

Specificity of the Reaction of 1,1-Dimethylhydrazine with Phenyl Isocyanate

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Abstract—According to the data of IR and NMR spectroscopy and ebullioscopy, the reaction of phenyl isocyanate with a large excess of 1,1-dimethylhydrazine gives 1,1-dimethyl-4-phenylsemicarbazide as the major product. At other reactant ratios, biuret-like structures are formed.

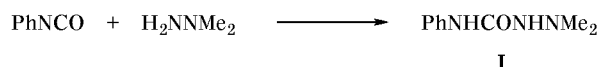
A well-known two-step process for preparation of polyurethanes is based on extension of a macro diisocyanate (MDI or prepolymer) via reaction with a difunctional compound having a labile hydrogen atom. For example, in the synthesis of film-forming polyurethanes, macro diisocyanate obtained from oligo-oxytetramethylene glycol and 4,4'-diisocyanatodiphenylmethane was extended by reaction with an equimolar amount of a low-molecular dihydrazide, diamine, or diol [1–4]. When the fraction of the latter is smaller, no linear polymer is formed, but a cross-linked product may be obtained. Macromolecular compounds are not formed in reactions of macro diisocyanates with aniline.

A different result was obtained by us when a solution of macro diisocyanate was treated with 1,1-dimethylhydrazine. High-molecular compounds soluble in DMF were formed with a two-, five-, and even tenfold excess of macro diisocyanate [5]. Removal of the solvent gave polymeric films whose physical and mechanical properties were similar to those of the polymers obtained with the use of low-molecular dihydrazides, diamines, and diols. The IR spectra of the above polymeric products (films) obtained at different reactant ratios were completely identical in the position of absorption bands. However, some differences were observed in the intensities of bands belonging to vibrations of the NH groups (1540 and 3300 cm^{-1}), C=O groups (1650, 1710, and 1730 cm^{-1}) and benzene rings (1600 cm^{-1}).

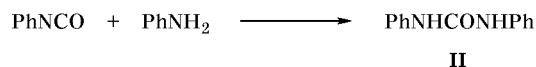
With the goal of understanding the mechanism of formation of macromolecular compounds on the basis

of 1,1-dimethylhydrazine (1,1-DMH) and the relations between the polymer structure and MDI:1,1-DMH ratio, we examined specific features of the reaction of 1,1-dimethylhydrazine with phenyl isocyanate as a process modeling formation of polyurethane.

Different interpretations have been reported for reactions of unsymmetrically substituted hydrazines with nucleophilic reagents [6–9]. According to the known concept [1], the reaction of 1,1-dimethylhydrazine with phenyl isocyanate should give 1,1-dimethyl-4-phenylsemicarbazide (**I**) as the only product.



This was reported, e.g., in [7] (see also references therein), but the reaction conditions were not given. We examined the structure of products formed in the same reaction at different reactant ratios (Table 1) by IR and NMR spectroscopy and ebullioscopy. When the amount of 1,1-dimethylhydrazine was equivalent to or lower than the amount of phenyl isocyanate, the IR spectra of the products were generally identical (samples M1, M2, and M3). The product obtained at a 1,1-dimethylhydrazine-to-phenyl isocyanate ratio of 3:1 (sample M4) had a considerably different IR spectrum. In order to identify this product we used the IR spectrum of *N,N'*-diphenylurea (**II**) which is the product of the reaction of phenyl isocyanate with aniline:



The reaction was carried out at aniline-to-phenyl isocyanate ratios of 1:1 and 1:3, as well as in dioxane solution using a 9-fold excess of phenyl isocyanate with respect to aniline. In all cases, we isolated crystal-like products whose IR spectra were similar to the IR spectrum of urea **II** [10]. These data indicated that in the reaction with aniline the NCO group of phenyl isocyanate did not react with the urea thus formed to give biuret structures.

Comparison of the IR spectra of M4 and *N,N'*-diphenylurea [10] led us to conclude that in this case only 1,1-dimethyl-4-phenylsemicarbazide (**I**) was formed. Stretching vibrations of the C=O and NH groups in the latter give rise to IR bands at 1680 and 3300 cm^{-1} . Bending vibrations of the NH groups appear as a strong absorption band at 1540 cm^{-1} , and a series of bands in the region 2760–2970 cm^{-1} can be assigned to stretching vibrations of C–H bonds in the NMe_2 moiety.

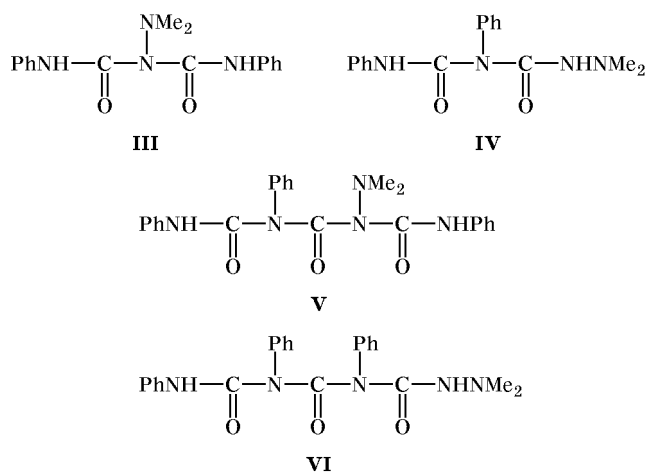
The IR spectra of products M1, M2, and M3 also contain absorption bands belonging to monosubstituted benzene rings and NMe_2 group. The main difference is that a strong band at 1720 cm^{-1} (free carbonyl group) is present in addition to the band at 1650 cm^{-1} corresponding to carbonyl group involved in hydrogen bonding. Stretching and bending vibrations of the NH groups are characterized by absorption at 3270 and 1560 cm^{-1} [11]. The bands are displaced relative to those observed in the spectrum of **I** (1680 to 1650, 3300 to 3270, and 1540 to 1560 cm^{-1}) due to specificity of hydrogen bonding in crystal [10].

The presence of the band at 1720 cm^{-1} may be explained as follows:

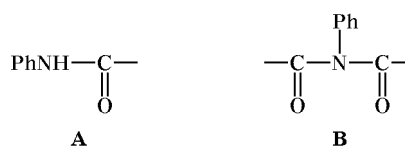
- (1) A structure is formed, in which some carbonyl groups are not involved in hydrogen bonding [6];
- (2) The reaction of phenyl isocyanate with dimethylhydrazine does not stop at the formation of urea **I**, and the subsequent process leads to biuret-like structures.

The appearance of a band belonging to free carbonyl group should be accompanied by appearance of a band due to absorption of free NH group at about 3440 cm^{-1} . However, π -system of benzene ring can also play the role of proton acceptor. In this case, the resulting hydrogen bond is weak, and a band at 3370 cm^{-1} should appear. The IR spectrum of M1 lacks absorption at 3440 and 3370 cm^{-1} , but a strong band is observed at 3270 cm^{-1} . This means that all NH groups in the molecule participate in formation of strong hydrogen bonds, but not all C=O groups are involved therein, so that a band at 1720 cm^{-1} appears in the experimental spectrum.

Taking into account that the IR spectra of M1, M2, and M3 differ only by the intensity ratios of absorption bands corresponding to carbonyl group (1650 and 1710 cm^{-1}), benzene ring (1600 cm^{-1}), and NH and CH_3 groups, we come to a conclusion that the reaction of 1,1-dimethylhydrazine with phenyl isocyanate does not stop at formation of 1,1-dimethyl-4-phenylsemicarbazide (**I**) as final product. Phenyl isocyanate reacts further with NH groups in **I** to give biuret structures like **III–VI**.



This assumption is confirmed by the ^1H NMR data. The ^1H NMR spectrum of product M4 contains signals from protons of monosubstituted benzene ring (δ 6.93, 7.23, and 7.6 ppm), NH group (δ 8.6 and 7.5 ppm), and methyl group (δ ~2.5 ppm). In the ^1H NMR spectrum of M3 we observed two sets of multiplet signals belonging to aromatic protons, which suggests the presence of two kinds of monosubstituted benzene rings in the molecule. In fact, only two kinds of phenyl-containing moieties, **A** and **B**, are possible (cf. structures **III–VI**).



In keeping with the intensity ratio of the aromatic proton signals, the ratio of phenyl groups **A** and **B** in M3 is about 2:3; such a ratio should be observed at an equimolar amounts of structures **IV** and **VI**. The above stated is supported by the data of ebullioscopic measurements. The experimental molecular weight of M4 is 188.9 against the calculated molecular weight of semicarbazide **I**, equal to 179.0. Almost ideal correspondence was found between the molecular weights of product M1 and compound **III**:

Table 1. Products of the reaction of *N,N*-dimethylhydrazine with phenyl isocyanate

<i>N,N</i> -Dimethylhydrazine, mol	Phenyl isocyanate, mol	Product
1	1	M1
1	3	M2
1	5	M3
3	1	M4

Table 2. Experimental and calculated molecular weights and structures of products M1–M4

Product	M_{exp}	M_{calc}	Assumed structure
M4	188.9	179	I
M1	307	298	III or IV
M2	417	417	V or VI
M3	357	298/417	IV/VI (1 : 1)

$M_{\text{calc}} = 298$ and $M_{\text{exp}} = 307$. Further decrease in the fraction of 1,1-dimethylhydrazine in the reaction mixture leads to formation products consisting of different amounts of biuret-like compounds (Table 2). The IR spectra of these products were identical in the position of absorption bands, but they differed by the relative band intensities.

Thus, analysis of the IR and ^1H NMR spectra and ebullioscopic data of the products obtained by reaction of *N,N*-dimethylhydrazine with phenyl isocyanate (as a model reaction for formation of polyurethanes) showed that 1,1-dimethyl-4-phenylsemicarbazide (**I**) is formed as the major product only when *N,N*-dimethylhydrazine is taken in a large excess relative to phenyl isocyanate. At other reactant ratios, including equimolar, biuret-like structures **III–VI** are obtained.

The analogy in the carbonyl absorption patterns observed in the above model reaction and in the synthesis of polyurethanes suggests that extension of a macrochain having terminal NCO groups with the aid of *N,N*-dimethylhydrazine occurs through formation of biuret-like fragments.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from samples pelleted with KBr. The ^1H NMR spectra were obtained on a WXR-300 instru-

ment (200.13 MHz) using DMSO- d_6 as solvent and TMS as internal reference. The molecular weights were determined on an EP-68 ebulliograph (Russia) using 4,4'-dibromodiphenyl ether (M 327.9) as reference and 1,4-dioxane as solvent.

N,N-Dimethylhydrazine was synthesized according to the procedure described in [12]. Phenyl isocyanate was commercial product [13].

Products M1–M4 were obtained as follows. Phenyl isocyanate and *N,N*-dimethylhydrazine were mixed at ratios specified in Table 1, and the mixture was kept for several hours at room temperature. Unchanged initial compounds were removed by evacuation for 4–6 h. The products were light yellow powders.

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