as presented by Stern, *et al.*,[4] has the valyl and leucyl peptide protons intramolecularly hydrogen bonded and the phenylalanyl and ornithyl peptide protons exposed to the solvent. It is, therefore, the resonances of the peptide protons exposed to the solvent which undergo the large upfield shift as the per cent of TFE is increased. The pmr spectra of gramicidin S in both deuteriomethanol and deuterio-TFE are very sharp suggesting no aggregation. As a reference compound, the position of the peptide proton resonance for DKP (L-alanyl-L-alanine diketopiperazine) was observed in various TFE–methanol mixtures. The result, as shown in Figure 1, is consistent with an upfield shift for solvent exposed peptide protons and very closely parallels the result for the nonintramolecularly hydrogen bonded protons of gramicidin S.

The exact nature of the solvent–peptide proton interaction giving rise to this phenomenon is not entirely clear at present. However, a decrease in the extent of hydrogen bonding with the solvent is consistent with an upfield shift for the corresponding resonance.[6] Goodman and Rosen[7] found for a series of L-glutamate oligomers that TFE induced secondary structure. Circular dichroism results by Urry, *et al.*,[8] indicate that TFE mimics the natural environment of membrane proteins insofar as the membrane proteins in 80% TFE give ellipticities very similar to those calculated for membrane proteins in their natural environment. We would like to raise the possibility that TFE does not hydrogen bond as well with the peptide protons as does methanol. This would in turn favor intramolecular hydrogen bonding, thereby increasing the probability of a fixed solution conformation.

There are other lines of experimental evidence supporting this idea. In deuteriomethanol the phenylalanyl and ornithyl peptide protons exchange very rapidly; whereas in deuterio-TFE exchange is slow. Also temperature dependence studies in TFE show the temperature coefficients for the ornithyl and phenylalanyl peptide protons to be very similar to the valyl and leucyl, in sharp contrast to methanol studies where the differentiation between internally and noninternally hydrogen bonded protons is very clearcut.[2] This means that in TFE, exposure of peptide protons to solvent has little effect on the temperature dependence.

The similar but opposing dipoles for the CF_3 and CH_2OH moieties may, in part, be responsible for the unusual solvent properties of TFE. This and other possible mechanisms are under consideration. The essential point of this communication, however, is the presentation of a third method for delineating peptide protons in small, relatively rigid cyclic polypeptides and thereby elucidating their secondary structure. Investigations are presently underway concerning the general applicability of this method.

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Reactions of Methylene in Solution. Formation of Olefins

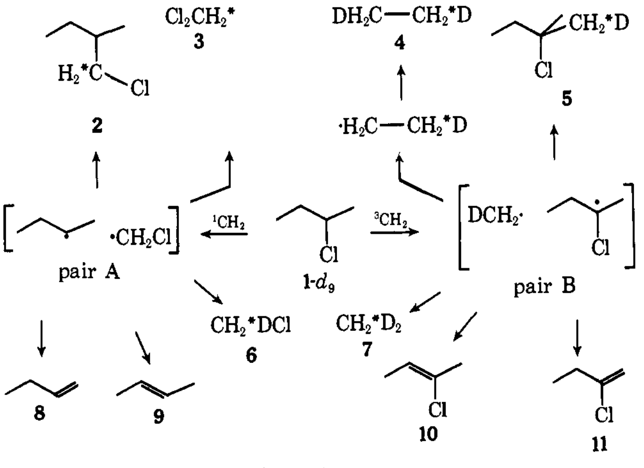
Sir:

Recently we described the application of chemically induced dynamic nuclear polarization (CIDNP) as a mechanistic tool in the study of carbene reactions.[1] In our continuing investigations we have uncovered a novel reaction of methylene, namely, the dehydrogenation or dehydrochlorination of suitable substrates to form olefins and, respectively, methane or chloromethane.

It had been observed that the insertion of methylene into the carbon–chlorine bond of optically active 2-chlorobutane (**1**) proceeded with a high degree of racemization.[2] We reinvestigated this reaction employing direct photolysis and photosensitized decomposition of diazomethane for generating ${}^1CH_2$ and ${}^3CH_2$, respectively. In order to simplify the nmr spectra of prospective polarized products a perdeuterated substrate was used (**1**-d_9). The resulting spectra are shown in Figure 1a, c. The signal directions of the polarized products were analyzed in the framework of the radical-pair theory.[3] We assumed that all radicals involved have π character ($a_\alpha < 0$; $a_\beta > 0$) and that radicals bearing a chlorine have larger g values than their alkyl counter radicals.

Similar to the reactions with $CDCl_3$[1b] the two spin states of methylene were selective in their abstraction reactions with 2-chlorobutane (Scheme I). Thus, the polarized products observed during direct irradiation could be explained by attack at the chlorine atom (${}^1CH_2$), whereas the polarized products observed in

Scheme I[a]



[a] An asterisk denotes polarization.

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[1] H. D. Roth, *J. Amer. Chem. Soc.*, 93, 1527, 4935 (1971).

[2] W. von E. Doering, private communication.

[3] R. Kaptein, *Chem. Commun.*, 932, (1971), has suggested simple qualitative rules for the evaluation of CIDNP spectra. References to the radical-pair theory of CIDNP may be found therein.

the photosensitized decomposition required abstraction of a hydrogen atom as the initial step ($^3CH_2$). During direct irradiation of diazomethane in **1**-d_9 nuclear spin polarization was observed in the products 1-chloro-2-methylbutane (**2**-d_9, A), dichloromethane (**3**, E), and monodeuteriochloromethane (**6**-d_1, A). During photolysis of diazomethane in a 1 *M* solution of benzophenone in **1**-d_9, three additional polarized products were observed: 2-chloro-2-methylbutane (**5**, A), methane-d_2 (**7**, A), and ethane-d_2 (**4**, E). The formation of **4** can occur by methyl-d_1-induced decomposition of diazomethane, yielding ethyl-*2*-d_1, and subsequent deuterium abstraction from the solvent. Radical-induced decomposition of diazomethane is well established[4] and it appears reasonable that the polarization of methyl-d_1 radicals escaping from pair A is in part preserved through a diffusion-controlled reaction with a substrate (CH_2N_2) of 0.1 *M* concentration. Spectrum 1c also showed weak signals of spin-polarized **2**, **3**, and **6** in the same directions that were observed during direct irradiation. These signals occur because some light is still being absorbed by diazomethane directly.

In-cage coupling of the radical pairs A and B accounts for the signal directions of 1-chloro-2-methylbutane (**2**, A) and 2-chloro-2-methylbutane (**5**, A), respectively. Dichloromethane (**3**, E) and ethane (**4**, E) could be formed by reactions of chloromethyl and methyl radicals, respectively, after escape from their counter radicals.

There remain the signals of CH_2DCl (**6**, A) and CH_2D_2 (**7**, A) which apparently are also formed by abstraction of deuterium atoms by the intermediate radicals. However, their signal directions were opposite to those of the cage escape products (**3** and **4**) and, therefore, indicated that **6** and **7** were formed in the primary encounter cage.[5] Potential hydrogen donors for $\cdot CH_2Cl$ and $\cdot CH_2D$ are solvent molecules in the cage (radical-pair substitution[6]) or the respective counter radicals (generation of olefins, "disproportionation"). Reactions of both general types are documented in the literature of CIDNP[6,7] but only abstraction from the counter radicals can lead to spin-polarized **6** and **7**.

The disproportionation products corresponding to **6** and **7** are not discernible by nmr, when **1**-d_9 is the substrate. Therefore, diazomethane was photolyzed in **1**-h_9 as solvent–substrate (Figure 1b, d). Even though wide areas of the spectra were obscured by the solvent lines, polarized products could clearly be observed in the olefinic region, in a pocket around the resonance of diazomethane, and in the high-field region near methane. Direct irradiation showed a weak CH_2Cl_2 signal, a *doublet* due to **2**-h_{11}, and a singlet due to CH_3Cl, but no olefinic products. In contrast, during the photosensitized decomposition a weak olefinic quartet (A) and a strong olefinic singlet (A) were observed, whose chemical shifts matched those of 2-chloro-2-butene (**10**) and 2-chloro-1-butene (**11**), respectively. The signal directions are in line with disproportionation of radical pair B, initially of triplet multiplicity.

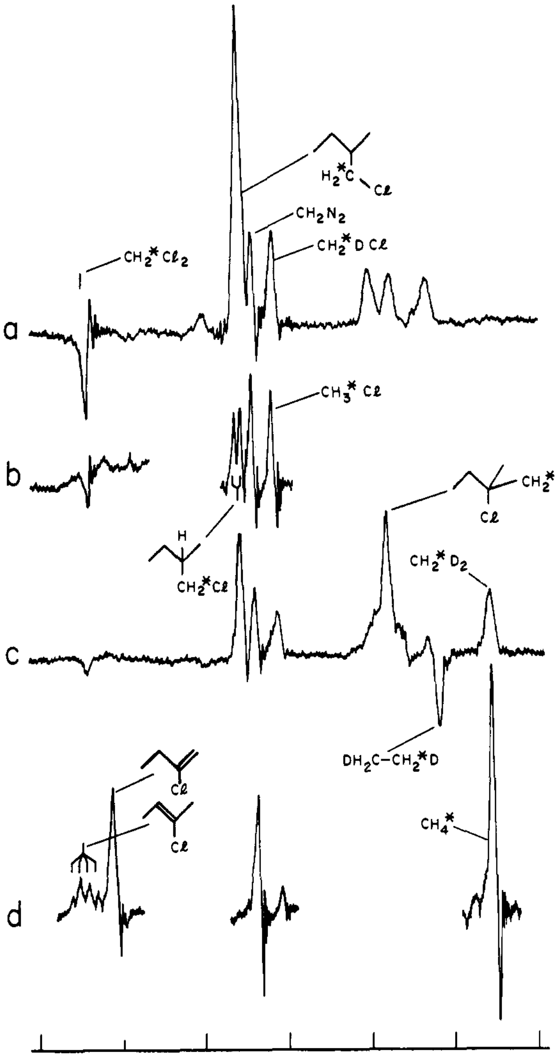

Figure 1. Pmr spectra (60 MHz) recorded during the direct (a,b) or sensitized (c,d) irradiations of diazomethane in **1**-d_9 (a,c) and **1**-h_9 (b,d) recorded at a sweep rate of 10 Hz/sec. At lower sweep rates (2 Hz/sec) fine structure was observed for the signals of **5**d_9-(triplet), **6**-d_1 (triplet), and **7**-d_2 (pentuplet). The frequency markers are separated by 61 Hz.

In summary, the results presented here show that singlet methylene selectively abstracts chlorine atoms, whereas triplet methylene selectively abstracts hydrogen atoms. The resulting radical pairs form products by recombination, by disproportionation, and after diffusive separation. The formation of olefins from methylene[8] (in yields of up to 10%) is not limited to 2-chlorobutane, nor to the triplet state of methylene, nor to dehydrogenation reactions. Additional polarized olefins observed were isobutylene (A; formed by dehydrochlorination of 2-chloro-2-methylpropane by $^1CH_2$), 1-chlorocyclohexene (A; $-H_2$ from chlorocyclohexane by $^3CH_2$), and trichloroethylene (E; $-HCl$ from

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[4] (a) W. H. Urry and J. R. Eiszner, *J. Amer. Chem. Soc.*, **73**, 2977 (1951); (b) W. H. Urry, J. R. Eiszner, and J. W. Wilt, *ibid.*, **79**, 918 (1957).

[5] Alteration of *two* parameters of Kaptein's formula[3] does not change the predicted signal direction, *e.g.*, **6**, A could arise *via* pair B (hydrogen abstraction by $^1CH_2$) and cage escape. This was ruled out because the coupling product **5** was not observed during the singlet reaction.

[6] (a) R. Kaptein, F. W. Verheus, and L. J. Oosterhoff, *Chem. Commun.*, 877 (1971); (b) R. A. Cooper, R. G. Lawler, and H. R. Ward, *J. Amer. Chem. Soc.*, **94**, 552 (1972).

[7] (a) H. R. Ward, R. G. Lawler, and R. A. Cooper, *J. Amer. Chem. Soc.*, **91**, 746 (1969); (b) H. R. Ward, R. G. Lawler, and T. A. Marzilli, *Tetrahedron Lett.*, 521 (1970).

[8] Olefin formation previously was observed in reactions of carbenes other than CH_2, *e.g.*, $:CHCOOCH_3$.[9] We have investigated the reactions of $:CHCOOCH_3$ with various substrates but so far have not found any indication of *polarized* olefins.

[9] A. P. Marchand and N. M. Brockway, *J. Amer. Chem. Soc.*, **92**, 5801 (1970), and literature cited therein.

1,1,1,2-tetrachloroethane by $^3CH_2$). Details of the reactions of methylene with these substrates will be published in a full paper. Scope and limitations of the reaction are under investigation.

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Molecular Structure of Tris(diphenylacetylene)tungsten Monocarbonyl

Sir:

Ever since the preparation of the novel complex tris(diphenylacetylene)tungsten monocarbonyl was reported several years ago,[1] there has been considerable speculation about its structure and mode of bonding.[1-3] Interest in this compound arose largely from its unexpected stoichiometry, which apparently was in violation of the effective atomic number rule. We submit here the results of a successful X-ray structure determination of this compound.

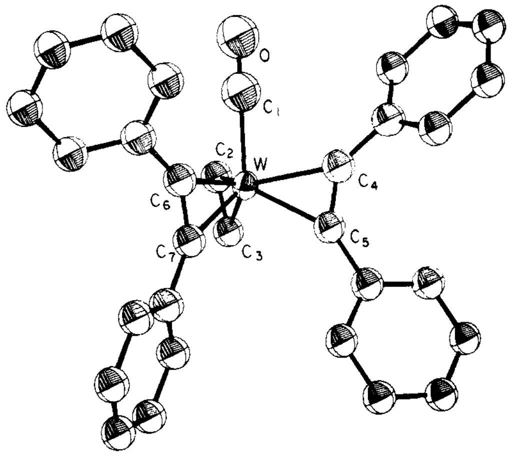

Figure 1. The molecular geometry of $(PhC{\equiv}CPh)_3W(CO)$ (the phenyl rings on carbons C_2 and C_3 have been omitted for clarity).

When prepared according to the published method[1] (reaction of $(CH_3CN)_3W(CO)_3$ and $PhC{\equiv}CPh$ in refluxing ethanol), $(PhC{\equiv}CPh)_3W(CO)$ can be obtained as large hexagonal plate-like crystals which, unfortunately, gave disordered, pseudotrigonal diffraction patterns. Better crystals were produced by utilizing an alternate preparative procedure whereby $W(CO)_6$ and $PhC{\equiv}CPh$ were refluxed directly in CH_3CN. From this reaction mixture, large yellow prismatic crystals were obtained and used in the subsequent analysis. Crystal data are as follows: triclinic; space group $P\bar{1}$; $a = 17.33$ Å, $b = 9.22$ Å, $c = 11.35$ Å, $\alpha = 99.1°$, $\beta = 106.7°$, $\gamma = 88.0°$; $V = 1715$ Å^3; ρ(obsd) = 1.43 g cm^{-3}, ρ(calcd) = 1.41 g cm^{-3} for $Z = 2$. The 2730 nonzero reflections, representing a half-sphere of data up to a 2θ maximum of 40°, were collected on a computer-controlled Nonius CAD-3 diffractometer using Mo Kα radiation. The structure was solved by conventional heavy atom techniques and refined to an R factor of 4.4%. In the least-squares refinement, the tungsten atom was refined anisotropically and the other nonhydrogen atoms refined isotropically. A final difference Fourier map showed no residual electron density (except near the W atom) greater than 0.6 e/Å^3.

We later found that $(PhC{\equiv}CPh)_3W(CO)$ forms other crystalline modifications, depending on the solvent used. A monoclinic variety[4] (space group $C2/c$; $a = 45.33$ Å, $b = 9.81$ Å, $c = 22.36$ Å, $\beta = 121.3°$, mol wt ≈ 825 for $Z = 8$), obtained *via* recrystallization from benzene, contains a C_6H_6 molecule of recrystallization, while an orthorhombic species[5] (space group $Pbca$; $a = 19.13$ Å, $b = 22.05$ Å, $c = 31.70$ Å, mol wt ≈ 745 for $Z = 16$), containing two independent molecules in the unit cell, can be obtained *via* recrystallization from CH_2Cl_2. The structures of both these species were subsequently solved by X-ray diffraction and shown to be similar to the triclinic variety.[4,5]

The geometry of the molecule, shown in Figure 1, has essentially C_{3v} symmetry (exclusive of the phenyl groups which are of course free to rotate). The coordination about the tungsten atom may be described as either a distorted tetrahedron or a tapered monocapped trigonal prism, depending on whether the complex is considered four coordinate or seven coordinate. The acetylene groups are inclined to the virtually linear (179.6°) WCO group by an average 13.4° angle of tilt. This tilting of the acetylenes away from the carbonyl group can also be appreciated by examining various nonbonding distances; the carbons C_2, C_4, and C_6, for instance, define a near equilateral triangle of length 3.56 Å, while C_3, C_5, and C_7 define a considerably smaller triangle of dimension 3.08 Å. The W–C and C–O distances associated with the carbonyl group are 1.99 and 1.16 Å, respectively. Various average molecular parameters are given as follows: W–C(ac) = 2.06 Å [where C(ac) = acetylene carbon], C(ac)–C(ac) = 1.30 Å, C(ac)–C(ph) = 1.46 Å [where C(ph) = *N*-carbon atoms of the phenyl groups], C(ac)–W–C(ac) = 36.4°, W–C(ac)–C(ac) = 71.6°, W–C(ac)–C(ph) = 148.7°, C(ac)–C(ac)–C(ph) = 139.6°. These figures indicate that the geometry of the acetylene group has been grossly altered upon coordination and has, in fact, approached the geometry of *cis*-stilbene. The decrease of the angle about a previously sp-hybridized carbon from 180° to about 140° is an expected feature in acetylene complexes[6,7] and has been observed in complexes of other linear ligands such as CS_2[8,9] and allenes.[10,11]

The finding that $(PhC{\equiv}CPh)_3W(CO)$ has C_{3v} symmetry provides support for the arguments of previous investigators,[1,2] who sought to rationalize the stoichiometry of the complex within the bounds of the effective

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