CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR V. V. KORSHAK, E. S. KRONGAUZ,

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Abstract

Full Text

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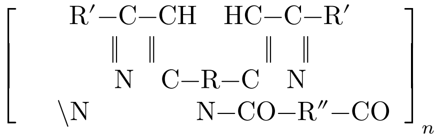
SYNTHESIS OF POLYPYRAZOLES

In recent years, in connection with the search for new polymers, polythiazoles and polybenzimidazoles have been synthesized; these represent a new type of polymer with a cyclolinear structure ($^{1-3}$).

Using the method we developed for the synthesis of tetraketones (^{6}), we have for the first time carried out the synthesis of high-molecular-weight compounds containing alternating pyrazole rings in the chain. The synthesis of polypyrazoles of the general formula



$$\left[\begin{array}{l} \quad R'{-}C{-}CH \quad HC{-}C{-}R' \\ \qquad \| \quad \| \qquad\quad \| \quad \| \\ \qquad N \quad C{-}R{-}C \quad N \\ \backslash N \qquad\quad N{-}CO{-}R''{-}CO \end{array}\right]_n$$

where $R = C_6H_4{-}O{-}C_6H_4;\ C_6H_4{-}CH_2{-}CH_2{-}C_6H_4;\ (CH_2)_8$

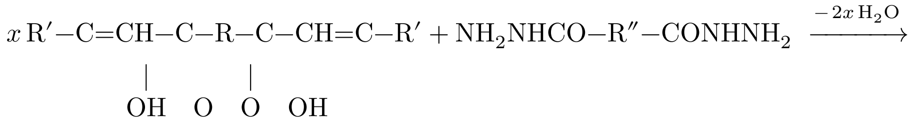
$R' = CH_3;\ C_6H_5$

$$R'' = (CH_2)_4$$

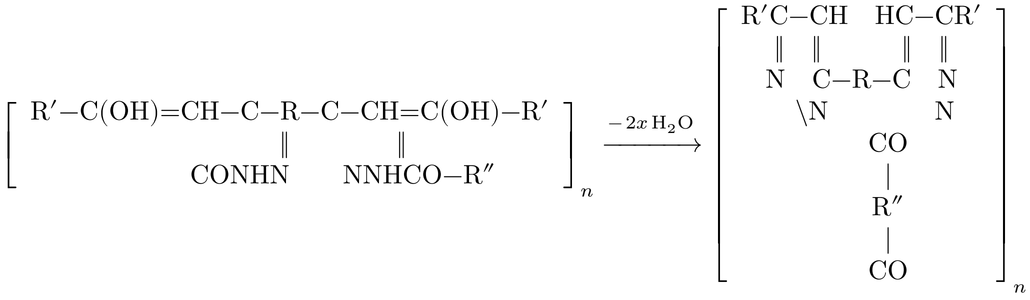
R″ = [[unclear: substituted phenylene ring]]

was carried out by the interaction of bis-(β-diketones) of the type $R'COCH_2CO{-}R{-}COCH_2COR'$ with dihydrazides of dicarboxylic acids. We have called this reaction polycyclization, since formation of the polymer takes place as a result of closure of a pyrazole or another ring.

A detailed study of the reaction products showed that polycyclization proceeds in two stages. In the first stage, formation of a polyhydrazone occurs; in the second, closure of the pyrazole rings occurs, leading to the formation of polypyrazoles. The overall reaction may be represented by the following scheme:



$$x\,\mathrm{R'{-}\underset{\displaystyle OH}{C}{=}CH{-}\underset{\displaystyle O}{C}{-}R{-}\underset{\displaystyle O}{C}{-}CH{=}\underset{\displaystyle OH}{C}{-}R'} + \mathrm{NH_2NHCO{-}R''{-}CONHNH_2} \xrightarrow{-2x\,\mathrm{H_2O}}$$



$$\left[\mathrm{R'{-}C(OH){=}CH{-}\underset{\displaystyle CONHN}{\overset{\Vert}{C}}{-}R{-}\underset{\displaystyle NNHCO{-}R''}{\overset{\Vert}{C}}{-}CH{=}C(OH){-}R'}\right]_n \xrightarrow{-2x\,\mathrm{H_2O}} \left[\begin{array}{c} \mathrm{R'C{-}CH \quad HC{-}CR'} \\ \Vert \quad \Vert \qquad \Vert \quad \Vert \\ \mathrm{N \quad C{-}R{-}C \quad N} \\ \backslash\mathrm{N} \qquad\qquad \mathrm{N} \\ \mathrm{CO} \\ | \\ \mathrm{R''} \\ | \\ \mathrm{CO} \end{array}\right]_n$$

polyhydrazone polypyrazole

Formation of polyhydrazones occurs upon boiling an equimolecular mixture of the bis-(β-diketone) and the acid dihydrazide in absolute ethyl alcohol. The use of glacial acetic acid as solvent, although it accelerates the process of polyhydrazone formation, leads to a decrease in the yield and molecular weight of the polymer formed. Polyhydrazones are greenish powders soluble in ordinary organic solvents; they have no sharp melting point, since upon heating of the polyhydrazones partial formation occurs.

polypyrazoles having higher melting temperatures. The reduced viscosity of 0.5% solutions of polyhydrazones in cresol reached 0.4.

Polypyrazoles are obtained in quantitative yield by heating polyhydrazones in vacuo in a nitrogen atmosphere at the melting temperature for 3–5 hr. They are yellowish powders, soluble in cresol, dimethylformamide, concentrated sulfuric and formic acids. In the process of formation of polypyrazoles as a result of ring closure, the length of the polymer chain decreases, which leads to a decrease in viscosity. Thus, the reduced viscosity of polymer solutions in cresol falls in this case from 0.4 to 0.1. The molecular weight of a polypyrazole with reduced viscosity 0.1, measured by the isopiestic method in dimethylformamide, is 9200. The synthesis of polypyrazoles can also be carried out in a single stage by conducting the reaction of 4,4′-bis(acetoacetyl)diphenylethane with adipic acid dihydrazide in boiling benzyl alcohol. An attempt to obtain polypyrazoles in the melt did not give positive results. The structure of the synthesized polyhydrazones and polypyrazoles is confirmed by elemental-analysis data, by the study of the infrared and ultraviolet spectra of model compounds, polymers, and the products of their alkaline and acid hydrolysis.

The ultraviolet spectra of the polyhydrazones had intense absorption bands in the regions of 270 mμ and 365 mμ, which was in good agreement with the spectrum of the model compound—acetylhydrazone of 4,4′-bis(acetoacetyl)diphenylethane. The ultraviolet spectra of the polypyrazoles also agreed well with the spectrum of the model compound, chosen as 4,4′-bis-[3-(5-methyl-N-acetylpyrazolyl)]diphenylethane, and had maxima in the regions of 270 mμ and 320 mμ. For methanol-soluble polymers obtained from sebacyl diacetophenone, the ultraviolet spectral curves were similar in appearance to those for the model compounds; however, a bathochromic shift of 40 mμ was observed: thus, the polyhydrazone had a maximum at 325 mμ, poly{4,4′-bis-[3-(1-adipyl-5-phenylpyrazolyl)]octamethylene} at 315 mμ, and the model compounds at 285 mμ and 275 mμ, respectively. An analogous picture was observed by Marvel and co-workers for polybenzimidazoles (2).

As the investigation of the polypyrazoles showed, they are products whose polymer chain, along with pyrazole units, also includes a certain number of unchanged hydrazone units. We carried out alkaline and acid hydrolysis of the products obtained.

Treatment of the polyhydrazone obtained from 4,4′-bis(acetoacetyl)diphenyl oxide with concentrated sulfuric acid led to destruction of the polymer chain and to the formation of bipyrazole—4,4′-bis-[3-(5-methylpyrazolyl)]diphenyl oxide, identical to the bipyrazole synthesized by us from the corresponding bis(β-diketone) and hydrazine hydrate. On the action of concentrated hydrochloric acid on the polyhydrazone, likewise as a result of complete hydrolysis, the hydrochloride salt of bipyrazole was isolated as the sole reaction product.

In contrast to polyhydrazones, polypyrazoles proved to be resistant to hydrolysis by water on boiling for 1 hr and to brief exposure (0.5 hr) to hot concentrated H_2SO_4. After this treatment, the polypyrazoles had the same melting temperature and viscosity as the starting sample. Prolonged action of concentrated sulfuric acid on polypyrazoles with heating leads to the formation of a complex mixture of sulfonated products, which we did not investigate.

Alkaline hydrolysis of a polyhydrazone and a polypyrazole with 25% KOH solution on boiling for 12 hr proceeds analogously to acid hydrolysis and is also accompanied by complete destruction of the polymer chain. But, in contrast to the action of acid on a polyhydrazone, alkali does not cause closure of the pyrazole ring; in connection with this, different substances are obtained as the final products of alkaline hydrolysis of the polyhydrazone and the polypyrazole.

This difference is especially clearly seen in studying the IR spectra of the initial and final hydrolysis products.

In the IR spectrum of the initial polypyrazole there is an intense band at 1725 cm^{-1}, which may be assigned to vibrations of the carbonyl group of the hydrazide residue bound to the pyrazole ring (^{4}); in the IR spectrum of the hydrolysis product of the polypyrazole this band is absent, and its spectrum is identical with the spectrum of authentic 4,4′-bis-[3-(5-methylpyrazolyl)]diphenylethane.

At the same time, in the IR spectrum of the product of alkaline hydrolysis of the polyhydrazone there is an intense absorption band at 1680 cm^{-1}, indicating the presence of a $-C=O$ group conjugated with the nucleus (^{5}).

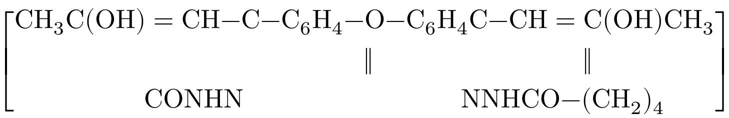
Table 1

Properties of polyhydrazones

No.	Reaction temp., °C; solvent	Duration, h	Melting temp., °C	Intrinsic viscosity	Found, % C	Found, % H	Found, % N	Calculated, % C	Calculated, % H	Calculated, % N
1	70; ethanol	40	185–210	0.4	63.67	6.41	11.47	65.54	5.88	11.76
2	70; ethanol	36	156–180	0.32	68.46	6.89	11.98	68.85	6.55	11.48
3	80; glacial CH_3COOH	0.5	65–75	0.08	70.50	7.42	9.90	70.58	7.35	10.29
4	70; ethanol	21	250–260	0.16	–	–	11.02	–	–	11.02
5	70; ethanol	10	165–170	0.08	58.20	7.17	15.62	57.20	7.14	16.66
6	70; ethanol	100	160–170	0.06	59.60	7.42	15.95	58.28	7.42	15.99

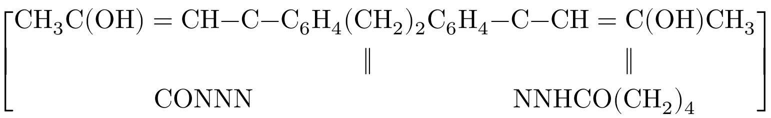
Repeating unit of the polymer

1



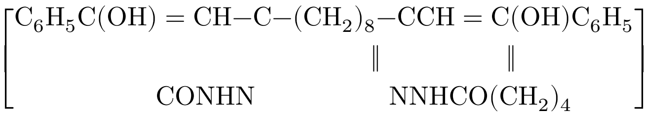
$$\left[\begin{array}{l}\mathrm{CH_3C(OH)=CH{-}C{-}C_6H_4{-}O{-}C_6H_4C{-}CH=C(OH)CH_3}\\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\| \qquad\qquad\qquad\qquad \|\\ \qquad\qquad\mathrm{CONHN}\qquad\qquad\qquad\qquad\mathrm{NNHCO{-}(CH_2)_4}\end{array}\right]$$

2



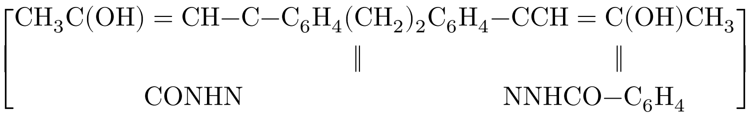
$$\left[\begin{array}{l}\mathrm{CH_3C(OH)=CH{-}C{-}C_6H_4(CH_2)_2C_6H_4{-}C{-}CH=C(OH)CH_3}\\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\| \qquad\qquad\qquad\qquad\qquad \|\\ \qquad\qquad\mathrm{CONNN}\qquad\qquad\qquad\qquad\qquad\mathrm{NNHCO(CH_2)_4}\end{array}\right]$$

3



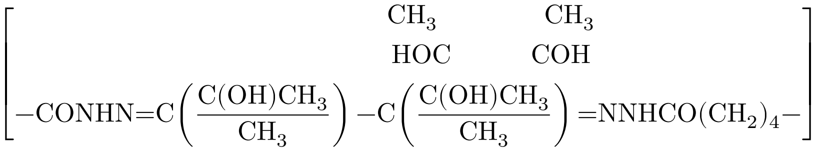
$$\left[\begin{array}{l} C_6H_5C(OH)=CH-C-(CH_2)_8-CCH=C(OH)C_6H_5 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \| \qquad\qquad \| \\ \qquad\qquad CONHN \qquad\qquad\quad NNHCO(CH_2)_4 \end{array}\right]$$

4



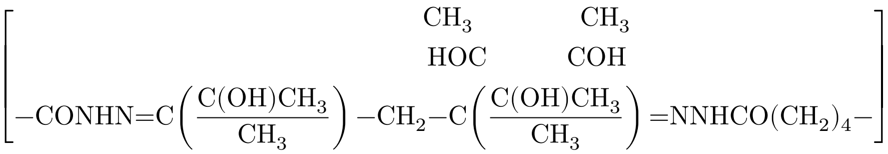
$$\left[\begin{array}{l} CH_3C(OH)=CH-C-C_6H_4(CH_2)_2C_6H_4-CCH=C(OH)CH_3 \\ \qquad\qquad\qquad\qquad\qquad\quad \| \qquad\qquad\qquad\qquad \| \\ \qquad\qquad CONHN \qquad\qquad\qquad\qquad NNHCO-C_6H_4 \end{array}\right]$$

5



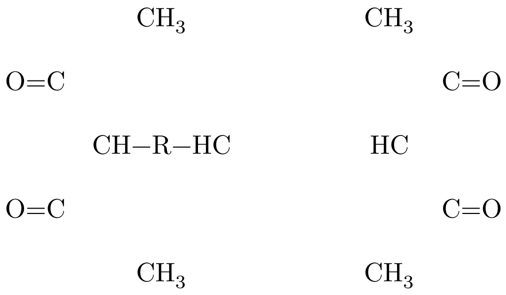
$$\left[\begin{array}{c} \qquad\qquad CH_3 \qquad\quad CH_3 \\ \qquad\qquad HOC \qquad\quad COH \\ -CONHN=C\left(\frac{C(OH)CH_3}{CH_3}\right)-C\left(\frac{C(OH)CH_3}{CH_3}\right)=NNHCO(CH_2)_4- \end{array}\right]$$

6



$$\left[\begin{array}{c} \qquad\qquad\qquad CH_3 \qquad\quad CH_3 \\ \qquad\qquad\qquad HOC \qquad\quad COH \\ -CONHN=C\left(\frac{C(OH)CH_3}{CH_3}\right)-CH_2-C\left(\frac{C(OH)CH_3}{CH_3}\right)=NNHCO(CH_2)_4- \end{array}\right]$$

In the course of the investigation we established that bis-(β-diketones) of branched structure:



$$\begin{array}{ccccc} & CH_3 & & CH_3 & \\ O=C & & & & C=O \\ & CH-R-HC & & HC & \\ O=C & & & & C=O \\ & CH_3 & & CH_3 & \end{array}$$

where $R =$ —, (CH_2), form only polyhydrazones. We were unable to convert the latter into polypyrazoles.

The characteristics of the synthesized polyhydrazones and polypyrazoles are given in Tables Nos. 1 and 2.

Table 2

Properties of polypyrazoles

No. p/p	Reaction temperature, °C, and vacuum	Melting temperature, °C	Intrinsic viscosity	Found, % C	Found, % H	Found, % N	Calculated, % C	Calculated, % H	Calculated, % N
1	200-210/1 mm	210-220	0.1	69.17	5.77	12.43	70.91	5.45	12.73
2	$200/10^{-4}$	218-225	0.14	73.04	6.36	12.38	74.24	6.23	12.42
3	225-235/1 mm	100-120	0.08	74.86	7.39	11.77	75.56	7.13	11.02
4	250/1 mm	260-280	0.12			12.59			11.86

Repeating unit of the polymer

1

$$\left[\begin{array}{c}\text{pyrazole ring with } CH_3C{-}CH \text{ and } N{-}C{-}C_6H_4{-}O{-}C_6H_4{-}C{-}N \\ \text{linked to a second pyrazole ring } HC{-}CCH_3, \text{ and } N{-}CO(CH_2)_4CO\end{array}\right]_n$$

2

$$\left[\begin{array}{c}\text{pyrazole ring with } CH_3C{-}CH \text{ and } N{-}C{-}C_6H_4(CH_2)_2C_6H_4{-}C{-}N \\ \text{linked to a second pyrazole ring } HC{-}CCH_3, \text{ and } N{-}CO(CH_2)_4CO\end{array}\right]_n$$

3

$$\left[\begin{array}{c}\text{pyrazole ring with } C_6H_5C{-}CH \text{ and } N{-}C{-}(CH_2)_8{-}C{-}N \\ \text{linked to a second pyrazole ring } HC{-}CC_6H_5, \text{ and } N{-}CO(CH_2)_4CO\end{array}\right]_n$$

4

$$\left[\begin{array}{c}\text{pyrazole ring with } CH_3C{-}CH \text{ and } N{-}C{-}C_6H_4(CH_2)_2C_6H_4{-}C{-}N \\ \text{linked to a second pyrazole ring } HC{-}CCH_3, \text{ and } N{-}CO{-}C_6H_4{-}CO\end{array}\right]_n$$

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Note: Figure translations are in progress. See original paper for figures.

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