Differential Effects of Radical *g*-Factors on the Polarization of ^1H and ^{19}F Nuclei in Products of Insertion of Diarylmethylenes into Benzyl Fluoride

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Summary Observable changes in the pattern of polarization of n.m.r. spectra of products $(XC_6H_4)(YC_6H_4)CH\cdot CHFPh$ from insertion of diarylmethylenes into the benzylic C–H bond of benzyl fluoride occur with different substituents X and Y and hence different *g*-values of the intermediate diarylmethyl radicals for ^1H and ^{19}F nuclei.

We report a systematic investigation of the effect of changing Δg-value on the pattern of chemically induced spin polarization (CIDNP) of two different nuclei within the same combination product of a radical pair. The series of products in question is the 2,2-diaryl-1-phenylethyl fluorides $(XC_6H_4)(YC_6H_4)CH\cdot CHFPh$ formed by insertion of triplet diarylmethylenes into the benzylic C–H bond of benzyl fluoride.[1] The results indicate a different sensitivity of the polarization of fluorine and the vicinal and geminal protons to changes in the substituents X and Y and provide the first examples where polarization of individual members of pairs of diastereoisomers has been observed.

The principal polarized signals in the ^{19}F spectrum (56·4 MHz) and the only observable polarized signals in the ^1H spectrum (60 MHz) during decomposition of diaryldiazomethanes (0·5—1M) at 120 °C in solvent benzyl fluoride are those attributable to the AMX spin system of the insertion product 2,2-diaryl-1-phenylethyl fluoride. The assignment is readily made by comparison of the essentially first-order spectra with that of the independently synthesised parent compound (X=Y=H). Patterns of polarization of the geminal and vicinal proton and fluorine parts of the spectra are in the Table, each line being indicated as displaying enhanced absorption (A) or emission (E). Line intensities in the polarized ^{19}F spectrum are not equal although they are in the depolarized spectrum observed by accumulation at the end of the reaction.

The patterns of polarization are different for the three types of nuclei and more importantly vary in different ways as the substituents in the carbene (and hence, by internal spin–orbit coupling, the *g*-factor of the intermediate diarylmethyl radical) change. Net polarization is much more important in ^{19}F than in ^{1}H spectra. Thus the gross pattern A + A/E for ^{19}F in the parent compound is unchanged until X = Y = 4-Cl when perfect multiplet polarization (integral over the multiplet is zero) is observed. At this point Δg = *ca.* 0 for the intermediate radical pair, indicating that g for the fluorobenzyl radical is *ca.* 2·0028.[2] Further increase in the g-value of the diarylmethyl radical leads to a phase inversion (E + A/E) and, when X = Y = 4-Br (Δg = *ca.* −0·0021), net polarization overwhelms the multiplet effect and all lines in the polarized ^{19}F spectrum appear in emission. In contrast, multiplet polarization is dominant in the proton spectra. For the geminal proton, the A/E pattern appears to be unchanged throughout the range of substituents although some lines are obscured by solvent signals. The vicinal proton, however, shows perfect multiplet polarization (E/A) in all cases except when X = Y = 4-Br, where net emission appears.

TABLE

Patterns of polarization of 2,2-*diaryl*-1-*phenylethyl fluoride* $(XC_6H_4)(YC_6H_4)CH_{vic}\cdot CH_{gem}$ F·Ph *at* 120 °C

X	Y	Pattern of polarization[a] H_{gem}	 H_{vic}	 F	$\Delta\delta_F$/Hz
H	H	AAEE	EEAA	AAEA	—
H	2-F	AAEE	EE(A)(A)	AAEA/AAEA[b]	58
H	3-F	AAE(E)	EEAA	AAEA/AAEA	34
H	4-F	AAE(E)	EEAA	AAEA/AAEA	54
4-F	4-F	AAE(E)	EEAA	AAEA	—
H	2-Cl	AAEE	EEAA	AAEA/AAEA	52
H	3-Cl	AAE(E)	EEAA	AAEA/AAEA	51
H	4-Cl	AAE(E)	EEAA	AAEA/AAEA	16
4-Cl	4-Cl	AAE(E)	EEAA	AAEE	—
H	2-Br	AAEE	EEAA	EAEE/EAEE	78
H	4-Br	AAE(E)	EEAA	EAEE/EAEE	5
4-Br	4-Br	AA(?)(?)	EEAE	EEEE	—

[a] Symbols in parentheses indicate the presumed phases of lines obscured by signals due to the solvent. [b] Additional doublet splitting of each line.

The differential behaviour is intelligible in terms of current theory[2,3] since, for collapse of a correlated radical pair of given multiplicity, the intensity of net polarization is determined by both the sign and magnitude of the product of Δg and the nuclear hyperfine coupling constant a. The implication of the present results is that a_F (α-fluorobenzyl) $>> -a_H$ (diarylmethyl)> $|a_H|$ (α-fluorobenzyl). Multiplet polarization is independent of Δg and thus remains constant throughout the series.

When X $\neq$ Y, Y = H, the 2-aryl-1,2-diphenylethyl fluoride contains two chiral centres and can exist in *erythro*- and *threo*-diastereoisomeric forms. Overlapping polarized quartets with separations ($\Delta\delta_F$) up to *ca.* 80 Hz are observable in the ^{19}F (but not ^{1}H) spectra during the formation of such compounds. In all cases, the diastereoisomers are formed in equal amounts and are polarized identically. However, when X = H and Y = 2-F, all the lines in the ^{19}F spectra of both diastereoisomeric products show an additional doublet splitting (*ca.* 3 Hz) which is absent in the depolarized spectrum.

Because of the simplicity of spectra, the sensitivity of the chemical shift to small structural alterations, the through-space contribution to H–F and F–F coupling,[4] and the large intensity of polarization, studies of ^{19}F CIDNP promise to be most valuable in mechanistic studies of organic reactions. An example of such an application is given in the following communication.

Financial support from the S.R.C. is acknowledged.

(*Received, 27th October* 1972; *Com.* 1828.)

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