in a "leopard" pattern such that the distance from the center of a spot to each of its six nearest neighbors was three times the diameter of the spot. Patterns for transmitting the light were kindly prepared by the Research Laboratories of the Eastman Kodak Company by photographing a master pattern at different distances with high contrast emulsion. The cell containing the solution was only 5 mm. thick to reduce light scattering, and the light traversed this cell vertically to reduce convection effects. Intensity of illumination in a spot and total area illuminated were the same in all experiments.

The average concentration of iodine atoms in the cell was determined by measuring the rate of isotopic exchange with *trans*-diiodoethylene.[2] Figure 1 shows a plot of relative atom concentration against log r_L where r_L is the radius of an illuminated spot. One anomalously low measurement at very small spot radius has been omitted from the plot.

The dashed horizontal lines denote the theoretical limits for large and small spots computed from measurements with homogeneous illumination at the same intensity as the local intensity in the spots. The curve illustrates the theoretical predictions of reference 1 in terms of ρ_L, the spot radius in units of the magnitude of the root-mean-square diffusion distance for an atom during its lifetime in a homogeneously illuminated solution. The curve has been shifted horizontally to provide a fit to the experimental points, this fit being such that ρ_L of unity corresponds to $r_L = 0.0040$ cm.

The theoretical analysis[1] predicts that

$$\rho_L = (4\phi q k/D^2)^{1/4} r_L \qquad (1)$$

where q = rate of absorption of radiation in an illuminated area = 7.71×10^{-10} einstein/liter sec., ϕ = quantum yield for iodine dissociation = 0.66,[3] and k = rate constant for iodine atom recombination = 1.3×10^{10} liter/mole sec.[4] Then D, the diffusion coefficient for iodine atoms in hexane, becomes 8.2×10^{-5} cm.²/sec.

This result is more than the value of 4.05×10^{-5} cm.²/sec. reported[5] for iodine molecules. It is also somewhat more than the 5.3×10^{-5} cm.²/sec. diffusion coefficient of iodine atoms predicted if the theory of diffusion controlled reactions in an isotropic medium[6] is applied to the observed[4] rate constant for iodine atoms of assumed diameter[7] 4.30 Å. Shifting the curve in Fig. 1 by 0.09 unit to the left would bring it into agreement with the predictions of the isotropic medium theory.

The experimental observations provide only a fair fit to the theoretical curve. At very large spot size, the concentration of isotopically labelled I_2 could become locally depleted. This effect can be corrected for and may be responsible for the one point below the theoretical minimum. At small spot size, any fuzziness of the boundary will make the average atom concentration greater than that predicted by the theory developed for a sharp boundary. This effect probably is responsible for the fact that the points in Fig. 1 rise more steeply than the theoretical curve, and such a steep rise makes the calculated diffusion coefficient larger than the true value. The theory of this diffuse boundary effect must be developed.

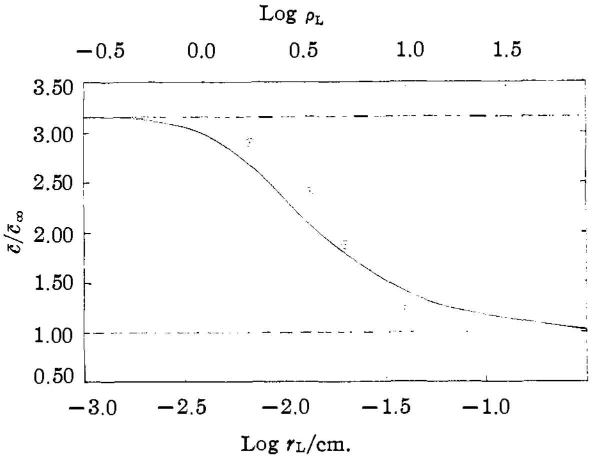

Fig. 1.—Ratio of average iodine atom concentration, $\bar{c}$, to average predicted for very large spots, $\bar{c}_\infty$. Measurements were made with same total intensity of illumination but different sizes of individual spots.

Although the method must be refined before it is possible to measure diffusion coefficients much more accurately than to about a factor of two, these results demonstrate unequivocally that at constant total illumination of a solution the average concentration of radicals increases with decrease in size of the individual illuminated areas and that the effect is of the magnitude predicted by the previously developed theory.

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RECEIVED DECEMBER 11, 1961

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REPORTING NUCLEAR MAGNETIC RESONANCE SHIELDING DATA

Sir:

Nuclear magnetic resonance spectral data are at present reported in a variety of units. This communication is not an endorsement of any particular one but instead points out certain incorrect usage.

In some current journals, *tau* (τ) values have been used to report positions of lines which were a part of spin multiplets[1] and coupling constants have been

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recorded in ppm. units.[2] Certainly this is improper because spin-spin coupling is independent of spectrometer frequency. Thus these line positions and coupling constants should not be subjected to a correction for a variable on which they are not directly dependent. Only measurements of *chemical shifts* may be reported in dimensionless, spectrometer-frequency-independent-units such as δ or τ. In multiplets, *line positions* are not measurements of chemical shifts and if reported they must be described in cps. units at a specified spectrometer frequency, relative to the absorption of a specified reference substance. Coupling constants must be reported in cps.

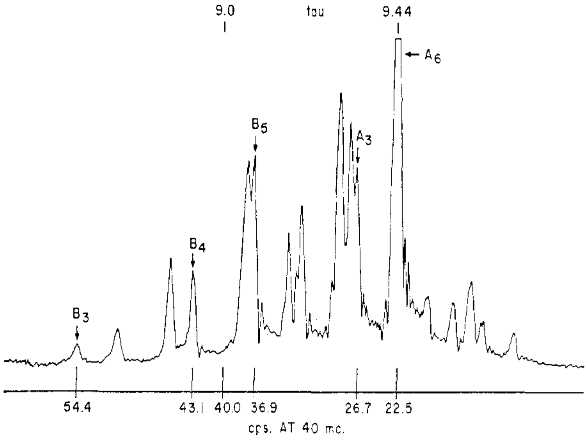

Fig. 1.—N.m.r. spectrum of tetraethylmethane (25 vol. % in CCl_4): $\delta\nu = 17.5 \pm 0.4$ cps., $J = 7.3 \pm 0.2$ cps., $J/\delta\nu = 0.4 \pm 0.02$. Replicate spectra were measured on a Varian 4300-2 spectrometer at 40 mc. and calibrated against internal tetramethylsilane at 26.5° by audiofrequency-sideband interpolations. The spectrum is calibrated in *tau* values and in cps. at 40 mc. downfield from TMS Pertinent lines are labeled in accordance with reference 8.

It is therefore recommended that when τ units are reported they refer only to the position of the origin of the multiplet (a measure of the chemical shift of the atom under observation). If possible, the multiplet should be further characterized by reporting its multiplicity and its coupling constant, J, in cps. The importance of establishing this practice is set forth below.

Reliable shielding values are obtained by internal calibration of n.m.r. spectra with tetramethylsilane[3] (TMS) (where applicable) and the dimensionless δ or τ units are used by some for presentation of spectral data in order that workers using different spectrometer frequencies may have a simple basis for comparison of data. These units by definition account for the dependency of shielding data (chemical shift) on spectrometer frequency and are independent of spectrometer frequency.

Since spectra ordinarily are calibrated by the use of audiofrequency side bands measured with a frequency counter the positions of the lines in the spectrum are *observed* in cps. relative to some standard. The dimensionless τ units may be *calculated* from these data using the equation: $\tau = 10 \times 10^6(\nu_{TMS} - \nu_{Line})/\nu_{spectrometer}$.

In the case of spin multiplets the absorption from a given hydrogen atom is perturbed by its coupled neighbors and may be widely separated into several lines of varying intensity whose spectral positions are related to a parameter, $J/\delta\nu$, which is by definition the quotient of the size of the coupling constant, J, divided by the separation of the two shifts, $\delta\nu$. This coupling constant is invariant when specified in units of cps. and does not change with spectrometer frequency. Therefore, there is no rationale for dividing these line positions or their coupling constants by the spectrometer frequency to convert them to dimensionless units. In fact, the same sample, when observed at different spectrometer frequencies, may give quite different τ values or coupling constants, when calculated in this way. This is especially true if the coupling constant is large, as it may often be when fluorene, carbon-13,[4] or boron[5] (where J may be as large as 60, 200, or 180 cps. respectively) is involved in the spin interaction.

For example, the absorption of the 21-hydrogen atom was seen in the n.m.r. spectrum of 21,21-difluoroprogesterone as a regular triplet at 4.30 τ with a J of 53 cps. The position of the low-field line of this triplet was calculated as 3.42 τ from the 60 mc. spectrum but was 2.98 τ from the 40 mc. spectrum, when converted to τ units in this irrational way. This difference is confusing and tends to void the advantages cited above for τ units.

Conversely, if the positions of the lines in a multiplet or the coupling constant are reported only in dimensionless units and the spectrometer frequency is not recorded,[2,6] it may be impossible to calculate the coupling constant or the positions of the lines from the data.

For these reasons dimensionless units should be attributed only to the chemical shift of the *origin* of the multiplet. The location of the origin requires factoring of the multiplet by inspection (for simple first-order spectra) or by the method of spin-spin analysis (for complex multiplets of higher order). In the spectrum of tetraethylmethane, for example (Fig. 1) the chemical shift of the CH_2 and CH_3 multiplets could only be obtained after the generalized A_3B_2-spin Hamiltonian had been solved for the various energy levels from which the expected line frequencies were calculated.[7,8,9]

Thus the origin of the B-multiplet is the tall line at 22.5 cps. in Fig. 1 and the origin of the A-multiplet is exactly the mean of the B_4- and B_5- transition lines and is at 40 cps.[10] The locations of the origins

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(2) K. Mislow and M. A. W. Glass, *J. Am. Chem. Soc.*, **83**, 278 (1961).

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(7) B. R. McGarvey and G. Slomp, *J. Chem. Phys.*, **30**, 1586 (1959).

(8) P. L. Corio, *Chem. Revs.*, **60**, 363 (1960).

(9) A detailed derivation of the A_3B_2-problem can be supplied by the author.

(10) For derivation of these results see reference 8, p. 397. J was accordingly found from the equation: $\delta - 5/2\,J = 2\nu A_6 - \nu A_3 - \nu B_3$. Several alternate equations are possible.

of these multiplets are chemical shifts and may be labeled in values of τ (see Fig. 1).

Other multiplets may be factored in a similar manner once they are recognized.

When the multiplet is partially obscured or cannot be analyzed, the positions of the lines must be reported in terms of the observed data, in cps., at a given spectrometer frequency, relative to some standard (if not TMS the conversion factor should be specified). Both methods were acclaimed at the Second Conference on Experimental Aspects of NMR Spectroscopy, Pittsburgh, Pennsylvania, February 24–25, 1961. The problem is under study by the ASTM Committee E-13.

The tetraethylmethane sample was kindly supplied by Dr. K. W. Greenlee of A.P.I. Project 45 and the difluoroprogesterone by Dr. E. V. Jensen of the University of Chicago. The author gratefully acknowledges the suggestions and criticisms of Drs. F. L. Anet, D. J. Cram, H. S. Gutowsky, W. S. Johnson, B. R. McGarvey, R. E. Richards, J. D. Roberts, W. G. Schneider, B. L. Shapiro and J. N. Shoolery.

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AN OPTICALLY INACTIVE INTERMEDIATE IN THE MULTIPLE REARRANGEMENT OF *EXO*-2-AMINOMETHYLNORBORNANE

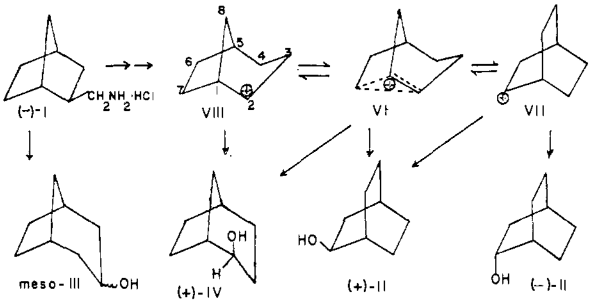
Sir:

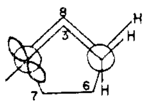
The behavior of *exo*-2-aminomethylnorbornane I on deamination provides an instructive comparison with that of the *endo*-isomer reported elsewhere.[1] In qualitative accord with a previous report,[2] we find that nitrous acid in acetic acid converts racemic I to a mixture of *ca.* 35–40% of the acetate of bicyclo[2.2.2]octanol-2, II; *ca.* 17–20% of the acetate of bicyclo[3.2.1]octanol-3, III; and *ca.* 35–40% of the acetate of a product previously identified[2] only as a bicyclo[3.2.1]octanol-2 but now shown to be the *exo*-(*axial*)-isomer IV by comparison of its properties with those known[3] to distinguish it from the *endo*-(*equatorial*)-isomer V. From deamination of optically active (−)-I hydrochloride, 40.7% optically pure,[4] lithium aluminum hydride cleavage of the mixture of acetates and repeated preparative vapor chromatography, there are obtained: optically active II, $[\alpha]_D$ +8.97° ($CHCl_3$); optically active IV, $[\alpha]_D$ +5.25° (ethanol); and optically inactive III, a *meso* compound (possibly a mixture of epimers). The latter substance presumably represents a mode of ring expansion alternative to that employed in the formation of II and IV.

Although we have no evidence yet on the degree of retention of optical purity in IV, II is partially racemized. The rotation of optically pure II is established by a modification of the isotope dilution method,[5-7] in which x g. of ^{14}C-labelled racemic II acid phthalate of specific radioactivity C_0 is added to B g. of partially resolved[8] acid phthalate of rotation α_0, the mixture again is resolved *via* the brucine salt until material having a new rotation α and radioactivity C is obtained, and the weight E of excess enantiomer in the starting sample is calculated from the equation

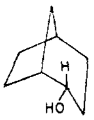
$$E^2 = \frac{B[(x + B)^2 - (C_0/C)x(x + B)]}{B - (C_0/C)x(\alpha/\alpha_0)}$$

On this basis, optically pure bicyclo[2.2.2]-2-octyl acid phthalate has $[\alpha]_D$ 30.5 ± 3.7° ($CHCl_3$), and optically pure II has $[\alpha]_D$ 40.0 ± 4.8° ($CHCl_3$). The stereochemical result in the deamination of I to II is therefore 49–63% retention of optical purity and 37–51% racemization.

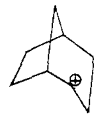




VIII a



V



IX

Although some of the product II apparently is formed *via* the optically active non-classical cation VI (previously postulated[8,9b] in the solvolysis of II, OBs instead of OH, and in the solvolysis of 3-cyclohexenylethyl *p*-bromobenzenesulfonate[9a]), VI cannot be the sole intermediate, since II then would be formed with complete retention of optical purity. The possibility is not excluded that transannular hydride shift in VI (from C.4 to C.2) may account for part of the racemization, but a simple explanation is provided by the inactive classical cation VII. Although partial racemization in the formation of II is established definitely by the above data, the experimental error in this result and in that reported[8] for the acetolysis of the optically active *p*-bromobenzenesulfonate of II (82 ± 15% retention) is almost large enough to allow the possibility that the two results are the same. It remains to be seen whether this is indeed the case.

The multiple rearrangement of I may be stepwise, like that of the *endo*-isomer,[1] since an initial

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[8] By the method of H. M. Walborsky, M. E. Baum and A. A. Youssef, *ibid.*, **83**, 988 (1961).

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