

Chapter 2

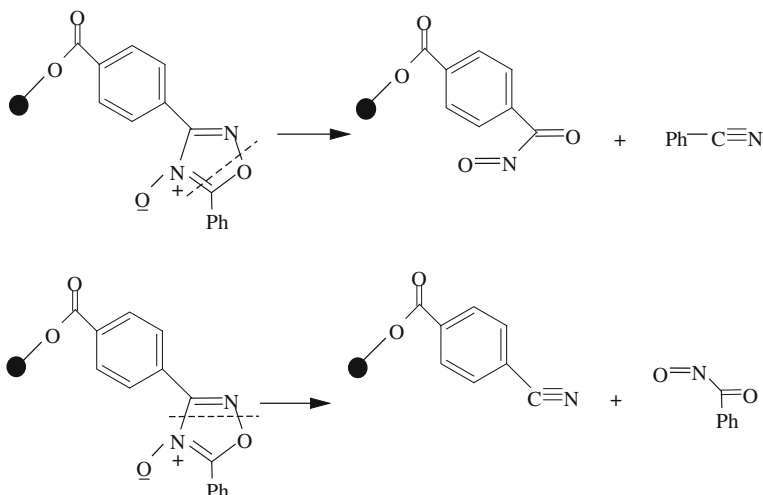
Resin-Docking, Polymer-Penetration, and Surface-Engrafting Effects

2.1 Introduction

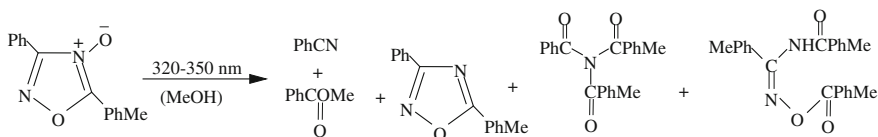
This chapter considers topics that up to now have remained beyond the scope of reviews or books relevant to confined chemistry. Among these are changes in organic reactivity resulting from docking to resins, transformations of substrates confined in polymer grinds (under conditions of ultrasmall scales), and polymer-penetration and surface-engrafting effects. Further development of these problems may provide innovative solutions for currently pressing problems related to energy, the environment, sustainability, and health.

2.2 Resin-Docking Effects

Docking resins contain only one side connected with organic substances. The literature does not pay much attention to effects of organic-substrate docking at resins. Nevertheless it exists, as shown by the following example. Quadrelli et al. (2005) studied photolytic splitting of 1,2,4-oxadiazole 4-oxide docked at Wang resin through the carboxy phenyl substituent (Scheme 2.1). The reactions were carried out in methanolic suspension at room temperature. The reaction depicted at the top of Scheme 2.1 shows the results of 2-h irradiation by an ultraviolet lamp. The nitroso-carbonyl was generated on the resin, while the benzonitrile was released in solution. The reaction at the bottom of Scheme 2.1 shows the results of 2-h exposure to sunlight. In this case, the nitrosocarbonyl was released in solution while the benzonitrile was generated on the resin. Consequently, the splitting direction depends on the intensity of photoexcitation. It is significant that the resin-supported reactions did not lead to deoxygenation of the *N*-oxide fragment as takes place upon light irradiation of free 1,2,4-oxadiazole 4-oxides (not docked at the resin) (cf. Scheme 2.2). Consequently, the resin docking changes the reactivity of the oxides, representing a kind of confinement effect.



Scheme 2.1 Light-irradiation intensity and splitting manner of oxadiazole docked at Wang resin

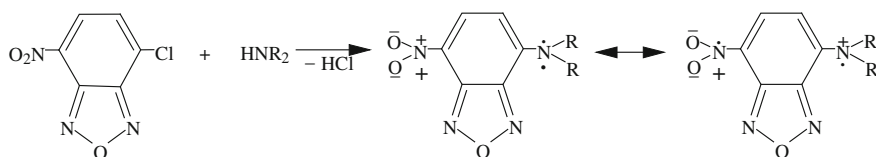


Scheme 2.2 Photolytic splitting and deoxygenation of oxadiazole N-oxide

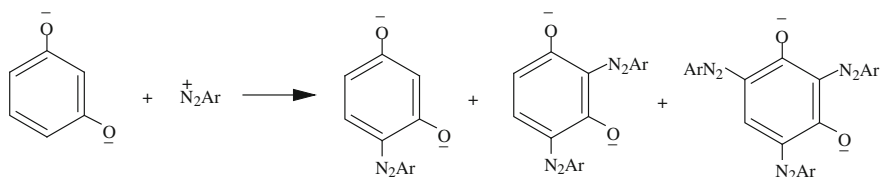
2.3 Polymer-Penetration Effects

It has been known for many years that polymer fibers can interact with each other after production. Anzenbacher and Palacios (2009) used the interaction between electrospun polyurethane fibers to deposit them in a rectangular grid and to overlay in a cross-hatch pattern. The authors doped the fibers with different reagents and heated the hatch or exposed it to solvent vapors. As a result, the fibers joined (welded) at the crossing points. The multiple junctions created during this process have a volume of a few attoliters (aL, 1 aL is 10^{-18} L). Because the polymer readily adsorbs hydrophobic compounds, these compounds occur very close to each other, in a confined space, and real chemistry is possible between them.

Scheme 2.3 shows the reaction between amines and α -chloro- α' -nitro-benzofurazan taking place in a nanofiber junction (Anzenbacher and Palacios 2009). The nucleophilic substitution leads to an intense intramolecular charge transfer, resulting in strong fluorescence; for analogs to this, see pp. 51, 52, 58, and 59 of Todres's monograph (2011). The fluorescent spectra registered in cases of ultrasmall-scale reactions are free from any artifacts caused by side-interactions. The reaction of Scheme 2.3 confirms not only that the content of the fiber junctions is physically mixed, but also that the reactant molecules diffuse close enough to enter into chemical interaction.



Scheme 2.3 Amine-chloronitrobenzofurazan reaction within polymer nanofiber junction

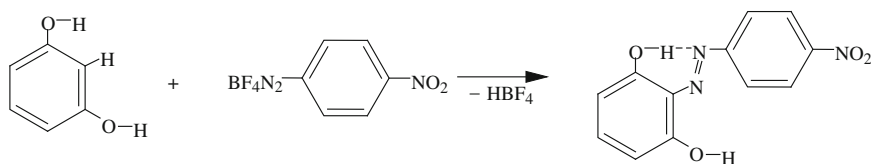


Scheme 2.4 Azocoupling of resorcinol

Resorcinol coupling with 4-nitrobenzenediazonium salts proceeds in alkali medium where the hydroxyl groups step forward in their high active anionic forms. Multiple substitution takes place: Even in the case of equimolar ratio of the azo and diazo components, resorcinol couples first at position 4, then easily transforms into a 2,4-bis(azo) compound and, eventually, into the 2,4,6-tris(azo) product (Scheme 2.4).

When resorcinol and 4-nitrobenzenediazonium tetrafluoroborate come into contact in a poly(ether-urethane) attoliter reactor, the hydroxyl groups of the azo component react in its neutral form and solely the monosubstituted product is obtained (Anzenbacher and Palacios 2009). According to the authors, the azocoupling proceeds at position 2. Obviously, the attoliter reactor cannot accommodate “shaggy” bis(azo) and tris(azo) compounds. Stabilization of the monoazo compound by intramolecular hydrogen bonding is also an important feature of the confined reaction (Scheme 2.5). This reaction provides another fundamental insight into the chemistry of confined spaces.

Carotenoids present some challenges in terms of their therapeutical application. The presence of a polyene chain and various terminal substituents in carotenoid molecules determines their near-zero inherent aqueous solubility, instability in the presence of oxygen, and high photosensitivity. Developing carotenoids into a pharmaceutical formulation requires a chemical delivery system that overcomes the problem



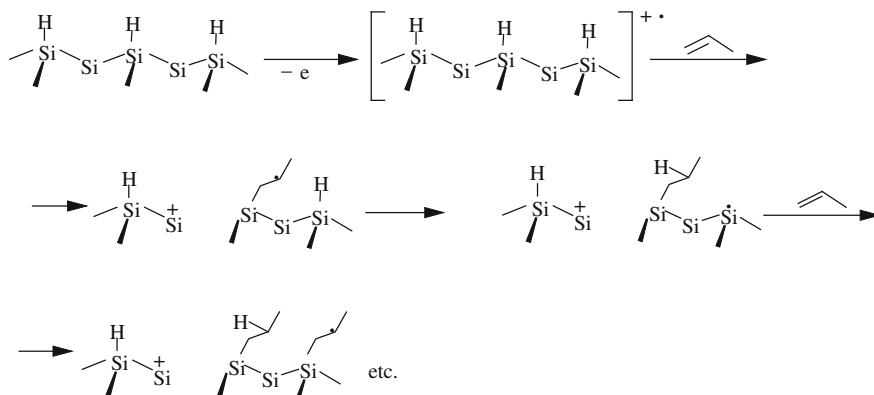
Scheme 2.5 Resorcinol coupling with nitrobenzene diazonium within poly(ether-urethane) nanofiber junction

with parenteral administration of a highly lipophilic, low-molecular-weight compound. Such a system was found in the complex between carotenoids and the natural polysaccharide arabinogalactan (Polyakov et al. 2009). This polysaccharide is a long, highly branched polymer composed of galactose and arabinose fragments in 6:1 ratio. Arabinogalactan is extracted from larch and approved for use by the U.S. Food and Drug Administration (FDA). Pharmaceutical-grade larch arabinogalactan is a fine, dry, beige powder with a slightly sweet taste and mild pine-like odor. It is low in viscosity, dissolves completely in water or juice, and is therefore easy to administer, even to children. Mixing a water solution of arabinogalactan with an ethanol solution of carotenoid did not result in complexation. However, it was found that an appropriate approach to complexation consists of cogrinding of a solid mixture of carotenoid crystals with arabinogalactan powder. This results in penetration of the carotenoid into the arabinogalactan polymer. Upon cogrinding, the crystal lattices of the starting materials are destroyed and reformed. The mechanochemical reaction leads to formation of supramolecular compounds or hybrid molecular crystals (Todres 2006). The resulting complexes are water soluble. Compared with pure carotenoids, these polysaccharide complexes showed enhanced photostability by a factor of 10 in water solution. A significant fall by a factor of 20 in the reactivity toward metal ions (Fe^{3+}) and reactive oxygen species was also detected. The carotenoid cation-radical imbedded into a polysaccharide host demonstrated greatly increased stability (Polyakov et al. 2009). The authors underline that this opens wide possibilities for application of these complexes in the design of artificial light-harvesting and photoredox devices.

2.4 Surface-Engrafting Effects

Surface-initiated and surface-confined polymerization has attracted great attention from specialists in material sciences. This approach provides rapid access to thick films or brushes with smooth surface and long-range order. The few defects and high precision of layers grown from the initiator-sown surface provide the possibility to generate a substantially enhanced photocurrent (Sakai et al. 2011). This approach can be exemplified by the work of Jones et al. (2002). In concrete language, the controlled radical polymerization of methyl methacrylate and glycidyl methacrylate from gold surface deserves to be mentioned. The gold surface was sown with mixed monolayers comprising undecanethiol (a confining component) and ω -mercaptoundecyl bromoisobutyrate (a fixed initiator of radical polymerization). The initiator density at the start of polymerization determines the ultimate “footprint” and hence the density of polymer molecules in the polymer brushes. The polymerization proceeds rapidly at room temperature in aqueous media. Sacrificial amounts of initiator are not needed, and polymerization in solution did not take place (Jones et al. 2002).

Jhon et al. (2008) used a flat silicon surface as a support and an initiator of styrene polymerization. The resulting polystyrene remained on the surface in the form of brushes. Bromination of the brushes led to substitution of the phenyl rings at their



Scheme 2.6 Alkene photoinoculation to silicon surface

para-positions. As that took place, the rate of reaction with the polystyrene brushes was much slower than bromination of free polystyrene in bulk solution. This behavior was attributed to steric hindrance due to the polystyrene confinement on the substrate.

Modification of the flat silicon surface is important for applications in electronic devices. Visible-light irradiation of Si(111) wafer in the presence of alkenes results in fast inoculation according to Scheme 2.6 (Rijksen et al. 2011). The reaction proceeds at room temperature and is distinguished by low activation energy. As seen from Scheme 2.6, the monolayer formation onto H-terminated Si progresses as cation-radical-induced initiation followed by radical recombination.

Adenier et al. (2005) grafted iron with 4-nitropobenzene diazonium cation so that a layer of 4-nitropolyphenylene was formed. The grafting was performed spontaneously by dipping the iron surface into 10 mM solution of the diazonium salt in acetonitrile. The immersion time governed the thickness of the layer: It was 2.8 nm after 1 min and 9.7 nm after 360 min. This simple method can be used to modify conductor and semiconductor surfaces.

2.5 Closing Remarks

Regardless of common opinion, chemical supports such as Wang resin really can change the reactivity of docked molecules. As seen from this chapter, the photoinduced splitting direction is different for docked oxadiazole oxides and for the same undocked compounds.

Polymer grinds readily absorb hydrophobic species, creating conditions of reactions in confined environments. These ultrasmall-scale reactions sometimes lead to products showing strong fluorescence, a property that can be used in practice without product isolation.

Penetration within polymers changes the physicochemical properties of organic compounds. Thus, carotenoids penetrated into arabinoglucan polymer become water soluble. Compared with pure carotenoids, these polysaccharide complexes showed enhanced photostability by a factor of 10 in water solution. A significant fall by a factor of 20 in the reactivity toward metal ions (Fe^{3+}) and reactive oxygen species is also important. This opens wide possibilities for application of these complexes in the design of artificial light-harvesting and photoredox devices.

By and large, further progress on the problems discussed in this chapter can bring about new developments of knowledge in organic and organometallic chemistry. At the same time, innovative developments that are potentially technologically useful can be made.

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