Electron Spin Resonance Spectra of Mercurated Arene Radical Cations

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When certain arenes are oxidized with mercury trifluoroacetate in trifluoroacetic acid, the ESR spectra of the arene radical cations observed show that progressive mercuration occurs. The aromatic protons with the largest hyperfine coupling constants are replaced by mercury, and satellites due to ^{199}Hg hyperfine coupling can be observed. Mercuration also reduces the *g* value of the radicals. This behavior is reported for acenaphthene, anthracene, biphenylene, pyracene, hexahydropyrene, triptycene, terphenyl, tetramethylnaphthopyran, and dibenzodioxin. The introduction of mercury causes a reduction in the *g* value of the radical cation, but it does not affect the hyperfine coupling constants of the remaining protons. For the nuclei involved in the mercurideprotonation process, $a(^{199}\mathrm{Hg})/a(^{1}\mathrm{H})$ = ca. 20.6.

Introduction

In 1982, Kochi and his co-workers reported that the ESR spectra of arene radical cations could be observed when solutions of the arenes in trifluoroacetic acid (TFAH) containing mercury(II) trifluoroacetate [$\mathrm{Hg(TFA)_2}$] were photolyzed.[1] From a study of various methylbenzenes, they concluded that the reactions followed the mechanism shown in eq 1. The arene and mercury trifluoroacetate form a charge-transfer complex that undergoes photoinduced electron transfer, and back electron transfer is minimized by dissociation of the radical ion $\mathrm{Hg(TFA)_2}^{\bullet -}$.

$$\begin{tikzcd}
\mathrm{ArH} + \mathrm{Hg(TFA)_2} \arrow[r] & {[\mathrm{ArH}, \mathrm{Hg(TFA)_2}]} \arrow[r, "h\nu"] & {[\mathrm{ArH}^{\bullet +}, \mathrm{Hg(TFA)_2}^{\bullet -}]} \arrow[d] \\
\mathrm{ArH}^{\bullet +} + {}^{\bullet}\mathrm{Hg(TFA)} + \mathrm{TFA}^{-} & & {[\mathrm{ArH}^{\bullet +}, {}^{\bullet}\mathrm{Hg(TFA)}, \mathrm{TFA}^{-}]} \arrow[ll]
\end{tikzcd} \quad (1)$$

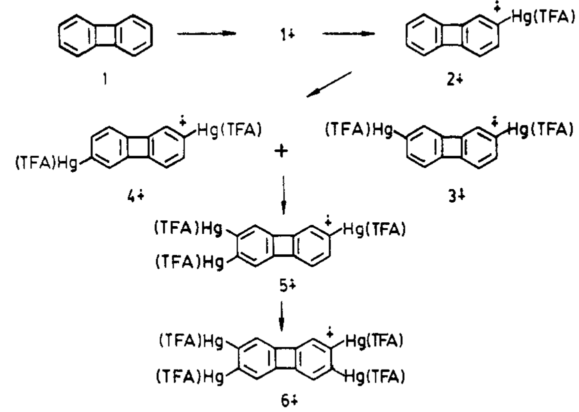
An alternative procedure, which probably follows a similar mechanism, makes use of thallium(III) trifluoroacetate in place of the mercury(II) salt;[2] the charge-transfer complex now involves the ion $\mathrm{Tl(O_2CCF_3)_2}^{+}$.

We have used these procedures extensively for preparing radical cations of aromatic[3] and, more recently, heteroaromatic compounds,[4] and we found that sometimes the aromatic ring was undergoing mercuration (eq 2).

$$\mathrm{ArH} + 2\mathrm{Hg(TFA)_2} \rightarrow \mathrm{Ar^{\bullet +}Hg(TFA)} + {}^{\bullet}\mathrm{Hg(TFA)} + \mathrm{TFA^{-}} + \mathrm{TFAH} \quad (2)$$

In particular, biphenylene was shown to undergo progressive mercuration in the β-positions, and during a period of about 3 h, the spectra of the zero-, mono-, di-, tri-, and tetra-β-mercurated biphenylene radical cations $1^{\bullet +}$–$6^{\bullet +}$ could successively be identified (eq 3).[5] Each mercuration step brought about a reduction in the *g* value of the radical.

We now report the similar behavior of a variety of other aromatic and heteroaromatic compounds.

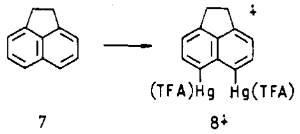


(3)

Results

Acenaphthene (7). An excellent spectrum of the acenaphthene radical cation ($7^{\bullet +}$) was observed by Livingston et al. from a solution of acenaphthene in antimony trichloride.[6] The hyperfine coupling constants are listed in Table I.

When acenaphthene is photolyzed in Kochi's reagent, however, the spectrum that is observed (see ref 7) consists of a central feature which can be simulated by using the hyperfine coupling constants for $7^{\bullet +}$, less the values ascribed to the protons at positions 4 and 5 [a(2 H) = 6.59 G]. This central feature is flanked by satellites of itself with a separation of about 142 G and a combined intensity of about 1:5. At the same time, the *g* value, which in $7^{\bullet +}$ is 2.0027, is reduced to 1.9950. We conclude that the species being observed is the dimercurated radical cation $8^{\bullet +}$ in which the hyperfine coupling constants at the non-mercurated positions are the same as they are in $7^{\bullet +}$ (see Table I) (eq 4).



(4)

Pyracene (9). In the dark, pyracene in trifluoroacetic acid containing thallium(III) trifluoroacetate gave rise to

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[1] (a) Lau, W.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 5515–5517. (b) Lau, W.; Kochi, J. K. *J. Org. Chem.* **1986**, *51*, 1801–1811. (c) Lau, W.; Kochi, J. K. *J. Am. Chem.* **1986**, *108*, 6720–6732.

[2] (a) Elson, I. H.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 5060–5062. (b) Lau, W.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *160*, 7100–7112.

[3] Courtneidge, J. C.; Davies, A. G. *Acc. Chem. Res.* **1987**, *20*, 97–107.

[4] Davies, A. G.; Julia, L.; Yazdi, S. N. *J. Chem. Soc., Chem. Commun.* **1987**, 929–930; *J. Chem. Soc., Perkin Trans. 2* **1989**, 239–244.

[5] Courtneidge, J. L.; Davies, A. G.; McGuchan, D. C.; Yazdi, S. N. *J. Organomet. Chem.* **1988**, *341*, 63–71.

[6] Buchanan, A. C.; Livingston, R.; Dworkin, A. S.; Smith, G. P. *J. Phys. Chem.* **1980**, *84*, 423–427.

[7] Courtneidge, J. L.; Davies, A. G.; Gregory, P. S.; McGuchan, D. C.; Yazdi, S. N. *J. Chem. Soc., Chem. Commun.* **1987**, 1192–1194.

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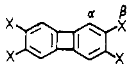
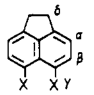
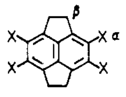
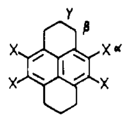
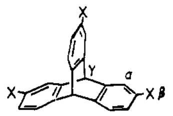
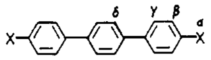
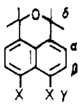
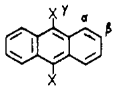
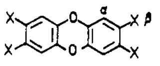
Table I. ESR Spectra of Mercurated Arene Radical Cations

		a(H)/G		a(X)/G (X = H or ^{199}Hg)		g	a(Hg)/a(H$_x$)
	**1**$^{\bullet+}$	4 H(α)	0.2	4 H(β)	3.6	2.0025	
	2$^{\bullet+}$	4 H(α)	0.2	3 H(β)	3.6	2.0014	
				1 Hg(β)	76.5		21.3
	3$^{\bullet+}$	4 H(α)	0.2	2 H(β)	3.6	2.0007	
				2 Hg(β)	76.5		21.3
	4$^{\bullet+}$	4 H(α)	0.22	1 H(β)	3.6	2.0007	
				2 Hg(β)	77.3		21.5
	5$^{\bullet+}$	4 H(α)	0.2	1 H(β)	3.6	ca. 2.0003	
				3 Hg(β)	75.5		21.0
	6$^{\bullet+}$	4 H(α)	0.24	4 Hg(β)	ca. 78	ca. 2.0003	21.7
	**7**$^{\bullet+}$	2 H(α)	3.13	2 H(γ)	6.59	2.0027	
		2 H(β)	0.59				
		4 H(δ)	13.18				
	8$^{\bullet+}$	2 H(α)	3.13	2 Hg(γ)	141.6	1.995	21.5
		2 H(β)	0.59				
		4 H(δ)	13.18				
	**9**$^{\bullet+}$	8 H(β)	12.96	4 H(α)	2.00	2.0030	
	10$^{\bullet+}$	8 H(β)	12.96	3 H(α)	2.00	2.0023	
				1 Hg(α)			
	11$^{\bullet+}$	8 H(β)	12.96	2 H(α)	2.00	2.0008	23.8
				2 Hg(α)	47.7		
	12$^{\bullet+}$	8 H(β)	12.96	1 H(α)	2.00		
				3 Hg(α)	48		ca. 24
	**13**$^{\bullet+}$	8 H(β)	18.3	4 H(α)	1.90	2.0026	
		4 H(γ)	0.38				
	14$^{\bullet+}$	8 H(β)	18.3	3 H(α)	1.90	2.0018	
		4 H(γ)	0.38	1 Hg(α)			
	**15**$^{\bullet+}$	6 H(α)	0.175	6 H(β)	2.27	2.0022	
		2 H(γ)	0.075				
	16$^{\bullet+}$	6 H(α)	0.175	3 H(β)	2.27	2.0004	
		2 H(γ)	0.075	3 Hg(β)	46.44		20.5
	**17**$^{\bullet+}$	2 H(α)	2.28	2 H(γ)	3.65	2.0025	
		4 H(β)	0.61				
		4 H()	1.22				
	18$^{\bullet+}$	2 H(α)	2.28	1 H(γ)	3.65	2.0016	
		4 H(β)	0.61	1 Hg(γ)	ca. 68		ca. 19
		4 H()	1.22				
	19$^{\bullet+}$	2 H(α)	2.28	2 Hg(γ)			
		2 H(β)	0.61				
		4 H(σ)	1.22				
	**20**$^{\bullet+}$	2 H(α)	2.45	2 H(γ)	6.05	2.0026	
		2 H(β)	1.15				
		12 H(4Me)	0.675				
	21$^{\bullet+}$	2 H(α)	2.45	2 Hg(γ)	127	2.0008	21.0
		2 H(β)	1.15				
		12 H(4Me)	0.675				
	**22**$^{\bullet+}$	4 H(α)	3.06	2 H(γ)	6.5	2.0027	
		4 H(β)	1.40				
	23$^{\bullet+}$	4 H(α)	3.06	2 Hg(γ)	ca. 138.5		21.3
		4 H(β)	1.40				
	**26**$^{\bullet+}$	4 H(α)	<0.005	4 H(β)	2.13	2.0039	
	27$^{\bullet+}$			3 H(β)	2.13	2.0031	20.1
				1 Hg(β)	42.90		
	28$^{\bullet+}$			2 H(β)	2.13	2.0024	21.2
				2 Hg(β)	45.12		
	29$^{\bullet+}$			2 H(β)	2.13	2.0024	21.7
				2 Hg(β)	46.20		
	30$^{\bullet+}$			1 H(β)	2.13	2.0019	21.5
				3 Hg(β)	45.07		
	31$^{\bullet+}$			4 Hg(β)	45.60	2.0014	21.4

a strong spectrum of the familiar pyracene radical cation (**9**$^{\bullet+}$)[8] (Figure 1) consisting of a nonet of quintets with the parameters listed in Table I. The intensity of the spectrum decreased when the solution was photolyzed.

If pyracene was dissolved in trifluoroacetic acid containing about one-fifth of the amount of mercury(II) trifluoroacetate needed to give a saturated solution, it gave rise to a very weak spectrum. When the sample was photolyzed with light from a mercury arc reduced to 3% in intensity through a neutral screen and filtered through Pyrex glass, the spectrum of **9**$^{\bullet+}$ was generated (eq 5).

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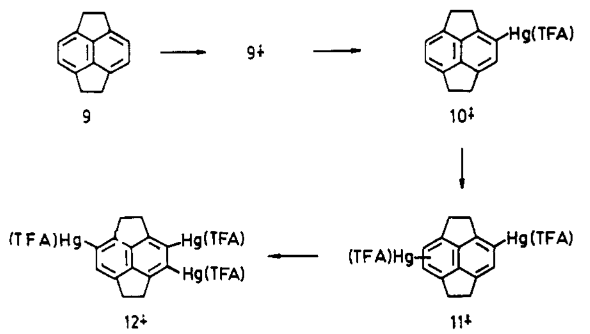
(8) Terahara, A.; Ohya-Nishiguchi, H.; Hirota, H.; Oku, A. *J. Phys. Chem.* **1986**, *90*, 1564-1571.



(5)

With prolonged photolysis, a spectrum which appeared to be that of the monomercurated radical cation was observed, but when the neutral screen was removed, the spectrum was rapidly lost.

When the solution was saturated with mercury trifluoroacetate, the spectrum of $9^{\bullet+}$ was not observed. When the sample was photolyzed with light at 3% intensity and filtered through Pyrex glass, the spectrum shown in Figure 1b was obtained; then after photolysis with 100% Pyrex-filtered light for 20 min, this was replaced by the spectrum in Figure 1d.

We assign spectrum 1b to the monomercurated radical cation $10^{\bullet+}$, contaminated with un-mercurated and dimercurated species. Figure 1c shows a simulation of the spectrum based on the assumption that only three of the four aromatic protons remain, with the same hyperfine coupling constants as in $9^{\bullet+}$, and the main features of the spectrum are seen to be reproduced. We estimate (see Discussion) that the hyperfine coupling by ^{199}Hg should be about 42 G. The principal ^{199}Hg satellites therefore lie within the main body of the spectrum and contribute to the complication.

The spectrum in Figure 1d can be simulated reasonably well in terms of a 1:0.3 mixture of the dimercurated species $11^{\bullet+}$ and the trimercurated species $12^{\bullet+}$, and the satellites due to ^{199}Hg hyperfine coupling in both species can be detected. With biphenylene[5] and dibenzodioxin (see below), we can observe pairs of dimercurated radical cations, and it is likely that an equivalent pair of isomers of $11^{\bullet+}$ is present but that they now have the same hyperfine coupling constants. Parameters that have been used in the simulation (Figure 1c) are given in Table I. In the spectra in Figure 1, d and e, the new outer features (labeled X) are composed of superimposed triplet and doublet primary ^{199}Hg satellites of the dimercurated and trimercurated radical cations $11^{\bullet+}$ and $12^{\bullet+}$, respectively. Secondary and tertiary ^{199}Hg satellites involving hyperfine coupling to two or three mercury atoms have been ignored in the simulations, although they will generate further weak lines in the spectra.

Further photolysis weakened the spectrum, and no evidence for tetramercuration could be obtained.

Hexahydropyrene (13). Hexahydropyrene (13) in trifluoroacetic acid containing thallium(III) trifluoroacetate gave a strong ESR spectrum in the dark.[9] With mercury(II) trifluoroacetate, no spectrum was obtained in the dark, but photolysis with 3% Pyrex-filtered light gave a spectrum that was similar to but weaker than that obtained with Tl(TFA)$_3$. With more intense light (30%), the quintet due to the four aromatic protons became progressively distorted, and the spectrum can be interpreted in terms of a superposition of the spectra of $13^{\bullet+}$ and of the monomercurated radical cation $14^{\bullet+}$ (eq 6). Spectral data are given in Table I.

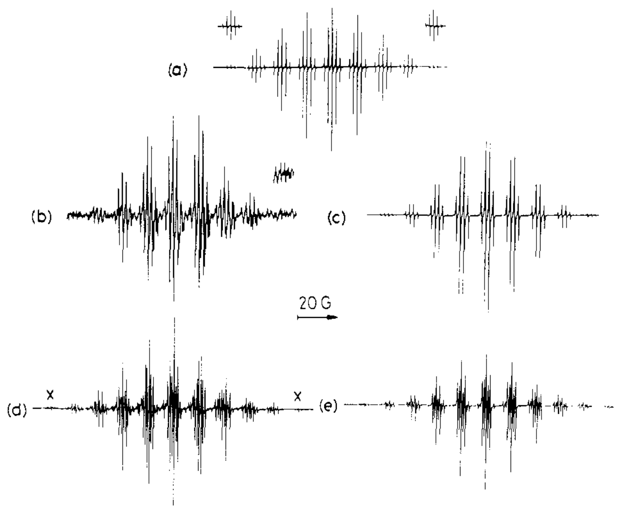
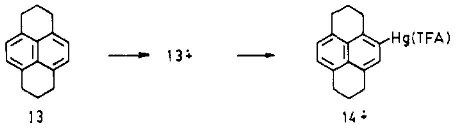


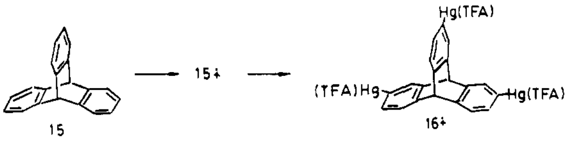
Figure 1. ESR spectra of radical cations in trifluoroacetic acid at 262 K. (a) Pyracene ($9^{\bullet+}$). (b) Monomercurated pyracene ($10^{\bullet+}$) contaminated with some dimercurated pyracene ($11^{\bullet+}$). (c) Computer simulation of the spectrum of $10^{\bullet+}$. (d) Di- and trimercurated pyracene $11^{\bullet+}$ and $12^{\bullet+}$. (e) Simulation of the spectrum of a mixture of 1.0 ($11^{\bullet+}$) + 0.3 ($12^{\bullet+}$). In (d) and (e), the features labeled X are ^{199}Hg satellites (see text).



(6)

The value of $a(^{199}\text{Hg})$ would be expected to be about 41 G, but the spectrum was not strong enough for the mercury satellites to be identified.

Triptycene (15). A solution of 15 in trifluoroacetic acid containing thallium(III) trifluoroacetate was photolyzed with 3% Pyrex-filtered light and gave rise to a strong spectrum of the radical cation $15^{\bullet+}$ (eq 7), which we have analyzed in terms of the hyperfine coupling constants $a(6\text{H}_\alpha) = 0.175$, $a(6\text{H}_\beta) = 2.28$, $a(2\text{H}_\gamma) = 0.075$ G.[10] When Tl(TFA)$_3$ was replaced by Hg(TFA)$_2$, the major septet was still obvious under the same conditions, but the smaller couplings could not be resolved.



(7)

However, with continuous photolysis signals rapidly developed further in the gaps between the septets, the character of the septet degenerated, and mercury satellites appeared with a separation of about 40 G. After 1 h of photolysis, the central feature resolved into a simple quartet, $a(3\text{ H}) = 2.27$ G, with ^{199}Hg satellites. We conclude that tri-β-mercuration has occurred, probably with one mercury in each ring. It is likely that more than one isomer is present, such as we observe with biphenylene and dibenzodioxin, but in the present case, the line width of ca. 1 G, which results in part from unresolved α and γ coupling, prevents the resolution of the similar spectra.

When the solution containing Tl(TFA)$_3$ was similarly photolyzed, signals developed in the gaps of the septets, and these appeared to retain the hyperfine pattern of

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[9] Cf.: de Boer, E.; Praat, H. P. *Mol. Phys.* **1964**, *8*, 291–293. Pijpers, F. W.; Arick, M. R.; Hendricks, B. M.; de Boer, E. *Mol. Phys.* **1971**, *22*, 781–787. Makela, R.; Oksanon, M.; Vuolle, M. *Acta Chem. Scand.* **1984**, *A38*, 73–78.

[10] Courtneidge, J. L.; Davies, A. G.; McGuchan, D. C. *Recl. Trav. Chim. Pays-Bas* 1988, *107*, 190–196.

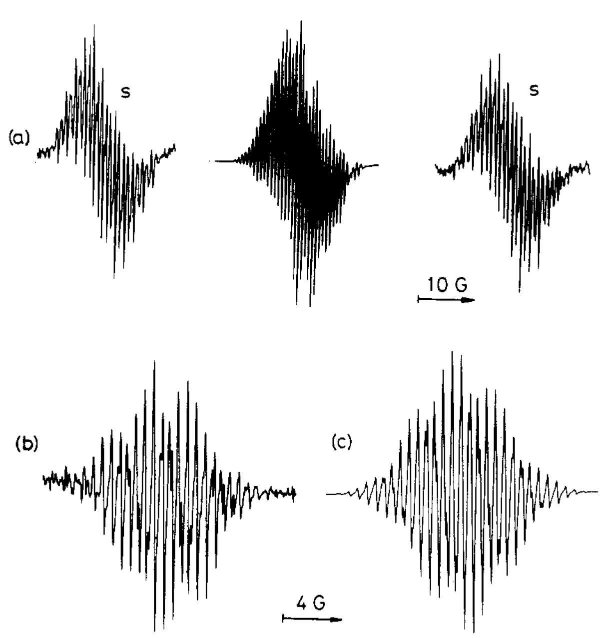
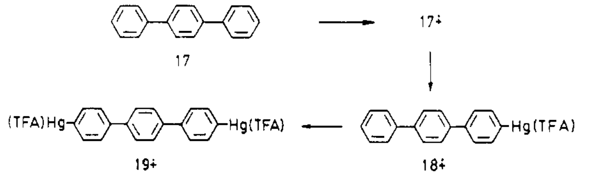


Figure 2. ESR spectra of radical cations in trifluoroacetic acid at 262 K. (a) Monomercurated *p*-terphenyl ($18^{\bullet+}$); the ^{199}Hg satellites (s) are shown at increased gain. (b) Dimercurated *p*-terphenyl ($19^{\bullet+}$). (c) Computer simulation of the spectrum of $19^{\bullet+}$.

$a(6H_\alpha) = 0.175$ and $a(2H_\gamma) = 0.075$ G. It seems unlikely that this could be due to thallation of the aromatic rings as ^{203}Tl (29.52% abundance) and ^{205}Tl (70.48% abundance) each have a nuclear spin of $^1/_2$ and no hyperfine coupling by these isotopes could be observed. Sullivan has reported,[11] and we have confirmed, that the $Tl(TFA)_3$ reagent brings about trifluoroacetoxylation of anthracene in the 9- and 9,10-positions, and it seems probable that we are observing a similar trifluoroacetoxylation[16] of triptycene in the β-position.

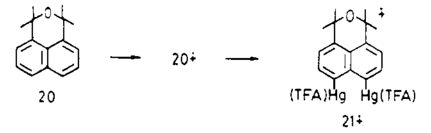
***p*-Terphenyl (17).** We have already described and analyzed the complex ESR spectrum of the *p*-terphenyl radical cation ($17^{\bullet+}$), which can be observed when *p*-terphenyl in trifluoroacetic acid containing mercury(II) trifluoroacetate is photolyzed with 3% Pyrex-filtered UV light.[10] With more intense (30%) light, the spectrum became distorted, and ^{199}Hg satellites developed. After ca. 30 min, the spectrum in Figure 2a was obtained, which can be simulated with the same hyperfine coupling constants as for $17^{\bullet+}$ but with the presence of only one para proton. Spectral data are given in Table I. We assume that monomercuration has occurred to give $18^{\bullet+}$ (eq 8).



(8)

Further photolysis gave a weaker spectrum, which, after about 1 h, had the appearance shown in Figure 2b. It was too weak to permit the observation of ^{199}Hg satellites, but the central spectrum can be simulated (Figure 2c) on the assumption that both para protons have been displaced, implying that the radical is $19^{\bullet+}$.

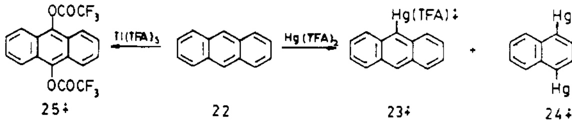
1,1,3,3-Tetramethyl-1*H*,3*H*-naphtho[1,8-*cd*]pyran (20). Photolysis of tetramethylnaphthopyran (20) in Kochi's reagent with 3% Pyrex-filtered light gave a well-resolved spectrum of the corresponding radical cation ($20^{\bullet+}$), (eq 9), which could be simulated with the hyperfine coupling constants given in Table I.



(9)

By analogy with the spectra of acenaphthene[6] and 1,8-dimethylnaphthalene,[12] the largest triplet coupling of 6.05 G can be ascribed to the protons at positions 7 and 8. The spectrum became distorted when photolysis was prolonged, and weak ^{199}Hg satellites (sl) developed with $a(^{199}Hg) = 127$ G. These satellites could be simulated by using the hyperfine coupling constants for $20^{\bullet+}$, less $a(2\ H_{7,8}) = 6.05$ G, and the central feature could be reproduced reasonably well by assuming that it arose from a 40:60 mixture of $20^{\bullet+}$ and $21^{\bullet+}$, with $21^{\bullet+}$ having a g value of ca. 2.0008. The presence of some monomercurated material cannot be ruled out.

Anthracene (22). The anthracene radical cation shows $a(2\ H_{9,10}) = 6.53$, $a\ (4\ H_{1,4,5,8}) = 3.06$ and $a(4\ H_{2,3,6,7}) = 1.40$ G.[13] In trifluoroacetic acid containing mercury(II) trifluoroacetate, 22 gave a blood red solution, which on photolysis with 3% Pyrex-filtered light showed an unsymmetrical spectrum with mercury satellites with $a(^{199}Hg)$ ca. 138.5 G. The magnitude of the coupling shows that the mercuration has occurred at the 9- and/or 10-position. The spectrum was too weak to allow secondary satellites, which would confirm dimercuration, to be detected, but the complexity of the central feature, which could not be satisfactorily simulated, suggests that both monomercuration and dimercuration occur to give the radical cations $23^{\bullet+}$ and $24^{\bullet+}$ (eq 10).



(10)

When thallium(III) was used instead of the mercury(II) salt, the deep green solution showed a strong spectrum of $22^{\bullet+}$ in the dark. This spectrum progressively changed when the sample was irradiated with Pyrex-filtered UV light, and after 40 min the spectrum of 9,10-bis(trifluoroacetate) **25** was obtained, $a(4\ H) = 3.13$, $a(4\ H) = 1.20$, and $a(6\ F) = 0.28$ G and $g = 2.0025$.[11]

Dibenzodioxin (26). Dibenzodioxin (26) in trifluoroacetic acid containing thallium trifluoroacetate at 258 K gave a blue solution that showed a very strong ESR spectrum of $26^{\bullet+}$ consisting of a simple quintet with $a(4\ H) = 2.13$ G, which is ascribed to coupling by the four β-protons[14] (eq 11). Hyperfine coupling to the α protons was undetectable at less than 0.005 G. Two sets of ^{13}C satellites could be detected, with $a(^{13}C, 2\ C) = 1.55$ and 2.60 G; the third ^{13}C coupling appears to be within the line width (Figure 3a). No change occurred on photolysis, and nothing that might be interpreted as implying thallation or trifluoroacetoxylation could be observed.

A solution of **26** in $TFAH/CH_2Cl_2$ containing $Hg(TFA)_2$ at 259 K was bright yellow and without photolysis showed

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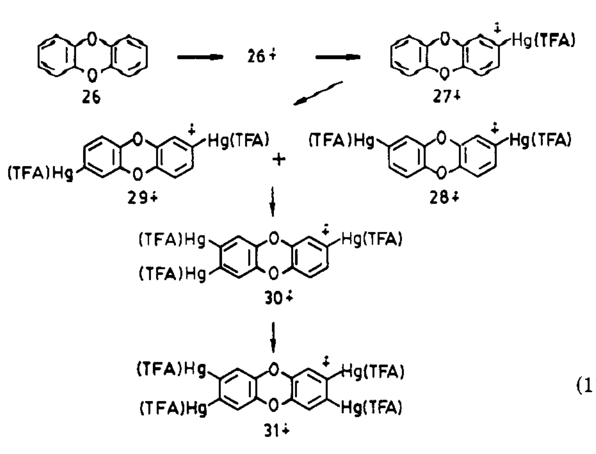


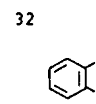
(11)

the quintet ESR spectrum of $26^{\bullet+}$. When the solution was prepared at 271 K in the dark, the quintet was distorted, indicating partial mercuration. Photolysis with 3% Pyrex-filtered UV light gave the spectrum of the monomercurated radical cation $27^{\bullet+}$ with $a(3\ H_\beta) = 2.13$ and $a(^{199}Hg) = 42.90$ G (Figure 3b); the ^{13}C satellites could still be detected with $a(^{13}C, 2\ C) = 1.55$ and 2.60 G. Continued photolysis gave further mercurideprotonation, and the succession of spectra shown in Figure 3c–e. Two dimercurated species could be detected in approximately equal concentration, showing two pairs of triplet primary satellites (s1) and two pairs of triplet secondary satellites (s2) separated from each other by twice as much as the primary satellites (Figure 3c). These two isomers are presumably $28^{\bullet+}$ and $29^{\bullet+}$. Further mercuration gave $30^{\bullet+}$ in which the secondary satellites (s2) are principally doublets (Figure 3d); weak tertiary satellites (s3) could also be detected as cleaner doublets. Finally, tetramercuration gave $31^{\bullet+}$, in which the central spectrum was contaminated with residual $30^{\bullet+}$, but the primary and secondary satellites were singlets (Figure 3e).

To investigate the part photolysis played in the mercuration, two identical samples were prepared at 258 K. One sample was handled in laboratory light, and the other was kept in the dark. The first sample, without UV irradiation, showed a quintet spectrum of the unmercurated radical cation $26^{\bullet+}$, and on photolysis with 10% Pyrex-filtered UV light, monomercuration occurred to give the quartet characteristic of $27^{\bullet+}$, which was complete in 45 min.

At this time, the second sample, which had been kept in the dark, showed no ESR signal, but on photolysis with 3% Pyrex-filtered UV light, it showed a spectrum that, though weaker than that of the first spectrum, showed principally the quartet spectrum of $27^{\bullet+}$. We conclude that mercuration proceeds in the absence of photolysis, though photolysis, if only by laboratory light, is necessary to generate the radical cations.

Phenoxazine (32), Phenoxathiin (33), Dihydrophenazine (34), Phenothiazine (35), and Thianthrene (36). Compounds 32–36 in trifluoroacetic acid were treated with mercury(II) trifluoroacetate and with thallium(III) trifluoroacetate. All were readily oxidized to the corresponding familiar radical cations, showing the same ESR spectra as those reported previously;[15] phenazine (34) gave the spectrum of the dihydrophenazine radical cation. With thianthrene (36), the wing lines of the ^{33}S ($I = {}^3/_2$) satellites could be resolved as clean quintets [$a(4\ H_\beta) = 1.28$ G], so that the hyperfine coupling could be measured more accurately than previously, with $a(^{33}S) = 8.98$ G.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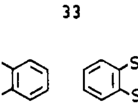
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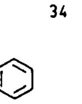
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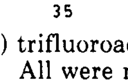
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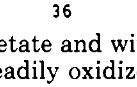
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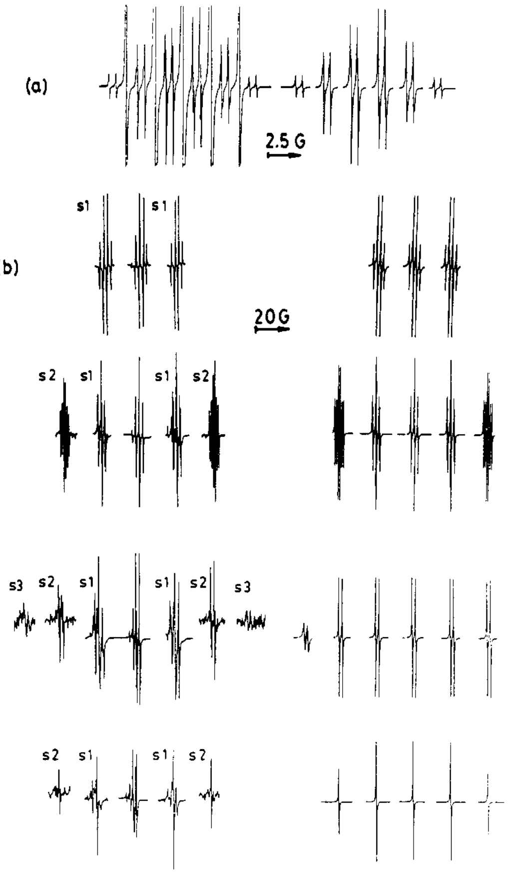
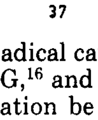


Figure 3. ESR spectra (left) and computer simulations (right) of radical cations in trifluoroacetic acid at 272–274 K, illustrating the progressive mercuration of dibenzodioxin (27). The features due to the primary (s1), secondary (s2), and tertiary (s3) satellites are recorded at ca. 10-fold, 100-fold, and 1000-fold gain, respectively. In the simulations, the intensities of the satellites are arbitrarily chosen to match approximately those in the recorded spectra. (a) Dibenzodioxin ($26^{\bullet+}$) showing the ^{13}C satellites. The simulation is of the ^{13}C satellites only. (b) Monomercurated dibenzodioxin ($27^{\bullet+}$). (c) Dimercurated dibenzodioxins ($28^{\bullet+}$) and ($29^{\bullet+}$); in the simulation, these are taken to be in equal concentration. (d) Trimercurated dibenzodioxin ($30^{\bullet+}$). (e) Tetramercurated dibenzodioxin ($31^{\bullet+}$).

Under no conditions of temperature or photolysis could we observe distortion of the spectra or the appearance of satellites, which could have indicated the occurrence of mercuration or thallation.

Tri-*tert*-butylbenzene (37), (Tri-*tert*-butylphenyl)mercury(II) Chloride (38), and Bis(tri-*tert*-butylphenyl)mercury(II) (39). In Kochi's reagent, 1,3,5-tri-*tert*-butylbenzene (37) showed a strong spectrum of the radical cation $37^{\bullet+}$ with $a(3\ H) = 5.19$ and $a(27\ H) = 0.95$ G,[16] and under no conditions of photolysis could mercuration be observed. Under the same conditions, (2,4,6-tri-*tert*-butylphenyl)mercury(II) chloride (38) and bis(2,4,6-tri-*tert*-butylphenyl)mercury (39) showed only the same spectrum of the hydrocarbon radical cation $37^{\bullet+}$, and no spectrum of a mercurated species could be detected.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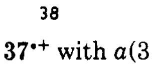

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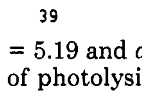

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Discussion

^{199}Hg Satellites. The nuclear spins and natural abundances of the various isotopes of mercury are ^{196}Hg, $I = 0$, 0.14%; ^{198}Hg, $I = 0$, 10.02%; ^{199}Hg, $I = {}^1/_2$, 16.84%; ^{200}Hg, $I = 0$, 23.13%; ^{201}Hg, $I = {}^3/_2$, 13.22%; ^{202}Hg, $I = 0$, 29.80%; ^{204}Hg, $I = 0$, 6.85%. The only ESR spectra of mercury-containing organic compounds in solution that have previously been reported appear to be complexes of some semiquinones[17] and nitroxyl radicals,[18] and these show ^{199}Hg but not ^{201}Hg hyperfine coupling. Similarly, as far as we are aware, ^{199}Hg–^{1}H coupling is familiar in NMR spectroscopy, but ^{201}Hg–^{1}H coupling has not been observed. Fullam and Symons, however, have detected ^{201}Hg hyperfine coupling in the radicals $^\bullet$CH$_2$HgMe and $^\bullet$CH$_2$HgBr in the solid state.[19]

It is not surprising, therefore, that in our spectra (see Table I) we observe ^{199}Hg but not ^{201}Hg coupling; presumbly rapid relaxation induced by the nuclear quadrupole broadens the signals of the ESR spectra beyond detectability.

The relative intensity of the combined pair of ^{199}Hg satellites to that of the spectrum due to the spin-free isotopomers in a monomercurated radical should therefore be 16.84:69.94, or 1:4.15, and this is approximately what we observe. Similarly, when they can be observed, the intensities of the secondary, and tertiary, ^{199}Hg satellites arising from the presence of radical cations containing two, three, or four ^{199}Hg atoms, respectively, agree approximately with predictions.

We hoped that we might be able to observe the spectrum of the radical cations of the preformed (2,3,6-tri-*tert*-butylphenyl)mercury compounds **38** and **39** by treating them with Kochi's reagent, but apparently protodemercuration occurs to give the radical cation of the parent hydrocarbon (**37**). Kochi[20] has shown that the *tert*-butyl groups sterically protect the ring against electrophilic substitution, but the hydrocarbon is very much more soluble in organic solvents than are the organomercury compounds, and it seems unlikely that **37** could have been present in **38** or **39** as an impurity.

Wan has rationalized the low g values that are observed in mercury-containing radical ions in terms of the spin–orbit coupling which results from p_π–d overlap.[17,18]

Site of Mercuration. When the parent hydrocarbon contains nonequivalent aromatic protons, mercurideprotonation occurs at the position where the proton hyperfine coupling is greatest, which is where the local coefficient of the MO of the HOMO of the hydrocarbon or the SOMO of the hydrocarbon radical cation is greatest. The mercuration occurs more readily when the concentration of mercury trifluoroacetate is increased. Photolysis with UV light filtered through Pyrex glass is usually necessary for mercuration to be observed, but the use of unfiltered UV light always led to a rapid decay of the intensity of the spectrum.

When mercuration occurs, the hyperfine coupling of the remaining protons and (when it can be observed) the ^{13}C hyperfine coupling is not changed. This implies that the substituent effect of mercury on the electron distribution is similar to that of hydrogen and that the coefficients of the SOMO are essentially unaffected by mercuration.

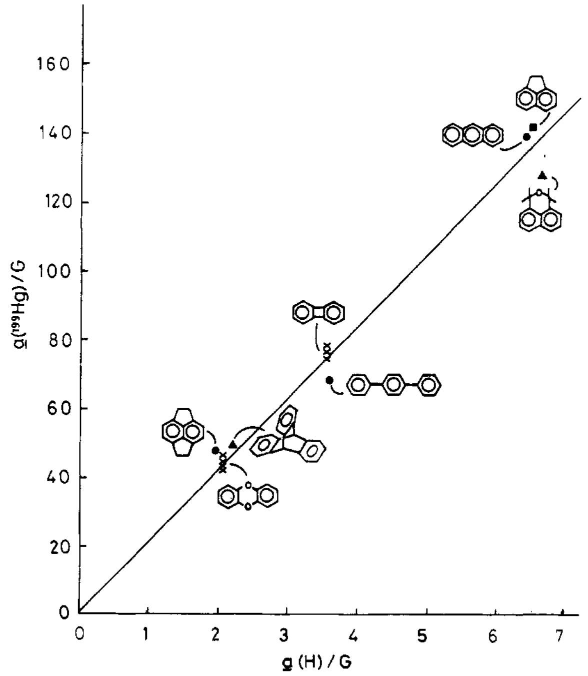

Figure 4. Plot of $a(^{199}\mathrm{Hg})$ against $a(^1\mathrm{H})$ for the process of mercurideprotonation.

Polymercuration, therefore, proceeds randomly at the remaining positions of highest electron density which were equivalent in the hydrocarbon, with the probable proviso that vicinal mercuration is sterically retarded.[21] Thus, triptycene (**15**) undergoes tri-β-mercuration. We assume that steric hindrance is directing one mercury substituent into each of the three rings; the two β-positions in any one ring probably show a similar reactivity irrespective of the position of substitution in the other two rings, leading to a mixture of the two possible dimercurated isomers, and of the two possible trimercurated isomers, with similar spectra. However, the ESR spectra show the presence of two dimercurated biphenylene radical cations, which we assume to be $\mathbf{3}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$, and similarly two dimercurated dibenzodioxin radical cations, presumed to be $\mathbf{27}^{\bullet+}$ and $\mathbf{28}^{\bullet+}$, could be observed. This is apparent because there are small differences between the values of $a(^{199}\mathrm{Hg})$ for the mercury atoms successively introduced at the various equivalent positions in the parent molecule. For example, in the various mercurated dibenzodioxins $a(^{199}\mathrm{Hg})$ varies between 42.90 and 46.20 G.

The Ratio $a(^{199}\mathrm{Hg})/a(^1\mathrm{H})$. As shown in Table I and Figure 4, the ratio of the hyperfine coupling by mercury-199 which is introduced to that by the proton which is displaced is approximately constant, with $a(^{199}\mathrm{Hg})/a(^1\mathrm{H})$ ca. 20.6, making it possible to predict the value of $a(^{199}\mathrm{Hg})$ in new species and to locate the ^{199}Hg satellites more readily. This revises our earlier estimate[7] of ca. 21.5, which was based on fewer data.

This implies a proportionality between the spin density on the ring carbon atom and on the attached mercury atom according to a McConnell-like equation[22]

$$a(^{199}\mathrm{Hg}) = Q_{\mathrm{CHg}}\rho_{\mathrm{C}_\alpha}$$

where the constant $|Q_{\mathrm{CHg}}| = 20.6Q_{\mathrm{CH}}$. Gerson[23] has recommended values of Q_{CH} for radical cations of −35.1 G

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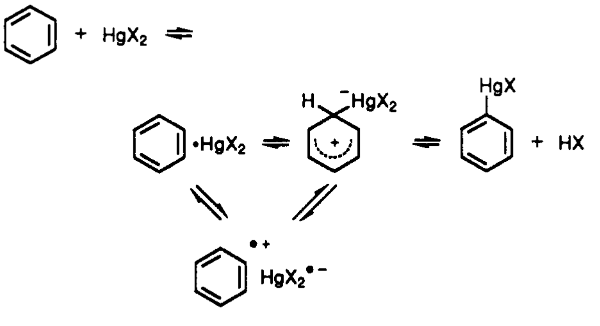
based on HMO electron densities c_j^2, and of −25.4 G based on the more accurate McLachlan spin densities, which leads to the corresponding values for Q_{CHg} of −723 and −523 G, respectively.

As replacement of hydrogen by mercury does not significantly perturb the SOMO of the radical cation, the spin polarization of the C–H and C–Hg σ-bonding electron pair should be similar, placing similar spin densities on hydrogen and mercury. In that case, if bonding by hydrogen utilizes the 1s orbital and that by mercury utilizes a pure 6sp hybrid, with 50% s character (and no p_π–p_π or p_π–d_π involvement), the ratio $a(^{199}\mathrm{Hg})/a(^{1}\mathrm{H})$ should be approximately equal to $A_0(^{199}\mathrm{Hg})/2A_0(^{1}\mathrm{H})$, where $A_0(^{199}\mathrm{Hg})$ is the isotropic coupling to mercury (41 880 MHz)[24] and $A_0(^{1}\mathrm{H})$ is the isotropic coupling to hydrogen (1422 MHz).

This predicts a value of $a(^{199}\mathrm{Hg})/a(^{1}\mathrm{H})$ of ca. 15, as compared with that of 20.6 which we observe. The discrepancy between these two values may be rationalized on the model proposed by Fullam and Symons, who generated radicals $^\bullet\mathrm{CH_2HgX}$ and $\mathrm{Me^\bullet CHHgX}$ (X = $\mathrm{CH_3}$, I, Br, or Cl) by γ-radiolysis of the solids at 77 K and found that $a(^{199}\mathrm{Hg})$ increased from 220 to 450 G as the electronegativity of X increased in the above sequence. They argued that when X was more electronegative than the organic ligand, the Hg–X bond involved mainly the mercury $6p_z$ orbital, so the C–Hg bond involved a large contribution from the 6s mercury orbital and hyperfine coupling by spin polarization of the C–Hg σ-bond was more effective. In our system, the ligand X in $\mathrm{ArHgX^{\bullet+}}$ is presumably the electronegative trifluoroacetate group. Therefore, the Hg–X bond has a p contribution greater than 50%, the Ar–Hg bond has an s contribution greater than 50%, and the divisor in the above expression for $a(^{199}\mathrm{Hg})/a(^{1}\mathrm{H})$ should be greater then 2. In the compounds we have studied, the largest s-electron density on mercury is less then 1%, and any accompanying change in a(H) would be commensurate with the probable error.

Mechanism of Mercuration. Aromatic mercuration is usually regarded to involve attack of the electrophile $\mathrm{HgX_2}$ to first form a charge-transfer complex, then a Wheland intermediate, followed by elimination of HX[25] (eq 12).



(12)

In some of the compounds we have studied (e.g., acenaphthene), the mercuration occurs before the sample is irradiated with UV light and could be accommodated by this mechanism.

With other substrates, however (e.g., biphenylene), the mercuration is at most slow in the dark, but it is relatively fast when the solution is photolyzed, and the conventional heterolytic mechanism cannot explain this photocatalysis. The ESR spectra show that this photolysis enhances electron transfer in the charge-transfer complex to give a radical ion pair, and it is reasonable to assume that it is collapse of the radical ion pair that leads to mercuration (see eq 12). By either mechanism, reaction would occur at the position where the coefficient at the HOMO or SOMO is largest, and as the HOMO of ArH and the SOMO of $\mathrm{ArH^{\bullet+}}$ have the same form, the two mechanisms would lead to similar products.

Indeed the electrophilic and the electron-transfer mechanisms need not necessarily be distinct, and Kochi has argued that a radical ion pair is a viable intermediate for these mercurations, which are usually discussed in terms of an electrophilic mechanism.[20]

The alternative of a dissociative mechanism seems unlikely. There appears to be no evidence that arene radical cations can lose a proton to give aryl radicals, and if the radicals cations described here are generated in deuteriotrifluoroacetic acid in the absence or presence of mercury(II) trifluoroacetate, many do not undergo deuteriation.

As aromatic mercuration and thallation by mercury(II) trifluoroacetate or thallium(III) trifluoroacetate occur at rather similar rates,[1c] and as we so frequently observe the ESR spectra of mercurated arenes, it may seem surprising that we have not yet observed the spectra of the thallated arenes. Two factors probably account for this. First, thalliodeprotonation is reversible, and under our conditions, the parent hydrocarbon ArH will be present together with the arenethallium compounds, $\mathrm{ArTl(TFA)_2}$. Second, whereas, as we have argued above, mercuration has little effect on the π-system, thalliation appears to attract electrons from the ring[26] and thereby increase the ionization potential of the arenethallium compound above that of the parent arene. Our systems will therefore show only the spectra of the arene radical cations, $\mathrm{ArH^{\bullet+}}$, although the degree of thallation may be considerable.

Trifluoroacetoxylation. It is also surprising that we do not observe trifluoroacetoxylation more frequently, because this should reduce the ionization potential of the arene. Sullivan has shown that anthracene undergoes trifluoroacetoxylation with $\mathrm{Tl(TFA)_3}$ at the 9- and 10-positions, to show the ESR spectrum of the 9,10-bis(trifluoroacetoxy)anthracene radical cations.[11] Photolysis of arenethallium bis(trifluoroacetates) has been shown to lead to the formation of some aryl trifluoroacetate,[27] and the more rapid generation of the spectrum of the 9,10-bis(trifluoroacetoxy)anthracene, which we observe when anthracene in trifluoroacetic acid is photolysed in the presence of $\mathrm{Tl(TFA)_3}$, may indicate that, at least in this system, trifluoroacetoxylation proceeds though thalliation.

The only other substrate that appeared to show the spectrum of a trifluoroacetoxy derivative was triptycene. Perhaps with other arenes, the trifluoroacetates may be formed, but protonation of the oxygen increases the ionization potential of the π-system so that the radical cation of the hydrocarbon is preferentially observed.

Experimental Section

Most of the reactants were commercial materials and were purified by recrystallization or by chromatography before use. The tetramethylnaphthopyran (**20**) was provided by Dr. J. E. Anderson. Dibenzodioxin (**26**) was prepared from *o*-chlorophenol.[28] (Tri-*tert*-butylphenyl)mercury chloride (**38**) and bis(tri-*tert*-butylphenyl)mercury (**39**) were prepared by Mr. C. J.

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Cooksey by the mercuration of tri-*tert*-butylbenzene.[29]

ESR Spectroscopy. ESR spectra were recorded by using a Varian E4 or E109 spectrometer, fitted with a 500-W high-pressure mercury arc that was focused on the cavity and provided with neutral density (metal gauze) and glass (soda and Pyrex) filters.

Mercury trifluoroacetate (ca. 70 mg) was added to TFAH (1.3 cm^3) in a Suprasil ESR tube to give a saturated solution at room temperature. This was cooled to 262 ± 1 K, just above the freezing point of TFAH, and dissolved oxygen was removed by bubbling nitrogen through the solution for 5 min. A solution of the substrate (ca. 1 mg) in a minimum volume of TFAH or dichloromethane was added, and the solution was degassed for a further 1 min and then transferred to the precooled ESR cavity.

Acknowledgment. We thank Dr. J. E. Anderson and Mr. C. J. Cooksey for their gift of samples and Dr. S. N. Yazdi for carrying out the work on the mercuration of anthracene. This work was supported by the SERC.

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Efficient Synthesis of Substituted Derivatives of (Naphthalene)chromium(0) Carbonyls

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Tricarbonyl(η^6-1,4-epoxy-1,2,3,4-tetrahydronaphthalene) complex is a source of "protected" naphthalene for the indirect synthesis of Cr(η^6-naphthalene)(CO)$_2$L complexes, which can then be used in arene-exchange experiments. Experiments are reported for when L is a chiral 1,3,2-dioxaphospholane made by condensation of a chiral diol and PPhCl$_2$. Direct photolysis reactions of these ligands with Cr(η^6-naphthalene)(CO)$_3$ gives the substituted complexes in very poor yield (<3%). In contrast, photolysis reactions with the 1,4-epoxy-1,2,3,4-tetrahydronaphthalene complexes proceed in good (ca. 60–65%) yields, and subsequent dehydration by HBF$_4$ and BF$_3$ (ca. 50–65% yields) gives the substituted naphthalene complexes in an overall yield of 30–40% from the tricarbonyl. It is possible to exchange the naphthalene with monoarenes, though poor selectivity is observed in ligand-exchange experiments of the chiral naphthalene complexes with prochiral arenes.

Naphthalene complexes of the transition metals are an important subgroup of the metal arenes.[1] The naphthalene ligand or any other polyaromatic ligand is usually thermodynamically susceptible to exchange reactions with monoarenes,[2] and because of facile η^6 to η^4 ring slippage reactions, naphthalene is typically also kinetically quite labile.[4] This reactivity can be very useful, as demonstrated by the extensive chemistry of Cr(CO)$_3$(η^6-naphthalene) in stoichiometric[5] or catalytic[6] applications.

The utility of the naphthalene ligand is, however, limited because the very reactivity of the naphthalene ligand precludes many high-energy thermal or photolytic synthetic techniques. Thus, there are no convenient routes to potentially important substituted Cr(CO)$_2$L(η^6-naphthalene) derivatives. It is certainly true that photolytic substitution of a monoarene tricarbonyl complex proceeds quite smoothly in many cases,[7] but reports of such substitution reactions with related polyaromatic complexes[8] are quite uncommon and we infer from those papers that the yields are low despite arduous experimental methods. This may well be because the extended aromatic system alters the chromophore[9] to drive reactions other than CO expulsion, such as arene activation or cleavage.

In this paper, we report an efficient and, we believe, more generally applicable route to such substituted naphthalene complexes using the simple monoaromatic ligand, 1,4-epoxy-1,2,3,4-tetrahydronaphthalene, **1** (available commercially or from the Diels–Alder reaction

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