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# ON THE PARAMAGNETIC SPECIES FORMED IN THE REACTION BETWEEN 2,4,6-TRI-t-BUTYLNITROSOBENZENE AND ORGANOALUMINIUM COMPOUNDS

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## Summary

ESR spectra are reported for long-lived paramagnetic products formed when 2,4,6-tri-t-butylnitrosobenzene reacts with $(CH_3)_3Al$, $(C_2H_5)_3Al$, $C_2H_5AlCl_2$ and t-$Bu_3Al$. The spectra are assigned to nitroxide, *N*-alkoxyanilino and ethyl 2,4,6-tri-t-butylphenoxyamino radicals. On the basis of the results it is suggested that nitroxides abstract a hydrogen atom from the methylene group in $(C_2H_5)_3Al$, and undergo 1,2 rearrangement under the action of $C_2H_5AlCl_2$.

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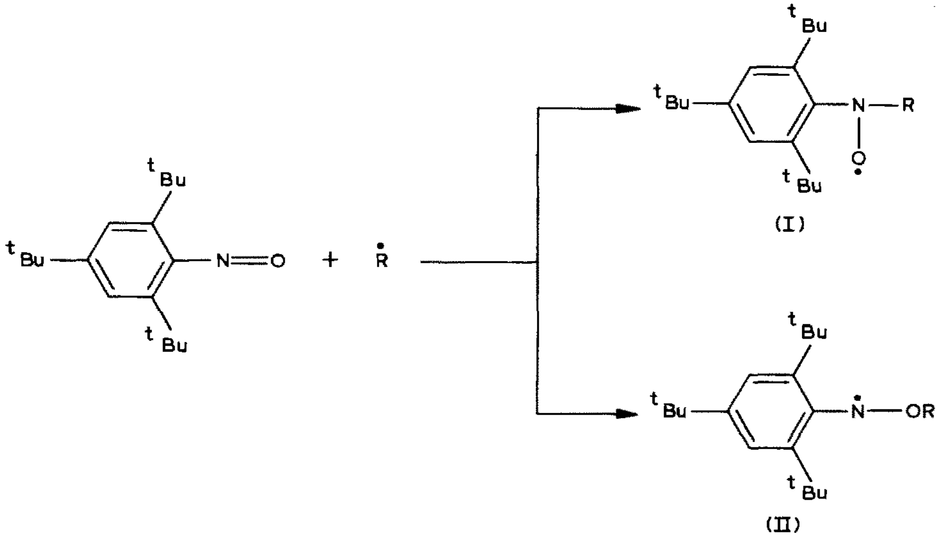
## Introduction

2,4,6-Tri-t-butylnitrosobenzene (TBNB) is a bifunctional spin-trapping agent which reacts with primary alkyl radicals to give nitroxide radicals (I) but with bulky radicals to give *N*-alkoxyanilino radicals (II) [1]. Both types of spin adducts I and II



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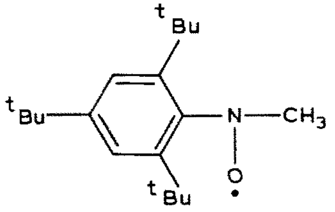
of methyl, ethyl and isobutyl radicals were detected by Yatsu et al. [2–4] in spin-trapping experiments involving use of TBNB in a mixture of an organic peroxide, γ-butyrolactone and a trialkylaluminium compound. According to these authors, in the reaction with a peroxide two kinds of alkyl radicals are formed from trialkylaluminium, one being the usual alkyl free radical and the second, a so called "coordinated" one, a sterically hindered species, probably involving interaction with the Al atom. Use of TBNB also indicated the participation of free and coordinated radical propagating species in polymerization processes initiated by the above system [2–5].

We have found that TBNB reacts very rapidly with organoaluminium compounds to produce various paramagnetic species even when no peroxide is introduced into the system. We describe below the ESR spectra observed in these reactions.

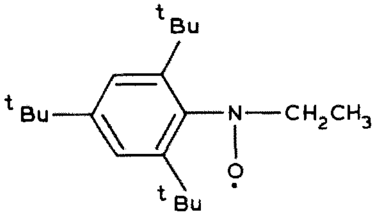
## Results and discussion

The compounds $(CH_3)_3Al$, $(C_2H_5)_3Al$ and $C_2H_5AlCl_2$ react with TBNB in the presence of strong Lewis bases like γ-butyrolactone, tetrahydrofuran and methyl acetate to give mainly nitroxide radicals III, IV provided the organoaluminium compound is not present in a large excess over the TBNB.



(III)

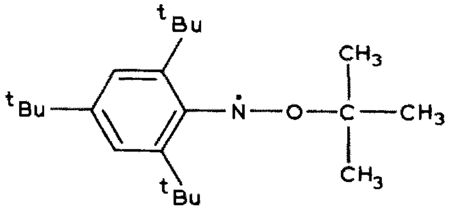
| found | lit. [1–4] |
|---|---|
| $g = 2.0064$ | 2.0060 |
| $a_N = 13.3$ G | 12.8–13.0 G |
| $a_{H(CH_3)} = 12.3$ G | 12.3–12.5 G |
| $a_{H(m)} = 0.8$ G | 0.81 G |



(IV)

| found | lit. [1–4] |
|---|---|
| $g = 2.0066$ | 2.0060 |
| $a_N = 13.4$ G | 13.5–13.6 G |
| $a_{H(CH_2)} = 18.0$ G | 18.0 G |
| $a_{H(m)} = 0.8$ G | 0.8 G |

In contrast t-$Bu_3Al$ reacts with TBNB to give *N*-t-butoxyanilino radicals V.



(V)

| found | lit. [1] |
|---|---|
| $g = 2.0045$ | 2.0040 |
| $a_N = 10.1$ G | 10.26 G |
| $a_{H(m)} = 1.8$ G | 1.90 G |

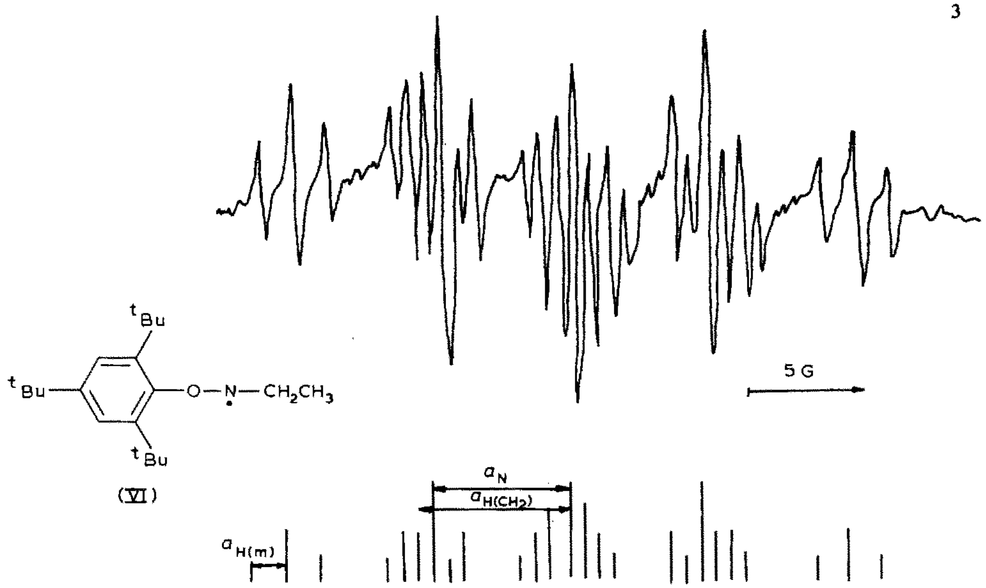
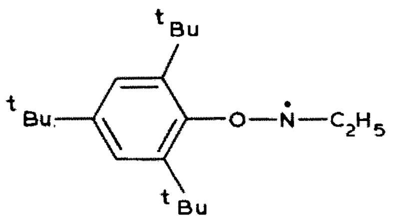


Fig. 1. ESR spectrum of the paramagnetic product formed in the system $C_2H_5AlCl_2$/methyl acrylate/TBNB (mole ratio 1/10/1, in toluene) after vanishing of the nitroxide radical.

The above radicals are formed immediately after mixing the reactants even at −80°C and vanish slowly after the samples are heated to about 60°C. The formation of radical V indicates that in the reaction between TBNB and an organoaluminium compound the alkyl radical is generated and subsequently trapped by TBNB. Nitroxides III and IV can be formed in the same manner. Another possibility is the scission of the Al–O bond in an aluminium derivative of the corresponding *N*-alkylhydroxylamine resulting from the 1,2-addition to the N=O group. This type of mechanism was proved in reactions of phenylmagnesium bromide with nitrosobenzene [6].

For the system containing $C_2H_5AlCl_2$, careful heating and cooling operations gave a clear spectrum of another radical (Fig. 1). The hyperfine structure exhibits splitting for one nitrogen and two pairs of protons. In our opinion the spectrum can be assigned to the ethyl 2,4,6-tri-t-butylphenoxyamino radical (VI). The rather small coupling constants of the nitrogen and methylene group protons can be explained in terms of a large spin delocalization on the 2,4,6-tri-t-butylphenoxy substituent.



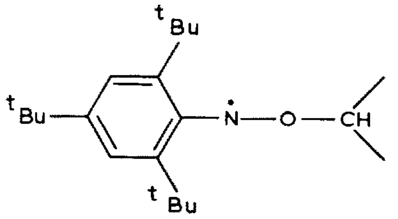
(VI)

$g = 2.0033$
$a_N = 5.3$ G
$a_{H(CH_2)} = 5.9$ G
$a_{H(m)} = 1.3$ G

The proton coupling constant of 1.3 G fits reasonably with the value expected for *meta* protons at the benzene ring in VI, i.e. it is greater than that for nitroxides (0.8 G) [1–4] and a little smaller than that for alkoxyanilino radicals (1.7–2.3 G) [1–4].

(The observed radical has spectral data differing from those for the ethoxyanilino radical reported by Yatsu ($g = 2.003$, $a_N = 10.6$ G, $a_H(CH_2) = a_{H(m)} = 2.3$ G) [2–4].) The amino radical VI may be formed by the 1,2-rearrangement of the aryl group in ethyl 2,4,6-tri-t-butyl nitroxide (IV) or in the aluminium derivative of ethyl 2,4,6-tri-t-butylhydroxylamine, followed by the cleavage of the O–Al bond.

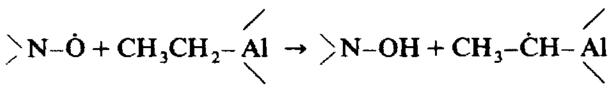
Another amino radical VII is formed when the system containing ethyl 2,4,6-tri-t-butylnitroxide (IV) is treated with an excess of the ethylaluminium compound. The spectrum observed after complete disappearance of the nitroxide (Fig. 2) exhibits features typical of anilino radicals containing one hydrogen atom bonded to the carbon atom which is itself linked to the oxygen atom [1,2].



(VII)

| found | lit. [1,2] |
|---|---|
| $g = 2.0047$ | 2.003–2.004 |
| $a_N = 11.2$ G | 10.9–11.0 G |
| $a_{H(CH)} = a_{H(m)} = 1.8$ G | 1.66–1.90 G |

It has been suggested that the nitroxide radicals can abstract a hydrogen atom from the methylene group in ethylaluminium compounds [7]:



$$>N\text{-}\dot{O} + CH_3CH_2\text{-}Al< \rightarrow >N\text{-}OH + CH_3\text{-}\dot{C}H\text{-}Al<$$

(VIII)

The radical VIII trapped by TBNB might produce the spectrum observed.

The signal of radical VII is observed together with that of the nitroxide when the reaction is carried out in toluene without a strong Lewis base. If a strong Lewis base is added to the product, the nitroxide signal predominates.

More detailed studies on the reactions between nitroso compounds and organoaluminium compounds will be described in a later paper.

## Experimental

All experiments with organoaluminium compounds were carried out using dry, oxygen-free solvents under nitrogen.

2,4,6-Tri-t-butylnitrosobenzene was obtained by a published method [8]. Methyl- and ethyl-aluminium compounds (commercial grade) were purified by distillation. Tri-t-butylaluminium diethyl etherate was prepared as previously described [9]. The toluene solutions of organoaluminium were introduced at −80°C into a Suprasil silica tube containing the required amount of TBNB in the appropriate solvent.

The ESR spectra were recorded on a Varian E 4 or JEOL JES ME-3X spectrometer.

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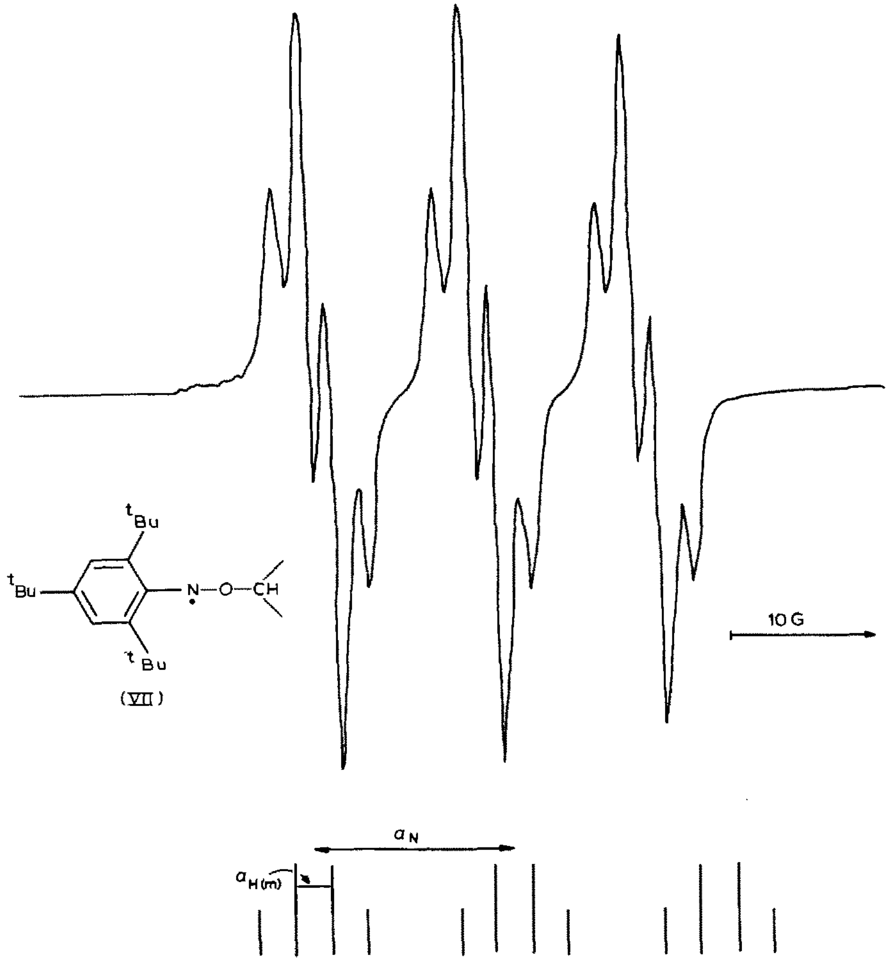

Fig. 2. ESR spectrum of the paramagnetic product formed in the system $(C_2H_5)_3Al$/THF/TBNB (mole ratio 1/10/1, in toluene) after introducing an excess of $(C_2H_5)_3Al$.

ments and for valuable discussions. This work was carried out as part of the research programme M.R.I.12 and was financed by the Polish Academy of Sciences.

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