ELECTROCHEMICAL REDUCTION OF DIPHENYLDIAZOMETHANE

by

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TABLE OF CONTENTS

LIST OF FIGURES

iii

Introduction

Sargent and coworkers[1] have recently shown that reductive dehalogenation of geminal dihalomethanes in aprotic media gives rise to ethene and methane as the two principal products. Although the formation of both products was postulated to involve the methylene radical anion, the generation of the latter species requires a total of three ele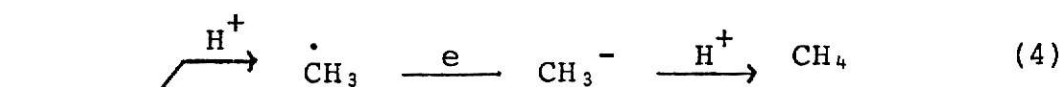ctrons and the intermediacy of a carbanion (eq. 1), and either a dianion radical (eq. 2) or a carbene (eq. 3) (Scheme I). Since these intermediates might

Scheme I

$$CH_2X_2 \xrightarrow{\;e\;} X^- + \overset{\bullet}{C}H_2X \xrightarrow{\;e\;} \overset{-}{C}H_2X \qquad (1)$$

$$\overset{-}{C}H_2X \begin{cases} \xrightarrow{\;e\;} [CH_2X]^{2\overline{\cdot}} \longrightarrow X^- + CH_2\overset{-}{\cdot} & (2) \\ \\ \xrightarrow{-X^-} :CH_2 \xrightarrow{\;e\;} CH_2\overline{\cdot} & (3) \end{cases}$$

$$CH_2\overline{\cdot} \begin{cases} \xrightarrow{H^+} \overset{\bullet}{C}H_3 \xrightarrow{\;e\;} CH_3^- \xrightarrow{H^+} CH_4 & (4) \\ \\ \xrightarrow{dimerize} \overset{-}{C}H_2\overset{-}{C}H_2 \xrightarrow{-2e} CH_2=CH_2 & (5) \end{cases}$$
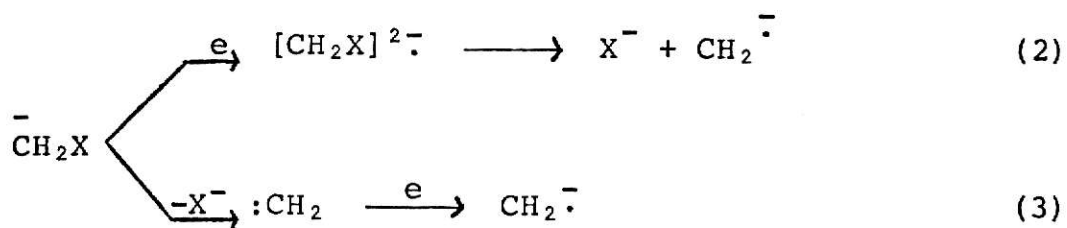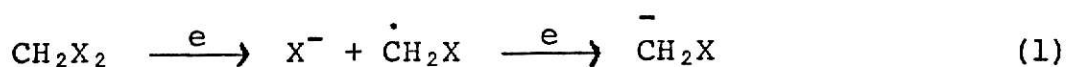
also give rise to the observed products, a more convenient, unequivocal method for the preparation and study of carbene

radical anions was sought. At the suggestion of Professor R. N. McDonald of this Department, and with his assistance, we have studied the electrochemical reduction of diphenyl-diazomethane (Ph_2CN_2) in aprotic media as a method to effect the intra muros generation of the diphenylmethylene radical anion.

EXPERIMENTAL

Instrumentation

Cyclic Voltammetry. The cyclic voltammetric experiments were performed on a transitorized, three-electrode potentiostat.[2] A digitally controlled, multipurpose function generator and a circuit for electronic compensation of ohmic potential loss between the reference and working electrodes were incorporated into the instrument. Readout in relatively slow cyclic voltammetric experiments (scan rates of 0.4 V/s or less) was to a Moseley 7035B X-Y recorder; readout for scan rates in the range from 0.5 to 100 V/s was to a Tektronix Model 564 oscilloscope. The latter was equipped with Type 2A63 and 2B67 plug-ins and a Model C-12 Polaroid camera.

Chronoamperometry and Coulometry. A simplified schematic of the potentiostat for chronoamperometric work is shown in Figure 1. The salient features of this potentiostat include (1) electronic compensation of ohmic potential loss between the reference and working electrodes which is independent of the current range setting, and (2) complete control from

Figure 1. Simplified schematic for the circuit used in
the computer-controlled and coulometer
potentiostats.
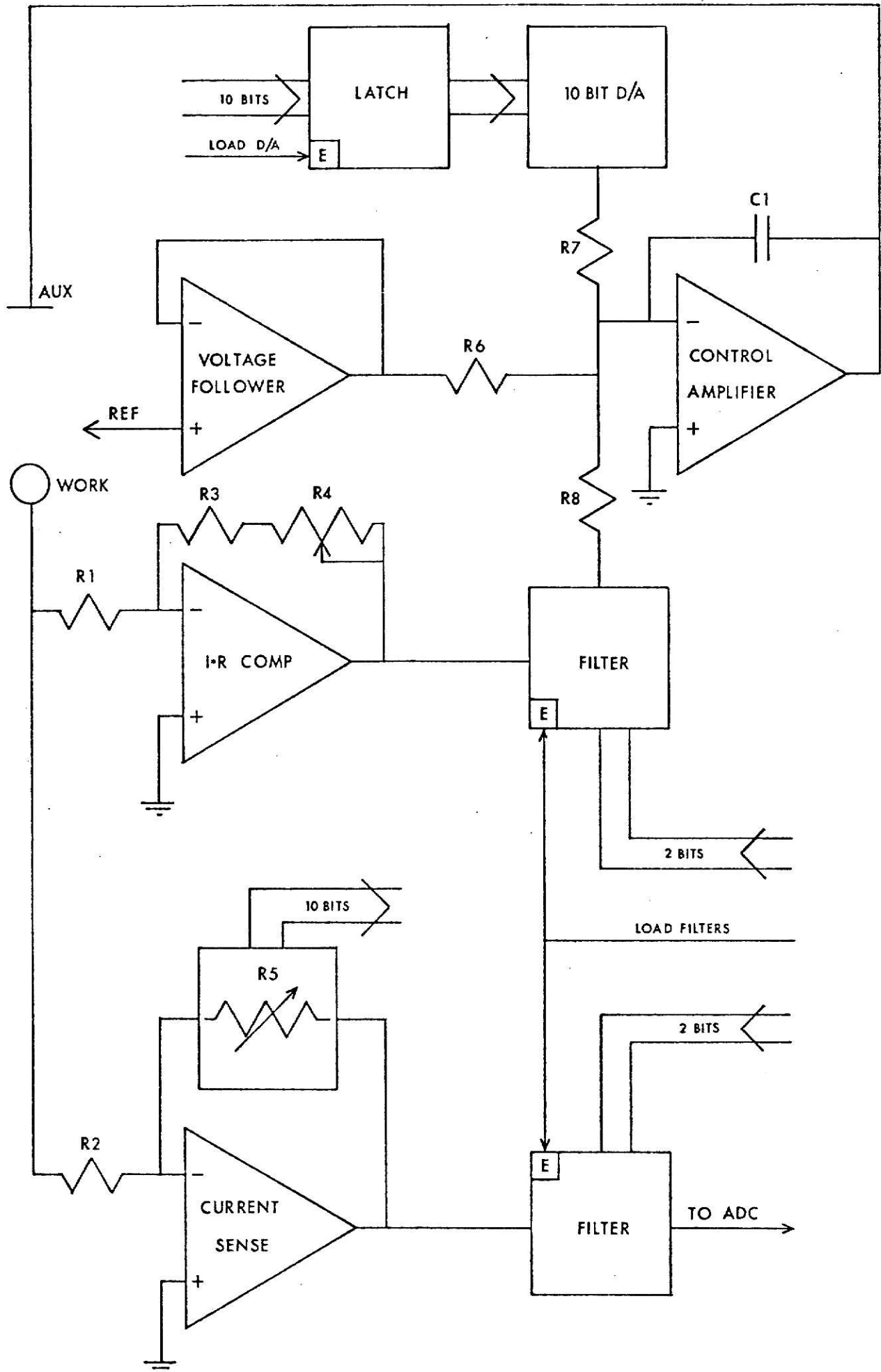
ment Corporation).[3]

A similar circuit was used for the potentiostat for controlled potential electrolyses. The control amplifier of this instrument has a voltage capability of ±100V and can deliver a sustained current of 100 mA. This potentiostat also incorporated circuits for digital integration of the cell current and the digital display of the number of coulombs passed.[4] A strip-chart recorder (Moseley Model 680) was used to record the current-time curve.

Cells and Electrodes

All cells used in this work were the three-electrode type previously reported.[5] Solvent was vacuum distilled into the cell and any traces of oxygen were removed with several freeze-pump-thaw cycles. The cell was returned to room temperature (22 ± 0.5°C) and pressure in the cell brought to atmospheric level with helium. Purification of the helium was achieved by passage through successive columns of BTS catalyst, anhydrous magnesium perchlorate, and a liquid nitrogen-cooled trap. With positive helium pressure the sample was introduced into the cell and the solution thoroughly stirred.

A saturated calomel electrode (SCE) was used as the reference electrode in all experiments. The SCE was isolated from the working and auxiliary electrodes by means of a glass frit

and bridge containing 0.1 M electrolyte. The auxiliary electrode used in the cyclic voltammetric and chronoamperometric studies was a piece of platinum foil positioned parallel to and about one half cm from the working electrode. The auxiliary electrode for coulometric studies was a coiled platinum wire isolated within the cell by means of a glass frit.

Most cyclic voltammetric and chronoamperometric experiments were performed using a platinum button working electrode with a geometric area of 0.25 cm.^{2} The working electrode in the coulometric experiments was a large cylindrical platinum gauze.

Chemicals

Most of the chemicals involved in this work were either prepared or purified by Dr. R. N. McDonald of the department. Diphenyldiazomethane was prepared according to the method of Miller[6] (30-31°C, lit. 29-32°C). Diphenylmethane was produced by the method of Huang-Minlon[7] (b.p. 73.5°/0.6 mm Hg). Benzophenoneazine was prepared according to Whitlock.[8]

Tetraphenylethene (Aldrich) was used as received (m.p. 225°). Tetraphenylethane (Columbia Products) contained large amounts of the ethene. Recrystallization from $CHCl_3$-EtOH did not remove all of the ethene. Therefore the tetraphenylethane was used primarily for qualitative work.

Dimethylforamide (Aldrich) was purified by storage over anhydrous copper sulfate and distilled at a pressure such that boiling occurred in the range 35°-40°C.[9] The middle 60% was saved and stored over Linde type 5A molecular sieves on the vacuum line.

Tetra-n-butylammonium perchlorate (TBAP), Eastman Chem. Co., was dried in a vacuum oven and used as received. Tetra-ethylammonium perchlorate (TEAP) was prepared by the method of Kolthoff and Coetzee.[10]

Separation

Immediately following electrolysis the DMF solution was transferred to a 250 ml separatory funnel and 10 ml benzene added with mixing. Then 100 ml water were added slowly, the funnel was shaken, and the layers allowed to separate. The benzene layer was drawn off and the aqueous layer was returned to the separatory funnel for further benzene extractions (50 ml total).

When TBAP was used as the electrolyte, it was also extracted into the benzene layer. However, upon standing at room temperature, the TBAP precipitated (this usually occurred even in the separatory funnel). After filtration to remove the TBAP, the benzene solution was dried with $CaCl_2$ and transferred to a 100 ml round bottom flask for solvent evaporation.

Since the tetraethylammonium perchlorate remained in the
water/DMF layer, the filtration steps were not necessary when
it was used as the electrolyte.

A Buchi Roto Vapor-R solvent evaporator was used to con-
centrate the benzene solution to a volume of about one ml.
A steam-warmed water bath was used to aid the evaporation.
The material was then transferred quantitatively to a five
ml volumetric flask and brought to volume with benzene.

The efficiency of the separations procedure was tested
using known amounts of the compounds which were shown by
chromatographic procedures to be present in the electrolyzed
solution. With the exception of tetraphenylethene, which is
present in only trace amount, the concentrations were chosen
to approximate product yields from an electrolysis of a dilute
solution of diphenyldiazomethane. Standard solutions were
prepared which were 0.2 mM diphenylmethane, 1 mM benzophenoneazine,
and 0.1 mM tetraphenylethene in 0.1 M electrolyte-DMF. The
extraction procedure, discussed above, was performed on three
similarly prepared standard solutions.

After extraction, the solutions were analyzed by glc.
The results are shown in Table 1. Reproducibility of re-
covery of the ethene and the azine was much better than for the
methane. One plausible explanation for poor reproducibility
in methane recovery is its higher volatility and solubility
in a wide range of solvents.

Table I

Percent Recovery of Material from Standard Mixtures

Compound	Exp #1		Exp #2		Exp #3		Average % Recovery
	mMoles	% Recovery	mMoles	% Recovery	mMoles	% Recovery	
Diphenylmethane	0.31	> 100	0.34	90	0.24	70	80
Tetraphenylethene	0.14	82	0.13	70	0.12	81	78
Benzophenoneazine	1.02	95	1.15	87	1.09	85	89

Product Analysis

Identification of products formed in the coulometric experiments was made by glc and nmr. Quantitation of the products was performed by glc and high pressure liquid chromatography (HPLC).

Gas chromatographic analysis was performed on a Hewlett Packard gas chromatograph with flame ionization detection. Stationary phases employed were 5% SE-30 (6 ft. column) and 3% OV-101 (4 ft. column), both on Chromasorb W. The columns were temperature programmed at 30°/min. from 110° to 290°C with a carrier gas flow rate of 30 ml/min.. The injector and detector were maintained at a temperature of 300°C.

No significant difference was seen in the data obtained from the two stationary phases. The longer column did display naturally longer retention times and somewhat more tailing. Results of glc analysis are shown in Table 2 and Figure 6.

Components used in HPLC analysis were a Waters Model M-6000A chromatography pump and a Schoeffel Model SF-770 variable wavelength uv detector. Injections were made through a Valco Model CV-6-UHPa-C-20, 7000 psig sample injection valve with 25 µl sample loop. Readout was made to a Honeywell Electronik 19 strip chart recorder. The 100 cm Waters stainless steel column was packed with Corasil II, 37-50µ. The

detector was operated at 285 nm with benzene as the mobile phase and a flow rate of 1.5 ml/min.

Due to problems encountered in trying to pump low boiling mobile phases, e.g. hexane, benzophenoneazine was the only product quantitated by HPLC. Other products were not seen in benzene since their absorption maxima are below the benzene cutoff.

Data obtained by HPLC are shown in Table 2. As shown in the table these results were found to be in excellent agreement with the results obtained by glc.
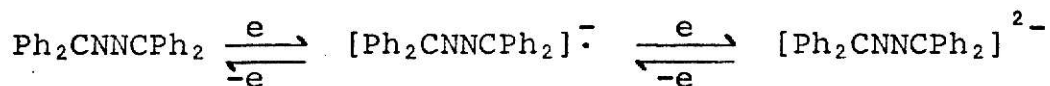
RESULTS

Cyclic Voltammetry

The cyclic voltammetric behavior of diphenyldiazomethane in dilute solution is shown in Fig. 2. At a scan rate of 0.2V/s the first cathodic scan shows a major cathodic peak at -1.74V and a relatively small cathodic peak near -2.12V. Upon reversal of the scan direction a small anodic peak appears which corresponds to reoxidation of the product formed in the second cathodic process. Two somewhat larger anodic peaks (shown in separate experiments to arise from decomposition of the solvent-electrolyte) appear at -0.60 and -0.25V. The only apparent change appearing on the second scan is some enhancement relative to the major peak of the small cathodic peak at -2.20V and its corresponding anodic peak.

In more concentrated solutions (Fig. 3) some enhancement is noted in the second cathodic peak and its corresponding anodic peak relative to the major cathodic process. Also, in solutions of concentration greater than about 3 mM, a new anodic process becomes discernible on the second scan near -1.66V.

At faster scan rates, up to 100V/s, the general appearance of the voltammogram remains about the same. No reversibility of the major process is ever observed on the first scan.

Figure 4 illustrates the cyclic voltammetry behavior of benzophenoneazine. The two reversible couples ($E_{p,c}$ = -1.72 and -2.12V) indicate a stepwise, two-electron reduction of azine to its dianion.

$$Ph_2CNNCPh_2 \underset{-e}{\overset{e}{\rightleftharpoons}} [Ph_2CNNCPh_2]^{\cdot -} \underset{-e}{\overset{e}{\rightleftharpoons}} [Ph_2CNNCPh_2]^{2-}$$

The position of the second azine process ($E_{p,c}$ = -2.12V) is at the same potential as the minor couple in Figures 2 and 3. Also, the anodic peak near -1.68V corresponds very closely to the anodic peak seen in the second scan of Fig. 3. This suggests that azine is formed in small amounts in the reduction of diphenyldiazomethane.

Chronoamperometry

In order to determine the number of electrons involved

Figure 2. Cyclic voltammogram of 0.98 mM diphenyldiazomethane
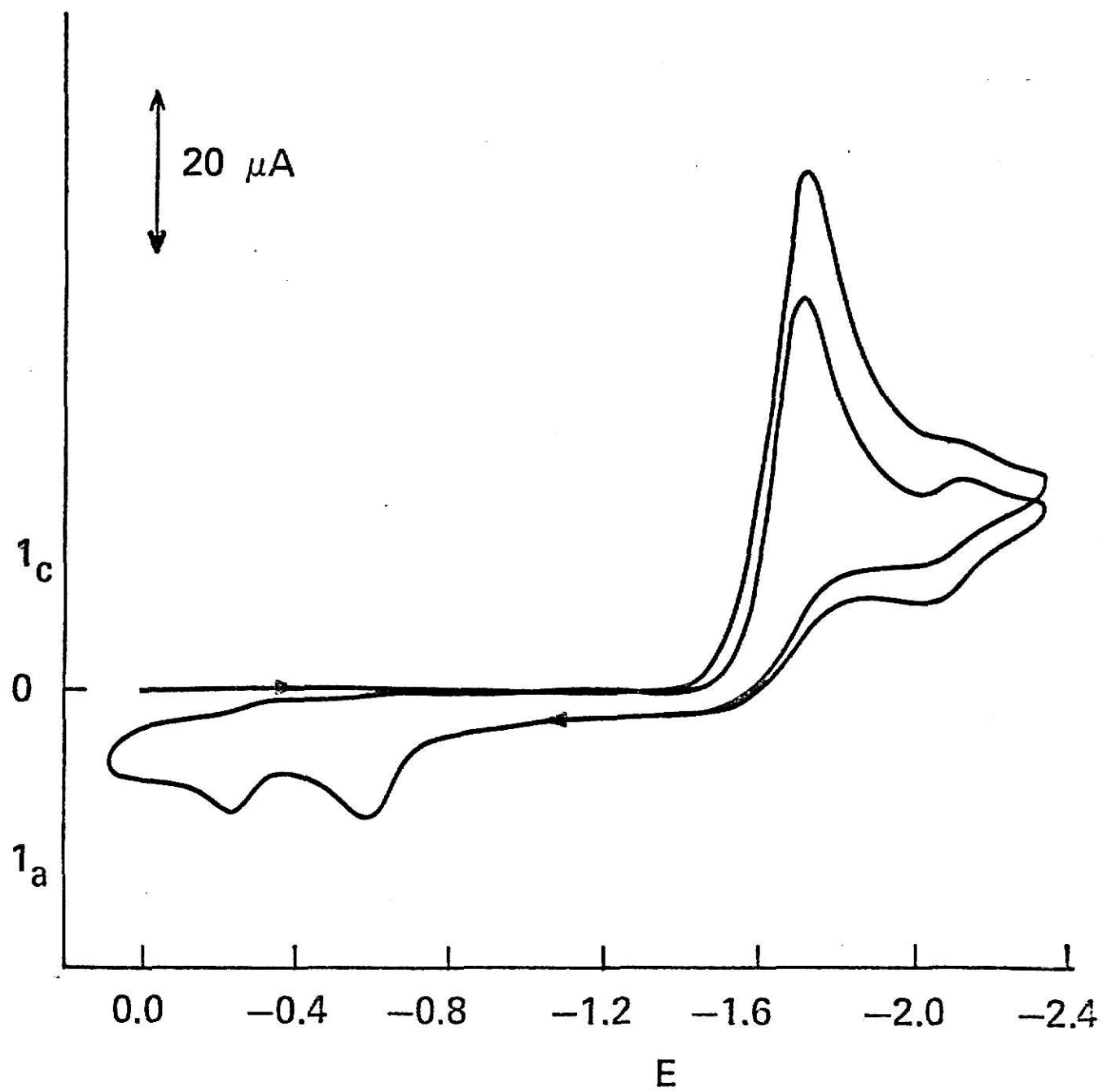in 0.1 M TBAP-DMF

Figure 3. Cyclic voltammogram of 4.70 mM diphenyldiazomethane
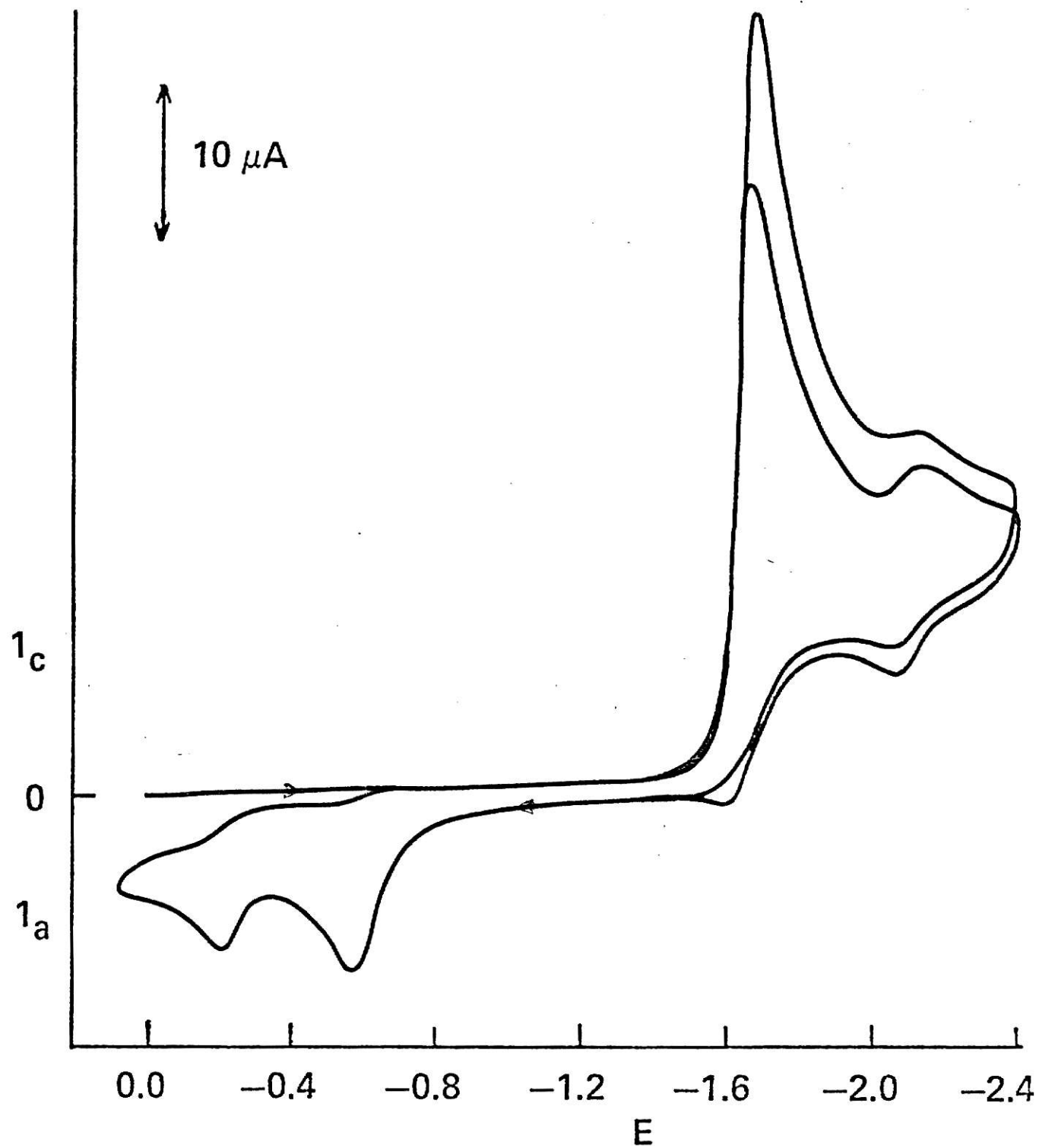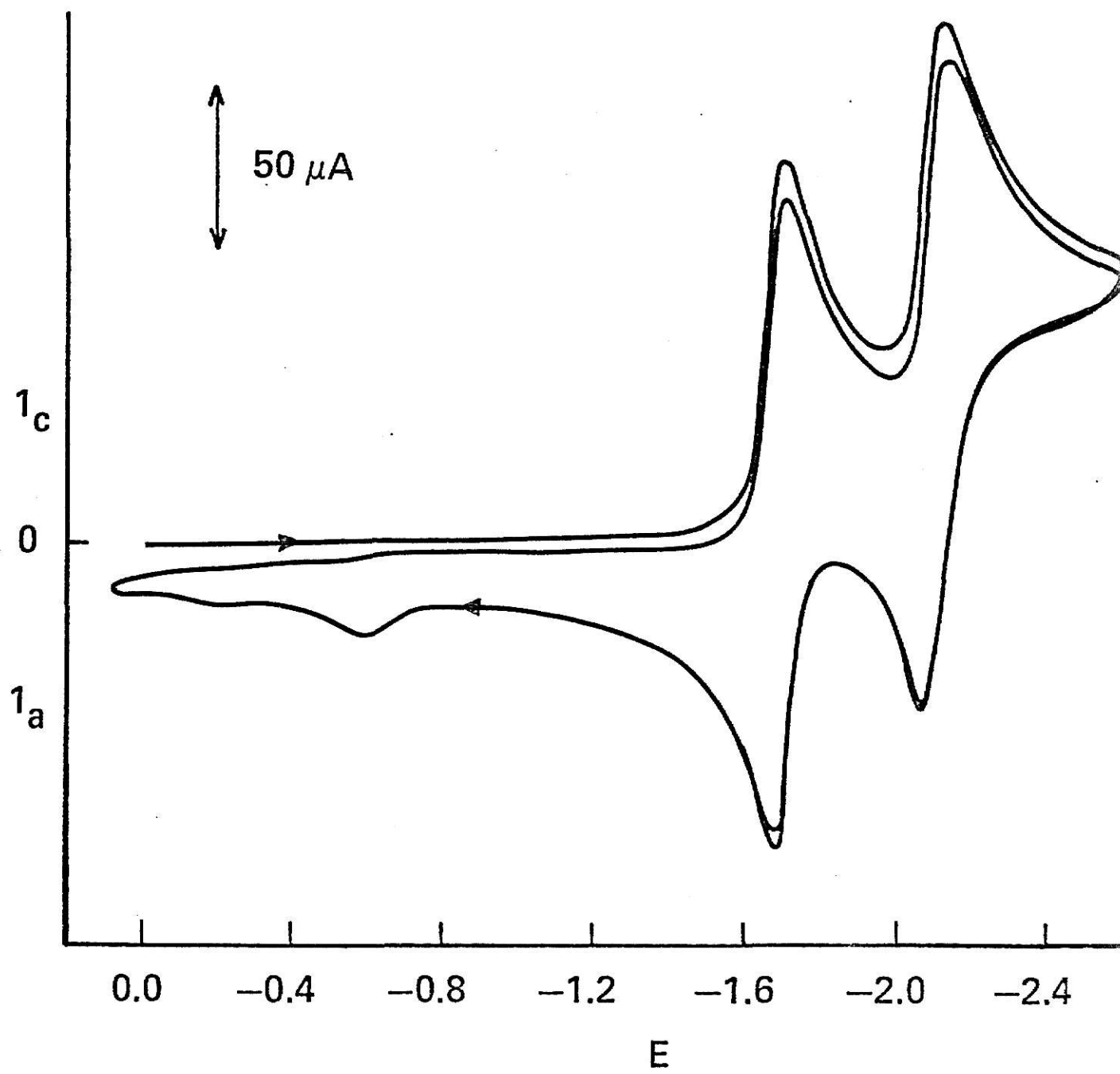in 0.1 M TBAP-DMF.

Figure 4. Cyclic voltammogram of 2.72 mM benzophenoneazine
in 0.1 M TBAP-DMF.

in the reduction of diphenyldiazomethane, chronoamperometric experiments were performed in the time range 3ms $\leq$ t $\leq$ 2s. The working potential was made negative enough to effect reduction of the diphenyldiazomethane (-2.00V). In dilute solution this resulted in a constant $it^{1/2}/c$ value of 37 (Fig. 5) indicating diffusion control throughout the experimental time range.

In more concentrated solutions, the $it^{1/2}/c$ value is no longer constant, but decreases slightly from the original value with increasing time. This is inconsistent with a strictly diffusion controlled process and indicates that a relatively small amount of the diphenyldiazomethane reacts via some pathway having an n-value less than one. As will be shown this decrease is due to production of benzophenoneazine in a chain process.

Also shown in the figure is the chronoamperometric data for benzophenoneazine. These data were taken over the same time range as above and show a diffusion controlled $it^{1/2}/c$ value of 29 at a potential negative enough to effect the reduction of the azine to its radical ion.

The reduction of azine to its radical ion was shown to be a one-electron process. Considering that the substantially larger size of the azine would give a smaller $it^{1/2}/c$ value, this strongly suggests that the reduction of diphenyldiazomethane is also a one-electron process.

Figure 5. Single potential step chronoamperometric data
            for the reduction of diphenyldiazomethane (o)
            0.77 mM, (v) 2.66 mM; and (o) 3.10 mM benzo-
            phenoneazine.
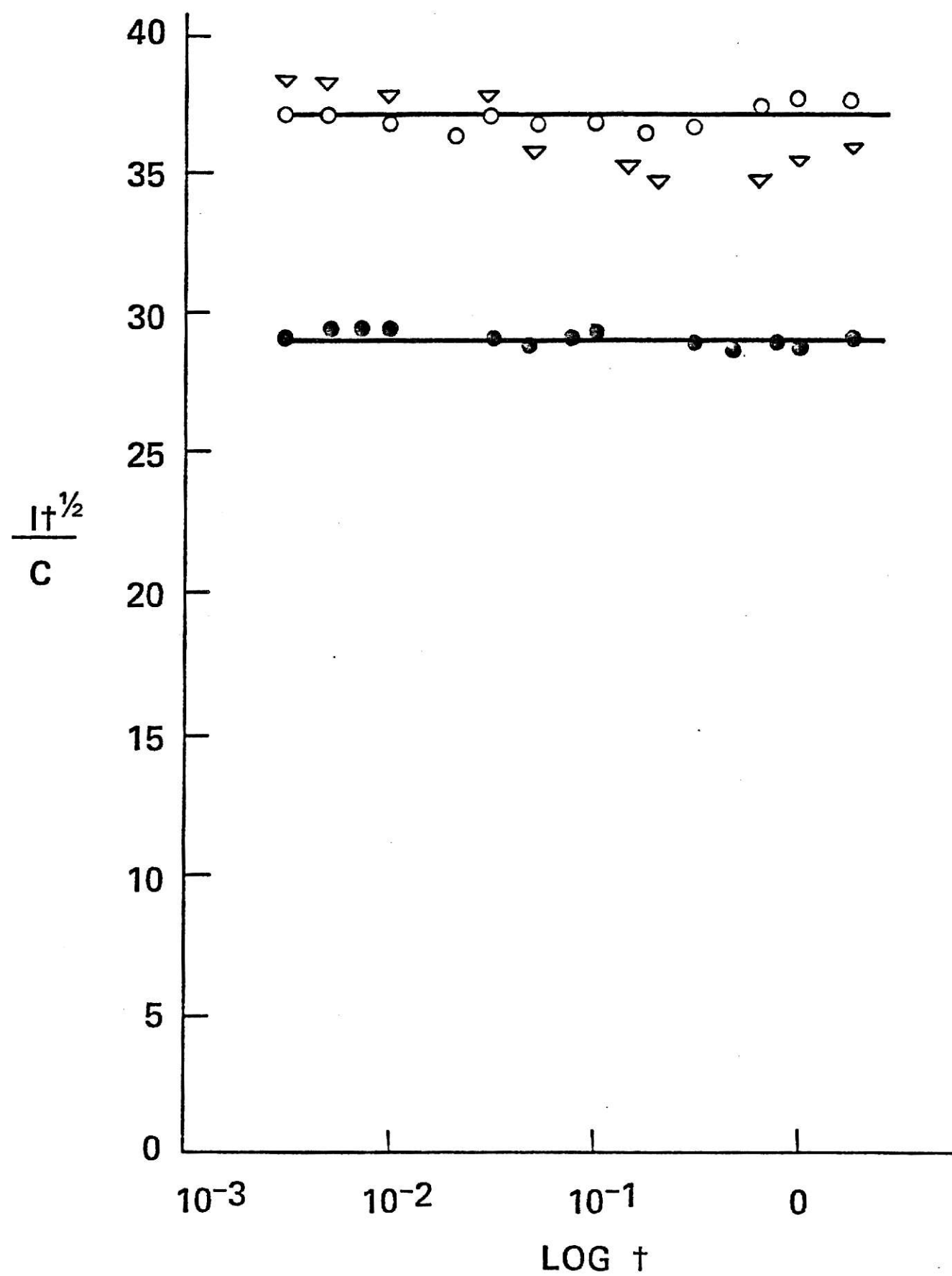
Coulometry

Both the n-value and the product distribution are markedly dependent upon the potential of the working electrode. When the applied potential was less negative than the cyclic voltammetric peak potential for the reduction of diphenyl-diazomethane ($E_{p,c} \cong -1.74V$), benzophenoneazine was formed as the principal product, along with minor amounts of diphenyl-methane and benzhydrylamine (Experiments 1-3, Table 2). Traces of tetraphenylethane and tetraphenylethene were also detected by gas chromatography (Fig. 6) and high-pressure liquid chromatography. However, since these materials are also formed during the slow, normal decomposition of diphenyl-diazomethane in the solid, they are not thought to be products of the electrolysis.

In contrast, when the potential was made sufficiently negative so as to render the concentration of starting material effectively zero at the working electrode surface, the principal product was diphenylmethane. The large increase in the yield of the methane was accompanied by a corresponding increase in the n-value and a concomitant decrease in the yield of benzophenoneazine (Experiment 4, Table 2). Benzhydrylamine was the only other product formed in significant yield.

The n-values which are listed in Table 2 are approximate values only. More accurate values could not be determined because benzophenoneazine, one of the products of the re-duction of diphenyldiazomethane, is also electroactive at the applied potential. Since the consumption of the starting

TABLE 2

Coulometric Data & Product Analysis from Controlled Potential
Reduction of Diphenyldiazomethane

Products Yields (%)

Exp #	$[Ph_2CN_2]$	Potential Range	$Ph_2CH_2^c$	$Ph_2CN_2CPh_2^c$	$Ph_2CH_2NH_2^c$	$Ph_2CHCHPh_2$	Ph_2CCPh_2
1	1.37mM (n ~0.6)	1.7–1.8V	11.3 ± 0.5	$49.9^a \pm 1.9$ / $46.7^b \pm 1.7$	6.5 ± 0.1	–	–
2	2.20mM (n ~0.5)	1.6–1.8V	5.6 ± 0.6	$64.1^a \pm 0.6$ / $60.8^b \pm 0.7$	3.9 ± 0.1	<1	<1
3	4.70mM (n ~0.25)	1.75–1.85V	2.7 ± 0.3	$69.3^a \pm 1.4$ / $72.9^b \pm 0.5$	5.5 ± 0.4	<1	<1
4	0.72mM (n > 1)	2.0–2.2V	40.6 ± 0.8	$17.6^a \pm 1.0$	6.3 ± 0.5	–	–

a. Data obtained by glc.

b. Data obtained by HPLC.

c. $(\pm)$ values indicates reproducibility of injections

Figure 6. A typical gas chromatogram of an electrolyzed
solution of diphenyldiazomethane showing (a)
diphenylmethane, (b) benzhydrylamine, (c)
tetraphenylethene, (d) tetraphenylethane, and
(e) benzophenoneazine.
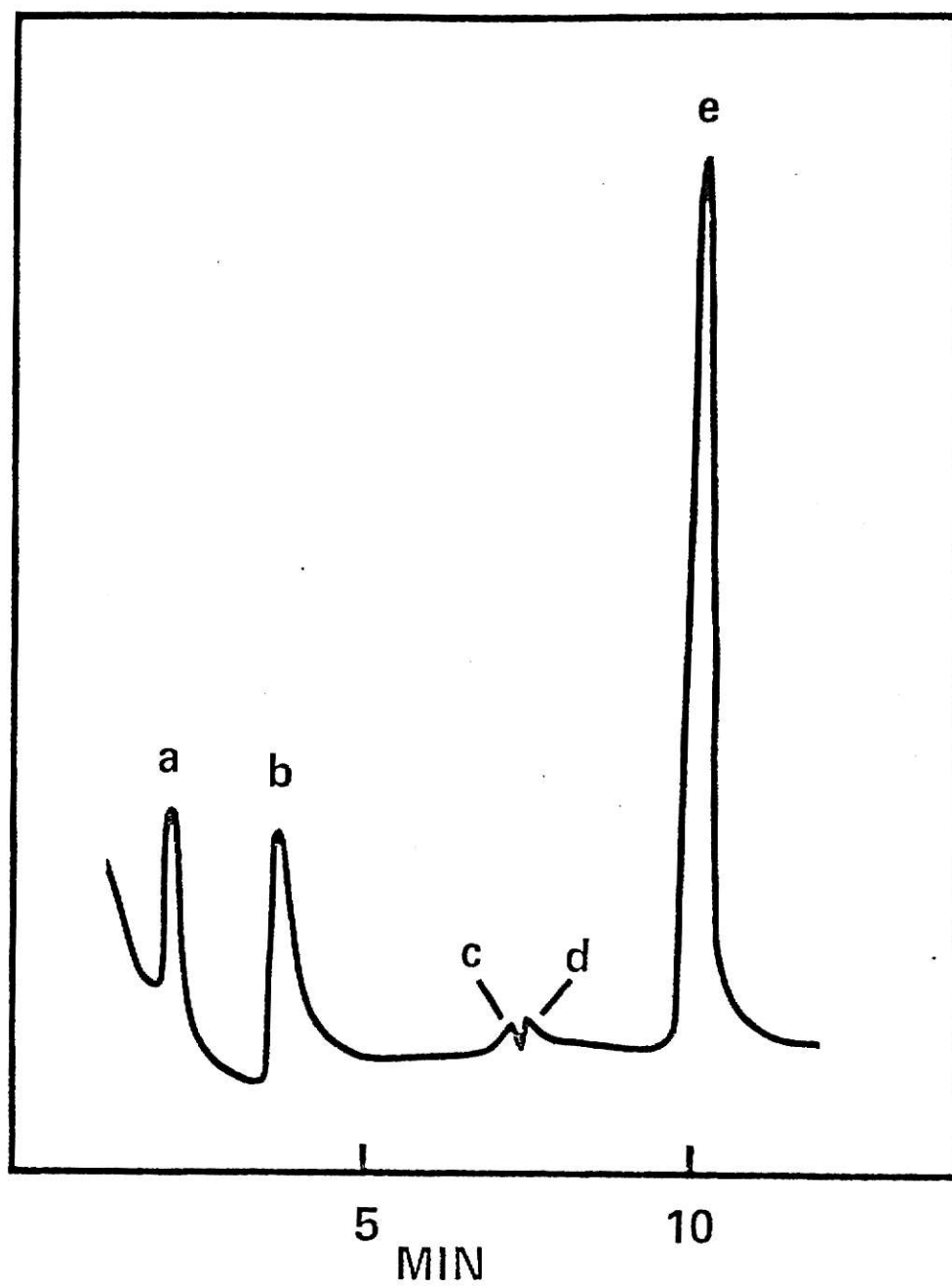
material is not accompanied by cessation of electrolysis current, the course of the reduction was monitored by cyclic voltammetry. Electrolysis was terminated when the magnitudes of the first (concurrent reduction of starting material and benzophenoneazine) and the second (further reduction of the azine radical anion to the dianion) cathodic peaks were deemed equal. The cyclic voltammogram of the electrolyzed solution (Fig. 7) indicates the presence of only the azine. With the exception of tetraphenylethene ($E_{p,c} = -2.2V$) which may be present in trace amount, none of the other products which were detected by chromatographic methods is electroactive in this potential range.

DISCUSSION

Results of the chronoamperometric experiments support a diffusion controlled one-electron reduction of diphenyldiazomethane. This suggests the formation of the corresponding radical ion which would then rapidly lose nitrogen to form

$$Ph_2CN_2 \xrightleftharpoons{e^-} Ph_2CN_2^{\cdot -} \longrightarrow Ph_2\overset{\cdot}{C}^{-}: + N_2 \qquad (1)$$
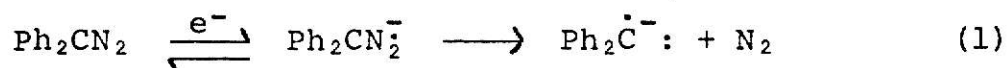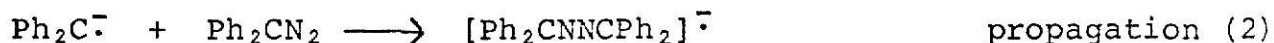
a carbene radical ion. This process was shown by cyclic voltammetry to be irreversible at scan rates up to 100V/s. Except for a small amount of azine which is formed, no other electroactive species was produced, indicating that the carbene radical ion reacts mainly with components of the solvent-electrolyte system to produce an electroinactive

Figure 7. Cyclic voltammogram of an electrolyzed solution
           of diphenyldiazomethane (12.6 mM) in 0.1 M
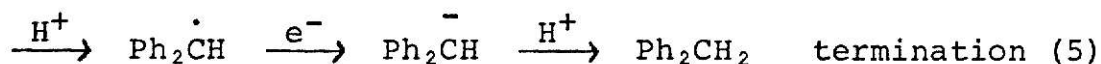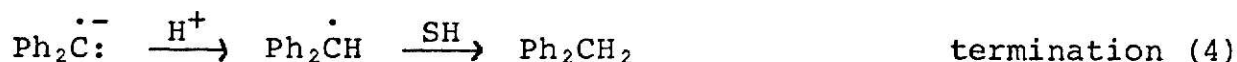   TBAP-DMF.
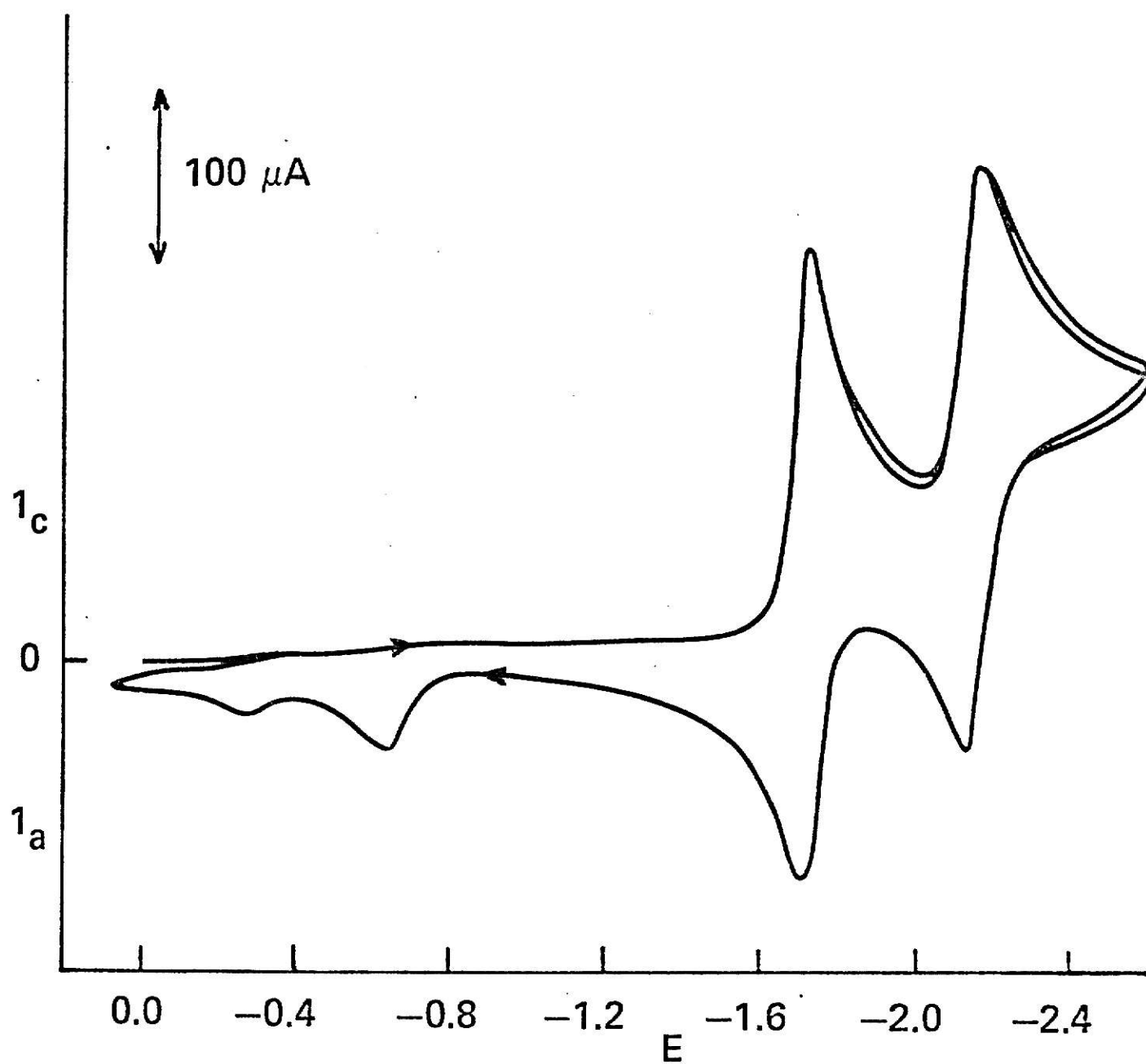
product. A likely product of this interaction would be diphenylmethane.

In contrast to the results which are obtained during the chronoamperometry experiment, reduction of diphenyldiazomethane in the coulometry cell at a potential less negative than its $E_{1/2}$ gives an n-value significantly less than 1.0 and benzophenoneazine as the principal product. These results can be rationalized if the intermediate carbene radical anion were now to consume starting material. The first step would involve coupling of the carbene radical ion with diphenyl-diazomethane to produce the azine radical ion. This species then electron transfers to a second molecule of starting material to produce azine and the diphenyldiazomethane radical anion. Decomposition of the latter species by loss of nitrogen gives the carbene radical ion which acts as the chain-carrying species in this chain reaction.

$$Ph_2C^{\cdot-} + Ph_2CN_2 \longrightarrow [Ph_2CNNCPh_2]^{\cdot-} \qquad \text{propagation (2)}$$

$$[Ph_2CNNCPh_2]^{\cdot-} + Ph_2CN_2 \longrightarrow Ph_2CNNCPh_2 + Ph_2\overset{\cdot}{C}{:} + N_2 \quad \text{propagation (3)}$$

Termination of the chain process occurs via interaction of the carbene radical ion with the solvent system to form diphenylmethane. Three mechanisms are postulated for this reaction.

$$\overset{\bullet\,-}{Ph_2C:} \xrightarrow{H^+} \overset{\bullet}{Ph_2CH} \xrightarrow{SH} Ph_2CH_2 \qquad\qquad \text{termination (4)}$$

$$\xrightarrow{H^+} \overset{\bullet}{Ph_2CH} \xrightarrow{e^-} \overset{-}{Ph_2CH} \xrightarrow{H^+} Ph_2CH_2 \qquad \text{termination (5)}$$

$$\xrightarrow{SH} \overset{-}{Ph_2CH} \xrightarrow{H^+} Ph_2CH_2 \qquad\qquad \text{termination (6)}$$

Equation (4) involves formation of the benzhydryl radical as an intermediate. In previous work with benzyl halides[11] formation of such radicals resulted in the corresponding dimer. In this case the dimer would be tetraphenylethane. As stated previously only traces of this compound were found in the electrolyzed solution and these probably do not arise from the electrolysis. In equation (5) the resulting benzyhydryl radical is reduced to the carbanion which then is protonated to form diphenylmethane. This mechanism is similar to equation (6) in which the carbanion is also formed. However, in (6) the carbanion is formed by first abstracting a hydrogen atom from the solvent system.

Although equations (5) and (6) both give diphenylmethane through the carbanion, equation (5) is a two-electron process whereas (6) involves one electron. Since results of the chronoamperometric and cyclic voltammetric experiments indicates that diphenylmethane is formed as the principal product in a one-electron step, equation (6) must be favored as the termination step in the chain process.
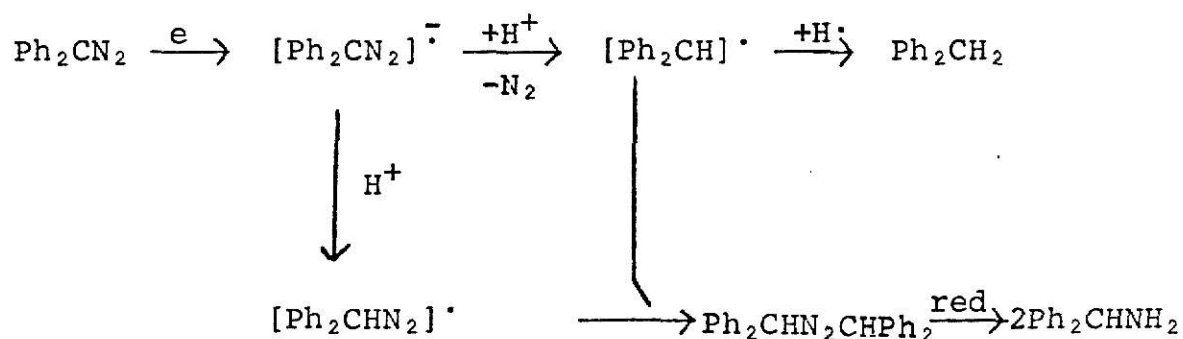
The absence of appreciable amounts of the dimeric products tetraphenylethene and tetraphenylethane has particular significance. As noted in the introduction, Sargent and co-workers[1] obtained ethene as the principal product from reductive dehalogenations of dichloro-, dibromo-, and di-iodomethanes. The pathway suggested for the formation of ethene involved dimerization of the methylene radical anions and the subsequent loss of two electrons from the dimeric dianion. Since substitution of the hydrogen on the methylene radical anion with phenyl should facilitate dimerization of the carbene radical anion, the absence of tetraphenylethene as an electrolysis product in our experiments vitiates Sargent's proposal. In view of the fact that electrolytic reduction of <u>vicinal</u> dihalides is known to give olefins,[12] an alternate pathway which involves nucleophilic attack on the parent compound by the monohalomethyl anion should be examined further (eq. 7). The validity of this suggestion may be

$$CH_2X^- + CH_2X_2 \longrightarrow XCH_2CH_2X + X^- \qquad (7)$$

$$XCH_2CH_2X + 2e \longrightarrow 2X^- + CH_2 = CH_2 \qquad (8)$$
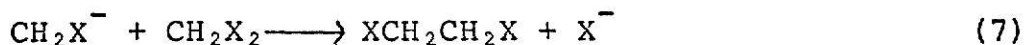
tested by searching for the formation of the 1,2-dihaloethane after the reaction of equimolar quantities of dihalomethane and the hydrocarbon radical anion reducing agent.

In other work with diphenyldiazomethane, Elofson, et al.[13] found in preliminary studies that the polarographic reduction
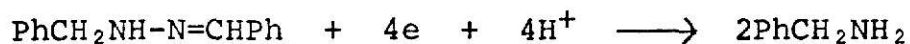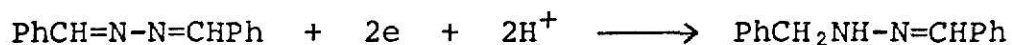
(n∿1) of this compound produced 40% diphenylmethane and 20% benzhydrylamine. They proposed the reactive intermediates to be the benzhydryl radical and a diazinile radical. This

$$Ph_2CN_2 \xrightarrow{e} [Ph_2CN_2]^{\overline{\cdot}} \xrightarrow[-N_2]{+H^+} [Ph_2CH]^{\cdot} \xrightarrow{+H\cdot} Ph_2CH_2$$

$$\downarrow H^+$$

$$[Ph_2CHN_2]^{\cdot} \qquad \longrightarrow Ph_2CHN_2CHPh_2 \xrightarrow{red} 2Ph_2CHNH_2$$

hypothesis was apparently largely based on the mass spectrometric determination of azodiphenylmethane as the third reduction product.

These results contrast somewhat with the work performed here. Benzophenoneazine was found to be the principal product when the working potential was less than ∿-1.84V. Also, electrolysis was found to be complete at n-values substantially less than one, suggesting a chain process as the major reaction pathway. Even at a more negative working potential (-2.0 to -2.2V) formation of azine in 17% overall yield (Exp. #4, Table 2) indicates that this remains an important reaction pathway.

Further support for the mechanisms and results postulated here comes from a paper by Lund.[14] Electrochemical reduction of benzalazine in protic solvents produced first benzaldehyde benzylhydrazone in a two-electron process and then benzylamine in an overall six-electron process.

$$PhCH=N-N=CHPh \ + \ 2e \ + \ 2H^+ \ \longrightarrow \ PhCH_2NH-N=CHPh$$

$$PhCH_2NH-N=CHPh \ + \ 4e \ + \ 4H^+ \ \longrightarrow \ 2PhCH_2NH_2$$

The salient features of this paper are production of an amine from the azine and the hydrazone intermediate. Implications of the former are obvious and the latter is important due to the fact that the other isomeric form of benzaldehyde benzylhydrazone is azotoluene, which is analogous to the azodiphenylmethane reported by Elofson. Lund discusses these isomers and reports that the azo form is known to rearrange to the hydrazone. Also, Lund suggests that reduction of the azo isomer would not yield an amine, but would yield the corresponding hydrazine instead.

Thus, from the information obtained in our lab, in conjunction with the works discussed above, we feel that we have expanded and improved upon the postulates of Elofson's group. The ultimate results, as set forth in this work, indicate that the electrochemical generation of carbene radical ions from diazo compounds is a viable technique.

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ELECTROCHEMICAL REDUCTION OF DIPHENYLDIAZOMETHANE

by

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Abstract

Diphenyldiazomethane has been studied in nonaqueous media by cyclic voltammetry, chronoamperometry, and controlled potential electrolysis. The results of these studies show that the product distribution is dependent upon the electrode potential. When the potential of the working electrode is significantly more negative than the peak reduction potential of diphenyldiazomethane, the principal product obtained is diphenylmethane. Reduction of diphenyldiazomethane at less negative potential results in a decreased yield of diphenyl-methane and a concomitant increase in the yield of benzo-phenoneazine. The reaction pathway which has been postulated for the formation of the principal products involves the initial one-electron reduction of diphenyldiazomethane to its corresponding radical anion (eq. 1) and the subsequent rapid loss of nitrogen from this species to give the di-phenylmethylene radical anion (eq. 2). A chain reaction then ensues which gives benzophenoneazine as its product. In the propagation step, the diphenylmethylene radical anion couples with starting material to give the radical anion of benzo-phenoneazine (eq. 3). This intermediate radical anion then transfers an electron to the starting material to give the azine and the radical anion of diphenyldiazomethane (eq. 4). Loss of nitrogen from this radical anion then results in the regeneration of the carbene radical anion, the chain-carrying

species. Chain termination occurs when the carbene radical anion abstracts a hydrogen atom from a component of the solvent-electrolyte system (eq. 5). Protonation of the diphenylmethyl anion gives diphenylmethane and completes the reduction process (eq. 6).

$$Ph_2CN_2 + e \; \underset{\longleftarrow}{\overrightarrow{\hspace{1cm}}} \; [Ph_2CN_2]^{\overline{\cdot}} \tag{1}$$

$$[Ph_2CN_2]^{\overline{\cdot}} \xrightarrow{fast} Ph_2C^{\overline{\cdot}} + N_2 \tag{2}$$

$$Ph_2C^{\overline{\cdot}} + Ph_2CN_2 \longrightarrow [Ph_2C=N-N=CPh_2]^{\overline{\cdot}} \tag{3}$$

$$[Ph_2C=N-N=CPh_2]^{\overline{\cdot}} + Ph_2CN_2 \longrightarrow Ph_2CNNCPh_2 + [Ph_2CN_2]^{\overline{\cdot}} \tag{4}$$

$$Ph_2C^{\overline{\cdot}} \xrightarrow{SH} Ph_2\overline{C}H + \text{solvent derived radical} \tag{5}$$

$$Ph_2\overline{C}H \xrightarrow{HA} Ph_2CH_2 \tag{6}$$