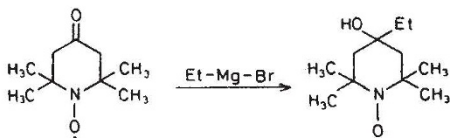


### A New Organic Radical Reaction involving No Free Valence

THE discovery of a fundamentally new type of organic radical reactions involving no unpaired electron has been already reported<sup>1-3</sup>. The work recorded here was concerned with a reaction between a free radical, triacetoneaminoxyl and the Grignard reagent. The reaction proceeding with conservation of free valence yielded a new organic free radical with a hydroxyl group:



After distillation in vacuum, the crude product appeared as a bright red oily substance readily soluble in water and in organic solvents. Analysis by means of paper chromatography has shown that the oil was a mixture of two radicals: 2,2,6,6-tetramethyl-4-ethyl-4-hydroxypiperidin-oxyl and triacetoneaminoxyl (Fig. 1).

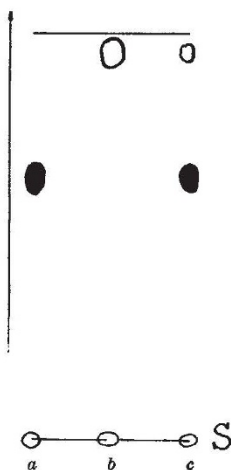
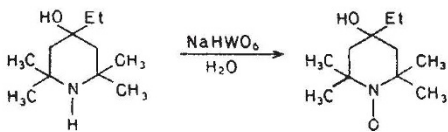


Fig. 1. Paper chromatography (methanol : acetone = 1 : 1). (a) 2,2,6,6-tetramethyl-4-ethyl-4-hydroxypiperidin-oxyl; (b) triacetoneaminoxyl; (c) paramagnetic red oil

An individual paramagnetic compound with a melting point of 67°–69° was obtained on chromatographic purification of the crude product on aluminium oxide (found: 0.480 per cent H (active); molecular weight 199.4; spin/mole  $5.0 \times 10^{23}$ ; calculated: 0.503 per cent H (active); molecular weight 200.3; spin/mole  $6.0 \times 10^{23}$ ).

The new free radical represented an orange-yellow crystalline compound, soluble in water and in organic solvents, suffering no change for a year under the usual conditions.

The ultra-violet ( $\lambda_{\max}$  227 and 235 m $\mu$ ) and infra-red absorption spectra (Fig. 2) were found to be identical to those of 2,2,6,6-tetramethyl-4-ethyl-4-hydroxypiperidin-oxyl obtained by direct catalytic oxidation of 2,2,6,6-tetramethyl-4-ethyl-4-hydroxypiperidine by the scheme:



The electron spin resonance spectrum of the crystalline radical represented a singlet type curve. When the sample was solved in benzene, it turned into a triplet similar to the initial ketone radical spectrum (Fig. 3).

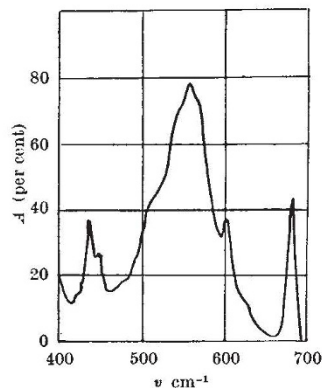


Fig. 2. Infra-red spectrum of a solid free radical

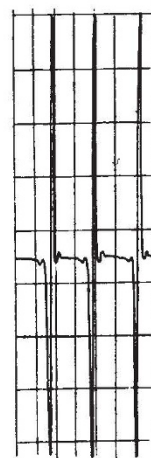


Fig. 3. Hyperfine structure of a free radical electron spin resonance spectrum

The low-intensity doublets in the hyperfine structure of the spectrum (splitting of 5.4 gauss) seem to be due to an admixture of a natural carbon-13 isotope (spin 1/2).

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<sup>1</sup> Rozantzev, E. G., Mamedova, Yu. G., and Neiman, M. B., *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, No. 12, 2250 (1962).

<sup>2</sup> Neiman, M. B., Rozantzev, E. G., and Mamedova, Yu. G., *Nature*, **196**, 472 (1962).

<sup>3</sup> Rozantzev, E. G., and Papko, R. A., *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, No. 3 (1963).

### A Direct Hydrocarbon/Air Fuel Cell

A CONSIDERABLE amount of effort is being expended at present to develop fuel cells capable of burning hydrocarbons directly and efficiently to carbon dioxide and water. Most of the work so far has been confined to temperatures below 100° C using sulphuric acid as the electrolyte and platinum metals as the catalytic surface. Under these conditions it has been possible to demonstrate current densities of up to 10 or 20 m.amp/cm<sup>2</sup> at very low cell voltages, leaving in considerable doubt the feasibility of making efficient working devices.

We have carried out investigations using phosphoric acid of various concentrations as the electrolyte up to temperatures of 220° C, also using platinum for the electrode catalytic surface. Fig. 1 shows the polarization obtainable on simple platinum black electrodes using propane as the fuel. Polarization is shown versus the reversible hydrogen electrode in the same electrolyte. It can be seen from these results that current densities