An E.S.R. Investigation of Radical Cations Formed in Friedel–Crafts Reactions

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The present study deals with the detection and identification of radical cations produced in a Friedel–Crafts alkylating system, with benzene, toluene, or ethylbenzene, and an alkyl chloride. Our results indicate that the observed e.s.r. spectra are due to polycyclic aromatic radical cations formed from the parent hydrocarbons.

It is suggested that benzyl halides produced in the Friedel–Crafts alkylating reaction undergo Scholl self-condensation to give polycyclic aromatic hydrocarbons, which are converted into the corresponding polycyclic aromatic radical cations in the presence of aluminium chloride.

It is well known, that the Friedel–Crafts alkylation is a classic electrophilic aromatic substitution, and is a method used in the preparation of alkyl substituted benzene. The catalyst used most often is aluminium chloride. Generally, it is considered that the mechanism for the reaction starts with the formation of a carbocation:

$$RCl + AlCl_3 \longrightarrow [RCl{\cdot}AlCl_3] \longrightarrow R^+ + AlCl_4^-$$

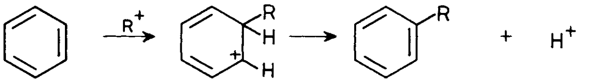
The carbocation then acts as an electrophile and attacks the benzene ring to form an arenium ion. The arenium ion then loses a proton generating the alkyl substituted benzene (Scheme 1). Based on these facts, we can see that Friedel–Crafts alkylation reactions do not involve any radical intermediates.

Rooney and Pink[1] discovered that a solution of anthracene and chrysene in chloroform gave e.s.r. signals in the presence of aluminium chloride. Adams and Nicksic[2] observed e.s.r. absorptions in the Friedel–Crafts system formed by benzene, alkylchloride, and aluminium chloride. In their work, only a *g* value and spectral widths were reported, the e.s.r. spectrum of the radical was not further analysed. Therefore, the type and mechanism of radical formation was not fully understood; it was not clear in either of these reactions whether the e.s.r. signal came from an intermediate or from a radical formed by the products of the reaction. The formation of a 9,10-diphenylanthryl radical cation from a mixture of benzene and chloroform in the presence of $AlCl_3$ has been confirmed.[3] We have reported recently[4] the resolution of the e.s.r. spectra of polycylic aromatic radical cations generated during Friedel–Crafts reactions with triphenylantimony. To understand the mechanism of the free-radical formation, it is necessary to detect and identify the radicals produced in the Friedel–Crafts alkylations, this paper describes the results of e.s.r. studies of such species, and proposes a possible mechanism for their formation.

Experimental

Materials.—The purity of aluminium chloride used was 99.9%.

Sample Preparation. The sample tubes used in these studies were 4 mm o.d. Pyrex tubes. The samples were prepared directly in e.s.r. tubes. As the mixture was heated gently, gases were released. The released gases were washed with water and collected for analysis. The samples were not degassed on a vacuum line. During a Friedel–Crafts reaction the evolution of gases removes the dissolved oxygen in the solution, so the resolved e.s.r. spectra can be observed. The sample was placed in the resonance cavity and its spectrum was recorded. The volume ratio of benzene or alkylbenzene to alkyl chloride was 1:1.



$$H^+ + AlCl_4^- \longrightarrow HCl + AlCl_3$$

Scheme 1.

E.s.r. Spectra.—Spectra were obtained on a Varian E-115 spectrometer operating at a microwave frequency of 9.5 GHz. The fields were calibrated with ^1H n.m.r. markers and the microwave frequency was measured with a frequency counter (model H/P 5342A). E.s.r. spectra were recorded at room temperature.

The coupling constants for the radicals were assigned by comparing the experimental spectra with those simulated by a Varian E-936 computer.

Hydrogen Analysis.—Hydrogen was analysed using a model 100 Gas Chromatograph. The chromatography column was 2 m long and contained 5 Å molecular seives. All the reactions discussed were carried out in the presence of anhydrous aluminium chloride. Gas chromatography results showed that hydrogen and hydrogen chloride were present in all gas mixtures released.

Results and Discussion

(i) *The Benzene and Chloroform System.*—When the reaction mixture is gently heated, the reaction takes place rapidly with large quantities of gas released. Figure 1 shows the e.s.r. spectrum observed. If chloroform is replaced by CCl_4, or CBr_4, the e.s.r. spectra observed are identical with Figure 1. The e.s.r. proton hyperfine coupling constants obtained from the analysis of this spectrum are given in the Table. The hyperfine splitting pattern proves to be almost identical to that observed for 9,10-diphenylanthracene in concentrated H_2SO_4.[5] This spectrum

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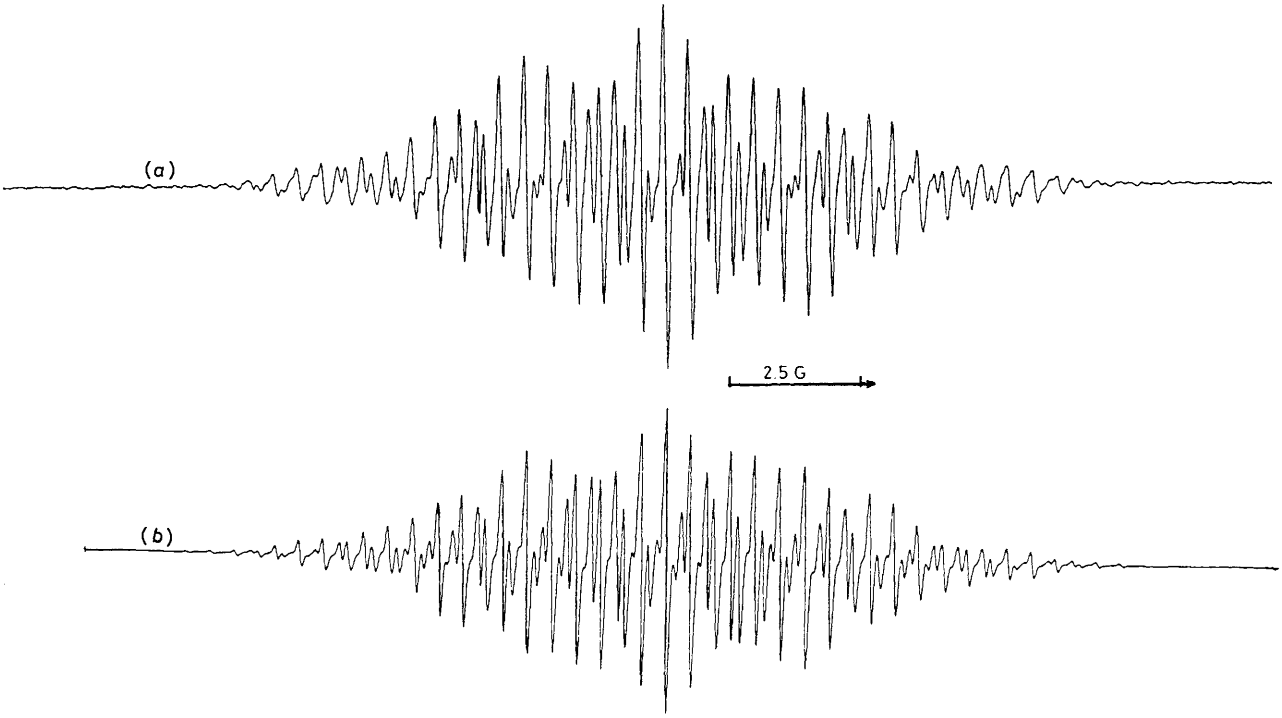
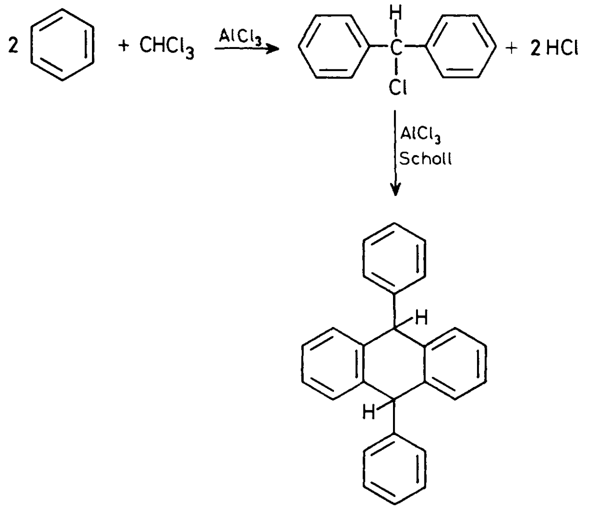
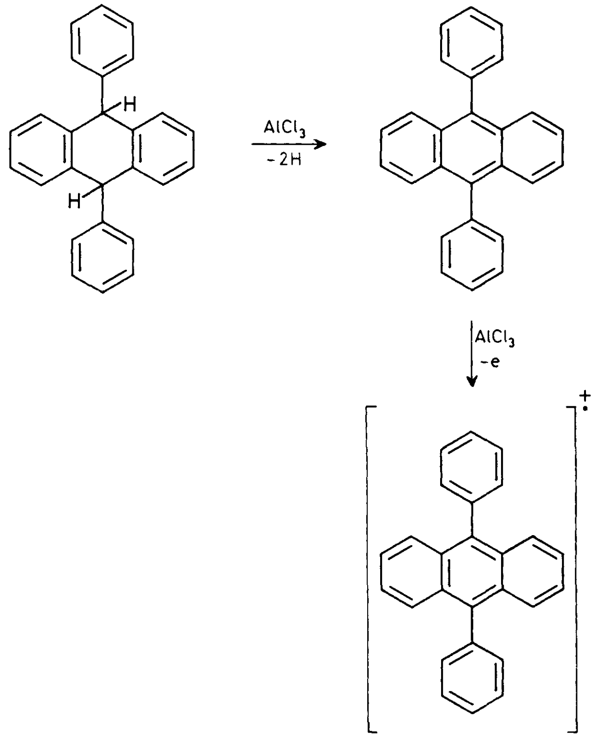


Figure 1. (*a*) E.s.r. spectrum of 9,10-diphenylanthryl cation radical obtained from C_6H_6 and $CHCl_3$ in $AlCl_3$; (*b*) Simulated spectrum.



Scheme 2.



Scheme 3.

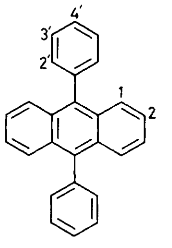
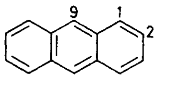
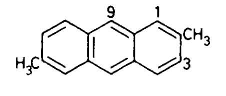
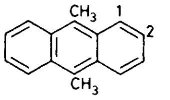
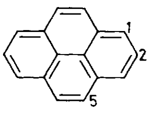
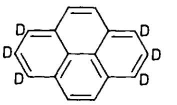
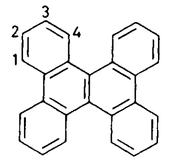
was, therefore, assigned to the 9,10-diphenylanthryl radical cation.

The formation of 9,10-diphenylanthracene in the Friedel–Crafts reaction can be interpreted in terms of the well-known Scholl condensation,[6] Scheme 2. $AlCl_3$ is known to have a powerful dehydrogenating action.[7] It catalyses the dehydrogenation of 9,10-diphenyl-9,10-dihydroanthracene to yield 9,10-diphenylanthracene. The 9,10-diphenylanthryl radical cations are produced by one electron transfer from 9,10-diphenylanthracene to $AlCl_3$, Scheme 3.

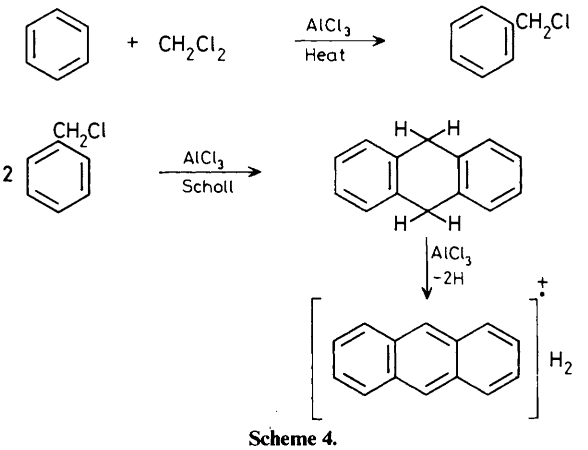
(ii) *The Benzene and Dichloromethane System.*—This reaction does not occur as rapidly as the reaction with C_6H_6 and $CHCl_3$. Figure 2 shows the e.s.r. spectrum observed for this system. This spectrum is identical with that for anthracene in concentrated H_2SO_4.[8] The hyperfine coupling constants are listed in the Table. The formation of anthryl radical cations proceeds according to Scheme 4. 9,10-Dihydroanthracene was formed through an intermolecular Scholl condensation reaction with benzyl chloride. The $AlCl_3$ catalyses the dehydrogenation of 9,10-dihydroanthracene to yield anthracene[9] which is converted into the corresponding radical cation in the presence of $AlCl_3$.

(iii) *The Toluene and Dichloromethane System.*—Figure 3 is the spectrum obtained from the study of the reaction of toluene with CH_2Cl_2 in the presence of $AlCl_3$. The reaction takes place rapidly when the mixture is gently heated. Although the e.s.r.

Table. E.s.r. coupling constants for some polycyclic aromatic radical cations in a Friedel–Crafts alkylation system in the presence of $AlCl_3$.

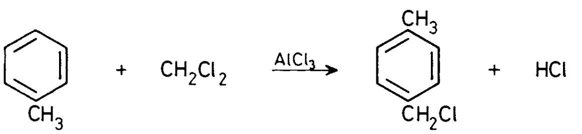
Reaction system	Structure	Position	a_H/G	a_H/G*[a]
$C_6H_6 + CHCl_3$		1	2.63	2.65[5]
		2	1.23	1.25
		2'	0.44	0.44
		3'	0.44	0.44
		4'	0.44	0.44
$C_6H_6 + CH_2Cl_2$		1	3.08	3.08[5]
		2	1.30	1.36
		9	6.58	6.51
$C_6H_5CH_3 + CH_2Cl_2$		1	3.19	3.18[10]
		CH_3	2.76	2.76
		3	0.56	0.56
		9	6.33	6.33
$C_6H_5CH_2CH_3 + CCl_4$		1	2.52	2.48[5]
		2	1.20	1.22
		CH_3	8.0	7.89
$C_6H_6 + ClCH_2CH_2Cl$		1	5.10	5.40[5]
		2	1.20	1.20
		5	2.50	2.10
$C_6D_6 + ClCH_2CH_2Cl$		1	0.46 (4 D)	
		2	0.23 (2 D)	
		5	3.75	
$C_6H_6 + Cl_2CHCHCl_2$		1	0.60	0.60[11]
		2	1.99	1.99
		3	<0.03	<0.03
		4	2.28	2.28

[a] Literature values.



Scheme 4.

signals are weak, the well-resolved hyperfine structure was observed. The e.s.r. hyperfine coupling constants obtained from the analysis of the spectrum are given in the Table. This spectrum is very similar to that obtained for 2.6-dimethylanthracene in concentrated H_2SO_4.[10] Based on these observations, the formation of 2,6-dimethylanthracene can be represented by Scheme 5. $AlCl_3$ catalyses the alkylation of toluene to yield a binary substituent product which proceeds *via* an intermolecular Scholl condensation reaction to yield 2,6-dimethylanthracene, the latter was converted into the corresponding radical cations under the influence of $AlCl_3$.



Scheme 5.

(iv) *The Ethylbenzene and Tetrachloromethane System.*—The reaction of this system proceeds smoothly at room temperature. The e.s.r. spectrum obtained is shown in Figure 4. The hyperfine coupling constants of the e.s.r. spectrum are identical with those of the 9,10-dimethylanthryl radical cation. Therefore, it is inferred that formation of 9,10-dimethylanthracene occurs *via* the well-known Scholl condensation of 1-chloroethylbenzene. This radical cation is produced by transfer of an electron from 9,10-dimethylanthracene to $AlCl_3$.

In a separate reaction, $AlCl_3$ was added to a solution of

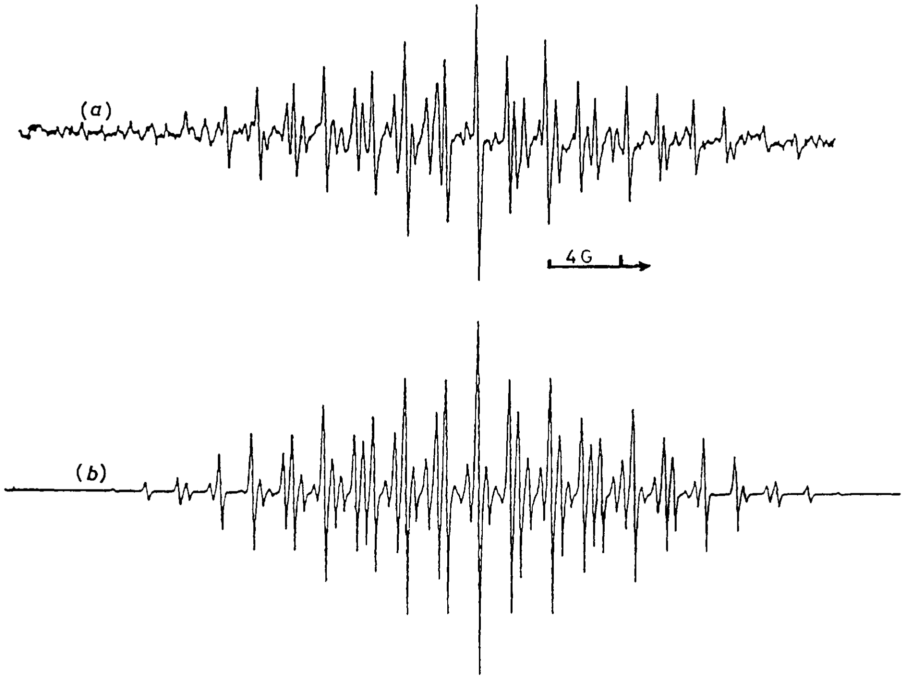


Figure 2. (*a*) E.s.r. spectrum of anthryl cation radical obtained from C_6H_6 and CH_2Cl_2 in $AlCl_3$; (*b*) Simulated spectrum.

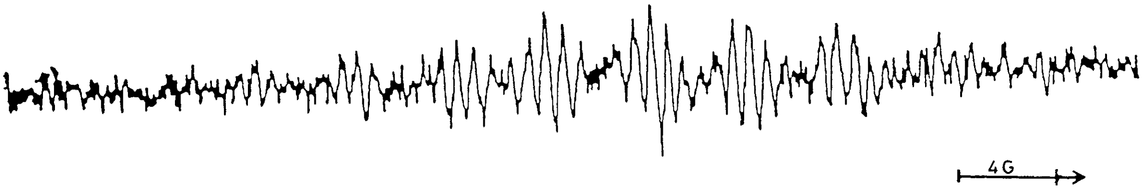


Figure 3. E.s.r. spectrum of 2,6-dimethylanthryl cation radical obtained from $C_6H_5CH_3$ and CH_2Cl_2 in $AlCl_3$.

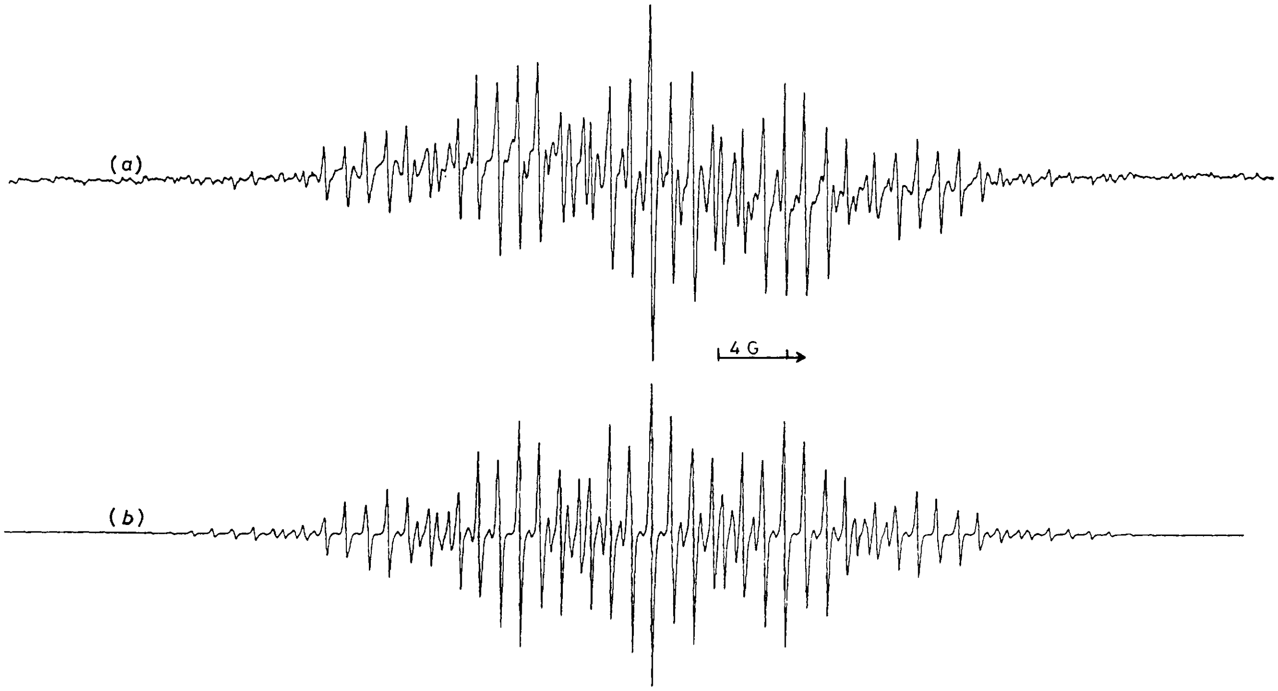


Figure 4. (*a*) E.s.r. spectrum of 9,10-dimethylanthryl cation radical obtained from $C_6H_5CH_2CH_3$ and CCl_4 in $AlCl_3$; (*b*) Simulated spectrum.

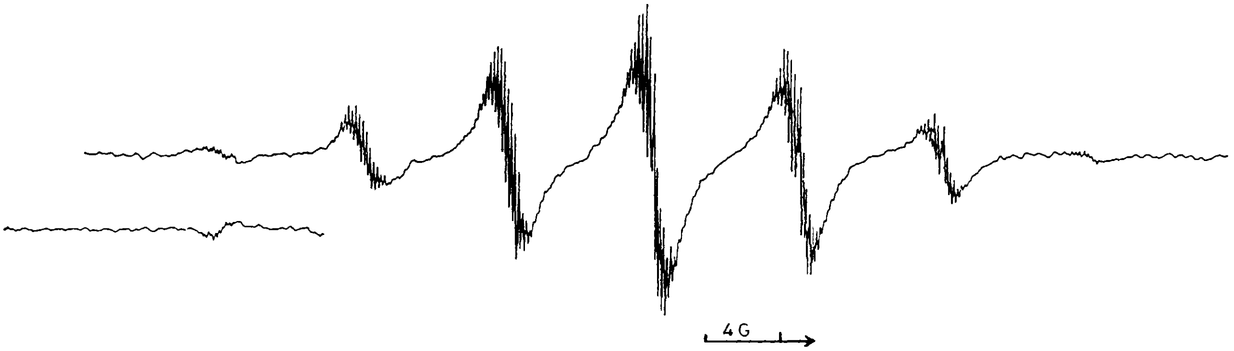


Figure 5. E.s.r. spectrum of deuteriated [$^2H_8$]-9,10-dimethylanthryl cation radical obtained from C_6D_6 + CH_3CH_2Br + CCl_4 in $AlCl_3$.

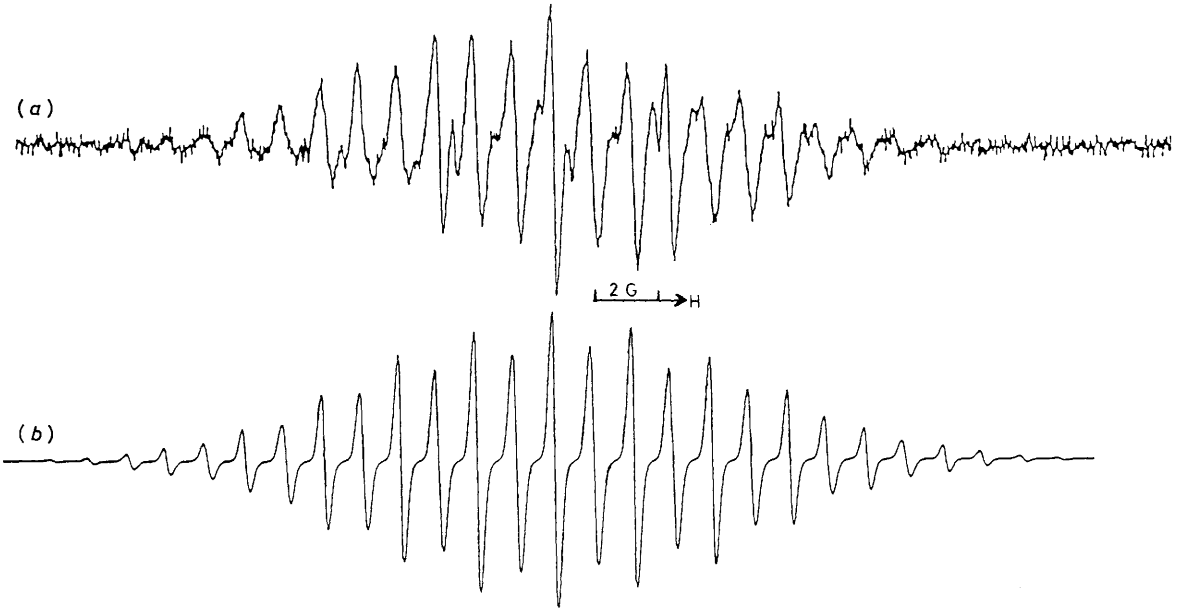


Figure 6. (*a*) E.s.r. spectrum of pyrenyl cation radical obtained from C_6H_6 and CH_2ClCH_2Cl in $AlCl_3$; (*b*) Simulated spectrum.

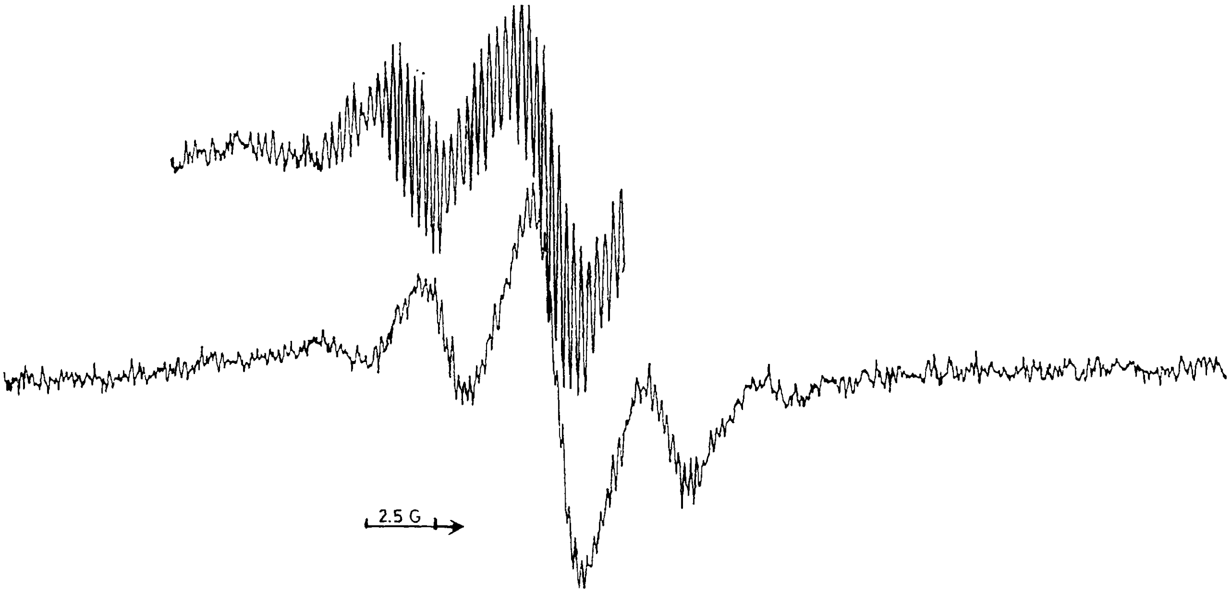


Figure 7. E.s.r. spectrum of deuteriated pyrenyl cation radical obtained from C_6D_6 and CH_2ClCH_2Cl in $AlCl_3$.

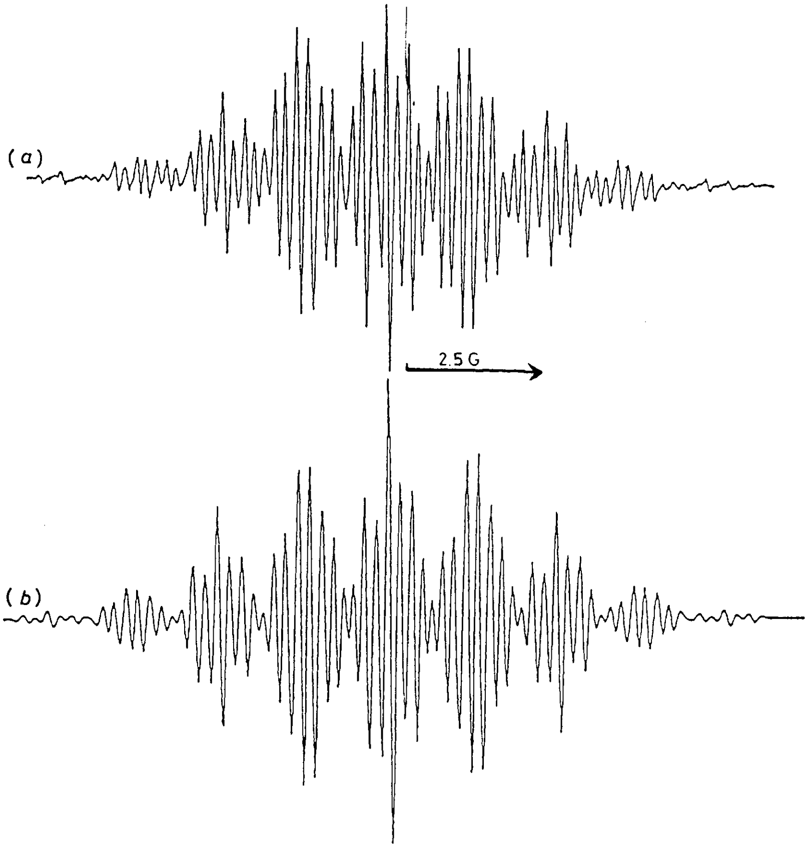
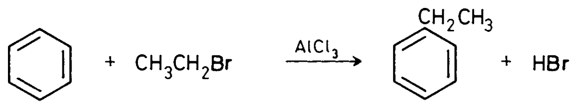


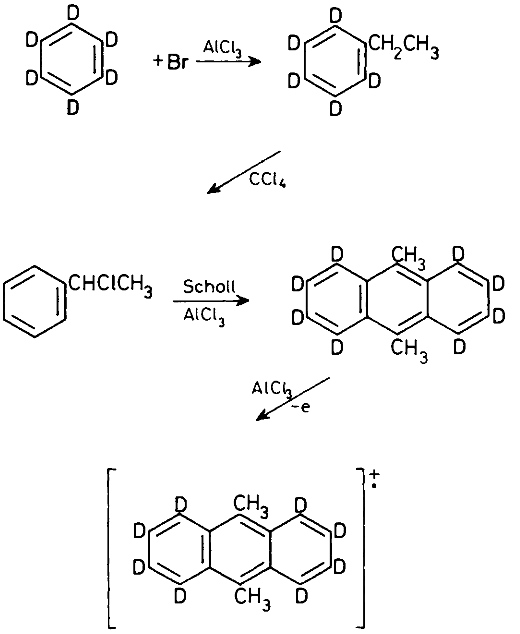
Figure 8. (*a*) E.s.r. spectrum of dibenzo[*a*,*c*]triphenylene cation radical obtained from C_6H_6 and $CHCl_2$ in $AlCl_3$; (*b*) Simulated spectrum.

benzene and bromoethane. On completion of the reaction CCl_4 was added to the mixture; this produced a violent reaction. The resulting material produced an e.s.r. spectrum quite similar to that shown in Figure 4. Therefore, we deduced that they were both due to the same radical and we assumed that the alkylation of benzene occurs to yield ethylbenzene (Scheme 6). Ethylbenzene undergoes the same reaction as discussed above to yield the 9,10-dimethylanthryl radical cation.



Scheme 6.

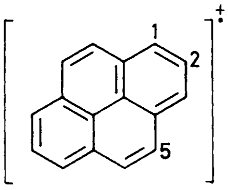
When benzene is replaced by C_6D_6, we can obtain the e.s.r. spectrum shown in Figure 5. The e.s.r. spectrum is assigned to the 1,2,3,4,5,6,7,8-octadeuterio-9,10-dimethylanthryl radical cation. Presumably the radicals are formed by the following sequence, Scheme 7.



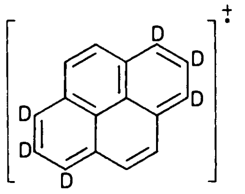
Scheme 7.

From the results discussed above we conclude that the Friedel–Crafts alkylation reaction of monocyclic aromatics with methyl halides yield alkyl aromatics which undergo an intermolecular Scholl condensation reaction to obtain the derivatives of anthracene, which, are then, converted to the corresponding radical cations under the influence of $AlCl_3$.

(v) *The Benzene* 1,2-*Dichloroethane System*.—The e.s.r. spectrum shown in Figure 6 was observed after the reaction mixture was gently heated in the presence of $AlCl_3$. The hyperfine coupling constants listed in the Table were obtained by comparison of the experimental with the computer-simulated spectra. If C_6H_6 is replaced by C_6D_6, the spectrum obtained is that shown in Figure 7. Based on the analysis of Figures 6 and 7, we believe that the spectra are due to the pyrenyl radical cation (**1**) and the deuteriated [$^2H_6$]pyrene (**2**) respectively. The hyperfine coupling constants of radical (**1**) are very similar to those obtained for the pyrenyl radical cation in a liquid $SbCl_3$[5] solution. For the radical, (**2**), the interactions between an unpaired electron and four protons splits the spectrum into five lines with relative intensities 1:4:6:4:1, and each of these five lines is split into a further multiplet by the

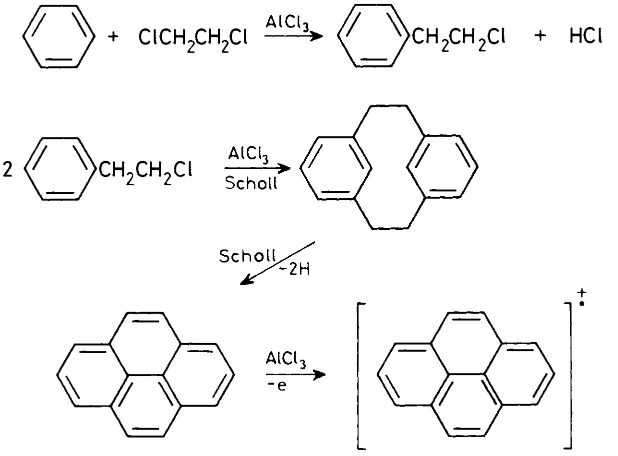


(1)



(2)

deuterons at positions 1 and 2 (Figure 7). The coupling constants are listed in the Table. The formation of the pyrenyl radical cation may be represented by the following reaction Scheme 8.



Scheme 8.

(vi) *The Benzene and* 1,1,2,2-*Tetrachloroethane System*.—Figure 8 shows the e.s.r. spectrum observed in the reaction of C_6H_6 with $CHCl_2CHCl_2$ in the presence of $AlCl_3$. This spectrum is identical to that of dibenzo[*a*,*c*]triphenylene[11] in an $SbCl_5$–CH_2Cl_2 solution. The proton hyperfine coupling constants are listed in the Table. The experimental spectrum is in good agreement with the computer-simulated spectrum. The same e.s.r. spectrum was observed when $CHCl_2CHCl_2$ was replaced by CHB_2CHBr_2.

Dibenzo[*a*,*c*]triphenylene is obtained through an intramolecular Scholl condensation of 1,1,2,2-tetraphenylethane. Dibenzo[*a*,*c*]triphenylene is then converted into the corresponding radical cations in the presence of $AlCl_3$.

The oxidants which are often used for the preparation of polycyclic aromatic radical cations reported in the literature are: concentrated H_2SO_4,[8] BF_3–CF_3CO_2H,[12] $SbCl_3$,[13] $SbCl_5$,[14] and $AlCl_3$.[1] Generally, the use of these oxidants results in the formation of well-resolved e.s.r. spectra.

Conclusions

Our results indicate that observed spectra in the Friedel–Crafts alkylation system are due to polycyclic aromatic radical cations formed from their parent hydrocarbons. The alkyl aromatics produced in Friedel–Crafts alkylation reactions undergo intermolecular or intramolecular Scholl condensation to give polycyclic aromatic hydrocarbons, which are converted into the corresponding polycyclic aromatic radical cations in the presence of $AlCl_3$. We have reason to believe that the observed radicals are neither the species involved in Friedel–Crafts alkylation reactions nor the ones involved in Scholl condensation reactions.

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