# SYNTHESIS OF SOME POLYUREAS BASED ON DIAMINO DERIVATIVES OF BIS-1,3,4-OXADIAZOLE

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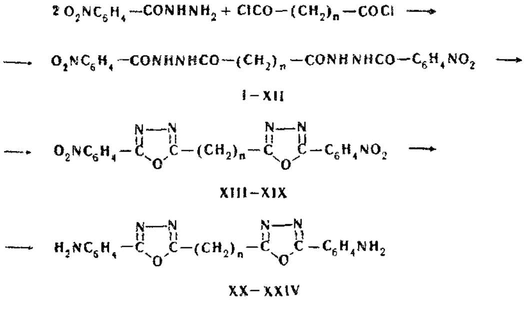
Ortho-, meta, and para-nitrobenzoyl derivatives of the dihydrazides of succinic, glutaric, adipic, and azelaic acids are prepared, from which are obtained nitro and amino derivatives of bis-1,3,4-oxadiazole. Various conditions for synthesizing these compounds are investigated. A series of polyureas is obtained by reacting diamino derivatives of bis-1,3,.4-oxadiaole with diisocyanates, and some of their properties are investigated.

Polymers containing oxadiazole rings, with high heat resistance and chemical stability [1–9] have of recent years attracted ever increasing attention. Some high molecular compounds of that type are film- and fiber-forming [4–6, 8]. Preparation of these polymers is usually based on cyclodehydration of the corresponding polyhydrazides at high temperature [2, 5–7], or by treatment with various cyclizing reagents [8,9]. However the polymers can also be synthesized from bifunctional derivatives of oxadiazole, which offers extensive possibilities of preparing such materials with diverse properties.

The present paper is devoted to the preparation of polymers from various diamino derivatives of bis-1,3,4-oxadiazole and diisocyanates.

Diamino derivatives of bis-1,3,4-oxadiazole were synthesized according to the following equation:



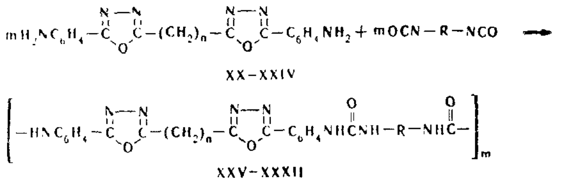
$n = 2, 3, 4$ and 7

Reaction of hydrazides of nitrobenzoic acids with chlroides of dicarboxylic acids proceeds readily at room temperature in dimethylformamide or pyridine as solvent, to give the corresponding products I–XII. When p-nitrobenzhydrazide is used, due to its lower solubility in the above solvents, the reaction is run at 40–50°. Usually the reaction between hydrazide and acid chloride is exothermic, so cooling must be used. Treatment of the reaction products with cold water gives high yields of compounds I–XII, given in Table 1, with a sufficient degree of purity. The same substances can be obtained from the dihydrazides of the carboxylic acids and nitrobenzoyl chloride, but often this method does not give satisfactory results, due to the low solubility of some dihydrazides in the usual solvents.

We found that cyclodehydration of compounds I–XII to the corresponding oxadiazoles XIII–XIX, takes place readily in solution in 20–24% oleum at 35–40°. Pouring the reaction products onto ice precipitated high yields of colorless crystalline products XIII–XIX (Table 2). Compounds I–XIII can be cyclodehydrated with phosphorus oxychloride, when the reaction is run at the boiling point of the latter, until a homogeneous solution is obtained, which usually requires 1–2 hr, after which most of the phosphorus oxychloride is distilled off, and the residue poured onto ice. The oily products precipitated slowly crystallize to the compounds XIII–XIX. As compared with the oleum cyclodehydration method, however, this one gives low yields of compounds XIII–XIX with low degrees of purity. Cyclodehydration was not possible in the case of o-nitrobenzoylhydrazides of dibasic carboxylic acids, as the dark oily product always formed was not susceptible to ordinary methods of purification. Evidently this is due to the ease with which they decompose in acid solution, since it is known that 2-aryl-5-alkyl-1,3,4-oxadiazoles are quite easily hydrolyzed with opening of the heterocyclic ring [10], a nitro group in the ortho position obviously considerably facilitating this process.

Reduction of nitro compounds XIII–XIX was carried out in α-methyl-naphthalene solution using phenylhydrazine at 190–210°, or in excess phenylhydrazine at 150–190°. Reduction of the nitro derivatives of the oxadiazole obtained starting from azelaic acid is difficult because of their low solubilities. Cooling or treating the reaction products with benzene precipitates amino compounds, which are submitted to the usual purification. All the meta-aminophenyl derivatives of oxadiazole (XX–XXIV) obtained in the present work fluoresce in UV light, and are soluble in dimethylformamide, formic acid, and hydrochloric acid. Their solubilities decrease as the length of the hydrocarbon radical increases.

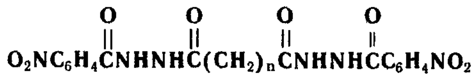
The diamines XX–XXIV prepared were condensed with diisocyanates according to the equations



R–$(CH_2)_6$, 1,4-$C_6H_4$, 2,4-$CH_3C_6H_3$; $n = 2, 3$ and 4.

Table 1

Nitrobenzoylhydrazides of Dibasic Carboxylic Acids

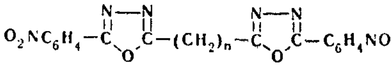


$$O_2NC_6H_4\overset{O}{\overset{\|}{C}}NHNH\overset{O}{\overset{\|}{C}}(CH_2)_n\overset{O}{\overset{\|}{C}}NHNH\overset{O}{\overset{\|}{C}}C_6H_4NO_2$$

| Compound | Position of nitro group | *n* | Mp, °C | Formula | N, % |  | Yield, % |
|---|---|---|---|---|---|---|---|
|  |  |  |  |  | Found | Calculated |  |
| I | o | 2 | 255—256 | $C_{18}H_{16}N_6O_8$ | 19.05 | 18.91 | 73 |
| II | m | 2 | 252—253 | $C_{18}H_{16}N_6O_8$ | 18.90 | 18.91 | 80 |
| III | p | 2 | 282—283 | $C_{18}H_{16}N_6O_8$ | 19.02 | 18.91 | 81 |
| IV | o | 3 | 303—304 | $C_{19}H_{18}N_6O_8$ | 18.00 | 17.80 | 85 |
| V | m | 3 | 293—294 | $C_{19}H_{18}N_6O_8$ | 17.71 | 17.80 | 94 |
| VI | p | 3 | 297—298 | $C_{19}H_{18}N_6O_8$ | 18.01 | 17.80 | 91 |
| VII | o | 4 | 275—276 | $C_{20}H_{20}N_6O_8$ | 18.60 | 18.33 | 90 |
| VIII | m | 4 | 255—256 | $C_{20}H_{20}N_6O_8$ | 18.34 | 18.33 | 91 |
| IX | n | 4 | 285—286 | $C_{20}H_{20}N_6O_8$ | 18.17 | 18.33 | 89 |
| X | o | 7 | 267—268 | $C_{23}H_{26}N_6O_8$ | 16.26 | 16.34 | 95 |
| XI | m | 7 | 227—228 | $C_{23}H_{26}N_6O_8$ | 16.16 | 16.34 | 96 |
| XII | p | 7 | 255—257 | $C_{23}H_{26}N_6O_8$ | 16.34 | 16.34 | 96 |

Table 2

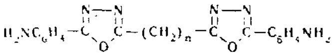
$\alpha$-$\omega$-Bis[2-(5-nitrophenyl-1,3,4-oxadiazolyl)]alkanes



| Compound | Nitro group position | *n* | Mp, °C | Formula | N, % |  | Yield, % |
|---|---|---|---|---|---|---|---|
|  |  |  |  |  | Found | Calculated |  |
| XIII | m | 2 | 255—256 | $C_{18}H_{12}N_6O_6$ | 20.64 | 20.58 | 82 |
| XIV | p | 2 | 284—285 | $C_{18}H_{12}N_6O_6$ | 20.48 | 20.58 | 80 |
| XV | m | 3 | 183—184 | $C_{19}H_{14}N_6O_6$ | 19.95 | 19.90 | 94 |
| XVI | n | 3 | 175—176 | $C_{19}H_{14}N_6O_6$ | 19.73 | 19.90 | 74 |
| XVII | m | 4 | 201—202 | $C_{20}H_{16}N_6O_6$ | 19.02 | 19.26 | 87 |
| XVIII | p | 4 | 224—226 | $C_{20}H_{16}N_6O_6$ | 19.13 | 19.26 | 85 |
| XIX | p | 7 | 135—136 | $C_{23}H_{22}N_6O_6$ | 17.52 | 17.56 | 60 |

Table 3

$\alpha$-$\omega$-Bis[2-(5-aminophenyl-1,3,4-oxadiazolyl)]alkanes



$H_2NC_6H_4-C(=N-N=)C(-O-)-(CH_2)_n-C(=N-N=)C(-O-)-C_6H_4NH_2$

| Compound | Nitro group position | *n* | Mp, °C | Formula | Found: Number of $NH_2$ groups | Found: N, % | Calculated N, % | Yield, % |
|---|---|---|---|---|---|---|---|---|
| XX | m | 2 | 231—232 | $C_{18}H_{16}N_6O_2$ | 1.98 | 23.94 | 24.12 | 72 |
| XXI | p | 2 | 310—315 (decomp.) | $C_{18}H_{16}N_6O_2$ | 1.92 | 24.14 | 24.12 | 74 |
| XXII | m | 3 | 169—170 | $C_{19}H_{18}N_6O_2$ | 2.10 | 23.40 | 23.19 | 80 |
| XXIII | m | 4 | 179—180 | $C_{20}H_{20}N_6O_2$ | 2.00 | 22.16 | 22.33 | 73 |
| XXIV | p | 4 | 293 (decomp.) | $C_{20}H_{20}N_6O_2$ | 1.86 | 22.11 | 22.33 | 80 |

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*Theoretical 2 amino groups.

The reaction is run in dimethylformamide or hexamethylphosphamide solution at room temperature, for 1 hr followed by heating at 60° for 4–5 hr. The resultant products are separated by pouring the reaction products into water.

The synthesized polymers are colorless substances with a logarithmic viscosity equal to 0.2–0.5, which fluoresce in UV light. They are insoluble in ordinary organic solvents, slightly soluble in dimethylformamide, m-cresol, and sulfuric acid, and heating the polymers in the last three solvents leads to their partial decomposition. They melt without decomposition in the temperature range 245–310°, use of diisocyanates with aromatic radicals giving polymers with a higher melting point and lower viscosity. Increasing the length of the hydrocarbon chain in the diamine molecule does not substantially effect polymer decomposition temperature or viscosity (Table 4).

## EXPERIMENTAL

**Preparation of the nitrobenzoylhydrazide of dicarboxylic acids (I–XII).** 0.05 mole of the dichloride of the appropriate acid was added to a stirred and cooled solution of 0.1 mole of the hydrazide of the nitrobenzoic acid in a mixture of 80 ml dry dimethylformamide and 10 ml pyridine, at such a rate that the temperature of the reaction mixture remained at 20–25°. For p-nitrobenzohydrazide the reaction mixture temperature was held inside the limits 40–50°. After adding all the acid dichloride the mixture was stirred for 30 min, and then treated with excess of cold water. The crystalline product was filtered off, washed first with dilute HCl (3–5%), then with water, and dried. Crystallization from dimethylformamide raised the mps of the compounds obtained by 2–5° (Table 1).

**Preparation of α, ω-bis-[2-(5-nitrophenyl-1, 3, 4-oxadiazolyl)]-alkanes (XIII–XIX).**

**a) Cyclization of nitrobenzoylhydrazides of dicarboxylic acids in oleum.** 0.02 mole of the starting hydrazide was slowly added, with cooling and stirring, to 30 ml 20–24% oleum (temperature not above 20–25°). After a homogeneous solution had been obtained, the temperature was raised to 35–40°, and kept there for 4 hr. Then the products were cooled and slowly dropped onto cracked ice; the crystalline product obtained was filtered off, washed with water, until neutral, then dried. The compounds were purified by recrystallizing from dimethylformamide-dioxane (1:1) (Table 2).

**b) Cyclization of nitrobenzoylhydrazides of dicarboxylic acids in phosphorus oxychloride.** A round-bottomed flask, fitted with a reflux condenser and bubbler, was filled with a weighed amount of the nitrobenzoylhydrazide of the dicarboxylic acid, and a 10-fold excess (by weight) of $POCl_3$. The mixture was refluxed in an oil bath until evolution of HCl ceased, when the mass of hydrazide dissolved up. When the reaction was complete, the contents of the flask were poured in small portions onto cracked ice. An oily product came out, and crystallized on stirring. The crystals were filtered off, washed with water until neutral, and dried, yield 30–45%.

**Preparation of α, ω-bis[2-(5-aminophenyl-1, 3, 4-oxadiazolyl)]-alkanes (XX–XXIV).**

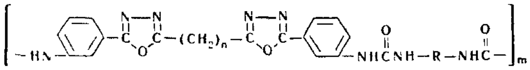
**a) Reduction of α, ω-bis[2-(5-nitrophenyl-1, 3, 4-oxadiazolyl)]-alkanes (XIII–XV).** A round-bottomed flask, fitted with air reflux condenser, bubbler, and dropping funnel, was filled with 3 g nitro compound and 20 ml purified α-methylnaphthalene. The mixture was heated to 200° in an oil bath, when the mass of nitro compound dissolved up. Then the calculated quantity of freshly distilled phenylhydrazine was added to the homogeneous solution, and heating continued until evolution of nitrogen ceased. When the reaction products were cooled, the product sought separated as pale yellow crystals, which were filtered off, washed with MeOH, then with ether, and dried. Compound XXI was purified by crystallization from dimethylformamide-dioxane (1:2); compounds XX and XXII were purified by fractional precipitation from aqueous hydrochloric acid solutions.

**b) Reduction of α, ω-bis[2-(5-nitrophenyl-1, 3, 4-oxadiazolyl)]-alkanes (XVII–XIX).** A mixture of 3 g dinitro compound and 8 ml freshly distilled phenylhydrazine was heated on an oil bath, when the solid gradually went into solution, which acquired a dark red color. At 140–150° an energetic reaction set in, accompanied by evolution of heat and vigorous evolution of benzene vapors, water, and nitrogen. When the reaction slowed down, as judged by the decreased nitrogen evolution, the oil bath temperature was raised to 185–190°, and heating continued until evolution of nitrogen ceased. Then the products were cooled and poured into excess benzene (20 ml). The product sought separated as crystals, which were separated off, washed with benzene, and dried (Table 3). Compound XXIII was purified by crystallization from MeOH or by fractional precipitation from hydrochloric acid solutions; compound XXIV was purified by recrystallizing from dimethylformamide.

**Preparation of polyureas (XXV–XXXII).** A solution of 0.005 mole diisocyanate in 5 ml dimethylformamide was added dropwise, with vigorous stirring, to a solution of 0.005 mole diamino compound in 40 ml purified dimethylformamide. After 1 hr the mixture was heated to 60°, and stirred and kept there for 4 hr. When p-phenylenediisocyanate was used, the resultant polymer separated out from the hot reaction products. When the reaction was complete, the polymer solution was cooled, and poured into excess water, MeOH, or other solvent. The polymer came out as white flocs, which were separated off and dried, yield quantitative (Table 4).

The polyureas from diamines XXI and XXIV and hexamethylenediisocyanate, were prepared in hexamethylphosphamide solution at 60°. The decomposition temperatures of the polymers, and the logarithmic viscosity in m-cresol, were 245° and $\eta_{\log}$ 0.15, 220° and $\eta_{\log}$ 0.14, respectively.

Table 4
Polyureas



| Compound | R | $n$ | T. decomp. °C | $\eta_{\log}$ In conc $H_2SO_4$ | $\eta_{\log}$ In m-cresol | Formula | N, % Found | N, % Calculated |
|---|---|---|---|---|---|---|---|---|
| XXV | $(CH_2)_6$ | 2 | 245 | 0.36 | 0.48 | $(C_{26}H_{28}N_8O_4)_m$ | 20.82 | 21.69 |
| XXVI | 1,4-$C_6H_4$ | 2 | 260 | 0.14 | 0.16 | $(C_{26}H_{20}N_8O_4)_m$ | 21.83 | 22.04 |
| XXVII | 2,4-$CH_3C_6H_3$ | 2 | 255 | 0.22 | 0.39 | $(C_{27}H_{22}N_8O_4)_m$ | 20.81 | 21.45 |
| XXVIII | $(CH_2)_6$ | 3 | 260 | 0.30 | 0 41 | $(C_{27}H_{30}N_8O_4)_m$ | 20.79 | 21.12 |
| XXIX | 2,4-$CH_3C_6H_3$ | 3 | 270 | 0.10 | 0.15 | $(C_{28}H_{24}N_8O_4)_m$ | 20 84 | 20.88 |
| XXX | $(CH_2)_6$ | 4 | 245 | 0.51 | 0.60 | $(C_{28}H_{32}N_8O_4)_m$ | 20.43 | 20.58 |
| XXXI | 1,4-$C_6H_4$ | 4 | 310 | 0.14 | 0.18 | $(C_{28}H_{24}N_8O_4)_m$ | 21.05 | 20.88 |
| XXXII | 2,4-$CH_3C_6H_3$ | 4 | 250 | 0.14 | 0.21 | $(C_{29}H_{26}N_8O_4)_m$ | 20.76 | 20.34 |

The amino group was estimated by potentiometric titration with sodium nitrite in hydrochloric, acetic, or formic acid, as described in [11]. The logarithmic viscosities of the polyureas were determined in conc $H_2SO_4$ (d 1.84) or m-cresol, with an Ostwald viscosimeter, at 25 ± 0.05°. The heat resistance of the polyureas were determined thermogravimetrically, the specimen being heated at the rate of 2°/min. Weight losses were determined at intervals with a torsion balance.

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