Intermediates in the Decomposition of Aliphatic Diazo-compounds. Part XII.[1] Chemically Induced Dynamic Polarisation of Fluorine-19 and Proton Nuclei in the Insertion of Diarylmethylenes into Benzyl Fluoride

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The patterns of polarisation of ^{19}F and ^{1}H n.m.r. signals of 2,2-diaryl-1-phenylethyl fluoride formed during thermal decomposition of diaryldiazomethanes in solvent benzyl fluoride are described. Using diphenyldiazomethane, the ^{19}F quartet shows net (A) + multiplet (A/E) polarisation and this changes to E + A/E as the g-factor of the intermediate diarylmethyl radical is increased beyond 2.003 0 using substituted diphenyldiazomethanes. With monosubstituted diphenyldiazomethanes, two diastereoisomeric products are formed in equal amounts, and these show identical polarisation. Over almost the whole range of substituents, little net polarisation is detectable in the n.m.r. signals of the protons geminal and vicinal to the fluorine despite wide variations in Δg; both ^{1}H quartets show strong multiplet polarisation, A/E for H-1 and E/A for H-2. By the use of phenyl t-butyl nitrone which traps intermediate free radicals it is shown that polarised insertion products arise from both recombination of geminate radical pairs and from diffusive encounter of diarylmethyl and fluorobenzyl radicals. The results, particularly the differential effect of substituent on the polarisation of ^{19}F and ^{1}H nuclei, are interpretable in terms of the radical-pair theory of CIDNP, but it is shown by simulation studies that nuclear spin relaxation can play a significant role in certain instances in modifying the relative intensities of polarised signals.

CHEMICALLY-INDUCED dynamic nuclear polarisation (CIDNP), the observation of transient enhanced absorption (A) and/or emission (E) signals in the n.m.r. spectrum of products of reactions of radical pairs when these are conducted in a magnetic field (the spectrometer probe), has brought new insights into radical chemistry.[2] Of particular importance is the mechanistic information which such studies provide.[2,3] In the field of carbene chemistry, CIDNP, by virtue of the dependence of patterns of polarisation on the electronic multiplicity of the radical-pair precursor, offers direct information about the nature of the carbene and also throws light on the path-

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[1] Part XI, D. Bethell and M. F. Eeles, *J.C.S. Perkin II*, 1974, 704.

[2] For reviews, see ' Chemically Induced Magnetic Polarization,' eds. A. R. Lepley and G. L. Closs, Wiley–Interscience, New York, 1973; C. Richard and P. Granger, ' Chemically Induced Dynamic Nuclear and Electron Polarizations—CIDNP and CIDEP,' ' NMR: Basic, Principles and Progress,' eds. P. Diehl, E. Fluck, and R. Kosfeld, Springer Verlag, Berlin, 1974, vol. 8.

[3] D. Bethell and M. R. Brinkman, *Adv. Phys. Org. Chem.*, 1973, **10**, 53.

ways by which individual reaction products are formed. The development of the currently accepted radical-pair theory of CIDNP owed much to carbene chemistry, however; the studies of Closs[4] in particular on benzylic insertion by triplet diarylmethylenes provided early quantitative tests of the theory since the radicals involved were ones for which the e.s.r. parameters *g* and *a* were well-known.

In this paper we report in detail[5] the results of our extension of Closs' studies to a fluorine-containing system. Our reasons for doing this were to explore the advantages which we expected to accrue from the use of ^{19}F n.m.r. as a result of the sensitivity of chemical shift to environment, the simplicity of spectra (almost all being first-order), and the generally longer spin-lattice relaxation time of ^{19}F than ^{1}H.[6] Benzyl fluoride was chosen as reactant and solvent, and we describe the nature of the polarised signals in both ^{19}F and ^{1}H spectra of the insertion products which result when diphenyldiazomethane and related diazoalkanes decompose thermally in it.

RESULTS

Reaction Conditions and Products.—Reaction conditions were chosen to maximise the intensity of the polarised signals. It was found necessary to employ benzyl fluoride as the solvent, and a temperature of 120 °C was found to be the lowest at which consistently satisfactory results could be obtained. In all cases the concentration of the diazoalkane was initially 1.0M. At this high concentration the formation of benzophenone azine is favoured, especially in glass vessels.[7] Nevertheless a substantial proportion of the diazoalkane yielded the insertion product, 2,2-diaryl-1-phenylethyl fluoride, although its final concentration was always too little to permit the depolarised n.m.r. signals to be detected by a single spectrometer scan. Depolarised spectra were, therefore, recorded by accumulation at the normal probe temperature (35—40 °C).

TABLE 1

Product analysis by g.l.c. for the thermal decomposition of diphenyldiazomethane (1.0M) in benzyl fluoride solution at 120 °C

Product [a]	Yield (%) [b]		
1,2-Difluorobibenzyl	1.8	1.4	1.5
Benzophenone	4.7	6.2	7.1
1,2,2-Triphenylethyl fluoride	12.5	12.2	11.9
Tetraphenylethane	23.4	21.8	20.9
Tetraphenylethylene	<0.5	<0.5	<0.5
Benzophenone azine	55.5	56.3	53.4

[a] In order of increasing retention time. [b] Percentage of the initial diphenyldiazomethane converted into each product; values are believed to be accurate to within 5% of that quoted.

Typical product analyses by g.l.c. for the reaction of diphenyldiazomethane in benzyl fluoride at 120 °C are in Table 1. The reproducibility of the results from run to run is quite good bearing in mind that no attempt was made rigorously to exclude oxygen from reaction mixtures; indeed, the thermal decomposition normally took place in an open n.m.r. tube. Thus the reaction of diphenylmethylene with oxygen yielding benzophenone competes with conversion of the carbene into a radical pair by hydrogen abstraction.[8]

Polarised N.m.r. Spectra.—The CIDNP studies were conducted for the most part at 56.4 MHz (^{19}F) and 60 MHz (^{1}H). Attempts to observe ^{13}C CIDNP in this system have so far proved unsuccessful.

Initial experiments using diphenyldiazomethane showed that there were two groups of polarised signals in the ^{19}F-spectrum. The less intense of the groups, centred some 1 280 Hz downfield from the solvent triplet showed perfect multiplet polarisation. It appeared in all experiments irrespective of substituents in the diazoalkane and has been assigned to the dimers of fluorobenzyl radical.[9] It will not be discussed further in this paper.

The other group of polarised ^{19}F signals was centred 1 825 Hz downfield of the solvent triplet and consisted of four lines of unequal intensity, the polarisation pattern being AAEA. The chemical shift and coupling constants corresponded exactly with those of an authentic specimen of 1,2,2-triphenylethyl fluoride. In the ^{1}H spectrum two polarised quartets were detectable corresponding in chemical shift and coupling constants with signals due to the aliphatic protons of 1,2,2-triphenylethyl fluoride; the quartets showed multiplet polarisation, A/E for H-1 and E/A for H-2. The polarised ^{19}F and ^{1}H spectra and those of the authentic product are shown in Figure 1, together with the depolarised ^{19}F spectrum. Accumulation of ^{1}H scans did not give satisfactory results because solvent side-bands and ^{13}C-satellites obscure the product signals.

In order to investigate the nature of the radical pair responsible for the polarised signals, the experiment was repeated in the presence of a trap for free radicals. Phenyl t-butyl nitrone was used since this is known to scavenge reactive radicals forming long-lived nitroxide radicals which are readily detectable by e.s.r. spectroscopy.[10] At a concentration of 0.2 and 0.4M the nitrone completely eliminates the polarised fluorobenzyl dimer signals and reduces the intensity of the polarised signals of the insertion product by *ca.* 50%. This indicates that polarised insertion product arises in part from the diffusive encounter of diphenylmethyl and fluorobenzyl radicals and in part from recombination of the geminate radical pairs resulting from hydrogen atom abstraction by diphenylmethane. Diffusive (F) and triplet (T) radical pairs are known to give rise to identical patterns of polarisation,[2] and consistently the nitrone reduced the total intensity of polarisation without affecting the relative intensity of individual lines in the multiplet.

Magnetic Field Effect.—The effect on the pattern of ^{19}F polarisation of changing the magnetic field was examined by carrying out the decomposition of diphenyldiazomethane in benzyl fluoride at 120 °C in the probes of spectrometers

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[4] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, 1969, **91**, 4549, 4550; G. L. Closs, *ibid.*, p. 4552; G. L. Closs and A. D. Trifunac, *ibid.*, 1970, **92**, 2183, 2186.

[5] Preliminary reports of part of this work: D. Bethell, M. R. Brinkman, and J. Hayes, *J.C.S. Chem. Comm.*, 1972, 475, 1323.

[6] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon Press, London, 1966, vol. I and II.

[7] D. Bethell, A. R. Newall, G. Stevens, and D. Whittaker, *J. Chem. Soc.* (*B*), 1969, 749.

[8] D. Bethell, G. Stevens, and P. Tickle, *Chem. Comm.*, 1970, 792.

[9] D. Bethell, M. R. Brinkman, and J. Hayes, *J.C.S. Chem. Comm.*, 1972, 1324.

[10] E. G. Janzen, *Accounts Chem. Res.*, 1971, **4**, 31; E. G. Janzen, C. A. Evans, and Y. Nishi, *J. Amer. Chem. Soc.*, 1972, **94**, 8236; E. G. Janzen and C. A. Evans, *ibid.*, 1973, **95**, 8205.

operating at 37.6 and 94.1 MHz. In the low field, the pattern of polarisation was unchanged, but at 94.1 MHz, the strong emission of line 3 of the quartet almost completely disappeared.

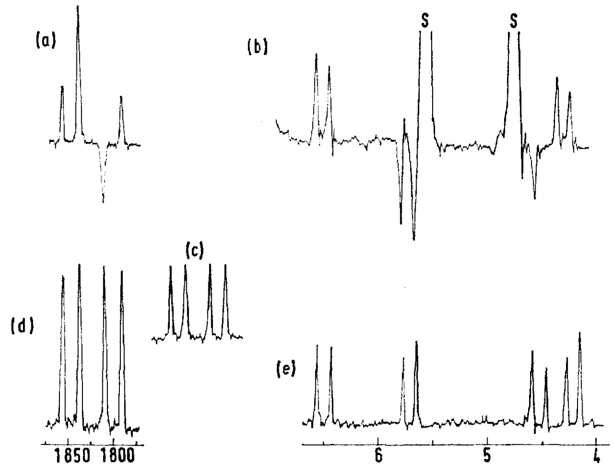

FIGURE 1 ^{19}F (56.4 MHz) and ^{1}H (60 MHz) n.m.r. spectra of 1,2,2-triphenylethyl fluoride. (a) Polarised ^{19}F spectrum recorded during thermal decomposition of diphenyldiazomethane in benzyl fluoride solvent at 120 °C. (b) Polarised ^{1}H spectrum under the same conditions; the peaks labelled S constitute the doublet due to the benzylic protons of the solvent. (c) Depolarised ^{19}F spectrum from (a) obtained by accumulation of scans at normal probe temperature. (d) ^{19}F and (e) ^{1}H spectra of independently synthesised material in $CDCl_3$ at normal probe temperature. The calibration of ^{19}F spectra is in Hz downfield from the $PhCH_2F$ triplet and of ^{1}H spectra in p.p.m. from internal Me_4Si

Rates of Depolarisation.—It was observed that, during the course of a given experiment, the pattern of ^{19}F polarisation of 1,2,2-triphenylethyl fluoride underwent modification. Lines 1(A) and 3(E) decreased in intensity relative to lines 2 and 4 and indeed only these latter two lines were detectable in the late stages of the reaction. To investigate this further, the three polarised multiplets of the combination product were separately scanned at 10-second intervals throughout the course of the reaction. For each line, the intensity rises rapidly, passes through a maximum at time $t_{max.}$, and then depolarises slowly until the intensity falls to the spectrometer noise level. After a time $2t_{max.}$, most of the diazoalkane has decomposed, and the decay of signal intensity follows a first-order kinetic law from which values of a decay constant, k_D, could be obtained. These k_D-values are given in Table 2 for the four lines of the fluorine spectrum and for the enhanced absorption lines of both the geminal and vicinal protons. It can be seen that k_D varies by a factor of three even within the same multiplet.

TABLE 2

Apparent first-order velocity constants k_D for depolarisation of ^{19}F and ^{1}H signals [a] of 1,2,2-triphenylethyl fluoride at 120 °C

	$10^3 k_D/s^{-1}$				
	F		H-1		H-2
A	12.1 ± 1.1	A	7.8 ± 0.8	E	
A	4.1 ± 0.4	A	7.1 ± 0.7	E	
E	8.8 ± 0.8	E		A	5.5 ± 0.6
A	4.7 ± 0.8	E		A	4.4 ± 0.5

[a] Lines are listed in order of decreasing frequency. The preceding letter indicates the phase (absorption or emission) of the line.

Substituent Effect on ^{19}F *and* ^{1}H *Polarisation.*—Because of the much larger internal spin-orbit coupling of halogen compared with hydrogen (*viz.* λ/cm^{-1}: H, 0.5; F, 272; Cl, 587; Br, 2 460; I, 4 060),[11] introduction of halogen substituents into the reactants, either the diazoalkane or benzyl fluoride, alters the electronic *g*-factor of the intermediate radicals and hence Δg for the pair. *p*-Fluoro- and *p*-t-butyl-benzyl fluoride gave patterns of polarisation with diphenyldiazomethane which were very similar to that observed with benzyl fluoride itself. Halogen substituents in the diazoalkane had much more pronounced effects on ^{19}F-polarisation in the insertion product. This is illustrated in Figures 2 and 3, and the complete patterns of polarisation of F, H-1, and H-2 are assembled in Table 3. All the results refer to the spectrum at maximum polarisation.

Two striking features in the patterns of polarisation stand out. One is that for protons multiplet polarisation is dominant throughout the whole series of substituents with the exception of the dibromo- and di-iodo-diazoalkane, whereas for fluorine polarisation net polarisation predominates. Pure multiplet ^{19}F-polarisation is observed in the case of 4,4′-dichlorodiphenyldiazomethane, but even the change to the 2,2′-dichloro-compound is sufficient to induce a substantial net effect such is the sensitivity to halogen substitution. In contrast, methyl substituents whether in the *para*- or *ortho*-positions do not appear to have a signifi-

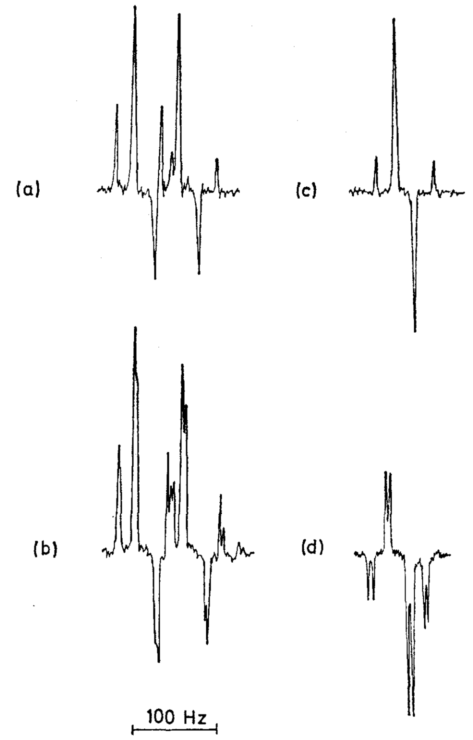

FIGURE 2 Polarised ^{19}F spectra (56.4 MHz) of the benzylic insertion product of substituted diphenylmethylenes into benzyl fluoride at 120 °C. (a) 4-Fluorophenyl(phenyl)methylene. (b) 2-Fluorophenyl(phenyl)methylene. (c) 4-Chlorophenyl(phenyl)methylene. (d) 4-Bromophenyl(phenyl)methylene

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[11] D. S. McClure, *J. Chem. Phys.*, 1949, **17**, 905.

cant effect either on the pattern or intensity of the polarised signals.

The other striking feature of the substituent effects is that when diphenyldiazomethane carrying a substituent in only one of its rings is used, two insertion products are formed, the *erythro*- and *threo*-diastereoisomers of 2-aryl-1,2-diphenylethyl fluoride. The ^{19}F chemical shifts of these are different and in consequence two polarised quartets are seen. From depolarised n.m.r. spectra, the two diastereoisomers can be seen to be formed in equal concentration as expected, and both the pattern and intensity of polarisation are the same. In general *ortho*-substituents give the largest separation of the ^{19}F n.m.r. signals of the diastereoisomers, the CF_3 substituent giving a 342 Hz shift at 56.4 MHz. In this instance a small separation is detectable in the polarised proton signals, although for all other pairs of diastereoisomers no such separation can be seen. The *ortho*-F substituents introduces a further complication in that all the lines in the two polarised ^{19}F-quartets show an additional *ca.* 3 Hz splitting (confirmed at 94.1 MHz) which seems to be somewhat greater in the high-field diastereoisomer than in the other. Although this is clearly resolved in polarised spectra, it was not detectable in the accumulated depolarised spectrum of the reaction product. Such additional splitting was also absent in the polarised insertion product obtained when 4-fluorodiphenyldiazomethane was used. The extra splitting in the *ortho*-fluoro-product is plausibly attributable to a five-bond F–F coupling. The failure to detect the coupling in depolarised spectra may simply stem from resolution difficulties in spectral accumulation over long periods.

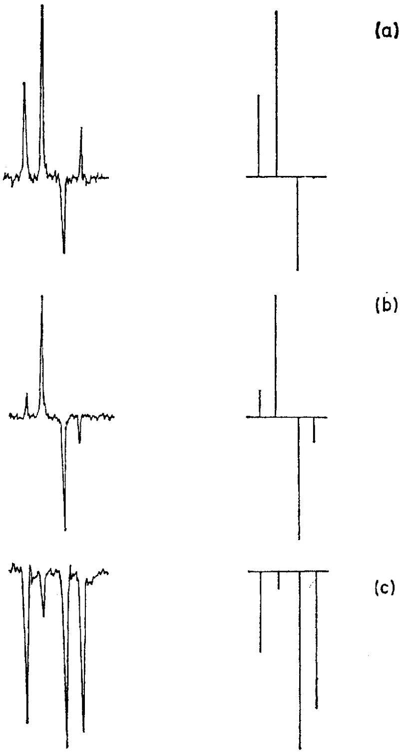

FIGURE 3 Observed and calculated ^{19}F spectra of polarised 2,2-diaryl-1-phenylethyl fluorides obtained by benzylic insertion of diarylmethylenes into solvent benzyl fluoride at 120 °C. (a) Diphenylmethylene. (b) Bis-(4-chlorophenyl)methylene. (c) Bis-(4-bromophenyl)methylene

Polarisation (E) of aromatic fluoro-substituents was observed only in the reaction of 4,4′-difluorodiphenyldiazomethane. Aromatic CF_3-substituents were not polarised appreciably in the present studies. Since CF_3-polarisation is detectable during benzylic insertion into benzyl chloride this absence is thought to stem from a low value of Δg for the radical pairs in the benzyl fluoride reaction rather than low values for a_F (see below).

DISCUSSION

Reaction Mechanism.—The expected mechanism for benzylic insertion by diphenylmethylene is hydrogen abstraction by the carbene in its triplet state followed by intersystem crossing from triplet to singlet state in the radical pair and rapid recombination. The experiments with phenyl t-butyl nitrone indicate that part of the insertion product does indeed arise from geminate radical pairs but a substantial proportion comes from chance encounter of freely diffusing diphenylmethyl and fluorobenzyl radicals.

The pattern of polarisation, A + A/E for fluorine, A/E for H-1, and E/A for H-2, is consistent with both these routes to 1,2,2-triphenylethyl fluoride as indicated by Kaptein's rules.[12] For the diphenylmethyl radical, $g = 2.002\,5$ [13] and the hyperfine splitting constant for the methine hydrogen, $a_H = -8.36$ G; [14] for the fluorobenzyl radical, spin-orbit coupling due to fluorine should lead to $g > 2.002\,5$, $a_F \simeq 50$ G by analogy with other α-fluororadicals and $a_H \simeq -16$ G by analogy with the benzyl radical itself.[15] INDO Calculations on fluorobenzyl radical give $a_F = 46.7$ G and $a_H = -16.7$ G. Thus for a triplet carbene precursor of the radical pair or for an F-pair ($\mu = +$) yielding 1,2,2-triphenylethyl fluoride as a combination product ($\varepsilon = +$), net polarisation is predicted to be A for ^{19}F ($\Gamma_{NE} = \mu\varepsilon\Delta g a_F = + + + + = + = $ A), E for H-1, and A for H-2. Kaptein's rule for multiplet polarisation strictly applies only to a system of two coupled nuclei, but can be applied to the three-spin systems by making use only of the coupling to the nucleus having the higher absolute a-value, the proton geminal to fluorine in the present case. Taking $^2J_{HF}$ to be positive,* the prediction is A/E for ^{19}F ($\Gamma_{ME} = \mu\varepsilon a_F a_H {}^2J_{HF}\sigma = + + + - + + = - = $ A/E), A/E for H-1, and E/A for H-2. These polarisations are exactly as observed except for the absence of significant net polarisation in the proton signals (discussed below).

This agreement does not rule out some participation of

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* Assuming $J(^{13}C-H)$ is positive, $^2J_{HF}$, $^3J_{HF}$, and $^3J_{HH}$ are all positive.[16]

[12] R. Kaptein, *Chem. Comm.*, 1971, 732; *J. Amer. Chem. Soc.*, 1972, **94**, 6251.

[13] G. L. Closs, ' Special Lectures presented at the XXIIIrd International Congress of Pure and Applied Chemistry, Boston, 1971,' vol. 4, Butterworths, London, p. 19.

[14] D. R. Dalton and S. A. Leibman, *J. Amer. Chem. Soc.*, 1969, **91**, 1194.

[15] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, 1968, **90**, 4201, and references therein.

[16] Ref. 6, Vol. II, pp. 682, 888.

singlet diphenylmethylene. Such a species could either insert into the benzylic C–H bond in a concerted fashion, when there would be no polarisation, or through a singlet (S) radical pair where a cage effect might give predominant recombination without polarisation. Benzylic insertion by singlet diphenylmethane into diastereoisomeric esters of α-fluorophenylacetic acid in small amount has been inferred from the difference in stereochemistry indicated by the n.m.r. signals due to the polarised and total (unpolarised) insertion product.[17] However, in the present instance, the dominant insertion processes seem to be those involving T and F radical pairs, since enhancement factors greater than 200 can be estimated for 1,2,2-triphenylethyl fluoride.

Radical-pair Theory: Qualitative Predictions.—Qualitatively, the results of the present study nicely illustrate the working of the currently accepted radical-pair theory of CIDNP, in which nuclear spin selection occurs during mixing of T_0 and S states of the radical pair.[2] According to this theory, for the first-order spectrum of the combination product AB of a radical pair A··B, the intensity I of the transition $m_i \longrightarrow m_i - 1$ of nucleus i in A is given by equation (1). The initial + sign refers to T or

$$I \propto \pm \frac{1}{2} a_i \left[\beta \hbar^{-1} (g_A - g_B) H_0 + \sum_{j \neq i}^{A} a_j \, . \, m_j - \sum_{k}^{B} a_k m_k \right] \quad (1)$$

F pairs and − to S pairs. The equation applies when the electron–electron exchange integral for the pair of radicals is very much greater than the off-diagonal matrix element connecting the T_0 and S states of the radical pair for a particular nuclear spin state. Of course, in assigning intensities to spectral lines, the signs of nuclear–nuclear coupling constants also need to be known since these determine whether lines with positive m_j and m_k appear at low or high field in the multiplet of nucleus i. In equation (1), the first term gives the net polarisation, which should thus show direct proportionality to Δg and the magnetic field H_0, and the remaining terms the multiplet polarisation dependent in intensity only on the electron–nuclear coupling.

The results of Table 3 can now be interpreted in terms of equation (1). The insertion product of bis-(4-chlorophenyl)methylene shows perfect multiplet polarisation of F, H-1, and H-2; in this system $\Delta g = 0$, and thus the g-factor for the fluorobenzyl radical must have a value very close to that of the bis-(4-chlorophenyl)methyl radical, namely, 2.003 0.[13] Using diphenyldiazomethane, and its mono- and difluoro-, and mono- and other dichloro-analogues, the net ^{19}F absorption signifies that the diarylmethyl radical has a g-factor less than that of fluorobenzyl. Introduction of bromo- or iodo-substituents reverses the situation giving the diarylmethyl component of the radical pair the higher g-value and so leading to net emission. Throughout this range of Δg the multiplet polarisation remains A/E as required by equation (1).

Net polarisation of the n.m.r. signals of H-1 and H-2 should change in the same way as that of the fluorine in the insertion product. However, the net effect is only clearly detectable in the dibromo- and (with some difficulty) in the di-iodo-case. Equation (1) permits us to explain this. The maximum ratio of intensities due to multiplet and net polarisation is proportional to $\Sigma a / |\Delta g| H_0$, where the summation is taken over all nuclei other than that being observed. In the present instance Σa will be smaller when fluorine is observed than for protons since in the latter cases the summation contains a_F which is in general $\geqslant$ *ca.* $3a_H$.[15] Net polarisation is, therefore, much more important for fluorine than for protons. In the same way it can be seen that multiplet polarisation increases in importance at low Δg and lower fields.

TABLE 3

Patterns of polarisation of 2,2-diaryl-1-phenylethyl fluorides $(XC_6H_4)(YC_6H_4)CH{\cdot}CHFPh$ at 120 °C

		Pattern of polarisation [a]			
X	Y	F	H-1	H-2	$\Delta\delta_F$/Hz
H	H	AAEA	AAEE	EEAA	
H	2-F	AAEA/ AAEA [b]	AAEE	EEAA	58
H	3-F	AAEA/ AAEA	AAE(E)	EEAA	34
H	4-F	AAEA/ AAEA	AAE(E)	EEAA	54
4-F	4-F	AAEA [c]	AAE(E)	EEAA	
H	2-Cl	AAEA/ AAEA	AAEE	EEAA	52
H	3-Cl	AAEA/ AAEA	AAE(E)	EEAA	51
H	4-Cl	AAEA/ AAEA	AAE(E)	EEAA	16
2-Cl	2-Cl	AAEA			
4-Cl	4-Cl	AAEE	AAE(E)	EEAA	
H	2,4-Cl_2	AAE(−)/ AAE [d]			46
H	3,4-Cl_2	AAEA/ AAEA			56
4-CH_3	2,4-Cl_2	AAE(−)/ AAE [d]			73
4-Cl	2-CH_3, 4-Cl	AAEE/ AAEE			3
H	2-Br	EAEE/ EAEE	AAEE	EEAA	78
H	4-Br	EAEE/ EAEE	AAE(E)	EEAA	5
4-Br	4-Br	EEEE	AA(?) (?)	EEAE	
4-I	4-I	EEEE	AAAA	EE [e]	
H	2-CF_3	AAEA/ AAEA	AAEE/ AAEE	EEAA/ EEAA	342 (3)
H	3-CF_3	AAEA/ AAEA	AAEE/ AAEE	EEAA	7 (3) [f]
H	4-CF_3	AAEA/ AAEA	AAEE	EEAA	60

[a] Symbols in parentheses indicate the presumed phases of lines obscured by signals due to the solvent. [b] Additional doublet splitting (3 Hz) of each line. [c] Aromatic F polarised E. [d] No polarisation of fourth line. [e] Two broad weak emission signals detected in this region. [f] $\Delta\delta_H$.

Radical-pair Theory: Quantitative Predictions and the Role of Nuclear Relaxation.—In the present study the predictions of the radical-pair theory have been made

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[17] D. Bethell and K. McDonald, *J.C.S. Chem. Comm.*, 1974, 467.

quantitative using a CIDNP computer simulation program devised by den Hollander. In this program, nuclear spin state populations are predicted on the basis of assumed precursor multiplicity, radical *g*-factors, *a*-values, coupling constants, and enhancement ratio, using either an exponential or diffusion model to express the time variation of the electron–electron interaction in the radical pair. Nuclear-spin relaxation is not a variable.

Figure 3 shows the results of calculations of the polarised ^{19}F- and ^{1}H-spectra of 1,2,2-triphenylethyl fluoride and the analogous insertion products resulting from the use of 4,4′-dichloro- and 4,4′-dibromo-diphenyldiazomethane. No appreciable difference was found between the results from calculations according to exponential and diffusion models. The perfect, multiplet polarisation in the dichloro-case is very satisfactorily reproduced. However, in the unsubstituted compound, the prediction of the ^{19}F spectrum at 56.4 MHz is appreciably closer to a perfect multiplet effect than is in fact observed, and line 3 of the quartet is predicted to remain a moderately intense emission at 94.1 MHz. In the dibromo-compound the predicted variation in intensity in the ^{19}F lines is greater than observed. In both cases the proton spectrum is well reproduced, but, as we have seen, ^{1}H polarisation is much less sensitive to the properties of the radical pair components.

Somewhat similar behaviour has been described by others. Thus Müller and Closs [13,18] reported changes in the intensity of polarisation of the starting material during the photolysis of phenyl α-phenylethyl ketone; this included a change from absorption to emission of one line in a polarised ^{1}H quartet. Similar changes of intensity in a polarised quartet from EEEA to EEEE have been described by Lawler in the spectrum of ethylbenzene produced in the decomposition of benzoyl propionyl peroxide.[19] These variations in intensity (I_{nm}) have been interpreted by Closs in terms of equation (2) where the first term refers to the rates of population of the nuclear spin states n and m and the remaining terms cover nuclear spin relaxation processes in a multilevel system. For correct simulation, it was found necessary to include both intermolecular spin-lattice relaxation and intramolecular nuclear dipole–dipole coupling,[18] and Lawler has drawn special attention to the latter interaction.

$$\begin{aligned} \mathrm{d}I_{\mathrm{nm}}/\mathrm{d}t = {} & k_{\mathrm{r}}[^{\mathrm{m}}\mathrm{M}](W_{\mathrm{n}} - W_{\mathrm{m}}) - 2w_{\mathrm{mn}}(N_{\mathrm{n}} - N_{\mathrm{m}}) \\ & + \sum_{\mathrm{i}\neq\mathrm{m}} w_{\mathrm{in}}(N_{\mathrm{i}} - N_{\mathrm{n}}) \sum_{\mathrm{i}\neq\mathrm{n}} w_{\mathrm{im}}(N_{\mathrm{i}} - N_{\mathrm{m}}) \quad (2) \end{aligned}$$

In the present instances, the discrepancies between observation and prediction (with neglect of relaxation) persist throughout each experiment. However, relaxation processes could be responsible for the differences since with three coupled nuclei both inter- and intramolecular effects could contribute. This leads to ' intensity borrowing ' from non-nearest neighbour lines in the multiplet and, in the case of 1,2,2-triphenylethyl fluoride for example, could well convert the predicted weak emission in line 4 of the ^{19}F quartet at 56.4 MHz into a weak absorption. The present results seem to bear out Closs' suggestion that relaxation effects should be most important in cases where Δg is of the same order of magnitude as the hyperfine coupling. However, the difference in polarisation of the fourth ^{19}F line between the product from 2,2′- and 4,4′-dichlorodiphenyldiazomethane is very similar to the difference between the observed and calculated polarised spectra for 1,2,2-triphenylethyl fluoride; relaxation rather than $\Delta g > 0$ may be responsible for the net absorption in the 2,2′-dichloro-case. If this is so, then a limit is placed on the accuracy with which radical *g*-factors can be determined by simulation of CIDNP signals.

EXPERIMENTAL

Materials.—Diaryldiazomethanes were prepared by oxidation of the corresponding benzophenone hydrazone as in earlier papers in this series. A number of the compounds were not previously known and these are listed in Table 4. Some of the diazoalkanes could not be obtained in crystalline form and were characterised by conversion into the triphenylphosphazene (triphenylphosphoranylhydrazone) by reaction with the stoicheiometric amount of triphenylphosphine in acetonitrile solution at room temperature.

Benzyl fluoride was commercial material used without further purification. No impurities were detectable in the ^{1}H and ^{19}F n.m.r. spectra.

1,2,2-*Triphenylethyl Fluoride.*—This was prepared by hydrogenation in cyclohexane over 10% Pd/C of triphenylvinyl fluoride obtained from the reaction of tetrafluoroethylene with phenyl lithium.[20] The hydrogenation was allowed to proceed until some 50% of the theoretical uptake of hydrogen had occurred and the product separated from the starting material by preparative t.l.c. Prolongation of the hydrogenation gave only triphenylethane. 1,2,2-Triphenylethyl fluoride had m.p. 81—82 °C (Found: C, 86.7; H, 6.35. $C_{20}H_{17}F$ requires C, 86.9; H, 6.2%).

Product Analyses.—These were carried out by g.l.c. using a Pye-Unicam 104 gas chromatograph with flame-ionisation detector in conjunction with a 5 ft × $\frac{1}{4}$ in glass column packed with 1% OV17 on Gas Chrom Q. Peak areas were measured using a Vidar 6300 electronic integrator. Identification of peaks was by comparison of retention times using authentic specimens.

CIDNP.—Spectrometers employed were a Varian A56/60 (^{19}F, 56.4; ^{1}H, 60 MHz) and HA100 (^{19}F, 94.1; ^{1}H, 100 MHz). These were equipped with variable-temperature accessories usually set at 120 °C with temperature calibration using the ^{1}H resonances of ethylene glycol. For the HA100 spectrometer, lock signals were provided by insertion of a sealed capillary containing dimethyl sulphoxide (^{1}H) or *p*-dichlorotetrafluorobenzene (^{19}F) into the n.m.r. tube.

The reaction mixture (0.5 ml) was placed in a 5-mm n.m.r. tube which was inserted into the heated probe of the spectrometer which had been tuned at the reaction tem-

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[18] K. Müller and G. L. Closs, *J. Amer. Chem. Soc.*, 1972, **94**, 1002.

[19] R. G. Lawler, Lecture presented at the Euchem. Conference on Chemically Induced Magnetic Polarisation, St. Pierre de Chartreuse, 1975.

[20] T. F. McGrath and R. Levine, *J. Amer. Chem. Soc.*, 1955, **77**, 4168.

TABLE 4

Characterisation of substituted diphenyldiazomethanes $(XC_6H_4)(YC_6H_4)CN_2$

				Analysis (%)					
				Found			Required		
X	Y	Formula	M.p. (θ_c/°C)	C	H	N	C	H	N
2-F		$C_{31}H_{24}N_2FP$ *	167—170	78.3	5.3	5.9	78.5	5.1	5.9
3-F		$C_{31}H_{24}N_2FP$ *	171—173	78.5	5.2	5.9	78.5	5.1	5.9
4-F		$C_{13}H_9N_2F$	34—35	73.5	4.7	13.0	73.6	4.3	13.2
2-Cl		$C_{13}H_9N_2Cl$	35—36	68.4	4.1	11.6	68.3	4.0	12.2
3-Cl		$C_{31}H_{24}N_2ClP$ *	155—157	75.6	4.6	5.8	75.8	4.9	5.7
2-Cl	2-Cl	$C_{31}H_{23}N_2Cl_2P$ *	143—145	70.8	4.6	5.4	70.9	4.4	5.3
2,4-Cl_2		$C_{31}H_{23}N_2Cl_2P$ *	152—154	70.7	4.4	5.5	70.9	4.4	5.3
3,4-Cl_2		$C_{13}H_8N_2Cl_2$	93—94	59.2	3.1	10.9	59.3	3.1	10.6
2-Me-4-Cl	4-Cl	$C_{32}H_{25}N_2Cl_2P$ *	149—151	70.9	5.0	5.2	71.2	4.7	5.2
2,4-Cl_2	4-Me	$C_{32}H_{25}N_2Cl_2P$ *	152—154	71.4	4.9	5.4	71.2	4.7	5.2
2-Br		$C_{31}H_{24}N_2BrP$ *	136—138	69.4	4.8	5.5	69.5	4.5	5.2
4-Br		$C_{13}H_9N_2Br$	39—41	57.3	3.4	9.7	57.2	3.3	10.3
4-Br	4-Br	$C_{13}H_8N_2Br_2$	100—102	44.1	2.3	7.7	44.3	2.3	8.0
2-CF_3		$C_{32}H_{24}N_2F_3P$ *	125—127	73.5	4.9	5.2	73.3	4.6	5.3
3-CF_3		$C_{32}H_{24}N_2F_3P$ *	117—119	73.3	4.5	5.4	73.3	4.6	5.3
4-CF_3		$C_{14}H_9N_2F_3$	35—37	64.5	3.8	9.4	64.1	3.5	10.7

* Diazoalkane not crystalline; analysis and m.p. refer to the corresponding triphenylphosphazene (triphenylphosphoranylhydrazone).

perature. After an initial warming-up period, polarised signals were detected by repetitive scanning of the appropriate spectral region. Maximum polarisation was some 2 min after insertion of the sample, whereafter the polarisation decayed and after *ca.* 10 min was indistinguishable from the spectrometer noise level.

For very rapid scanning of polarised signals, such as in measuring the rate of depolarisation, a Varian C1024 CAT accessory was used to trigger repeated scans of narrow spectral regions, the n.m.r. signals being continuously recorded on an auxiliary chart recorder connected to the ' external recorder ' terminals of the spectrometer.

Depolarised spectra were recorded at probe temperature (*ca.* 40 °C) using the CAT accessory. Typically 50—150 scans were necessary to obtain a satisfactory spectrum.

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