

THE ESR SPECTRUM OF THE DIPHENYLMETHYL RADICAL

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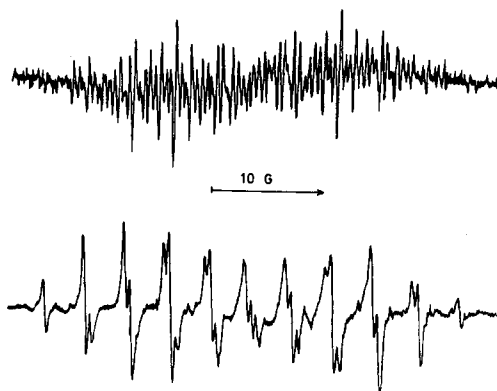
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In a recent note Neugebauer and Groh¹⁾ have shown that published data on the solution esr spectrum of diphenylmethyl are based on a wrong identification of the radical species. They were unable, however, to obtain a resolved esr spectrum of unsubstituted diphenylmethyl and concluded that its identification remains a challenge. We report that diphenylmethyl is conveniently generated by the reaction²⁾ of triethylsilyl radicals with diphenylmethyl bromide. The esr spectrum observed at -40°C is shown in the upper part of the figure. Analysis of the spectrum, checked by computer simulation, yields the coupling constants $a_{\text{H}}^{\alpha} = 14.7$, $a_{\text{H}}^{\text{O}} = 3.7$, $a_{\text{H}}^{\text{M}} = 1.35$ and $a_{\text{H}}^{\text{P}} = 4.2$ G. We have likewise generated the di(3,5-di-t-butylphenyl)methyl radical. The comparatively simple spectrum shown in the lower part of the figure gives $a_{\text{H}}^{\alpha} = 14.6$, $a_{\text{H}}^{\text{O}} = 3.7$ and $a_{\text{H}}^{\text{P}} = 4.1$ G in good agreement with the values for the unsubstituted species. We have also been able to obtain the t-butyl substituted radical from the thermal reaction of t-butyl peroxyoxalate and di(3,5-di-t-butylphenyl)methane in benzene at 40°C [$a_{\text{H}}^{\alpha} = 14.4$, $a_{\text{H}}^{\text{P}} = 4.0$ and $a_{\text{H}}^{\text{O}} = 3.6$ G]. The α -hydrogen coupling constant are slightly smaller than those found for ortho alkyl-substituted diphenylmethyl radicals³⁾ and the ring coupling constants are slightly

greater indicating reduced twisting of the phenyl groups and greater delocalisation of the unpaired electron in the absence of steric hindrance. The value of $a_{\text{H}}^{\alpha} = 15.92\text{G}$ for di(2-t-butylphenyl)methyl reported by de Jong *et al.*³⁾ appears more consistent with our results than the value of 18.18G assigned to the same radical by Bölsing and Korn⁴⁾ which seems improbably high.



Esr spectra of diphenylmethyl (top) and di(3,5-di-t-butylphenyl)methyl (bottom).

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