(100% D incorporated), optical purity 0%. IR and NMR spectra were identical with those of an authentic sample.

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Radical Detection in Benzylic Halide–Aromatic Radical Anion Reactions by Continuous Flow Electron Spin Resonance Spectroscopy

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Abstract: An apparatus for the study of radical intermediates in the reaction of sodium naphthalene with organic halides in tetrahydrofuran by the continuous flow ESR method is described. The successful detection of bis(3,5-di-*tert*-butylphenyl)methyl radicals, **2**, from bis(3,5-di-*tert*-butylphenyl)methyl bromide has provided direct physical evidence for the existence of radical intermediates in reductions of halides by aromatic radical anions.

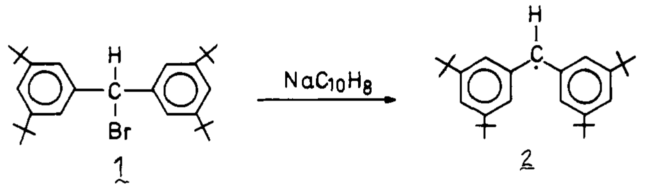
The reaction of aromatic radical anions with alkyl halides is believed to produce radical and carbanion intermediates sequentially as precursors to products.[2a–c] The currently accepted mechanistic scheme is shown in schematic form in eq 1.

$$RX + NaC_{10}H_8 \rightarrow R\cdot \xrightarrow{NaC_{10}H_8} R:^- \rightarrow \text{products} \qquad (1)$$

The evidence for the existence of radicals as intermediates comes from CIDNP records of associated radical pairs,[2d,3] from kinetic and product analyses of the 5-hexenyl halide sodium–naphthalene system,[4] as well as from a comparative study of the 3,5-cyclocholestan-6-yl chloride system's rearrangement behavior with sodium biphenyl- vs. triphenyltin hydride.[9]

In order to secure direct physical evidence for the existence of a radical precursor to the carbanion intermediate, ESR spectroscopy of continuously flowing solutions[10] offered the most reasonable chance for producing a steady state concentration of radicals under conditions where the further reduction of radicals to carbanions could be minimized, if not eliminated completely. For ESR measurement by means of a flow method to be successful, a radical having a lifetime in the millisecond range had to be selected.

The reaction of bis(3,5-di-*tert*-butylphenyl)methyl bromide (1) with sodium naphthalene to form **2** was chosen for several reasons: (1) the ESR spectrum of the bis(3,5-di-*tert*-butylphenyl)methyl radical had been secured previously by two alternative methods,[18,19] (2) recently it has been demonstrated that steric factors are more significant than resonance factors in determining radical lifetimes,[20] and (3) during prior studies on benzylic halide reactions with lithium naphthalene where it was shown that the major product is a dimer, we decided that a diphenylmethyl radical should possess a long enough lifetime for detection by ESR spectroscopy.[21]



Experimental Section

The apparatus consisted of a high vacuum line and tetrahydrofuran (THF) purification manifold, a cylindrical reaction vessel A for preparing sodium naphthalene, a pair of equal-sized cylindrical reagent vessels B and C joined by an inverted 25-mm diameter glass T tube and connected by capillary tubes to the commercially available mixing chamber-ESR cell[23] shown schematically in Figure 1, and a specially constructed holding device whose purpose was to suspend reagent vessels B and C and the flow cell in the space between the pole shoes of the Varian EE-15 ESR spectrometer by fastening securely to the lower wave guide tube.

The high vacuum line system had a mercury diffusion, ejector pump (Leybold-Heraus, Model Hg-12) capable of an ultimate pressure of 10^{-7} Torr (liquid N_2 traps). Pressures were read on a McLeod compression, vacuum meter (Leybold-Heraus no. 16126) and could be read as low as 1×10^{-6} Torr.

The THF reservoir (4 L) was connected to the solvent manifold and the high vacuum line by a system of stopcocks similar to that portrayed in the literature[24] except that stainless steel (SS) packless bellows valves (Nupro Co. 8 BK-TSW) were used to introduce THF vapor into the lower line and vessels A and B-C.

The solvent line was also provided with a vacuum-tight glass line connected to a source of highly purified argon (Messer Griesheim, Gmbh, 99.999%) which was further purified in a Normag gas purification apparatus.[25]

THF was exhaustively purified in the usual way[24] except that the final two distillations from sodium benzophenone ketyl involved the use of 4.0-L receivers which had been evacuated to 0.1 Torr and filled with ultrapure argon.

Vessel A (l = 23.0 cm, d = 8.0 cm, $V \geq 1$ L) was provided with side arms for sodium metal and naphthalene. It had a 0.5 in. diameter glass to flexible stainless steel (SS) transition tube (Cajon Co. G 321-8-GX3) for connection to the solvent manifold by means of high-vacuum tight SS couplings using Cajon Co. SS-8-VCR glands, nickel washers, and SS male and female nuts through a Nupro Co. bellows valve. Vessel A also possessed an internal tube (i.d. 10 mm) having a fritted disk (Coarse D-O) for transferring freshly prepared sodium naphthalene solutions to vessel B. The naphthalene side arm was separated from the main vessel by a break seal so that the sodium mirror could be generated first by gentle flaming. Doubly sublimed naphthalene was placed in the $C_{10}H_8$ side arm and sealed in a vacuum (P = 0.1-0.2 mmHg). After the break seal was crushed with the magnetic stirring bar, $C_{10}H_8$ was sublimed with liquid N_2 cooling of vessel A at $P = 1 \times 10^{-5}$ Torr and with the valve to A closed so as to ensure no loss of $C_{10}H_8$. During this operation the pressure in A was maintained at 10^{-5}-5×10^{-6} through the transfer tube to B.

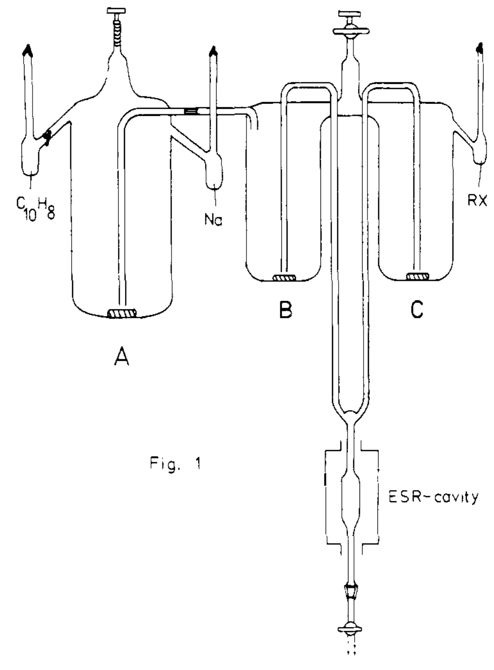


Figure 1. Apparatus for continuous flow ESR spectroscopy.

The organic substrate, RBr, and the sodium were placed into C's and A's side arms with a countercurrent of ultrapure argon flowing out of the side arms. After side arm sealing, evacuation to 5×10^{-6} Torr, Na-mirror formation, and naphthalene sublimation, THF was distilled into vessels A (650-750 mL) and C (600-650 mL) by condensing with liquid N_2 at pressures of 1 Torr. After the sodium naphthalene solution was warmed to ambient temperatures the system was stirred magnetically overnight. By closing A's valve to the common solvent line and chilling C, the sodium naphthalene solution was drawn into B until it was full 625 ± 25 mL. B was sealed away from A, and argon was admitted to a pressure in excess of 760 Torr (until the Hg over pressure bubbler in the Normag system vented) and the valve to the inverted T tube of B and C was closed. The system was now ready for disconnection from the solvent manifold for transport to the ESR spectrometer.

Vessels B and C (d = 7.4 cm, l = 20.0 cm, V = 710 ± 10 mL) as portrayed in Figure 1 were fitted with 5 mm i.d. capillary tubes located along the cylinder axis running from the bottom through the glass ring seal at the top and thence via two right angle turns into a downward direction to the quartz mixing chamber-flat ESR cell (60 × 10 × 0.25 mm). The apparatus is so constructed as to (1) fit in the 23 mm of space between the pole shoes of the Varian EE-15's magnet and (2) to permit the cavity's lower wave guide extension tube leading upward toward the microwave bridge to pass directly between vessels B and C without touching the T tube or the capillaries but allowing the mixing chamber and the ESR cell to enter the cavity.

Preparation of Bis(3,5-di-*tert*-butylphenyl)carbinol. To an ether solution of 3,5-di-*tert*-butylphenyllithium which had been prepared from lithium (1.75 g, 0.25 mol) and 3,5-di-*tert*-butylbromobenzene[26] (23. g, 0.136 mol) was added dropwise 3,5-di-*tert*-butylbenzaldehyde[27] (12.3 g, 0.055 mol) in 25 mL of ether. The reaction mixture was refluxed for 1.0 h, hydrolyzed, and then dried ($MgSO_4$), and the ether layer was distilled to separate the solvent and the 1,3-di-*tert*-butylbenzene by-product. The solid residue was recrystallized from petroleum ether (bp 40-60 °C) giving white needles (14 g, 65%): mp 142-143 °C; NMR (CCl_4) δ 7.17 (t, 2 H), 6.99 (d, 4 H), 5.60 (s, 1 H), 1.73 (s, 1 H, D_2O), 7.30 (s, 36 H).

Anal. Calcd for $C_{29}H_{44}O$ (408): C, 85.23; H, 10.85. Found: C, 85.30; H, 11.13.

Bis(3,5-di-*tert*-butylphenyl)methyl Bromide (1). Method 1. Gaseous HBr was bubbled through a petroleum ether solution of bis(3,5-di-*tert*-butylphenyl)carbinol at 0 °C until saturation. The excess of HBr was expelled with a strong nitrogen current. After drying over $MgSO_4$ and filtration, petroleum ether was evaporated at reduced pressure. The yield is quantitative, mp 75 °C (uncorrected).

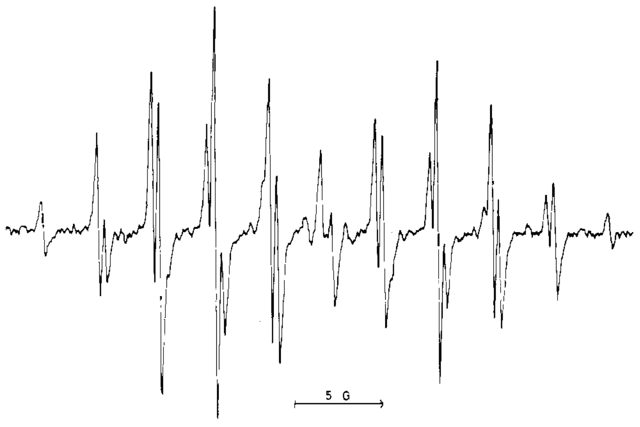


Figure 2. ESR spectrum of bis(3,5-di-*tert*-butylphenyl)methyl radical in THF at 25 °C.

Method 2. Bis(3,5-di-*tert*-butylphenyl)carbinol (8.16 g, 0.02 mol), 100 mL of petroleum ether, and 10 mL of phosphorus tribromide were refluxed for 6 h and poured into 100 g of ice. The organic layer was separated, dried over Na_2SO_4, and concentrated by distillation giving 9.0 g (95%) of bis(3,5-di-*tert*-butylphenyl)methyl bromide: mp 70-71 °C; NMR δ 1.4 (s, 36 H), 6.7 (s, 1 H), and 7.8 (s, 6 H).

1,1,2,2-Tetrakis(3,5-di-*tert*-butylphenyl)ethane. Method 1. Bis(3,5-di-*tert*-butylphenyl)methyl bromide (4.08 g, 0.01 mol) in 100 mL of THF at 0 °C was treated with 0.01 mol of *n*-butyllithium (Alfa Inorganics) and stirred for 1.0 h before addition of $FeCl_3$ (1.62 g, 0.01 mol). After 30 min of stirring at room temperature, the mixture was quenched with 30 mL of H_2O followed by 100 mL of 6 N HCl. The ether layer was dried (Na_2SO_4) and removed in the rotary evaporator to give a crude solid. Dissolving in the minimum amount of hot $HCCl_3$ was followed by the addition of excess absolute ethanol and cooling overnight at 5 °C to give 2.90 g (83%) of 1,1,2,2-tetrakis(3,5-di-*tert*-butylphenyl)ethane: mp 270-271 °C; NMR ($CDCl_3$) δ 7.0 (m, 12 H), 4.60 (s, 2 H), 1.20 (s, 72 H).

Anal. Calcd for $C_{58}H_{86}$: C, 88.93; H, 11.07. Found: C, 88.67, 88.60; H, 10.82, 10.90.

Method 2.[21] Naphthalene (12.8 g, 0.01 mol) in 50 mL of dry THF was converted into lithium naphthalene with excess lithium.[21] Bis(3,5-di-*tert*-butylphenyl)methyl bromide (4.71 g, 0.01 mol) was added to the naphthalenide ion solution discharging the green color in 1.0 min. The reaction mixture was treated with 100 mL of saturated NH_4Cl and extracted (2 × 50 mL) with ether, dried (Na_2SO_4), and recrystallized as described above to give 2.5 g (72%) of the title dimer, mp 260-261 °C. Needles for analysis can be grown by the slow evaporation of ether solutions. This melting point (uncorrected) was run on a Mel-Temp apparatus; when run on the C. Reichert Co. hot stage with microscope (Vienna), it had mp 270-271 °C.

Reaction of Sodium Naphthalene and Bis(3,5-di-*tert*-butylphenyl)methyl Bromide in a Flow Cell. Twice sublimed naphthalene (0.70 g, 5.47 mmol) was placed in the left side arm of vessel A and was sealed in a vacuum of 0.15 Torr. Excess sodium and bis(3,5-di-*tert*-butylphenyl)methyl bromide (2.72 g, 5.77 mmol) were placed in the side arms of vessels A and C in a countercurrent of pure argon. The side arms were sealed with an internal argon pressure of 1 atm. The entire system was evacuated to a pressure of 2.5×10^{-5} Torr.

The sodium mirror was generated and the naphthalene was sublimed into vessel A using liquid nitrogen cooling. The solvent was condensed from the reservoir at pressures of 1 Torr until vessel A had about 680 mL and vessel C from 600 to 650 mL. The green-colored radical anion formed instantaneously in the solid state on the interior walls of vessel A. After warming to room temperature the sodium naphthalene solution was stirred overnight and about 600-650 ml was sucked into vessel B by liquid N_2 cooling of C after the valve into A was closed. The capillary tube to B was sealed under reduced pressure; argon was introduced until the pressure exceeded 760 Torr; the valve on the T tube to B and C was closed and the system was disconnected from the vacuum line and attached to the upper wave guide arm that leads to the microwave bridge in the ESR spectrometer.

During the pressurization process naphthalene radical anion was always forced through the mixing chamber and measuring cell first because there was a slight excess of reagent solution in B vs. C. This permitted tuning of the spectrometer.

Table I. Coupling Constants for Bis(3,5-di-*tert*-butylphenyl) Radical (G)

	This work	Ref 18	Ref 19
a_H^{α}	14.6	14.4	14.6
a_H^{β}	4.1	4.0	4.1
a_H^{0}	3.6	3.6	3.7
Line width	0.26	0.6	

By means of an evacuated 4.0-L single-necked flask (P = 0.1 Torr) and partial opening of the stopcock, the solutions from B and C were drawn through the flow cell at a total rate of 2.1 mL/s during the 4.0 min that the spectrum of Figure 2 was secured. This consumed about half of the solution in each vessel.

After all of the solutions had been drawn through the mixing cell, the combined solution was evaporated on the rotary evaporator and the residue was triturated with petroleum ether (bp 60-70 °C) giving 0.37 g of 1,1,2,2-tetrakis(3,5-di-*tert*-butylphenyl)ethane, mp 270.0-271.0 °C.

Results

The ESR spectrum (40-G range) shown in Figure 2 agrees well with literature spectra as may be seen by a comparison of the coupling constants in Table I. In fact the resolution of the spectrum in Figure 2 is much better than that secured earlier.[18,19] This spectrum was secured during a 4-min scan time (total flow rate = 2.1 mL/s) and demonstrates that a steady state concentration of radical **2** was formed in the reaction of eq 2 at 25 °C.

In the run shown in Figure 2, a 16.4% yield of 1,1,2,2-tetrakis(3,5-di-*tert*-butylphenyl)ethane (**3**) was isolated. As expected[21] addition of 0.01 mol of **1** to 0.2 M lithium naphthalene (0.01 mol) gave a 72% yield of **3**.

Discussion

The ESR spectrum of Figure 2 demonstrates that a steady state concentration of radical **2** was formed in the reaction of eq 2 at 25 °C. It provides direct physical evidence that radicals are intermediates in the mechanistic scheme due to Garst[2] and shown in a simplified schematic form in eq 1.

It seems reasonable to speculate on the existence of a bromo radical anion precursor ($RBr^{-}\cdot$) to **2**, since ESR evidence for $ArF^{-}\cdot$ intermediates has been obtained during reductions of 2-fluoropyridine by sodium in liquid ammonia.[13b] If such precursor radical anion intermediates are still present, they do not have ESR signals that overlap with the spectrum of **2**.

On the other hand, the amount of dimer that was isolated in the flow system experiment (16.4%) of Figure 2 compared to preparative scale experiments[21] (see Experimental Section) was surprisingly large. It has already been adequately demonstrated[22] that *excess* amounts of radical anion at ***high*** concentrations can reduce benzylic halides to the carbanion stage fast enough so as to diminish the amounts of dimer formed by slower addition of 0.039 M lithium naphthalene solutions.[21b] Whether the dimer formed in the flow experiments of Figure 2 acted to diminish the rate of radical production by being reduced to carbanion and then reacting with more halide[21] or to increase the rate of radical disappearance by radical coupling[20c] or by the carbanion route,[21,22] they are poor model compounds for a study of the mechanism of dimer formation in radical anion studies.

Producing radicals for ESR studies in flow systems by reaction of aromatic radical anions with halides possesses several potential advantages over more widely utilized methods in that

(1) only one type of radical is produced as the paramagnetic precursor vanishes; (2) the amount, concentration, and rate of radical production can be controlled in a known way; (3) the radical site can be controlled unambiguously. Thus the resolution of the spectrum in Figure 2 is much greater than that of the previously secured spectra.[18,19]

The two biggest problems with our apparatus are (1) the slow flow rates and (2) the generation of vapor bubbles in the capillary tubes near the end of a run where the pressures in vessels B and C decrease toward the room temperature boiling point of THF. Both of these problems arise because of our modus operandi in which the solutions are sucked through the mixing cell. Pumping with dry, purified argon would lead to destruction of the naphthalene radical anion by residual impurities in the gas.[28]

We are working on a modification of our apparatus that will allow volatilization of ether from a side arm vessel through a glass break seal in the hopes that both problems will be solved allowing study of other interesting radical species.

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