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John A. Horsley, Yves Jean, Carl Moser
Lionel Salem,* Richard M. Stevens, James S. Wright
Laboratoire de Chimie Théorique[21] *(490)*
and Centre Européen de Calculs Atomiques et Moléculaires
du Circe (506)
Université de Paris-Sud, Centre d'Orsay
91-Orsay, France

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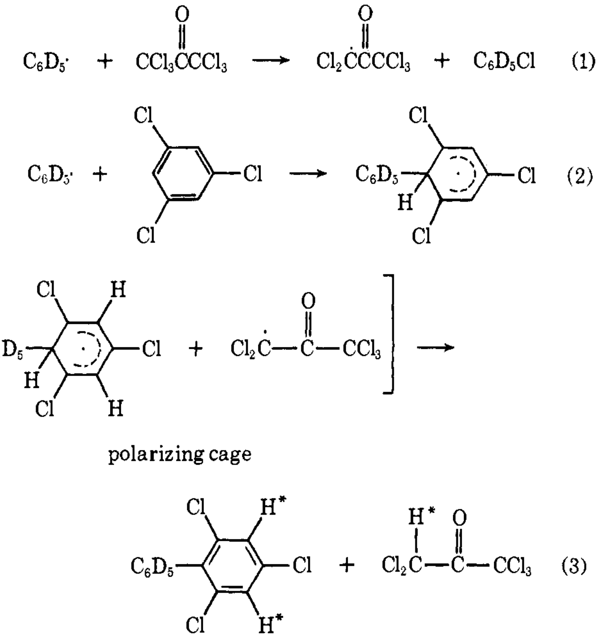
Chemically Induced Dynamic Nuclear Polarization Techniques in the Study of the Arylation Reaction. A Novel Demonstration of the Intermediacy of the Aryl Cyclohexadienyl Radical[1]

Sir:

The phenylcyclohexadienyl radical (PCD·) has been assumed to be the key intermediate in the extensively studied free-radical arylation of aromatic compounds.[2] While the presence of this radical had been inferred from chemical evidence we have been able to obtain physical evidence for it by the use of CIDNP techniques.[3] The CIDNP effect detects electron-nuclear spin interactions between unsymmetric radical pairs by a net polarization in the nmr spectrum of the resulting products.[4]

Phenyl radicals are most conveniently produced by the thermal or photochemical decomposition of benzoyl peroxide (BPO). Whatever the source, phenyl radicals will react with aromatic substrates by a complicated mechanism leading to arylated products.[2] In fact, it has been calculated that there are 100 significant steps in the decomposition of BPO in benzene.[5] In order to simplify the nmr spectra, perdeuterated BPO was used as the source of phenyl radicals, and 1,3,5-trisubstituted benzenes were used as the aromatic substrate. Thus, the reaction produced a single biphenyl containing only one kind of hydrogen. Furthermore, perchlorinated radicals were used as acceptors for any abstractable hydrogens which thereby appeared in a one-line spectrum. The perchlorinated radicals are formed by chlorine abstraction of excess radicals during the BPO decomposition. For example, see eq 1-3, where an asterisk denotes polarization.



The perchlorinated radicals also served the purpose of providing a radical with a different *g* value from that of the PCD·, a condition which must be met for net polarization.[4c,6] (Normally the predominant reactions are the coupling and disproportionation of two PCD· radicals.[2f])

We observed polarized nmr spectra from both products of reaction 3, the biphenyl and the pentachloroacetone, the polarized hydrogens being those of the PCD·. Similarly, an emission spectrum of pentachloroethane or chloroform was observed when hexachloroethane or carbon tetrachloride[7] was the chloro substrate. Among the aromatic compounds which were used successfully as hydrogen sources to produce these one-line nmr spectra were benzene, toluene, xylene, mesitylene, chlorobenzene, 1,3,5-trichlorobenzene, diphenylmethane, and naphthalene. The corresponding biphenyl polarization, however, an enhanced absorption, is easily obscured by the solvent spectrum and was only observed in the substrates mesitylene and 1,3,5-trichlorobenzene. These 1,3,5-substituted benzenes also provide more favorable conditions for biphenyl formation since coupling of their PCD radicals is sterically inhibited. For a typical run see Figure 1. The observed polarization may be analyzed on the basis of a simple formulation used to predict the sign of nmr enhancement.[8] Then the emission spectrum of the pentachloroacetone (chloroform or pentachloroethane) is consistent with hydrogen abstracted from the PCD· within the polarizing cage. The perchlorinated radicals are expected to have a higher *g* value than any

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[1] Presented in part at the 159th National Meeting of the American Chemical Society, Houston, Tex., Feb 1970, Abstract No. ORGN-42. For Part I, see S. R. Fahrenholtz and A. M. Trozzolo, *J. Amer. Chem. Soc.*, **93**, 251 (1971).

[2] Most of the important references are included in the following: (a) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp 474–491; (b) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, Elmsford, N. Y., 1960; (c) M. Eberhardt and E. L. Eliel, *J. Org. Chem.*, **27**, 2289 (1962); (d) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, pp 91–99, 251–263; (e) D. H. Hey, K. S. Y. Kiang, M. V. Perkins, and G. H. Williams, *J. Chem. Soc.*, 1153 (1967); (f) D. F. DeTar, R. A. V. Long, J. Rendleman, J. Bradley, and P. Duncan, *J. Amer. Chem. Soc.*, **89**, 4051 (1967); (g) J. Saltiel and H. C. Curtis, *ibid.*, **93**, 2056 (1971).

[3] (a) The presence of a cyclohexadienyl radical in the decomposition of BPO in C_6H_6 has been confirmed by recent esr evidence: J. H. Marshall, private communication. (b) The low-temperature γ radiolysis of biphenyl gives an isomer of PCD·: C. Chachaty, *J. Chim. Phys. Physicochim. Biol.*, **64**, 614 (1967). (c) The perfluorinated benzoyloxycyclohexadienyl radical has recently been observed by CIDNP: J. Bargon, *J. Amer. Chem. Soc.*, **93**, 4630 (1971).

[4] (a) R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195 214 (1969); (b) G. L. Closs, *J. Amer. Chem. Soc.*, **91**, 4552 (1969); (c) G. L. Closs and A. D. Trifunac, *ibid.*, **92**, 2183, 7227 (1970); (d) H. Fischer, *Chem. Phys. Lett.*, **4**, 611 (1970); (e) H. R. Ward, *Accounts Chem. Res.*, **5**, 24 (1972); R. G. Lawler, *ibid.*, **5**, 32 (1972).

[5] D. F. DeTar, *J. Amer. Chem. Soc.*, **89**, 4058 (1967).

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[7] Photochemical decomposition was used when low boiling solvents were present. We are indebted to Dr. A. A. Lamola for suggesting and installing a magnet external to the nmr apparatus. The irradiations took place in this field as in M. Lehnig and H. Fischer, *Z. Naturforsch. A*, **24**, 1771 (1969).

[8] R. Kaptein, *Chem. Commun.*, 732 (1971).

corresponding PCD· in the radical pair.[6,9] Since the hyperfine coupling constant of the allylic hydrogens in the unsubstituted cyclohexadienyl radical has a large positive value (+47.7 G),[10a] we expect the corresponding PCD· coupling constant to be positive also. Applying the rules[8] for a "disproportionation reaction" between independently generated radicals as in eq 3 with a negative Δg and a positive hyperfine coupling, an emission line is predicted for the pentachloroacetone (pentachloroethane or chloroform) as we observe. The 3,5-hydrogens of the *biphenyl*, however, appear in enhanced absorption in the nmr spectrum. This cannot be compared with prediction as the absolute value of the hyperfine coupling constant in that position of the best available model, the cyclohexadienyl radical, is too small to presume that the sign of the highly substituted radicals is the same.[10a] The calculations of hyperfine coupling constants also require considerable approximations.[10b]

In toluene, xylene, mesitylene, and diphenylmethane direct abstraction of the benzylic protons by the pentachloroacetonyl radical competes with phenyl addition to the aromatic ring. Such a chain-transfer process does not contribute to polarization;[4] it merely lessens the emission from the pentachloroacetone, formed by reaction 3. Indeed, the pentachloroacetone produced from a hexamethylbenzene substrate is not polarized since by far the major process there is not arylation but direct abstraction. We obtained additional experimental evidence that hydrogen is not polarized in a chain-transfer step, from the earlier studied BPO–cyclohexanone system.[11] We decomposed 5% solutions of BPO-d_{10}[12] or BPO-f_{10}[12] in cyclohexanone under conditions in which even a 1% solution of BPO-h_{10} gave a large benzene emission signal. No polarization was observed in the abstraction products. Therefore, polarization was not induced when only a single radical was involved. The perchloro *and* the PCD· radical are both required in the polarizing step.

So far we have discussed the polarization of the protons on the cyclohexadienyl ring of the PCD·, as produced from the reaction of BPO-d_{10} with hydrogen-containing aromatic compounds. When BPO-h_{10} is decomposed in benzene-d_6, the PCD· is deuterated in the radical-containing ring and polarized biphenyl is not expected. Nevertheless, an nmr emission spectrum corresponding to the ortho protons of biphenyl is observed[13] particularly in the absence of perchloro compounds. This polarization must be due to phenyl radicals which have escaped the initial polarizing cage and retained some polarization throughout the arylation reaction. In the same spectrum a large enhanced absorption nmr signal from phenyl benzoate is observed from the in-cage combination of benzoyloxy and phenyl radicals. Addition of only 5% perchloroalkane reduced the enhanced absorption to the much smaller peak usually observed for phenyl benzoate in aliphatic solvents.[14] We assume that this is due to solvent interference in the geminate recombination reaction.[15]

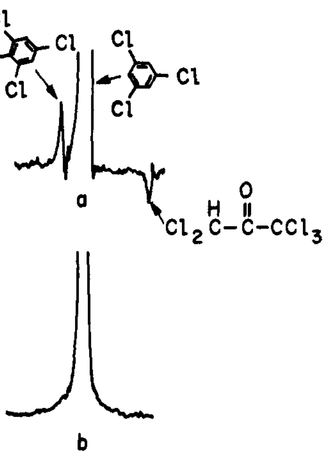
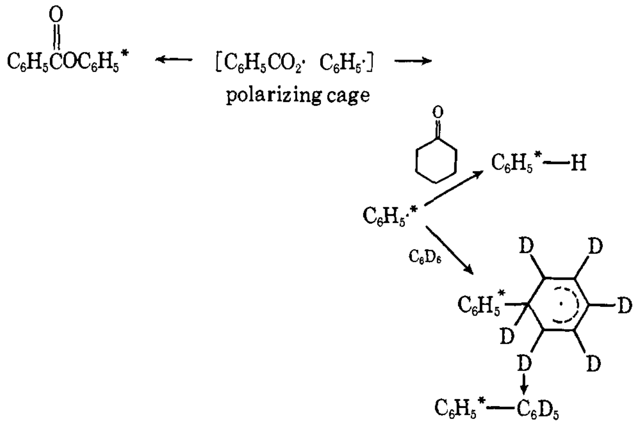


Figure 1. Nmr spectra of a BPO-d_{10}–1,3,5-trichlorobenzene–hexachloroacetone solution (molar ratio, 0.1:1:1): (a) after 3 min at 127° in nmr probe; (b) after 10 min at 127° in nmr probe.



By using selectively substituted (Cl, D, or alkyl) reactants, we have been able to detect three kinds of protons of the PCD· intermediate by CIDNP. The role of the PCD· radical in the arylation reaction is thus demonstrated by a physical technique.

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Susan R. Fahrenholtz,* Anthony M. Trozzolo*
Bell Laboratories
Murray Hill, New Jersey 07974

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Quantum Yields of Silver Ion Reduction on Titanium Dioxide and Zinc Oxide Single Crystals

Sir:

Photochemical electron transfer reactions at the surfaces of solids in contact with metal ion solutions have been the subject of numerous investigations.[1-4]

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