Chemically Induced Dynamic Nuclear Spin Polarisation in Products of Reactions of Diphenylmethylene with Benzyl Fluorides: Novel Effects Arising from Intramolecular Interactions of Polarised ^{1}H and ^{19}F Nuclei

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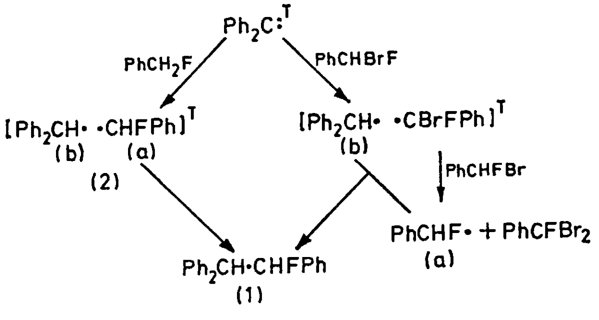
Summary Polarised ^{19}F n.m.r. spectra of 1,2,2-triphenylethyl fluoride, produced during the reaction of diphenylmethylene with either benzyl fluoride or α-bromobenzyl fluoride, show unusual relative line intensities and doublet splittings which are thought to stem from the coupling of the polarised ^{19}F nucleus with a polarised vicinal proton which is undergoing nuclear spin relaxation more rapidly.

THE theory of chemically induced dynamic nuclear spin polarisation (CIDNP) has been developed largely in terms of proton polarisation.[1] The only reported examples of polarised ^{19}F-spectra have been in spin-delocalised fluoroaromatic systems:[2,3] polarised ^{1}H-spectra were not observed in these experiments, and the ^{19}F-spectra were not interpreted in terms of CIDNP theory. We report an example of a reaction in which polarisation of both ^{1}H and ^{19}F nuclei occurs, and we show that this gives rise to novel effects.

1,2,2-Triphenylethyl fluoride (**1**) is formed together with other products when diphenylmethylene, generated thermally (120 °C) from diphenyldiazomethane (1M), reacts with solvent benzyl fluoride or α-bromobenzyl fluoride. Its identity was established by comparison with material independently synthesised by catalytic hydrogenation of 1,2,2-triphenylvinyl fluoride.[4] Plausible routes to (**1**) in the two solvents are shown in the Scheme, the key feature of which is that in-cage collapse of the first-formed radical pair can yield (**1**) in benzyl fluoride, but out of cage reaction is necessary in the other solvent.

When the reactions are carried out in the pre-heated n.m.r. probe, polarisation is observed in both ^{1}H- and ^{19}F-spectra. While other polarised products are formed in both reactions, we concern ourselves here only with (**1**). When produced in the reaction of diphenylmethylene with benzyl fluoride, (**1**) shows a quartet polarised AAEA in the 56·4 MHz ^{19}F-spectrum 1910 Hz downfield from the solvent triplet† and two polarised quartets in the 60 MHz ^{1}H-spectrum (H_{gem}, AAEE; H_{vic}, EEAA) representing the AMX spectrum of (**1**), with $J^{\mathrm{HF}}_{\mathrm{gem}}$ 46·5 Hz, $J^{\mathrm{HC}}_{\mathrm{vic}}$ 18·0 Hz and $J^{\mathrm{HH}}_{\mathrm{vic}}$ 7·3 Hz. While the integrals over the polarised quartets in the ^{1}H-spectrum are zero, that for the fluoride is not. The intensity of all three quartets reaches a maximum at roughly the same time (3 min) after the n.m.r. tube is inserted into the heated probe, but the polarisation of H_{vic} decays to the thermal distribution of nuclear spin states much faster (4 min) than that of H_{gem} (*ca.* 6 min) and F (*ca.* 10 min). As indicated in the Scheme, (**1**) is thought to arise in this reaction from combination of radicals (**2a**) and (**2b**), and this requires that F and H_{gem} be polarised concomitantly.‡ Now, the polarisation of ^{19}F is substantially greater than that of H_{gem}. In contrast to Rakshys,[2] we suggest that the relative magnitude of polarisation is determined by the ratio of isotropic hyperfine interaction constants $A(\mathrm{F})/A(\mathrm{H}_{\mathrm{gem}})$, since all other factors



SCHEME

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† The same pattern of polarisation with the same relative line intensities was observed when the reaction was conducted outside the n.m.r. probe (approximately zero field) and the sample tube rapidly transferred to the probe maintained at slightly above room temperature.

‡ T_0–S mixing occurs when the electron exchange energy J_{ee} is equal to the isotropic hyperfine splitting constant A. Since $A(\mathrm{F}) \neq A(\mathrm{H})$, F and H_{gem} need not be polarised simultaneously.

which might influence it are the same for the two nuclei in radical (**2a**).

Compared with the 56·4 MHz ^{19}F-spectrum, the maximum emission intensity of line 3 at 94·1 MHz is much reduced, and lines 3 and 4 are broadened and split into doublets (splitting *ca.* 4·5 Hz). Such a field dependence of polarisation is quite novel, although the intensity of polarisation in certain ^{1}H-spectra has been shown to be dependent on magnetic field.[5]

Analogous experiments at 56·4 MHz using α-bromobenzyl fluoride as solvent produced ^{19}F-spectra showing a chemical shift and coupling constants identical with those of (**1**) and polarised EEEE. The maximum intensity was some six times less than for the reaction in benzyl fluoride and no polarisation was detectable in the ^{1}H-spectrum. However, in the ^{19}F-spectrum, lines 1 and 2 were always of greater intensity than lines 3 and 4 which were broader and split into doublets (splitting *ca.* 3·5 Hz).

We regard the pattern of ^{19}F-polarisation of (**1**) as a perturbed AAAA in benzyl fluoride. Since the pattern is EEEE when (**1**) is produced by a route which must, from the structure of the reactants, be out of cage, the polarisations are qualitatively consistent with the Scheme and Kaptein's rules.[6] The ^{1}H-spectrum of (**1**) from benzyl fluoride is A/E for H_{gem} and E/A for H_{vic} as expected if J^{HF}_{vic} (included in the expression for Γ_{ME} for H_{vic}) and J^{HF}_{gem} (in Γ_{ME} for H_{gem}) have opposite signs. The other factors controlling Γ_{ME} are identical for H_{vic} and H_{gem}.

The perturbations of the ^{19}F spectra of (**1**) are unprecedented in CIDNP studies. They appear, however, to be general in products formed by combination of pairs of radicals one of which carries a polarised fluorine nucleus and the other a polarised proton.[7] Changes in relative line intensities and doublet splittings of certain lines within a multiplet would be expected if an external field were applied, as in spin-tickling or INDOR double resonance experiments.[8] No such external field has been applied in the experiments described above.

We suggest that these phenomena result from the combination of the following circumstances: (a) the nuclear spin substates of H_{gem}, H_{vic} and F are unequally populated by T_0–S mixing; (b) the gyromagnetic ratio of ^{1}H is greater than that of ^{19}F; (c) polarised H_{vic} nuclei relax much faster than H_{gem} and F nuclei. Thus a certain transition in the ^{1}H spectrum (H_{vic}) relaxing faster than connected transitions in the ^{19}F-spectrum should produce the effect of a time-dependent perturbation on the connected nuclear spin substates of the fluorine nucleus similar to the effect of an externally applied field. The strength of this perturbation should be related to the rate of depolarisation of the connected transitions in the H_{vic}-spectrum. The signs of the polarisations would thus be affected by a nuclear Overhauser effect, and the nature of the doublet splitting would be a function of whether the lines were progressively or regressively connected.[8]

Homo- and heteronuclear double resonance experiments on (**1**) are in hand with a view to quantifying these effects which will, we believe, ultimately lead to hitherto unavailable information concerning radical pair reactions.

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