

BRIEF
COMMUNICATIONS

Synthesis of 1,4-Diphenyl-3-phenylimino-1,2-dihydro-1,2,4-triazolium Hydroxide (Nitron)

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Abstract—1,4-Diphenyl-3-phenylimino-1,2-dihydro-1,2,4-triazolium hydroxide (Nitron) is prepared by the reaction of Pb_3O_4 with diphenylthiourea, followed by the reaction of the obtained diphenylcarbodiimide with phenylhydrazine to form triphenylaminoguanidine, whose heterocyclization yields 1,4-diphenyl-3-phenylimino-1,2-dihydro-1,2,4-triazole, which is subsequently oxidized.

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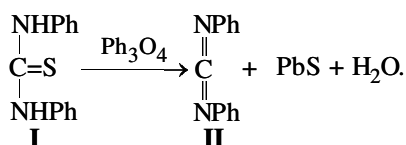
1,4-Diphenyl-3-phenylimino-1,2-dihydro-1,2,4-triazolium hydroxide (Nitron) is a well-known reagent for analysis of nitrate, perchlorate, tungstate, rhuthenate, and iodide anions [1], as well as silicon, germanium, arsenic, and phosphorus [2, 3]. Nitron was used for preparing lithium iodide power sources utilized in manufacture of electrocardiostimulators [4].

The published method of preparation of Nitron [5] allows its synthesis in a yield of $\leq 20\%$ based on diphenylthiourea **I** because of incomplete conversion in the step of the reaction of phenylhydrazine with diphenylcarbodiimide and formation of a tautomer decreasing the yield and purity of the final product.

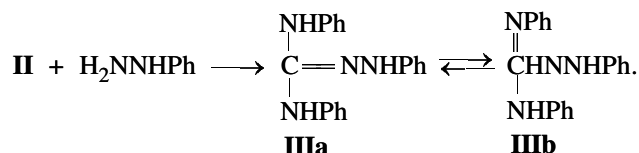
In this study we developed the conditions for synthesis of purer Nitron reagent in higher yields.

EXPERIMENTAL

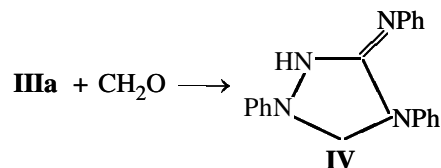
The synthesis includes four steps. First, thiourea is desulfurized with Pb_3O_4 into *N,N*-diphenylcarbodiimide **II**:



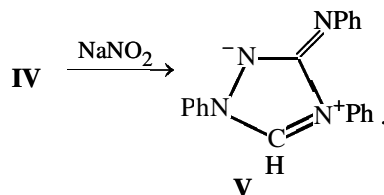
Addition of phenylhydrazine to diimide **II** at 29–31°C yields the desired triphenylaminoguanidine tautomer **IIIa** in 80% yield, which is virtually free of impurity tautomer **IIIb** transforming under the reaction conditions into the ballast “pseudonitron”:



Condensation of guanidine **IIIa** with formaldehyde in isopropanol at 55–60°C yields 1,4-diphenyl-3-phenylimino-1,2-dihydro-1,2,4-triazole **IV** in 87–89% yield:



This is followed by oxidation of triazole **IV** into Nitron by the reaction with sodium nitrite; the final product is isolated by reprecipitation from a mixture of acetic acid and 25% ammonia solution:



The resulting Nitron **V** is 98 wt % pure, which corresponds to the analytically pure grade.

The yield of Nitron based on diphenylthiourea was 43%, which is virtually 2 times that reported in [5].

The IR spectra were recorded on an FSM-1201 Fourier spectrometer in Nujol, and the ^1H NMR spec-

tra, on a Varian FT 80A (80 MHz) spectrometer in CDCl_3 (with TMS as internal reference).

***N,N*-Diphenylcarbodiimide II.** Thiourea **I** (300 g) in 700 ml of benzene was refluxed with vigorous stirring until water ceased to liberate (Dean–Stark trap), and 300 g of Pb_3O_4 was added in portions. Desulfurization was regarded as complete when water ceased to liberate. The sludge was separated, and diphenylcarbodiimide **II** was taken to the next step without isolation.

Triphenylaminoguanidine IIIa. To the solution of diimide **II** (see above), cooled to 10°C , 136 ml of phenylhydrazine was added dropwise so that the temperature in the reaction mixture was about 30°C . Then 100 ml of benzene was distilled off at atmospheric pressure; 300 ml of isopropanol was added to the remaining solution, and the resulting mixture was kept at 0°C for 8–10 h. The crystalline reaction product was filtered off and dried in air; yield 350 g (88%), mp $156\text{--}158^\circ\text{C}$.

1,4-Diphenyl-3-phenylimino-1,2-dihydro-1,2,4-triazole IV. To 200 g of compound **IIIa**, 200 ml of 40% aqueous solution of formaldehyde and 1.0 l of isopropanol were added. The reaction mixture was heated at $55\text{--}60^\circ\text{C}$ for 0.5 h and cooled to 22°C . The reaction product was filtered off, washed with 150 ml of isopropanol, and dried in air, which yielded 184 g (89%) of triazole **IV**; mp $126\text{--}128^\circ\text{C}$.

1,4-Diphenyl-3-phenylimino-1,2-dihydro-1,2,4-triazolium hydroxide V. To a solution of 240 g of triazole **IV** in 1 l of isopropanol, glacial acetic acid was added at $65\text{--}67^\circ\text{C}$ until complete dissolution of crystalline substance **IV**, which required 200 ml of the acid. Then a solution of 88 g of sodium nitrite in 200 ml of water was added. The reaction was regarded as complete when the color of the solution changed

from light green to red. The reaction mass was cooled to room temperature and poured into a 25% aqueous ammonia solution with ice. The resulting finely divided yellow precipitate of Nitron **V** was filtered off and reprecipitated from a mixture of glacial acetic acid and ammonia solution (1 : 3 by volume). The reaction product was dried in a vacuum oven at $50\text{--}60^\circ\text{C}$ and a pressure of 0.2 kg cm^{-2} . The yield of Nitron reagent was 176 g (74%), mp $186\text{--}188^\circ\text{C}$ (dec.). Published data: mp 189°C (dec.).

Found (%): C 76.89, H 5.20, N 18.01.
 $\text{C}_{20}\text{H}_{16}\text{N}_4$.

Calculated (%): C 76.92, H 5.13, N 17.95.

IR spectrum (cm^{-1}): 3052 [$\nu(\text{CH}_{\text{arom}})$], 2924 [$\nu(\text{CH})$], 572 [$\delta(\text{CH}_{\text{arom}})$]. ^1H NMR spectrum (CDCl_3), δ (ppm): 6.64–7.64 m (16H, Ph, CH).

CONCLUSION

Conditions were developed for synthesis of high-purity (98 wt %) Nitron reagent in the preparative yield of 43% with the use of Pb_3O_4 instead of lead oxide (PbO_2) and 2-propanol instead of ethanol.

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