

## Selectivity in the Photo-Fries Reaction of Phenyl Phenylacetates Included in a Nafion Membrane

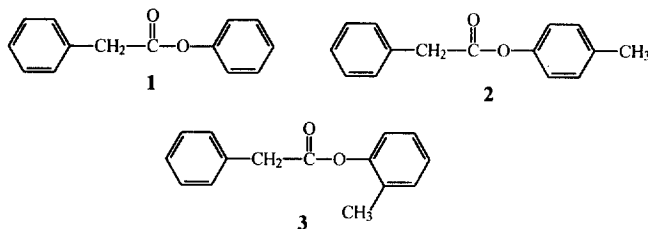
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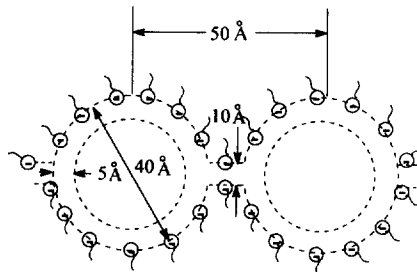
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**Abstract.** Photoirradiation of phenyl phenylacetates included within a Nafion membrane exclusively resulted in *ortho*-hydroxyphenones, thus achieving high selectivity in the photo-Fries reaction. © 1998 Elsevier Science Ltd. All rights reserved.

Selectivity in organic phototransformations continues to be one of the main topics of current interest. Of the various approaches the use of organized and constrained media has shown considerable promise.<sup>1</sup> We show below that by inclusion of substrate within a Nafion membrane one can control product distribution in the photo-Fries rearrangements of phenyl phenylacetate (**1**), *p*-tolyl phenylacetate (**2**) and *o*-tolyl phenylacetate (**3**) and can selectively achieve the formation of a single product.



Nafion represents a novel and unique family of polymers which consists of a perfluorinated backbone and short pendant chains terminated by sulfonic groups. When swollen in water, the structure of Nafion is believed to resemble that of an inverse micelle (Scheme 1).<sup>2-4</sup> The hydrated SO<sub>3</sub><sup>-</sup> head groups are clustered together in a



Scheme 1. Schematic representation of the two-phase cluster-network model for Nafion membranes

water-containing pocket of ca. 40 Å in diameter, which are interconnected by short channels (ca. 10 Å in diameter) within the perfluorocarbon matrix. This polymer in water-swollen form can incorporate a high concentration of aromatic hydrocarbons<sup>5-7</sup> and has been utilized as a medium for photophysical and photochemical studies in recent years.<sup>8-11</sup> However, the use of Nafion to control product distribution in a photochemical reaction has scarcely been reported.<sup>12</sup>

The Nafion membrane used in this study was Nafion 117 (Du Pont) in its sodium form (Nafion-Na<sup>+</sup>). 1-3 was easily adsorbed into Nafion by immersing the polymer in a well stirred aqueous solution of 1-3. The solubility of these substrates in Nafion-Na<sup>+</sup> can be rather high ( $4 \times 10^{-2}$  M calculated in its swollen form). By using the parameters reported in the literature,<sup>4,13</sup> we could calculate the average occupancy numbers (the number of substrate molecules contained in each water cluster of Nafion) of the samples to be ca. 3.5. Considering the hydrophobicity of the substrates, it is likely that the molecules of 1-3 are located in the fluorocarbon/water interface of the Nafion membrane. The water adsorbed into the sample can be removed under reduced pressure ( $10^{-4}$  Torr) to prepare a dry sample. Photoirradiation was performed both with water-swollen and dry samples. After irradiation, the products were extracted with methanol and analyzed by GC, and identified on the basis of known retention times of authentic compounds, then confirmed by GC-MS. Generally, after 7 h irradiation, the conversion was near 100%. Similar conversion was achieved in acetonitrile after the same period of photoirradiation. For all three substrates, the yield of the isolated products was greater than 90% based on the consumption of the starting materials. The product distributions are presented in Table 1.

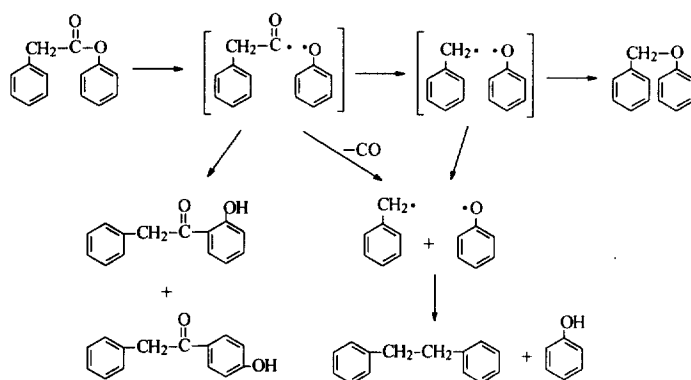
Table 1. The product distribution upon photolysis of esters 1-3<sup>a</sup>

Substrate	Medium	Phenol	Diphenyl-ethane	Ether <sup>b</sup>	<i>Ortho</i> <sup>c</sup>	<i>Para</i> <sup>d</sup>	<i>Ortho</i> / <i>Ortho</i> + <i>Para</i> <sup>e</sup> %	Cage Effect <sup>f</sup> %
1	acetonitrile	19	9	1	65	15	81	81
	water-swollen Nafion	4	2	0	85	11	89	96
	dry Nafion	0	0	0	100	0	100	100
2	acetonitrile	41	18	5	54	--	--	58
	water-swollen Nafion	2	1	0	98	--	--	98
	dry Nafion	0	0	0	100	--	--	100
3	Acetonitrile	33	16	5	50	12	81	66
	water-swollen Nafion	3	2	0	89	8	92	97
	dry Nafion	0	0	0	100	0	100	100

a. Error limit on yields was  $\pm 2\%$ . b. Phenyl benzyl ether. c. *Ortho*-hydroxyphenone. d. *Para*-hydroxyphenone. e. *Ortho*-hydroxyphenone/(*ortho*- + *para*-hydroxyphenone). f. (Phenyl benzyl ether + *ortho*-hydroxyphenone + *para*-hydroxyphenone)/(phenol + phenyl benzyl ether + *ortho*-hydroxyphenone + *para*-hydroxyphenone)

Table 1 indicates that the product distribution of the photochemical reaction of 1-3 in Nafion membrane is dramatically altered from that in homogeneous solution. First, while in acetonitrile considerable amounts of phenols and diphenylethane are formed, production of these products is significantly suppressed in the water-swollen Nafion membrane, and in dry Nafion samples no trace of such products was detected. Second, in acetonitrile both *para*- and *ortho*-hydroxyphenones are formed, whereas within dry Nafion membrane *ortho*-hydroxyphenones are the exclusive products. The first observation can be understood by considering the factor that the diffusion of the reactive intermediates is restricted in a Nafion membrane. The second observation can be interpreted by considering the suppression of the rotation of the intermediates imposed by the Nafion cluster structure.

The photo-Fries reaction has been established to occur predominantly from the singlet excited state.<sup>14,15</sup> Scheme 2 shows the photochemical reaction of 1 as representative of the esters studied in the present



Scheme 2

work. Upon photoirradiation, 1 undergoes C-O bond homolytic cleavage resulting in two paired radicals (termed a primary geminate radical pair). The solvent molecules create a "cage" surrounding the radical pair. This geminate radical pair in the cage recombines to form photo-Fries rearrangement products: *para*- and *ortho*-hydroxyphenones. The phenylacetyl radical may undergo decarbonylation to produce the secondary radical pair which in turn produces phenyl benzyl ether. Thus, the hydroxyphenones and phenyl benzyl ether may be viewed as "cage" products. The radical pair may also undergo diffusive separation to yield "escape" products: phenol and diphenylethane. The cage effect is usually defined as the yield ratio of the cage products to the total products. Restriction on the diffusion of the radicals would increase the cage effect. In acetonitrile the cage effects are 81%, 66% and 58% for esters 1, 2, and 3, respectively, while in water-swollen Nafion samples these values are increased to 96%, 97% and 98% respectively, and in dry Nafion samples no escape product is detected. This observation suggests that a Nafion membrane significantly restricts the diffusion of the photogenerated radicals.

An even more spectacular control of product selectivity is that the ratio of the *ortho*-hydroxyphenone to the total photo-Fries products in the photochemical products of 1 and 2 in the Nafion membrane is remarkably increased. While in acetonitrile both *ortho*- and *para*-rearrangement products were obtained for 1 and 2, the *ortho*-hydroxyphenones were the unique products in the Nafion membrane. As shown in Scheme 2, upon

recombination the primary geminate radical pairs lead to the formation of either *ortho*- or *para*-hydroxyphenones. In solution, the relative yield of the two isomers is determined by the electron densities at the *ortho*- and *para*- positions of the phenoxy radical. Evidently, this is not the controlling factor within Nafion. The formation of a *para*- product requires a greater extent of rotation of the radicals than the formation of an *ortho*- product. The exclusive formation of *ortho*-hydroxyphenones in a Nafion membrane suggests that the rotational motion of the radicals was significantly suppressed.

We have shown that by using a Nafion membrane as reaction medium one can achieve very high selectivity in photochemical reactions.

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