are readily assigned to the γ-methylene and methyl carbons by comparison with the liquid-phase spectrum. These resonances are only slightly shifted upon adsorption. The remaining four resonances arise from the two α- and β-methylene carbons, from which we conclude that a least two types of chemically different butylamine species are present on the surface.

The existence of well-resolved resonances demonstrates that if surface diffusion is occurring, then the rate is not comparable to the spinning rate (~3.2 kHz).[13] Further, if site exchange is occurring, then the rate must be slow compared to the chemical-shift difference between the two species on the surface. Therefore, this spectrum is consistent with a picture whereby the nitrogen of the *n*-butylamine is firmly anchored to the surface. In all probability the system is executing rapid albeit limited angular diffusion about the bond axis connecting the surface to the nitrogen, with the motion of the alkyl chains increasing as one moves away from the surface.

The appearance of four resonances in the region expected for the two α and β carbons of the alkyl group is consistent with there being two quite different sites available to the amine. Two candidates are the classic Lewis and Brönsted sites. In order to check this possibility we obtained the CP-MAS ^{13}C spectra of two solid adducts of *n*-butylamine (Figure 1b,c). Those resonances for the solid HCl adduct match closely to four of the resonances for the surface adsorbed species. The resonances corresponding to the α and β carbons of the solid BCl_3 adduct are deshieled relative to the corresponding carbons within the HCl adduct but shielded relative to the analogous carbons of the adsorbed amine. Hence, we conclude that the most deshielded set of resonances correspond to the *n*-butylamine which is attached to the surface via Lewis bonds to an aluminum atom. That the chemical shifts of this species are deshielded relative to those of the BCl_3 adduct we attribute to the fact that the acid site in this surface is a stronger Lewis acid than BCl_3.

The breadth of the resonances for the α and β carbons may arise from several factors. An important consideration for the α carbon is the presence of nitrogen-14 dipolar coupling. The fact that we do not observe "well-resolved" doublets[14] for this carbon may be due in part to the angular diffusion of the molecule and/or the strength of the applied magnetic field relative to the nitrogen-14 quadrupolar coupling constant. Perhaps of equal importance to the line width is a heterogeneity of the acid sites on the surface of the alumina. The presence of a distribution of site acidities would lead to a corresponding distribution of chemical shifts and hence appear as a line-broadening mechanism.

In summary, it is clearly evident that ^{13}C NMR spectroscopy in conjunction with CP-MAS methods can be used to probe the interactions between small molecules and surfaces even when the surface is of moderately low specific area. Compared to other spectroscopies carbon-13 CP-MAS NMR spectroscopy appears to provide a facile method to distinguish between different types of surface bonding sites and their relative acidity. Within the limitations of cross-polarization dynamics the relative populations of these sites can be quantified.

Acknowledgment. We thank Z. Szafran for his assistance in preparing the amine and F. D. Doty for the MAS probe design used for this work. We are indebted to Dr. R. C. Schoening for his useful advice. The encouragement and support of the management of union Carbide Corporation is gratefully acknowledged. The use of the facilities at the University of South Carolina Regional NMR Center, funded by the National Science Foundation Grant CHE78-18723, is acknowledged.

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(10) The γ-alumina (SA = 220 m^2/g) employed in this study was pretreated at 350 °C in vacuum. The *n*-butylamine was laid down on the surface by using entrainment in a helium flow. The basis of a weight increase of approximately 0.5%, the surface covered by the butylamine is estimated to be 10 m^2/g or roughly one-twentieth of a monolayer. Operating under a dry nitrogen atmosphere the granular alumina sample was packed into an aluminum oxide NMR rotor.

(11) An important experimental difficulty that had to be overcome with these relatively dilute samples (typically 40 mM in amine based on the total volume of the NMR rotor) was the carbon background signal from the NMR probe. We accomplished this using sample machined from aluminum oxide and a stator from Macor. The Delrin end caps of the rotor leave a small signal at 90 ppm which we use for reference.

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Laser Photochemical Production of Vitamin D[†]

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The complex photochemistry of 7-dehydrocholesterol (7-DHC) and ergosterol (E) is now moderately well understood due, in large part, to the elegant studies of Havinga and co-workers.[1-9] Table I shows how the distribution of products depends on photolyzing wavelength.[10] Photolysis in the range 270–310 nm gives relatively high yields of previtamin D (P); shorter wavelengths lead to a predominance of tachysterol (T) and longer wavelengths to lumisterol (L).[11] The interrelations between the various products are shown in Figure 1.

Using laser photolysis, we have confirmed the main aspects of the dependence of the product array on wavelength and have gone further by demonstrating that by a two-stage photolysis we can "engineer" a desirable product distribution with improved yields. This approach may offer an attractive alternative to the commercial method of vitamin D production, which requires a number of fractional crystallizations.[15]

Photolysis at KrF (248 nm) and XeCl (308 nm) wavelengths was carried out with an excimer laser (Lumonics Research Limited, Model 861), which gives average powers in the 1–10-W range. Photolysis at 337 nm used a nitrogen laser (Molectron, Model UV 1000) with an average power of 0.2 W while at 353 nm a YAG laser (Molectron, Model MY 34) with an average power of 0.4 W was used. The reaction mixtures were analyzed by high-performance LC[20] (Varian 8500) on a silica Si-5 column (5

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(17) The cis–trans isomerization of the $C_{6,7}$ double bond can be brought about by triplet sensitization[18,19] to give a photostationary state (80% P_3; 20% T_3).

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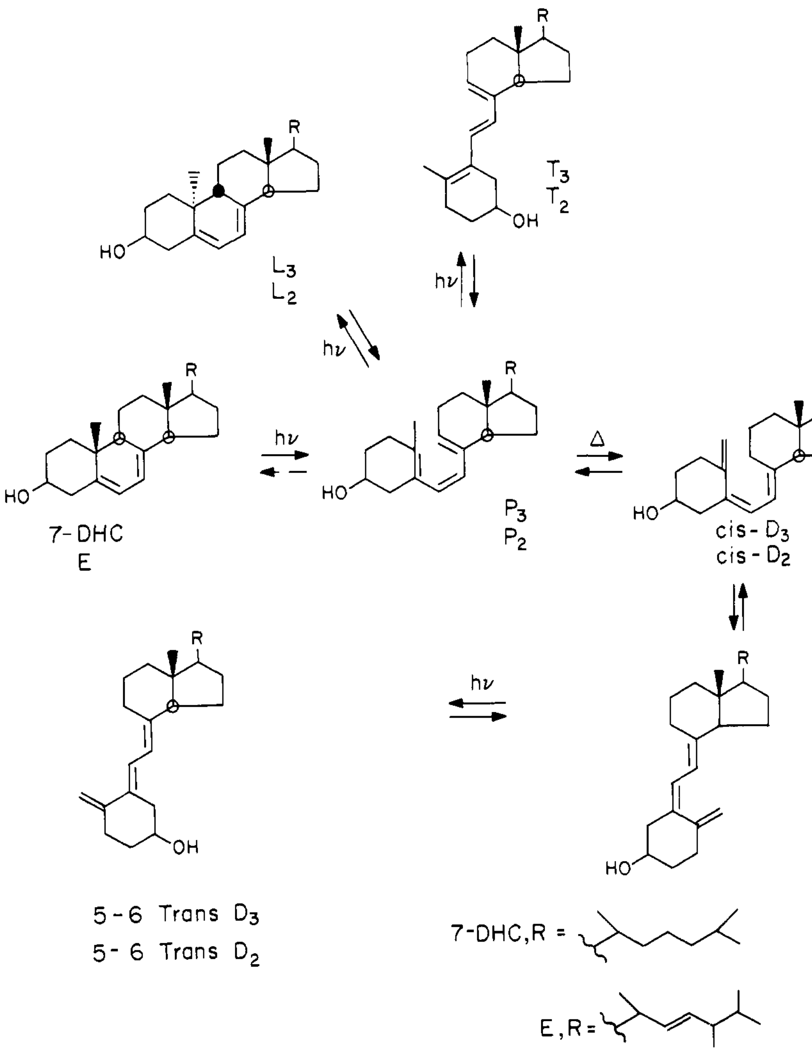

Figure 1.

Table I. Composition of the Photostationary State at Various Wavelengths

wavelength/ nm	% E	% P_2	% T_2	% L_2	% D_2	ref
248	2.9[a]	25.8[b]	71.3[c]	nd		this work
254	1.5	20	75	2.5		16
302	3.4	53	26	17		14
308	13.3[a]	35.5[b]	3.41[c]	42.3[d]	4.5[e]	this work
(248 + 337)[f]	8.8[a]	79.8[b]	1.5[c]	9.8[d]		this work[g]
(248 + 353)[f]	0.1[a]	80.1[b]	11.0[c]	8.7[d]		this work

[a] 7-DHC. [b] P_3. [c] T_3. [d] L_3. [e] *cis*-D_3. [f] Photolyzed to a photostationary state at 248 nm and then photolyzed at the second wavelength. Because of the long photolysis times (95 min at 337 nm and 180 min at 353 nm), complete photoequilibrium might not have been attained. [g] A better separation between P_3 and L_3 is obtained when a mixture of n-hexane and n-amyl alcohol (0.3%) is used as eluent. (M. P. Rappoldt, personal communication).

μm) at a flow rate of 0.5 cm^3 min^{-1} under an operating pressure of 90 atm. The eluent used was 70:30:2 chloroform–hexane–ethyl acetate and the compounds were identified by UV monitoring at 282 nm. The relative concentration was calculated from relative area after allowance was made for extinction coefficient at the monitoring wavelength.

The photoproduct yields we observe in single-wavelength photolysis are included in Table I and agree with the general features previously established. Irradiation at 248 nm of a 6.4 × 10^{-5} M solution of 7-DHC in O_2-free diethyl ether (0 °C) distilled from benzophenone ketyl gives a conversion of about 96% (15 W·min incident) with L_3 below our limits of detection. This agrees with the results of Pfoertner,[12,13] who found that a solution of ergosterol irradiated at 254 nm gave only T_2. Similarly, the observations at 308 nm agree with those of Yakhimovich et al.,[14] who, using a lamp with maximum output at 302–305 nm, showed it was possible to minimize the amount of T_3 when the conversion of 7-DHC is kept to 40–45%. The yields of T_3 and L_3 after 248-nm photolysis support the scheme proposed by Havinga,[16] where, of the three possible photoproducts from previtamin D_2 (T_2, E, and L_2), only T_2 has a significant forward quantum yield whereas the other two have high reverse quantum yields.

Significant improvement in overall yield and decrease in side-product contamination is possible by two-stage laser photolysis. Taking the mixture produced by photolysis with the KrF laser at 248 nm (25.8% P_3, 71.3% T_3, 2.9% 7-DHC), photolysis with an N_2 laser (14 W·min, 337 nm, at room temperature) isomerizes T_3 to previtamin D_3[17] (79.8% P_3, 1.5% T_3, 8.8% 7-DHC, 9.8% L_3). At this wavelength a small amount of P_3 is photolyzed back to 7-DHC and L_3. A series of weak absorption bands of the *cZc* triene (P_3) which occur around 337 nm (ε 60) may account for the cycloaddition reactions $P_3 \rightarrow$ 7-DHC and $P_3 \rightarrow L_3$.

At longer wavelength T_3 is the only compound having appreciable absorption (ε 175 at 350 nm) and the $E \rightarrow Z$ isomerization of the $C_{6,7}$ double bond of the *cEc* triene (T_3) should be the only photoreaction taking place. Indeed room-temperature photolysis with the third harmonic of a YAG laser smoothly converts T_3 to P_3 with minimization of the ring closure to 7-DHC and L_3 (P_3

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80.1%, T_3 11.0%, 7-DHC 0.1%, L_3 8.7%).

Thus by two-stage photolysis using narrow spectral width laser sources it is possible to greatly reduce or eliminate competing photoreactions leading to photoequilibria of complex composition and to have *high conversion* of 7-DHC (>90%) to P_3 with very low final yields of T_3 and L_3.

Acknowledgment. We wish to express our thanks to Drs. N. Thompson and K. Pfoertner for their helpful suggestions. Samples of tachysterol$_3$ 4-methyl-3,5-dinitrobenzoate, lumisterol$_3$, and lumisterol$_2$ were generous gifts of Dr. K. Pfoertner (Hoffmann-La Roche & Co. Ltd., Basel, C.H.) and Dr. M. P. Rappoldt (Duphar Co., Weesp, N.L.).

Spinning Near the Magic Angle: A Means of Obtaining First-Order Dipolar NMR Spectra of Molecules Dissolved in Nematic Liquid Crystals

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Chemical applications of the dipolar NMR spectra obtained from molecules dissolved in nematic crystals are limited by the difficulty of solving the complicated multispin second-order patterns which arise from the large values of the partially averaged dipolar interactions. As a consequence the only spectra which have been interpreted have been those from molecules either with a small number of resonating nuclei or with high symmetry. Large or nonsymmetrical molecules have not been successfully studied with this otherwise powerful method of determining the molecular geometry.

This communication reports a technique which obtains first-order spectra from such systems by reducing the averaged dipole coupling by any factor up to 100. Such reduction is accomplished by making the angle α between the nematic director and the magnetic field any value between 0° and the magic angle, 54.73°, at which point the averaged dipole interaction is null. This is accomplished by spinning the sample at a moderate speed (ca. 50 Hz) about an axis which makes an angle less than the magic angle with the magnetic field. The director aligns along the spinning axis instead of along the magnetic field if the rate of spinning exceeds the rate of director reorientation. Large reductions in the dipole interaction are obtained as α approaches the magic angle. When the director of the liquid crystal is aligned at an angle α with the magnetic field all the tensor contributions (e.g., the dipole–dipole interaction, the chemical shift anisotropy, the anisotropy of the scalar spin–spin coupling, and the quadrupolar coupling for nuclei with spins greater than $^1/_2$) in the Hamiltonian are reduced[1,2] by a factor $R = (1/2)(3\cos^2\alpha - 1)$.

Previous attempts to orient the director of a nematic liquid crystal at a variable angle from the magnetic field have not successfully approached the magic angle. The use of electric fields[3,4] apparently presents serious technical problems which have limited their utility to values of α near 0 and 90°. Spinning the sample below a critical rotation rate around an axis perpendicular to the magnetic field has also been used to change the director orientation[5,6] from 0 to 45° from the magnetic field,[2] thus missing the magic angle by almost 10°. Furthermore, at rotation speeds which should produce angles larger than 30°, the director is distributed in such a way that the line widths become large. All previous work on rotating liquid crystals has used two particular orientations of the spinning axis relative to the field, viz, 90° in classical electromagnets and 0° in superconducting magnets. Thus, the very interesting region about the magic angle and between these two limiting cases has been neglected.

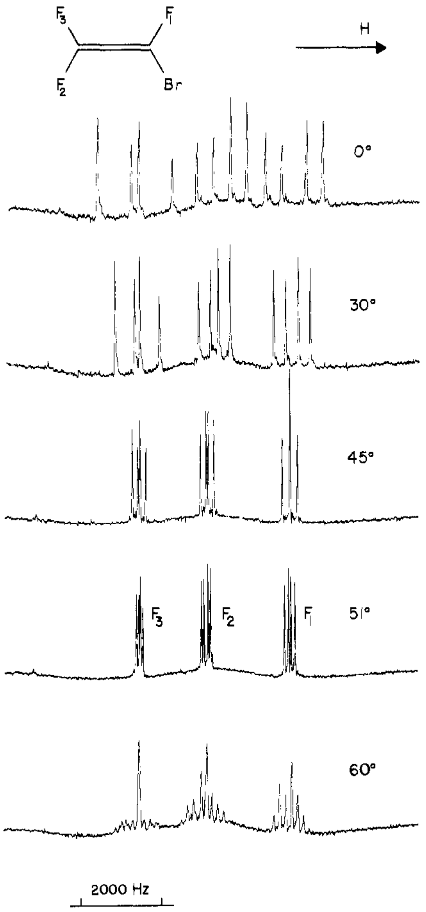

Figure 1. ^{19}F spectra of $CF_2{=}CFBr$ in liquid crystal as a function of the angle between the axis of rotation and the magnetic field. Spinning rate 70 rps.

For this work a spinner has been constructed for 10-mm NMR tubes with a length of 23 mm. The sample spins at frequencies between 20 and 100 Hz around an axis which is horizontal. The spinning axis may be rotated around the vertical so as to make any angle with the horizontal magnetic field of our wide-gap electromagnet.

Fluorine-19 spectra obtained at 75.25 MHz on trifluorobromoethylene dissolved in the liquid crystal *p*-pentylphenyl 2-chloro-4-(*p*-pentylbenzoyloxy)benzoate are shown in Figure 1. It is quite apparent that a second-order spectrum of the ABC type is obtained when spinning the sample parallel to the field. Upon spinning about an axis which is 3° less than the magic angle, the spectrum is clearly of the AMX type. The couplings are no longer dominated by the large dipolar terms, but they are now comparable with the scalar interactions. Note that resolution increases when the sample is oriented closer to the magic angle. When α is greater than the magic angle, a new pattern is observed. In this situation the director of the liquid crystal no longer reaches a homogeneous steady state but instead distributes in the plane perpendicular to the spinning axis. The result is a frequency modulated spectrum

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