2,4,6-TRIPHENYLPYRIDINE N-OXIDE ANION RADICAL

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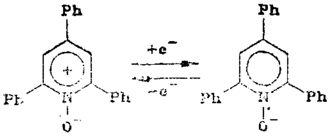
The existence of anion radicals of quinoline and acridine N-oxides has been proved by cyclical voltammetry and EPR spectroscopy [1]. The electrochemical reduction of the N-oxides of pyridine and picolines in aprotic solvents proceeds irreversibly with the consumption of two electrons, and intermediately formed anion radicals cannot be detected under ordinary conditions [2]. However, we have found that the corresponding anion radical is completely stable in the case of 2,4,6-triphenylpyridine N-oxide. The reduction of this oxide under the conditions of classical polarography (anhydrous DMF, dropping mercury electrode, and 0.1 mole/liter tetrabutylammonium perchlorate) proceeds in two one-electron steps ($-E_{1/2}$ = 2.18 and 2.38 V relative to a saturated calomel electrode). The existence of a commutated polarogram [3] with $-E_{1/2}$ = 2.20 V indicates the existence of a stable anion radical:



The anion radical is easily detected by EPR spectroscopy in the reduction of the N-oxide on a potassium mirror in tetrahydrofuran (THF). The triplet spectrum is due to interaction of the unpaired electron only with the ^{14}N nuclei (a_N = 6.7 Oe; g = 2.033).

The anion radical is stable *in vacuo* for a long time. It is characteristic that, in contrast to picoline N-oxide, 2,4,6-triphenylpyridine N-oxide does not react with benzophenone ketyl [4].

2,4,6-Triphenylpyridine, which was obtained from 2,4,6-triphenylpyrylium perchlorate [5], was converted to the N-oxide by the action of excess 30% H_2O_2 in the presence of urea (24 h on a water bath); the product had mp 182°C (from isopropyl alcohol). IR spectrum (oil): 1270 (N—O bond); 680-710, 1500-1560 cm^{-1} (aromatic C—H). The results of elementary analysis for C, H, and N were in agreement with the calculated values.

LITERATURE CITED

1. H. Tiyasaki, J. Matsuhisa, and T. Kubota, Bull. Chem. Soc. Jpn., 54, 3850 (1981).
2. G. Antoine, J. Nasielski, D. E. Vander, and N. Vanlauter, Bull. Soc. Chem. Belg., 76, 230 (1967).
3. J. Heyrovsky and J. Kuta, Principles of Polarography, Academic Press (1966).
4. A. S. Kurbatova, Yu. V. Kurbatov, and D. A. Niyazova, Khim. Geterotsikl. Soedin., No. 5 655 (1979).
5. G. N. Dorofeenko and S. V. Krivun, Zh. Obshch. Khim., 34, 105 (1964).

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