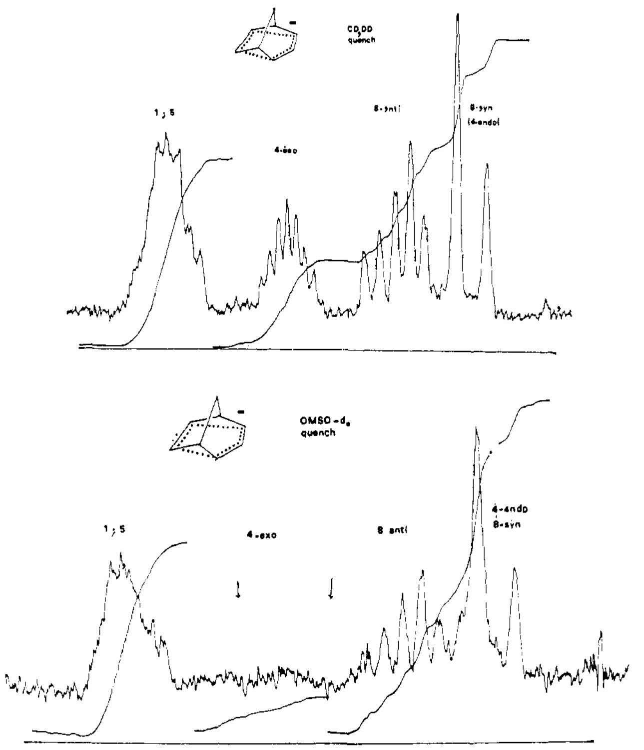

Figure 1. Nmr spectra (100 MHz) of quenches (A) and (B) taken between τ 6.5 and 8.5 at 250-Hz sweep width in CCl_4, showing $H_{1,5}$ at τ 7.38, $H_{4\ exo}$ at 7.74, $H_{8\ anti}$ at 8.10, $H_{4\ endo}$ (partly obscured) at 8.23, and $H_{8\ syn}$ at 8.33.

signal, and in (B) has largely disappeared. We estimate the stereoselectivity of quenching to be better than 85% in both cases. In one run under condition (C) assayed at 220 MHz an intermediate result was obtained with *ca.* 50% *exo* and 50% *endo* deuteration.

We find a probable explanation for result (A) by considering that III, which is strongly basic, exists as a contact ion pair with potassium cations in association with the more delocalized *endo* face of the carbanion. In their extensive study on hydrogen isotope effects attending proton transfer to carbanions, Pocker and Exner[8] considered that alcohols displaced the metal cation to produce hydrogen-bonded carbanion which rapidly collapsed. Cram has used the concept of specific hydrogen bonds between methanol and carbanions in his extensive studies on the stereochemistry of electrophilic substitution processes.[9] On these precedents, therefore, specific *endo* protonation is to be expected.

Conversely, it is probable that quenching by dimethyl sulfoxide occurs without the involvement of hydrogen bonding, since this solvent has little tendency to form hydrogen bonds to carbanions.[10] One must therefore look to other factors to explain the *exo* selectivity and we suggest that torsional effects[11] may operate to produce a selectivity of this magnitude. Given that ΔpK_a between I and dimethyl sulfoxide will be about 4–6 units, one might expect that rehybridization at C_4 is not very greatly advanced at the transition state. Examination of molecular models makes it clear that in this situation, less torsional strain is introduced on reprotonation from the *exo* direction.

Radlick and Rosen[12] have studied deprotonation leading to IV and quenching of this anion in dimethyl sulfoxide and explain the high *endo* specificity of these

IV

reactions on stereoelectronic grounds. It is clear from our results that if stereoelectronic factors operate at all in the formation and quench of III, they are mitigated by steric effects and ion-pairing considerations.

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[13] Award of an Australian National University Postdoctoral Traveling Fellowship is gratefully acknowledged by E.N.C. We are most grateful to Dr. Robin Goodfellow, University of Bristol, for 100-MHz nmr spectra and Mr. M. C. McIvor, I.C.I. Runcorn, for 220-MHz spectra.

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Simultaneous Biradical 1,2 and Concerted 1,4 Cycloaddition of *cis*- and *trans*-1,2-Dichloro-1,2-difluoroethylene to Cyclopentadiene

Sir:

Mechanistic studies of competition between thermal 1,2 and 1,4 cycloaddition of fluoroalkenes to conjugated dienes have been reported[1–7] and reviewed.[8] Orientation in the products, absence of major solvent effects, and greater loss of configuration in the cycloadducts than in the recovered diene establish the first step in the 1,2 cycloaddition as reversible biradical formation. Evidence regarding the 1,4-addition mechanism is mostly ambiguous: trace 1,4 adducts form with essentially the same activation energy as accompanying 1,2 adducts, and those factors which destabilize *s-trans* conformation in the ground-state[2,3] or excited[9] diene also favor 1,4 cycloaddition. However, *s-cis* or skew conformation in the diene is not a sufficient condition for 1,4 addition of fluoroalkenes.[10] Only in one case of substantial competition between 1,2- and 1,4-cycloaddition modes (2,4-hexadiene with α-acetoxyacrylonitrile[11]) has the 1,4 cycloaddition been shown by configurational evidence to be concerted.

Following stereochemistry in the thermal addition

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[5] P. D. Bartlett and L. K. Montgomery, *ibid.*, **86**, 628 (1964).

[6] P. D. Bartlett, C. J. Dempster, L. K. Montgomery, K. E. Schueller, and G. E. H. Wallbillich, *ibid.*, **91**, 405 (1969).

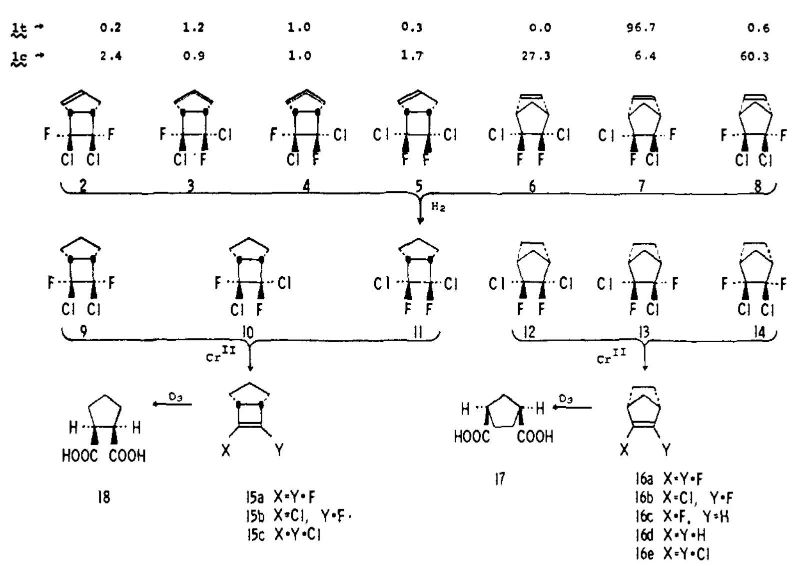
[7] P. D. Bartlett and G. E. H. Wallbillich, *ibid.*, **91**, 409 (1969).

[8] P. D. Bartlett, *Science*, **159**, 833 (1968).

[9] W. L. Dilling, *J. Amer. Chem. Soc.*, **89**, 2742 (1967).

[10] P. D. Bartlett, A. S. Wingrove, and R. Owyang, *ibid.*, **90**, 6067 (1968), and especially footnote 6.

[11] P. D. Bartlett and K. E. Schueller, *ibid.*, **90**, 6077 (1968).



of 1,2-dichloro-1,2-difluoroethylene (**1**) to cyclopentadiene indicates that 1,2 adducts are indeed formed by a biradical mechanism whereas 1,4 adducts are simultaneously formed by a concerted mechanism. A mixture of *cis*- and *trans*-1,2-dichloro-1,2-difluoroethylene is heated with about one-third of its weight of cyclopentadiene at 180–195° for 8 hr under nitrogen in a sealed Pyrex tube. On vapor phase chromatography the adducts elute from Carbowax 20M in the order **2**, **3**, **4**, **5**, **6** + **7**, **8**. Hydrogenation reorders the elution on Carbowax 20M to **9**, **10**, **11**, **13** + **14**, **12**, allowing preparative vpc separation of all adducts in their hydrogenated form.

Degradation distinguishes 1,2 from 1,4 adducts. Chromous ion effects vicinal dehalogenation and partial reduction to **15a,b** and **16a–d**.[12,13] Ozonolysis and subsequent oxidation of the dehalogenated olefins derived from the saturated 1,4 adducts give *cis*-1,3-cyclopentanedicarboxylic acid (**17**) in contrast to *cis*-1,2-cyclopentanedicarboxylic acid (**18**) from saturated 1,2-adduct dehalogenation products.

Structural assignments can be completed on the basis of ^{19}F nmr spectra. A single symmetrical multiplet immediately identifies those hydrogenated adducts with equivalent fluorines (*cis* to each other) while two unsymmetrical multiplets identify those with nonequivalent fluorines (*trans* to each other). Virtual coupling results in a 1:2:1 triplet for *exo-cis*-difluoro adduct **12**[14,15] while coupling to the *anti* bridge proton results in a 1:1 doublet for *endo-cis*-difluoro adduct **14**.[16] Based on angular dependence of vicinal J_{HF},[17,18] the broader ^{19}F AA′XX′ spectrum is assigned to *exo-cis*-difluoro adduct **11** and the narrower AA′XX′ spectrum to *endo-cis*-difluoro adduct **9**.

Chemical evidence confirms spectral structure assignments. Adducts **3** and **4** hydrogenate to the same compound **10**; positions of the double bond in isomers **3** and **4** were not assigned. This remaining uncertainty is indicated by the dotted double bonds in the figure. Direct fluorination[19] of **15c** and **16e** give[5] *exo-cis*-difluoro adducts **11** and **12** in preference to *endo-cis*-difluoro adducts **9** and **14**. Iodobenzene dichloride chlorination[20] of **15a** and **16a** gives *exo-cis*-dichloro adducts **9** and **14** in preference to *endo-cis*-dichloro adducts **11** and **12**.

As final confirmation compounds **9–16c** and **16e** give mass spectra with parent peaks of correct exact mass, with acceptable chlorine isotope ratios, and with reasonable fragmentation patterns.

Separation on preparative vpc affords 95% *cis*-1,2-dichloro-1,2-difluoroethylene (**1c**) contaminated with 5% *trans*-1,2-dichloro-1,2-difluoroethylene (**1t**) and 99% pure **1t** contaminated with 1% **1c**. A 5% DMSO on 80–100 Alcoa F-20 chromatographic alumina column at 0–25° gives particularly good separation.

The product distribution from addition of 99% pure **1t** to cyclopentadiene is shown as the upper row of numbers in the above chart with each number corresponding to the adduct directly below. The product distribution from addition of 95% pure **1c** to cyclopentadiene is shown in the second row of numbers. The numbers represent uncorrected vpc trace areas for the adducts adjusted to a total area of 100. Control experiments indicate that all adducts as well as **1c** and **1t** are stable to the reaction conditions; they neither decompose nor interconvert. Considering the 1% *cis* impurity in **1t** and the 5% *trans* impurity in **1c**, one concludes that the 1,4 adducts were formed with retention of *cis–trans* fluoroalkene configuration. On the other hand the 18–32% loss of configuration in the 1,2 adducts is not only too large an effect to be accounted for by 1–5% *cis–trans* impurity in **1** but also compares well with loss of configuration in other biradical additions.[4,6,7]

Thus in the present instance the products of 1,2 addition are formed by a two-step biradical mechanism while the 1,4 addition occurs simultaneously by a one-step concerted mechanism.[21] Cyclopentadiene, among

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(21) The conditions under which a rapid two-step cycloaddition may yield retention of configuration, which do not apply here, are discussed in a Centenary Lecture in press in *Quarterly Reviews*. The 1,6 biradical involved in the addition of maleonitrile to bicyclo[2.1.0]pentane loses configuration to the extent of 19% in the dicyanonorbornane product [P. G. Gassman, R. J. Mansfield, and T. J. Murphy, *J. Amer. Chem. Soc.*, **91**, 1684 (1969)].

dienes, is strongly predisposed to the concerted 1,4 mechanism;[5] **1t** (2.7% 1,2 addition) and **1c** (6.0% 1,2 addition) are both intermediate in their behavior toward cyclopentadiene between ethylene (no 1,2 addition) and 1,1-dichloro-2,2-difluoroethylene, which yields 16.6% of the 1,2 adduct.[3]

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Excitation Profiles of Laser Raman Spectra in the Resonance Region of Two Carotenoid Pigments in Solution

Sir:

Using the emissions at the frequencies available from the argon-ion laser, we have obtained the excitation profiles of resonance-enhanced Raman spectra,[1–16] well within the lowest optical absorption band, of two carotenoid pigments[17–19] in solution. These profiles differ substantially from the absorption spectrum and therefore contain new information concerning the electronic structure of the pigment molecules. Although one expects the resonance-enhanced Raman effect (RRE) to be quite a general phenomenon, its applicability to the study of electronic structures of molecules still hinges on the availability of suitable excitation sources in the shorter wavelengths. The extreme sensitivity attainable by the RRE makes it a potentially powerful analytical tool.[5,15] In particular, it has been applied to detect spectra of pigments in live tissue.[20] The experiment amounts to measuring the intensities of the Raman lines[3,15] as a function of the excitation frequency, as the latter is swept through the regions of electronic absorption (excitation profile, EP).[14] Before the advent of lasers, most of these experiments were carried out indirectly (using one or two excitation frequencies and shifting the absorption spectrum by changing temperature or molecules in a homologous series).[3,21–23] The eight emissions from an A-ion laser allowed the direct acquisition of EP data of all-*trans* β-carotene and lycopene[17–19] with much finer grain than in the experiments cited above.

In addition to the two Raman lines reported in the past for β-carotene[4,24,25] at $\bar{\nu}_1$ 1158 and $\bar{\nu}_2$ 1527 cm^{-1}, assigned, respectively, to single- and double-bond stretching modes of the conjugated chain,[26,27] we have observed a number of additional transitions in the region of fundamental vibrations; the shoulder on the $\bar{\nu}_1$ transition was resolved into three sharp transitions at 1215, 1193, and 1176, $\bar{\nu}_4 = 1006$, and $\bar{\nu}_5 = 961$ cm^{-1}. The strongest overtones were found at $\sim 2\bar{\nu}_1 = 2313$, $\sim \bar{\nu}_1 + \bar{\nu}_2 = 2679$, $\sim \bar{\nu}_1 + \bar{\nu}_4 = 2163$, and $\sim 2\bar{\nu}_2 = 3048$. The spectrum of lycopene was quite similar, with $\bar{\nu}_1 = 1158$ and $\bar{\nu}_2 = 1515$ cm^{-1}. Figure 1 shows examples of the Raman spectra. Vibrational assignments are not discussed here.

As an internal standard of intensity we used the lines of the *n*-hexane solvent, which does not absorb in the visible and has Raman lines within 100 cm^{-1} (in most cases within 50 cm^{-1}) of the carotenoid lines; this separation is sufficiently small so that differential absorption corrections[15] can be neglected—this was checked by carefully studying the location of the lines within the absorption spectrum of the pigments. The $\bar{\nu}^4_{\mathrm{Raman}}$ correction[15] was also found to be negligible. As a measure of intensity, we take ratios of the areas of the pigment and the adjacent hexane lines. The relative intensity factors thus obtained for a fixed sample at variable excitation frequencies represent the excitation profile. The EP's for fundamentals were taken in very dilute solutions ($c \lesssim 1\ \mu M$) using a transmission setup.[28] The more concentrated samples, used to study the overtones, were examined by a reflection technique.[28] The samples were repeatedly checked for chemical stability by remeasuring the fundamental Raman lines and the optical absorption spectrum (using a Cary 14).

In Figure 2 we plotted the excitation profiles for various Raman lines of the two pigments studied and compared them to the corresponding absorption spectra.

In both cases, the longest wavelength of excitation exceeds that of the first absorption peak. Nevertheless, enhancement is already appreciable—as evidenced by the observability of the lines at 10^{-7} *M* concentrations.

In β-carotene we see two well-defined intensity peaks: the peak at $\lambda \sim 476$ nm in the EP of the fundamentals is quite close to the lowest absorption peak, being, however, much sharper than the latter; the peak in the EP of the overtones occurs at $\lambda \sim 467$ and is distinct

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