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SYNTHESIS OF NITROPHENYL DERIVATIVES OF 1,3,4-OXADIAZOLE

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Acylation of nitrobenzhydrazides with nitrobenzoyl chlorides and ethyl chlorocarbonate yielded a number of corresponding 1,2-diacylhydrazines, which were converted by the action of phosphorus oxychloride to nitro-substituted 2,5-diphenyl- and 2-phenyl-5-ethoxy-1,3,4-oxidazoles.

2,5-Diphenyl-1,3,4-oxadiazole derivatives containing various substituents (Cl, Br, Alk, OAlk) in the phenyl rings are finding extensive application in scintillation technology and in other fields of science and technology [1-3].

The present paper is devoted to the synthesis of the little-studied nitro-substituted 2,5-diphenyl- and 2-phenyl-5-ethoxy-1,3,4-oxidiazoles via the scheme

I-VI VII-XI XII-XXI XXII-XXIX

We obtained starting 1,2-diacylhydrazines XII-XXI by acylation of the hydrazides of benzoic (I), 2-nitro- (II), 3-nitro- (III), 4-nitro- (IV), 3,5-dinitro- (V), and 2,4,6-trinitrobenzoic (VI) acids with the appropriate benzoyl chlorides, as well as ethyl chlorocarbonate. They were subsequently cyclized to oxidiazoles by the action of $POCl_3$.

The formation of nitro derivatives of 2-phenyl-5-ethoxy-1,3,4-oxadiazole is possible when there is only one nitro group in the benzene residue of the starting hydrazone (oxidiazoles XXVIII and XXIX). Di- and trinitro-substituted 1-benzoyl-2-carbethoxyhydrazines (XX

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TABLE 1. Synthetic Conditions and Characteristics of 1,2-Diacylhydrazines XII-XXI

Compound	Starting compounds		R	R′	Reaction conditions			mp, °C (crystallization solvent)	Found, %			Empirical formula	Calc., %			Yield, %
	hydrazide	chloride			solvent	temp., °C	time, h		C	H	N		C	H	N	
XII	II	X	2-$NO_2C_6H_4$	Pic[a]	EtOH	80	4,0	245–246 (AcOH)	39,7	1,9	19,8	$C_{14}H_8N_6O_{10}$	40,0	1,9	20,0	65
XIII	VI	VIII	Pic	3-$NO_2C_6H_4$	EtOH	35–40	4,0	240–241 (80% dioxane)	39,9	1,8	20,2	$C_{14}H_8N_6O_{10}$	40,0	1,9	20,0	70
XIII	VI	VIII	Pic	3-$NO_2C_6H_4$	Dioxane	20–25	1,5	240-241 (80% ")	39,9	1,8	20,2	$C_{14}H_8N_6O_{10}$	40,0	1,9	20,0	70
XIV	IV	X	4-$NO_2C_6H_4$	Pic	EtOH	80	4,0	262–263 (dioxane)	40,0	1,8	19,7	$C_{14}H_8N_6O_{10}$	40,0	1,9	20,0	67
XV	I	X	C_6H_5	Pic	Dioxane[b]	40–45	1,5	265–266 (dioxane)	44,5	2,4	18,3	$C_{14}H_9N_5O_8$	44,8	2,4	18,7	74
XV	XI	VII	Pic	C_6H_5	Dioxane	20–25	1,5	The same	44,5	2,4	18,3	$C_{14}H_9N_5O_8$	44,8	2,4	18,7	86
XVI	VI	IX	Pic	3,5-$(NO_2)_2C_6H_3$	Dioxane	50–55	1,5	279–280 (dioxane)[c]	36,3	1,6	21,2	$C_{14}H_7N_7O_{12}$	36,1	1,5	21,1	83в
XVII	VI	X	Pic	Pic	Dioxane	60–65	1,5	244–245[d] (AcOH)	32,8	1,2	21,7	$C_{14}H_6N_8O_{14}$	32,9	1,2	22,0	70
XVIII	III	XI	3-$NO_2C_6H_4$	OC_2H_5	AcOEt	20	2,0	147–149 (benzene)	47,2	4,0	16,4	$C_{10}H_{11}N_3O_5$	47,4	4,3	16,6	90
XIX	IV	XI	4-$NO_2C_6H_4$	OC_2H_5	AcOEt	20	2,0	185–187 (toluene)	47,4	4,7	16,6	$C_{10}H_{11}N_3O_5$	47,4	4,3	16,6	82
XIX	IV	XI	4-$NO_2C_6H_4$	OC_2H_5	AcOEt[b]	8–10	1,0	The same	47,4	4,7	16,6	$C_{10}H_{11}N_3O_5$	47,4	4,3	16,6	99
XX	V	XI	3,5-$(NO_2)_2C_6H_3$	OC_2H_5	AcOEt	25–30	2,0	160–161 (EtOH)	40,4	3,3	18,6	$C_{10}H_{10}N_4O_7$	40,3	3,3	18,8	90
XXI	VI	XI	Pic	OC_2H_5	AcOEt	35–40	2,0	206–207[e] (acetone–toluene)	35,0	2,7	20,2	$C_{10}H_9N_5O_9$	35,0	2,6	20,4	87
XXI	VI	XI	Pic	OC_2H_5	AcOEt[b]	10–15	1,0	The same	35,0	2,7	20,2	$C_{10}H_9N_5O_9$	35,0	2,6	20,4	99

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[a] Pic = 2,4,6-$(NO_2)_3C_6H_2$. [b] The experiments were carried out in the presence of pyridine. Pyridine was added dropwise to a suspension of hydrazone VI and acid chloride XI. [c] Compound XVI was obtained in 7-10% yield at 20-25°C. [d] IR spectrum: 3344 (NH) and 1728 cm^{-1} (C=O). [e] IR spectrum: 3200 (NH) and 1720 cm^{-1} (C=O).

TABLE 2. Yields and Characteristics of 2-Picryl-5-aryl-1,3,4-oxadiazoles XXII-XXVII [R = 2,4,6-$(NO_2)_3C_6H_2$]

Compound	Starting compound	R′	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
				C	H	N		C	H	N	
XXII	XII	2-$O_2NC_6H_4$	202—203	41,7	1,4	20,6	$C_{14}H_6N_6O_9$	41,8	1,5	20,9	50
XXIII	XIII	3-$O_2NC_6H_4$	245—246	41,6	1,6	20,7	$C_{14}H_6N_6O_9$	41,8	1,5	20,9	38
XXIV	XIV	4-$O_2NC_6H_4$	239—240	41,8	1,2	20,6	$C_{14}H_6N_6O_9$	41,8	1,5	20,9	48
XXV	XV	C_6H_5	237—238[a]	47,4	2,3	19,8	$C_{14}H_7N_5O_7$	47,1	2,0	19,6	56 b
XXVI	XVI	3,5-$(O_2N)_2C_6H_3$	263—264	37,2	1,0	22,1	$C_{14}H_5N_7O_{11}$	37,5	1,1	21,9	45
XXVII	XVII	2,4,6-$(O_2N)_3C_6H_2$	310—311[a]	34,3	0,8	23,0	$C_{14}H_4N_8O_{13}$	34,1	0,8	22,8	54

[a] From 90% dioxane. [b] Reaction time 10 h.

and XXI) remain unchanged even when they are refluxed in $POCl_3$ for a long time. This makes it possible to conclude that as the number of nitro groups in the phenyl ring of the diacylhydrazines (XX and XXI) increases, their ability to undergo closure to an oxadiazole ring decreases.

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil were recorded with a UR-10 spectrometer.

2,4,6-Trinitrobenzoyl Chloride (X). A 12.5-mmole sample of pyridine was added dropwise with stirring at 10-15°C to 52.5 mmole of $POCl_3$, after which 10 mmole of 2,4,6-trinitrobenzoic acid was added, during which the temperature of the reaction mixture was raised to 60-65°. The mixture was then stirred at 95-100° for 1 h, after which it was cooled to 10°. After 1 h, the solid material was removed by filtration, washed with two 10-ml portions of chloroform and ice water to neutrality, and dried to give acid chloride X, with mp 160-161°, in 92% yield.

2,4,6-Trinitrobenzhydrazide (VI). A solution of 11 mmole of 85% hydrazine hydrate in 5 ml of water was added dropwise with stirring at 15-20° to a solution of 5 mmole of 2,4,6-trinitrobenzoyl chloride in 35 ml of benzene. After 30 min, the temperature was raised to 40-45° and held there for 10 min. The mixture was then cooled to room temperature, and treated with 25 ml of water. The resulting precipitate was removed by filtration, washed with water, and dried to give 1.1 g (80%) of dark needles of VI with mp 187-188° (from water). Found: C 30.8; H 2.0; N 25.4%. $C_7H_6N_5O_7$. Calculated: C 31.0; H 1.8; N 25.8%. IR spectrum: 3280 (NH), 1668 (CO), 1609 (ring), and 1517 and 1353 cm^{-1} (NO_2).

1,2-Diacylhydrazines (XII-XXI). The synthetic conditions, yields, and characteristics of the nitrophenyl-substituted 1,2-diacylhydrazines are presented in Table 1.

The 1,2-diacylhydrazines XII-XXI were obtained as white crystalline substances that were quite soluble in pyridine, dioxane, and acetone, moderately soluble in acetic acid, and insoluble in ethanol, benzene, and water. They react with alkalis to give salts that decompose readily even under the influence of acetic acid. They are only slightly soluble in concentrated H_2SO_4 and practically insoluble in hydrochloric acid. When they are dissolved in concentrated HNO_3, they undergo oxidative destruction to the corresponding nitrobenzoic acids.

2,5-Diaryl-1,3,4-oxadiazoles (XXII-XXVII). A suspension of 2 mmole of 1,2-diacylhydrazine (XII-XVII) in 100 ml of $POCl_3$ was refluxed for 20 h, after which it was cooled to 0°, and the precipitated crystals were removed by filtration or the mixture was poured into water. The crystals were washed thoroughly with water, 3% KOH solution, alcohol, and ether, and dried. They were then recrystallized from dioxane. Oxidiazoles XXII-XXVII were obtained as colorless acicular crystals that were quite soluble in pyridine, dimethylformamide (DMF), and concentrated nitric and sulfuric acids, slightly soluble in alcohols, AcOH, and ethyl acetate, and insoluble in benzene, ether, and water. The yields and characteristics of the products are presented in Table 2. IR spectrum of XXVII: 1660 (oxadiazole ring); 1560 and 1350 cm^{-1} (NO_2).

2-(3-Nitrophenyl)-5-ethoxy-1,3,4-oxadiazole (XXVIII). A suspension of 5 mmole of 1-(3-nitrobenzoyl)-2-carbethoxyhydrazine in 10 ml of $POCl_3$ was refined for 4 h, after which it was cooled to 0°, and the solid material was removed by filtration, washed with petroleum ether and ethanol, and dried to give 0.9 g (76%) of oxadiazole XXVII in the form of white acicular crystals with mp 189-190° (from aqueous alcohol or acetone). Found: C 50.8; H 3.9

N 18.0%. $C_{10}H_9N_3O_4$. Calculated: C 51.0; H 3.8; N 17.8%.

2-(4-Nitrophenyl)-5-ethoxy-1,3,4-oxadiazole (XXIX). This compound, with mp 246-247° (acetone), was obtained in 60% yield as white crystals by the method used to prepare XXVIII. Found: C 51.2; H 3.7; N 17.9%. $C_{10}H_2N_3O_5$. Calculated: C 51.0; H 3.8; N 17.8%. IR spectrum: 1540 and 1350 (NO_2); 1610 (phenyl ring); 1250, 1120, and 1140 cm^{-1} (C-O-C).

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SIDE PRODUCTS IN THE ROSENMUND REDUCTION OF BENZOFURAN-2-CARBOXYLIC ACID CHLORIDES

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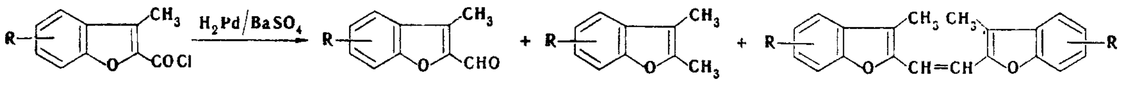
The corresponding 1,2-bis(2-benzofuryl)ethylenes and 2-methylbenzofurans were isolated as side products, along with the principal reaction products (2-formylbenzofurans), in the Rosenmund reduction of 3-, 5-, and 7-alkylbenzofuran-2-carboxylic acid chlorides. The bis(2-benzofuryl)ethylene structure was confirmed by the IR and PMR spectra data and alternative synthesis by reduction of the corresponding benzofuroins, obtained by benzoin condensation of 2-formylbenzofurans, with zinc amalgam in acidic media. The side formation of desoxybenzofuroin derivatives was noted in some cases in the benzoin condensation.

We have previously established (for example, see [1]) that, in addition to the chief reduction products (aldehydes II), small amounts of 2-methylbenzofurans (III) and crystalline side-unsaturated compounds are always formed in the Rosenmund reduction [2] of alkylbenzofuran-2-carboxylic acid chlorides (I). The IR spectra of the crystalline side-unsaturated compounds contain absorption bands at 1615-1620 cm^{-1}, and the PMR spectra contain a two-proton singlet at 7.03-7.06 ppm and a number of other features typical for the CH=CH increment. These data, together with the results of elementary analysis, make it possible to assign to them the structure of 1,2-dibenzofuryl derivatives of ethylene of the general formula IV.



Ia-e IIa-e IIIa-e IVa-e

I–IV a[*] R=H; b R=5-CH_3; c R=7-CH_3; d R=5-C_2H_5; e R=7-C_2H_5

For the alternative synthesis of IV we selected the method proposed by Ballard and Dehn [3] — preparation of 1,2-disubstituted ethylenes with aromatic groups by reduction of the corresponding benzoins. From 2-formylalkylbenzofurans II we obtained the corresponding benzofuroins V, which gave the expected ethylenes IV by reduction with zinc amalgam in

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[*] In what follows, the R values for V-VII for the letters are corresponding to those presented here.

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