LITERATURE CITED

1. B. A. Trofimov, S. G. Shevchenko, S. E. Korostova, A. I. Mikhaleva, and V. V. Shcherbakov, Khim. Geterotsikl. Soedin., No. 11, 1573 (1985).

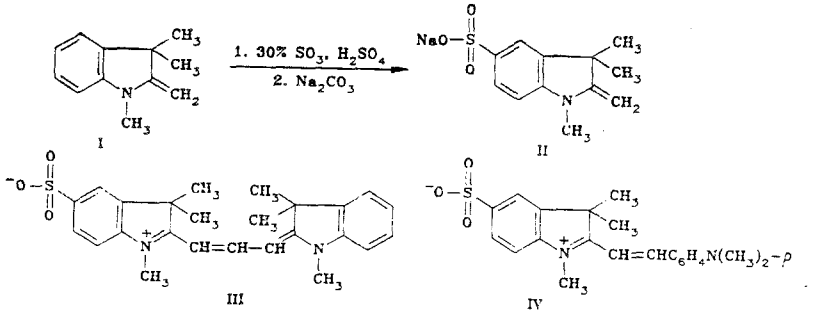
DIRECT SULFONATION OF 1,3,3-TRIMETHYL-2-METHYLENEINDOLINE

V. S. Tolmacheva, A. A. Tolmachev, L. I. Shevchuk, and F. S. Babichev

UDC 547.753.04:542.945.24

Except for 2-oxo derivatives, compounds of the indole series have not been sulfonated in the benzene ring because of their tendency to undergo oxidation [1].

We have found that when 1,3,3-trimehyl-2-methyleneindoline (I) is sulfonated with 30% oleum, 1,3,3-trimethyl-2-methylene-5-sulfoindoline (II) is formed practically quantitatively. It is of interest that, like other electrophilic substitutions, sulfonation of compound (I) in sulfuric acid medium [2] gives a 5-substituted, not a 6-substituted 2-methyleneindoline. This is shown for certain by the PMR spectrum of sulfoindoline (II) (in DMSO-D_6): 1.28 (6H, s, 3-CH_3); 3.01 (3H, s, N-CH_3O: 3.90 (2H, s, =CH_2); 6.58 (1H, d, J = 7.8 Hz, 7-H); 7.35 (1H, s, 4-H); 7.38 (1H, d, J = 7.8 Hz, 6-H). The PMR spectra of a large number of 5- and 6-substituted 2-methyleneindolines are shown in [2, 3]. Furthermore, to prove the structure of (II), carbocyanine (III) and styryl dye (IV) were prepared by condensation with the respective aldehydes in pyridine in the presence of trifluoroacetic acid. The synthesis of some 5-sulfoindolines (by Fischer's procedure) and of type (III) and (IV) dyes is described in a patent [4].



Compound (II). Yield 97%. mp 265°C.

Compound (III). Yield 43%. mp >300°C. UV spectrum, λ_{max} (in methanol): 547 nm.

Compound (IV). Yield 72%. mp >300°C. UV spectrum, λ_{max} (in methanol): 555 nm.

S and N contents agree with the calculated values.

LITERATURE CITED

1. K. Unverferth and G. Ohms, Pharmazie, 42, 132 (1987).
2. D. J. Grale, J. Lin, and J. F. K. Wilshere, Austr. J. Chem., 30, 689 (1977).
3. A. A. Tolmachev, V. S. Tolmacheva, L. I. Shevchuk, E. S. Kozlov, and F. S. Babichev, Khim. Geterotsikl. Soedin., No. 7, 919 (1989).
4. French Pat. 886,294; Chem. Zbl., 1, 599 (1944).

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1567-1568, November, 1989. Original article submitted January 31, 1989.

