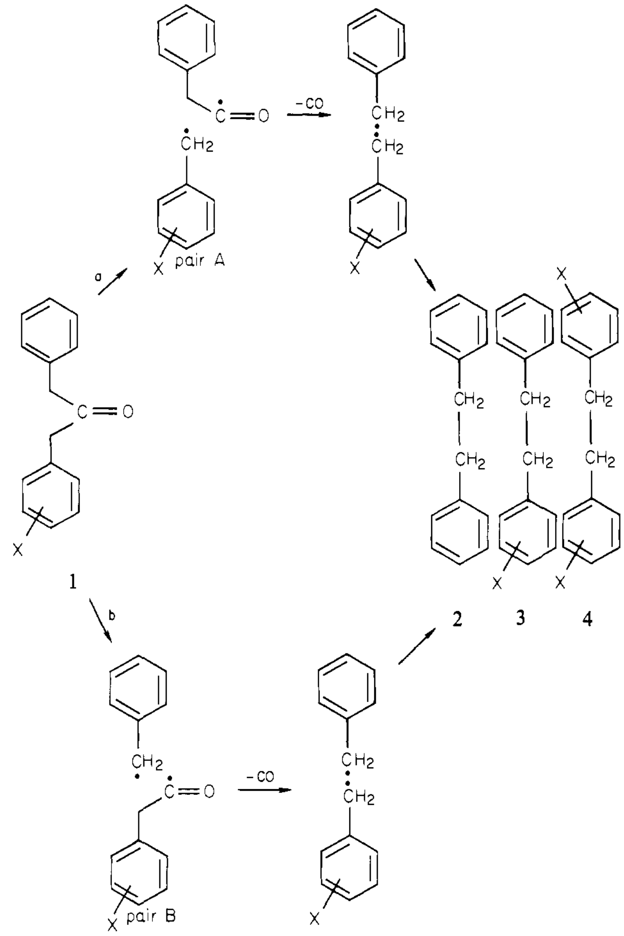
The rate of α cleavage of triplet dibenzyl ketones (Type I photolysis) has been estimated to be at least 10^{10} s^{-1}.[2,3] While we were investigating the behavior of radical pairs on a silica gel surface in comparison with that in solution and micelles,[4] an opportunity presented itself to measure directly the relative rates of the type I reaction. These rates have been correlated with the Hammett equation by using σ^+. The technique of chemically induced dynamic nuclear polarization (CIDNP) was especially well suited for this investigation, the results of which we now wish to report.

The stepwise homolytic α cleavage as well as the nature of the excited precursor in the photolysis of the parent dibenzyl ketone has been clearly demonstrated from CIDNP effects by Fischer et al.[5] These authors observed the methylene protons in strong emission for the starting material and in enhanced absorption for the decarbonylation product, dibenzyl. When a monosubstituted dibenzyl ketone is photolyzed, the possibility of two competitive α cleavages, a and b (Scheme I), exists although the same three final coupling products (dibenzyls **2**–**4**) may result, as indicated. When the photolysis was carried out in the high magnetic field of an NMR spectrometer,[6] the absorptions of the methylene protons of all starting materials (**1a**–**e**) were converted into emission but to different extents. In Figure 1, we show the results obtained from *p*-methoxydibenzyl ketone (**1a**). The *p*-methoxybenzyl methylene protons exhibit a much stronger emission than do the unsubstituted benzyl methylene protons, thus indicating the nonequivalent properties of these two different methylene groups. However, the distribution of dibenzyl products **2**, **3a**, and **4a**, obtained in the ratio of 1:2:1 expected from the statistical coupling of the free benzyl and *p*-methoxybenzyl radicals, fails to indicate the possibility of selective α cleavage. The CIDNP nonequivalence of the methylene protons can, thus, be related to two different radical pairs, A and B, generated from the two possible competitive α cleavages.

Scheme I



a, X = *p*-MeO
b, X = *p*-Me
c, X = *p*-F
d, X = *p*-Cl
e, X = *m*-Cl
f, X = H

The CIDNP emissive character of the methylene protons of the starting materials is fully accounted for by the Kaptein rule:[7] that is, pairs A and B are generated from a triplet state ($\mu > 0$), the recombination is a cage process ($\epsilon > 0$), the methylene protons of the benzyl radicals have negative hyperfine coupling constants ($A_H < 0$), and the g factors of benzyl radicals (2.0025) are larger than those of acyl radicals (2.0007) ($\Delta g > 0$). Since the parameters affecting the CIDNP effects for pair A and pair B are almost the same,[8] we interpret the different signal intensities as being derived from a larger concentration of radical pair A, resulting from a preferred cleavage at the methoxybenzyl–carbonyl bond. A similar interpretation has been put forward by Hutton

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(1) Publication No. 000 from the Photochemistry Unit, London, Ontario.

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(6) CIDNP experiments were performed on a Varian XL-100A NMR spectrometer with a Photochemical Research Associates light source (a 200-W Hg–Xe lamp with an ellipsoidal mirror).

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(8) The diffusion behavior, the recombination probability, and Δg of pair A and pair B may be considered to be identical. There is a slight variation in hyperfine coupling constants of methylene protons of benzyl radicals (*p*-MeO, −15.93 G; *p*-Me, −16.07 G; *p*-F, −16.43 G; h, −16.34 G; *p*-Cl, −16.08 G. Neta, P.; Schuler, R. H. *J. Phys. Chem.* **1973**, *77*, 1368). The β protons of the phenylacetyl radicals ($a_H \sim 1$ G; $\Delta g < 0$) can induce a CIDNP effect of the same direction, but this is smaller than that induced by benzylic methylene protons. It is interesting to note that the hyperfine interaction of nuclei other than the methylene protons, particularly those of the ortho and para hydrogens of the benzyl radicals, the paramethyl hydrogens, and the para-fluorine atom, is expected to have a minor influence on the amplitude of the methylene polarization. This is because the present CIDNP effect is basically a Δg effect and because the effect of the hyperfine interactions of other nuclei are averaged to null as far as the polarization of the methylene protons is concerned.

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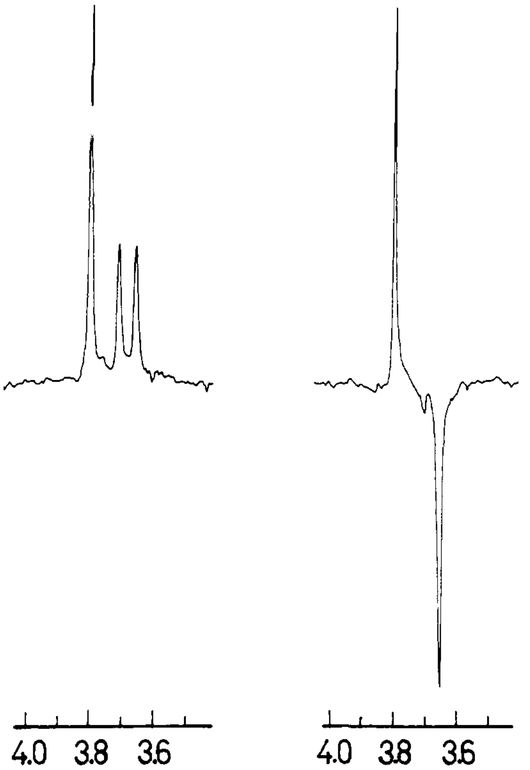

Figure 1. ^{1}H NMR spectrum (3.5–4 ppm, 100-MHz, Me_4Si as reference) of *p*-methoxydibenzyl ketone ($\sim 1 \times 10^{-2}$ M in $CDCl_3$) in the dark (left) and during UV irradiation (right). Peaks at 3.65, 3.70, and 3.79 ppm are assigned to *p*-methoxybenzyl methylene, benzyl methylene, and methoxy protons, respectively.

et al.[9] for the photolysis of *p*-methyldibenzyl ketone (**1b**). This effect provided us with an opportunity for the direct measurement of the relative rate of α cleavage within the same molecule based on the relative emission intensities of specific methylene protons. In the case of **1a**, the cleavage at the *p*-methoxybenzyl–carbonyl bond is preferred by a factor of 3.2 times over that at the unsubstituted benzyl–carbonyl bond.

The effective relative concentrations of radical pair A and B may be affected by the possible different rates of decarbonylation of the acyl radicals. In the extreme case we might be monitoring the relative rates of decarbonylation of various acyl radicals rather than the type I cleavage. Experimentally, we could not exclude this possibility, but from the following considerations we still favor our original interpretation. The rate constant for decarbonylation of the phenylacetyl radical is $\sim 5 \times 10^7$ s^{-1} [3,19,20] at 25 °C, but the lifetime of a radical pair in a nonviscous solvent such as $CDCl_3$ is believed to be shorter than 10^{-9}s. It is therefore not to be expected that decarbonylation could affect our major conclusion. Moreover, it is generally believed that the reason that the quantum yield of the formation of dibenzyl is less than unity ($\phi = 0.7$) is because of efficient geminate recombination. If decarbonylation of the acyl radicals were to compete effectively with recombination, then one would expect the quantum yields to vary with different substituents; the reported values are essentially the same.[3]

Ketones **1a–e** were prepared,[10] and their relative rates of type I cleavages were measured and are summarized in Table I: they give a better fit to the Hammett equation with σ^+ values[11] ($\rho^+ = -0.65$; correlation coefficient = 0.997) than with σ values[11] ($\rho = -1.03$; correlation coefficient = 0.937) or a more recently defined $\sigma\cdot$ scale[12] ($\rho\cdot = 0.55$; correlation coefficient 0.655), as shown in Figure 2. The correlation of σ^+ with a negative ρ^+ implies a polar transition state which can be stabilized by electron-donating aromatic substituents. This resembles a previous, but less direct, study of the photolysis of deoxybenzoin by Lewis et al.[15] who obtained a ρ^+ value of −1.1. Walling and Clark[16] have shown that the relative rates of α cleavage of substituted alkoxy radicals derived from dibenzylmethylcarbinols correlate with σ^+ ($\rho^+ = -1.04$). The general parallel made[17] for the α cleavage between the alkoxy radical and the ketone in the n,π^* triplet state is established here in detail. The smaller absolute value for ρ^+ in our system may reflect a faster rate of homolysis as compared with those in dibenzylmethylcarbinol radicals and deoxybenzoins ($\sim 10^{10}$ s^{-1} for dibenzyl ketones,[2,3] $\sim 10^7$ s^{-1} for alkoxy radicals,[16] and $\sim 4 \times 10^6$ s^{-1} for deoxybenzoins[15,18]). It is remarkable that with rates as fast as 10^{10} s^{-1} one is still able to measure the relative

Table I. Relative Rates of Type I Reactions[a]

X	k_X/k_H[b]	log k_X/k_H	σ^+[c]	σ[c]	$\sigma\cdot$[d]	T_1,[f] s
p-MeO	3.18	0.502	−0.78	−0.27	0.24	1.8
p-Me	1.53[e]	0.185	−0.31	−0.17	0.11	2.0
p-F	1.05	0.021	−0.07	0.06	−0.08	2.2
H	1	0	0	0	0	2.2
p-Cl	0.90	−0.045	0.11	0.23	0.12	2.0
m-Cl	0.52	−0.284	0.40	0.37	0.04	2.0

[a] Determined from the emission intensities, which have been corrected for initial absorption intensities and spin-lattice relaxation times. The assignment of methylene groups is based on the chemical shifts and is referenced to parent dibenzyl ketone as the internal standard. [b] Reproducible within ±5%. [c] See ref 10. [d] See ref 11. [e] Hutton et al.[9] obtained 1.5. [f] Spin-lattice relaxation times of the benzylic methylene protons of the ketones.

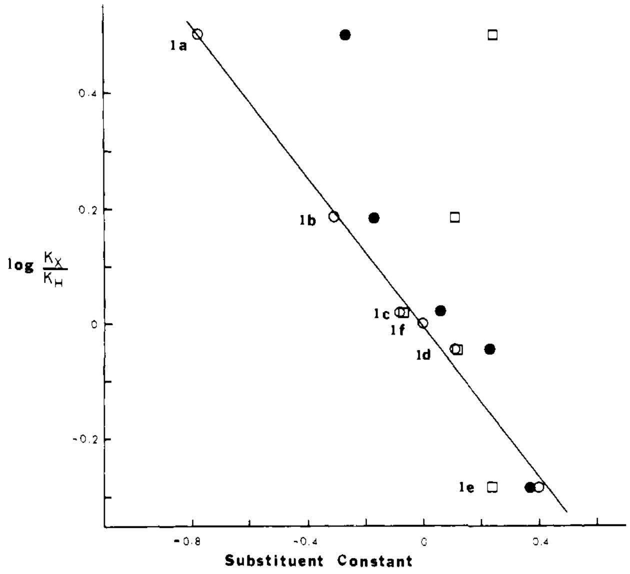

Figure 2. Hammett plot of log (k_X/k_H) vs. substituent constant for α cleavage of substituted dibenzyl ketones (○, σ+; ●, σ; □, $\sigma\cdot$). See text for labels **1a–f**.

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values and study the structure–reactivity relationship.

Acknowledgment. P.deM. and S.K.W. wish to thank the Natural Sciences and Engineering Research Council of Canada for its support of this research. P.deM. also thanks the Ontario Ministry of the Environment and the donors of the Petroleum Research Fund administered by the American Chemical Society, for partial support. We also thank Heather Schroeder for the measurement of spin–lattice relaxation times.

Registry No. 1a, 29917-69-9; **1b**, 35730-02-0; **1c**, 330-97-2; **1d**, 35730-03-1; **1e**, 73178-50-4; **1f**, 102-04-5.

Inversion at Tetracoordinate Silicon in Nucleophilic Media. Ligand Permutation in 3,3,3′,3′-Tetrakis(trifluoromethyl)-1,1′(3*H*,3′*H*)-spirobi[2,1-benzoxasilole]

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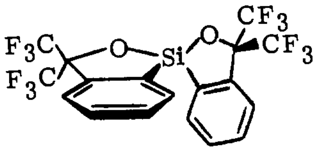
Intramolecular ligand permutation (inversion) at tetracoordinate silicon in nucleophilic media has been observed for a variety of halo- and aminosilanes.[1] As the inversion process is always second order (or higher-order) with respect to the nucleophile, the mechanism is generally thought to involve reversible stepwise attack of two molecules of nucleophile to give a symmetrical penta- or hexacoordinate intermediate or transition state. We wish to present the first example known to us of inversion at tetracoordinate silicon in nucleophilic media which occurs at a rate showing a first-order dependence on the concentration of the nucleophile.

The spirosilane **1**[2] exhibits an A_3B_3 ^{19}F NMR spectrum in nonnucleophilic solvents (e.g., chloroform, toluene) which, upon addition of weak nucleophiles, shows the coalescence of trifluoromethyl peaks expected for the interconversion accompanying inversion at silicon.



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Kinetic studies on **1** were carried out by visual fit of observed and calculated spectra[3] to determine the pseudo-first-order rate constant ($k_1 = k_2\,[\mathrm{Nu}]^n$). The order of inversion with respect to the nucleophile is given by the slope of a plot of ln k_1 vs. ln [Nu] and is clearly unity for nucleophiles tetrahydropyran (0.984 ± 0.009) or benzaldehyde (0.97 ± 0.02). Quoted errors are standard deviations, calculated from points for at least four different concentrations of nucleophile (ca. 0.05–0.5 M).

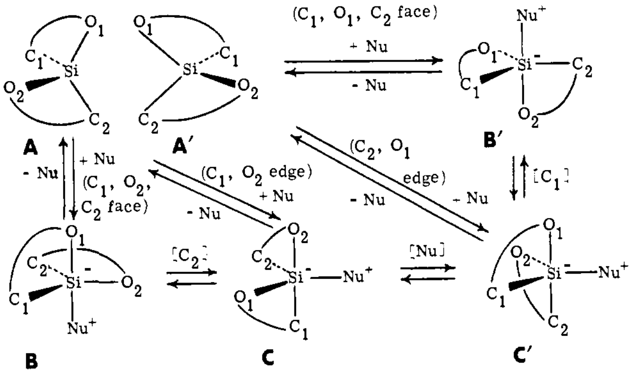

Figure 1. Selected pathways for the racemization of **1** by nucleophilic attack on a tetrahedral face opposite oxygen (A ⇄ B ⇄ C ⇄ C′ ⇄ B′ ⇄ A′), or on a C,O edge (A ⇄ C ⇄ C′ ⇄ A′) of the tetrahedral silicon, with intervening Berry pseudorotation steps about the pivot ligand indicated in brackets.

The effect of substituents on the rate of inversion was investigated by using a series of para-substituted benzaldehydes as nucleophiles.[4] The best correlation was obtained by using the Yukawa and Tsuno modification of the Hammett–Brown equation[5]: $\log k/k_0 = [\sigma + 0.39\,(\sigma^+ - \sigma)]\rho$ with a ρ value of -1.52 ± 0.03.[6] Activation parameters determined from the temperature dependence of k_2 with benzaldehyde as nucleophile are $\Delta H^* = 6.9 \pm 0.2$ kcal/mol, $\Delta S^* = -27.9 \pm 1.2$ eu, and $\Delta G^*_{298} = 15.2 \pm 0.4$ kcal/mol.

Inversion of **1** by ionization to a zwitterionic silicenium ion appears unlikely as the rate of inversion shows no relation to the polarity of the nucleophile.[7] A mechanism involving attack of one molecule of nucleophile at silicon to give a pentacoordinate intermediate is consistent with all of these findings, including first-order kinetics in the nucleophile and a moderately negative activation entropy (an ordered transition state). The transition state, with its developing positive charge at the nucleophilic center, is stabilized by electron-releasing substituents on benzaldehyde, giving rise to the negative value of ρ.

One plausible mechanism for the inversion of **1** involves attack of the nucleophile[8] on the O,O edge of the tetrahedron of **1** to give **2**, followed by the sequence of five pseudorotation steps necessary to invert the chirality of a trigonal-bipyramidal species.[9] Loss of the nucleophile then gives silane of inverted configuration. Although several such pseudorotation sequences are possible starting from **2**, all involve high energy intermediates[9,10] having two apical carbons or a diequatorial five-membered ring and one apical carbon ligand.

Pseudorotation mechanisms have been invoked to explain ligand permutation of a few fluorosiliconates[11] and most recently and most convincingly for the isolable siliconate **3** (the report of which[12] appeared shortly after this paper had been submitted). The structure of **3** was confirmed by an X-ray crystal structure determination and is essentially that which was proposed for similar siliconates prepared in this laboratory,[2] on the basis of data obtained on the solution phase.

While the reported nondissociative inversion of **3** most probably involves a sequence of five pseudorotation steps, such a mechanism

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