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Chemical and Electrochemical Reduction of 1,2-Dihalobenzocyclobutene[1]

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Abstract: The treatment of 1,2-dibromobenzocyclobutene with an excess of solvated electrons or with biphenyl radical anion results in the formation of benzocyclobutene. Benzocyclobutene is proposed to arise by the intermediate benzocyclobutadiene radical anion or dianion. Polarographic, cyclic voltammetric, and controlled potential electrolytic reduction studies of the generation of benzocyclobutadiene from the corresponding dihalide indicate dimerization to be faster than further reduction to benzocyclobutadiene radical anion.

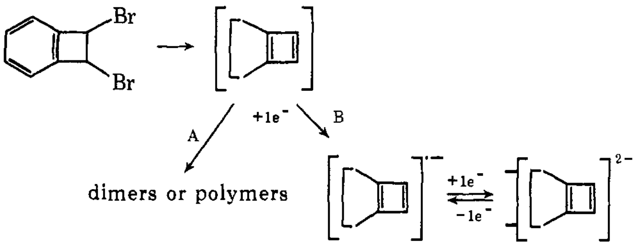
The cleavage of carbon–halogen bonds upon treatment with naphthalene or biphenyl radical anion solutions is well documented.[2–11] We recently reported on an attempt to extend this reaction toward the generation of reactive neutral unsaturated hydrocarbons.[1] The hope was that, in the presence of excess electrons, the neutral hydrocarbon would be reduced to its radical anion in a diffusion-controlled process. The radical anion in turn might be stable enough to allow its study by epr.

We wish to present our results on the treatment of 1,2-dihalobenzocyclobutene with solutions of solvated electrons in ethereal solvents and with naphthalene and biphenyl radical anions. We also studied the electrochemical reduction of the dihalides to examine the possibility that the reduction potential of benzocyclobutadiene might be found. Also, the 1,2-dihalobenzocyclobutenes were reduced in the presence of $MgBr_2$ with biphenyl radical anion.

Results

The initial attempts to generate the benzocyclobutadiene radical anion involved the reduction of *trans*-1,2-dibromobenzocyclobutene with ethereal solutions of solvated electrons. The solution of alkali metals in polyethereal solvents, giving rise to blue solutions of solvated electrons in concentrations of up to 1×10^{-2} *M*, has been extensively investigated,[12–16] Reduction of the dihalide was expected to give the very reactive benzocyclobutadiene as has been demonstrated by Cava using zinc as a reducing agent.[17] This could then dimerize, as shown in Scheme I, or it could be reduced to the radical anion or dianion in a diffusion controlled process.

Scheme I



Solutions of solvated electrons were prepared at −78° under high vacuum in one side of a tube of H-design (see Figure 2) which has an epr side arm attached. The concentration of solvated electrons was in large excess over that of the benzocyclobutene dihalide, which was contained in the other side of the double tube. Upon treatment of the dihalide with excess solvated electrons, a paramagnetic species resulted immediately. The paramagnetic species displayed the temperature dependence shown in the epr spectrum in Figure 1. At temperatures lower than −50°, the epr spectrum consisted of approximately 65 lines with apparent coupling constants of 7.60, 5.75, 5.25, and 1.45 G for four sets of two equivalent pro-

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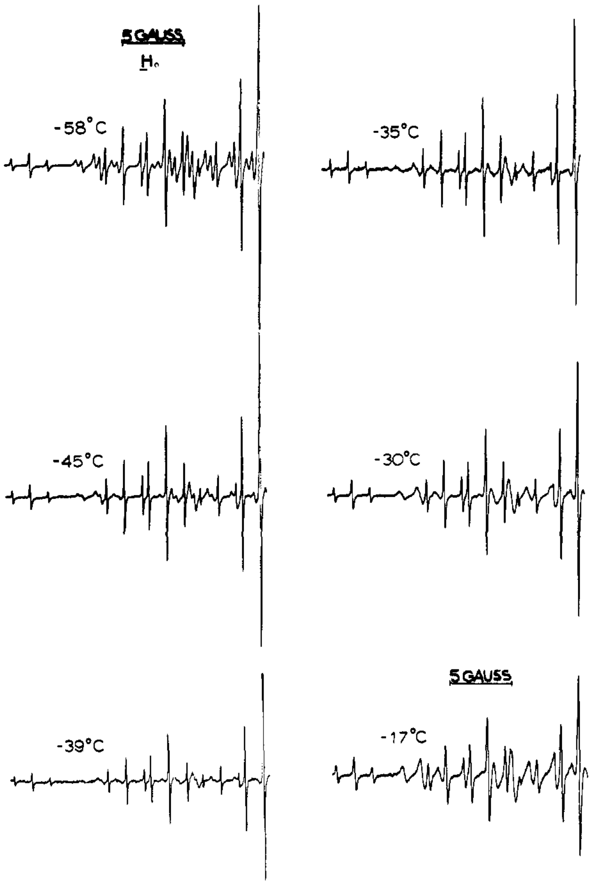

Figure 1. Epr spectral temperature dependence of the radical anion of benzocyclobutene radical anion in a glyme–diglyme mixture.

tons. At temperatures above −30°, the spectrum was 45 lines with hyperfine splitting constants of 7.50 and 1.45 G for two sets of two equivalent nuclei and 5.50 G for one set of four equivalent protons. Between these two extremes (*ca.* −40°) the epr spectrum consisted on only 27 sharp lines, the number expected for the benzocyclobutadiene radical anion. However, the intensities of the lines were not consistent with a simple 27-line spectrum. Analysis was complicated by variations in these intensities in spectrum to spectrum. There was no sign of any hyperfine splitting due to the metal cation. In addition, the same spectrum resulted when the diiodide was reduced.

The initial studies were also hampered by the low concentration of the species, which limited the temperature range to −50 to −30°. In this temperature range, the epr spectrum was characterized by the sharp 27-line spectrum. This spectrum was not at all similar to that of benzocyclobutene (BCB) radical anion which we had prepared under a variety of conditions.[18,19]

Additional attempts resulted in higher concentrations of the paramagnetic species and allowed its study at higher and lower temperatures. Marked changes in the spectra were observed, as is shown in Figure 1, and now great similarities to the BCB radical anion were noted. When BCB was reduced with potassium in a mixture of glyme and diglyme, an identical spectrum was obtained. It is interesting to note that only with one particular combination of glyme and diglyme does one see the extensive line broadening to such an extent that only 27 sharp lines remain.

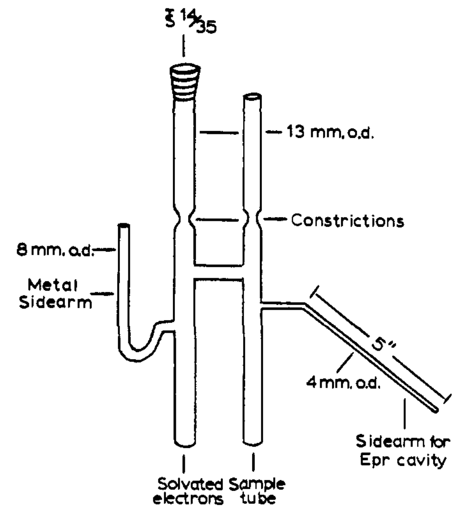

Figure 2. Double tube design for excess solvated electron reductions.

The formation of BCB in the solvated electron reduction of benzocyclobutene dibromide is evidence that the technique of solvated electron reductions does indeed work quite well, but rapid protonation of the resulting anions interferes with the observation of the benzocyclobutadiene radical anion. The use of a flow system employing the Jeolco JES-SM-1 sample mixing kit with the Jeolco JES-ME-3X epr spectrometer was undertaken in hopes of seeing the radical anion of benzocyclobutadiene before protonation occurs. However, all attempts to see the epr spectrum of the benzocyclobutadiene radical anion were negative under a variety of experimental conditions, including attempts to computer-time average any signal.

Deuterium Quenching Studies. During the course of this investigation, S. Bank and J. F. Bank[20] reported the use of anhydrous magnesium bromide as a trapping agent for the anion intermediate formed from the reaction of alkyl halides with sodium naphthalene radical anion, Scheme II. The halogen–metal interchange proceeds both rapidly and irreversibly, giving rise to a stable Grignard reagent which is converted to a deuterated hydrocarbon in 80–100% yield by quenching with deuterium oxide at ambient temperatures. It appeared that the procedure of Bank might be employed in the reduction of 1,2-dibromobenzocyclobutene to stabilize the dianion. The results from the solvated electron reduction of benzocyclobutene dibromide suggested that the electron density on the carbon atoms exocyclic to the benzene ring in the radical anion or dianion is quite large. HMO calculations predict almost one-half of each of the electrons in the antibonding MO to be located at these two positions. The large amount of electron density on these atoms could explain why the radical anion or dianion behaves as a base, showing a great deal of carbanionic character.

Scheme II

$$\text{R–X} \xrightarrow{\text{Naph}\cdot^-} \text{R}\cdot + \text{X}^- \xrightarrow{\text{Naph}\cdot^-}$$

$$\text{R}^- \xrightarrow{\text{MgBr}_2} \text{RMgBr} \xrightarrow{\text{D}_2\text{O}} \text{R–D}$$

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(18) R. D. Rieke, S. E. Bales, P. M. Hudnall, and C. F. Meares, *J. Amer. Chem. Soc.* **92**, 1418 (1970); **93**, 697 (1971).

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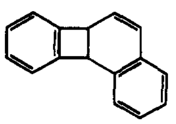
Biphenyl radical anion was employed in these investigations as the electron transfer agent. Treatment of the dibromide with biphenyl radical anion and $MgBr_2$ in THF at −78° for 30 min, followed by D_2O quench, resulted in a 4.7% yield of BCB. The product was gas chromatographed, collected, and analyzed by mass spectrometry to reveal 40% dideuteration, 30% monodeuteration, and 30% undeuterated BCB. The same experiment with DME as the solvent resulted in an overall smaller yield of BCB (*ca.* 2%) with no dideuteration and only 10% monodeuteration. The greater solvating power of DME may be responsible for the formation of a less tightly bound dianion with the metal counterion and consequently greater reactivity. The dideuterated product in THF was obviously arising from either the dianion or by an exchange process from undeuterated BCB under the conditions of the reaction upon quenching. However, the latter possibility was negated when BCB was submitted to the reaction conditions and quenched with D_2O. Analysis of the product showed no deuterium incorporation.

A repeat of the THF experiment omitting the magnesium bromide gave lower yields of BCB (1.3%) and much less deuterium incorporation (dideuterio 5%, monodeuterio 30%). Under these conditions, the deuterated product must be arising from D-abstraction by the radical or dianion of benzocyclobutadiene upon quench. The amount of deuteration found in this experiment indicates that the use of $MgBr_2$ effectively increases both the total yield and quantity of deuterium found in the product. A similar experiment with magnesium bromide using 1,2-diiodobenzocyclobutene and quenching with D_2O 30 sec after mixing yielded a 4.10% yield of BCB. Analysis indicated almost quantitative incorporation of two deuterium atoms in the product.

In these experiments with magnesium bromide present, only slight amounts of dimeric products of benzycyclobutadiene could be detected. The remainder was assumed to be polymeric. No starting material was discovered in the quenched product. However, in those experiments where magnesium bromide was absent, a 30% yield of Diels–Alder dimer (I) was found. Furthermore, when the Diels–Alder dimer I was subjected to these reaction conditions without magnesium bromide, only about 30% of the initial material was reclaimed. This indicates that in this experiment with the dibromide, nearly all the generated benzocyclobutadiene dimerizes before further reduction and subsequent formation of BCB, and that the Diels–Alder dimer I detected represents nearly the balance of material in the reaction.

A normal Grignard reaction with 1,2-diidobenzocyclobutene and quenched with D_2O resulted in a 15.8% yield of Diels–Alder dimer I and 13.4% of head-to-head dimer II, the remainder being unreacted diiodide. A small amount of BCB (0.57%) was formed, not enough for collection and determination of per cent deuteration. The results are explained by asserting the reaction pathway is similar to that for other 1,2-dihalides; that is, predominantly elimination. This supports the contention of a somewhat different mechanism in the biphenyl radical anion electron transfer–$MgBr_2$ quench technique which gives much higher yields of BCB and very high deuterium incorporation.



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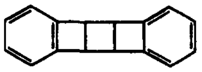


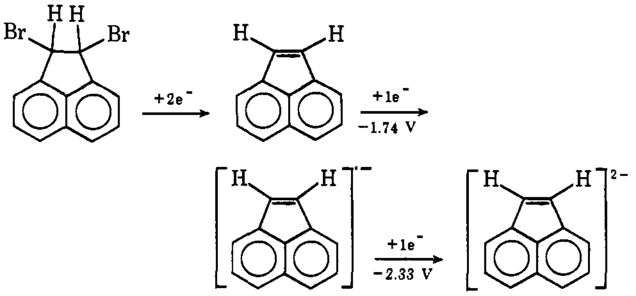
II

Electrochemical Investigations. In order to gain additional information on the benzocyclobutadiene molecule, we attempted to study its electrochemical generation. Covitz[21] has reported the electrochemical reduction of α,α′-dibromo-*p*-xylene in which two polarographic and cyclic voltammetric waves are observed, the second and more cathodic of which is ascribed to the reduction wave for the unstable *p*-xylene intermediate. Thus, it appeared possible to electrochemically determine the reduction potential of benzocyclobutadiene.

The electrochemical reduction of vicinal dihalides to yield olefins has received considerable attention.[22,23]

The cathode generation of acenaphthylene from 1,2-dibromoacenaphthene was initially studied as a model compound. Cyclic voltammetry on platinum showed a broad irreversible wave at E_p = −0.73 V, a reversible couple at E_p = −1.74 V, and on mercury a broad irreversible wave at E_p = −2.33 V. Acenaphthylene on platinum showed the −1.74 V reversible couple, and on mercury both the −1.74 V reversible couple and the irreversible wave at −2.33 V were observed. The overall sequence is depicted in Scheme III. A constant potential electrolysis (cpe) at −1.0 V on 1,2-dibromoacenaphthylene resulted in a nearly quantitative yield of acenaphthylene. Coulommetry indicated the passage of 2 electron equiv/mol with a 97% conversion based on residual current.

Scheme III



The polarographic reduction of 1,2-dibromobenzocyclobutene showed two cathodic waves. The first of these was extremely broad with an $E_{1/2}$ of −1.04 V, and the second wave was found at −1.92 V. The wave heights were approximately 2:1, respectively. Cpe at −1.3 V resulted in the isolation of the Diels–Alder dimer I of benzocyclobutadiene in greater than 90% yield. Coulommetry determined that n = 1.96, or the passage of 2 electron equiv/mol of the dibromide.

Cyclic voltammetry on benzocyclobutene dibromide was performed on both platinum and mercury with the results tabulated in Table I. The first wave was broad and irreversible with a peak potential of −1.30 V. The second wave was irreversible at sweep rates up to 100 V/sec, and its peak potential was found at −2.05 V.

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Table I. Cyclic Voltammetric Results for Benzocyclobutene Dibromide

	E_p^1, V	E_p^2, V	Solvent
Hg	−1.23	−2.04	CH_3CN
Pt	−1.32	−2.10	BuCN

Discussion

Benzocyclobutadiene has been generated as a reactive intermediate from the zinc reduction of the 1,2-dihalobenzocyclobutene[17] and trapped with various dienophiles. The generation of BCB from the treatment of the corresponding dihalide with solutions of solvated electrons provides strong evidence that the benzocyclobutadiene radical anion or dianion was an intermediate in this reaction. One of the most unusual features of this species is its high basicity. The exact pK_a of the species is not known but can be assumed to be greater than 38. Part of the increase in the pK_a of this species is most likely due to I-strain but this effect is expected to only be a small part of the large increase in basicity.[24,25]

The large increase in the yield of dideuteriobenzocyclobutene when $MgBr_2$ is present in the reduction of 1,2-dibromobenzocyclobutene suggests that it is stabilizing the intermediate radical anion or dianion in some manner. This observation suggests that the dianion is involved and some sort of di-Grignard was formed. If this were the case, the two carbon atoms in the four-membered ring are most likely not sp^2 hybridized.

The high reactivity of the benzocyclobutadiene radical anion or dianion does not suggest much resonance stabilization and can best be described as antiaromatic as defined by Breslow.[24] It is interesting to note that Pettit has recently published similar results for cyclobutadiene itself.[26] Thus, the addition of the benzo group does little to stabilize this species.

The investigation of the cathodic electrochemical generation of benzocyclobutadiene from the 1,2-dibromide was undertaken for two reasons. First, it was hoped that the reduction potential of benzocyclobutadiene might be determined and second, it was hoped that some information on the cleavage of the two bromine atoms would result.

Benzocyclobutadiene, from the energy of the first antibonding MO in HMO calculations and using the correlation of $E_{1/2}$ with HMO energies, is predicted to reduce around −1.63 V. It is apparent from the electrochemical results that the rate of dimerization of benzocyclobutadiene is fast compared to electron transfer for further reduction to the radical anion. It is possible that a small per cent was reduced to the radical anion or dianion and that it occurred at −1.90 V; however, if it did exist it would have been masked by the reduction wave for the Diels–Alder dimer I which occurs at this potential. The first broad two electron wave can only be taken as suggestive evidence that both bromine atoms are coming off in a concerted or nearly concerted process. This, however, would be consistent with quenching studies where we never observed the presence of any monobromobenzocyclobutene, even in those experiments where we recovered 60% starting dibromide.

It is interesting to note that the first wave in the polarographic reduction of 1,2-dibromoacenaphthene on mercury occurs at −0.30 V, while the first wave for the reduction of 1,2-dibromobenzocyclobutene occurs at −1.04 V. While both these waves are very broad and irreversible, a large cathodic shift is noted for the 1,2-dibromobenzocyclobutene. It is possible that this shift in reduction potential is due to the antiaromatic character of benzocyclobutadiene.

Experimental Section

Epr spectra were recorded on a Varian E-3 spectrometer or a Jeolco JES-ME-3X spectrometer at X band frequencies. Temperatures were regulated on the Varian spectrometer with the E-3 variable-temperature accessory and checked using a Honeywell Model 2746 potentiometer and copper–constantan thermocouple. Temperature control on the Jeolco spectrometer was accomplished with the accompanying variable-temperature unit. All glassware, epr tubes, and solvent bumpers were thoroughly cleaned and dried at 140° for 24 hr prior to use.

Usual high-vacuum procedures employing alkali metals and ethereal solvents were used to prepare the radical anions. DME, THF, and DG (Aldrich) were distilled from lithium aluminum hydride under nitrogen and passed through a column of dry alumina (3 × 15 cm). It was then redistilled as before into a flask containing lithium aluminum hydride. The purified solvent was attached to a vacuum line and degassed several times by a freeze-pump–thaw technique. The solvent was vacuum distilled into a round-bottom flask fitted with a high-vacuum stopcock and containing 1.0 ml of sodium–potassium alloy (MSA Research Corp), and stored there. Hexamethylphosphoramide (Aldrich) was stored overnight with $CuSO_4$ and vacuum distilled twice from fresh portions of 4A molecular sieves. It was stored in a desiccator over sieves in a septum sealed flask.

The compounds used in this investigation were prepared by published syntheses. The preparation of 1,2-dibromoacenaphthylene was effected by the method of Cristol, Stermitz, and Ramey[27] by treatment of acenaphthylene (Columbia) with bromine. The mixture of 1,2-dihalocyclobutenes was prepared by treatment of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene (Aldrich) with sodium iodide (Mallinckrodt) as described by Cava and Napier.[28] Gc analysis of the product of the ring-closure reaction above indicated three products in the ratio of 47:47:6. One product, not reported by Cava, was collected and identified as 1-bromo-2-iodobenzocyclobutene as 47% of the total yield: mp 47.6–48.0°; nmr τ (ppm, TMS, $CDCl_3$) 2.5–3.0 (complex m, 6 H), 4.48, 4.53 (AB q, J = 1.1 Hz, 2 H); high-resolution mass spectral mol wt 307.8705, calcd 307.8696 for C_8H_6BrI. The method of Cava and Muth[29] was used to prepare pure 1,2-dibromobenzocyclobutene. Treatment of the mixture of benzocyclobutene dihalides with iodine and sodium iodide yielded pure 1,2-diiodobenzocyclobutene.[28] Benzocyclobutene was synthesized by the method of Cava and Napier.[30] Zinc dehalogenation of 1,2-dibromobenzocyclobutene, described also by Cava and Napier,[28] was used to prepare the Diels–Alder dimer I of benzocyclobutadiene.[28] All the analytical data gathered was in agreement with that reported by the above authors. Gas chromatography was performed on the Hewlett–Packard Model 5750 using a 6 ft × 0.25 in. column of 20% SE-30 on Chromosorb W.

Solvated Electron Reductions. A double tube was used in the excess solvated electron reductions and is shown in Figure 2. The tube, after being properly cleaned and dried, was removed from the oven and flushed with dry nitrogen for about 5 min. The dihalohydrocarbon to be reduced was placed in one main tube designated sample tube, usually in a melting point capillary tube about 1-cm long. The amount of compound used was such that the resulting final solution was 10^{-3} *M*. This tube was then sealed off at the constriction with a torch. Potassium or sodium metal (Baker) was

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[24] R. Breslow, J. Brown, and J. Gajewski, *J. Amer. Chem. Soc.*, 89, 4383 (1967).

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[28] M. P. Cava and D. R. Napier, *ibid.*, 79, 1701 (1957).

[29] M. P. Cava and K. Muth, *J. Org. Chem.*, 27, 757 (1962).

[30] M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.*, 80, 2255 (1958).

placed under heptane and a rectangular piece about 3 × 2 × 15 mm was cut to expose clean metal surface. This piece of metal was quickly transferred into the metal side arm and, after flushing for about 5 more min, the side arm was tipped off with a torch. The tube was then attached to a high-vacuum system and evacuated after the bottom portion of the tube containing the sample was cooled with liquid nitrogen to retard loss of sample by sublimation. After a vacuum of about 1 μ was achieved, a portion of the metal was vacuum distilled with a torch to form a metal mirror in the tube designated solvated electrons and the side arm tipped off near the main tube. After the metal had cooled, the tube was pumped down to a vacuum of about 0.1 μ and 5 ml of diglyme was distilled into the tube containing the metal mirror by cooling with liquid nitrogen. Glyme (5 ml) was then distilled from a solvent bumper to the sample side of the double tube. The tube was sealed at the remaining constriction.

The solvents were allowed to thaw and then the tube was placed in a Dry Ice–acetone bath where a solution of solvated electrons was generated with diglyme in contact with the metal in one side of the tube. Studies have shown that a maximum solution of metal is attained in approximately 30 min.[14,15] The solution of dihalocyclobutene in glyme was poured slowly into the solution of solvated electrons in diglyme. The mixed solution was run into the epr side arm and inserted into the epr cavity. The remainder of the solution was kept cold in a Dry Ice–acetone bath.

Flow system studies were performed using the Jeolco JES-ME-1 sample mixing kit attachment to the JES-ME-3X epr spectrometer. This consists of two sample cylinders in which the solutions to be mixed are placed. The solutions were drawn into two calibrated injection syringes by raising a cross bar which is attached to both plungers through three-way stopcocks. The stopcocks were repositioned and the crossbar, with a certain amount of plumb weights attached, was released to force the solution through plastic tubing into the mixing chamber. When the flow system was used not in conjunction with the epr spectrometer, the mixed solution was run directly into a D_2O quench. In the spectrometer a quartz tube (JES-LC-01) was fitted into the end of the mixing chamber, which was placed in the cavity of the spectrometer, and the mixed solution was run through the tube and its effluent tube into a waste liquid receiver.

Electrochemical Studies. All electrochemical experiments were performed on the Fox-Reilly electroanalytical instrument heretofore described.[31] The cell design for polarography and cyclic voltametry has been discussed.[32] The reference electrode was aqueous sce with a nonaqueous salt bridge. The dc polarography was conducted at a dropping mercury electrode (dme) using triple distilled mercury. The cyclic voltammetric (CV) experiments were performed using a spherical platinum bead electrode (spe) or a hanging drop electrode (hmde) with which was employed Bethlemen Instrument Grade mercury.

Coulometric determinations and constant potential bulk electrolyses were conducted on a triple distilled mercury pool used as the cathode. The pool was magnetically stirred. The sce reference electrode was placed approximately 2 ml from the center of the pool. Two platinum gauze auxillary electrodes were separated from the cathodic compartment by fine sintered glass frits. The number of coulombs (Q) passed were determined by measuring the potential change across a 0.1 ± 1% ohm resistor *vs.* time. All i *vs.* t curves were exponential as expected for an EC (electron transfer–chemical reaction) reduction and final residual currents were below 50 μA.

Spectrograde acetonitrile (MCB) was treated with dry alumina and the bottle sealed with a septum under nitrogen. The alumina was dried at 250° for 24 hr in a muffle furnace before using. The water content of acetonitrile treated in this manner has been determined to be about 0.5 mM, a very acceptable level.

Butyronitrile (Eastman White Label) was heated to 75° and stirred for several hours with a mixture of 7.7 g of Na_2CO_3 and 11.5 g of $KMnO_4$/liter of butyronitrile (BN). After cooling, BN was distilled under a nitrogen pressure of 15 mm and collected over activated alumina as described for acetonitrile.

All studies were conducted with 0.1 M tetraethylammonium perchlorate (TEAP) as supporting electrolyte. TEAP (Eastman) was dried at 100° under vacuum for several hours before use.

Data were recorded on a Sargent Model SR strip chart recorder or a Hewlett-Packard Model 7004B X-Y recorder. Alternatively, a Tektronix Type R564B oscilloscope equipped with a Tektronix C-12 polaroid camera unit was employed.

The solutions for electrochemical experiments were degassed with nitrogen which had been passed through Drierite and a Dry Ice–acetone trap, then bubbled through the same dry solvent as used in the experiment. When degassing was complete prior to commencing the experiment, the nitrogen flow was diverted over the solution surface where an inert atmosphere was maintained.

Procedure. For polarography and CV, dry TEAP (0.6 g) was weighed into a dry 50-ml erlenmeyer flask and sealed with a septum. All glassware was oven dried at 140° before using. With a syringe, 25 ml of dry solvent was injected into the erlenmeyer, giving a 0.10 M electrolyte solution. The compound under investigation was weighed into a second dry flask and sealed as before. The solvent-electrolyte solution (15 ml) was introduced into this flask with a syringe to dissolve the compound. The amount of compound used resulted in a 1.0 mM solution. This solution was injected into the dry cell and degassed. The remaining solvent–electrolyte solution was utilized in the salt bridge and the reference electrode added.

Coulommetric determinations were made in conjunction with constant potential bulk electrolyses. The same procedures and precautions were used as described above, but approximately 30 ml of a 1 mM solution of compound was electrolyzed per experiment. The work-up following constant potential bulk electrolysis first involved adding distilled water and distilling the acetonitrile–water azeotrope at 45 mm at 30°. The remainder, consisting of water, electrolyte, and electrolysis products, was extracted several times with anhydrous ether, dried over sodium sulfate, and evaporated to dryness. The remaining solid was analyzed.

Reduction in Presence of Magnesium Bromide. Biphenyl Radical Anion Solutions. To a 1000-ml three-necked flask with a coarse frit and Teflon stopcock on the bottom, tetrahydrofuran (THF, Matheson Coleman Bell, 800 ml) was distilled from lithium aluminum hydride (LAH) under a nitrogen purge. Biphenyl (37.68 g, 0.3056 mol, Eastman, sublimed) was added along with freshly cut pieces of potassium metal (Baker, 12.121 g, 0.31 g-atom). The flask was then stoppered; reduction of biphenyl was noted almost immediately. After several hours, a dark green-black solution was generated. This radical anion solution served as a reservoir and electron source for the di-Grignard experiments.

Anhydrous magnesium bromide ($MgBr_2$) was prepared separately for each experiment. THF (50 ml) was distilled from $LiAlH_4$ under nitrogen into a dry 500-ml reaction flask with nitrogen inlet and reflux condenser. Magnesium turnings (Baker, 350 mg, 0.0144 g-atom) which had been dried overnight in a 140° oven were added, followed by the volumetric addition through a rubber septum of ethylene bromide (Eastman, 3.0 g, 0.016 mol, 1.38 ml at 2.18 g/ml). Gentle heating was normally all that was required to initiate the reaction. Initially a very exothermic reaction took place and was continued for 30 min at reflux with external heating. The solution was then distilled nearly to dryness under nitrogen with removal of THF. The $MgBr_2$ was dried by placing the flask in a 150° mineral oil bath and pumping the powder to dryness under vacuum. A fine white powder resulted.

General Procedure. Into the reaction flask with anhydrous $MgBr_2$ was poured, under nitrogen, 100 ml of the biphenyl radical anion solution (*ca.* 0.03 mol radical anion) and the mixture was stirred to dissolve the $MgBr_2$. The temperature was adjusted to that desired and, with stirring, the benzocyclobutene dihalide (1.0 g, 0.00349 mol) was added in 10 ml of dry THF. The reaction was allowed to progress the desired length of time and then quenched with 2.0 ml of D_2O (MSD, 99.7+% isotopic purity). Those reactions at −78° were warmed rapidly to 0° or slightly above with a warm water bath before quenching. Water (100 ml) was then added to the mixture and the aqueous layer was neutralized with dilute aqueous HCl. The mixture was then extracted twice with ether (100 ml). The ether extracts were combined, dried over $MgSO_4$, and concentrated carefully by distillation through a packed column with an external oil bath, the temperature of which never exceeded 100°. After concentrating to approximately 10 ml, the solution was gas chromatographed and analyzed by a Xerox cut-and-weigh technique *vs.* a standard.

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