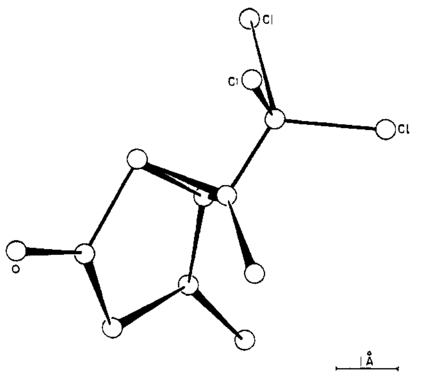
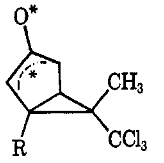


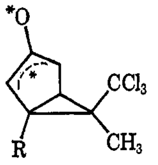
Figure 1. Crystal structure of 4-methyl-*endo*-6-methyl-*exo*-6-trichloromethylbicyclo[3.1.0]hex-3-en-2-one. The view is down the C^* axis perpendicular to the xy plane.

$P2_1/c$ with cell dimensions $a = 13.11$, $b = 8.00$, $c = 11.90$ Å, $\beta = 115.9°$. Figure 1 is drawn from the final parameters obtained for the structure when the agreement factor, R, has been reduced to 0.14. Full details of the solution will be reported separately elsewhere. This absolute structure determination provides a firm foundation for the spectroscopic analyses given above and in related investigations.[4,5,7,10b]

The factors influencing the stereochemistry of the dienone–lumiketone photorearrangement have been discussed in detail elsewhere.[5,10b,11] Briefly, this is the result of the stereoselectivity associated with (1) electrocyclic ring closure to a 3,5-bonded intermediate V or VI, and (2) the stereochemistry of the final [1,4]-sigmatropic shift.[11a–c] If step 2 occurs with inversion of configuration, by analogy with established ground-state reactions,[11–14] then the selective formation of IIIb must be due to preferential formation of intermediate Vb as opposed to VIb. This is contrary to the prediction[5] based only on the steric size of the substituents at C-4, but is consistent with repulsion of the C–O and C–CCl$_3$ dipoles in the ring closure leading to VI.



V



VI

In the light of these observations and the near identity of the chemical shift of the 6-methyl (δ 1.55) for the lumiketone from dienone Ia and the 6-methyl in IIIb (δ 1.54), we now propose that structure IIIa be assigned to the lumiketone derived from dienone Ia, rather than IVa as tentatively suggested earlier.[3] The effect of the added methyl group in Ib is to introduce some steric interference in the route to Vb,[5] and to divert some of the reaction *via* VIb to IVb. Thus both steric and electronic effects must be considered in rationalizing and predicting the course of these photochemical rearrangements.

[11] (a) H. E. Zimmerman and D. S. Crumrine, *J. Amer. Chem. Soc.*, **90**, 5612 (1968); (b) H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *ibid.*, **91**, 434 (1969); (c) H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969); (d) R. B. Woodward and R. Hoffmann, *ibid.*, **8**, 781 (1969).

[12] T. M. Brennan and R. K. Hill, *J. Amer. Chem. Soc.*, **90**, 5614 (1968); R. F. Childs and S. Winstein, *ibid.*, **90**, 7146 (1968); H. Hart, T. R. Rodgers, and J. Griffiths, *ibid.*, **91**, 754 (1969).

[13] This assumes that deactivation from the electronic excited state precedes rearrangement, which has not been unequivocally established [see D. I. Schuster and D. J. Patel, *ibid.*, **90**, 5145 (1968), and ref 10b]. The stereochemistry of the final sigmatropic rearrangement can be established experimentally by study of a chiral cyclohexadienone, which is in progress in these laboratories.

[14] In ref 4d, it is claimed that a dienone–lumiketone phototransformation has been observed in which the final [1,4]sigmatropic rearrangement occurs with retention of configuration, *i.e.*, by a pivotal motion involving exo–endo interconversion of substituents on proceeding from the 3,5-bonded intermediate to the product. However, the assignment of configuration to the intermediate in this case is dubious,[4d] since it ignores precisely those stereochemical factors which were pointed out by Rodgers and Hart.[5]

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Segmental Motion in Liquid 1-Decanol. Application of Natural-Abundance Carbon-13 Partially Relaxed Fourier Transform Nuclear Magnetic Resonance[1]

Sir:

In a previous report[2] we showed that carbon-13 spin–lattice relaxation times (T_1), measured by means of partially relaxed Fourier transform (PRFT) nmr,[2–4] could be used to monitor segmental motion of biopolymers in solution. Such measurements on smaller molecules also yield detailed information about relative rotational mobility in carbon chains. In general, the ^{13}C spin–lattice relaxation of a protonated carbon is overwhelmingly dominated by dipole–dipole interactions with the attached protons,[5] and T_1 is given by[6]

$$1/T_1 = N\hbar^2\gamma_C{}^2\gamma_H{}^2r_{CH}{}^{-6}\tau_C \qquad (1)$$

where γ_C and γ_H are the gyromagnetic ratios of ^{13}C and ^{1}H, N is the number of directly bonded hydrogens, r_{CH} is the C–H distance, and τ_C is the effective correlation time for rotational reorientation. Equation 1 applies in the "extreme narrowing" limit, when $1/\tau_C$ is much greater than the resonance frequencies of the ^{13}C and ^{1}H nuclei, and is thus usable for small molecules in liquids of low viscosity.

Individual carbon-13 T_1 values in liquid 1-decanol were determined from the peak intensities in partially relaxed frequency-domain spectra obtained by Fourier transformation of accumulated time-domain signals following 180°–τ–90° pulse sequences.[3,7] Details have

[1] Carbon-13 Fourier Transform Nuclear Magnetic Resonance. IV. For part III see ref 2.

[2] A. Allerhand, D. Doddrell, V. Glushko, D. W. Cochran, E. Wenkert, P. J. Lawson, and F. R. N. Gurd, *J. Amer. Chem. Soc.*, **93**, 544 (1971).

[3] R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.*, **48**, 3831 (1968).

[4] R. Freeman and H. D. W. Hill, *ibid.*, **53**, 4103 (1970).

[5] K. F. Kuhlmann, D. M. Grant, and R. K. Harris, *ibid.*, **52**, 3439 (1970).

[6] H. G. Hertz, *Progr. Nucl. Magn. Resonance Spectrosc.*, **3**, 159 (1967).

[7] A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961, p 64.

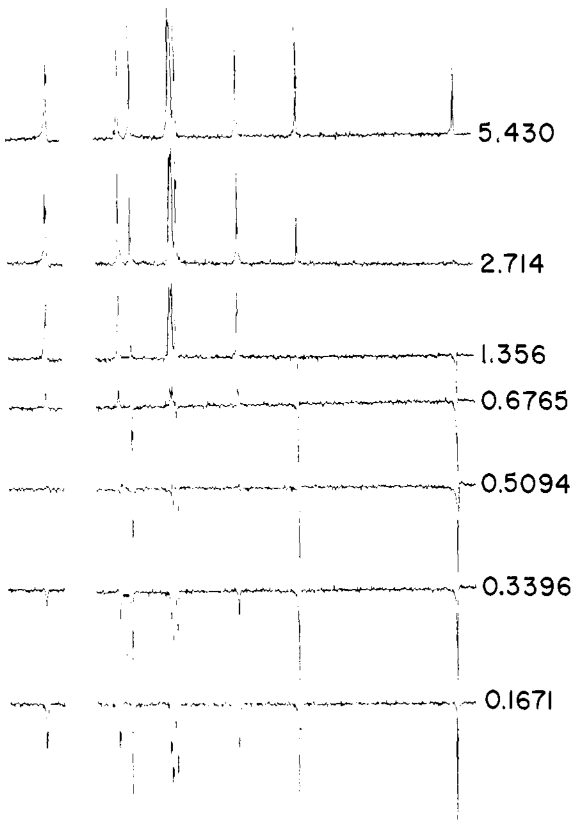

Figure 1. Proton-decoupled natural-abundance carbon-13 PRFT spectra of neat-liquid 1-decanol at 42° and 15.08 MHz. Each spectrum is the result of four accumulations, with a recycle time of 21.7 sec, and covers the ranges 129.0–132.1 ppm and 159.0–180.2 ppm upfield from neat carbon disulfide. The interval τ between each 180° pulse and the subsequent 90° pulse is indicated next to each spectrum, in seconds.

been given elsewhere.[2] A set of such PRFT spectra is shown in Figure 1. The assignments in the ^{13}C spectrum of 1-decanol, made by Roberts and coworkers,[8] are indicated in Figure 2. The spin–lattice relaxation times extracted from Figure 1 are also shown in Figure 2, together with the effective correlation times computed from eq 1.

There is more than a factor of 7 increase in τ_C when going from the CH_2OH carbon to the methyl carbon. This indicates a large degree of internal motion of the methyl group. Methylene carbons close to the methyl group also show evidence of appreciable segmental motion. The internal motion becomes more and more restricted as one approaches the hydroxyl end of the molecule.

Large variations of ^{13}C relaxation times within a molecule are not observed in the case of straight-chain hydrocarbons.[4] It appears that internal motion will have a large effect on carbon-13 T_1 values of alkyl chains only when the overall reorientation of the molecule is restricted. In the case of 1-decanol, this restriction is caused by intermolecular hydrogen bonding. Let us assume that

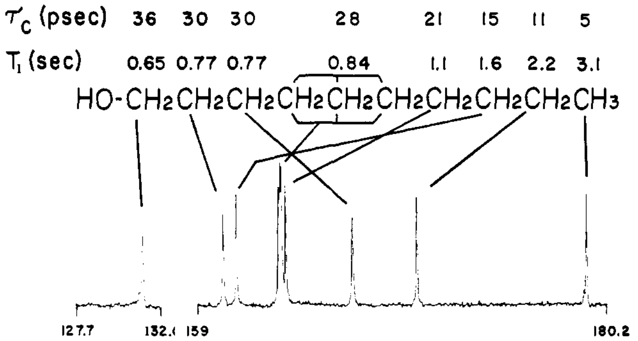

Figure 2. Normal proton-decoupled natural-abundance carbon-13 Fourier transform nmr spectrum of neat-liquid 1-decanol at 42° and 15.08 MHz, after four accumulations, with a recycle time of 21.7 sec. Horizontal scale is in parts per million upfield from neat carbon disulfide. The indicated assignments are taken from ref 8. Spin–lattice relaxation times and effective rotational correlation times are indicated above each carbon.

$$1/\tau_C \approx 1/\tau_R + 1/\tau_G \qquad (2)$$

where τ_R is the correlation time for overall reorientation of the molecule and τ_G is an effective correlation time for internal motion of a group in a molecule. It follows that the measurable effect of τ_G increases as the overall motion becomes slower. In 1-decanol, τ_R and the various τ_G values are of the same order of magnitude, with τ_G decreasing with increasing distance from the hydroxyl group. In straight-chain hydrocarbons[4] the absence of hydrogen bonding yields a shorter τ_R and a dominant contribution from $1/\tau_R$ to $1/\tau_C$.

Carbon-13 PRFT nmr spectroscopy is becoming an increasingly useful technique. One can use the T_1 values of individual transitions to identify carbons with a large degree of internal motion. PRFT spectra appear to have a bright future in spectral assignments.

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[8] J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Amer. Chem. Soc.*, 92, 1338 (1970).