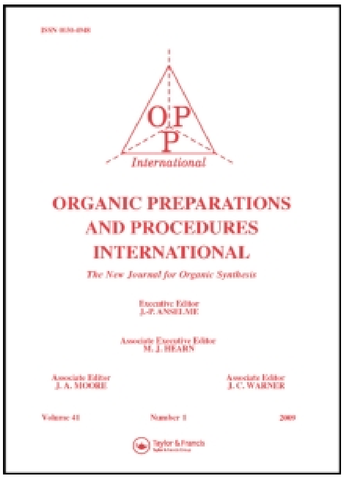

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SYNTHESIS OF N-PHENYLTETRAMETHYLSUCCINIMIDE

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SYNTHESIS OF N-PHENYLTETRAMETHYLSUCCINIMIDE

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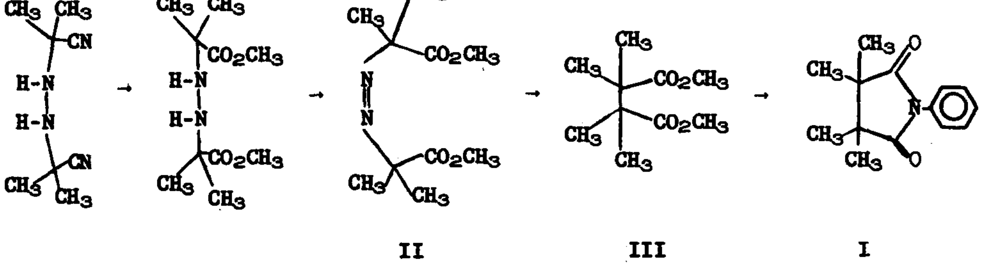
Recently in these laboratories, the necessity arose for analytically pure N-phenyltetramethylsuccinimide (I) for use as a host crystal in esr studies. Although several methods are known for the general synthesis of N-aryl succinimides, the customary synthesis[1], ie. the reaction of an anhydride with a substituted aniline, has an inherent limitation due to the difficulty in removing side products. We now report an improved synthesis of I, which meets the purity requirements for an esr host crystal.

2,2'-Hydrazoisobutyronitrile[1] after esterification was oxidized with bromine water to give a 95% yield of dimethyl 2,2'-azoisobutyrate (II).[2] The thermal decomposition of II by the method of Bickel and Waters[3] gave a 50% yield of the crystalline methyl tetramethylsuccinate (III).[4] Refluxing III in excess aniline under nitrogen gave a 70% yield of I, mp 88-89°, which was shown to be analytically pure.



EXPERIMENTAL

2,2'-Hydrazoisobutyronitrile was prepared as previously described[1] in quantitative yield, mp. 88-89°, lit.[1] mp. 87.5-89.5°.

Dimethyl 2,2'-azoisobutyrate (II) was prepared[1] by esterification of 2,2'-hydrazoisobutyronitrile with methanol-HCl affording dimethyl 2,2'-hydrazoisobutyrate (bp. 70-71°/1 mm, lit.[3] bp. 126-130°/26 mm), which was then oxidized (95%) with bromine water giving II, mp. 31-32°, lit.[3] mp. 31-32°.

Methyl tetramethylsuccinate (III). - Dimethyl 2,2-azoisobutyrate (76.14g, 0.33 mol) in benzene (200 ml) was added dropwise under nitrogen to 500 ml of refluxing benzene. The solution was refluxed for an additional 20 hours or until evolution of nitrogen cases. The benzene was removed in vacuo affording the crude III, bp. 210-220°/750 mm, lit.[4] bp. 104-107°/20 mm. There was obtained 33 g (50%) after preparative gas chromatography[5] of III, bp. 71-71.5°/1.25 mm, mp. 24-26°; nmr ($CDCl_3$-1% TMS) δ 1.22 (s, $\underline{CMe_2}$, 12H) and δ 3.65 (s, $CO_2\underline{CH_3}$, 6H).

N-Phenyltetramethylsuccinimide (I). - A mixture of III (10 g, 0.05 mol) in anhydrous aniline (100 ml) was refluxed under nitrogen for 20 hours. The aniline was removed by distillation and the residue dissolved in ether and washed successively with an 1N hydrochloride acid solution, water, saturated salt solution and dried over magnesium sulfate. The solid, which remained after evaporation of solvents, was dissolved in benzene-petroleum ether and recrystallized from cyclohexane affording (70%) analytically pure N-phenyltetramethylsuccinimide, mp. 88-89°, lit.[6] mp 88°; nmr ($CDCl_3$) δ 1.25 (s, $\underline{CMe_2}$, 12H) and δ 7.28 to 7.48 (m, $C_{aromatic}$-H, 5H).

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5. Preparative chromatography was carried out on a Perkin-Elmer Model F-21 instrument equipped with a flame ionization detector and a copper column (20 ft. x 0.5 in., 15% Carbowax on 60-80 mesh chromosorb w, flow rate of 1000 ml./min., column temperature 120°).

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