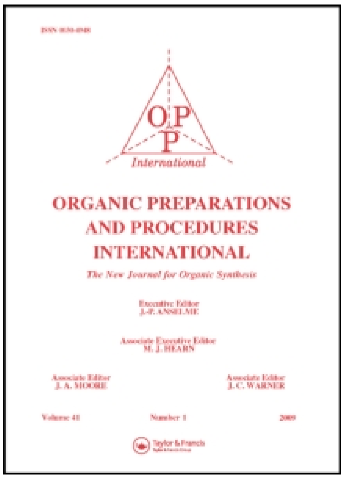

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AN IMPROVED SYNTHESIS OF FLUORENONE METHYLNITRONE

Magid A. Abou-Gharbia[a]; Madeleine M. Joullié[a]
[a] Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania

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AN IMPROVED SYNTHESIS OF FLUORENONE METHYLNITRONE

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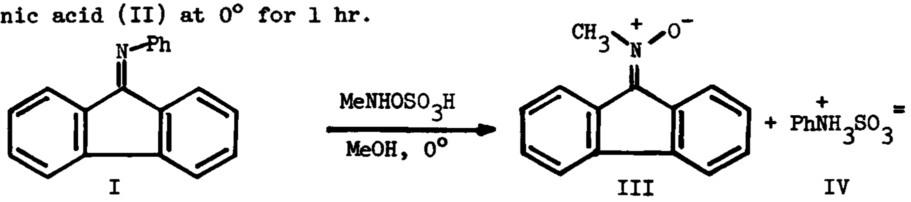
Magid A. Abou-Gharbia and Madeleine M. Joullié*

Department of Chemistry
University of Pennsylvania
Philadelphia, Pennsylvania 19104

Fluorenone methylnitrone (III) was originally prepared from fluorenone in an overall yield of 47%, using drastic conditions for two days.[1] We now report a convenient synthesis of the title compound (III) in 90% yield by treating N-fluorenylideneaniline (I) with N-methylhydroxylamine-O-sulfonic acid (II) at 0° for 1 hr.

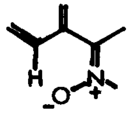


The reaction is general for aldimines and ketimines and was found to be independent of the substituents on the imines.[2] When aldehyde imines are used, the methylnitrones obtained are in the more stable *trans* configuration.

EXPERIMENTAL

N-Fluorenylideneaniline (I).- This compound was prepared in 82% yield from commercially available 9-fluorenone (Aldrich Chemical Co.) *via* its condensation with freshly distilled aniline using zinc chloride as catalyst[3] mp. 87-89°, lit.[3] mp. 88-89°.

N-Methylhydroxylamine-O-sulfonic Acid (II).- This compound was prepared in 89% yield from N-methylhydroxylamine hydrochloride with chlorosulfonic acid.[4] The reagent is very hygroscopic and should be used within 1 hr. The reagent may be stored in chlorosulfonic acid for a period of three weeks and regenerated prior to its use by addition of dry ether.

Fluorenone methylnitrone (III). Typical Procedure.- N-Methylhydroxylamine-O-sulfonic acid (II) (0.7 g, 5.5 mmoles) was added slowly, over a period of 10 mins., to a stirred solution of 1.28 g (5.0 mmoles) of I in 50 ml of methanol at 0-10°. The reaction mixture was stirred for an additional hour at 0-10° and then diluted with 100 ml of ice water. The deep yellow solution was extracted with 90 ml of methylene chloride.[5] The organic layer was washed three times with water, dried over anhydrous sodium sulfate, filtered and the solvent removed in vacuo. The remaining solid was recrystallized from 10 ml of absolute ethanol to afford 0.94 g (90% yield) of pure nitrone (III) as yellow needles, mp. 143-145°, lit.[1] mp. 145-146°; IR (KBr): 1550 cm^{-1} (C=N), 1290 cm^{-1}, 1200 cm^{-1} ($N \rightarrow O$); NMR ($CDCl_3$): δ 4.25 (s, 3H, CH_3), 7.2-7.8 (m, 7H, aromatic), and 8.6-8.8 (m, 1H ).

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