INVESTIGATIONS OF 2,1,3-THIA- AND SELENADIAZOLES LXV.* AMINATION OF METHYLBENZO-2,1,3-THIADIAZOLES WITH HYDROXYLAMINE SULFATE IN CONCENTRATED SULFURIC ACID

V. A. Sergeev and V. G. Pesin

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All three possible isomeric amines are obtained by the reaction of 4- or 5-methylbenzo-2,1,3thiadiazoles with hydroxylamine sulfate in concentrated sulfuric acid. Under similar conditions, 5,6-dimethyl-4-aminobenzo-2,1,3-thiadiazole is obtained from 5,6-dimethylbenzo-2,1,3thiadiazole.

In [1] it was shown that a mixture of equal amounts of 4- and 5-aminobenzo-2,1,3-thiadiazoles (II and III) is formed by the reaction of benzo-2,1,3-thiadiazole (I) with hydroxylamine sulfate in concentrated sulfuric acid (the Turskii reaction) at 150° C for 1-10 h.

In this paper we present the results of a study of the behavior of 4- (IV) and 5- methyl- (V) and 5,6- dimethylbenzo-2,1,3-thiadiazoles (VI) in the presence and absence of a vanadium pentoxide catalyst.

*See [8] for communication LXIV.





Chromatogram zones	Amine	R	R'	R″	R ‴	Color	mp	Yield g, %
Jpper, yellow-green	VII	CH3	NH₂	н	H	Yellow	118	0,12
/iddle, yellow-green	VIII	CH3	H	NH ₂	Н	Yellow	116-	0,07
ower, yellow	IX	CH₃	H	н	NH₂	Red	83— 85 ^{2, 3}	(13) 0,13 (24)
Jpper, yellow-green	х	NH2	CH₃	Н	Н	Yellow	80-	0,10
Aiddle, yellow	Хĭ	Н	CH3	NH ₂	н	Dark-yellow	171-	0,05
ower, yellow	XII	Н	CH₃	Н	NH₂	Light-yellow	91 92 ⁷	(9) 0,12 (22)
(ellow	XIII*	NH2	СН₃	CH3	н	Yellow†	111— 113 ⁷	0,35 (60)
	Chromatogram zones pper, yellow-green fiddle, yellow-green ower, yellow pper, yellow-green fiddle, yellow ower, yellow cellow	Chromatogram zonesA mine/pper, yellow-greenVII/diddle, yellow-greenVIII/wer, yellow-greenX/diddle, yellow-greenX/diddle, yellowXI/wer, yellowXII/wer, yellowXII/wer, yellowXII/wer, yellowXII	Chromatogram zonesA mineRSpper, yellow-greenVIICH3fiddle, yellow-greenVIIICH3ower, yellowIXCH3Jpper, yellow-greenXNH2fiddle, yellowXIHower, yellowXIIHower, yellowXIIHower, yellowXIIIHYellowXIIIH	Chromatogram zonesA mineRR'Spper, yellow-greenVIICH3NH2Addle, yellow-greenVIIICH3Hower, yellowIXCH3HIpper, yellow-greenXNH2CH3Addle, yellowXIHCH3Addle, yellowXIHCH3Addle, yellowXIHCH3YellowXIIHCH3YellowXIIIHCH3YellowXIIIHCH3	Chromatogram zonesAmineRR'R''Spper, yellow-greenVIICH3NH2HAddle, yellow-greenVIIICH3HNH2ower, yellowIXCH3HHAddle, yellow-greenXNH2CH3HAddle, yellow-greenXNH2CH3HAddle, yellow-greenXNH2CH3HAddle, yellowXIHCH3NH2ower, yellowXIIHCH3HAddle, yellowXIIIHCH3HAddle, yellow	Chromatogram zonesAmineR R' R'' R''' Spper, yellow-greenVII CH_3 NH_2 HHAddle, yellow-greenVIII CH_3 H NH_2 Hower, yellowIX CH_3 HH NH_2 Ipper, yellow-greenX NH_2 CH_3 HHAddle, yellowXIH CH_3 HHAddle, yellowXIIH CH_3 NH_2HOwer, yellowXIIH CH_3 NH_2HCellowXIII* NH_2 CH_3 CH_3H	Chromatogram zonesAmineRR'R''R'''ColorIpper, yellow-greenVIICH3NH2HHYellowfiddle, yellow-greenVIIICH3HNH2HYellowower, yellowIXCH3HHNH2RedIpper, yellow-greenXNH2CH3HHYellowower, yellow-greenXNH2CH3HHYellowdiddle, yellowXIHCH3NH2HDark-yellowower, yellowXIIHCH3HNH2Light-yellowcellowXIII*NH2CH3CH3HYellow+	Chromatogram zonesA mineRR'R''R'''ColormpSpper, yellow-greenVII CH_3 NH_2 HHYellow118Addle, yellow-greenVIII CH_3 H NH_2 HYellow116ower, yellowIX CH_3 H NH_2 HYellow116iddle, yellow-greenX NH_2 CH_3 HHYellow813ipper, yellow-greenX NH_2 CH_3 HHYellow803iddle, yellowXIH CH_3 NH_2 HDark-yellow813iddle, yellowXIIH CH_3 NH_2 HDark-yellow91 72^6 XIII* NH_2 CH_3 CH_3 HYellow $+$ 111 113^7

† The XIII obtained in [7] was brown.

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The isomeric amines 4-methyl-5-amino- (VII), 4-methyl-6-amino- (VIII), and 4-methyl-7-aminobenzo-2,1,3-thiadiazoles (IX) were isolated by heating equimolecular amounts of IV and hydroxylamine sulfate at 100° for 5 h in the presence of vanadium pentoxide.

Under similar conditions, V forms a mixture of 5-methyl-4-amino- (X), 5-methyl-6-amino- (XI), and 5-methyl-7-aminobenzo-2,1,3-thiadiazole (XII), while VI forms the single possible product, 5,6-dimethyl-4-aminobenzo-2,1,3-thiadiazole (XIII). The same results were obtained when the experiments were carried out under nitrogen. Only traces of the corresponding amines were detected when the reaction was carried out without a catalyst.

EXPERIMENTAL

A total of 0.27 g (0.0033 mole) of hydroxylamine sulfate and 0.02 g of vanadium pentoxide were added at 100° to a solution of 0.0033 mole of 4-methyl- [2, 3], 5-methyl- [2, 3], or 5,6-dimethylbenzo-2,1,3thiadiazole [4] in 10 ml of concentrated sulfuric acid, and the mixture was stirred at this temperature for 5 h. It was then cooled and poured with stirring into 100 ml of water. This mixture was then made alkaline in the cold with 20% sodium hydroxide and extracted with 200 ml of carbon tetrachloride (ten 20-ml portions).* The combined extracts were dried with anhydrous sodium sulfate and passed through a column filled with activated aluminum oxide.

The chromatogram was developed with carbon tetrachloride; the colored zones were separated and eluted with acetone. The eluates were evaporated, and the residues were weighed and characterized from their appearance and melting points. The amines obtained did not depress the melting points of the genuine compounds (Table 1).

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^{*}In the amination of VI, 100 ml $(10 \times 10 \text{ ml})$ of carbon tetrachloride was used for the extraction.