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A Chemically Induced Dynamic Nuclear Polarization Study of the Neophyl Radical Rearrangement

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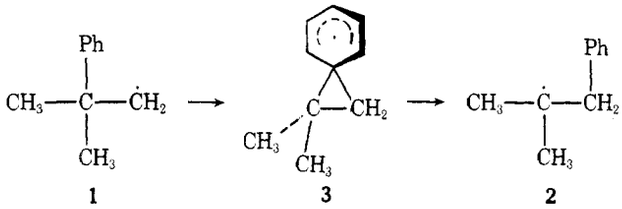
A CIDNP study of the thermolysis of benzoyl β-phenylisovaleryl peroxide and β-phenylisovaleryl peroxide has been carried out. Polarized signals in products resulting from both the 2-methyl-2-phenyl-1-propyl radical and from the rearranged 2-methyl-1-phenyl-2-propyl radical are observed. The CIDNP signals were consistent with a mechanism in which the majority of phenyl migration is not concerted with loss of CO_2 and occurs after diffusion from the cage. When β-phenylisovaleryl peroxide was decomposed, no polarization of aromatic ^1H signals was observed. Thus, if a phenyl-bridged intermediate is involved in the rearrangement, it does not have sufficient lifetime for spin selection and its consequent polarization to occur.

Although 1,2 migrations in free radicals are rather rare, they have been observed in a number of instances.[1] An extremely interesting example is the migration of a phenyl group in the 2-methyl-2-phenyl-1-propyl radical (**1**) which yields the 2-methyl-1-phenyl-2-propyl radical (**2**).[1,2] This rearrangement owes its thermodynamic driving force of approximately 8 kcal/mol[3] to the production of a tertiary radical from a primary radical. In addition, the kinetic barrier to rearrangement

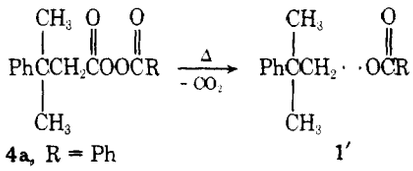


1 **3** **2**

is lowered by the known tendency for phenyl group rearrangement in radicals.[1] This propensity for phenyl migration has been ascribed to delocalization of the unpaired electron in an intermediate spiro radical such as **3**. Simple molecular-orbital calculations predict that, if **3** is involved, the energy of the transition state for this rearrangement will be lowered over that for a simple alkyl migration.[4]

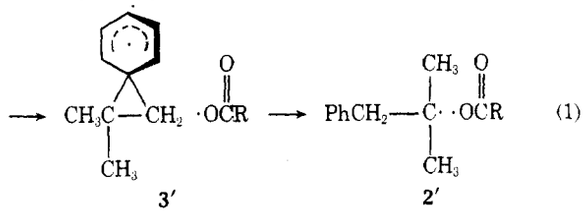
ESR studies of both **1**[5] and **2**[6] and of the rearrangement of **1** to **2**[3,7] have been reported. However, in none of these investigations was the bridged structure **3** detected. These results indicate that, if **3** is an intermediate, it does not have sufficient lifetime to permit its detection by ESR. Hence, it is not clear at this time whether **3** is an intermediate, lying in a shallow minimum on the energy surface between **1** and **2**, or simply a transition state for this rearrangement.

NMR–CIDNP studies have become an important means of detecting short-lived radical intermediates.[8] If an intermediate radical lives longer than $\sim 10^{-10}$ s as a member of a radical pair, spin selection and its consequent nuclear polarization can result.[9] In the rearrangement of **1** to **2**, CIDNP has the potential of providing a means for the detection of **3** if it is a short-lived intermediate. This is illustrated in eq 1 for the decomposition of a β-phenylisovaleryl peroxide (**4**).



4a, R = Ph **1′**

b, R = $-CH_2C(CH_3)_2Ph$



3′ **2′** (1)

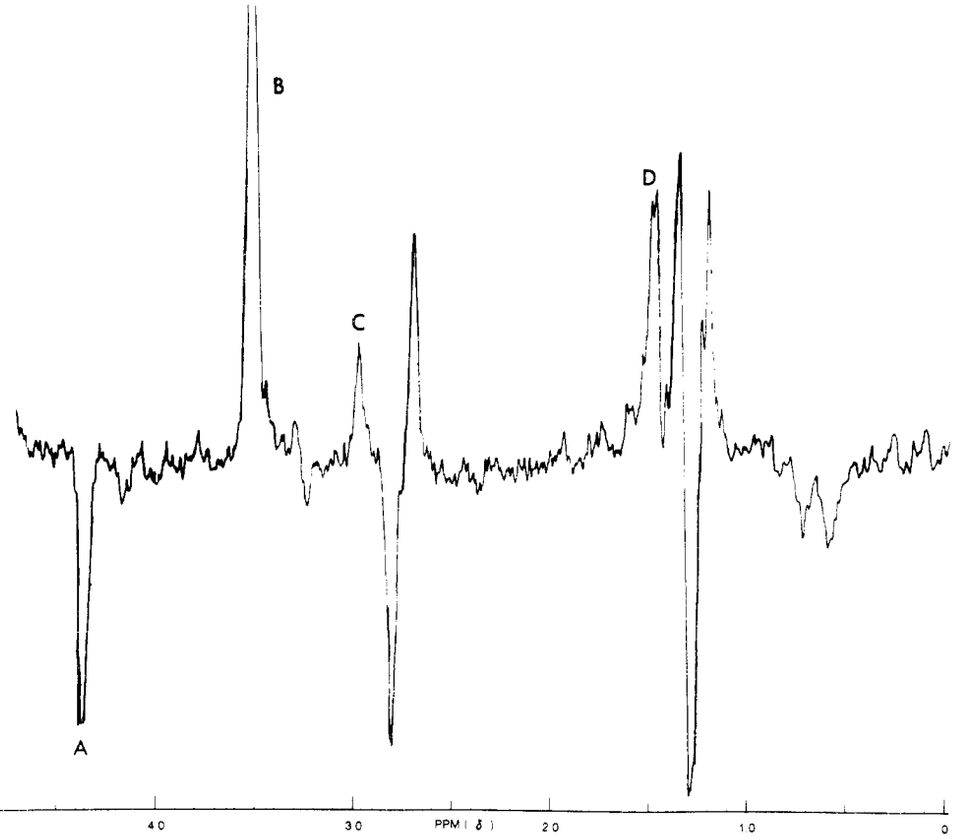
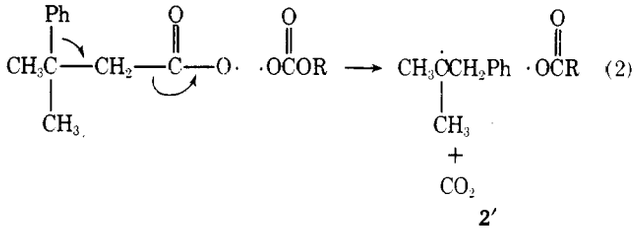


Figure 1. ^{1}H NMR spectrum recorded during the thermolysis of **4a** in HCA at 105 °C. Revelant assignments are: A, methylene protons in **7a**; B, methylene protons in **5**; C, methylene protons in **6**; D, methyl protons in **8a**.

Initial decomposition of **4** gives radical pair **1′** which will rearrange to pair **2′** via **3′**. In radical pair **3′**, unpaired spin is delocalized on the phenyl ring. Hence, phenyl protons in products resulting from **3′** are expected to be polarized if **3′** lives longer than 10^{-10} s.

In addition to providing information regarding the intermediacy of **3**, a CIDNP study of the decomposition of **4** can provide important information regarding the timing of phenyl migration with respect to decarboxylation. If decarboxylation is assisted by concerted phenyl migration (eq 2), all products



resulting from **2′** will show only polarization derived from spin selection in **2′** and none from **1′**.

In order to provide further information regarding the mode of decomposition of **4** and the mechanism of the rearrangement of **1** to **2**, we have conducted a CIDNP study of the thermolysis of **4**.

Results and Discussion

When the decomposition of **4b** was carried out in either hexachloroacetone (HCA) or *m*-dichlorobenzene, no polarization of any aromatic protons was observed. However, the polarizations observed in the aliphatic protons of rearranged cage product (vide infra) established that some rearrangement of **1′** to **2′** occurs. These results may be taken to indicate that the spiro radical pair **3′** does not have sufficient lifetime for spin selection and its consequent polarization of aromatic protons to occur.

However, a number of polarized signals were observed during the thermolysis of either **4a** or **4b**. Figure 1 shows the NMR spectrum taken during the 105 °C thermolysis of **4a**. Although the identity of all polarizations has not been established, a number of interesting points emerge from a consideration of the spectrum.

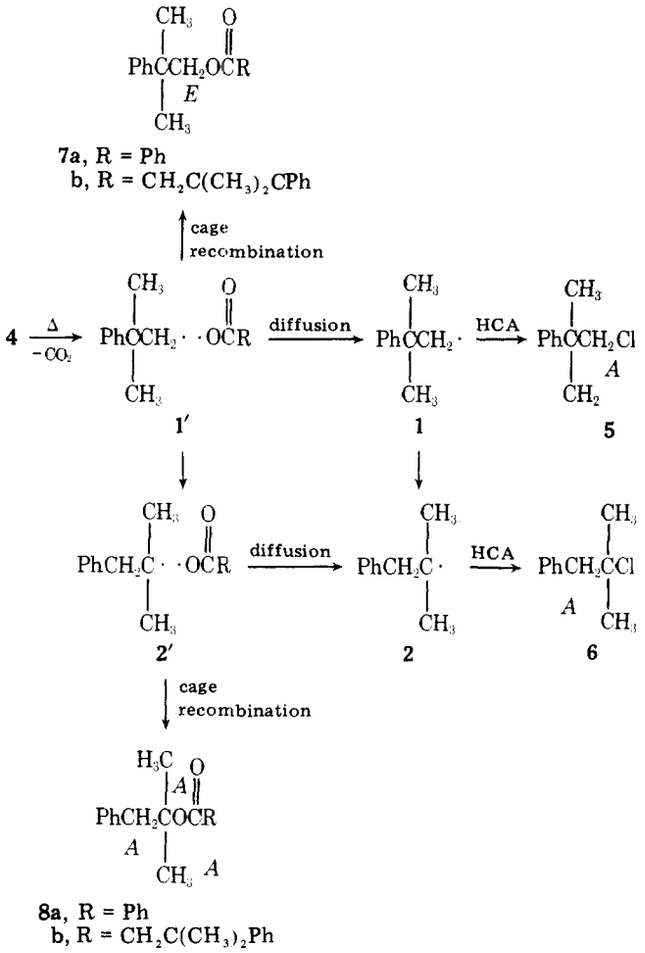
In the thermolysis of **4a** and **4b**, the products of initial interest were the unrearranged and rearranged cage recombination products and those products corresponding to diffusion of **1** and **2** from the cage. In order to simplify the product spectrum, the decomposition was initially carried out in hexachloroacetone (HCA), a solvent in which 1-chloro-2-phenyl-2-methylpropane (**5**) and 2-chloro-2-methyl-1-phenylpropane (**6**) are expected to be the major products of diffusion from the cage. The product of recombination within radical pair **1′** is the 2-phenyl-2-methyl-1-propyl ester **7**, while ester formation within pair **2′** will result in the 1-phenyl-2-methyl-2-propyl ester **8**.

These four products, **5**, **6**, **7**, and **8**, were detected in this study. The polarizations of the ^{1}H CIDNP signals resulting from them are shown in Scheme I, where *A* denotes enhanced absorption and *E* emission. Scheme I also depicts mechanisms of product formation consistent with the observed polarization.

Application of Kaptain's rules[10] to determine the polarization in unrearranged cage recombination product **7** and unrearranged diffusion product **5** is straightforward and leads to the conclusion that the methylene protons in **7** should exhibit emission while those in **5** should give enhanced absorption. These are the polarizations observed (Figure 1).

A prediction of the polarization expected for the methylene protons in rearranged cage product **8** is slightly more complicated. Kaptain's rules predict enhanced absorption for the methylene protons when **8** is produced from **2′** as the primary radical pair. In the present case, however, **2′** is a secondary

Scheme I



radical pair derived from the initial pair 1′. Since cage products from 1′ should exhibit methylene proton emission, the situation is ambiguous.

den Hollander[11] and Schwerzel, Lawler, and Evans[12] have recently examined systems in which secondary radical pairs are formed. Although these authors do not consider a case exactly analogous to the present system, they conclude that polarizations may be predicted using Kaptain's rules and summing the parameters for both primary and secondary radical pairs.

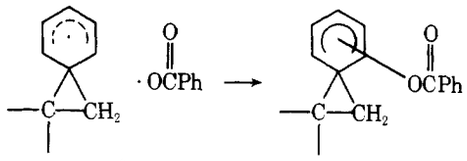
In the present case, only the values of the hyperfine splittings (a_H) in the two radical pairs differ. Since the sign of a_H in 1′ is opposite to that in 2′, the a_H values tend to cancel and little polarization of the methylene protons in 8 is expected. In fact, no polarized signal for these protons at δ 3.20 is observed in HCA (Figure 1). However, when the thermolysis of **4a** is carried out in *m*-dichlorobenzene, a weak enhanced absorbtion at δ 3.20 attributed to the methylene protons of **8a** is observed. The fact that a slight enhanced absorption actually occurs may reflect a longer lifetime of 2′ as compared to 1′.

Since a_{CH_3} is much larger in 2′ than in 1′,[3] a prediction of the polarization of methyl signals in 8 is unambiguous. The positive sign of a_{CH_3} in 2′ leads one to predict the enhanced absorption for the methyl protons in 8 which is observed in the spectrum (Figure 1).

Scheme I shows that the polarization of CIDNP signals from rearranged chloride, **6**, can be used to deduce the sequence of events leading to its formation. If **6** results mainly from a sequence involving 1′ → 2′ → 2 → **6**, its methylene protons should show a net emission as spin selection will occur in pair 2′. However, the fact that the methylene protons in **6** show enhanced absorption implies that the major pathway leading to **6** is 1′ → 1 → 2 → **6**. That is, most of the rearrangement of 1 to 2 occurs after diffusion from cage 1′. This must be true as the polarization observed in **6** is that predicted to be the result of diffusion from pair 1′ rather than from pair 2′.

The polarization of the methylene protons in **6** also establishes that the majority of the rearrangement cannot be concerted with decarboxylation, as this process would lead directly to 2′ which would yield **6** with methylene protons polarized oppositely to that observed.

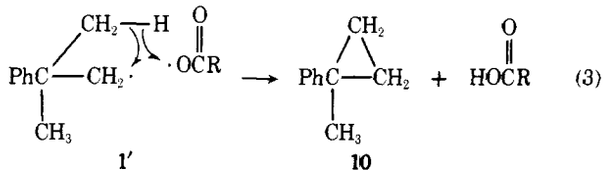
When the pyrolysis of **4a** was carried out in HCA, a CIDNP emission consisting of a multiplet centered at δ 0.67 was observed. Since this chemical shift is that expected for cyclopropyl protons, we first thought that this emission resulted from a structure such as **9** in which the spiro radical **3** is captured by benzoyloxy radical.



3′ 9

However, it was subsequently found that the *E* at δ 0.67 was identical with the multiplet for the cyclopropane protons in 1-methyl-1-phenylcyclopropane (**10**). Rickatson and Stevens[2c] have reported that **10** is produced when **4b** is decomposed in refluxing benzene. It is interesting that **10** is not reported when radical 1 is produced by other methods.[2a,b,d]

The most probable mechanism for the formation of **10** is via the radical disproportionation shown in eq 3. This process would produce **10** with the observed polarization of the cyclopropane protons. Polarization of either the phenyl or methyl protons in **10** is not observed nor is it expected, since there is little hyperfine splitting by these protons in radical 1.[3,5]



1′ 10

Conclusion

This CIDNP study of the decomposition of **4** has established that phenyl migration in the intermediate neophyl radical is not concerted with the loss of carbon dioxide. Furthermore, phenyl migration has been found to occur both within the cage and after diffusion of the neophyl radical from the cage. ESR studies have failed to produce evidence for a spiro radical intermediate in this rearrangement.[3,5-7] Likewise our search for this intermediate using the CIDNP technique has provided no evidence for its existence. Hence, we conclude that, if a spiro radical intermediate exists, it must live less than 10^{-10} s.

Experimental Section

Procedure for Obtaining CIDNP Spectra. All CIDNP spectra were obtained on a Varian A-60 NMR spectrometer. The appropriate peroxide, **4a** or **4b**, was weighed and dissolved in 0.4 mL of solvent, hexachloroacetone or *m*-dichlorobenzene, to give a 0.43 M solution. The probe of the spectrometer was heated to 105 °C and allowed to equilibrate, and the tube containing the solution of the peroxide was introduced. The CIDNP signals were observed while sweeping the field with a sweep time of 100 s. After completion of the reaction, a small amount of *o*-xylene was added to the solution as an internal standard. The positions of the CIDNP signals were obtained in ppm relative to the methyl signals in *o*-xylene at 105 °C. The identity of the signals was established by adding a small amount of each product to the hot solution and observing the growth of signal intensity. Al-

though NMR signals from **10** were not present at the conclusion of the reaction, addition of authentic **10** to the reaction mixture produced signals identical with the emissions assigned to **10.** In order to further confirm the identity of the products, the reaction mixtures were analyzed by gas chromatography on an 8-ft 3% SE-30 on 60/80 Supelcopert column. The GC analysis consisted of coinjection with known samples of **5, 6, 7,** and 8 and observing peak uniformity.

Benzoyl β-Phenylisovaleryl Peroxide (4a). Perbenzoic acid (108 mL, 54.3 mmol in chloroform) was placed in an ice-cooled 200-mL three-necked flask. β-Phenylisovaleryl chloride (10.7 g, 54.3 mmol) was then added all at once with stirring. A solution of 50 mL of methylene chloride and 4.4 mL of pyridine was added dropwise over a period of 1 h and the stirring continued for an additional hour. The reaction mixture was washed with four 50-mL portions of saturated sodium bicarbonate solution. The organic layer was dried over anhydrous sodium sulfate and the solvent removed on a rotary evaporator at room temperature. Upon cooling in a dry ice–acetone slush (−78 °C) and adding a small amount of petrolium ether, the oil crystallized. After repeated recrystallizations from methylene chloride–petroleum ether, then from petroleum ether, the pure peroxide was obtained, 6.5 g (40%): mp 65.5 °C; NMR (CCl_3D) δ 7.25–8.2 (m, 10 H, ArH), 2.86 (s, 2 H, CH_2), 1.6 (s, 6 H, CH_3); IR (CCl_3H cm^{-1} 3100–3010 (ArH), 2980 (CH_3), 1805, 1770 (C=O), 1060–1000 (COO).

β-Phenylisovaleryl Peroxide (4b). The symmetric peroxide was prepared according to the general procedure of Price and Krebs:[13] mp 42.5–43.8 °C, dec 75 °C; NMR (CCl_3D) δ 7.49 (s, 10, Ar–H), 2.72 (s, 4 H, CH_2), 1.5 (s, 12 H, CH_3); IR (CCl_3H) cm^{-1} 3030, 3060, 3090 (t, Ar–H), 1810, 1780 (C=O), 1055 (COO).

Reaction Products. The ester products of the peroxide decompositions (**7a, 7b, 8a,** and **8b**) were prepared by dissolving x mL of the alcohol in $3x$ mL of pyridine and adding $0.5x$ mL of the acid chloride. This solution was refluxed for 1 h, washed with 5% sodium carbonate, then with 1 N sulfuric acid, dried, and distilled through a small distillation apparatus with a Claison head.

2-Methyl-1-phenylprop-2-yl benzoate (8a): bp 105 °C (0.15 Torr); NMR (CCl_4) δ 7.08–8.14 (m, 10 H, ArH), 3.22 (s, 2 H, CH_2), 1.57 (s, 6 H, CH_3); IR (CCl_4) cm^{-1} 3040, 3070, 3090 (ArH), 2980 (CH_3), 1715 (C=O), 1115 (CO).

2-Methyl-2-phenylprop-1-yl benzoate (7a): bp 105 °C (0.15 Torr); NMR (CCl_4) δ 7.08–8.12 (m, 10 H, ArH), 4.35 (s, 2 H, CH_2), 1.42 (s, 6 H, CH_3); IR (CCl_4) cm^{-1} 3040, 3060, 3090 (ArH), 2970 (CH_3), 2930 (CH_2), 1740 (C=O), 1110 (CO).

2-Methyl-1-phenylprop-2-yl 3-methyl-3-phenylbutanoate (8b): bp 110 °C (0.15 Torr); NMR (CCl_4) δ 7.16–7.6 (m, 10 H, ArH), 2.91 (s, 2 H, CH_2), 2.52 (s, 2 H, CH_2), 1.46 (s, 6 H, CH_3), 1.24 (s, 6 H, CH_3); IR (CCl_4) cm^{-1} 3030, 3060, 3080 (ArH), 2970 (CH_3), 2930 (CH_2), 1720 (C=O(= {[[] (CO).

2-Methyl-2-phenylprop-1-yl 3-methyl-3-phenylbutanoate (7b): bp 110 °C (0.15 Torr); NMR (CCl_4) δ 7.26 (s, 10 H, ArH), 4.0 (s, 2 H, CH_2), 2.52 (s, 2 H, CH_2), 1.27 (s, 6 H, CH_3), 1.2 (s, 6 H, CH_3); IR (CCl_4) cm^{-1} 3020, 3060, 3080 (ArH), 1720 (C=O), 1110 (CO).

1-Chloro-2-methyl-2-phenylpropane (5) was prepared by the procedure of Whitmore, Weisgerber, and Shabica.[14]

2-Chloro-2-methyl-1-phenylpropane (6). This chloride was synthesized by refluxing 2-methyl-3-phenylpropan-2-ol with a molar excess of thionyl chloride. The thionyl chloride was removed by distillation under reduced pressure. The residue was washed with water, dried over sodium sulfate, and used without further purification: NMR (CCl_4) δ 7.25 (s, 5 H, ArHO), 3.01 (s, 2 H, CH_2), 1.5 (s, 6 H, CH_3); IR (CCl_4) cm^{-1} 3030, 3060, 3080 (ArH), 2970 (CH_3), 2920 (CH_2).

1-Methyl-1-phenylcyclopropane (15) was prepared by dechlorination of the adduct of dichlorocarbene with α-methylstyrene according to literature procedures.[15]

Acknowledgment. We express our appreciation to Professor James W. Wilt for an extremely helpful correspondence.

Registry No.—**4a,** 62698-29-7; **4b,** 62726-47-0; **5,** 515-40-2; **6,** 1754-74-1; **7a,** 19284-03-8; **7b,** 62698-30-0; **8a,** 16737-31-8; **8b,** 62698-31-1; perbenzoic acid, 93-59-4; β-phenylisovaleryl chloride, 4094-64-8; 2-phenyl-2-methylpropan-1-ol, 2173-69-5; benzoyl chloride, 98-88-4; 3-methyl-3-phenylbutanoyl chloride, 4094-64-8; 1-phenyl-2-methylpropan-2-ol, 100-86-7; thionyl chloride, 7719-09-7.

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