

## SYNTHESIS AND TRANSFORMATIONS OF ACIDS OF THE TRIAZOLE SERIES.

## IV.\* 3,5-BIS(CARBOXYPHENYL)-1,2,4-TRIAZOLES AND THEIR DERIVATIVES

R. G. Sultangareev, V. A. Lopyrev, L. G. Rozinova,  
and M. G. Voronkov

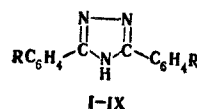
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3,5-Di(*m*- and *p*-tolyl)-1,2,4-triazoles were obtained by reaction of formalin with 2,5-ditolyl-1,3,4-oxadiazoles and subsequent hydrolysis of the resulting formyl derivatives. 3,5-Di(*o*-tolyl)-1,2,4-triazole cannot be obtained by this method. The oxidation of 3,5-ditolyl-1,2,4-triazoles leads to 3,5-bis(carboxyphenyl)-1,2,4-triazoles, which were converted to diesters and dihydrazides.

2,5-Bis(carboxyphenyl)1,3,4-oxadiazoles are intermediates for the preparation of polycondensed heat-resistant polymers [2, 3]. Previously unknown analogs of these monomers containing a 1,2,4-triazole ring were synthesized in the present research. Up until now very little study has been devoted to monomers of this type. The synthesis of 3,5-bis(carboxyphenyl)-1,2,4-triazoles has been only briefly indicated [4].

The oxidation of the corresponding 3,5-ditolyl-1,2,4-triazoles was used for the synthesis of 3,5-bis(carboxyphenyl)-1,2,4-triazoles (III, IV). 3,5-Ditolyl-1,2,4-triazoles (I, II) were obtained by reaction of readily accessible ditolyloxadiazoles [5, 6] with formalin and subsequent hydrolysis of the formyl derivatives [7]. We were unable to obtain 3,5-bis(*o*-tolyl)-1,2,4-triazole by means of this method, possible because of steric hindrance.

During the oxidation the starting triazoles undergo partial decomposition to give isophthalic or terephthalic acid (they are the principal products in acidic media). Pure 3,5-bis(carboxyphenyl)-1,2,4-triazoles were obtained by saponification of their esters (V-VII). We also synthesized the dihydrazides (VIII, IX) of the acids. The triazoles obtained in this research are presented in Table 1.



I R=*m*-CH<sub>3</sub>; II R=*p*-CH<sub>3</sub>; III R=*m*-COOH; IV R=*p*-COOH; V R=*m*-COOCH<sub>3</sub>;  
VI R=*p*-COOCH<sub>3</sub>; VII R=*p*-COOC<sub>2</sub>H<sub>5</sub>; VIII R=*m*-CONHNH<sub>2</sub>; IX R=*p*-CONHNH<sub>2</sub>

The IR spectra of these compounds contain four absorption bands that are characteristic for the stretching vibrations of the triazole ring at 1100-1505 cm<sup>-1</sup>, the deformation vibrations of the triazole ring appear at 950-1050 cm<sup>-1</sup>, and absorption bands of benzene rings and C=O groups are present at, respectively, 1650 and 1680-1730 cm<sup>-1</sup>. The absorption bands at 2800-3200 cm<sup>-1</sup> are related to the stretching vibrations of the NH bond [9, 10].

## EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded. The purity of the compounds was monitored by repeated recrystallization from appropriate solvents and determination of the melting points.

**3,5-Ditolyl-1,2,4-triazoles (I, II).** A mixture of 30 mmole of the appropriate 2,5-ditolyl-1,3,4-oxadiazole [5] and 70 ml of formalin was heated with stirring at 170-180°C for 8 h. After cooling, the mixture began to crystallize. It was then treated with water, and the precipitate was removed by filtration, washed with water, refluxed with 10% HCl, washed again with water, dried, and recrystallized from Methyl Cellosolve.

\*See [1] for communication III.

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of USSR, Irkutsk 664033. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 6, pp. 848-849, June, 1978. Original article submitted March 26, 1977.

TABLE 1. Synthesized Triazoles

Com- pound	mp, °C	Found, %			Empirical formula	Calc.,			Yield, %
		C	H	N		C	H	N	
I	154—155	71,6	6,4	15,7	$C_{16}H_{15}N_3 \cdot H_2O$	71,9	6,4	15,7	36
II	245—246*	77,4	6,0	16,8	$C_{16}H_{15}N_3$	77,0	6,0	16,8	55
III	~380†	62,6	3,3	13,2	$C_{16}H_{11}N_3O_4$	62,1	3,5	13,5	48
IV	~390†	58,4	4,4	12,7	$C_{18}H_{11}N_3O_4 \cdot H_2O$	58,7	4,0	12,8	59
V	196	63,0	4,3	12,5	$C_{18}H_{15}N_3O_4$	64,0	4,4	12,4	63
VI	273	63,0	4,4	12,0	$C_{18}H_{15}N_3O_4$	64,0	4,4	12,4	78
VII	181	64,3	5,4	11,0	$C_{20}H_{19}N_3O_4$	65,7	5,2	11,5	70
VIII	>450	—	—	30,0	$C_{16}H_{15}N_7O_2$	—	—	29,1	60
IX	>460	54,5	4,9	26,5	$C_{16}H_{15}N_7O_2 \cdot H_2O$	54,0	4,8	27,5	41

\*According to [8], this compound has mp 248°C.

†With decomposition.

3,5-Bis(carboxyphenyl)-1,2,4-triazoles (III, IV). A) A mixture of 12 mmole of I or II, 56 mmole of  $KMnO_4$ , 1-2 g of  $NaHCO_3$ , and 100 ml of  $H_2O$  was heated for 8 h, after which the  $MnO_2$  was removed by filtration, and dilute HCl was added to the filtrate with stirring. The resulting precipitate was removed by filtration, washed with water, dried, and reprecipitated from a hot solution in Methyl Cellosolve by the addition of water.

B) The calculated amount of a 10% solution of KOH in alcohol was added dropwise in the course of 15-20 min to a hot solution of 20 mmole of V or VI in methanol, after which the mixture was cooled and acidified with HCl, and the precipitate was removed by filtration and washed with water.

3,5-Bis(carbalkoxyphenyl)-1,2,4-triazoles (V-VII). A) A mixture of 13 mmole of III or IV, 15 ml of methanol or ethanol, and 0.5 ml of concentrated  $H_2SO_4$  was refluxed for 4 h, after which it was cooled and treated with alcoholic KOH solution to pH 6-7. The resulting ester was recrystallized from methanol.

B) Excess dry HCl was bubbled into a suspension of 78 mmole of the dipotassium salt of IV in 90 ml of methanol, after which the mixture was poured into water, and the precipitated VI was removed by filtration, washed with water, and recrystallized from methanol.

3,5-Bis(carbohydrazidophenyl)-1,2,4-triazoles (VIII, IX). A mixture of 10 mmole of V or VI and 50 ml of hydrazine hydrate was refluxed for 6 h, after which the excess hydrazine hydrate was removed by vacuum distillation. The fine acicular crystals that formed when the residue was cooled were recrystallized from formamide.

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