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TRIARYLAMINE-N-OXIDES. I. THE FIRST ATTEMPT OF (4,4´,4´´-TRIMETHYL)TRIPHENYLAMINE-N-OXIDE SYNTHESIS AND DIRECT PROOF OF ITS FORMATION

Vladimir N. Bulavka[1], Alexandr E. Gekhman[2], Konstantin K. Koshelev[1]

[1]Slavich Company, 2 Mendeleev sq., Pereslavl-Zalessky, Yaroslavl region, 152020, Russian Federation
E-mail: nifti@slavich.ru

[2]N. S. Kurnakov Institute of Inorganic Chemistry RAS, 31 Leninsky Pr., Moscow, 117071, Russian Federation

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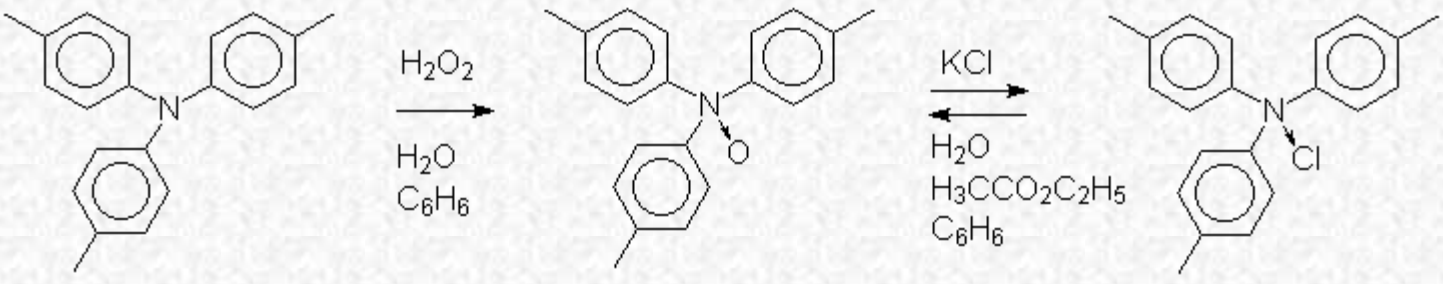
Triarylamine-N-oxides are mainly of interest to theoretical organic chemists. The first mention of triphenylamine-N-oxide (**I**) [1] was an erroneous one. In fact, in the original paper [2] **I** has not been described. In reference [3] the acetone solution of the **I** : UO_2Cl_2 1:1 complex was described without any experimental data for the above mentioned complex or for the ligand preparation. Up to the present time no synthetic procedure for triarylamine-N-oxide preparation were described. Their stability seems to be much lower than the stability of other known amine-N-oxides. In our opinion, (4,4¢,4¢¢-trimethyl)-triphenylamine (**II**) forms a relatively stable (4,4¢,4¢¢-trimethyl)-triphenylamine-N-oxide (**III**).

Earlier, **III** was mentioned in one patent publication (without any experimental description) together with a wide variety of all known types of amine-N-oxides as useful lubricant additives for the prevention of PH_3 formation in phosphorus containing alloys [4].

Oxidation of **II** dissolved in benzene with a large excess of 50% aqueous hydrogen peroxide leads to the formation of **III**. A saturation of the reaction mixture with solid potassium chloride and extraction with ethyl acetate gives mixtures of **II**, **III**, and (4,4¢,4¢¢-trimethyl)triphenylamine-N-chloride (**IV**).



II **III** **IV**

GC-MS analyses of the so obtained extracts shows a direct proof for the formation of **III**: 16.91 min, 96.48% **II**, M^+ 287; 18.02 min, 1.98% **III**, M^+ 303; 18.14 min, 1.53% **IV**, M^+ 321 [5].

The fragmentation of **III** begins with loss of m/z 16 (single oxygen atom) and formation of the 287 m/z fragment. Similarly, **IV** initially loses a chlorine mass fragment (35 and 37 m/z) and forms the 287 m/z fragment. As 287 is the molecular mass of **II**, this fragmentation process confirms the chemical structures of **III** and **IV**.

The stability of **II** in solutions is low. The presence of **II** and **III** in solution is detectable only immediately after oxidation. After standing of the solution for 1 hour at room temperature no **II** and **III** were detected by GC-MS method.

References

1. *Chemical Abstracts*. 1972-1976 9th Collective Formula Index, p. 9636F. Benzeneamine, N,N-diphenyl-N-oxide [41864-95-3] **79**: 35604h.

2. *Doklady Acad. Sci. USSR*, 1973, 209(6), 1369-1972 (Russian), (*Chemical Abstracts* **79**: 35604h).

3. Kobets, L.V. The energetics of uranylchloride iteraction with neutral oxygen-containing bases. *Koord. Khim.*, 1987, 13(1), 85-91 (Russian).

4. Schulz J. (Rhenus Wilhelm Reiners GmbH & Co.) *Schmiermittel sowie Additiv fur die mechanische Bearbeitung eines Werkstoffes.* Offen. **DE 19535517** (C 10 M 133/02), 27.03.1997; 19535517.2, 25.09.1995. (Germany).

5. Mass-spectra, m/z (%):

II: 287 (100), 271 (5), 257 (1), 194 (1), 180 (10);

III: $(M+1)^+$: 304(27), M^+: 303(100), 287(6), 197 (7), 196 (4), 182 (5), 178 (9), 177 (12), 92 (3);

IV: $(M+1)^+$: 324 (10), M^+: 323 (33), $(M+1)^+$: 322 (42), M^+: 321 (100) (isotopic peaks relative intensity is in accordance with ^{37}Cl : ^{35}Cl =1:3 natural content), 287 (3), 286 (20), 284 (2.5), 272 (17), 271 (68), 269 (2), 254 (2.5), 194 (23), 192 (2), 191 (1.5) 178 (15), 152 (1), 135 (7), 134 (6), 63 (2).
