Oligomerization in the Reaction of Acetylacetone with Organic Diisocyanates

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Diisocyanates are organic monomers [1] widely used in the polymer chemistry [2–4]. They are highly reactive compounds toward various nucleophiles such as alcohols, phenols, and primary amines [5]. The corresponding reactions underlie large-scale processes for manufacture of polyurethanes and polyureas. CH Acids are less reactive toward isocyanates. However, such CH acids as malonic acid esters, ethyl acetoacetate, nitroalkanes, and acetylacetone are known [2, 3] to react with diisocyanates at the activated C–H bonds to give substituted amides.

Compounds containing both isocyanato group and β-diketonate moiety, e.g., like O=C=N–X–NHC(O)-C[C(O)CH$_3$]$_2$, can be used as starting materials in the synthesis of luminescent labels for biochemical and microbiological studies [6], as well as for the preparation of functionalized polymers. The presence of a reactive isocyanato group provides the possibility for chemical binding of difunctional molecules to proteins and polyols, whereas β-diketonate fragment is a well known chelating ligand capable of forming complexes with various metals, including luminescent rare earths. Our attempts to synthesize such compounds did not result in isolation of expected products. The reactions of 2,4-diisocyanatotoluene (**I**) and 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane (**II**) with acetylacetone (Hacac) at a molar ratio of 1:1 was accompanied by formation of oligomers. No reaction occurred in the absence of catalyst. Addition of a small amount of triethylamine (0.2–0.5 wt %) strongly accelerated the process (3–4 h at 80–120°C). Diisocyanate **I** slowly reacted with acetylacetone at room temperature (20–25 h). During the process, the reaction mixture turned more viscous to form finally a colored transparent glassy material. When the reactions were carried out using 3 equiv of acetylacetone, we observed coloration and increase in viscosity of the reaction mixture, but it did not turn glassy. The products were reprecipitated from THF with hexane, and were isolated as yellow or brown powders which underwent thermal decomposition upon attempted vacuum sublimation (no sublimation or melting was observed). The IR data indicated that the products contained both isocyanato groups and β-diketonate fragments. In addition, absorption bands assignable to amide groups were observed. Diisocyanates characteristically show in the IR spectra a very strong absorption band due to stretching vibrations of isocyanato groups at 2270–2260 cm^{-1}. In the IR spectra of the products, this band was not maximal in intensity and was comparable with νC=O (1710 cm^{-1}, amide; 1662, 1599 cm^{-1}, β-diketone, urethane) and δNH bands (1535 cm^{-1}).

According to the data of gel permeation chromatography (GPC), the molecular weights of oligomers **III** (from diisocyanate **I**) and **IV** (from **II**) varied over a wide range, and their polydispersity indices were 1.9–2.4; the weight-average and number-average molecular weights of oligomer **IV** were, respectively, $M_w = 1100$ and $M_n = 490$; $M_w/M_n = 2.3$.

In the ^{1}H NMR spectra of the oligomeric products, protons in methyl groups [CH$_3$C(O), CH$_3$C(OH)=, CH$_3$C–O–C(O)] give a set of signals in the range

I   II

Scheme 1.

III, X = 4-methylbenzene-1,3-diyl, n = 3; **IV**, X =


, n = 2.
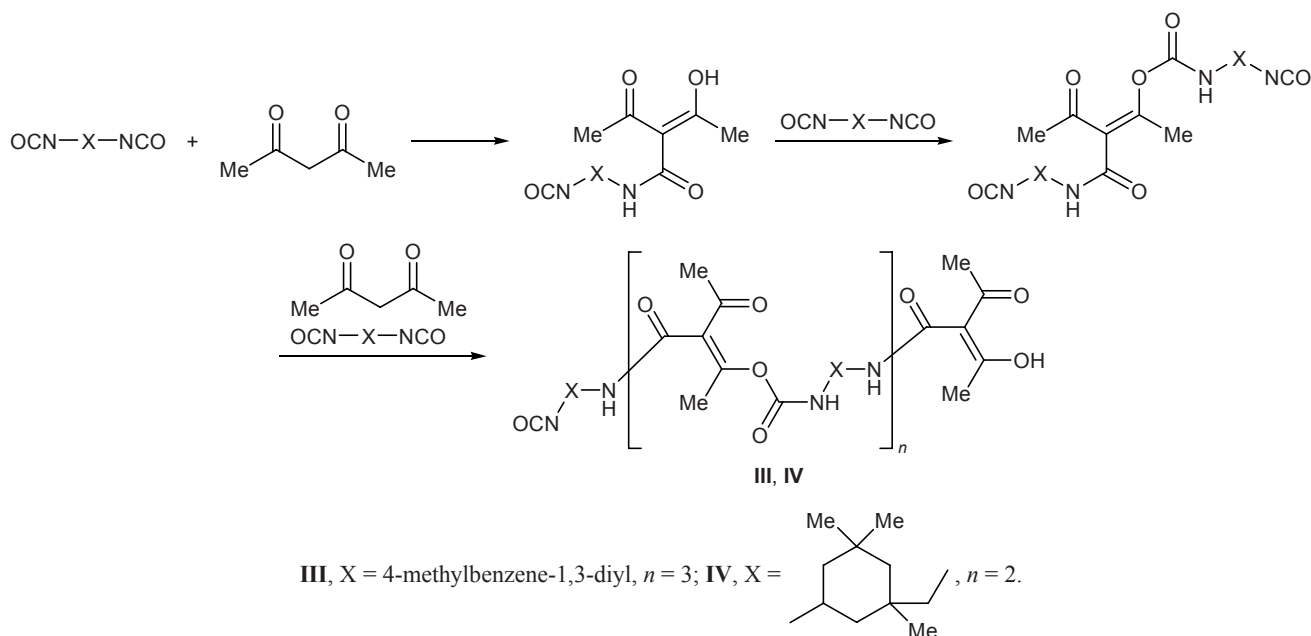
δ 1.6–2.6 ppm; protons in the aromatic methyl group of oligomer **III** resonated at δ 2.3 ppm, and CH$_3$ groups at the cyclohexane ring in oligomer **IV** gave signals at δ 0.9–1.1 ppm. Signals from protons in the CH$_2$NH and terminal CH$_2$NCO groups in the spectrum of **IV** were located at δ 3.0 and 3.4 ppm, and CH$_2$ protons in the cyclohexane ring appeared at δ 1.5–1.7 ppm. Downfield signals at δ 10.1 and 11.9 ppm were assigned to hydroxy protons in the terminal enol fragments. The spectrum of **III** contained a set of signals from aromatic protons in the region δ 6.8–7.4 ppm. Oligomeric structure of the products also follows from broadening of all signals.

Among the initial compounds, only diisocyanates **I** and **II** are difunctional monomers suitable for condensation polymerization. However, taking into account the ability of acetylacetone to undergo enolization, it is also capable of acting as such monomer due to formation of hydroxy group which may be involved in condensation with isocyanates. Scheme 1 illustrates a probable mechanism of oligomerization. In the first step acetylacetone as CH acid adds at one NCO group of diisocyanate **I** or **II** to give the corresponding amide, and enol form of the latter undergoes condensation with the second diisocyanate molecule. A sequence of such transformations gives rise to oligomers having terminal isocyanato groups and β-diketonate fragments.

The low molecular weights of the oligomeric products may be rationalized in terms of reduced reactivity of the terminal enol group in oligomer toward NCO group. Another reason is the formation of terminal carbamate fragment which is incapable of reacting with isocyanate. The resulting oligomers should be classed with amidourethanes, for they contain both amide NHC(O)C and carbamate NHC(O)O moieties. The formation of a viscous rather than glassy material in the presence of excess acetylacetone may be explained by predominant formation of terminal carbamate groups (Scheme 2).

Scheme 2.
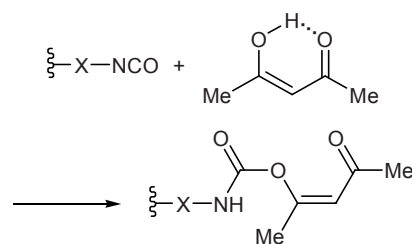
As a result, compounds with a relatively low molecular weights are obtained, and their solution in excess acetylacetone looks like a viscous liquid. After reprecipitation, the oligomeric products were isolated as solids.

Reaction of acetylacetone with 2,4-diisocyanatotoluene (I). An ampule was charged with 0.70 g (7 mmol) of acetylacetone, and 1.23 g (7 mmol) of diisocyanate **I** and one drop of triethylamine were added. The mixture slightly warmed up. The ampule was

frozen, evacuated, and sealed. After 20 h, the mixture was a yellow transparent glassy material. The ampule was opened, the products were dissolved in THF and reprecipitated with hexane to a THF–hexane ratio of 1:3. The precipitate was filtered off, washed with hexane, and dried under reduced pressure at 70–80°C. Yield of oligomer **III** 1.33 g, yellow powder. IR spectrum, v, cm^{-1}: 3475 w (OH), 3291 m (NH), 2270 v.s (NCO), 1710 sh (C=O, amide), 1662 v.s, 1599 v.s [C(O)C=C–O, C(O)OC], 1535 v.s (δ NH, amide). Found, %: C 66.20; H 5.60; N 11.05. $C_{56}H_{55}N_8O_{10}$. Calculated, %: C 67.24; H 5.54; N 11.21. $M_w = 451$, $M_n = 214$, $M_w/M_n = 2.1$.

Reaction of acetylacetone with 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane (II). An ampule was charged with 1.66 g (17 mmol) of acetylacetone, and 1.23 g (6 mmol) of diisocyanate **II** and two drops of triethylamine were added. The ampule was frozen, evacuated, sealed, and heated for 4 h at 100–120°C. The ampule was cooled and opened, and the dark orange viscous liquid was dissolved in THF. Hexane was added to the solution, and the yellow solid was filtered off, washed with hexane, and dried under reduced pressure at 70–80°C. Yield of oligomer **IV** 0.81 g, yellow powder. IR spectrum, v, cm^{-1}: 3493 sh (OH), 3312 s (NH), 2261 v.s (NCO), 1705 sh (C=O, amide), 1650 v.s, 1630 v.s sh [C(O)C=CO, C(O)OC], 1551 v.s (δ NH, amide). Found, %: C 64.57; H 8.80; N 10.40. $C_{49}H_{77}N_6O_{10}$. Calculated, %: C 64.55; H 8.53; N 9.24. $M_w = 1100$, $M_n = 490$, $M_w/M_n = 2.3$.

The ^{1}H NMR spectra were recorded at 25°C from solutions in CDCl$_3$ on a Bruker Avance DPX-200 instrument (200 MHz) using tetramethylsilane as internal reference. The IR spectra were obtained on an FSM 1201 spectrometer with Fourier transform from samples dispersed in mineral oil. The molecular weights were determined by gel permeation chromatography on a Knauer Smartline chromatograph equipped with Phenogel Phenomenex 5-µ columns (300×7.8 mm); refractometric detector, eluent THF.

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