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AZO BİLEŞİKLERİNİN HİDRAZİN HİDRAT İLE REDÜKTİF BÖLÜNMESİ VE BAZI YENİ 1,3,4-TİYADİAZOL TÜREVLERİ

REDUCTIVE CLEAVAGE OF AZO COMPOUNDS WITH HYDRAZINE HYDRATE AND SOME NEW 1, 3, 4-THIADIAZOLE DERIVATIVES

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SUMMARY

In this study, the azo groups of 2-aryl/alkylamino-5-[p-(1'-phenyl-3',5'-dimethyl-4'-pyrazolylazo)-phenyl]-1,3,4-thiadiazoles which were previously prepared by us were reduced with hydrazine hydrate without a catalyst in ethanol and the following compounds were obtained: 2-n-propylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (I), 2-n-buthylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (II), 2-cyclohexylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (III), 2-phenetylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (IV), 2-phenylamino-5-(p-aminophenyl) 1,3,4-thiadiazole (V). The structures of these substances were elucidated using UV, IR and NMR spectral methods besides elementary analysis.

ÖZET

Bu çalışmada, daha önce tarafımızdan hazırlanmış olan 2-aril/alkil'-1'-amino-5-[p-1'-fenil-3'5-dimetil-4'-pirazolilazo)-fenil]-1,3,4-tiyadiazollerin, azo grubu katalizörsüz olarak etanollü ortamda hidrazin

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hidratla redüksiyona uğratılarak, 2-n-propilamino-5-(p-aminofenil)-1, 3, 4-tiyadiazol (I), 2-n-butilamino-5-(p-aminofenil)- 1, 3, 4-tiyadiazol (II), 2-sikloheksilamino-5-(p-aminofenil)-1, 3, 4-tiyadiazol (III), 2-fenetilamino-5-(p-aminofenil)- 1, 3, 4-tiyadiazol (IV) ve 2-fenilamino-5-(p-aminofenil)-1, 3, 4-tiyadiazol (V) kazanılmıştır. Maddelerin yapıları, elemanter analiz ve UV, IR, NMR spektral bulguları yardımı ile aydınlatılmıştır.

INTRODUCTION

We have previously reported (1) the synthesis and spectroscopic analysis of 1, 3, 4-thiadiazoles with azo groups. It is known that hydrazine hydrate reduces the azo groups to amino groups in the presence of a catalyst (2). We had observed that hydrazine hydrate also reduced the azo group without a catalyst (3-5).

Owing to our interest in the synthesis of 2-alkyl/arylamino-5-(p-aminophenyl)-1, 3, 4-thiadiazoles, we attempted to prepare it by reductive cleavage with hydrazine hydrate.

EXPERIMENTAL

Melting points were taken on apparatus Buchi (Flawil/Schweiz) and are uncorrected. UV spectra were obtained with a 25 Model Beckman recording spectrophotometer. IR spectra were recorded on a Perkin-Elmer 577 Spectrophotometer in KBr. NMR spectra were recorded on a Varian A 60 D intrument using TMS as an internal standard.

General method for the preparation of the compounds

A mixture of the azo compound (0.0025 mol), hydrazine hydrate (3 ml of 99 %) and ethanol (30-40 ml) was stirred for 30 45 min at 60-65 C°. Excess ethanol was removed by distillation, when the water was added to the solution, white or pale yellow crystalline product was obtained and recrystallized from aqueous ethanol (1:1).

2-n Propylamino-5-(p-aminophenyl)-1, 3, 4-thiadiazole (I)

The substance was prepared according to the general method

from 1.03 g of 2-allylamino-5-[p-(1′-phenyl-3′, 5′-dimethyl-4′-pyrazolylazo) phenyl]-1, 3, 4-thiadiazole (Pale yellow needles).

2-n-Buthylamino-5-(p-aminophenyl)-1, 3, 4-thiadiazole (II)

The substance was prepared according to the general method from 1.07 g of 2 n-buthylamino-5-[p-(-1′-phenyl-3′, 5′-dimethyl-4′-pyrazolylazo) phenyl]-1, 3, 4-thiadiazole (White needles).

2-Cyclohexylamino-5-(p-aminophenyl)-1, 3, 4-thiadiazole (III)

The substance was prepared according to the general method from 1.14 g of 2-cyclohexylamino-5-[p-(1′-phenyl-3′ 5′-dimethyl-4′-pyrazolylazo) phenyl]-1, 3, 4-thiadiadiazole (White needles).

2-Phenethylamino-5-(p-aminophenyl)-1, 3, 4-thiadiazole (IV)

The substance was prepared according to the general method from 1,2 g of 2-phenethylamino-5-[p-(1′-phenyl-3′,5′-dimethyl 4′-pyrazolylazo) phenyl]-1,3,4-thiadiazole (White needles).

2-Phenyl-5-(p-aminophenyl)-1, 3, 4-thiadiazole (V)

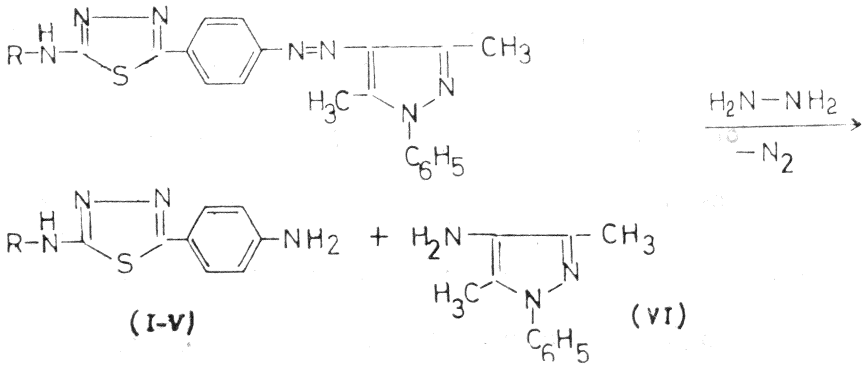
The substance was prepared according to the general method from 1.12 g of 2-phenylamino-5-[-1′-phenyl-3′, 5′-dimethyl-4′-pyrazolylazo) phenyl]-1,3,4-thiadiazole (White needles).

RESULTS and DISCUSSION

In our previous paper, 4-aminopyrazole derivatives were prepared by reducing the azopyrazole derivatives with hydrazine hydrate without a catalyst in ethanol (3-5). This method provides an easy hydrogenolysis with good yield without the need of the usual hydrogenation equipment. The aromatic amines have been isolated in high purity.

In the present investigation, as shown in scheme 1, the treatment of 2-aryl/alkylamino-5-[p-(1′-phenyl-3′, 5′-dimethyl-4′-pyrazolylazo) phenyl]-1,3,4-thiadizoles with hydrazine hydrate resulted the formation of two products.

When the reaction medium was diluted water, compounds I-V were obtained, and then when the mother liqour was extracted with chloroform, compound VI was also isolated.



Scheme — 1

The starting substance of I contains an allyl group. When the NMR spectrum of compound I was investigated, it was found that allyl group was also reduced with hydrazine hydrate to propyl group (Fig. 1).

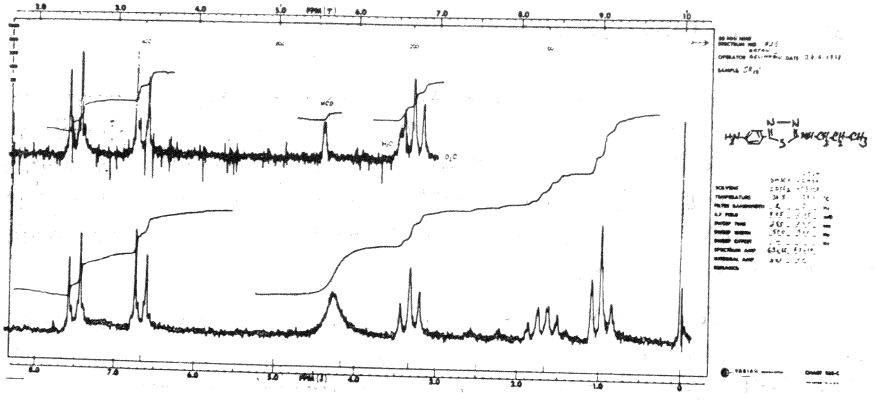
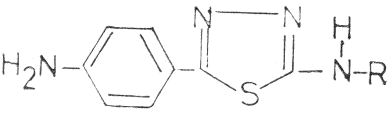


Fig. — 1 : NMR Spectrum of 2-n-Propylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (I).

Table — I : Some characteristics of 2-aryl/alkyl-amino-5-(p-aminophenyl)-1,3,4-thiadiazole detivatives.



Compound	R	Yield %	Molecular Formula	m.p. C° (EtOH)	Analysis Calculated/found C	H	N
I	n-C_3H_7	68	$C_{11}H_{14}N_4S$ (234.32)	118-9°	56.38 56.26	6.02 5.79	23.91 23.85
II	n-C_4H_9	56	$C_{12}H_{16}N_4S$ 1/2 H_2O (257.36)	82-4°	56.00 56.06	6.65 7.22	21.77 21.70
III	C_6H_{11}	41	$C_{14}H_{18}N_4S$ H_2O (292.40)	99-101°	57.50 57.67	6.89 6.87	19.16 18.74
IV	CH_2-CH_2-C_6H_5	54	$C_{16}H_{16}N_4S$ (296.40)	139-40°	64.83 65.17	5.44 5.54	18.90 18.87
V	C_6H_5	59	$C_{14}H_{12}N_4S$ (268.34)	188-9°	62.66 62.73	4.50 4.86	20.88 20.79

The IR spectra of I, IV and V showed the characteristic bands of —NH_2 asimetric and simetric stretching vibration at 3320-3286 cm^{-1} in addition to the other characteristic bands. The IR spectra of II and III contained water of cristallization not showed the characteristic band of —NH_2 streching vibration. (Fig. 2 6).

The —NH_2 protons of I-V appeared as a broad singlet at δ 3.10-5.10 ppm. The other NMR spectral data are listed in Table II.

Table — II : UV and NMR, Data of 2-aryl/alkylamino-5-(p-aminofenil)-1,3,4,-thiadiazole derivatives.

Compound	U.V. (EtOH) λmax (nm) ε (log)	^{1}H-NMR ($CDCl_3$+DMSO/TMS) δ (ppm)
I	327 (4.438)	0.98 (t,3H,CH_3); 1.63 (m,2H,CH_2); 3.33 (t,2H,CH_2-N); 3.90-4.50 (br. peak, 2H, NH_2); 6.68 (d,2H$_{arom.}$, J = 8.5 Hz); 6.90-7.38 (br. peak, 1H, NH); 7.51 (d, 2H$_{arom.}$, J = 8.5 Hz).
II	327 (4.398)	0.75-1.83 (m,7H,CH_2-CH_2-CH_3); 3.10-3.70 (4H, CH_2-N and NH_2, br. peak, exchanged with D_2O); 5,90-6.50 (br. peak, 1H,NH); 6.70 (d,2H$_{arom.}$, J = 8.5 Hz); 7.58 (d,2H$_{arom.}$, J = 8.5 Hz).
III	328 (4.459)	0.90-2.40 (m,10 H, cyclohexyl); 2.83-3.70 br. peak, 5H, CH_2-N,NH_2,OH); 5.10-5.90 (br. peak, 1H,NH); 6.66 (d,2H$_{arom.}$, J = 8.5 Hz 7.58 (d,2H$_{arom.}$, J = 8.5 Hz).
IV	325 (4.469)	2.96 (t,2H,CH_2); 3.63 (t,2H,CH_2-N); 4.33-4.83 (br. peak, 2H,NH_2) 6.68 d,2H$_{arom.}$, J = 8.5 Hz); 7.16 (br. peak, 1H,NH); 7.26 (s,5H,C_6H_5); 7.53 (d,2H$_{arom.}$, J = 8.5 Hz)
V	239 (Sholder) (3.811) 342 (4.480)	3.90-5.10 (br. peak, 2H,NH_2); 6.70 (d, 2H$_{arom.}$, J = 8.5 Hz); 6.90-7.78 (m,8H,NH, C_6H_5 and 2H$_{arom.}$).

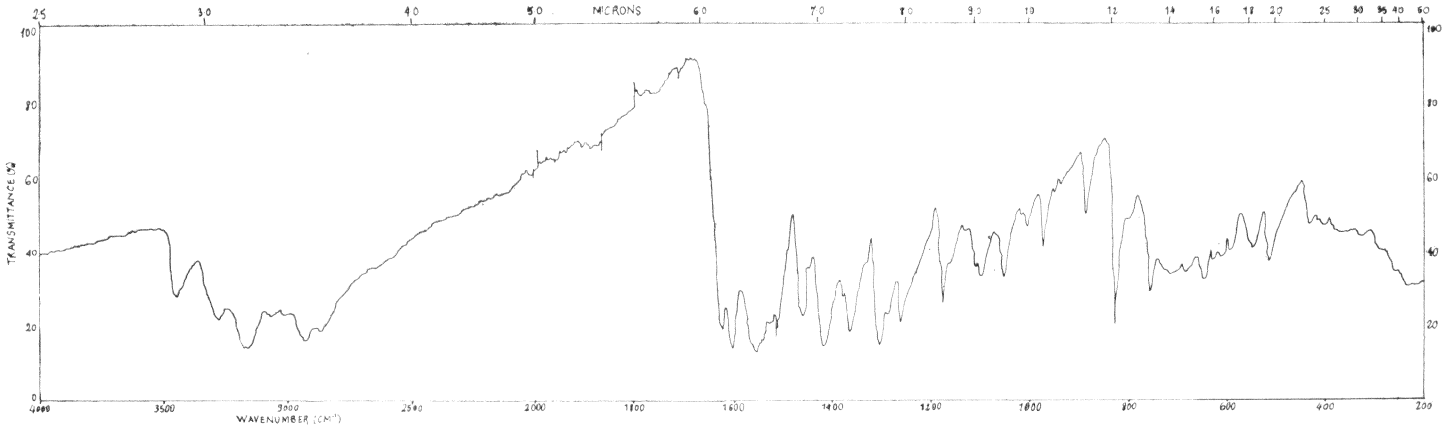


Fig. — 2 : IR Spectrum of 2-n-Propylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (I)

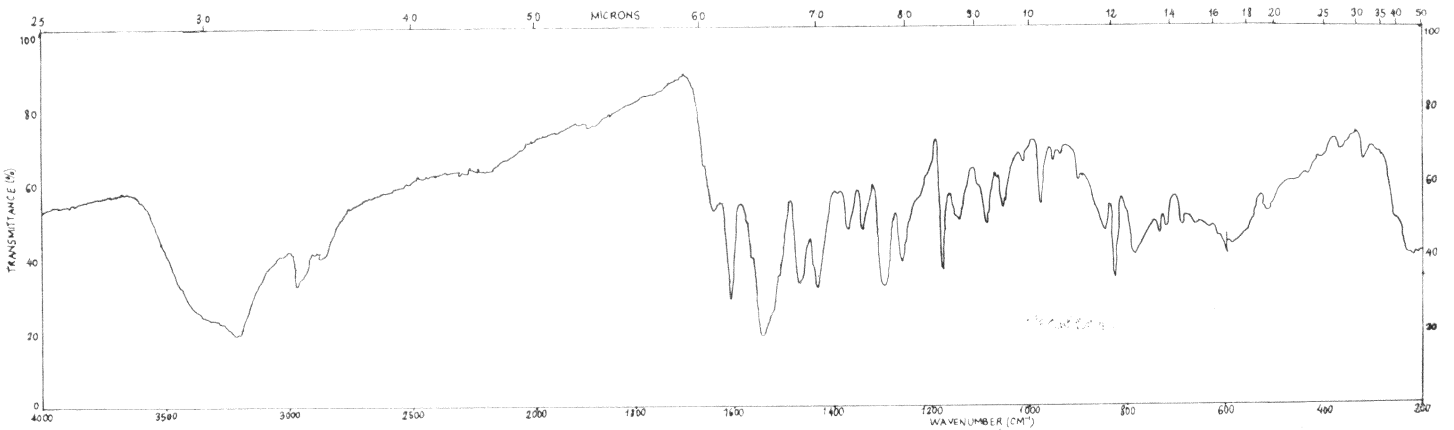


Fig. — 3 : IR Spectrum of 2-n-Buthylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (II).

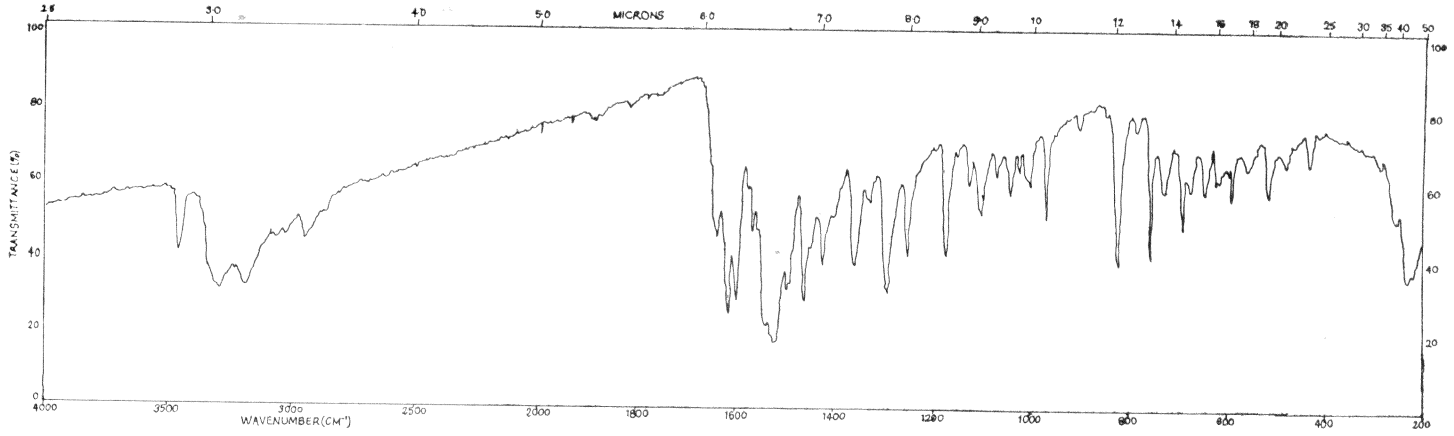


Fig. — 4 : IR Spectrum of 2-Cyclohexylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (III).

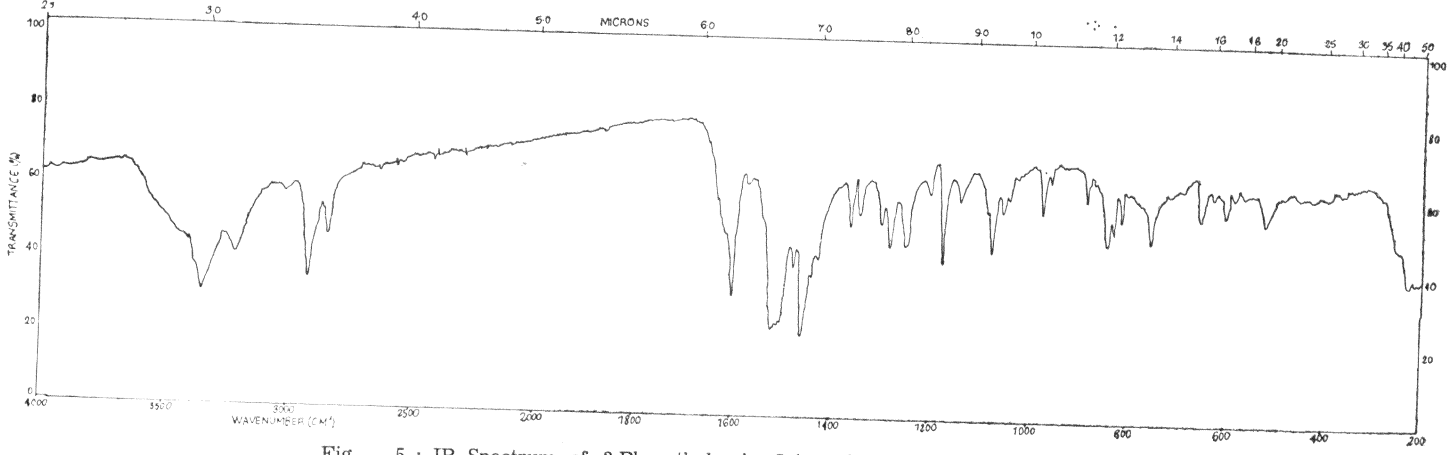


Fig. — 5 : IR Spectrum of 2-Phenethylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (IV).

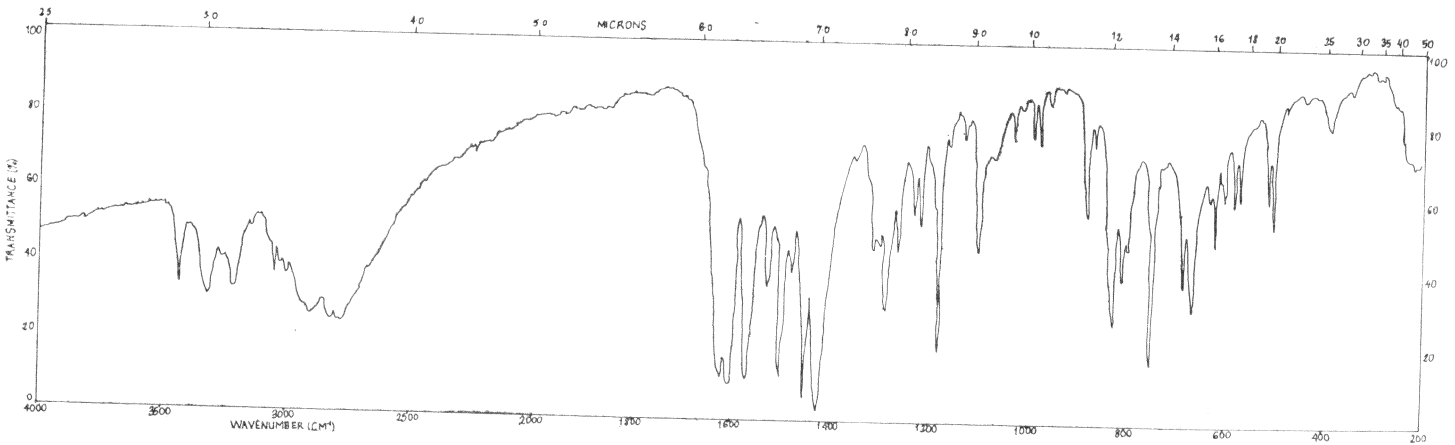


Fig. — 6 : IR Spectrum of 2-Phenylamino-5-(p-aminophenyl)-1,3,4-thiadiazole (V).

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