# Communications

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## CIDNP Evidence for Radical Pair Mechanism in Photo-Fries Rearrangement

*Summary:* Photolysis of *p*-cresyl *p*-chlorobenzoate (**1**) affords *p'*-chlorobenzoyl-*p*-cresol (**2**) as the major and *p*-cresol (**3**) as the minor product *via* aryloxy–aroyl radical pair intermediates **4**, derived from singlet excited state precursors **1***.

*Sir:* CIDNP (chemically induced dynamic nuclear polarization) is a powerful diagnostic tool for radical cage reaction,[1] and we wish to communicate our CIDNP evidence for a radical pair mechanism of the photo-Fries rearrangement. A recent review on this reaction[2] reveals still numerous mechanistic uncertainties in regard to whether a concerted or stepwise process is involved and whether the rearrangement products are derived from singlet or triplet precursors, although, quite recently, flash photolysis[3] and gas phase photolysis[4] have demonstrated the involvement of free radicals in the rearrangement of aryl esters. For our model study we selected *p*-cresyl *p*-chlorobenzoate (**1**), a choice dictated by practical considerations for CIDNP detection. Thus, the *p*-cresyl and *p*-chlorobenzoyl moieties would assure rapid conversion, minimal overlap of the aromatic protons, relatively simple nmr spectra, and only ortho rearrangement product, and the *p*-methyl substituent would serve as an effective polarization probe.

Irradiation of a 0.1 *M* $CH_2Cl_2$ solution of ester **1** in a quartz tube directly in the Varian HA-100D nmr spectrometer with an unfiltered 1000-W mercury arc produced the spectra (sets A, B, and C) in Figure 1. It is evident that the ortho protons of the *p*-cresyl moiety in ester **1** (compare top and center spectra in set A) and in the phenol **2** (compare bottom and center spectra in A) exhibit enhanced absorption, while the ortho protons in phenol **3** (compare spectra in set B) and the *p*-methyl protons in ester **1** (compare top and center spectra in set C) and in phenol **2** (compare bottom and center spectra in set C) display emission. To pronounce the observed CIDNP effects in the starting material, in the top spectra of sets A and C, which refer, respectively, to the ortho protons and the *p*-methyl protons of the *p*-cresyl moiety of **1**, we show as well signal intensities during (broken line) and after (solid line) irradiation. Unfortunately, on careful comparison of the resonances of the *p*-methyl protons with those of authentic products, it was found that in $CH_2Cl_2$ the $\delta$ 2.34 ppm emission (center spectrum in set C) corresponds to superimposed polarizations of the *p*-methyl protons of phenols **2** and **3** (bottom spectrum in set C). For this reason we examined the photolysis of ester **1** in benzene (0.02 *M*) since now the *p*-methyl proton resonances of **1**, **2**, and **3** are all sufficiently separated to permit individual detection (set D). Now the *p*-methyl protons of ester **1** show clearly emission at $\delta$ 2.03 ppm (compare top and center spectra in set D), of phenol **2** strong emission at 1.88, and of phenol **3** weak enhanced absorption at 2.05 (compare center and bottom spectra in set D).[5] None of these CIDNP effects could be observed when authentic products were irradiated under similar photolysis conditions as controls.[6] These CIDNP results of the photorearrangement of ester **1** in $CH_2Cl_2$ and $C_6H_6$ are summarized in Table I. The same polarization signs were also observed in $CCl_4$, $CH_3OCH_2CH_2OCH_3$, and $CH_3OH$, although the proportion of products varied in these solvents.

Table I

Photo-CIDNP of *p*-Cresyl *p*-Chlorobenzoate (**1**)

| | | $CH_2Cl_2$[b] | | $C_6H_6$[c] | |
|---|---|---|---|---|---|
| Products | Type of protons[a] | $\delta \times 10^6$ [d] | $\Gamma$[e] | $\delta \times 10^6$ [d] | $\Gamma$[e] |
| Ester **1** | *p*-Methyl | 2.46 | E | 2.03 | E |
| | *o*-Cresyl | 7.12 | A | | *f* |
| | | 7.20 | | | |
| Phenol **2** | *p*-Methyl | 2.34 | E | 1.88 | E |
| | *o*-Cresyl | 7.01 | A | | *f* |
| | | 7.05 | | | |
| | | 7.10 | | | |
| Phenol **3** | *p*-Methyl | 2.34 | *g* | 2.05 | A |
| | *o*-Cresyl | 6.74 | E | | *f* |
| | | 6.83 | | | |

[a] Assignments were made by comparison of product resonances with authentic samples. [b] Sets A, B, and C in Figure 1. [c] Set D in Figure 1. [d] Relative to TMS and within ±0.01 ppm. [e] Owing to extensive overlapping of the aromatic protons of **1**, **2**, and **3** it was not possible to diagnose a multiplet effect. [f] Aromatic protons are masked by benzene. [g] Obscured because of superposition with *p*-methyl of phenol **2**.

With the help of Kaptein's formula for net polarization[7] and the esr parameters for the related phenoxy and benzoyl radicals,[8] we find perfect agreement between the observed (Table I) and the predicted CIDNP effects if we assume that $\mu < 0$ (singlet precursor) and $\epsilon > 0$ (cage products) for ester **1** and phenol **2** and $\epsilon < 0$ (escape product) for phenol **3**. Thus, our CIDNP data support the radical pair mechanism suggested for the photo-Fries rearrangement.[3,4] However, as shown in Scheme I, photoactivation of ester **1** leads first to the singlet excited state **1*** which subsequently suffers principally carbon–oxygen bond rupture into

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[1] H. Fischer, *Top. Curr. Chem.*, **24**, 1 (1971); G. L. Closs, *Spec. Lect. Int. Congr. Pure Appl. Chem.*, *28th*, **4**, 19 (1971); H. Ward, *Accounts Chem. Res.*, **5**, 18 (1972).

[2] D. Bellus, *Advan. Photochem.*, **8**, 109 (1971).

[3] C. E. Kalmus and D. M. Hercules, *Tetrahedron Lett.*, 1575 (1972).

[4] J. W. Meyer and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 2219 (1972).

[5] It was not possible to record the polarizations of the aromatic protons since $C_6H_6$ masked this region. Even $C_6D_6$ was not suitable since the aromatic protons of **1**, **2**, and **3** overlapped still more severely than in $CH_2Cl_2$.

[6] H. D. Becker, *J. Org. Chem.*, **32**, 2140 (1967).

[7] R. Kaptein, *J. Chem. Soc., Chem. Commun.*, 732 (1971).

[8] K. Scheffler and H. B. Stegmann, "Elektronenspinresonanz," Springer Verlag, Berlin, Germany, 1970: $g\,(\mathrm{PhO}\cdot) = 2.0047$, $a(p\text{-Me}) = +11.95\ G$ and $a(\text{ortho H}) = -6.0\ G$. H. Paul, University of Zürich, personal communication: $g(\mathrm{PhCO}\cdot) = 2.0006$, $a(\text{ortho H}) \cong 0$ and $a(\text{meta H}) \cong +1.2\ G$. In view of the small hyperfine coupling constants of the aromatic protons and overlapping resonances it was difficult to trace the *p*-chlorobenzoyl radical by CIDNP.

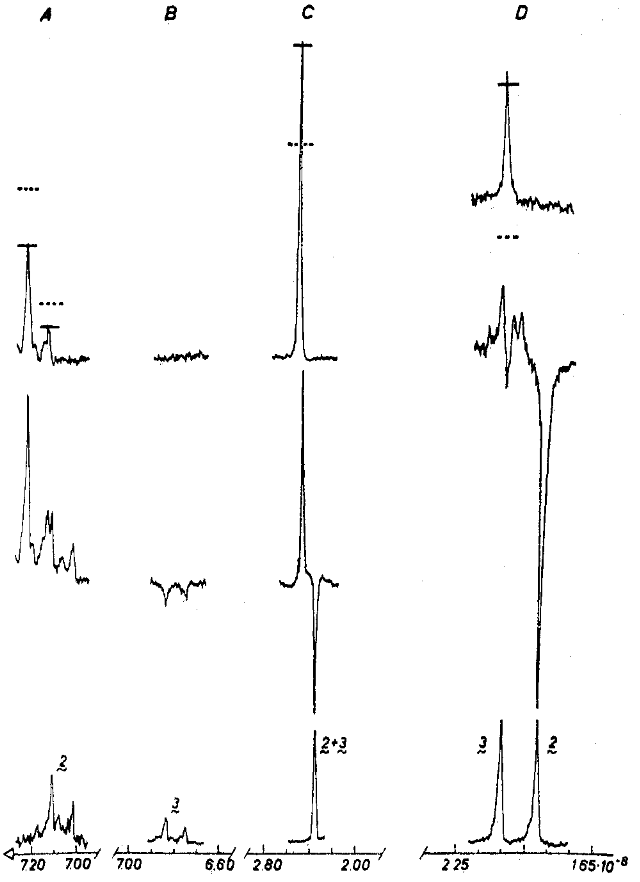
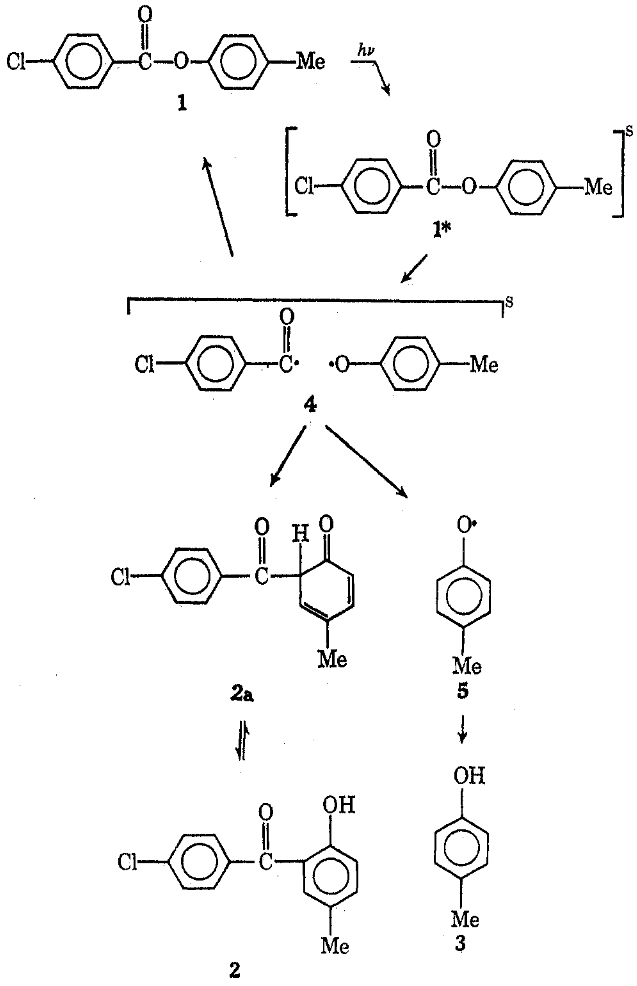


Figure 1.—CIDNP during photolysis of *p*-cresyl *p*-chlorobenzoate (1). Sets A, B, and C are in $CH_2Cl_2$, set D in $C_6H_6$. Bars in the top spectra of sets A, C, and D refer to signal intensities of the polarizations in ester 1 during (broken) and after (solid) irradiation. The reference numbers in the bottom spectra of sets A, B, C, and D refer to the proton resonances of authentic *p*′-chlorobenzoyl-*p*-cresol (2) and *p*-cresol (3) products relative to TMS.

SCHEME I



the aroyl–aryloxy radical pair **4** prior to intersystem crossing. Cage combination results in ester **1** or phenol **2** *via* its **2a** tautomer, the latter having a lifetime ($t$) considerably shorter than the relaxation times ($T_1$) of its polarized protons, *i.e.*, $t \ll T_1$. Some aryloxy radicals **5** escape the cage and on hydrogen abstraction give phenol **3**.

It is unlikely that a concerted pathway[2] is of major importance in the photo-Fries rearrangement of *p*-cresyl *p*-chlorobenzoate (**1**), at least in the solvents used here. For example, measurement[9] of the enhancement factor ($V_{exp}$) for the *p*-methyl polarization of the rearrangement product **2** gave $V_{exp} = -243 \pm 13$. With the help of Adrian's high field CIDNP treatment,[10] employing a one-proton model and making reasonable assumptions about the time between diffusive pair displacements ($10^{-12} \leq \tau \leq 10^{-11}$ sec),[9] the calculated enhancement factor ($V_{calcd}$) for the formation of **2** entirely from radical pair **4** *via* a singlet reaction is $V_{calcd} = 200 \pm 50$. We anticipate that analogous radical pair mechanisms obtain quite generally for the related photorearrangements of aryl ethers[11] and amides.[12]

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[9] M. Lehnig and H. Fischer, *Z. Naturforsch.*, **27a**, 1300 (1972).

[10] F. J. Adrian, *J. Chem. Phys.*, **75**, 3410 (1971).

[11] F. A. Carroll and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 7152 (1972).

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## A Stereoselective Trans-Trisubstituted Olefin Synthesis *via* Rearrangement of Allylic Sulfonium Ylides

*Summary:* The [2,3]-sigmatropic rearrangement of α-substituted methallylsulfonium ylides results in a stereoselective formation of trans-trisubstituted olefins.

*Sir:* The need for stereoselective methods for olefin synthesis continues as demonstrated by several recent