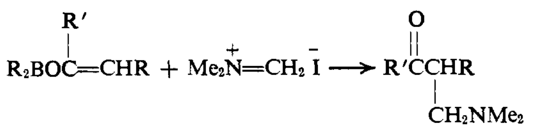
Table I. Formation of Mannich Bases by Reaction of Enol Borinates with Dimethyl(methylene)ammonium Iodide

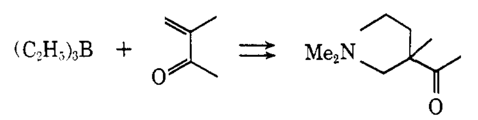


$$R_2BOC(R'){=}CHR + Me_2\overset{+}{N}{=}CH_2\,\overset{-}{I} \longrightarrow R'C(=O)CH(CH_2NMe_2)R$$

R_3B,[a] R	R'$COCHN_2$, R'	Product[b]	Yield, %[c]	Picrate mp, °C
C_2H_5[d]	C_6H_5	1-Phenyl-2-dimethylaminomethyl-1-butanone	92	157–158
C_2H_5[d]	$(CH_3)_2CH$	2-Methyl-4-dimethylaminomethyl-3-hexanone	94	128–129
C_6H_{13}	C_6H_5	1-Phenyl-2-dimethylaminomethyl-1-octanone	86	126–127
C_6H_{13}	$(CH_3)_2CH$	2-Methyl-4-dimethylaminomethyl-3-decanone	84	116–118
C_7H_{15}	C_6H_5	1-Phenyl-2-dimethylaminomethyl-1-nonanone	80	114–115
C_7H_{15}	$(CH_3)_2CH$	2-Methyl-4-dimethylaminomethyl-3-undecanone	100	113–113

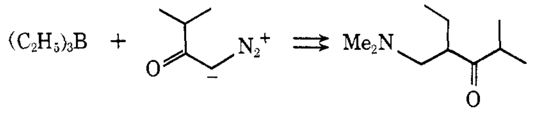
[a] Organoboranes (except $(C_2H_5)_3B$[d]) were prepared by hydroboration of the appropriate olefin. [b] Products were analyzed by glc, isolated, and characterized by spectroscopic methods (compatible ir and nmr spectra) and satisfactory (±0.3%) elemental analyses. [c] Based on diazo ketone, using a molar ratio of R_3B : diazo ketone : "Mannich reagent" of 1:1:1.15 (except for the preparation of **5** which employed 1.75 equiv of R_3B), and determined by glc analysis. [d] From Alfa Inorganics, Inc.

rived from reaction of triethylborane and 3-methyl-3-butenone. Subsequent reaction with **3** (in DMSO) provided (eq 5) the corresponding Mannich base in



(5)

87% yield. By way of comparison, an example which illustrates the versatility of the method, by enabling the construction of other Mannich base isomers (*i.e.*, at either secondary or tertiary positions), is the synthesis (94%) of **6** *via* the α-diazo ketone route (eq 6).



(6)

6

Mannich bases (and their functional equivalents) are useful intermediates for several important processes (*e.g.*, Michael, Diels-Alder, Robinson annelation). The present development illustrates that, by suitable choice of substrates (all of which are easily accessible), the simplicity, regiospecificity, and high yields of this method allow the unambiguous synthesis of certain Mannich bases which would not be readily available using conventional methods.

A typical experimental procedure, illustrated for the synthesis of 1-phenyl-2-dimethylaminomethyl-1-butanone, is as follows.[11] To a cooled (0°), magnetically stirred solution of 20 mmol of triethylborane (Alfa Inorganics, Inc.) in 40 ml of anhydrous THF was gradually added a solution of 2.92 g (20 mmole) of 2-diazoacetophenone in 20 ml of THF. The ice bath was removed, and the mixture was stirred at room temperature (90 min), at which time nitrogen evolution was complete. Then a solution of 22.5 mmol of dimethyl(methylene)ammonium iodide[4] in 20 ml of anhydrous DMSO was added to the stirred solution. The initial precipitate gradually dissolved and a yellow solution formed. After stirring at room temperature (3 hr), the mixture was cooled to 0°, and 20 ml of 3 *N* NaOH solution was added. The mixture was stirred vigorously (15 min), poured into ice-water (200 ml), and extracted with pentane (five 50-ml portions). After concentration (rotary evaporator), the residue[12] was extracted with cold 5 *N* HCl solution, and the aqueous layer was made basic with NaOH. The mixture was extracted with pentane (five 50-ml portions), and the residue remaining after concentration of the dried ($MgSO_4$) extract was distilled to afford 2.86 g (70%) of 1-phenyl-2-dimethylaminomethyl-1-butanone, bp 84–86° (0.75 mm), mp 42–44°, picrate mp 157–158°.

Acknowledgment. We thank the National Research Council of Canada for financial support.

[11] Anhydrous solvents, reagents, and equipment are necessary; without these precautions, yields of Mannich base diminish and concomitant formation of ketone occurs *via* hydrolysis of the enol borinate.[5]

[12] Distillation at this stage gives considerably lower yields of product.

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Received September 26, 1972

Raman Scattering of Circularly Polarized Light by Optically Active Molecules

Sir:

In a recent letter, Bosnich, Moskovits, and Ozin reported observations of the differential Raman scattering of right and left circularly polarized light by the optically active liquid α-phenylethylamine.[1] We have been unable to reproduce their results but have observed different effects which correspond more closely with theoretical expectations.

The effect may be expressed as[2]

$$\Delta = (I^R - I^L)/(I^R + I^L)$$

where I^R and I^L are the intensities of the scattered light in right and left circularly polarized incident light.[3] Δ can be defined for light scattered at 90° which is linearly polarized perpendicular (Δ_x) and parallel (Δ_z) to the scattering plane.

[1] B. Bosnich, M. Moskovits, and G. A. Ozin, *J. Amer. Chem. Soc.*, **94**, 4750 (1972).

[2] L. D. Barron and A. D. Buckingham, *Mol. Phys.*, **20**, 1111 (1971).

[3] The name Raman circular dichroism[1] is not recommended since the word dichroism refers to differential absorption. The fundamental process responsible for Raman scattering is different from that producing infrared absorption, and the effect cannot be regarded as a manifestation of infrared circular dichroism although both are forms of vibrational optical activity. We use the name Raman circular intensity differential (CID).

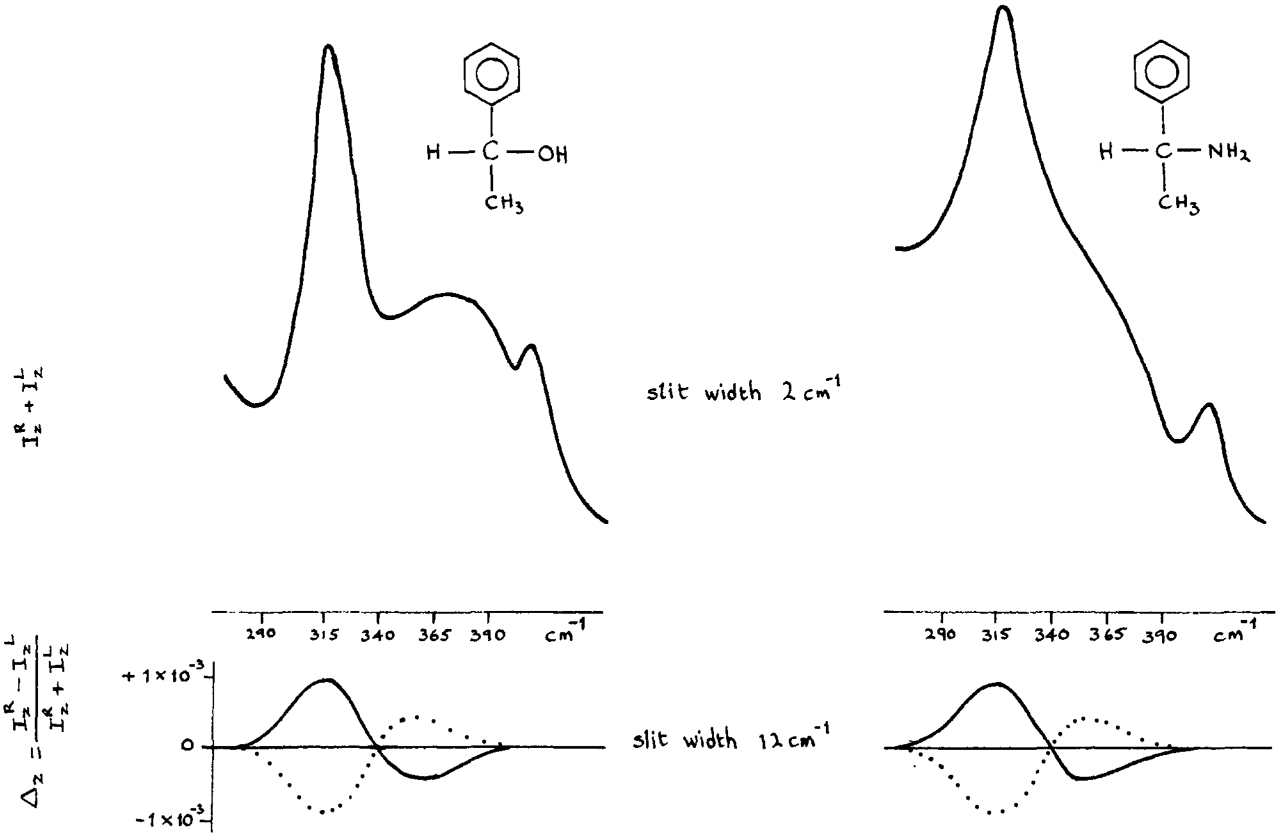

Figure 1. The Raman and Raman CID spectra of α-phenylethanol and α-phenylethylamine for scattered light linearly polarized parallel to the scattering plane. (——) is the (−) enantiomer and (· · ·) is the (+) enantiomer. The background has been subtracted from the Raman intensities in estimating Δ_z.

The features of the results of Bosnich, *et al.*,[1] are: (1) Δ_z was as large as 10^{-1}; (2) the effect was significant only in parallel polarization; (3) the sign of Δ_z for each Raman band in a particular enantiomer was the same and of the same magnitude but of opposite sign for the other enantiomer.

Our reasons for suggesting that these observations arise through a spurious mechanism are as follows. (1) Δ_z was expected to be $\sim 10^{-3}$.[2] (2) The intensities of the light scattered at 90° linearly polarized perpendicular (I_x) and parallel (I_z) to the scattering plane are

$$I_x \propto 3\alpha^2(5 + 7\kappa^2) + 3\alpha^2(5 + \kappa^2)P \cos 2\eta \cos 2\theta + (2/c)[3\alpha G'(5 + 7\gamma) + \omega\alpha\zeta]P \sin 2\eta$$

$$I_z \propto 18\alpha^2\kappa^2 + (4/c)[9\alpha G'\gamma - \omega\alpha\zeta]P \sin 2\eta$$

where θ is the azimuth of the major axis of the polarization ellipse of the incident light ($\theta = 0$ corresponds to the major axis perpendicular to the scattering plane), η is the ellipticity ($\eta = 0$ corresponds to linear polarization and $\eta = \mp\pi/4$ to circular polarization, the upper and lower signs referring to right and left), P is the degree of polarization (P varies between 0 for unpolarized light and 1 for polarized light), $\boldsymbol{\alpha}$ is the transition polarizability tensor, $\mathbf{G}'$ is the electric dipole–magnetic dipole polarizability tensor, and $\mathbf{A}$ is the electric dipole–electric quadrupole polarizability tensor.[2] The anisotropies in $\boldsymbol{\alpha}$, $\mathbf{G}'$, and $\mathbf{A}$ are

$$\kappa^2 = (3\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta})/2\alpha_{\gamma\gamma}\alpha_{\delta\delta}$$

$$\gamma = (3\alpha_{\alpha\beta}G'_{\alpha\beta} - \alpha_{\alpha\alpha}G'_{\beta\beta})/2\alpha_{\gamma\gamma}G'_{\delta\delta}$$

$$\zeta = \alpha_{\alpha\beta}\mathcal{A}_{\alpha\beta}/2\alpha_{\epsilon\epsilon} = \alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}/2\alpha_{\epsilon\epsilon}$$

and the mean values are $\alpha = {}^1/_3\alpha_{\alpha\alpha}$, $G' = {}^1/_3G'_{\alpha\alpha}$, and $\mathcal{A} = {}^1/_3\mathcal{A}_{\alpha\alpha} = 0$. The square of the mean polarizability, α^2, makes the largest contribution to the intensity of polarized Raman bands, whereas the anisotropy makes the largest contribution to depolarized bands through $\alpha^2\kappa^2$. The optically active scattering producing the CID arises from $\alpha G'$, $\alpha G'\gamma$, and $\alpha\zeta$, and modulation of η enables this to be detected as the part of the scattered light modulated in phase with η. Imperfections in, or misalignments of, the modulating device can give rise to spurious effects since the more intense scattering from α^2 and $\alpha^2\kappa^2$ contributes to I_x through terms which depend on θ, η, and P. The modulated part of I_z should be much less susceptible to error. We observed large contributions to the modulated part of I_x but these depended critically on the alignment of the modulator; however, the modulated part of I_z is insensitive to the alignment, and the corresponding spurious values of Δ_z were reduced to less than $\pm 2 \times 10^{-4}$. We could easily induce Δ_x values of 10^{-2} in the strongly polarized bands favored by Bosnich, *et al.*,[1] but the signs and magnitudes were the same for (+), (−), and (±) forms. If genuine effects of the size reported[1] exist, we should have found large differences between these three forms. (3) Different signs for Δ are to be expected among the Raman bands of a particular enantiomer. The constant but opposite signs for Δ_z found in the two enantiomers by Bosnich, *et al.*,[1] could originate in the opposite optical rotations.

We have observed Raman CID couplets in α-phenylethanol and α-phenylethylamine consisting of positive and negative components associated with two adjacent weakly polarized Raman bands common to both molecules at ~315 and ~365 cm^{-1}. The peaks of the sharp bands at ~315 cm^{-1} are associated with values of $|\Delta_z| \sim 1 \times 10^{-3}$, and the peaks of the broad bands at ~365 cm^{-1} with values of $|\Delta_z| \sim 0.5 \times 10^{-3}$. The (+) and (−) enantiomers give mirror-image couplets. The CID's of the alcohol (+) and (−) enantiomers have the same signs as the corresponding amine enantiomers. No significant Raman CID was detected in any other band.

We used a Coderg Model PH1 Raman spectrometer equipped for photon counting and a Coherent Radiation Laboratories Model 52A argon ion laser set at 4880 Å. The polarization of the incident laser beam was modulated directly between right and left circular at 90 Hz with a KDP crystal driven by an appropriate square-wave alternating voltage; square-wave modulation can, in principle, eliminate the spurious contributions to I_x arising from the term dependent on θ, η, and P since this term no longer contributes. The component of the Raman light modulated at 90 Hz was the difference in the Raman intensity in right and left circularly polarized light. The noise level of the phase-sensitive detection system corresponded to a value of $\Delta \sim \pm 2 \times 10^{-4}$. The component of the light scattered at 90° and linearly polarized parallel to the scattering plane was sampled since, as stated above, only this component was free from spurious contributions in our instrument.

Acknowledgment. This work was supported by the National Research Development Corporation.

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Electron Spin Resonance and Electronic Structure of Organic Radicals Containing α-Bromine Atoms

Sir:

Despite the fact that a very wide range of organic radicals have been studied by esr spectroscopy, both in solution and in the solid state, very few have been interpreted for $R_2\dot{C}X$ radicals, where X = Cl, Br, or I. Recently, various $R_2\dot{C}Cl$ radicals have been detected in the liquid state[1] and this has enabled others[2] to interpret esr spectra for such radicals in the solid state that had previously defied complete interpretation.[3] Very recently, a full analysis of the radical $F\dot{C}(CONH_2)Cl$ has been described[4] formed in γ-irradiated $FCH(CONH_2)Cl$ crystals.[5]

Although $H_2\dot{C}Br$ radicals have been matrix isolated and studied by infrared spectroscopy,[6] we know of only one tentative esr identification, in which a multiline esr spectrum for an irradiated single crystal of bromoacetic acid was obtained but was not analyzed.[7] The results reported are of little diagnostic value and, indeed, need not have been due to an α-bromo radical.

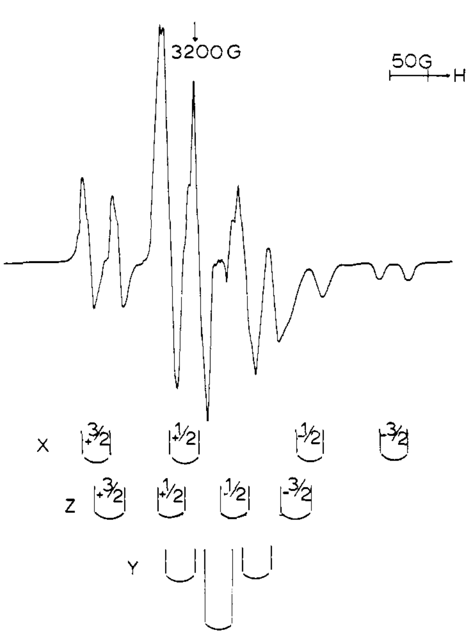

Figure 1. First derivative esr spectrum for powdered α-bromomaleic acid after exposure to ^{60}Co γ-rays at 300 K. This spectrum, especially the features marked A_z, is completely characteristic of $R_2\dot{C}Br$ radicals and can be taken as being diagnostic of their formation.

We have studied a wide range of aliphatic bromides after exposure to ^{60}Co γ-rays at 77 K and have obtained esr spectra which are clearly characteristic of $R_2\dot{C}Br$ radicals. A typical spectrum is given in Figure 1, and such a spectrum may be taken as diagnostic of the formation of such radicals.

In order to proceed with a proper analysis of these spectra, we began by studying the X-band and Q-band powder spectra of typical α-chloro radicals, especially that of $H\dot{C}(CO_2H)Cl$ formed from chloroacetic acid by γ irradiation. Our results (Table I) compare very well with those from single crystals and give us confidence in our procedure.

Analysis of spectra such as that in Figure 1 [for $Br\dot{C}CO_2H(CH_2CO_2H)$] was helped by the following observations. There is a clear set of four doublets (marked A_z). The doublet of *ca.* 40 G stems from hyperfine coupling to one of the β protons and should be nearly isotropic. The quartet is unequally spaced in a manner characteristic of a nuclear quadrupole effect with the magnetic field perpendicular to the major electric field gradient (in this case, the C–Br bond direction). We conclude that this corresponds to a direction perpendicular to the radical plane.[8] Then we expect to find a set of four evenly spaced lines with a high g value for the magnetic field parallel to the C–Br bond (z) and a multiplet at intermediate g values whose form depends upon the relative magnitudes of the hyperfine coupling and $^1/_2e^2Qq_z$, the quadrupole interaction term. The value of $^1/_2e^2Qq_z$ is expected to be close to that for normal C–Br bonds which usually fall close to 80 G.[9] Thus the A_z features

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