SYNTHESIS OF BIS(ISOINDOLO-1,2-sym-TRIAZOL-5-ON-2-YLS) AND 10,10'-ARYLENEBIS[7H-BENZO-[de]-sym-TRIAZOLO[5,1-a]ISOQUINOLIN-7-ONES]

V. V. Korshak, A. L. Rusanov,
S. N. Leont'eva, and T. K. Dzhashiashvili

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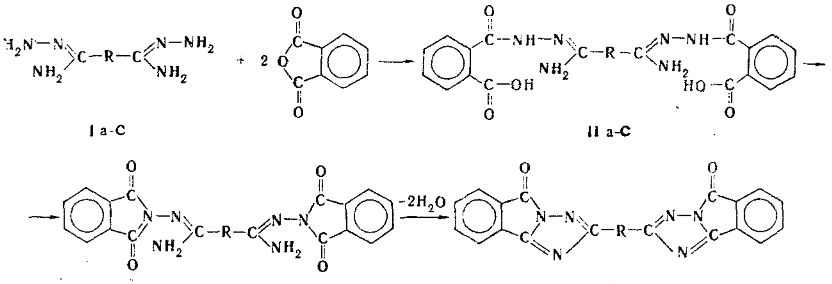
Compounds with a bistriazolone structure were obtained by reaction of bisamidrazones of oxalic, isophthalic, and terephthalic acids with phthalic and naphthalic anhydrides. The heterocyclic products of the reaction of the bisamidrazones with phthalic anhydride react with o-phenylenediamine and are converted to arylenebis[1-(3-sym-triazol-5-yl)-2-(benzimidazolyl)phenylenes].

In 1968 we proposed [1] that the final products of the reaction of bisamidrazones with tetracarboxylic acid dianhydrides are polybenzoylene-sym-triazoles (polytriazoloisomidolones) rather than poly(o-carboxy)-phenyl-sym-triazoles [2] or polyamidinoimides [3]. We carried out model reactions of bisamidrazones of dicarboxylic acids – oxalic, isophthalic, and terephthalic – with phthalic and naphthalic anhydrides in order to establish the structures of the polymeric products and select the optimum conditions for the synthesis of polyaroylene-sym-triazoles. The reaction with phthalic anhydride was carried out in polyphosphoric acid (PPA) [4] at 160-180°C and also under the conditions of a multistep reaction of the starting compounds in polar organic solvents with subsequent heat treatment of the products. Condensation in PPA gives a mixture that is difficult to separate, whereas the multistep process makes it possible in all cases to obtain the desired bis(isoindol-1,2-sym-triazol-5-on-2-yls) (IVa-c):



I-IV a R=p-C_6H_4; b R=m-C_6H_4; c R=–

The first step was realized in diemthylformamide (DMFA) or dimethyl sulfoxide (DMSO) and gave quantitative yields of products that can be considered to be N,N'-di-(o-carboxybenzoyl)bisamidrazones IIa-c: when they were heated they melted twice, solidified, and, finally, melted without subsequent solidification. According to the IR spectra, when IIa-c are heated to 200° they are apparently converted to N,N'-di(phthalimido)diamidines (IIIa-c), which are converted to IVa-c at 370°.

The relatively low yields of IVa-c, which, in contrast to the data in [5], reach 50-54%, are probably explained by partial decomposition of IIIa-c under the severe cyclization conditions, which are due to the low nucleophilicity of the amide NH_2 group in IIIa-c. In addition, the reduction in the yields of IVa-c may

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TABLE 1. Characteristics of the Compounds Obtained

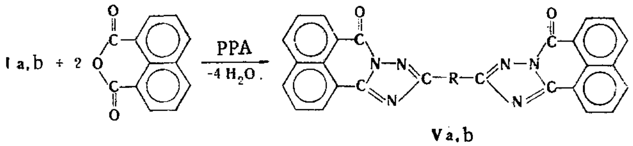
Compound	mp, ℃	Empirical formula	Found, %			Calc., %			UV spectra		IR spectra*, cm⁻¹		Yield, * %
			C	H	N	C	H	N	λ_{max}, nm	lg ε	C=O	C=N	
IVa	387	$C_{24}H_{12}N_6O_2$	69,8	3,0	20,4	69,2	2,9	20,3	245 285	4,64 4,86	1760 1790	1620	54
IVb	350	$C_{24}H_{12}N_6O_2$	69,6	2,9	20,3	69,2	2,9	20,3	242 282	4,18 3,90	1760 1790	1610	52
IVc	420	$C_{18}H_8N_6O_2$	63,4	2,1	25,4	63,5	2,4	24,7	217 287	4,85 4,28	1760 1790	1630	50
Va	410	$C_{32}H_{16}N_6O_2$	73,8	3,1	16,2	74,4	3,1	16,3	224 250 273 380	4,88 4,65 4,62 4,72	1750	1595	84
Vb	361	$C_{32}H_{16}N_6O_2$	74,1	3,1	16,5	74,4	3,1	16,3	240 292 390 412	4,23 4,34 4,79 4,76	1750	1590	82
VIa	420	$C_{36}H_{24}N_{10}$	72,1	4,5	24,1	72,5	4,1	23,5	224 295	4,78 4,81	—	1620	60
VIb	430	$C_{36}H_{24}N_{10}$	71,6	4,7	22,6	72,5	4,1	23,5	218 277	4,88 4,75	—	1630	62

* Recorded from 10^{-5} M solutions in H_2SO_4.

† Determined after two high-vacuum sublimations.

be associated with the possibility of opening of the isoindolo-1,2-sym-triazol-5-one ring, as in the case of 1,2-benzoylenebenzoimidazole rings [6]. This is also possibly responsible for the difficulties associated with the synthesis of IVa-c in PPA.

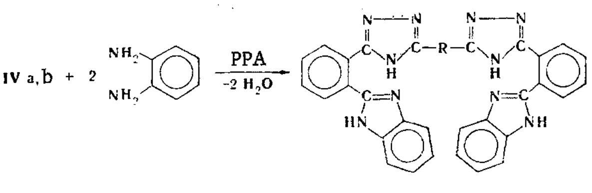
In contrast to IVa-c, 10,10'-arylenebis(7-H-benzo[de]-sym-triazolo[5,1-a]isoquinolin-7-ones) (Va, b) can be obtained by both the multistep method and in one step in PPA; in agreement with the data in [7], the reaction in PPA gives better results.



Va,b

Compound Vc could not be obtained; this is possibly explained by the decomposition of Ic in PPA in analogy with oxalic acid dihydrazide [8].

A comparative study of the chemical stability of IV and V showed that, in contrast to V, IV readily react with nucleophiles with opening of the CO–N bond. Thus the reaction of IVa, b with o-phenylenediamine in PPA, in analogy with 1,2-benzoylenebenzimidazoles [6], led to the production of arylenebis-1-(3-sym-triazol-5-yl)-2-(2-benzimidazolyl)phenylenes:



VI a,b

EXPERIMENTAL

The synthesis and purification of I were realized by known methods (a [2], b [5], and c [9]).

Compounds IVa-c. A 0.02-mole sample of phthalic anhydride was added to a solution of 0.01 mole of Ia-c in 20 ml of DMFA (or DMSO), and the mixture was stirred at 20° for 3 h. The solution was poured into 500 ml of acetone, and the precipitated II was removed by filtration, washed successively with cold DMFA and diethyl ether, and dried at 20° (10^{-3} mm), for 20 h. Reaction products II were heated to 370° (10^{-3}mm), during which sublimation of the resulting products was observed. The sublimates were collected and sublimed twice at 340-370° (10^{-3} mm). The principal characteristics of products IVa-c are presented in Table 1.

Compounds Va,b. A mixture of 0.01 mole of Ia,b, 0.02 mole of naphthalic anhydride, and 90 ml of 116% PPA was heated slowly with stirring to 170-180° for 10 h, after which it was stirred at this temperature for another 12 h. It was then poured into water, and the products were removed by filtration, washed with aqueous sodium bicarbonate solution, and extracted with ethanol. The products were dried and subjected to two sublimations at 330° (10^{-3} mm). The principal characteristics of Va,b are presented in Table 1.

Compounds VIa,b. A mixture of 0.01 mole of IIIa-c, 0.02 mole of o-phenylenediamine, and 20 ml of 116% PPA was heated gradually to 200-210°, after which it was stirred at this temperature for 8-9 h. It was then poured into water, and the white precipitate was removed by filtration, washed successively with cold DMFA, water, and acetone, dried, and recrystallized from DMFA. The principal characteristics of VIa,b are presented in Table 1.

According to thin-layer chromatography, all of the compounds obtained are individual substances.

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