NEW METHOD FOR THE PREPARATION OF N-OXIDES OF AROMATIC NITROGENOUS HETEROCYCLES

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It is well known that the N-oxides of pyridines, quinolines, and other nitrogen-containing aromatic heterocycles are obtained by the oxidation of the bases by various peracids. We have shown that the hydroperoxide-molybdenum salt oxidative system recently [1] proposed for the epoxidation of olefins is not only a superb reagent for preparing various N-oxides but also has a number of advantages over peracids. For example, the oxidation of pyridine with tert-amyl hydroperoxide (TAHP) in the presence of MoC $\rm I_5$ proceeds more rapidly than the oxidation with peracids, and the yields of N-oxides are close to quantitative. An advantage of the proposed reagent is shown in the case of the oxidation of acridine, the yield of the N-oxide of which reaches 90%, while the yield when perbenzoic acid is used does not exceed 50%, even after prolonged reaction [2]. The melting points in degrees centigrade and the percent yields of the N-oxides are indicated in parentheses: pyridine (65-67, 100), α -picoline (hydrochloride, 124-125, 100), β -picoline (33-34, 100), collidine (from -4 to -2, 100°), γ , γ '-dipyridyl (dioxide, 305-310, 100), methyl nicotinate (38-39, 90), diethyl 2,6-dimethylpyridine-3,5-dicarboxylate (108-110, 80), 4-acetamidopyridine (265-266, 40), quinoline (61-62, 100), quinaldine (hydrate, 77-78, 90), phenazine (dioxide, 202-204, 100), acridine (168-169, 100), and papaverine (168-170, 85).

The method has some limitations. Thus, we could not oxidize α, α' -dipyridyl and o-phenanthroline. Satisfactory elementary analysis results were obtained for all of the compounds.

LITERATURE CITED

- 1. M. N. Sheng and J. G. Zajacek, International Oxidation Symposium, Vol. 2, San Francisco (1967), p. 243.
- 2. H. Kliege, Ber., 89, 197 (1936).

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