

51.66; H, 9.11; N, 3.03; S, 6.92. In spite of careful handling, elemental analyses (three separate trials) did not give satisfactory results. This may be due to the strong deliquescence of the quaternary salt as verified by the IR and ^1H NMR spectra.

N-Methyl-N-octylmorpholinium 15-crown-5 ether methyl sulfate (3b): waxy, deliquescent solid: Yield, 0.44 g (2 mmol scale) (44%); mp 120.5–121.6 °C; ^1H NMR (CDCl_3) δ 0.88 (t, 3 H), 1.20–1.52 (m, 10 H), 1.68–2.04 (br, 2 H), 3.12–3.96 (m, 28 H) 3.96–4.80 (m, 2 H); MS, *m/e* (rel intensity) 389 (1), 373 (4), 274 (100); IR (neat) 2940, 2875, 1475, 1360, 1120 cm^{-1} . Anal. Calcd for $\text{C}_{22}\text{H}_{46}\text{NO}_9\text{S}$: C, 52.98; H, 9.08; N, 2.80; S, 6.42. Found: C, 52.85; H, 8.90; N, 2.84; S, 6.29.

N-Octylmorpholino 15-Crown-5 N-Oxide (4b); Typical Procedure. To N-octylmorpholino 15-crown-5 ether (2b) (2.24 g, 6 mmol) heated to 60 °C was added 35% aqueous hydrogen peroxide (2.92 g, 30 mmol) dissolved in 7 mL of acetone dropwise during a period of 3 h. The solution was kept at the same temperature for 42 h. After the removal of the solvent, the reaction product was purified by column chromatography on alumina using benzene/2-propanol (98:2) as eluent to give 4b as a white waxy solid: yield, 1.55 g (66%); mp 138.0–139.0 °C; ^1H NMR (CDCl_3) δ 0.89 (t, 3 H), 1.20–1.56 (m, 10 H), 1.78–2.20 (br, 2 H), 2.80–4.00 (m, 22 H), 4.18–5.20 (m, 2 H); ^{15}N NMR ($\text{CHCl}_3\text{-CDCl}_3$) 300.6 ppm from NO_3^- and 99.4 ppm from NH_3 ; MS, *m/e* (rel intensity) 373 (5), 274 (100), 112 (34) 43 (84); IR (neat) 2920, 2850, 1465, 1350, 1115 cm^{-1} . Anal. Calcd for $\text{C}_{20}\text{H}_{35}\text{NO}_6$: C, 61.67; H, 10.09; N, 3.60. Found: C, 61.39; H, 9.81; N, 3.41.

N-Octylmorpholino 12-crown-4 N-oxide (4a): white waxy solid; yield, 1.57 g (6 mmol scale) (76%); mp 133.1–134.0 °C; ^1H NMR (CDCl_3) δ 0.89 (t, 3 H), 1.14–1.64 (m, 10 H), 1.64–2.24 (br, 2 H), 2.66–4.16 (m, 18 H), 4.16–5.24 (m, 2 H); MS, *m/e* (rel intensity) 329 (11), 230 (100), 112 (34), 43 (55); IR (neat) 2940, 2870, 1460, 1370, 1125 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{35}\text{NO}_5$: C, 62.58; H, 10.21; N, 4.05. Found: C, 62.25; H, 9.84; N, 3.91.

N-Octylmorpholino 18-crown-6 N-oxide (4c): white waxy solid; yield, 2.10 g (6 mmol scale) (81%); mp 126.0–127.0 °C; ^1H NMR (CDCl_3) δ 0.89 (t, 3 H), 1.20–1.56 (m, 10 H), 1.76–2.20 (br, 2 H), 2.92–4.04 (m, 26 H), 4.20–5.04 (m, 2 H); MS, *m/e* (rel intensity) 417 (1), 318 (27), 112 (17), 43 (100); IR (neat) 2940, 2870, 1470, 1360, 1125 cm^{-1} . Anal. Calcd for $\text{C}_{22}\text{H}_{43}\text{NO}_7$: C, 60.94; H, 10.00; N, 3.23. Found: C, 60.79; H, 9.76; N, 3.10.

Registry No. 1a, 117021-77-9; 1a', 106576-28-7; 1b, 117021-75-7; 1b', 106576-29-8; 1c, 117021-76-8; 2a, 117039-38-0; 2a', 117039-39-1; 2b, 117021-62-2; 2b-HCl, 117021-64-4; 2b', 117021-63-3; 2c, 117021-61-1; 2c-HCl, 117021-65-5; 3a, 117021-69-9; 3b, 117021-71-3; 3c, 117021-67-7; 4a, 117021-73-5; 4b, 117021-72-4; 4c, 117021-74-6; 5b, 75006-54-1; 5c, 75006-58-5; 6a, 74649-87-9; 6b, 75507-22-1.

EPR Studies of Polycyclic Aromatic Cation Radicals Generated during Friedel-Crafts Reactions with Triphenylantimony

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Introduction

Radical cations have been detected by EPR measurements of Friedel-Crafts reactions¹⁻³ and resolved EPR spectra of the anthracene (I),² and 9,10-dimethylanthracene (II)³ cation radical have been reported. It has

recently been reported by ourselves⁴ and others⁵ that resolved EPR spectra can in general be observed from a Friedel-Crafts type reaction with benzene or substituted benzene carried out in originally air-saturated systems without degassing the samples on a vacuum line. HCl gas evolved during the Friedel-Crafts type reaction removes the dissolved oxygen in the solution, so that high-resolution EPR spectra are observed.

Previously^{4,5} it was shown that a well resolved EPR spectrum of 9,10-diphenylanthracene (III) cation radical appeared whenever benzene was reacted with excess AlCl_3 in either CHCl_3 , CBr_4 , CCl_4 , CDCl_3 , and PhCCl_3 or upon reaction of Ph_3SiH^5 or Ph_3SiOH^5 in place of benzene. On the other hand, the reaction of benzene with AlCl_3 in CH_2Cl_2 solvent gave a resolved EPR spectra due only to the anthracene cation radical.⁴ Presumably methylene chloride reacts with benzene in the presence of AlCl_3 to form benzyl chloride, which reacts further to give 9,10-dihydroanthracene in low yield. In the presence of excess AlCl_3 , 9,10-dihydroanthracene reacts⁶ to yield I. Reaction of I with excess AlCl_3 forms the anthracene radical cation⁷⁻⁹ in millimolar concentrations, so that narrow line EPR spectra are observed from the HCl degassed solutions. However upon reaction with alkyl-substituted benzenes, the EPR pattern became extremely complex, presumably due to the appearance of several radicals, and is not as such interpretable. It seems likely that ENDOR methods may be extremely useful in analyzing the EPR spectra.

We have extended this work to the study of radical formation when triphenyl antimony (SbPh_3) reacts with an alkyl chloride as the solvent in the presence of excess aluminum chloride. It is known¹⁰ that trialkyl- and triarylstibines (R_3M) react with alkyl halides (RX) and upon heating in the presence of AlCl_3 from a halide salt ($\text{R}_3\text{R}^+\text{M}^-\text{X}^-$). On the other hand triarylstibines¹¹ do not react with the alkyl halides above. Here we will show that the number and type of radicals identified by EPR methods depend on the concentration of the reactant. Highly resolved spectra, equal in quality to that produced by chemical oxidation of the parent material, have been observed. The added advantage with the Friedel-Crafts method is that various deuteriated radical cation radicals can be formed with relative ease.

Experimental Section

Materials. Triphenylantimony and 9,10-phenylanthracene were purchased from Aldrich Chemical and used without further purification. The various alkylating agents were purified by the usual methods prior to use.

Sample Preparation. Triphenylantimony was dissolved in an alkyl chloride solvent, and the solution was placed in a sample tube (4 mm o.d.) containing a 3-fold or more of solid anhydrous aluminum chloride. Gases evolved from the reaction mixture were found to be H_2 and HCl. EPR measurements indicated that

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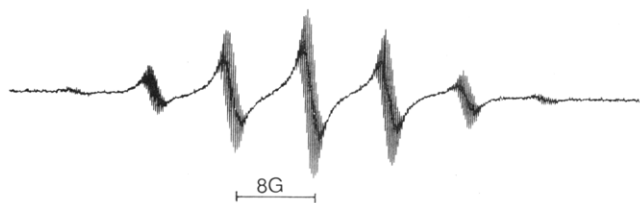


Figure 1. EPR spectrum of deuteriated 9,10-dimethyl(9,10-dimethylanthracene- d_8) cation radical obtained from $\text{SbPh}_3 + \text{C}_6\text{D}_6$ and excess AlCl_3 .

radicals formed during the reaction were stable for several hours. A mixture of aluminum chloride and the alkyl chloride solvent resulted in a broader, unresolved less intense adsorption peak than when triphenylantimony was present.

Spectra. Spectra were obtained on a Varian E-115 spectrometer at the Lanzhou Institute of Chemical Physics operating at a microwave frequency of 9.5 GHz. The magnetic field was calibrated with a Varian E-500 NMR gaussmeter, and the microwave frequency was measured with a frequency counter Model H/P 5342A. EPR spectra were recorded at room temperature. The coupling constants for the radicals obtained by analysis are refined by simulating the spectra on a Varian E-936 computer.

Results and Discussion

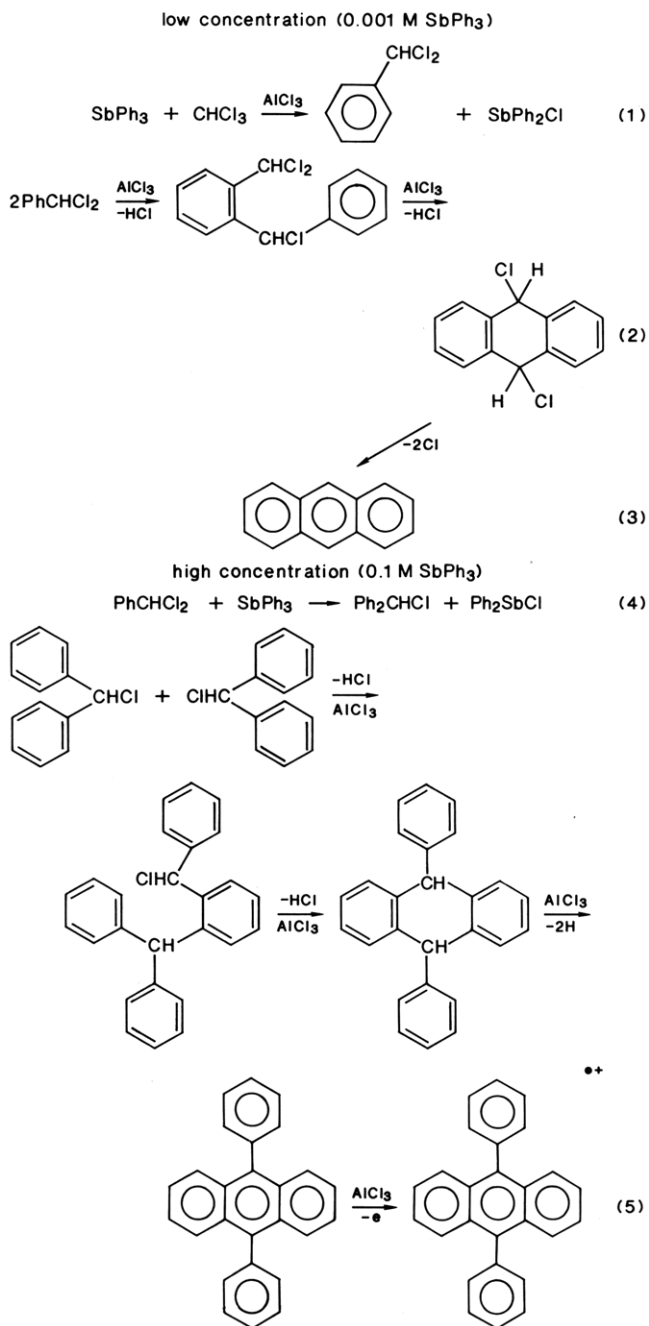
1. $\text{SbPh}_3 + \text{CH}_2\text{Cl}_2$ System. The reaction between a CH_2Cl_2 solution of SbPh_3 (I) (0.05 M) and an excess of AlCl_3 at 40 °C resulted in an EPR spectrum (Figure S1¹²) virtually identical with that observed when anthracene is reacted with concentrated H_2SO_4 .¹³ The proton hyperfine coupling constants of 3.08, 1.35, and 6.48 G (Table S1¹²) obtained from a computer simulation confirmed the assignment as the anthracene radical cation.¹³ Presumably, the reaction between SbPh_3 and AlCl_3 in CH_2Cl_2 forms anthracene by a Friedel-Crafts alkylation at the ipso position. Aluminum chloride is known¹⁴ to be a powerful dehydrogenating agent and catalyzes the dehydrogenation of 9,10-dihydroanthracene at room temperature to yield anthracene. The anthracene radical cations are produced by electron transfer⁷⁻⁹ from anthracene to AlCl_3 .

2. $\text{SbPh}_3 + \text{CHCl}_3$ System. EPR spectra were also observed for a chloroform solution of I in the presence of excess AlCl_3 ; however, the EPR pattern depended on the concentration of I in the CHCl_3 solvent. At 0.1 M I in CHCl_3 , a well-resolved EPR spectrum (Figure S2a¹²) was observed quite similar to that observed for III in concentrated H_2SO_4 (Figure S2b¹²). Computer simulation resulted in the proton hyperfine coupling constants of 2.65, 1.25, 0.45, 0.45, and 0.45 G (Table S1¹²).

Upon decreasing the concentration of SbPh_3 in CHCl_3 to 0.05 M, an EPR spectrum (Figure S3¹²) was observed consisting of a mixture of III and I. At a concentration of 5×10^{-3} M in CHCl_3 , the EPR spectrum (Figure S4a¹²) is that of I; the hyperfine coupling parameters deduced by computer simulation (Figure S4b¹²) are in good agreement with the anthracene cation radical in concentrated H_2SO_4 .¹

If the solvent is CDCl_3 , then the 9,10-dideuterioanthracene radical is observed (Figure S5a¹²). A computer simulation of the EPR spectrum using coupling constants of $a_{\text{H}} = 3.08$ G, $a_{\text{H}} = 1.35$ G, and $a_{\text{D}} = 1.00$ G and a 0.040-G linewidth gave good agreement with the experimental spectrum (Figure S5b¹²).

Presumably the radicals are formed via the following sequence of steps (1-5):



These experiments indicate that the formation of polycyclic aromatic hydrocarbons depends on the concentration of SbPh_3 . This is in contrast to the reaction of benzene with AlCl_3 in CHCl_3 where only EPR spectra due to III was observed, independent of the benzene concentration.

In the first step, presumably chloroform in the presence of AlCl_3 reacts with triphenylantimony to give benzal chloride. However at high concentration of SbPh_3 (step 4) further reaction of benzal chloride with additional triphenylantimony forms Ph_2CHCl , which forms a condensation product in step 5 of 9,10-diphenyl-9,10-dihydroanthracene. This undergoes hydrogen elimination¹⁴ to form 9,10-diphenylanthracene (DPA). At millimolar concentration, apparently the concentration of Ph_2CHCl is too low to form detectable DPA and thus step 2 occurs to form 9,10-dichloro-9,10-dihydroanthracene, which eliminates HCl ¹⁵ to yield anthracene.

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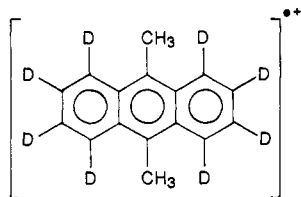
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3. SbPh₃ + 1,1,2,2-Tetrachloroethane System. The reaction of SbPh₃ (0.05 M) and 1,1,2,2-tetrachloroethane in the presence of aluminum chloride resulted in an EPR spectrum (Figure S6a¹²) identical with that of the dibenzo[*a,c*]triphenylene radical cation in SbCl₅-CH₂Cl₂ solution.¹⁶ Proton hyperfine coupling constants of 0.60, 2.00, 2.27, and <0.03 G (Table S1¹²) were used to simulate the spectrum (Figure S6b¹²).

This radical cation occurs by first the formation of 1,1,2,2-tetraphenylethane upon reaction of SbPh₃ with the alkyl carbonium ion. Formation of dibenzo[*a,c*]triphenylene occurs via the well-known Scholl condensation for 1,1,2,2-tetraphenylethane. If 1,1,2,2-tetrachloroethane is replaced by 1,1,2,2-tetrabromomethane, an identical spectrum is observed. This same spectrum is also observed when benzene reacts with 1,1,2,2-tetrachloro- or 1,1,2,2-tetrabromomethane in excess AlCl₃.

4. SbPh₃ + 1,1-Dichloroethane System. The ESR spectrum (Figure S7¹²) observed in the reaction of SbPh₃ (0.05 M) with 1,1-dichloroethanes, under the influence of AlCl₃, is identical with that of the 9,10-dimethylantracene radical cations in the molten SbCl₃.¹⁷ Proton hyperfine coupling constants of $a_H = 2.52$, $a_H = 1.20$, and $a_{CH_3} = 7.98$ G (Table S1¹²) were used to simulate the spectrum in (Figure S7b¹²).

The EPR spectrum and coupling constants of the 9,10-dimethyl-1,2,3,4,5,6,7,8-octadeuterioanthracene radical cation is unreported in the literature. In this work, we found that the precursor molecule can be synthesized by the Friedel-Crafts alkylating reaction. Figure 1 shows the EPR spectrum of paramagnetic species formed in the reaction of the benzene-*d*₆ with 1,1-dichloroethane. We note that this pattern consists of seven equally spaced lines, with relative intensities 1:6:15:20:15:6:1, and that the separation between any two adjacent lines gives the value of 8.00 G, fairly close to methyl proton coupling constant in the nondeuteriated 9,10-dimethylantracene radical cation. Each of these seven lines is split into a further multiplet line due to interaction with other magnetic nuclei. We assigned this EPR spectrum to the radical cation as shown below. The hyperfine coupling constants



were assigned by comparing the experimental spectrum with those simulated by a computer. The observed hyperfine coupling constants are listed in Table S1 (see the supplementary material).

Summary

Careful control of SbPh₃ concentration enables resolved EPR spectra that can be analyzed in a straightforward manner. This suggests that more complex EPR patterns may be simplified if the concentration of the reactants are carefully considered. This method may also permit various new deuteriated radical cations to be studied.

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useful discussions with M. Cava.

Registry No. CH₂Cl₂, 75-09-2; CHCl₃, 67-66-3; CDCl₃, 865-49-6; SbPh₃, 603-36-1; 1,1,2,2-tetrachloroethane, 79-34-5; 1,1-dichloroethane, 75-34-3; anthracene cation radical, 34512-28-2; 9,10-dideuterioanthracene cation radical, 117178-97-9; dibenzo[*a,c*]triphenylene radical cation, 34478-92-7; 9,10-dimethylantracene radical cation, 34526-95-9; 9,10-dimethyl-1,2,3,4,5,6,7,8-octadeuterioanthracene radical cation, 117095-79-1; 1,1,2,2-tetrabromoethane, 79-27-6.

Supplementary Material Available: EPR spectra and hyperfine coupling constants (Figures S1-S7 and Table S1) (8 pages). Ordering information is given on any current masthead page.

Boron Trifluoride Mediated Reaction of 1,9-Dihalopentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-diones with Ethyl Diazoacetate: A Novel Synthetic Entry into the Cyclopent[*a*]indene Ring System

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As part of a program that is concerned with the synthesis and chemistry of substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes (PCUD),¹ we have recently undertaken a study of the Lewis acid promoted reaction of substituted PCUD-8,11-diones with ethyl diazoacetate (EDA).^{2,3} Thus, reaction of 1-substituted PCUD-8,11-diones (1) with EDA (1 equiv) in the presence of boron trifluoride etherate has been shown to afford the corresponding monohomologation product (2 or 3, Scheme I). We now report the results of a study of the corresponding reactions of 1,9-dibromo- and 1,9-dichloro-PCUD-8,11-diones (4 and 5, respectively) with EDA (1 equiv)-F₃B·OEt₂.

It has been shown that, when α -halo ketones are employed as substrates in the homologation reaction with EDA-F₃B·OEt₂, the presence of the halogen atom effectively suppresses migration of the terminus to which it is attached.⁴ Since 4 and 5 contain two α -halo ketone moieties, it was of interest to determine which carbonyl group would prove to be the preferred reaction site. It was anticipated that the presence of the halogen atom adjacent to the reaction site would lead to regiospecific ketone homologation by EDA-F₃B·OEt₂.⁴

In our hands, the reaction of 4 with EDA (excess) in the presence of F₃B·OEt₂ afforded a single product, 6, in 42% yield. The proton and carbon-13 NMR spectra of 6 indicated the presence of an aromatic ring (see the Exper-

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