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Note

Note on the Formation of 2,5-Dianilino-1,3,4-thiadiazole

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Received July 28, 1964

In a previous paper[1] we have described the formation of 2,5-dianilino-1,3,4-thiadiazole and other 2,5-diarylamino compounds from 4-phenylthiosemicarbazide or other 4-arylthiosemicarbazides and diethyl carbonate. The same reaction product was also obtained by other workers when reacting 4-phenylthiosemicarbazide with acetic acid[2], concentrated sulfuric acid[3], sulfur monochloride[4] or with urea in amyl alcohol[1]. Furthermore, many reactions are known starting with 1,6-diphenylbithiourea[5] and leading similarly to 2,5-dianilino-1,3,4-thiadiazole.

In an attempt to react 4-phenylthiosemicarbazide with ethylene glycol carbonate we have now isolated as the sole reaction product 2,5-dianilino-1,3,4-thiadiazole. Experiments, in which only solvent, as for example 2-ethoxyethanol, was used, confirmed our presumption that heat alone is necessary to form the reaction product. Thus heating 4-phenylthiosemicarbazide alone in a solvent with boiling point below the melting point of the starting compound afforded always the mentioned thiadiazole derivative. Therefore the unusual formation of 2,5-dianilino-1,3,4-thiadiazole in this and in all other cases mentioned above can be explained in terms of a thermally proceeding transformation of 4-phenylhiosemicarbazide.

EXPERIMENTAL

2,5-Dianilino-1,3,4-thiadiazole

a) A mixture of 4-phenylthiosemicarbazide (1.67 g., 0.01 mole), 2-ethoxyethanol (15 ml.) and ethylene glycol carbonate (0.88 g., 0.01 mole) was refluxed on an oil bath for 4 hrs. After cooling the reaction mixture, it was poured into 50 ml. of iced water. The formed precipitate was filtered, washed with water, with a few drops of ethanol and dried, yielding 0.8 g. (60%) of the crude product. This was recrystallized from ethanol affording colorless crystals, m.p. 247°C, undepressed with an authentic specimen.

b) 4-Phenylthiosemicarbazide (1.67 g., 0.01 mole) when heated to reflux with 2-ethoxyethanol (15 ml.) for 4 hrs. and treated as above, afforded the same product (yield 56%, 0.75 g.). Mixed m.p. with an authentic specimen was undepressed and infrared spectra were identical. Instead of 2-ethoxyethanol other higher boiling solvents (b.ps. 100—135°C) can be used.

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IZVLEČEK

Beležka o tvorbi 2,5-dianilino-1,3,4-tiadiazola

Pri reakciji med 4-feniltiosemikarbazidom in etilenglikol karbonatom nastane 2,5-dianilino-1,3,4-tiadiazol. Ugotovili smo, da poteka tvorba tega tiadiazolovega derivata izključno potom termične reakcije brez vpliva drugih reagentov.

ODDELEK ZA KEMIJO
FAKULTETA ZA NAROVOSLOVJE IN TEHNOLOGIJO
LJUBLJANA

Sprejeto 28. julija 1964.