

An ESR study of the mercuration of the biphenylene radical cation. Evidence for a homolytic mechanism of mercuration *

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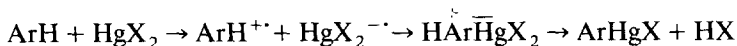
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Abstract

When a solution of biphenylene in trifluoroacetic acid containing mercury(II) trifluoroacetate is photolysed with ultraviolet light, the ESR spectra show the progressive mercuration of the biphenylene radical cation in the β -position. β -Proton hyperfine coupling [$a(\text{H}_\beta)$ 3.58 G] is lost, and ^{199}Hg primary, secondary, and tertiary satellites [$a(^{199}\text{Hg}_\beta)$ 76–77 G] appear until tetra- β -mercuration is complete.

It is concluded that, apart from the usual electrophilic mechanism, an alternative mechanism for mercuration exists, and that this probably involves collapse of the aromatic radical cation, $\text{ArH}^{+\cdot}$, with its counterion, $\text{HgX}_2^{-\cdot}$:



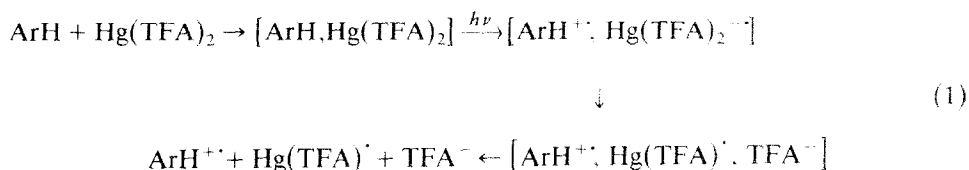
Introduction

One of the most useful techniques for the one-electron oxidation of π -conjugated organic compounds to the corresponding radical cations was developed recently by Lau and Kochi, and involves photolysis of a solution of the substrate in trifluoroacetic acid (TFAH) containing mercury(II) trifluoroacetate [1–3].

From a thorough study of the oxidation of the homologous methylbenzenes, Lau and Kochi concluded that the reaction involved the initial formation of a charge-transfer complex between the hydrocarbon and the mercury(II) trifluoroacetate; the complex of hexamethylbenzene was isolated as a crystalline solid, and its structure was determined by single crystal X-ray diffraction. Irradiation into the charge-trans-

* Dedicated to Professor Colin Eaborn in recognition of his important contributions to organometallic chemistry, including the mechanisms of organometallic aromatic substitution.

fer band then induced electron transfer, and back-transfer was minimised by rapid dissociation of the counterion $\text{Hg}(\text{TFA})_2^{-+}$ [2,3] (eq. 1).

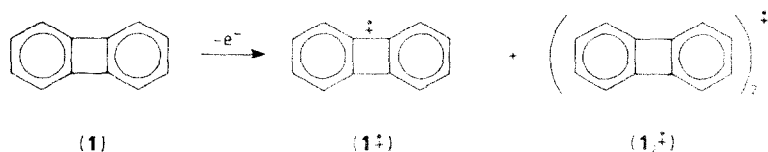


An alternative procedure, with probably an equivalent mechanism, involves the photolysis of a solution of the substrate in trifluoroacetic acid containing thallium(III) trifluoroacetate [3–5].

We are using both these techniques for generating radical cations for study by electron spin resonance spectroscopy [6], and in an increasing number of cases we have observed metallodeprotonation of the substrates [7]. In the ESR spectra, this becomes apparent by the loss of hyperfine coupling by protons, and the development of ^{199}Hg satellites. We describe here the behaviour of biphenylene, which provides the clearest example which we have found of progressive mercurydeprotonation.

Results

Biphenylene **1** was subjected to one-electron oxidation under a variety of conditions, when the spectra of the monomeric ($\mathbf{1}^{+\cdot}$) and dimeric ($\mathbf{1}_2^{+\cdot}$) radical cations were observed.



A solution of the hydrocarbon in sulfuric acid, or in trifluoroacetic acid containing thallium(III) trifluoroacetate, showed in the dark only the familiar spectrum of the monomeric radical cation $\mathbf{1}^{+\cdot}$; $a(4\text{H}_a)$ 0.20, $a(4\text{H}_\beta)$ 3.58 G, g 2.0025 [8–11]. A typical spectrum is shown in Fig. 1, together, at higher gain, with the ^{13}C satellites which can be simulated in terms of the coupling constants $a(^{13}\text{C}_a)$ 3.06, $a(^{13}\text{C}_\beta)$ 2.50 G. The assignments of these coupling constants is discussed below.

A solution in trifluoroacetic acid alone, or in dichloromethane containing aluminium(III) chloride, on the other hand, showed superimposed spectra of the monomeric and dimeric radical cations, $\mathbf{1}^{+\cdot}$ and $\mathbf{1}_2^{+\cdot}$ [11]. For example, the spectrum shown in Fig. 2 represents largely the dimer $\mathbf{1}_2^{+\cdot}$; $a(8\text{H}_a)$ 0.15, $a(8\text{H}_\beta)$ 1.75 G, g 2.0026. When this solution was warmed to about 220 K, the dimer dissociated to show a spectrum consisting predominantly of the monomer. This behaviour is typical of arene radical cations.

Different spectra were observed when biphenylene was treated with Kochi's reagent of trifluoroacetic acid containing mercury(II) trifluoroacetate.

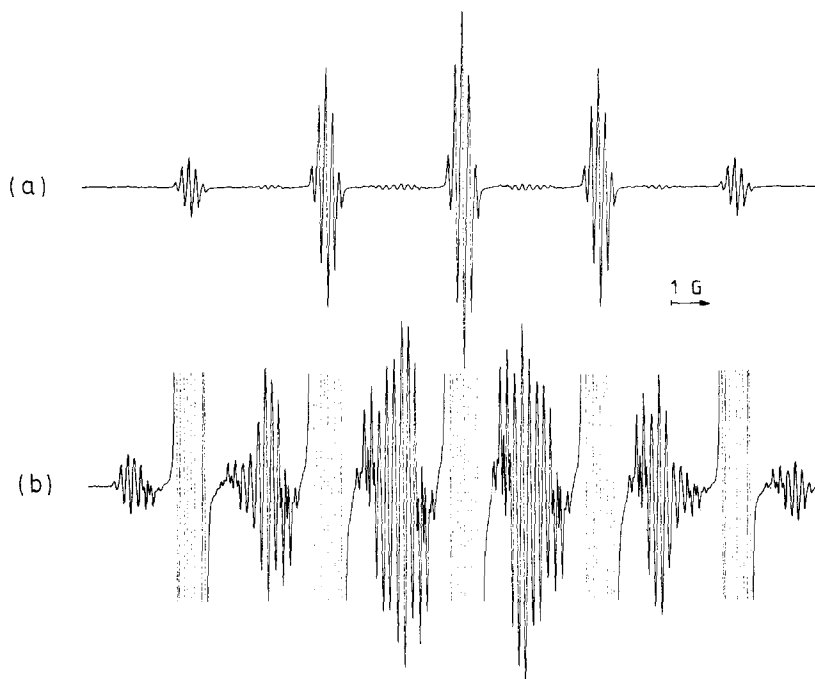


Fig. 1. ESR spectrum (a) of the biphenylene radical cation 1^{++} in trifluoroacetic acid at 260 K, together with, (b), the ^{13}C satellites.

In the dark, the initial spectrum which was observed was essentially that of the monomeric radical cation, 1^{+} .

When this solution was irradiated with Pyrex-filtered UV light, the spectrum changed progressively as shown in Fig. 3, where the magnetic field scale is such that only the larger proton hyperfine coupling of 3.58 G is apparent. The initial quintet

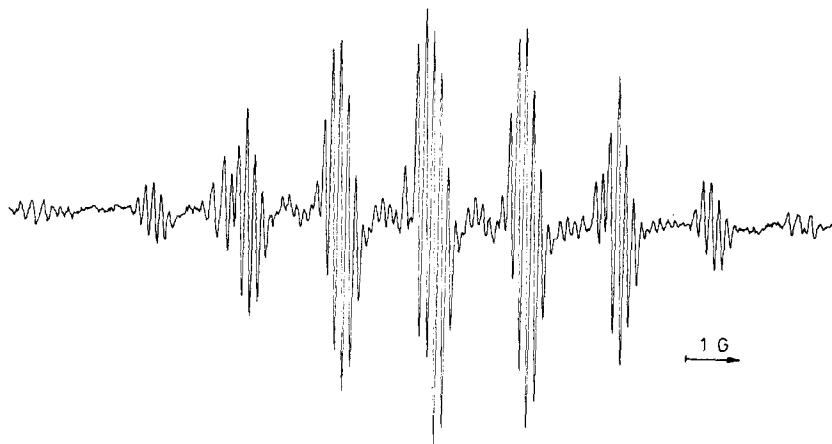


Fig. 2. ESR spectrum of the biphenylene dimer radical cation 1_2^{++} in dichloromethane at 180 K.

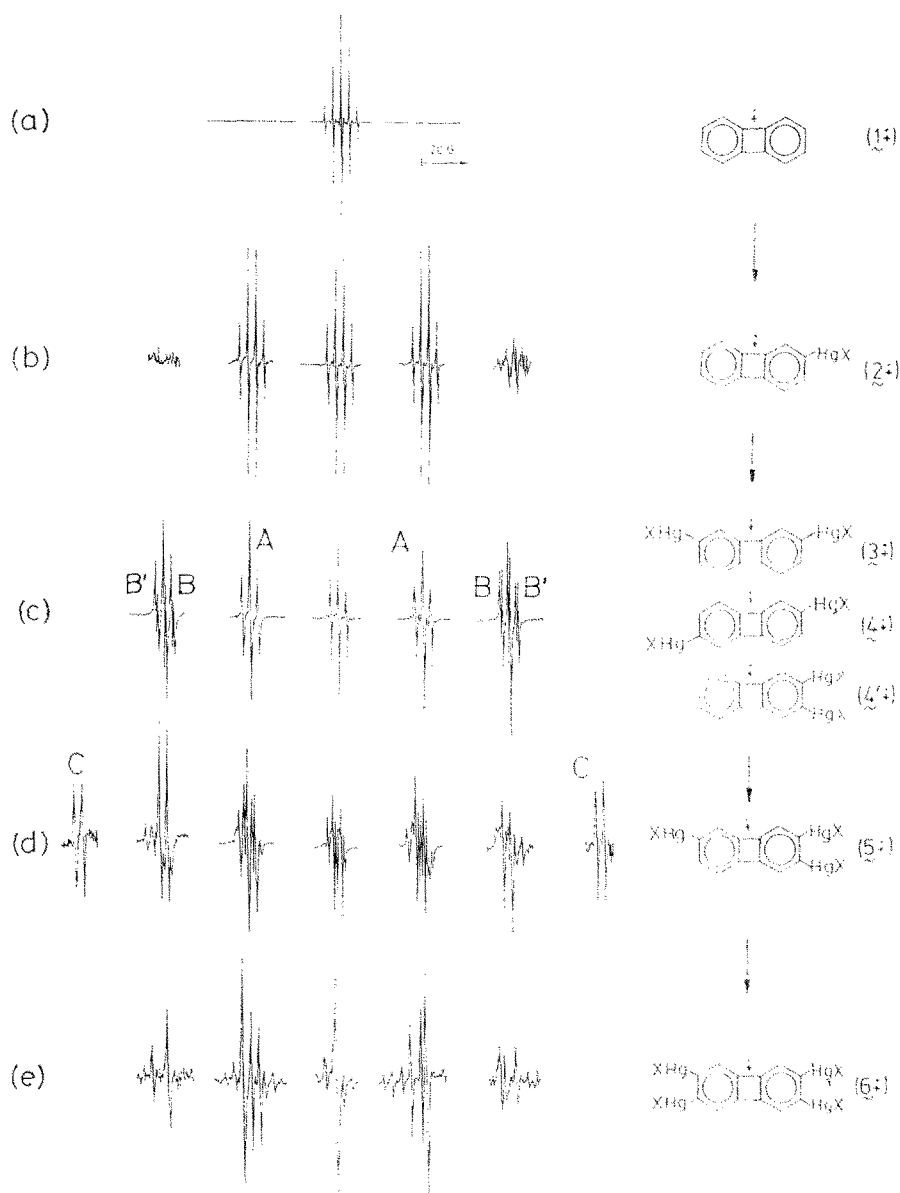


Fig. 3. ESR spectra observed on photolysis of a solution of biphenylene in trifluoroacetic acid containing mercury(II) trifluoroacetate at 293 K.

(Fig. 3) became distorted, then after about 20 min simplified to a quartet (g 2.0014) indicating hyperfine coupling by only three of the original four β -hydrogen atoms (Fig. 3b). Proof that the fourth β -hydrogen atom had been replaced by a mercury substituent is given by the appearance of ^{199}Hg satellites at the appropriate intensity; these are shown in Fig. 3b at a 10-fold spectrometer gain. This spectrum can be simulated with a program which takes account of the second order coupling

by the mercury with $a(^{199}\text{Hg})$ 76.5 G *. Expansion of any line in the central quartet or in its ^{199}Hg satellites, shows that the quintet coupling $a(4\text{H}_\alpha)$ 0.20 G, is still present.

We conclude therefore that the biphenylene radical cation, $1^{+\cdot}$ has been replaced by the β -mercurated radical cation $2^{+\cdot}$ (Fig. 3).

As the photolysis is continued, the spectrum changes further. After about 1 h, the central feature is reduced to a triplet indicating that two of the four β -protons have been replaced by two mercury atoms (Fig. 3c). The primary mercury satellites (A), in the appropriate intensity for dimercuration, show the same triplet pattern as the central feature, although the lines are broader.

In a fraction of the dimercurated molecules, both the mercury atoms will consist of the ^{199}Hg isotope, and these molecules will give rise to a secondary set of satellites, which will appear as 1/2/1 triplets.

On Fig. 3c, these outer, secondary, satellites (B and B') are shown at enhanced gain, and it will be seen that they each consist of a partially resolved pair of triplets. Di- β -mercuration can lead to the three possible isomers $3^{+\cdot}$, $4^{+\cdot}$, and $4'^{+\cdot}$; and spectrum 3c can be simulated assuming that two isomers are present in equal concentration, one showing $a(2\ ^{199}\text{Hg})$ 76.45 G, and the other $a(2\ ^{199}\text{Hg})$ 77.32 G. In the primary satellites, the resulting triplets cannot be resolved, and they show their presence only by conferring an enhanced line width. When the coupling by a second ^{199}Hg atom is imposed, the separations between the superimposed triplets is doubled, and the separate triplets can be partially resolved.

As the intensities of the overlapping triplets are approximately equal, it seems likely that only two isomers are present, and that they are in approximately equal amount, and therefore that the activation energies for the reactions by which they are formed are approximately equal. This suggests that the two isomers are the structurally similar pair, $3^{+\cdot}$ and $4^{+\cdot}$.

Further photolysis then introduces a third β -mercury atom, yielding only one possible isomer, $5^{+\cdot}$. Some remaining triplet character can still be seen in the central feature of the spectrum (Fig. 3d), but the secondary satellites are cleaner, and now, at higher gain, tertiary satellites, C, can be identified, and these, as they should be, are free from the contaminating triplets relating to the residual dimercurated biphenylenes, $3^{+\cdot}$, $4^{+\cdot}$, or $4'^{+\cdot}$.

Finally, after about 3 h of photolysis, the central feature of the spectrum is reduced to a singlet (Fig. 3e). The spectrum is now weaker, but the primary and secondary singlet satellites can still be distinguished, and the principal species present is the tetramercurated radical cation $6^{+\cdot}$, with evidence of some β -mercuration.

Expansion of any one line in any of these spectra in Figs. 3a–3e showed that the quintet pattern due to hyperfine coupling by the α protons, $a(4\text{H}_\alpha)$ 0.20 G was still

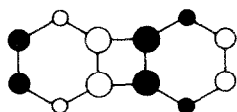
* Natural isotopic nuclear spins and abundances: ^{196}Hg , I 0, 0.14%; ^{198}Hg , I 0, 10.02%; ^{199}Hg , I $\frac{1}{2}$, 16.84%; ^{200}Hg , I 0, 23.13%; ^{201}Hg , I $\frac{3}{2}$, 13.22%; ^{202}Hg , I 0, 29.80%; ^{204}Hg , I 0, 6.85%. From the values of $a(^{199}\text{Hg})$ and the magnetogyric ratios of ^{199}Hg and ^{201}Hg , the expected values of $a(^{201}\text{Hg})$ can be calculated. No satellites due to ^{201}Hg could be detected. Similarly in NMR spectroscopy, ^{199}Hg –H coupling but not as far as we are aware, ^{201}Hg –H coupling, has been observed. The signals are probably broadened beyond detection by the quadrupole moment of the nucleus, I $\frac{3}{2}$. This has been taken into account in calculating the expected intensities of the ^{199}Hg satellites.

present, confirming that mercuration occurred only at the β -position. The spectroscopic properties of the radicals $2^{+\cdot}$ – $6^{+\cdot}$ are collected in Table 2.

Experiments which led to the sequence of spectra in Fig. 3a–3e were carried out in which duplicate samples were prepared, and the second was kept in the dark while the first was photolysed in the cavity until it gave a clean spectrum of dimercurated biphenylene (cf. Fig. 3c). This sample was then replaced in the cavity by the second sample, which showed a spectrum which was still essentially that of biphenylene itself $1^{+\cdot}$; with some slight contamination from monomercured biphenylene $2^{+\cdot}$. This establishes that the mercuration is photo-dependent.

Discussion

We first rationalise the spectrum of the biphenylene radical cation itself ($1^{+\cdot}$), then discuss the implications of the spectra of the mercured derivatives $2^{+\cdot}$ – $6^{+\cdot}$.



(7)

The form of the SOMO of $1^{+\cdot}$ is shown in 7 and the absolute values of the Hückel coefficients are given in the first row of Table 1. Subsequent rows then list the electron density ($q = e^2$), and the values of the proton hyperfine coupling constants as calculated by the Heller–McConnell equation [12]. Row 4 then gives the McLachlan spin densities ($\lambda = 1.1$) [13] followed by the derived values of $a(\text{H})$, and the values which are observed experimentally *.

Table 1
Calculated and observed ESR spectra of the biphenylene radical cation

	Position		
	α	β	γ
1 $ c $	0.164	0.296	0.368
2 q	0.027	0.088	0.135
3 $a(\text{H})_{\text{calc}} (\text{G})^{a,b}$	0.72	2.34	
4 ρ	–0.006	0.091	0.139
5 $a(\text{H})_{\text{calc}} (\text{G})^c$	–0.16	2.42	–
6 $ a (\text{H})_{\text{obs}} (\text{G})$	0.20	3.58	–
7 $a(^{13}\text{C})_{\text{calc}} (\text{G})^d$	–2.14	+1.53	–0.01
8 $a(^{13}\text{C})_{\text{calc}} (\text{G})^e$	–2.56	+1.98	+0.95
9 $a(^{13}\text{C})_{\text{obs}} (\text{G})$	3.06	2.50	– f

^a Hückel–McConnell. ^b $G \cdot 10^{-4}$ T. ^c Hückel–McConnell–McLachlan. ^d Fraenkel–Karplus.

^e Yonezawa–Kawamura–Kato. ^f Hindle, dos Santos Viegas, and Bolton arrived at a similar assignment from a consideration of the line-widths of the ^{13}C satellites [10].

* Carrington and dos Santos Viegas [9] calculated Hückel electron densities [$q(\alpha)$ 0.013, $q(\beta)$ 0.094, $q(\gamma)$ 0.143] and McLachlan spin densities [$\rho(\alpha)$ –0.025, $\rho(\beta)$ 0.101, $\rho(\gamma)$ 0.174] using different resonance integrals to accommodate the fact that the central “cyclobutadiene” unit in biphenylene is rectangular rather than square. The differences between these values and ours are not large enough to affect our argument.

Table 2
ESR spectra of mercurated biphenylene radical cations ^a

Radical cation	Hyperfine coupling constants (G)			g
	H _α	H _β	Hg _β	
1 ⁺⁺	0.21	3.58	—	2.0025
2 ⁺⁺	0.21	3.58	76.5 (1Hg)	2.0014
3 ⁺⁺ ^b	0.21	3.58	76.45 (2Hg)	2.0007
4 ⁺⁺ ^b	0.21	3.58	77.32 (2Hg)	2.0007
5 ⁺⁺	0.21	3.58	75.50 (3Hg)	ca. 2.0003
6 ⁺⁺	0.21	3.58	ca. 78 (4Hg)	ca. 2.0003

^a In trifluoroethanoic acid at 262 K. ^b The assignment of the spectra of the structures 3⁺⁺ and 4⁺⁺ is arbitrary; see text.

The correlation between the observed and calculated hyperfine coupling constants, $a(\text{H})$, is seen to be rather better using McLachlan spin densities (ρ) rather than Hückel electron densities (q), both underestimating the value of $a(\text{H}_\beta)$. The differences between the magnitudes of $a(\text{H}_\alpha)$ and $a(\text{H}_\beta)$, however, is so large that the assignment is unambiguous.

Rows 7 and 8 of Table 1 then list the values of the ¹³C hyperfine coupling constants calculated on the basis of the Karplus–Fraenkel [14] and Yonezawa–Kawamura–Kato [15] models. This suggests the assignment of the observed values of $a(^{13}\text{C})$ as shown in row 9.

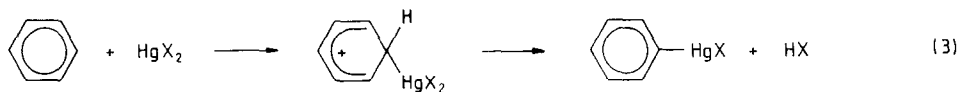
For comparison, the radical anion shows the values of $a(\text{H}_\alpha)$ 0.21, $a(\text{H}_\beta)$ 2.86, and $a(^{13}\text{C})$ 2.44 and 2.86 G [9]. As biphenylene is an alternant hydrocarbon, by the pairing principle, the values of $a(^1\text{H})$ and of $a(^{13}\text{C})$ (on the Karplus–Fraenkel model) should differ only insofar as the appropriate McConnell constants vary ($Q^+ > Q^-$) [16].

As progressive mercuration results in the loss of protons identified by $a(\text{H}_\beta)$ 3.58 G, and the preservation of those with $a(\text{H}_\alpha)$ 0.21 G, the mercury deprotonation is established to occur regiospecifically at the β -positions. The values of $a(\text{H}_\beta)$ and $a(\text{H}_\alpha)$ in 2⁺⁺–6⁺⁺ are the same as in 1⁺⁺, hence the introduction of the mercury does not alter the electron distribution in the SOMO, as shown in 7 and in the Table 1.

We appear then to be justified in describing ¹⁹⁹Hg hyperfine coupling by a McConnell relationship as shown in eq. 2, where $Q_{\text{Hg}}^+ \approx 77/3.58 \times Q_{\text{H}}^+ \approx 21.5 \times 26.6 \text{ G} \approx 572 \text{ G}$ *.

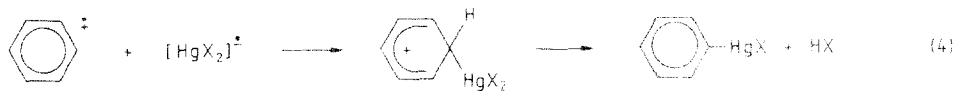
$$a(^{199}\text{Hg}) = \rho_{ca} Q_{\text{Hg}}^+ \quad (2)$$

Aromatic mercuration is usually accepted to proceed by a classical electrophilic substitution mechanism as illustrated in eq. 3.



* Previous observations of ¹⁹⁹Hg hyperfine coupling appear to be limited to complexes of semiquinones [18,19] and of nitroxyl radicals [20]. It is interesting that Wan finds, as we do, that ²⁰³Hg hyperfine coupling cannot be detected, and that mercuration reduces the g value of the radical.

We have demonstrated here however that, at least under photolytic conditions, there exists an alternative mechanism of mercuration which is associated with the formation of radical ions. The simplest picture of this is that the radical ion pair in Lau and Kochi's mechanism (eq. 1) collapses before the $[\text{HgX}_2]^{--}$ species can dissociate (eq. 4).



Oxidation of the aromatic mercury compound then gives the ArHgX^{+} radical cation.

The attack of HgX_2^{--} would be expected to occur at the site where the coefficient in the SOMO 7 in the radical cation is largest, i.e. the β -position, as is observed. As the electron distribution in the HOMO of **1** and the SOMO of **1**⁺ has the same form, electrophilic attack on **1** similarly occurs at the β -position [17]. Reactions 3 and 4 involve the same Wheland intermediate, and hence lead to the same products.

It is interesting that Lau and Kochi identified similar competing electrophilic and electron-transfer pathways for the thallation of homologous methylbenzenes, but not for mercuration [3,5], whereas we, by ESR spectroscopy find evidence for mercuration but not for thallation of biphenylene*. Our observations however do not preclude the possibility that thallation does take place. Thallation might increase the ionization potential of the π -electron system, in which case the ESR spectrum of the biphenylene radical cation would be observed until all the biphenylene was thallated.

Experimental

ESR spectra were recorded using a Varian E109 spectrometer fitted with a 500 W high pressure mercury arc with neutral (metal gauze) and glass filters, focussed on the cavity.

Oxidation of biphenylene

In H_2SO_4 . Biphenylene (ca. 10 mg) was dissolved in concentrated sulfuric acid at 291 K, when it showed the spectrum of **1**⁺.

In $\text{TFA}/\text{Th}(\text{TFA})_3$. A solution of biphenylene (ca. 0.5 mg) in CH_2Cl_2 (50 μl) was added to a solution of thallium(III) trifluoroacetate (50 mg) in trifluoroacetic acid (0.5 ml), yielding a red solution which showed the spectrum illustrated in Fig. 1.

In TFA . A solution of biphenylene (ca. 5 mg) in dichloromethane (ca. 50 μl) was added to trifluoroethanoic acid (0.5 ml), when a pink colour developed. This solution showed a spectrum which could be simulated on the basis of $[\mathbf{1}^{+}]/[\mathbf{1}_2^{+}] = 1.16/1$. Photolysis of this solution with Pyrex-filtered UV light produced a more complex spectrum which has not been identified.

In $\text{CH}_2\text{Cl}_2/\text{Al}_2\text{Cl}_6$. A solution of biphenylene (ca. 5 mg) in dichloromethane (50 μl) was added to dichloromethane (500 μl) containing aluminium(III) chloride

* We have found however ESR evidence for the thallation of triptycene [21].

(ca. 50 mg) at 178 K. This solution was green and showed a weak spectrum with no fine structure. Photolysis with UV light, attenuated to 3% intensity and filtered through Pyrex glass, gave a spectrum which was principally that of the dimer 1_2^{+} ; as shown in Fig. 2.

(5) *In TFA/Hg(TFA)₂*. Biphenylene (ca. 5 mg) in dichloromethane (100 μ l) was added to a solution of mercury(II) trifluoroethanoate (ca. 50 mg) in trifluoroacetic acid (500 μ l). With no photolysis other than that from ambient light, the solution showed an ESR spectrum which was essentially that of the radical cation 1^{+} , with some distortion by the spectrum of the monomercurated species 2^{+} . When the sample was prepared in the dark, this distortion was absent.

Photolysis of this solution with light from the mercury arc, attenuated to 3% and filtered through Pyrex glass, gave rise to the sequence of spectra shown in Fig. 3b–3e.

Acknowledgement

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