

## Dimerization of $\alpha$ -Fluorobenzyl Radicals: Mechanistic Evidence from Chemically Induced Dynamic Polarization of $^{19}\text{F}$ Nuclei

By D. BETHELL,\* M. R. BRINKMAN, and J. HAYES

(The Robert Robinson Laboratories, The University, P.O. Box 147, Liverpool L69 3BX)

*Summary* Differences between the polarized and depolarized  $^{19}\text{F}$  n.m.r. spectra of solutions in which 1,2-difluorobenzyl is formed by dimerization of  $\alpha$ -fluoro-

benzyl radicals are interpreted as evidence for the intermediate formation of a pair of diastereoisomeric methylcyclohexa-2,4-dienes.

IN the course of a study<sup>1</sup> of substituent effects on chemically induced dynamic nuclear spin polarization (CIDNP) in the product of insertion of diphenylmethylene into the benzylic C-H bond of solvent benzyl fluoride we observed an additional <sup>19</sup>F polarization *ca.* 1280 Hz downfield from the triplet due to the solvent. The polarized multiplet (E/A) [Figure (a)] had an integral of zero, indicating that  $\Delta g$  for the precursor radical pair is zero, and was essentially invariant with changing substituent in the carbene. Moreover, the same polarized spectrum could be observed when

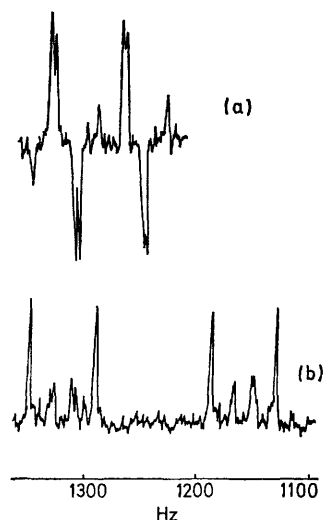
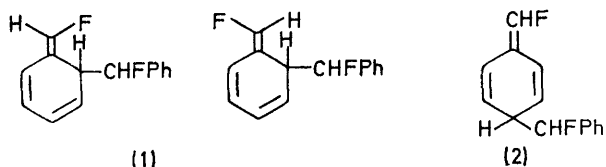


FIGURE. Typical <sup>19</sup>F n.m.r. spectra (56.4 MHz) of  $\alpha$ -fluorobenzyl radical dimers formed by decomposition (120 °C) of diphenyldiazomethanes in solvent benzyl fluoride: (a) during reaction; (b) by accumulation (106 scans) after completion of the reaction. 4-Chlorodiphenyldiazomethane was used in the example illustrated. The scale gives the chemical shift (Hz) downfield from the solvent triplet.

benzoyl peroxide decomposed thermally in benzyl fluoride. Dimerization of solvent radicals is thus indicated. In no case could corresponding polarization be detected in the <sup>1</sup>H spectrum. After the polarization had decayed a quite different depolarized spectrum [Figure (b)] was obtained by accumulation. The two identical multiplets each show the pattern of signals characteristic of an AA'XX' system of coupled nuclei<sup>2</sup> expected for ( $\pm$ )- and *meso*-1,2-difluorobenzyl. Confirmation of this assignment was provided by the identity of the <sup>19</sup>F spectrum of authentic ( $\pm$ )-1,2-difluorobenzyl [synthesized by reaction of tetrafluoroethylene with excess of phenyl-lithium followed by reduction

(H<sub>2</sub>/Pd) of the difluorostilbene] with the depolarized product multiplet at lower field. The problem therefore is to relate the polarized and depolarized spectra, since the current theory of CIDNP requires that these should be identical in all respects save relative line intensity.

We believe that these results indicate that the dimerization of  $\alpha$ -fluorobenzyl radicals to form ( $\pm$ )- and *meso*-1,2-difluorobenzyl (the thermodynamically controlled products) is a two-step reaction. The intermediate kinetically controlled product, giving rise to the polarized <sup>19</sup>F spectrum as a result of  $T_0$ -S mixing in an uncorrelated (encounter) radical pair<sup>3</sup> is thought to be the pair of diastereoisomeric fluoromethylenecyclohexa-2,4-dienes (**1**), formed by attack of one fluorobenzyl radical on the aromatic ring of the other (*cf.* the dimerization of triphenylmethyl radicals<sup>4</sup>). The polarized <sup>19</sup>F-multiplets are due to the fluorine bound to *sp*<sup>3</sup>-hybridized carbon in the two diastereoisomers and coupled to a geminal and vicinal proton (AMX system). Consistently, the separation between the two pairs of intensely polarized lines was found to be proportional to the magnetic field. However, polarized signals attributable to the vinylic fluorines in (**1**) could not be detected. Coupling of  $\alpha$ -fluorobenzyl radicals could also take place through the *para*-position of the aromatic ring as in (**2**). The doublet splitting [*ca.* 2.5 Hz (56.4 and 94.1 MHz spectra)] observed for the most intensely polarized lines in the <sup>19</sup>F spectrum<sup>†</sup> leads us to prefer formulation (**1**) since the relative disposition of the two fluorine nuclei is then very similar to that in *erythro*- and *threo*-2-(*o*-fluorophenyl)-1,2-diphenylethyl fluoride, where doublet splitting is also observed in the polarized spectrum.<sup>1</sup>



Rearrangement of methylenecyclohexadienes to aromatic structures ('semibenzene rearrangement') is well documented,<sup>5</sup> and migration of benzyl groups is known to be particularly rapid.<sup>5a</sup> There is strong evidence of radical intermediates in these rearrangements but CIDNP has not previously been reported; nor have we been able to detect polarization of 1,2-difluorobenzyl in the present instance.

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<sup>†</sup> In general, the splitting was more marked in the low-field half of the spectrum.

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<sup>3</sup> G. L. Closs, XXIIIrd International Congress of Pure and Applied Chemistry, Boston, 1971, Special Lectures Vol. 4, p. 19; R. Kaptein, Thesis, Leiden, 1971; *J. Amer. Chem. Soc.*, 1972, **94**, 6251, 6262; H. Fischer, *Z. Naturforsch.*, 1970, **25a**, 1957; R. G. Lawler, *Accounts Chem. Res.*, 1972, **5**, 25.

<sup>4</sup> H. Lankamp, W. T. Nauta, and C. MacLean, *Tetrahedron Letters*, 1968, 249.

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