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FREE RADICALS DERIVED FROM 1,4-DIAZA-1,3-BUTADIENE

II *. ADDUCTS WITH METAL CARBONYLS AND REACTIONS WITH DERIVATIVES OF GROUP VB ELEMENTS

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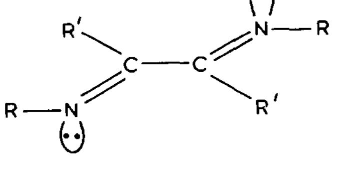
Summary

The paramagnetic adducts formed when photochemically generated $\mathrm{M\dot{n}(CO)_5}$ or $\mathrm{R\dot{e}(CO)_5}$ radicals are trapped by *N,N'*-di-t-butyl-1,4-diaza-1,3-butadiene (t-Bu-DAB) have been characterized by ESR spectroscopy. Adducts containing phosphorus have also been observed but attempts to produce adducts containing As, Sb or Bi have been unsuccessful. In a number of systems an identical ESR spectrum was observed. This has been shown to arise from the *N,N'*-di-t-butylpyrazinium cation.

Introduction

In the first paper of this series [1] we described the ESR spectra of adducts formed by *N,N'*-di-t-butyl-1,4-diaza-1,3-butadienes (I) with silyl, germyl and stannyl



(I)

radicals. The results obtained for t-Bu-DAB (I, R = t-Bu, R' = H) were similar to

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* For part I see ref. 1.

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those found in numerous studies of analogous reactions involving α-diketones or *ortho*-quinones. The reactions of 1,2-diones with transition metal carbonyls have also been the subject of several ESR investigations [2,3] but the only reported species containing R-DAB ligands are radical anions derived from Cr, Mo and W carbonyls [4]. We now report on the reactions of t-Bu-DAB with $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$.

The reaction of *ortho*-quinones with derivatives of Group VB elements has also been shown to give radical adducts with characteristic ESR spectra [5]. The behaviour of t-Bu-DAB with similar compounds is less straightforward and reveals a number of unexpected features.

Reactions of t-Bu-DAB with metal carbonyls

Irradiation with unfiltered ultraviolet light of a solution of t-Bu-DAB in benzene containing $Mn_2(CO)_{10}$ gives an ESR spectrum consisting of a single broad line but, when an aqueous $CuSO_4$ solution (5 cm path length) is inserted into the optical path, a well resolved spectrum is observed which is readily analysed in terms of coupling to two protons (4.65 G), two ^{14}N nuclei (7.94 G) and a single ^{55}Mn nucleus (8.49 G) with $g = 2.0020$.

A similar experiment with $Re_2(CO)_{10}$ gave an intense ESR spectrum (Fig. 1). This adduct is much more persistent than the corresponding manganese radical and can be detected practically unaltered after several days in the absence of UV irradiation. The spectrum is unchanged by the addition of triphenylphosphine, whereas addition of PPh_3 to a solution of the manganese radical results in a vigorous evolution of gas and loss of the ESR signal. The spectrum (Fig. 1) can be interpreted in terms of the coupling to two protons (4.81 G), two ^{14}N nuclei (7.29 G), and a single rhenium (^{185}Re 36.44 G, ^{187}Re 36.82 G) with $g = 2.0029$. Varying the temperature did not lead to any significant changes in the appearence of the spectrum. The metal coupling decreased slightly as the temperature was raised.

The addition of $Co_2(CO)_8$ to a degassed solution of t-Bu-DAB in benzene

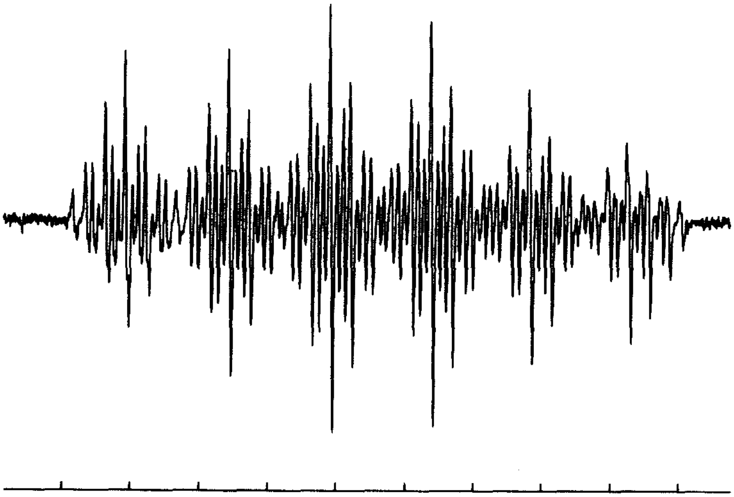
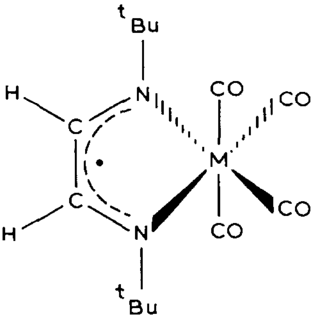


Fig. 1. Room temperature ESR spectrum of radical II (M = Re). 25 G spacing between marks.

resulted in a vigorous evolution of gas but no ESR signals were detected either in the dark or during UV irradiation.

The behaviour of t-Bu-DAB with $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ shows strong parallels with that reported [2,3] for α-diketones and *ortho*-quinones and we assign the observed radicals to the general structure II. They are isoelectronic with the radical anions containing Cr, Mo and W investigated by tom Dieck and his coworkers [4]. The probable mode of formation is addition of photolytically generated $\dot{M}n(CO)_5$ or $\dot{R}e(CO)_5$ to t-Bu-DAB followed by loss of carbon monoxide.



(II)

Structurally related species have recently been postulated as paramagnetic intermediates in the reactions of *ortho*-quinones with chromium, molybdenum and tungsten hexacarbonyls [6].

The radical complexes formed by *ortho*-quinones with manganese, rhenium, chromium, molybdenum and tungsten carbonyls have been shown to undergo a variety of ligand exchange reactions [2,3,6]. As indicated above, our initial attempts to substitute the t-Bu-DAB complexes II with PPh_3 have not produced new

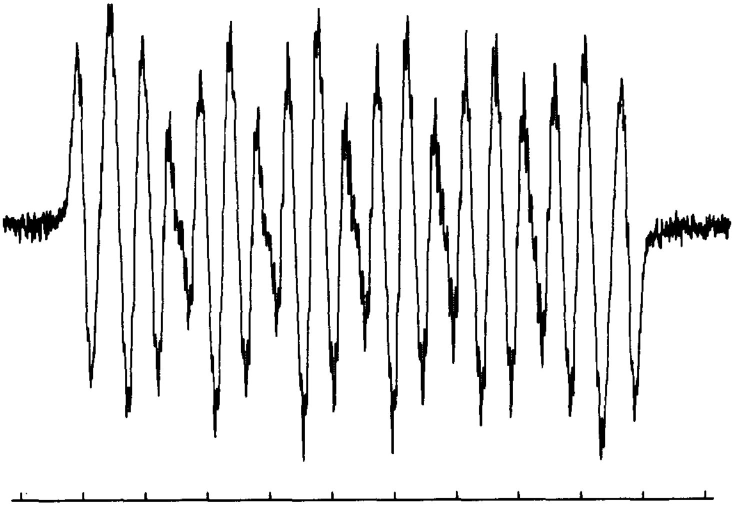
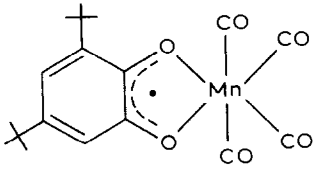


Fig. 2. Room temperature ESR spectrum of the radical obtained by adding some t-Bu-DAB to a solution of radical III. 5 G spacing between marks.

paramagnetic species. We have, however, performed one experiment which suggests that the investigation of substitution reactions involving R-DAB may prove worthwhile.

Irradiation of a solution of $Mn_2(CO)_{10}$ and 3,5-di-t-butyl-*ortho*-benzoquinone in benzene gives the known complex III with a(H) 3.30, a(Mn) 7.07, a(H)(decet) 0.29 G and $g = 2.0032$. If, in the absence of UV irradiation, some t-Bu-DAB is then added to the solution, the spectrum changes to that shown in Fig. 2. This can be analysed in terms of similar couplings to those found for III together with splitting from a single ^{14}N nucleus (a(H) 2.74, a(Mn) 7.11, a(H) (decet) 0.28, a(N) 2.58 G, $g = 2.0035$) suggesting that one CO ligand has been replaced by t-Bu-DAB acting as a monodentate ligand. An alternative possibility is t-Bu-DAB replaces two CO ligands, one apical and one equatorial, but only one of the two non-equivalent ^{14}N nuclei gives a detectable hyperfine coupling.



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Reactions of t-Bu-DAB with compounds of Group VB elements

Paramagnetic intermediates formed during the thermal reaction of *ortho*-quinones with compounds containing P, As, Sb and Bi have been described previously [5]; for example an ESR spectrum observed during the reaction of phenanthraquinone with $SbCl_3$ was assigned to $(PQ)\dot{S}bCl_2$.

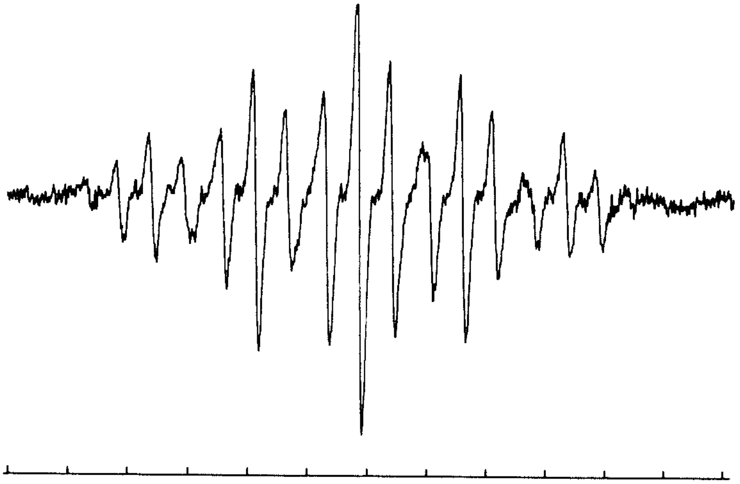
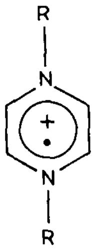


Fig. 3. ESR spectrum of the pyrazinium radical cation IV (R = t-Bu) recorded at 70°C. 5 G spacing between marks.

The spectrum obtained when a similar reaction was carried out using t-Bu-DAB in place of PQ is shown in Fig. 3. The same spectrum was observed when $SbCl_3$ was replaced by $AsCl_2Ph$, $SbCl_2Ph$ or $AlCl_3$ and in a number of solvents (THF, t-butylbenzene, diglyme, tetraglyme). It can be analysed as a quintet of quintets (a(4H) 2.74, a(2N) 8.62 G), a small coupling of 0.11 G from 18 equivalent protons, and $g = 2.0031$. In the more viscous solvents the wings of the spectrum exhibit strong line broadening.

After considering a number of possible structures which might account for the observed hyperfine pattern, we have come to the conclusion that the spectrum is that of *N*,*N*′-di-t-butyl-pyrazinium radical cation IV (R = t-Bu). We have confirmed the



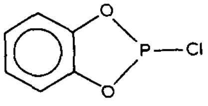
(IV)

assignment by establishing that the same spectrum is obtained by addition of t-butyl iodide to *N*-t-butyl-1,4-pyrazinium iodide or to pyrazine itself. Further support for the formation of a pyrazinium cation is provided by the observation that reaction of i-Pr-DAB with $SbCl_3$ in THF gives the spectrum of IV (R = i-Pr with a(2H) 2.90, a(4H) 2.56, a(2N) 8.40 G and $g = 2.0034$.

The signals attributed to pyrazinium radical cations develop slowly at ambient temperature but increase rapidly in intensity at 70°C; once formed the radicals persist for several days.

A further complication is that similar experiments with $AsClPh_2$, $SbClPh_2$, and, in some cases, $AlCl_3$ gave a different ESR spectrum which could also be simulated as a quintet of quintets but with a(2N) 7.79, a(4H) 3.10 G, and $g = 2.0032$. We have not been able to identify the radical responsible for this spectrum; one possibility is that radical cation IV is complexed with the counterion in these systems.

No radicals were detected in the reactions of PPh_3, $AsPh_3$ or $SbPh_3$ with t-Bu-DAB. However the chlorophosphole V reacts rapidly to give the pyrazinium cation IV (R = t-Bu) provided the temperature is kept below ca. 400 K. Above that



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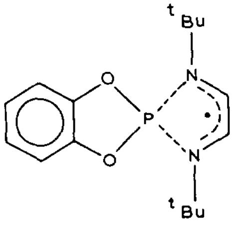

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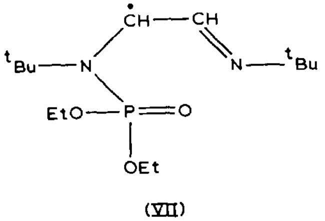

(VII)

temperature the spectrum is replaced by a pattern corresponding to coupling with two protons (5.67 G), two ^{14}N nuclei (6.79 G) and one ^{31}P nucleus (13.58 G) which we assign to VI existing as either the symmetric adduct depicted above, or as a rapid equilibrium between unsymmetrical adducts.

Phosphonyl radicals obtained by photolysis of tetraethylpyrophosphite in di-t-butyl peroxide react readily with t-Bu-DAB to give the adduct VII with a(H) 6.23, a(N) 4.48, a(N) 6.29 and a(P) 17.22 G.

Discussion

The reaction of t-Bu-DAB with $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ was as expected but the formation of pyrazinium cations in the reactions with Group VB halides was not anticipated. The identity of the observed radical has been established but its mode of formation is still not clear. However, the value of R-DAB as a trap for organometallic radicals has been established in Part I [1] for Group IVB radicals and, in this paper, for metal carbonyls and phosphorus centred radicals.

Experimental

The preparation of R-DAB [1] and the ESR techniques [5] have been described previously.

Acknowledgement

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