CIDNP Evidence for a 'Hot' Carbocation formed by Electron Transfer between Two Radicals

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The radical pair (**2**), containing 2-phenylethyl and *m*-chlorobenzoyloxy radicals, produced from β-phenyl[α,α-$^2H_2$]propionyl *m*-chlorobenzoyl peroxide (**1**), gives rearranged products; the observations of CIDNP and product analyses suggest that the 2-phenylethyl carbocation initially produced by electron transfer within the radical pair is a 'hot' carbocation which retains the ground state configuration of its neutral radical precursor.

The use of CIDNP has permitted the observation of electron transfer between two neutral organic radicals in solution.[1] Evidence is accumulating that this reaction is a general one occurring whenever unsymmetrical diacyl peroxides decompose.[2] We now report CIDNP evidence for a conformationally excited, or 'hot', carbocation produced by electron transfer within a radical pair. The radical pair precursor employed was β-phenyl[α,α-$^2H_2$]propionyl *m*-chlorobenzoyl peroxide (**1**).‡ Thermal decomposition of (**1**) (Scheme 1) may proceed by either an ionic pathway to produce ion pair (**4**) or a radical pathway to yield radical pair (**2**).[3] A subsequent electron transfer reaction of radical pair (**2**) would produce ion pair (**3**).[1] Wagner–Meerwein rearrangement of 2-phenylethyl cation (**3**) will form rearranged cations (**5**), (**6**), and (**7**) to yield esters (**8**), (**9**), and (**10**) and styrenes (**11**), (**12**), and (**13**). Ion pair (**4**) will produce the carboxy inversion product (**14**)§ and possibly other ionic products.[4] Yields of all identified products from the decomposition of (**1**) in *o*-dichlorobenzene (ODCB), as determined by 250 MHz ^1H n.m.r. spectroscopy of partially

Table 1. Yields and relative CIDNP enhancement factors of products from the thermolysis[a] of (**1**).

Product	Yield[b]/%	V_{rel}[c]
$\mathrm{PhC}H\mathrm{{=}CD_2}$ (**11**)	3.8 (±0.2)	+100[c]
$\mathrm{PhCH_2CD_2O_2CAr}$ (**8**)	32.7 (±4.4)	+23 (±2)
$\mathrm{PhCD_2C}H_2\mathrm{O_2CAr}$ (**9**)	9.7 (±0.9)	—[d]
*$\mathrm{PhC}H\mathrm{(CHD_2)O_2CAr}$ (**10**)[e]	1.9 (±0.1)	+35 (±7)
*(*Z*)-$\mathrm{PhCH{=}CD}H$ (**12**)	0.61(±0.03)	+33 (±5)
*(*E*)-$\mathrm{PhCH{=}CD}H$ (**13**)	0.71(±0.04)	+23 (±5)
$\mathrm{PhC}H_2\mathrm{CHD_2}$[f]	7.5 (±0.04)	−120 (±10)
$\mathrm{PhCH_2CD_2O_2CAr}$ (**8**)	32.7 (±4.4)	+23 (±2)

[a] 0.5 M, *o*-dichlorobenzene, 125 °C. [b] Yields are based on initial peroxide (100%) and determined by 250 MHz ^1H n.m.r. integration for an average of three runs. [c] CIDNP enhancement factors[5] for indicated protons relative to [2,2-$^2H_2$]styrene which was arbitrarily set to 100. Relative enhancements were obtained by dividing the observed *relaxation free* CIDNP intensity[5] per proton by the product yield. Ratios and errors for minor products were estimated by visual comparison between the observed CIDNP spectrum and one simulated using product ratios as shown in Figures 1(a) and (c), respectively. [d] No detectable CIDNP (see Figure 1). [e] Asterisk indicates rearranged products which also exhibit CIDNP. [f] Product formed by scavenging of the 2-phenylethyl radical by addition of solvent-derived H atom. CIDNP at δ 2.67 not shown in Figure 1. [g] Product of carboxy inversion.§ No CIDNP or rearrangement expected or observed.

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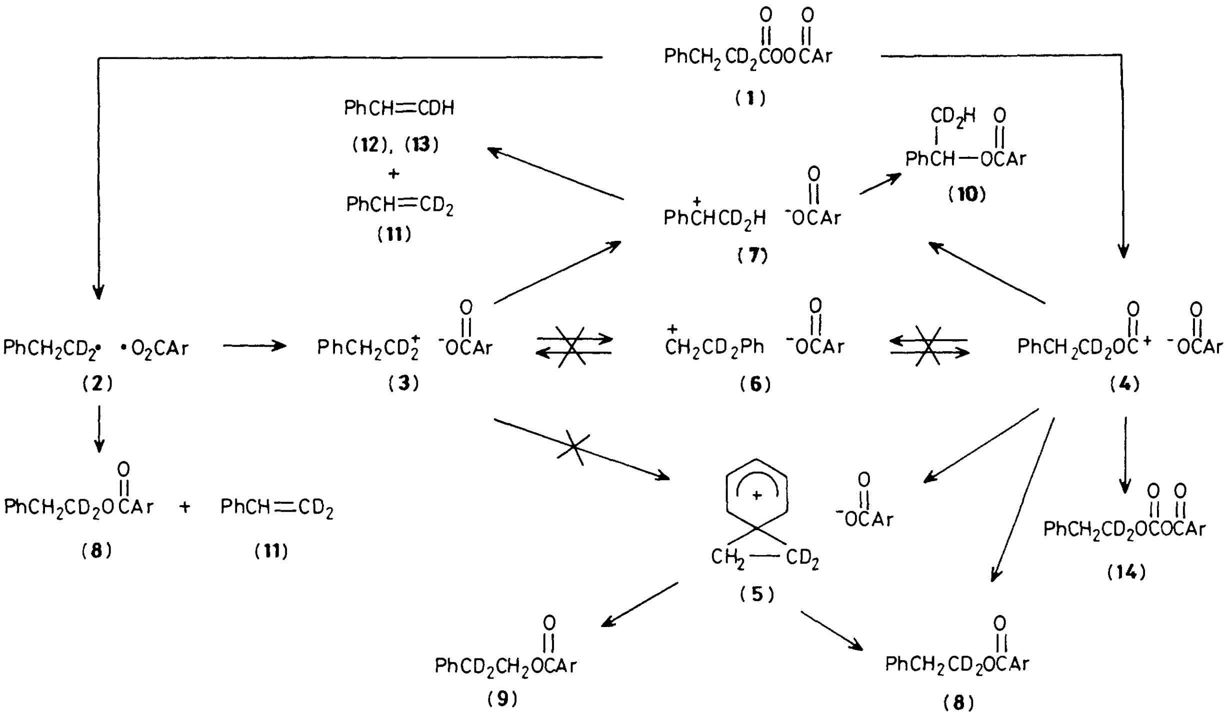
‡ Peroxide (**1**) was synthesized in 90% yield from *m*-chloroperbenzoic acid and β-phenyl[α,α-$^2H_2$]propionyl chloride. The amount of deuterium incorporated was 95.1 (±0.2)% determined by integration of the ^1H n.m.r. peaks. β-Phenyl[α,α-$^2H_2$]propionic acid was prepared from β-phenylpropionic acid (hydrocinnamic acid) by deuterium exchange with D_2O in the presence of sodium methoxide and converted into the acid chloride with excess of refluxing thionyl chloride.

§ The carboxy inversion product is formed in 13.4% yield but does not exhibit CIDNP. This product is stable under the reaction conditions, indicating a negligible yield of esters and rearranged products from this source.



Scheme 1. Ar = m-ClC$_6$H$_4$

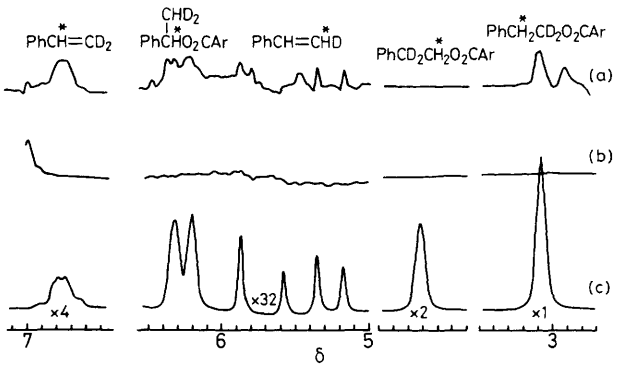
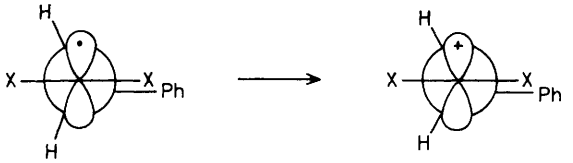


Figure 1. (a) Observed CIDNP spectrum recorded during the thermolysis of peroxide (**1**) (0.5 M) in ODCB at 140 °C. The spectrum is one scan in a series recorded with 90° pulse angle, repetition rate of one scan every 7.2 s, and delay time (τ) of 5 s. (b) The spectrum obtained from the sample under identical spectrometer conditions after thermolysis. The peak at δ 2.93 in spectrum (a) arises from the coupling product between m-chlorophenyl and β-phenylethyl radicals and was not simulated.[12] (c) Spectrum predicted on the basis of relative product yield.

decomposed samples, and relative CIDNP enhancements[5] are presented in Table 1.¶

On the basis of Scheme 1 it would be expected that the CIDNP enhancement factors would be identical for all the products arising from ion pair (**3**) and also for the ester (**8**) and styrene (**11**) formed by recombination of the corresponding radical pair. The data in Table 1 and the spectra in Figure 1 show that this is, in fact, the case for ester (**10**) and styrenes (**12**) and (**13**), consistent with their formation *via* a radical-derived 1-phenylethyl cation (**7**). The observed enhanced absorption for all of these protons is consistent with CIDNP produced in the protons of the 2-phenylethyl radical in the radical pair (**2**).[6] In striking contrast to this, however, the methylene protons in the rearranged ester (**9**) exhibit no detectable CIDNP.|| Furthermore, there is some evidence that the 1-phenylethyl cation is also formed to some extent by a purely ionic pathway.[7] The enhancement factors for (**10**), (**12**), and (**13**) are all lower by a factor of 3—4 than that of the radical-derived styrene (**11**). The lower enhancement factor for ester (**8**) is also explainable by invoking the portion of this product derived from the ion (**5**).



(**2A**) (**3A**)

X = H, D

It may thus be concluded that the 1- and 2-phenylethyl cations formed in the above reactions have different origins, the latter arising exclusively from non-radical pathways but the former having at least some contribution from a precursor free radical. A possible explanation for these observations may be found by considering the structure (**2A**) for the 2-phenylethyl radical. This structure is supported by e.s.r. and

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¶ When hexachloroacetone is used as solvent, β-phenylethyl chloride replaces ethylbenzene as the product of radical scavenging. The rearranged alkyl chloride, PhCD$_2$CH$_2$Cl and PhCH(Cl)CHD$_2$, could not be detected (<0.1%) by either CIDNP or product analysis, indicating that the β-phenylethyl radical does not rearrange before it is scavenged.

|| The possible product, PhCD=CH$_2$, from (**6**) was not observed in the 250 MHz ^{1}H n.m.r. spectrum. It has also been reported that bridged ion (**5**) may not produce styrenes.[9d]

CIDNP studies[6b,8] which indicates a non-bridged conformation in which the phenyl group lies close to the node of the half-filled p-orbital. If (**2A**) were suddenly ionized without conformational change, as expected for an electron transfer reaction, the resulting cation (**3A**) would possess a geometry favouring a hydride shift to form the more stable 1-phenylethyl cation (**7**) but unsuitable for phenyl migration to yield the cation (**5**). Evidence from a variety of sources,[9—11] however, indicates that the ground state of (**3**) is the bridged structure (**5**). In this sense, then, the structure (**3A**) corresponds to a vibrationally excited, or 'hot', isomer of (**3**). We are not aware of any direct evidence for the formation of such species in solution other than that presented here.

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