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USE OF ^{19}F CIDNP IN REACTION MECHANISM STUDIES. EVIDENCE FOR THE INTERMEDIACY OF BENZYL ANION IN THE REACTION OF BENZYL HALIDES WITH SODIUM NAPHTHALENE

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The mechanism for the reaction of alkyl halides with sodium naphthalene has been widely discussed, one of the more interesting topics being the relative importance of the direct radical combination route (eq 2) and the carbanion route (eq 3).[1-5] It is now generally thought[4] that alkyl chlorides and bromides

$$\text{RX} + \text{Naph}^{\overline{\cdot}} \longrightarrow \text{R}\cdot + \text{X}^- \qquad (1)$$

$$2\text{R}\cdot \longrightarrow \text{R-R; RH} + \text{R (-H)} \qquad (2)$$

$$\begin{tikzcd}[row sep=small] & & \text{RH} \\ \text{R}\cdot + \text{Naph}^{\overline{\cdot}} \arrow[r] & \text{R}^- \arrow[ur, "\text{SH}"] \arrow[dr, "\text{RX}"'] & \\ & & \text{R-R} \end{tikzcd} \qquad (3)$$

react mainly by eq 3. The situation for iodides is less clear; although eq 3 probably dominates, both routes may be important.[4,5]

We were concerned with the mechanism for the reaction of benzyl halides with sodium naphthalene, since the above conclusions do not necessarily apply to benzylic systems where both the radical and carbanion species are strongly stabilized. This paper describes experiments, involving the combined use of the Banks' anion-trapping technique[4] and ^{19}F CIDNP observations for p-fluorobenzyl halides, which demonstrate that both benzyl chlorides and iodides react mainly by the carbanion route (eq 3).

Reaction of equal volumes of THF solutions of benzyl chloride or iodide (0.6 M) and sodium naphthalene (0.25 M) yields bibenzyl in high yield. When the experiments are performed differently and the benzyl halide solutions are first saturated with anhydrous magnesium bromide, then reacted with sodium naphthalene, and finally treated with water, benzyl chloride yields toluene as the major product (toluene-bibenzyl molar ratio is ca. 5).[6] However, benzyl iodide still yields bibenzyl as the major product (less than 10% toluene forms).[6]

The above experiments were also performed with p-fluorobenzyl halides by mixing the reagents in an nmr sample tube in the probe of an nmr spectrometer (14KG, 56.4 MHz). The region of the ^{19}F spectrum associated with p-fluorobenzyl derivatives was scanned within 15 sec. of mixing. For both the chloride and iodide, in the absence of $MgBr_2$, an intense polarized resonance was observed (Fig. a) at the frequency expected for p,p'-difluorobibenzyl. No other polarized resonances were observed. A similar polarized resonance was also observed for the iodide in the presence of $MgBr_2$. However, no polarization could be observed during the reaction of the chloride in the presence of $MgBr_2$.

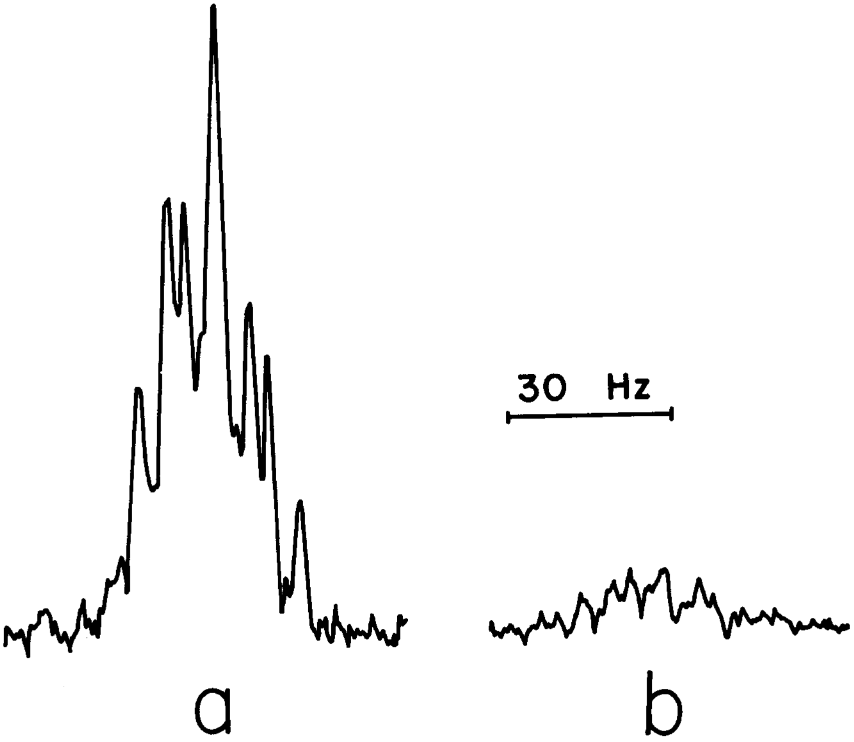
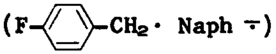


Figure. a) Polarized ^{19}F spectrum for p,p'-difluorobibenzyl obtained 15 sec. after mixing reagents in the spectrometer probe.
b) Equilibrium spectrum obtained 1 min. after mixing.

Anhydrous magnesium bromide has been suggested[4] as a reagent which effeciently and selectively traps the carbanion of eq 3, forming a Grignard reagent. Addition of water then converts the Grignard reagent to a hydrocarbon. Accordingly, the involvement of the Grignard reagent in the benzyl halide reactions would cause formation of toluene. Therefore, the observation of toluene as the major product in the presence of $MgBr_2$ indicates that benzyl chloride reacts with sodium naphthalene mainly by the carbanion route (eq 3). Unfortunately, the product analysis for benzyl iodide provides no information on its reaction mechanism. The absence of toluene in the presence of $MgBr_2$ does not necessarily indicate that radical coupling occurs; the carbanion route could be operative and still lead to exclusive bibenzyl formation.[7] Fortunately, the ^{19}F CIDNP experiments allow differentiation between these two possibilities and demonstrate that the latter one is correct.

CIDNP for reaction products results from time-dependent nuclear spin-electron spin interactions in radical pair intermediates.[8,9] CIDNP experiments are useful in mechanistic studies since the appearance of the polarized resonance is dependent on, and thus can provide information about, the reaction mechanism. The most likely radical pair to be of consequence in these reactions is I, formed as an intermediate in the electron transfer step of eq 3.



I

The radical pair consisting of two *p*-fluorobenzyl radicals might also be important in the reaction mechanism, but could not lead to the net polarization observed in Fig. a.[8] That polarization results during the formation of benzyl anion from I is confirmed for the chloride by the observation that no polarized *p*,*p*'-difluorobibenzyl resonance is observed when the benzyl anion is trapped by $MgBr_2$. This finding eliminates the possibility that the polarization results entirely from a small amount of *p*,*p*'-difluorobibenzyl formed by some other mechanism. The important point is that since a) *p*,*p*'-difluorobibenzyl formed *via* the two different mechanisms would exhibit different polarized spectra,[8] b) identical polarized resonances are observed for benzyl chloride and iodide in the absence of $MgBr_2$, and c) the polarization observed for the chloride does result during formation of the carbanion, it is probable that both the iodide and the chloride react mainly by the same mechanism; *i.e.*, by the carbanion route (eq 3).

The observation of CIDNP in this system is apparently associated with the great sensitivity of the ^{19}F polarization intensity for *p*-fluorobenzyl derivatives to small Δg values (*i.e.*, 10^{-4}) for the critical radical pairs;[10] polarization of the methylene and aromatic protons in this system was searched for but not observed. ^1H CIDNP has been observed for the reactions of sodium naphthalene with other alkyl halides,[11] but only at low magnetic fields[12] where the polarization has a different origin and provides less mechanistic information.

References

1. G. D. Sargent, J. N. Cron, and S. Bank, J. Am. Chem. Soc., 88, 5363 (1966); G. D. Sargent and G. A. Lux, ibid., 90, 7162 (1968).
2. J. F. Garst, P. W. Ayers, and R. C. Lamb, ibid., 88, 4260 (1966); J. F. Garst, J. T. Barbas, and F. E. Barton, ibid., 90, 7159 (1968).
3. S. J. Cristol and R. V. Barbour, ibid., 88, 4262 (1966).
4. S. Bank and J. F. Bank, Tetrahedron Letters, 4533 (1969).
5. J. F. Garst and J. T. Barbos, ibid., 3125 (1969).
6. The product analysis was performed by both glc and ^1H nmr integration.
7. The more reactive benzyl iodide might win out in competition with $MgBr_2$ for benzyl anion, or react with the benzyl Grignard reagent prior to the water quench.
8. G. L. Closs and A. D. Trifunac, J. Am. Chem. Soc., 92, 2183, 2186 (1970); G. L. Closs, C. E. Doubleday, and D. R. Paulson, ibid., 92, 2185 (1970).
9. R. Kaptein and L. J. Oosterhoff, Chem. Phys. Lett., 4, 195, 214 (1969).
10. a) J. W. Rakshys, Jr., Chem. Communications, 588 (1970).
    b) Submitted to J. Am. Chem. Soc.
11. J. F. Garst, R. H. Cox, J. T. Barbas, R. D. Roberts, J. I. Morris, and R. C. Morrison, J. Am. Chem. Soc., 92, 5761 (1970).
12. The ^{19}F resonance for p,p'-difluorobibenzyl shows emission when the reactions of p-fluorobenzyl halides are run under these conditions.