

Syntheses of isocyanates via amines and carbonyl fluoride



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ABSTRACT

Isocyanates are widely used in many different areas, but the most common synthesis route—phosgene route cannot fit the more and more rigorous restriction of safety and environment. Here, a facile synthesis method of isocyanates via amines and carbonyl fluoride is proven feasibly by expanding its applications to the syntheses of nine different isocyanates. And two differences with the phosgene route are proposed. The reaction could occur under milder conditions and afford isocyanates in good yields, especially for the isocyanates containing electron withdrawing groups. It is appealing for industrial application.

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1. Introduction

Isocyanates, such as toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), and methylenediphenyl diisocyanate (MDI), 5-Isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane (IPDI), are important commercial raw materials in the synthesis of polyurethanes and are manufactured on a very large scale for a broad range of applications. Currently, the global isocyanate market grows by 5% per year, stimulated primarily by the polyurethane output expansion [1]. Furthermore, isocyanates can be used as precursors in the synthesis of herbicides [2], in gun spray painting, in the formulation of varnish, as a component in thermo-plastic resins, printing ink, foundry moulds [3], and isocyanate-based coatings [4].

Nowadays, phosgenation of both aliphatic and aromatic amines is the most common and versatile method for the synthesis of isocyanates in the commercial processes, but there are some assignable drawbacks. Given (i) phosgene (COCl_2) is extremely toxic (TLV–TWA (ACGIN): 0.1 ppm) and difficult to be transported, stored, and handled in bulk quantities, and (ii) that large amounts of corrosive HCl are produced as a side-product, and (iii) that the hard-to-remove hydrolysable chlorines contained in the final products can be detrimental for the further

applications [5–8]. Hence, many efforts have been made to develop alternative reagents or processes, such as triphosgene method, β -elimination of haloform method, Curtius rearrangement, Lossen rearrangement, Hoffmann rearrangement, reductive carbonylation of nitro compounds, dehydration of carbamate anions, thermal decomposition of carbamates [2,9]. To the best of our knowledge, except the production of IPDI and HDI through the thermal decomposition of the corresponding carbamates which are prepared by a phosgene-free urea-based technology [10], all the other routes are still laboratory procedures for several drawbacks.

Carbonyl fluoride (COF_2) is similar to phosgene in structure and chemical property, and can react with amines at a relatively low temperature. Moreover, the toxicity of COF_2 (TLV–TWA (ACGIN): 2 ppm) is about equivalent to one twentieth of phosgene. Besides, our laboratory has developed an efficient synthesis method of COF_2 which made a large scale production in industry with low cost possible [11]. Therefore, using the reactions of amines with COF_2 to produce isocyanates is attractive industrially.

Practically, several literatures referred to the reactions of amines with COF_2 have been reported and isocyanates such as $(\text{CF}_3)_2\text{CFN}=\text{C}=\text{O}$, $\text{SF}_5\text{N}=\text{C}=\text{O}$, and $\text{ArCF}_2\text{N}=\text{C}=\text{O}$ were obtained [12]; but the investigations about this kind of reactions are still quite inadequate. Herein, we synthesized two different types of isocyanates by reacting COF_2 with amines. One was isocyanates without electron withdrawing groups, the other was isocyanates containing electron withdrawing groups. The discussion about the differences between the phosgene route and the COF_2 route were also conducted.

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Scheme 1. The main reactions of COF₂ with amines.

2. Results and discussion

The synthesis process is consisted of two steps. The first step is the reaction between COF₂ and the aromatic or aliphatic amines at the room temperature or near. The second step is the decomposition of the intermediate produced in the first step at a higher temperature (Scheme 1, R is the aromatic or aliphatic substituent).

2.1. Syntheses of isocyanates without electron withdrawing groups

Several widely-used commercial diisocyanates without electron withdrawing groups (Fig. 1.) were synthesized and the results are listed in Table 1. The intermediates and products were identified by nuclear magnetic resonance (NMR).

According to Table 1, the two-step process using COF₂ instead of phosgene is feasible to produce TDI, MDI, HDI, and TODI. Unlike examples of (CF₃)₂CFN=C=O [12a] and SF₅N=C=O [12c], there were no catalysts required. The experimental conditions were mild, which the first steps were carried out at room temperature, and the second steps were conducted at the temperature no higher than 160 °C. However, compare to the phosgene route, the yields of the final products presented here are relatively lower. For example, by reacting TDA, HDA, and MDA with the phosgene, the TDI, HDI, and MDI were obtained by Biskup et al. [13], Perret and Revelant [14], and Lichty and Seeger [15] in >99.5% yield, 97% yield, and 93.7% yield, respectively. Moreover, the main intermediates were found to be formed with the structure of “FOCHN–R–NHCOF”, and the compounds that only one amine group reacting with COF₂ were not detected. But for phosgene, only one amine group will react with COCl₂ at beginning stage and the second one will react with phosgene after the first one is reacted completely, which the main intermediates are in the structure of “ClOCHN–R–NH₂·HCl” [16,17]. This is very different between COF₂ and COCl₂.

Table 1

The syntheses of the isocyanates without electron withdrawing groups.

Entry	Substrate		COF ₂ (mmol)	Intermediate		Product	
	Name	Chemical amount (mmol)		Name	Yield (%)	Name	Yield (%)
1 ^a	TDA	8	76	1	94	TDI 2	93
2 ^b	MDA	5	53	3	66	MDI 4	81
3 ^c	HDA	9	53	5	92	HDI 6	77
4 ^d	TODA	5	88	7	98	TODI 8	74

First step: room temperature for 6 h; second step: 160 °C for 30 min, for Entry 1–3. The yields of intermediates and final products were determined by ¹⁹F NMR and ¹H NMR.

^a Solvent, chlorobenzene 15 g.

^b Solvent, dichloromethane 15 g.

^c Solvent, chlorobenzene 15 g.

^d Solvent, acetone 15 g, and chlorobenzene 15 g; first step: room temperature for 3 h; second step: reflux temperature, 132 °C.

2.2. Syntheses of isocyanates containing electron withdrawing groups

Isocyanates containing electron withdrawing groups (Fig. 2) were synthesized by COF₂ route, and the results are listed in Table 2. The intermediates and products were identified by NMR.

Generally, isocyanates containing withdrawing groups, which can be used as medical intermediates, precursors of pesticides, and in some other special fields, are reported relatively difficult to be obtained by the phosgene route or just prepared by other methods. For examples, Pohls et al. [18] reported a process to prepare BSDI based on a reaction of BSDA with phosgene in *ortho*-dichlorobenzene solvent at 180 °C, and Heymann et al. [19] used the same substrates but the solvent was changed to be dioxane; Neither of them presented the yield data. TFMPI was reported to be prepared from the reaction of *p*-aminobenzotrifluoride hydrochloride and phosgene in toluene solvent with a low yield just 42% [20]. Franz and Osuch [21] synthesized *p*STI by pyrolysis of *p*-toluenesulfonyloxamoyl chloride (obtained in 90% yield from the reaction of *p*STA with oxalyl chloride) in *o*-dichlorobenzene solvent with 79% yield. Obviously, from Table 2, using the COF₂ method, satisfactory yields of intermediates and final

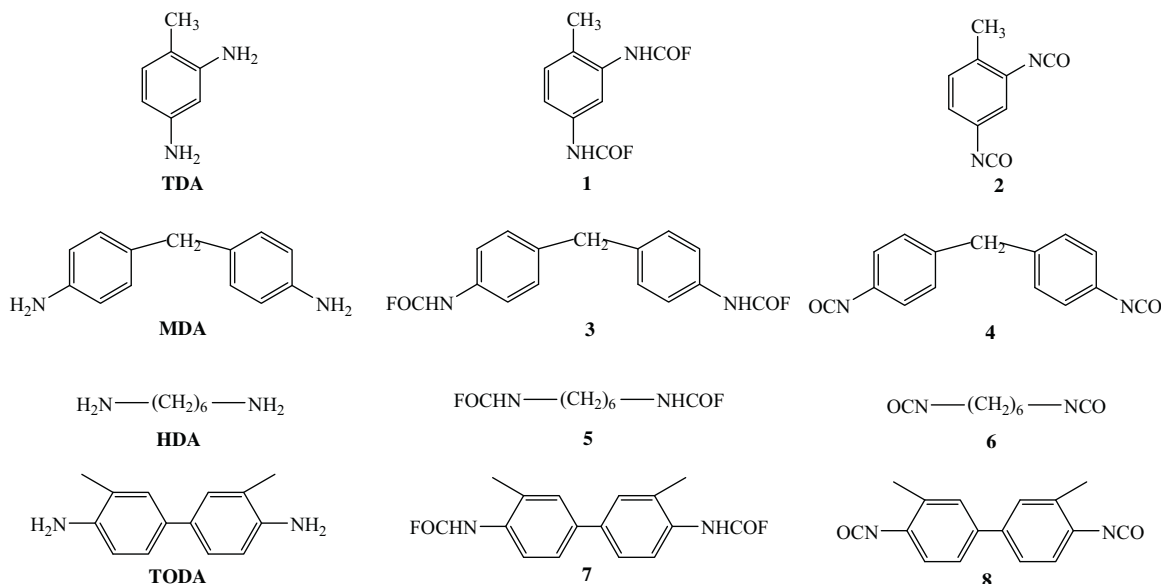


Fig. 1. Structures of the substrates, the corresponding intermediates, and the isocyanates without electron withdrawing groups.

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