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REACTIONS OF TRIPHENYLBORANE WITH PHOTOEXCITED KETONES AND WITH DIAZODIARYLMETHANES

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Summary

Aromatic ketones and diones when exposed to UV irradiation in the presence of triphenylborane give $R_2\dot{C}-OBPh_2$ radicals through an S_H2 displacement of phenyl from BPh_3 by the excited triplet state of the carbonyl derivative. Very persistent radicals, characterized by *g*-factors higher than 2.0040, are obtained when boron is compelled to lie in the molecular plane owing to chelation by an electron-rich atom, such as oxygen (diones) or nitrogen. In some of these radicals, coupling of the unpaired electron with protons of the BPh_2 group was also observed. Diazodiarylmethanes react spontaneously with triphenylborane by a heterolytic pathway, which eventually leads to the formation of triphenylmethyl radical.

Introduction

Davies et al. [1,2] reported that UV irradiation of mixtures of dialkyl ketones and trialkylboranes at low temperature inside the cavity of an ESR spectrometer leads to observation of the superimposed spectra of two radicals. These two radicals were identified as $R_2\dot{C}-OBR'_2$ (I) and $R'\cdot$, formed in reaction 1.

$$R_2C{=}O^{\star} + BR'_3 \rightarrow R_2\dot{C}-OBR'_2 + R'\cdot \qquad (1)$$

This has been taken as evidence that ketones, photoexcited in their triplet state, react with the borane to give a bimolecular homolytic substitution (S_H2) at boron, thus behaving similarly to the related alkoxyl radicals [1,2]. The radicals I were characterized by *g*-factors of 2.0034 and ^{11}B hyperfine splittings of ca. 8–9 G.

ESR signals were also detected when aromatic ketones or diones, such as acetophenone, benzophenone, benzil, etc., were used but the ESR parameters of the resulting boron-containing radicals were not determined [1]. For benzophenone and several ring substituted acetophenones, conventional techniques were used instead to determine the $S_{H}2$ process rate constants, which were found to be of the order of 10^8 M^{-1} s^{-1} at room temperature [3].

Since alkoxyl radicals can also displace phenyl radicals from BPh_3 [4], we irradiated a number of carbonyl compounds in the presence of triphenylborane, instead of trialkylboranes, in order to see whether a similar substitution reaction could also be induced by ketone triplets. Very strong ESR spectra of the radicals resulting from homolytic displacement of phenyl from BPh_3 were detected when diones and some aromatic ketones were used. These radicals were in some cases persistent at room temperature even for days in the absence of oxygen.

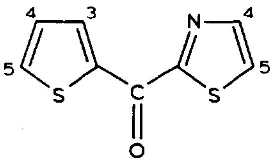
With the aim of establishing whether other triplets can bring about displacements at boron, we also brought BPh_3 into reaction with precursors of diarylcarbenes, i.e. diazodiarylmethanes. In this case, however, a non-radical reaction between the dioazomethane and triphenylborane takes place upon mixing the two reactants, giving eventually phenyldiarylmethyls.

Results and discussion

(a) Reactions with aromatic ketones and 1,2-diones

The aromatic carbonyl derivatives we investigated were benzophenone (**1**), bis(2-thienyl) ketone (**2**), 2-tienyl-2-thiazolyl ketone (**3**), bis(2-pyridyl) ketone (**4**), phenyl triphenylsilyl ketone (**5**), 4-chlorophenyl triphenylsilyl ketone (**6**), 9,10-phenanthraquinone (**7**), benzo(2,1-*b*;3,4-*b*′)dithiophen-4,5-dione (**8**), *α*-furyl (**9**), 4,4′-dimethoxybenzil (**10**) and 3,5-di-butyl-*o*-benzoquinone (**11**).

When a deoxygenated benzene solution of benzophenone (~ 0.2 M) and triphenylborane (~ 0.4 M) is irradiated at room temperature, an ESR spectrum is observed which can be interpreted on the basis of the coupling of the unpaired electron with the protons of two phenyl rings and with a boron nucleus. The



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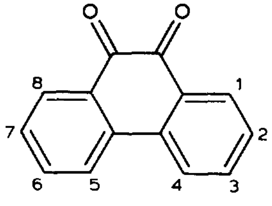

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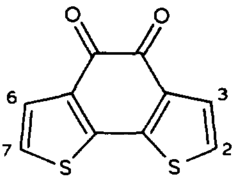

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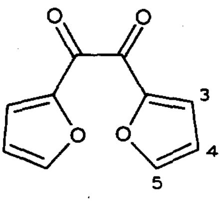

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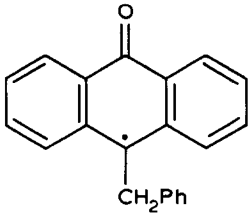
intensity of the ESR signal can be enhanced by raising the temperature, and a better spectrum was recorded at 343 K *. The boron splitting is almost temperature independent and its magnitude (5.80 G for ^{11}B) is comparable with the values observed for $R_2\dot{C}-OBR'_2$ radicals (R and R' = alkyl) after taking into account the reduction of spin density at the radical centre due to delocalization of the unpaired electron into the aromatic rings. We therefore attribute the observed ESR spectrum to the radical $Ph_2\dot{C}-OBPh_2$, formed by an S_H2 displacement of phenyl by the benzophenone triplet from the boron atom (eq. 2).

$$Ph_2C{=}O \rightarrow Ph_2C{=}O^{\star} \xrightarrow{BPh_3} Ph_2\dot{C}-OBPh_2 + Ph^{\cdot} \quad (2)$$

Bis(2-thienyl) ketone (**2**) behaves similarly, although the related radical, 2-$Th_2\dot{C}-OBPh_2$, is observable in much lower concentration and at higher temperature (403 K). No radical species were instead observed when fluorenone or xanthone were irradiated with BPh_3. The failure to detect the expected radicals I (R = aryl and R' = phenyl) should probably be attributed to the fact that their dimerization is faster than in the case of non-cyclic ketones, where the radical centre is more sterically hindered owing to non-coplanarity of the aromatic rings.

This possibility appears to be substantiated by the special behaviour displayed by 9-methyleneanthrone, the reaction of which with triphenylborane did not afford any boron-containing radical, but gave rise to a strong ESR spectrum attributable to radical II ($a_{1,8}$ 2.98, $a_{2,7}$ 0.83, $a_{3,6}$ 3.33, $a_{4,5}$ 1.01, $a(CH_2)$ 6.32, $a_{Ph}(2H)$ 0.17 G, $g = 2.0034$ at 296 K). The trapping of phenyl radicals by the C=C double bond of 9-methyleneanthrone provides evidence for the occurrence of the displacement reaction analogous to eq. 2, even though the primary $Ar_2\dot{C}-OBPh_2$ could not be detected.



(II)

Boron-containing radicals showing an ^{11}B splitting of about 7.5 G are also detected when mixtures of BPh_3 with the aroylsilanes $Ph(Ph_3Si)C{=}O$ or 4-$ClPh(Ph_3Si)C{=}O$ are irradiated. Although the identification of these species as $Ar(Ph_3Si)\dot{C}-OBPh_2$ (III) seems straightforward, the photolability of aroylsilanes [5,6] poses some problems, and the alternative structure $Ar(Ph_2B)\dot{C}-OSiPh_3$ (IV) must also be considered in the light of the results of an earlier study involving

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* The temperature dependence of the ESR signal intensity is similar to that of the related $Ph_2\dot{C}OMR_3$ (M = Si, Sn) radicals described by Neumann et al. [11], and explained in terms of monomer-dimer equilibria.

TABLE 1

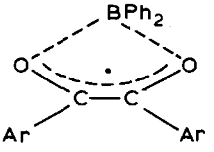
ESR SPECTRAL PARAMETERS FOR THE RADICALS $RR'\dot{C}OBPh_2$ (I) OBTAINED BY IRRADIATING MIXTURES OF KETONES AND TRIPHENYLBORANE

Ketone	$a_{^{11}B}$(G)	a_{other}(G)	g	T(K)
1	5.80	3.33($4H_o$), 1.27($4H_m$), 3.70($2H_p$)	2.0028	343
2	5.03	5.35(2H(3)), 1.11(2H(4)), 4.55(2H(5))	2.0036	403
3	3.54	3.08(N), 0.65(H′(4)), 3.78(H′(5)) 3.93(H(3)), 0.77(H(4)), 3.64(H(5))	2.0046	298
4	12 equally spaced lines with ΔH 2.24 G		2.0041	298
5	7.63	4.27, 4.52($2H_o$), 1.48($2H_m$), 5.12(H_p)	2.0029	298
6	7.48	4.33, 4.63($2H_o$), 1.56($2H_m$), 0.43(^{35}Cl)	2.0034	296

tetraethylpyrophosphite [7]. Since, however, the measured ^{11}B coupling is intermediate between those of the dialkyl, $R_2\dot{C}{-}OBR'_2$, and diaryl, $Ar_2\dot{C}{-}OBPh_2$, derivatives we favour structure III over IV.

Very strong ESR spectra are obtained even at room temperature when solutions of BPh_3 and 2-thienyl 2-thiazolyl ketone (**3**) or bis(2-pyridyl) ketone (**4**) are irradiated. These spectra are characterized by large linewidth (ΔH_{pp} 0.38 G for the adduct from **3** against 0.22 G for $Ph_2\dot{C}{-}OBPh_2$) and g-factors (see Table 1). Since both **3** and **4** contain at least one heterocyclic nitrogen β to the carbonyl group, it seems reasonable to attribute the greater persistence of their boron adducts to stabilization through chelation of boron by the nitrogen lone pair.

Since chelation is also expected with α-diones, we treated a number of diketones and *ortho*-quinones with BPh_3. In all cases very long-lived radicals were obtained; in particular, with dione (**8**) the radical adduct did not appreciably decay during several days. Likewise for the adducts of ketones **3** and **4**, the radicals show spectra with large linewidth and g-factors ($g \geqslant 2.0040$). The former feature can be attributed to hyperfine structure from the ten phenyl ring protons of BPh_2 which is generally unresolved. Only in the cases of the adducts of **8** and **9**, did second derivative recording of the ESR spectra allow these splittings to be measured, as 0.15 and 0.13 G, respectively, thus providing further evidence that BPh_2 is the group attached to the carbonyl oxygen. The observed equivalence of the two aryl rings of the dione moiety suggests that the radicals adopt the chelated structure V, in which boron is equally bound to the two oxygen atoms. Although the retention of the original symmetry in the radical adducts of diones may be only apparent, and the result of rapid migration of the BPh_2 group between the two oxygens, giving rise to averaging of the proton splittings in the two rings, such a fluxional process if present should be extremely fast, since even at temperatures close to the freezing point of toluene no



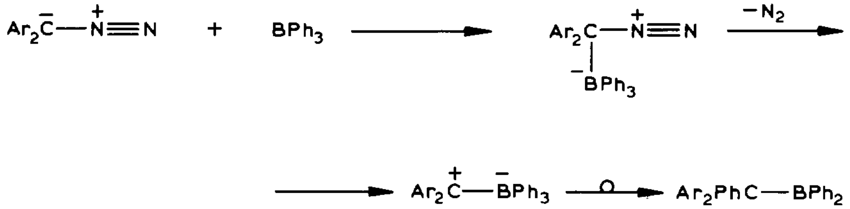
(V)

selective line broadening was detected. In view of the ease with which coordination takes place between boron and oxygen lone pairs, we favour the chelated structure V.

(b) Reactions with diazodiarylmethanes

In an attempt to establish whether triplet diarylcarbenes could also give homolytic substitution at boron, we treated BPh_3 with Ph_2CN_2 and diazofluorenylidene. In both cases simple mixing the reactants led to the appearance of strong ESR signals, which could be unambiguously attributed to triphenylmethyl and 9-phenylfluorenyl radicals, respectively. Irradiation of the solution did not result in any appreciable variation of the signal height.

The probable explanation of this finding is that triphenylborane undergoes nucleophilic attack by the diazodiarylmethane, and this is followed by a rearrangement involving a 1,2-shift of a phenyl group of BPh_3 to give $Ar_2PhC{-}BPh_2$ (eq. 3) *.



$$Ar_2\overset{-}{C}-\overset{+}{N}\equiv N + BPh_3 \longrightarrow Ar_2\underset{\overset{|}{^{-}BPh_3}}{C}-\overset{+}{N}\equiv N \xrightarrow{-N_2} Ar_2\overset{+}{C}-\overset{-}{B}Ph_3 \xrightarrow{\frown} Ar_2PhC-BPh_2 \quad (3)$$

Subsequently, as has been reported by Hoberg and Ziegler for the analogous $Ph_3C{-}AlPh_2$ derivative [8], cleavage of the C–B bond will lead to the stable and persistent triarylmethyl radical. However, in view of the results obtained by Roberts et al. [9] indicating that α-azidostyrene reacts with trialkylboranes via a homolytic rather than a heterolytic mechanism, the possibility of a radical chain reaction cannot be ruled out a priori in the present case also. We therefore carried out the reaction in the ESR cavity by using Ph_2CN_2 in the presence and in the absence of oxygen, and monitored the growth of the triphenylmethyl signal. In both cases the spectrum increased smoothly with time, reaching a plateau in ca. 1 h after the initial mixing. The addition of galvinoxyl to the solution of one of the reactants before mixing also had no apparent inhibiting effect on the rate of formation of $\cdot CPh_3$. We therefore believe that eq. 3 adequately describes the reaction between diazodiarylmethanes and BPh_3.

While attempting to gain evidence for a possible homolytic pathway for the above reaction, we added some phenyl-t-butylnitrone (PBN) to the BPh_3/Ph_2CN_2 mixture in order to scavenge possible phenyl radicals. Superimposed on the usual triphenylmethyl spectrum there were strong signals from $Ph_2CHN(O^{\cdot})Bu^t$ (VI). However the spectrum of this nitroxide was also observed in a blank experiment in which solutions of BPh_3 and PBN were mixed in the absence of diazodiphenylmethane, indicating that the trapping of phenyl radicals is not connected with the occurrence of an homolytic reaction between triphenylborane and Ph_2CN_2.

Further investigation of the reaction between BPh_3 and PBN showed that when

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* Insertion of a methylene unit into the R–B bond has been reported also by Davies et al. [12] in the reaction of diazomethane with boron compounds.

TABLE 2

ESR SPECTRAL PARAMETERS FOR RADICALS II OBTAINED BY IRRADIATING MIXTURES OF DIONES AND TRIPHENYLBORANE AT ROOM TEMPERATURE

Dione	$a_{^{11}B}$(G)	a_H(G)	a_{other}(G)	g
7	3.87	n.r.	0.46(4H(1,3,6,8)), 1.95(4H(2,4,5,7))	2.0042
8	3.96	0.15 [a]	0.15(2H(3,6)), 0.99(2H(2,7))	2.0051
9	3.57 [b]	0.13 [a]	2.59(4H(3,5,3′,5′)), 0.30(2H(4,4′))	2.0041
10	3.98	n.r.	1.27(4H$_o$)	2.0044
11	4.71	n.r.	3.78(H(4))	2.0043

[a] 10 protons from BPh_2 moiety. [b] $a_{^{10}B}$ 1.20 G.

the solutions containing each reactant were carefully deoxygenated before mixing, very weak spectra of VI, whose intensity did not change with time, were detected. Bubbling a small amount of oxygen through the solution produced a sudden increase of the ESR signal (by up to two orders of magnitude), without causing appreciable line broadening. Prolonged bubbling of O_2 resulted in a further increase of the spectral intensity, up to a maximum beyond which the ESR lines started to be severaly broadened. These results are a clear indication that no reaction takes place between BPh_3 and PBN in an oxygen-free atmosphere, and suggest that phenyl radicals originate from autoxidation of triphenylborane.

Experimental

Triphenylborane (Aldrich) and all other commercially available compounds were used as delivered. Compounds **2**, **3**, **5**, **6**, **8**, **10**, and diazodiphenylmethane were synthesized by established methods.

ESR measurements (Tables 1 and 2) were carried out by irradiating, where necessary, carefully deoxygenated benzene, toluene or t-butylbenzene solutions of the reactants with unfiltered UV light from a 1 kW high pressure mercury lamp. A Bruker ER-200 spectrometer was used, equipped with standard variable temperature accessories, an NMR gaussmeter (for field calibration), and a frequency counter (for g-factor determination).

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