Isolation of a Nitrogen-centred Radical, *N*-(4-Nitrophenylthio)-2,4,6-tri-t-butylphenylaminyl

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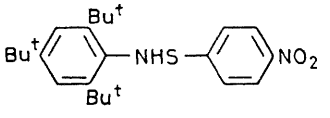
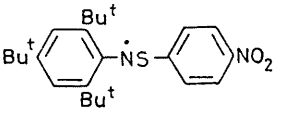
Summary The title radical has been isolated as dark brown needles which are stable in the presence of oxygen although the radical reacts very rapidly with oxygen when in solution.

ALTHOUGH free radicals are generally recognized to be transient, some exceptionally stable free radicals have been prepared.[1] For example, 2,2-diphenyl-1-picrylhydrazyl, nitroxides, and verdazyls have been isolated as pure crystals. In the course of an e.s.r. investigation of thioaminyls,[2] $R^1\dot{N}SR^2$, we isolated the sterically protected thioaminyl, *N*-(4-nitrophenylthio)-2,4,6-tri-t-butylphenylaminyl (**2**), as pure crystals.



(1)



(2)

In a typical procedure, *N*-(4-nitrophenylthio)-2,4,6-tri-t-butylaniline (**1**) (0·10 g, 0·24 mmol) was treated in benzene (10 ml) for 10 min with PbO_2 (0·5 g) and K_2CO_3 (0·5 g) under nitrogen. After filtration, the solvent was removed by freeze-drying, giving a dark brown powder, which was recrystallized from methanol under nitrogen to afford dark brown needles, m.p. 127—129 °C (in a degassed capillary) in 45% yield. The crystals gave a strong e.s.r. signal but the strong NH absorption which was observed in the i.r. spectrum of (**1**), disappeared completely in the i.r. spectrum of the crystals. The crystals were confirmed to be completely pure by t.l.c. analysis (alumina; benzene–hexane 3 : 7) and gave satisfactory elemental analyses.

The crystals dissolved in benzene, to give a dark brown solution which showed a strong e.s.r. signal due to (**2**) (a_N 12·30 G; *g* value 2·0066). The radical in solution reacted rapidly with oxygen, but was very stable in the crystal structure even in the presence of oxygen and, on standing for a month exposed to the atmosphere showed no detectable decomposition.

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[1] A. R. Forrester, J. M. Hay, and R. H. Thomson, in 'Organic Chemistry of Stable Free Radicals,' Academic Press, London, New York, 1968.

[2] Y. Miura, Y. Katsura, and M. Kinoshita, *Bull. Chem. Soc. Japan*, 1979, **52**, 1121.