Reactions of Methylene in Solution. Insertion into the Carbon–Hydrogen Bond

Sir:

The most characteristic reaction of methylene, the divalent carbon intermediate obtained by thermolysis or photolysis of diazomethane, diazirine, or ketene, is the unique insertion into carbon–hydrogen bonds. This reaction was discovered in ethers by Meerwein and coworkers[1] and established in hydrocarbons by Doering and coworkers.[2] One could conceive a radical mechanism for this reaction, either *via* the sequence abstraction–recombination[3] or by a pathway involving a radical chain.[4] However, an elegant study of the photolysis of diazomethane in 2-methylpropene-*1*-^{14}*C* furnished unequivocal evidence for a direct insertion mechanism.[5]

In line with our studies of carbene reactions[6] we reinvestigated the reactions of methylene with hydrocarbons by employing the CIDNP technique.[7,8] This mechanistic tool allows one to detect minor by-products of reactions proceeding *via* radical pairs, or the minor fraction due to a radical mechanism of a product predominantly formed by a nonradical mechanism. Since the differences in the *g* values of hydrocarbon radicals are minimal, the potential CIDNP spectra should be dominated by the *multiplet* effect.[9] The choice of substrates thus is limited to cases where the product nmr spectra have multiplets (aside from being sufficiently separated from the substrate signals).

When a solution of diazomethane in toluene containing benzophenone (1 mol/l.) was irradiated in the probe of an nmr spectrometer, strongly enhanced signals of phase A/E were observed for the triplet of ethylbenzene (Figure 1a). These signals disappeared completely as soon as the irradiation was discontinued. Obviously, the amount of ethylbenzene formed during the short irradiation time was too small to allow its detection next to the ^{13}C satellite of toluene (Figure 1b).

The observation of CIDNP signals indicates that the product was formed *via* a pair of radicals, in this case benzyl–methyl. According to the radical-pair theory[9] the observed multiplet phase (A/E) is consistent with the following assumptions, all of which appear reasonable. We assign triplet multiplicity to the geminate radical pair and to the parent methylene, since it was generated by photosensitized decomposition of diazomethane. Benzyl and methyl are π radicals; their α protons should have negative hyperfine coupling constants. The vicinal nuclear–nuclear coupling constant of ethylbenzene, the in-cage coupling product, should be positive ($^3J_{\mathrm{H,H}} > 0$). The corresponding quartet of ethylbenzene is obscured by the methyl signal of the substrate–solvent. Potential cage-escape products such as bibenzyl, ethane, and methane (and toluene) have single nmr signals, so that their polarization cannot be observed in the absence of a *net* CIDNP effect.[6]

Figure 1. Pmr spectra (60 MHz; $\tau \sim 8.3$–9.2): (a) of a toluene solution containing 1 mol/l. each of diazomethane and benzophenone during irradiation; (b) of a toluene solution containing 1 mol/l. of diazomethane, but no sensitizer during uv irradiation. The signal in trace b is the high-field ^{13}C satellite of the solvent methyl group.

The multiplet phase of spin-polarized ethylbenzene formed from $^3CH_2$ and toluene is consistent with an abstraction–recombination mechanism. An analogous mechanism was established for the reaction of (triplet) diphenylmethylene with toluene.[10] The polarization-determining parameters of the intermediate radical pair, in this reaction benzyl–diphenylmethyl, have the same signs as discussed above. The product, 1,1,2-triphenylethane, showed the same multiplet phase (A/E) as ethylbenzene, thus supporting the concept of similar mechanisms in both reactions.

In contrast to the photosensitized reaction no enhanced signals were observed during the direct photolysis of diazomethane in toluene even though ethylbenzene was isolated in substantial yield. Normally, a failure to observe enhanced spectra in CIDNP experiments is far from being sufficient for establishing a reaction mechanism or even excluding a mechanism from consideration. In the case of the reaction of $^1CH_2$ with toluene, however, such a negative result is significant, because the enhanced signals observed in the analogous reaction of $^3CH_2$ had shown that in principle the polarization induced in a methyl–benzyl pair could be observed.

It is well established in the literature of CIDNP that a change in initial spin multiplicity of a given radical pair results in alteration of the multiplet phase[11] or

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(1) (a) H. Meerwein, H. Rathjen, and H. Werner, *Chem. Ber.*, **75**, 1610 (1942); (b) H. Meerwein, H. Disselnkötter, F. Rappen, H. v. Rintelen, and H. van de Vloed, *Justus Liebigs Ann. Chem.*, **604**, 151 (1957).

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(3) H. M. Frey and G. B. Kistiakowsky, *ibid.*, **79**, 6373 (1957).

(4) *Cf.* W. H. Urry and J. R. Eiszner, *ibid.*, **73** 2977 (1951); **74**, 5822 (1952).

(5) W. von E. Doering and H. Prinzbach, *Tetrahedron*, **6**, 24 (1959).

(6) H. D. Roth, *J. Amer. Chem. Soc.*, **93**, 1527, 4935 (1971); **94**, 1400 (1972).

(7) J. Bargon, H. Fischer, and U. Johnson, *Z. Naturforsch. A*, **22**, 1551 (1967).

(8) H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5518 (1967).

(9) R. Kaptein, *Chem. Commun.*, 732 (1971), has suggested simple qualitative rules for the evaluation of CIDNP spectra. References to the radical-pair theory of CIDNP may be found therein.

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(11) G. L. Closs and A. D. Trifunac, *ibid.*, **91**, 4554 (1969).

the signal direction[6,12–14] of the polarized products. For example, the multiplet phase of 1,1,2-triphenylethane[10] (formed *via* a pair initially of triplet multiplicity) was altered to E/A when it was generated from an azo compound (*via* a pair initially of singlet multiplicity).[11] Products derived from phenyl–benzoyloxy[12,13] or chloromethyl–trichloromethyl radical pairs[6] showed alterations of signal directions, when the precursor multiplicity was changed by triplet sensitization. Finally, the benzylic emission signals observed during pyrolysis (singlet reaction) of various hydroxyphenanthrone derivatives were altered when these compounds were photolyzed (triplet reaction).[14]

In the light of these results one would have expected an E/A multiplet during the reaction of $^1CH_2$ with toluene to form ethylbenzene, if radical pairs with separations and lifetimes large enough to permit exchange ("singlet–triplet mixing") were involved. The failure to observe any polarization in this reaction indicates a fundamentally different path for the singlet reaction, namely the one-step insertion process previously proposed by Doering and Prinzbach.[5,15]

Richardson, Simmons, and Dvoretzky[17] had suggested that in the analogous gas-phase reactions $^1CH_2$ (one-step insertion) and $^3CH_2$ (abstraction) attack carbon–hydrogen bonds in different ways. In contrast, DeMore and Benson[18] favored a single reaction mechanism for both species. In their scheme abstraction is chiefly associated with a high-energy precursor. The CIDNP results presented here, the selectivity exerted by triplet methylene,[6b,c] and the almost total lack of selectivity displayed by the singlet species[2] clearly demonstrate that in solution the reaction mechanism is determined by the spin multiplicity and not the energy of the precursor.

The concept of fundamentally different reaction mechanisms for the reactions of $^1CH_2$ and $^3CH_2$ is in full agreement with results obtained with various other substrates such as chloroform,[6b] 2-chlorobutane,[6c] 2-chloro-2-methylpropane, cyclohexane-d_{12}, and isobutylene. Details of the reactions of CH_2 with these substrates will be discussed in a full paper.

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Intensity Decontrasting in Pulse Fourier-Transform Carbon-13 Nuclear Magnetic Resonance. Effective Signal–Noise–Time Enhancement by New Use of Paramagnetic Additives

Sir:

Carbon magnetic resonance finds rapidly increasing application for complex molecules.[1] Even with the pulse Fourier-transform (PFT) technique, the signal–noise–time problem, determined by the *smallest peaks* in a spectrum, is serious. The intensity of the single lines in proton-decoupled spectra is the outcome of opposing factors. On one hand, favorable nuclear Overhauser enhancement (NOE) occurs mainly for the proton-substituted carbons. On the other hand, saturation decreases the intensity of carbons having long relaxation times, typically those without proton substituent and with minimum NOE. Saturation can be decreased or avoided by driven equilibrium Fourier-transform (DEFT)[2] or spin–echo Fourier-transform (SEFT)[3] techniques or by employing long time spaces between pulses, a time-consuming luxury reserved for special experiments. Typical PFT cmr employs either a short rest time (*e.g.*, 1.5 sec) or no rest time between the end of the scan and the next pulse, leading to extensive saturation of quaternary, substituted aromatic and chlorine- and especially deuterium-bearing carbons. The result is a high "contrast" spectrum, where the intensity ratio between equimolar carbons can easily reach 1:10. This contrast is structurally diagnostic but leads to mistaking peaks for noise and *vice versa*.

We reasoned that a means of correcting this situation is available in the form of odd-electron, paramagnetic additives.[4] Shifts[5] are comparatively small and relaxation enhancement of nuclei is efficient when the electron spin has long relaxation time,[6] *e.g.*, in stable organic radicals and compounds of several members of the first transition metal series. Such additives have been used for selective and nonselective influencing[7,8] of relaxation time, T_1, and for the more specific and relevant decrease and elimination[9] of the NOE enhancement in continuous wave (CW) cmr. We expected that for typical PFT cmr the decrease of saturation experienced by the weaker carbons would be of greater significance than the decrease of NOE enhancement for the stronger carbons. Selectivity of the decrease of relaxation time is to be avoided in the initial and general use by employing a nonpolar, unreactive, nonassociating agent (*e.g.*, with fully occupied coordination sphere and hydrocarbon or fluorocarbon surface); later use will surely exploit specific interactions for diagnostic purposes, as is done for biomolecules with metal ions.[8]

Our preliminary experiments with CW pmr showed that β-diketonates of Cu^{2+} and Fe^{3+} at low concentration in CCl_4 and $CHCl_3$ with a mixture of a large variety of typical organic substrates showed no noticeable chemical shift, but gave nonselective broadening (except for the OH peak). A concentration of the paramagnetic agent was selected which broadened proton peaks to ~2.5-Hz width at half-height, knowing

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