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Photo-Fries Rearrangements of Phenyl Phenylacylates in Polyethylene Films. Comparison of Reactivity and Selectivity with 1-Naphthyl Phenylacylates

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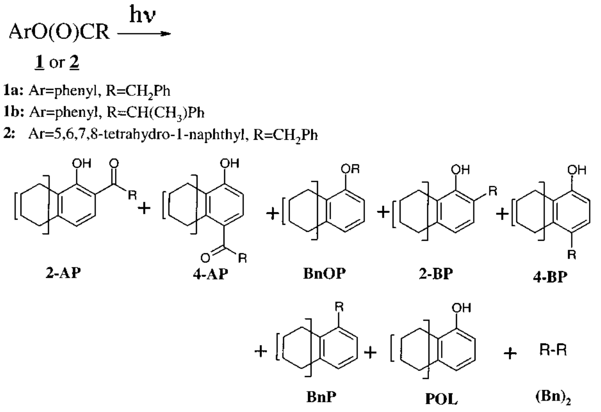
The fates and kinetics of recombination of singlet radical pairs generated by photolyses of three phenyl phenylacylates have been examined in unstretched and stretched polyethylene films. Comparisons with results from photolyses of analogous 1-naphthyl phenylacylates in the same media lead to the conclusions that (1) phenoxy is less reactive overall than 1-naphthoxy toward a common phenylacyl radical but (2) the constrained cages in which the radical pairs reside exert greater control over the movements of the 1-naphthoxy/phenylacyl pairs. The reasons for these observations are discussed in the context of the shapes and van der Waals volumes of the radical pairs, the void volumes of sites in native polyethylene films, and the electronic properties of the aryloxy radicals.

Introduction

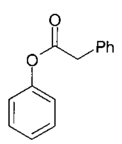
Investigations of the factors influencing the selectivity and kinetics[1] of radical-pair recombination processes in cages provided by polymeric media have led to several interesting discoveries, as well as many questions. Our approach to answering these questions has involved studies of the photo-Fries rearrangements of 1- and 2-naphthyl esters[2−4] and photo-Claisen rearrangements of aryl benzyl ethers[5] in polyethylene (**PE**) and other polyolefinic media.[3,6] The difference between the size and shape of the intermediate phenylacyl radicals (from lysis of the esters) and benzylic radicals (from lysis of the ethers or decarbonylation of the initially formed phenylacyl moieties upon irradiation of the esters) has been found to influence the selectivity and kinetics of their addition to aryloxy partners in the confines of **PE** cages.[5] In addition, the large van der Waals volumes of the reactant esters and ethers (with respect to the mean hole free volumes of the polyethylene media) and slow rates of relaxation of reaction cavity walls (with respect to the rates of in-cage radical-pair recombinations) suggest that product formation is mediated by "templating" effects, also.[3]

Despite these efforts, several important mechanistic questions remain unanswered. Among them is, "*Are rates and modes of recombinations dictated principally by the manner in which a singlet radical-pair interacts with its cage or with itself?*" Here, we address this question by comparing the photo-Fries reactions of some phenyl phenylacylates (**1**) and 5,6,7,8-tetrahydro-1-naphthyl phenylacetate (**2**) with those from analogous 1-naphthyl phenylacylates in **PE** films (eq 1).[1] The van der Waals size and volume of the highly substituted phenyl ester **2** are near those of the corresponding 1-naphthyl ester, 1-naphthyl phenylacetate (**3a**). Our previously developed radical-clock method for measuring the rates of in-cage radical recombinations[1] has been employed in the analyses. From these results, it is possible to determine whether the size (and shape) or reactivity of an aryloxy radical has the greater influence on the kinetics of photoproduct formation during recombination with its acyl partner in a constrained environment.

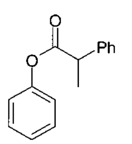


1a: Ar=phenyl, R=CH_2Ph
1b: Ar=phenyl, R=$CH(CH_3)Ph$
2: Ar=5,6,7,8-tetrahydro-1-naphthyl, R=CH_2Ph

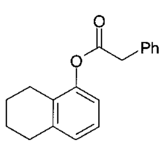
(1)



1a



1b



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Results

General Description of Reaction Pathways of 1 and 2. Photo-Fries rearrangements of phenyl esters

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10.1021/jo001455+ CCC: $20.00

Scheme 1

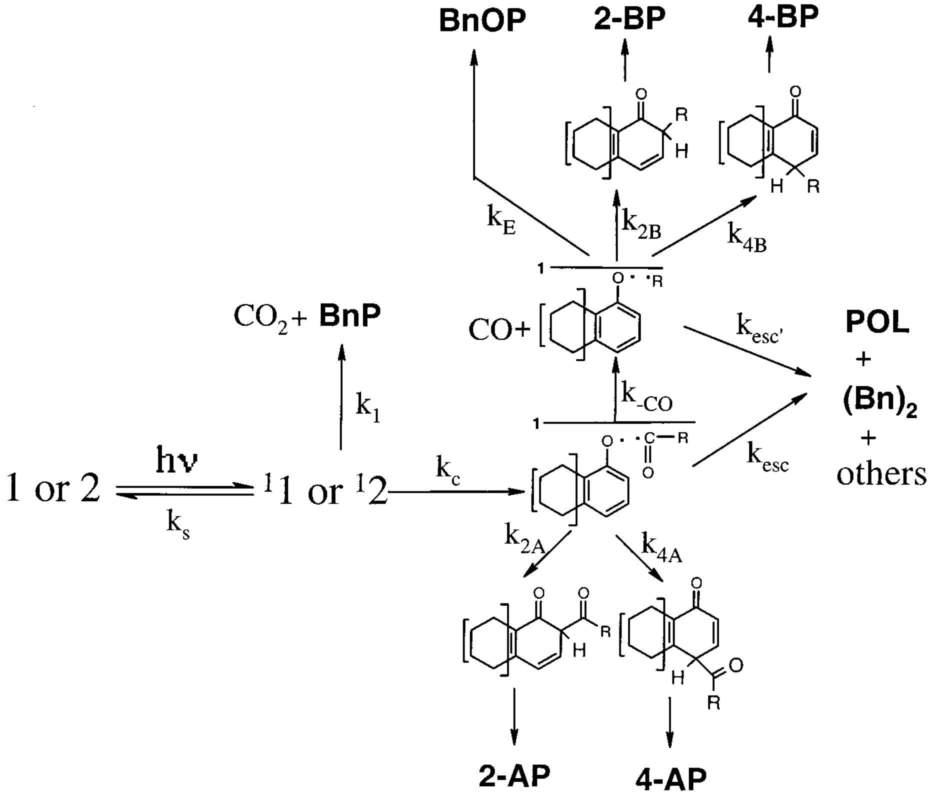

Table 1. Relative Photoproduct Yields (%) from Irradiations of 2 mM 1 and 2 to ≤ 20% Conversions in N_2-Saturated Solutions at 22 °C

ester	solvent	2-AP	4-AP	2-BP	4-BP	BnOP	BnP	POL	Sol-Bn[d]	$(Bn)_2$
1a[a]	hexane	35.2 ± 0.6	12.8 ± 1.2	1.6 ± 0.1	1.0 ± 0.1	6.0 ± 0.2	0.8 ± 0.1	19.8 ± 0.2	2.7 ± 0.3	14.3 ± 0.4
	cyclohexane	41.9 ± 1.1	11.7 ± 0.5	1.2 ± 0.1	0.4 ± 0.1	5.0 ± 0.2	1.7 ± 0.1	17.3 ± 0.9	2.6 ± 0.1	10.9 ± 0.4
1b	hexane	37.2 ± 0.2	22.0 ± 1.8	0.8 ± 0.3	1.3 ± 0.4	10.6 ± 0.5	0.6 ± 0.2	10.1 ± 1.4	2.0 ± 0.4	15.4 ± 0.5
2[b]	hexane	42.9 ± 0.5	*c*	7.1 ± 0.1	*c*	5.4 ± 0.1	3.0 ± 0.1	21.5 ± 0.4	3.9 ± 0.1	7.9 ± 0.1
	cyclohexane	55.2 ± 0.4	*c*	5.2 ± 1.7	*c*	4.0 ± 0.3	4.1 ± 0.8	14.8 ± 1.0	3.4 ± 1.5	5.9 ± 0.5

[a] There were 3 unidentified peaks in each solvent, accounting for 5.8% (hexane) and 7.2% (cyclohexane) of the total product yields. [b] The yields for the two unidentified products: **u-1**, 3.9% in hexane and 3.2% in cyclohexane. **u-2**, 4.4% in hexane and 4.2% in cyclohexane. [c] <0.1%.

proceed via homolytic bond scission predominantly from excited singlet states[7,8] to form geminate radical pairs.[9] Photoreactions of phenyl phenylacetate (**1a**) have been studied by Tung et al. in isotropic organic and aqueous cyclodextrin solutions, on silica surfaces, and in zeolites.[9] The reactive pathways for **1** and **2** (eq 1; Scheme 1) are analogous to those for 1-naphthyl acylates.[1] k_{2A} and k_{4A}, the rate constants for singlet radical-pair recombination leading to keto precursors of the Fries rearrangement products, can be calculated using eqs 2 and 3, provided two conditions are met:[1]

(1) Fries products are formed in-cage (i.e., within the original cavity where ester lysis occurred). This requires that radicals that escape their initial cage be scavenged efficiently.[1]

(2) The values of k_{-CO}, the decarbonylation rate constants from phenylacyl radicals, are the same in the polyethylenes as in isooctane. This assertion is supported by the known insensitivity of k_{-CO} to viscosity.[10] At 22 °C in isooctane, k_{-CO} is 4.8×10^6 s^{-1} for phenylacetyl (from **1a**) and 4.0×10^7 s^{-1} for 2-phenylpropanoyl (from **1b**).[11]

The rate constants calculated in this way do not depend on the extent to which the radical pairs recombine to yield their original esters.

$$k_{2A} = k_{-CO}[\textbf{2-AP}]/\{[\textbf{2-BP}] + [\textbf{4-BP}] + [\textbf{BnOP}]\} \quad (2)$$

$$k_{4A} = k_{-CO}[\textbf{4-AP}]/\{[\textbf{2-BP}] + [\textbf{4-BP}] + [\textbf{BnOP}]\} \quad (3)$$

Irradiations in Isotropic Solutions (Table 1). The photoproduct ratios from irradiations of **1** in alkanes at 22°C, **[2-AP]/[4-AP]**, are between 1.7 and 3.6. There are also significant amounts of cage-escape products, **POL** and $\mathbf{(Bn)_2}$, and a small amount of decarboxylation product (**BnP**).[12] The presence of $\mathbf{(Bn)_2}$ indicates that a large fraction of the decarbonylation products, **2-BP**,

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Table 2. Relative Photoproduct Yields (%) from Irradiations of 3−7 mmol/kg of 1a and 1b to < 30% Conversions in Unstretched (u) and Stretched (s) PE Films under N$_2$ Atmospheres at 22 °C

ester	film	2-AP	4-AP	2-BP	4-BP	BnOP	BnP	POL	(Bn)$_2$
1a	**NDLDPE** (u)	63.0 ± 2.7	29.1 ± 3.0	2.3 ± 0.1	0.7 ± 0.2	1.4 ± 0.1	<0.1	3.2 ± 0.1	0.3 ± 0.2
	NDLDPE (u)[a]	63.3 ± 0.3	29.2 ± 0.2	2.2 ± 0.1	0.6 ± 0.1	1.4 ± 0.1	<0.1	3.1 ± 0.2	<0.1
	NDLDPE (s)	66.8 ± 0.5	24.1 ± 0.3	3.9 ± 0.1	1.5 ± 0.3	2.0 ± 0.1	1.7 ± 0.2	<0.1	<0.1
	BHDPE (u)	60.6 ± 0.1	34.9 ± 0.1	2.0 ± 0.2	1.4 ± 0.1	1.1 ± 0.1	<0.1	<0.1	<0.1
	BHDPE (s)	59.2 ± 0.9	32.1 ± 1.1	2.6 ± 0.1	2.4 ± 0.1	1.3 ± 0.1	2.4 ± 0.2	<0.1	<0.1
1b	**BHDPE** (u)	59.7 ± 0.4	25.1 ± 0.6	2.3 ± 0.3	2.6 ± 0.2	3.6 ± 0.5	1.2 ± 0.7	2.2 ± 1.2	0.7 ± 0.1[b]
	BHDPE (s)	50.0 ± 0.6	19.7 ± 1.3	3.4 ± 0.3	2.2 ± 0.2	4.6 ± 0.2	4.6 ± 0.2	5.5 ± 2.8	4.1 ± 0.1[d]
	BHDPE (u)[c]	58.5 ± 0.4	27.8 ± 3.8	1.6 ± 0.6	2.3 ± 0.1	3.2 ± 0.3	1.9 ± 0.8	2.2 ± 1.4	1.1 ± 0.5[d]

[a] Concentration of **1a** in unstretched **NDLDPE** was ca. 0.1 mmol/kg. [b] 0.7% unidentified products were formed whose molecular weight was the same as **(Bn)$_2$** from GC/MS analyses. [c] At 5 °C. [d] The yields correspond to an unidentified product whose molecular weight was the same as **(Bn)$_2$** from GC/MS analyses.

Table 3. Relative Photoproduct Yields (%) from Irradiations of 3−7 mmol/kg of 2 to < 30% Conversions in Unstretched (u) and Stretched (s) PE Films under N$_2$ Atmospheres at 22 °C

film	2-AP	2-BP	u-1[a]	BnOP	u-2[a]	BnP	POL
NDLDPE (u)	78.1 ± 1.2	4.4 ± 0.4	1.3 ± 0.1	3.5 ± 0.4	2.8 ± 0.2	3.2 ± 0.6	6.7 ± 1.3
NDLDPE (s)	74.3 ± 1.9	4.7 ± 0.2	1.2 ± 0.1	3.7 ± 0.2	2.8 ± 0.2	7.8 ± 1.2	5.5 ± 0.4
BHDPE (u)	72.3 ± 0.7	4.3 ± 0.2	1.1 ± 0.1	3.7 ± 0.2	3.1 ± 0.1	5.6 ± 0.3	9.9 ± 1.2
BHDPE (s)	67.2 ± 4.3	5.8 ± 0.1	2.1 ± 0.4	4.2 ± 0.6	2.1 ± 0.2	8.3 ± 1.2	10.3 ± 2.2

[a] **u-1** (MW 238) and **u-2** (MW 266); see text.

4-BP, and **BnOP**, is also from out-of-cage radical recombinations.[1] Benzylic groups attached to solvent molecules (**Sol-Bn**) also were detected[13] despite their formation from benzyl or phenoxy, the expected radicals, and a solvent molecule being endothermic: the homolytic dissociation energies of PhO−H, PhCH$_2$−H, and a secondary C−H bond in alkanes are 88 ± 5 kcal/mol,[14] 83 ± 1 kcal/mol,[15] and 95 ± 1 kcal/mol,[15] respectively; abstraction of H• by benzyl or phenoxy is not favored energetically.

Photoproduct distributions from irradiations of **2** were somewhat similar to those from **1**. Large amounts of cage-escape products, **POL** and **(Bn)$_2$**, and small amounts of **BnP** and **Sol-Bn** were formed. However, the 4-position rearrangement products, **4-BP** and **4-AP**, were absent.[16] GC/MS analyses indicate that two unidentified products are a decarbonylated species like **BnON** (**u-1**) and an isomer of **2c** (**u-2**).[17]

Irradiations in PE Films. The [**2-AP**]/[**4-AP**] product ratios from phenyl esters **1** in unstretched or stretched **PE** films, ca. 2−3 (Table 2), are similar to those in hexane (vide ante). No cross-coupling product, **(Bn)$_2$**, was detected upon irradiations of **1a** except at 3−7 mmol/kg in unstretched **NDLDPE**. Small, but perceptible, concentrations of **(Bn)$_2$** were present upon irradiations of **1b** in unstretched and stretched **BHDPE** at 22 or 5 °C. Decarboxylation products from both **1a** and **1b** increased upon film stretching. Decarboxylation is known to emanate from excited singlet states,[18] to be conformationally controlled, and to increase upon film stretching as a result of an increase in the mole fraction of appropriate conformers.[12]

Irradiation of **2** in **PE** films (Table 3) led to no **(Bn)$_2$**, or, as in isotropic solutions, **4-AP** or **4-BP**. **u-1** and **u-2** were also detected, and film stretching increased the yield of **BnP**.

Rate Constants, k_{2A} and k_{4A}, from Reactions of 1 and 2 in PE Films. The absence of **(Bn)$_2$** is our indicator that the Fries recombination products are formed completely in-cage and that rate constants for the formation of the keto precursors in Scheme 1 can be calculated from eqs 2 and 3. Because **(Bn)$_2$** was present, no rate constants for in-cage recombination reactions of **1b** radical pairs in **BHDPE** are reported. In calculations of k_{2A} from irradiations of **2**, **u-1** was considered to be a decarbonylation product and its concentration was one of the terms in the denominator of eq 2. The calculated rate constants from **1a** and **2**, together with rate constants from rearrangements of 1-naphthyl phenylacetate (**3a**) and 1-naphthyl 2-phenylpropanoate (**3b**)[1] for comparison purposes, are collected in Table 4.

Discussion

Photo-Fries rearrangement products are formed from in-cage radical-pair recombinations.[1,19] The Fries rearrangement product ratios from irradiations of **1** in

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(13) **Sol-Bn** was benzylcyclohexane (from **1a** or **2** in cyclohexane); **Sol-Bn** consisted of two isomeric benzyl-hexane isomers (from **1a** or **2** in hexane) or three isomeric benzylic-hexane isomers (from **1b** in hexane). The suggested structures of **Sol-Bn** are based upon molecular weight and fragmentation pattern of the peaks during GC-MS analyses only. Confirmation by comparison with authentic compounds was not possible.

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(16) Assignments are based on the assumption that GC retention times of **4-AP** and **4-BP** from **2** and 1-naphthyl phenylacetate should be similar. No peaks (<0.1%) at retention times near those expected of 4-position products of **2** were detected.

(17) The molecular massesof **u-1** and **u-2** are 238 and 266, respectively. The MS fragmentation pattern of **u-1** is almost the same as that of **BnON**. Their GC retention times differ from those of authentic benzyl 5,6,7,8-tetrahydro-2-naphthyl ether or 5,6,7,8-tetrahydro-2-naphthyl phenylacetate. **5,6,7,8-Tetrahydro-2-naphthyl phenylacetate**, a colorless oil (> 99% by GC), was synthesized in 85% yield from 5,6,7,8-tetrahydro-2-naphthol (Aldrich, 98%) by a similar procedure to that employed for 5,6,7,8-tetrahydro-1-naphthyl phenylacetate except that **DCC** was used instead of **DICI**. IR (neat): 3031, 3062 (w, aromatic), 1752 cm^{-1} (s, C=O). ^{1}H NMR (CDCl$_3$/TMS, 300 MHz): 6.75−7.40 (m, 8H, aromatic), 3.84 (s, 2H, C(O)CH_2Ph), 2.73 (m, 4H, −CH_2CH$_2$CH$_2$$CH_2$−), 1.77 ppm (m, 4H, aliphatic −CH$_2$$CH_2CH_2CH_2$−). Mass *m*/*z* calculated for C$_{18}$H$_{18}$O$_2$ 266, found 266. **5,6,7,8-Tetrahydro-2-naphthyl benzyl ether**, a colorless oil (>99% by GC), was synthesized by a procedure analogous to that for 5,6,7,8-tetrahydro-1-naphthyl benzyl ether in 80% yield. IR (neat): 3033, 3062 (w, aromatic), 1026 and 1259 cm^{-1} (m−s, C.-O). ^{1}H NMR (CDCl$_3$/TMS, 300 MHz): 6.69−7.45 (m, 8H, aromatic), 5.02 (s, 2H, OCH_2Ph), 2.72 (m, 4H, −CH_2CH$_2$CH$_2$$CH_2$−), 1.77 ppm (m, 4H, aliphatic −CH$_2$$CH_2CH_2CH_2$−). Mass *m*/*z* calculated for C$_{17}$H$_{18}$O 238, found 238.

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Table 4. Photo-Fries Rearrangement Rate Constants (10^7 s^{-1}) for the Formation of the Keto Precursors of 2-AP and 4-AP in Unstretched (u) and Stretched (s) PE Films at 22 °C

	1a		**2**	**3a**[a]		**3b**[a]	
film	k_{2A}	k_{4A}	k_{2A}	k_{2A}	k_{4A}	k_{2A}	k_{4A}
NDLDPE (u)	7.2 ± 0.3	3.3 ± 0.1	4.1 ± 0.1	15 ± 2	1.3 ± 0.3	52 ± 9	3.9 ± 0.9
NDLDPE (s)	4.3 ± 0.2	1.6 ± 0.1	3.7 ± 0.3	16 ± 3	1.4 ± 0.3	22 ± 1	1.7 ± 0.4
BHDPE (u)	6.5 ± 0.4	3.7 ± 0.2	3.8 ± 0.2	20 ± 3	1.3 ± 0.3	35 ± 5	3.1 ± 0.5
BHDPE (s)	4.5 ± 0.1	2.4 ± 0.1	2.7 ± 0.1	10 ± 1	0.7 ± 0.1	13 ± 1	1.1 ± 0.1

[a] Reference 1.

Table 5. Relative Spin Densities at Selected Positions within Phenoxy and 1-Naphthoxy Radicals Calculated at the HF/6-31g* Level

radical	2-position	4-position	oxygen
phenoxy	0.86	0.88	0.72
1-naphthoxy	0.91	0.94	0.64

hexane, ca. 2−3, cannot be explained on the basis of electronic attraction by an acyl radical to the 2- and 4-positions on the phenoxy ring; as calculated from EPR spectra,[20] the free electron densities on phenoxy are 0.282 and 0.435 at positions 2 and 4, respectively. The existence of a large amount of **(Bn)$_2$** from irradiations of **1** indicates that most of the decarbonylation products are probably formed from out-of-cage radical recombinations. However, the relative yields of **2-BP** and **4-BP** are much lower than that of **BnOP**. The opposite trend was observed when 1-naphthyl phenylacylates were irradiated in hexane.[1] In addition, the ([**2-BP**] + [**4-BP**])/[**(Bn)$_2$**] product ratio is 0.2 and 4.5 from **1a** and **3a**, respectively, while the corresponding [**BnOP**]/[**(Bn)$_2$**] ratios are 0.4 and 0.3.[1] Qualitatively, these ratios indicate that the 2- and 4-positions on phenoxy are less reactive toward recombination than the analogous positions on 1-naphthoxy, despite there being two *ortho* positions on phenoxy. Again, these photoproduct distributions do not correlate with the relative spin densities on aryloxy rings. The free electron densities on 1-naphthoxy (as calculated from EPR spectra[21]), 0.353 and 0.459 at positions 2 and 4, respectively, are similar to those on phenoxy.[20] For comparison purposes, spin densities, including that on oxygen, were also calculated from ab initio calculations at the HF/6-31g* level (Table 5).[22] The result that the spin densities on oxygen atoms are lower than at the 2- or 4-positions of naphthoxy radicals does not correlate with the relative yield of **BnOP**. The yields of **BnOP** from both phenyl phenylacylates and 1-naphthyl phenylacylates are larger when the benzylic radicals are more stable (i.e, more substituted).

The absence of **4-AP** and **4-BP** products from irradiations of **2** is probably due to steric hindrance at the 4-position of the 5,6,7,8-tetrahydro-1-naphthoxy radical. In addition, the dialkyl substitution pattern of the 5,6,7,8-tetrahydro-1-naphthoxy radical may change somewhat its electronic preference for radical recombination and lead to the formation of the two unidentified products.

[**2-AP**]/[**4-AP**] ratios from **1** in unstretched *or* stretched **PE** films are nearly the same as those in hexane. By contrast, Fries rearrangement product ratios from the corresponding 1-naphthyl esters were usually much larger in **PE** films than in hexane.[1,3] This suggests that the larger size and greater shape anisotropy of 1-naphthoxy make it more difficult to move translationally or rotationally than phenoxy within **PE** cavities. Additionally, at the moment of its formation from a phenylacyl radical within a **PE** reaction cavity, a benzylic radical is expected to be farther removed, on average, from the oxygen atom of phenoxy (i.e., during photolysis of **1**) than the oxygen of 1-naphthoxy (i.e., during photolysis of **3**).

Although **(Bn)$_2$** cross-coupling products were either completely or nearly absent in **PE** films, they were present in reasonable yields in isotropic solutions: a small amount of **(Bn)$_2$** or unidentified products with the same molecular mass persisted in photoproduct mixtures from **1b** in **PE**; under the same experimental conditions, no **(Bn)$_2$** from irradiations of **3b** was detected.[1] 1-Phenylethyl radicals, generated after decarbonylation of 2-phenylpropanoyl (from **1b** or **3b**), are more stable and bulkier than the benzyl radicals produced after decarbonylation of phenylacetyl (from **1a** or **3a**). Consequently, 1-phenylethyl is expected to add more slowly than benzyl to phenoxy. Although data to test this prediction clearly are lacking, the much higher yields of **POL** and **(Bn)$_2$** from irradiations of **1b** than from **1a** in **BHDPE** (Table 2) provide inferential support; more cage escape occurs upon irradiation of **1b** despite the faster Fries reactions by 1-phenylethyl with an aryloxy radical (Table 4[1]).

Furthermore, the relatively higher yields of cage-escape products from **1b** than **3b** in the same **PE** film indicate that the 1-naphthoxy radical is more reactive than the phenoxy radical. The rate data in Table 4 provide a quantitative measure of this difference. We have not been able to find another example in the literature that compares the reactivity of phenoxy and naphthoxy toward a common radical. In fact, the k_{2A} of **1a** is less than that of **3a** (or **3b**), while k_{4A} is greater than or equal to that of **3a** (or **3b**).

The ester **2** resembles **1a** electronically and **3a** sterically. More importantly, the aryloxy/phenylacetyl radical pair derived from **2** is similar to that from **1a** in electronic character and to the radical pair from **3a** in size and shape. The fact that k_{2A} values from **2** are very near those of **1a** is a clear indication that *the electronic nature of an aryloxy radical plays a much more important role than its size in determining the rates of radical-pair reactions, even in* ***PE*** *cages*. However, the [**2-AP**]/[**4-AP**] ratios in **PE** films at 22 °C from **1a** and **1b** (Table 2), ca. 2−3, demonstrate that the smaller and more symmetrical phenoxy radical allows formation of **2-AP** and **4-AP** at similar rates. By contrast, the corresponding [**2-AP**]/[**4-AP**] ratios from **3a** and **3b**, ca. 12,[1] indicate that the larger size and shape anisotropy of the 1-naphthoxy

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Table 6. Mean Free Void Volumes (V_{PE}) Measured by Positron Annihilation Lifetime Spectroscopy (V_{PE}),[3] Crystallinities, Densities,[6] and Functional Group Frequencies[6] for Unstretched (u) and Stretched (s) PE Films Employed in This Work

film	V_{PE} (Å^3)	% crystallinity (±2%)[a]	density (g/cm^3)	C=C/1000CH$_2$	CH$_3$/1000CH$_2$
BHDPE (u)	124	51	0.945	0	12
BHDPE (s)	113	52			
NDLDPE (u)	139	26	0.918	0.50	38
NDLDPE (s)	121	34			

[a] By differential scanning calorimetry (DSC). Previously reported crystallinities,[6] calculated from DSC data obtained with a less precise instrument, differ somewhat from the data presented here.

radical attenuates motions that bring phenylacyl radicals into proximity with the 4-position. Statistical corrections-to-these ratios to normalize the site preferences (i.e., to account for the presence of only one 2-position on 1-naphthoxy and two on phenoxy) would only increase the disparities between the photochemical behaviors of **1** and **3**. These data demonstrate that the size and shape anisotropy of an aryloxy radical do influence the position at which a phenylacyl radical adds to its partner within a **PE** cage.

The van der Waals volume of **1a** (194 Å^3) is smaller than that of **3a** (237 Å^3) or **3b** (254 Å^3), which, in turn, are smaller than that of **2** (262 Å^3).[23] All are much larger than 113−139 Å^3, the range of mean free volumes of holes in the unstretched and stretched native **PE** films employed here (Table 6).[3] Although not necessarily the same sizes as the reaction cavities occupied by the aryl esters, the hole volumes must be sufficiently near to them such that all of our guest molecules should feel some compression by vicinal **PE** chains. Were the degree of compression, as expressed by the difference between the van der Waals volume of a guest and the hole free volume of its host, the determining factor for rates of in-cage radical-pair recombinations, $k_{\mathbf{2A}}$ from **2** should have been very similar to the value from **3a**. As mentioned, $k_{\mathbf{2A}}$ from **2** is ca. 4× *smaller* than that from **3a** but comparable to the value from **1a**; electronic factors intrinsic to the guest molecules (and their radical pairs) are the dominant factor controlling the *overall* rates of radical-pair recombinations. However, steric factors imposed by the cavity walls are evident from comparisons of $k_{\mathbf{4A}}$ from **1a** and **3a**. The lower $k_{\mathbf{4A}}$ values from **3a** are consistent with impediments to motion within **PE** cages caused by the greater shape anisotropy of 1-naphthoxy radicals and the relatively stiff cavity walls. Were the $k_{\mathbf{4A}}$ differences electronic in origin, the electron spin densities at the 2- and 4-positions of phenoxy and naphthoxy predict $k_{\mathbf{2A}} < k_{\mathbf{4A}}$ for both **1a** and **3a**; they are for neither. Although overall reactivity seems to be determined by electronic factors, positional reactivity is more sensitive to constraints imposed by reaction cages.

At present, we cannot explain all of the relative rate differences in Table 4. Studies of photochemically induced decarboxylations of aryl esters[12,18] suggest that some of the results, especially those dealing with variations in [**2-AP**]/[**4-AP**] ratios from one ester in different **PE** films or from related esters (like **1a** and **1b** or **3a** and **3b**) in one film type, may depend on subtle changes in populations of ground-state conformations caused by selective interactions between the guest molecules and the walls of their **PE** cages. If conformational relaxation rates in the **PE** cages are slow with respect to lysis after electronic excitation,[24] each ground-state population can lead to the lysis of excited singlet states and radical pairs in which the initial phenylacyl trajectories have a predisposition for recombination at the 2- or 4-position of aryloxy.

Conclusions

Photo-Fries rearrangements of two phenyl phenylacylates (and one ester with a highly substituted phenyl ring) have been investigated in isotropic solutions and in **PE** films. Results are compared with those from the analogous 1-naphthyl phenylacylates. Unlike those from the 1-naphthyl esters, photoproduct distributions and rates of radical-pair recombinations from the phenyl esters are only slightly sensitive to film stretching or the type of **PE** employed. The relatively smaller size and more circular shape of the phenoxy radical from **1a** or **1b** (as compared to the 1-naphthoxy radical from **3a** or **3b**) facilitate the motions necessary to effect radical-pair recombination processes at both the 2- and 4-positions; the relative rates of phenylacyl addition to the 2- and 4-positions of the aryloxy radicals do not correlate with the spin densities. In addition, the 1-naphthoxy radical is intrinsically more reactive than the phenoxy radical toward phenylacyl radicals. Results from irradiation of 5,6,7,8-tetrahydro-1-naphthyl phenylacetate, a molecule similar in size to the 1-naphthyl phenylacylates, but similar electronically to the phenyl phenylacylates, demonstrate that *electronic*, and not *steric*, attributes of the two aryloxy radicals are principally responsible for differences in the *overall* rates of recombinations of the intermediate radical pairs.

Experimental Section

Instrumentation. Melting points are corrected. IR spectra (in Nujol mulls or KBr pellets) were recorded on a MIDAC FT-IR spectrometer. ^{1}H NMR spectra, referenced to internal TMS, were obtained on a Varian Mercury 300 MHz NMR spectrometer interfaced to a Sun SparcStation 5. UV/vis absorption spectra were recorded on a Perkin-Elmer Lambda 6 UV/vis spectrophotometer. Gas chromatography (GC) was conducted on a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector, a Hewlett-Packard 3393A integrator, and a 0.25 μm Alltech DB-5 (15 mH0.25 mm) column. GC-MS was performed on a FISONS MD-800 GC-MS instrument using the same DB-5 column.

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(24) The relaxation times of occupied sites in polyolefins are difficult to estimate because the size and shape of each guest will influence the chain segments constituting its host cage differently. However, the NMR determined correlation time of C−H dipolar interactions in the amorphous regions of polyethylene[24a] and polypropylene[24b] are ≤50 ns. The correlation time of pyrene, which is expected to disturb its cage environment much more than molecules of **1**, is ca. 2 orders of magnitude shorter than that of its host, an ethylene-propylene rubber.[24a] (a) Tai, Y.; Okazaki, M.; Toriyami, K. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 23. (b) Tanaka, H.; Inoue, Y. *Eur. Polym. J.* **1993**, *29*, 569.

Reagents. Diisopropylcarbodiimide (**DICI**; 99%), *N*,*N*-dimethylaminopyridine (**DMAP**; 99%), *p*-toluenesulfonic acid monohydrate (**PTSA**; 99%), benzyl phenyl ether (98%), 1-naphthol (99%), diphenylmethane (99%), phenylacetyl chloride (98%), bibenzyl (99%), and 2-benzylphenol (98%) were from Aldrich. 2-Phenylpropanoic acid (98%), 4-benzylphenol (96%), and 5,6,7,8-tetrahydro-1-naphthol (99%) were from ACROS. *N*,*N*′-Dicyclohexylcarbodiimide (**DCC**) and phenol were ACS reagents from Sigma. Phenyl phenylacetate (99%, Aldrich) was recrystallized from hexane, mp 40−41 °C (lit.[25] mp 40−41.5 °C), before use. Chloroform (stabilized with 0.8% (v/v) ethanol) and methylene chloride (stabilized with 56 ppm amylene) were HPLC grade from Fisher and used as received. Hexane (Aldrich, 99+%) was distilled before use. Cyclohexane (Aldrich, spectrophotometric grade) was used as received.

PE Films and film Doping. High-density **PE** films (**BHDPE**; type ES-300; Polialden Petroquimica, Brasil) and low-density **PE** films (**NDLDPE**; DuPont of Canada) have been characterized previously (Table 6).[3,6] The **PE** films were immersed in 3 separate chloroform aliquots during 1 week to remove additives, dried, and placed overnight in methylene chloride solutions of **1a** (ca. 10 mM), **1b** (ca. 10 mM), or **2** (ca. 15 mM). The doped **PE** films were dried and rinsed with the nonswelling solvent, methanol, to remove surface-occluded molecules. The resulting dopant concentrations were determined from UV/vis absorption spectroscopy and Beer's law using averaged optical densities from at least 3 different parts of each film, the film thickness,[6] density of the film,[6] and the appropriate molar extinction coefficients (assumed to be the same as measured in cyclohexane or hexane: **1a** (ϵ_{220} 7100, ϵ_{258} 470 in cyclohexane), **1b** (ϵ_{220} 6800, ϵ_{258} 440 in cyclohexane), and **2** (ϵ_{220} 8400, ϵ_{258} 430 in hexane).

Irradiations and Analyses. Solutions or doped **PE** films, sealed in quartz tubes with rubber septa, were purged with nitrogen for > 10 min immediately before being irradiated with the ethanol-filtered output of an Ultra-Violet Products, Inc. low-pressure mercury lamp (principal λ 254 nm). Aliquots of irradiated solutions were analyzed directly by GC. Photoproducts and unreacted esters in **PE** films were extracted exhaustively with CH_2Cl_2, and the combined extracts were analyzed by GC. Photoproducts from **1a** were identified by overlap of peaks during co-injections of reaction mixtures and authentic samples in GC analyses and by comparison of fragmentation patterns for those peaks and authentic samples during GC-MS analyses. Photoproducts from **1b** were identified by analogy with the patterns of their GC traces and those of **1a** and fragmentation patterns of individual peaks from GC-MS analyses. Photoproduct peaks from GC traces of **2** reaction mixtures were identified by comparison with those of 1-naphthyl phenylacylates as well as by molecular masses and fragmentation patterns from GC-MS analyses of the individual peaks. The distributions of photoproducts showed no systematic deviations up to 30% conversions of starting esters. Relative photoproduct yields are the averages from 3 GC injections of each of at least 2 separate solutions or films; precision errors are 1 standard deviation. Mass balances were > 90%.

Syntheses. Phenyl 2-Phenylpropanoate (**1b**). A dried flask was charged with phenol (1.4 g, 15 mmol), 2-phenylpropanoic acid (2.1 mL, 15 mmol), **PTSA** (2.8 g, 15 mmol), **DMAP** (1.8 g, 15 mmol), **DICI** (3.0 mL, 19 mmol), and 50 mL of methylene chloride. After the mixture had been stirred for 1 h, the liquid was removed (rotary evaporator) to yield a colorless oil. It was chromatographed on a silica gel column (3% ethyl acetate in hexanes) to yield 3.0 g of a white solid that contained ~2% phenol (GC analysis). The solid was dissolved in methylene chloride, and the solution was extracted with 4% aqueous NaOH and water and then dried (anhydrous Na_2SO_4). A colorless oil, obtained after removal of the liquid (rotary evaporator), was recrystallized from hexane to yield white needle crystals (2.4 g, 71%; >99.5% by GC): mp 40.9−42.1 °C (lit.[27] mp 40 °C). IR (KBr): 1747 cm^{-1} (s, C=O). ^{1}H NMR ($CDCl_3$/TMS, 300 MHz): 6.97−7.41 (m, 10H, aromatic), 3.96 (q, *J* = 6.9 Hz, 1H, C(O)*CH*(CH_3)Ph), 1.61 ppm (d, *J* = 6.9 Hz, 3H, C(O)CH(*CH_3*)Ph). UV/vis (cyclohexane) λ_{max} (ϵ) (258) 440; mass *m*/*z* calculated for $C_{15}H_{14}O_2$ 226, found 226.

2-Phenylacetylphenol (1-(2-Hydroxyphenyl)-2-phenylethanone) and 4-Phenylacetylphenol (1-(2-Hydroxyphenyl)-2-phenylethanone). A dried flask was charged with phenyl phenylacetate (1.0 g, 5 mmol), $AlCl_3$ (3.2 g, 24 mmol), and 50 mL of CS_2. After 36 h of refluxing, the reaction mixture contained mainly phenol, 2- and 4-phenylacetylphenol (GC analysis). The volatile liquid was distilled, and crushed ice and 10 mL of concentrated hydrochloric acid were added to the residue. The mixture was extracted with methylene chloride (3 × 50 mL), and the combined organic layers were thoroughly extracted with water and dried (anhyd Na_2SO_4). Liquid was removed (rotary evaporator), and the residue was eluted through a silica gel column (3% ethyl acetate in hexanes) to yield 2-phenylacetylphenol as a white solid (0.25 g, 25%): mp 57−59 °C (lit.[27] mp 60 °C). IR (KBr): 3300 (s and b, −OH), 1644 cm^{-1} (s, C=O). ^{1}H NMR ($CDCl_3$/TMS, 300 MHz): 12.22 (s, 1H, -*OH*), 6.85−7.85 (m, 9H, aromatic), 4.31 ppm (s, 2H, C(O)*CH_2*Ph). Mass *m*/*z* calculated for $C_{14}H_{13}O_2$ 212, found 212. 4-Phenylacetylphenol (0.18 g, 18%), mp 145−8 °C (lit[27] mp 151 °C), was obtained as a yellow solid using chloroform as eluent. IR (KBr): 3369 (s, OH), 1666 cm^{-1} (s, C=O). ^{1}H NMR ($CDCl_3$/TMS, 300 MHz): 6.82−7.95 (m, 9H, aromatic), 4.24 ppm (s, 2H, C(O)*CH_2*Ph). Major peak from MS was 121 (molecular ion peak missing).

5,6,7,8-Tetrahydro-1-naphthyl phenylacetate (**2**). A dried flask equipped with a magnetic stir bar was charged with 5,6,7,8-tetrahydro-1-naphthol (2.2 g, 15 mmol), phenylacetic acid (2.1 g, 15 mmol), **PTSA** (2.9 g, 15 mmol), **DMAP** (1.8 g, 15 mmol), **DICI** (3.3 mL, 20 mmol), and 50 mL of methylene chloride. After 2 h of stirring, the liquid was removed (rotary evaporator) and the residue was extracted with Et_2O (3H50 mL), water, 5% aqueous NaOH (3 × 30 mL), and water. The liquid, after being dried over anhydrous Na_2SO_4, was removed (rotary evaporator) to yield a pale yellow oil. It was chromatographed on a silica gel column (2% ethyl acetate in hexanes) to yield a colorless oil (2.2 g, 58%; >99% by GC) which solidified (white) when left at ~ −15 °C but melted at ca. 5 °C. IR (neat): 3015, 3065 (w, aromatic), 1755 cm^{-1} (s, C=O). ^{1}H NMR ($CDCl_3$/TMS, 300 MHz): 6.78−7.38 (m, 8H, aromatic), 3.86 (s, 2H, C(O)*CH_2*Ph), 2.75 (t, *J* = 6.6 Hz, 2H, benzylic *CH_2*), 2.38 (t, *J* = 6.6 Hz, 2H, benzylic *CH_2*), 1.70 ppm (m, 4H, aliphatic $-CH_2$*CH_2CH_2*CH_2-); UV/vis (hexane) λ_{max} (ϵ) (258) 430. Mass *m*/*z* calculated for $C_{18}H_{18}O_2$ 266, found 266.

5,6,7,8-Tetrahydro-1-naphthyl Benzyl Ether. A mixture of 5,6,7,8-tetrahydro-1-naphthol (0.75 g, 5 mmol), benzyl bromide (0.6 mL, 5 mmol), K_2CO_3 (10 g), and 50 mL of 2-butanone was stirred and refluxed under a dry atmosphere overnight, the liquid was removed (rotary evaporator), and the residue was extracted with Et_2O (3 × 40 mL), water, 5% aqueous NaOH (3 × 30 mL), and water. After being dried over anhydrous Na_2SO_4, the liquid was removed (rotary evaporator) to yield a yellowish oil that became colorless (1.0 g, 81%; >99% by GC) after silica gel chromatography (hexanes). IR (neat): 3032, 3064 (w, aromatic), 1091 and 1253 cm^{-1} (m−s, C−O). ^{1}H NMR ($CDCl_3$/TMS, 300 MHz): 6.70−7.47 (m, 8H, aromatic), 5.07 (s, 2H, O*CH_2*Ph), 2.75 (m, 4H, -*CH_2*CH_2CH_2*CH_2*−), 1.77 ppm (m, 4H, aliphatic $-CH_2$*CH_2CH_2*CH_2-). Mass *m*/*z* calculated for $C_{17}H_{18}O$ 238, found 238.

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