

3.4: Green Technologies for Safer Chemical Production

Since the fallout from the Bhopal tragedy, efforts have centered on avoiding storage of methyl isocyanate (MIC). The final product, Sevin, is no longer being manufactured by a two-step process. The process now consists of no longer reacting naphthol with MIC (one step), but sequentially with phosgene and methyl amine. The basis for the Bhopal tragedy was the reaction shown in Figure 3.4.1.

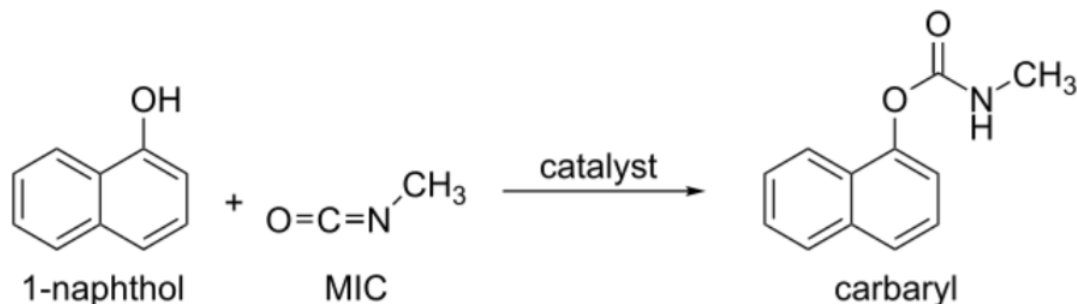


Figure 3.4.1: The original process that DuPont had in place to make Sevin (the commercial pesticide) through methyl isocyanate (MIC). http://www.wikiwand.com/en/Methyl_isocyanate

Polyurethanes

Polyurethane is a polymer composed of carbamate (urethane) linkages. Polyurethanes are traditionally formed by reacting a di- or polyisocyanate with a polyol (alcoholic polymer such as PEG, polyethylene glycol). Both the isocyanates and polyols used to make polyurethanes contain, on average, two or more functional groups (either on termini or within the molecule, hence being telechelic, i.e., a di-end-functional polymer where both ends possess the same functionality) per molecule. Recent efforts have been dedicated to minimizing the use of isocyanates to synthesize polyurethanes because isocyanates are toxic. Non-isocyanate-based polyurethanes (NIPUs), especially made from soybean oils, have recently been targeted as a new greener class of polyurethanes. Shown in Figure 3.4.2 is a molecular representation of polyurethane linkages (highlighted in blue). The carbamate linkages are composed of a central carbonyl moiety that has two heteroatoms attached to it – a nitrogen and an oxygen. From an organic perspective, it is an ester/amide hybridized molecular system. Interestingly, telechelic monomers such as adipic acid chloride (left telechelic monomer) and hexamethylene diamine (right telechelic monomer) such as shown in Figure 3.4.3.

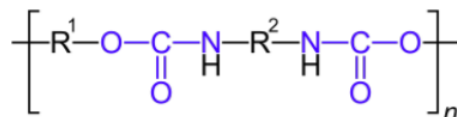


Figure 3.4.2: A simplified representation of urethane (carbamate) linkages in polyurethane polymers. de.wikipedia.org/wiki/Polyurethane#/media/File:Polyurethane-allg.svg

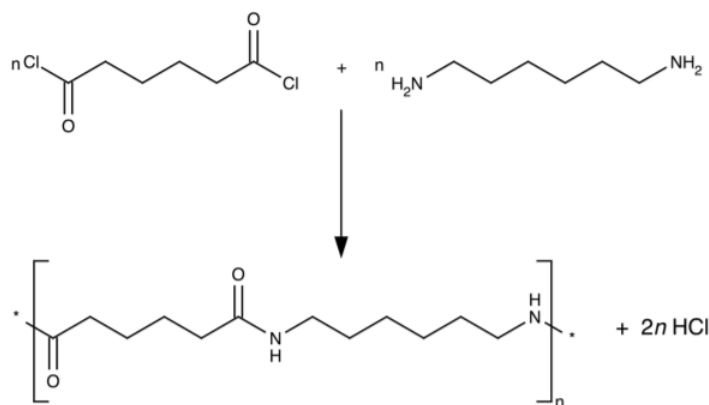


Figure 3.4.3: A simplified representation of the telechelic nature of the starting materials (monomers) that upon coupling form a telechelic polymer. commons.wikimedia.org/wiki/File:Nylon_synthesis_from_chloride_and_amine.svg

What is immediately noticeable is that the final polymer is a blend of two distinct monomers; thus, the final properties can be tailored by judicious (and discrete) choice of the monomers. More specifically, prepolymers (> 10-12 monomer units) of each monomer may be coupled to provide distinct segments having specific properties. For example, polyethylene glycol (PEG) is a polymer that is hydrophilic, soft, rubbery, and flows well. However, the phenyl-based di-isocyanate segment is much more rigid, tough, and non-stretchable. Therefore, the overall final physical and thermal properties of the polyurethane can be tuned. The opportunity to enhance the polymerization reactivity inherent for polyurethanes can be catalyzed by a non-nucleophilic base (such as DABCO – diazabicyclooctane) shown in Figure 3.4.4

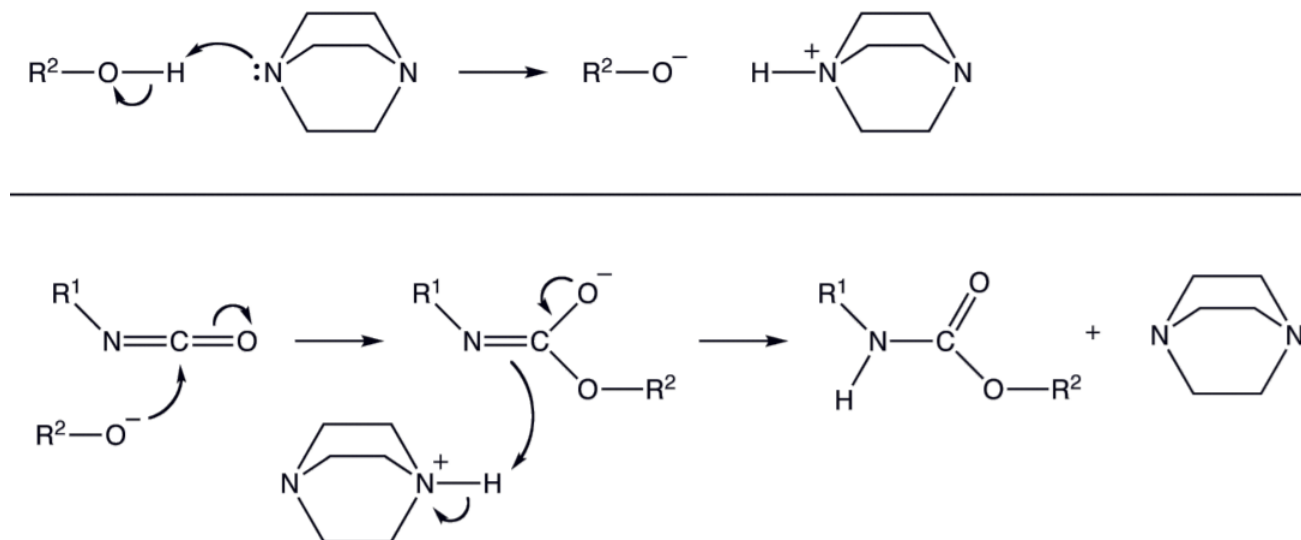


Figure 3.4.4: The molecular steps in the formation of a urethane bond by base catalysis. <http://www.wikiwand.com/en/Polyurethane>

In Figure 3.4.4, DABCO is able to abstract a proton from an alcohol (say ethylene glycol) to allow for the nucleophilic reactivity at the cumulated carbon of the isocyanate.

Curtius Rearrangement to Form Isocyanates

An additional “greener” approach to forming isocyanates, an important class of starting material in the formation of many highly important materials, is through the Curtius Rearrangement (RAR) Reaction, an example of which is shown in Figure 3.4.5.

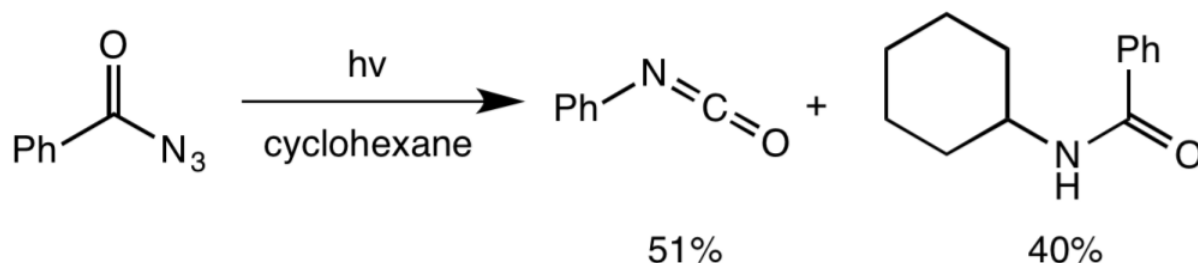
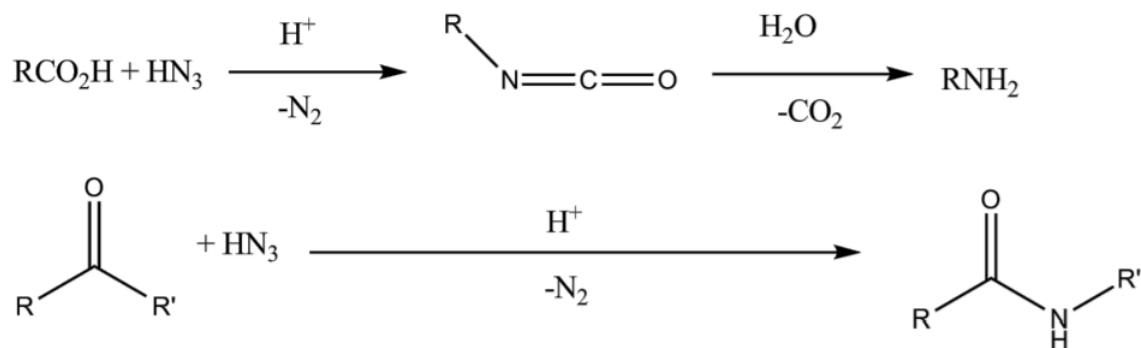


Figure 3.4.5: The Curtius RAR reaction http://www.wikiwand.com/en/Curtius_rearrangement

The Curtius Rearrangement is a thermal or photochemical decomposition starting from carboxylic azides (left structure in reaction above) to an isocyanate (first product in reaction above). In the above reaction, the solvent also plays the role of a reactant as shown by N atom insertion into cyclohexane via a radicaloid mechanism. These intermediates may be isolated, or their reaction or hydrolysis products can be obtained.

The reaction sequence that includes the subsequent reaction with water that leads to amines is called the Curtius Reaction. This reaction is similar to the Schmidt Reaction, shown below in Figure 3.4.6 (https://www.wikiwand.com/en/Schmidt_reaction), with acids that differs in that the acyl azide is prepared from the acyl halide and an azide salt.

Schmidt Reaction:



Mechanism of the Curtius Rearrangement:

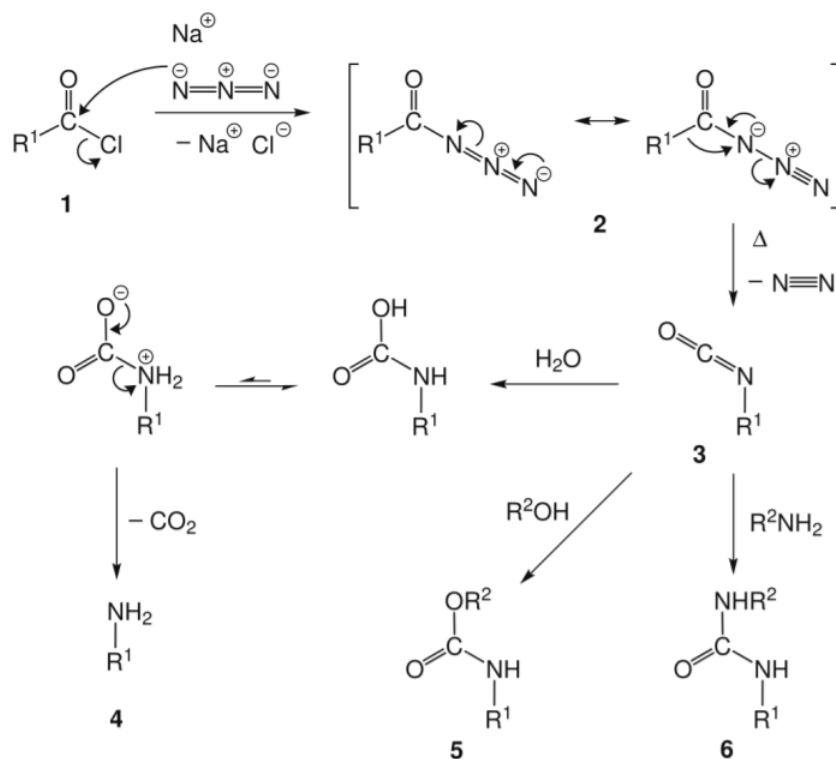


Figure 3.4.6: Two different reactions to form amines, one showcasing the green chemistry principles

For the Curtius RAR, the following steps take place: Starting Reagent 1 undergoes an electrophilic attack by an anionic azide molecule to produce an azide whose mesomerism is shown in brackets 2. It then undergoes decomposition under the appropriate stressor (heat, pressure, etc.), which leads to the isocyanate 3 with the loss of nitrogen (denitrogenation). This can react with water to yield a carbamate-like molecule (carbamic acid, urethane-like) which can spontaneously decompose thru decarboxylation to a primary amine 4. In the presence of an alcohol or an amine, 3 can yield an ester, 5, and an amide, 6, respectively.

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