Experimental Section

Acetic Acid. Fisher reagent ACS, 99.7%, was diluted to 90 and 95% (w/w) aqueous solutions, respectively.

Chromic Acid. The solutions were made from chromium trioxide by weighing and the concentrations were checked by determining molar absorbtivity at 350 mμ. Solutions of higher concentrations were normally prepared and diluted to kinetic conditions. The solutions were stored in the cold.

Perchloric Acid. Baker reagent $HClO_4$ (70%) was diluted to 1 *M* aqueous solution and standardized against standard NaOH to methyl red indicator end point. This solution was then diluted with 99.7% acetic acid to stock solutions in 90 or 95% acetic acid. Solutions were checked for 100% transmission at 350 mμ; they had no absorption compared to solvents as blank.

Alcohols. Cyclopentanol, cyclohexanol, and *trans*-2-acetoxycyclohexanol-1 were purified by preparative gas–liquid partition chromatography (10% Carbowax, 100° and 10% diethylene glycol succinate, 110°, respectively) until a purity of at least 98% was achieved.

Kinetic Measurements. The reaction rates were followed spectrophotometrically in a thermostated cell holder of a Carl Zeiss PMQ spectrophotometer at 350 mμ at 31 ± 0.02°. The cells were placed in the cell compartment at least 15 min before the start of the run in order to assure full temperature equilibration. The solvent was checked for stability. The reaction of the acetic acid solvent with chromic acid was negligibly slow in the absence of perchloric acid, but was measurable in solutions containing $HClO_4$. All rate constants were therefore corrected for solvent oxidation. The corrections were very low for reactive alcohols (*e.g.*, 0.2% of the rate constant for cyclopentanol in 0.02 *M* $HClO_4$), but could not be neglected for the least reactive compound (9% correction for hydroxy lactone **7**).

The concentration of chromic acid in all kinetic runs was about 5×10^{-4} *M*. A 20-fold excess of the organic substrate was generally used. Good straight-line plots of log *A vs.* time were obtained and used for the determination of first-order rate constants. The second-order rate constants (obtained from the first-order rate constants and the initial alcohol concentrations) showed good reproducibility, usually within ±5%; for the most reactive alcohol (bicyclooctanol) the variation was somewhat greater (±10%). The values given in Table I are averages from at least two measurements.

6-Oxatricyclo[3.2.1.1^{3,8}]nonan-4β-ol (4) was prepared according to the method of Henbest and Nichols[19] and had mp 114–115° (lit.[19] 115°).

6-Oxatricyclo[3.2.1.1^{3,8}]nonan-4β-ol acetate (6) was prepared by acetylation of **4** and had mp 50–51° (lit.[19] 50–52°).

6-Oxatricyclo[3.2.2.1]decan-4β-ol (5). A 4-g portion (0.029 mole) of the 2-*endo*-hydroxymethylbicyclo[2.2.2]octene-5[20] was treated with 4.0 g (0.029 mole) of perbenzoic acid in chloroform at 0°. The reaction mixture was left overnight in a refrigerator and then tested for excess perbenzoic acid by means of starch–iodide paper. The mixture was washed successively with potassium iodide, sodium thiosulfate, potassium carbonate, and water, dried over anhydrous magnesium sulfate, and then evaporated to dryness. The residue left was distilled *in vacuo*, and the distillate, bp 110–115° (1.3 mm), was collected as a hygroscopic solid (mp 110–120°), yield 1.8 g (40%).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.83; H, 8.98.

5-*exo*,6-*endo*-Dihydroxy[2.2.1]heptane-2-*endo*-carboxylic acid lactone (7) was prepared according to the method of Henbest and Nichols[19] and had mp 155–157° (lit.[19] 160°).

5-*exo*,6-*endo*-Dihydroxy[2.2.2]octane-2-*endo*-carboxylic acid lactone (8) was prepared according to the method of Crundwell and Templeton[7] and had mp 230–233° (lit.[7] 235–237°).

***trans*-2,3-Dihydroxy-1-cyclopentenylacetic acid γ-lactone (9)** was prepared according to the method of Hill and Edwards[21] and had bp 123–124° (0.4 mm).

***trans*-1,2-Dihydroxycyclohexane monoacetate (10)** was prepared according to the method of Auwers and Dersch[22] and had bp 123° (0.14 mm).

Acknowledgments. The support of this work by grants of the National Science Foundation (GP 737) (J. R.) and of the U. S. Army Research Office, Durham (AROD-31-124-G871) (J. R.), is gratefully acknowledged. Syntheses of many of the compounds used in this study were carried out by H. Gopal of this laboratory.

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(19) H. B. Henbest and B. Nichols, *J. Chem. Soc.*, 227 (1959).

(20) H. W. Whitlock, *J. Am. Chem. Soc.*, **84**, 3412 (1962).

(21) R. K. Hill and A. G. Edwards, *Tetrahedron*, **21**, 1501 (1965).

(22) K. V. Auwers and F. Dersch, *J. Prakt. Chem.*, **124**, 235 (1930).

The Electrochemical Reduction of α,α′-Dibromo-*p*-xylene

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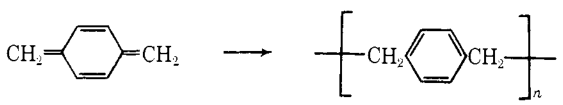
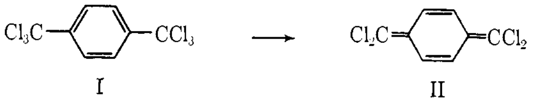
Received April 22, 1967

Abstract: Polarographic reduction of α,α′-dibromo-*p*-xylene occurs in two discrete steps. Evidence is presented that *p*-xylylene is formed during the first wave, and that this intermediate reacts rapidly to yield poly-*p*-xylylene and a small amount of [2.2]paracyclophane. The data suggest that *p*-xylylene, at very low concentration, can be reduced further polarographically. The mechanism of the electrochemical reduction of α,α′-dibromo-*p*-xylene is discussed in terms of the results of polarography, controlled-potential electrolysis, coulometry, and cyclic voltammetry.

The electrolysis of some α,α′-dihalo-*p*-xylenes was first examined in these laboratories by Gilch.[1] Several of these compounds were shown to be reduced at a mercury cathode to the corresponding *p*-xylylene polymers. It was postulated that *p*-xylylene was an intermediate in these cases, since, under appropriate conditions, this reactive species polymerizes rapidly.[2]



In the electrolysis of α,α,α,α′,α′,α′-hexachloro-*p*-xylene (I), α,α,α′,α′-tetrachloro-*p*-xylylene (II) was isolated at low temperatures.[1]



I II

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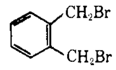
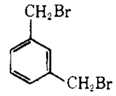
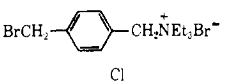
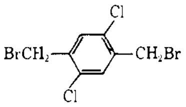
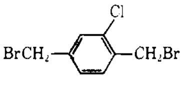
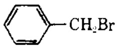
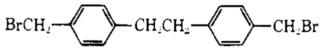
(1) H. G. Gilch, *J. Polymer Sci.*, **4**, 1351 (1966).

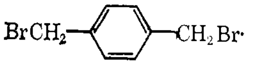
(2) L. A. Errede and J. M. Hoyt, *J. Am. Chem. Soc.*, **82**, 436 (1960), and references cited therein.

Table I. Polarographic Data[a]

	Compound	$-E_{1/2}$, v (*vs.* sce)	I_D (μa $m^{2/3}$ sec$^{1/6}$/10^{-3} M)[b]
1		0.80 (αn_a = 0.28) 1.72 (αn_a = 0.77)	4.10 2.78
2		0.61 1.58	4.50 2.52
3		1.32	7.58
4		0.79 1.72	3.64 1.57
5		0.45 1.36	3.90 0.42
6		0.61 1.59	4.12 2.06
7		1.22	4.13
8		1.15	4.40

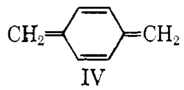
[a] Capillary constant $m^{2/3}t^{1/6}$ = 1.252 at −1.0 v, 1.237 at −2.0 v. [b] Concentration ~2 × 10^{-3} M.

This report deals primarily with the further elucidation of the mechanistic aspects of the electrochemical reduction of α,α'-dibromo-*p*-xylene (III). The results of this investigation clearly establish the presence of



III

p-xylylene (IV) as an intermediate.



IV

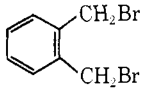
Moreover, the xylylenes, in general, are shown to be capable of further reduction, which can at present only be detected by polarography. This may serve as a diagnostic test for their presence as intermediates.

Results

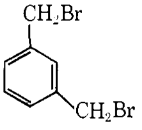
Electrode potentials cited below are all referenced to the saturated calomel electrode (sce), and all experiments were conducted in dimethylformamide (DMF) as solvent and tetraalkylammonium halides as supporting electrolyte.

Polarography. A typical polarogram of α,α'-dibromo-*p*-xylene is shown in Figure 1. Two waves appear, and a plot of limiting current *vs.* concentration for both waves is shown in Figure 2. The limiting current for the first wave is linearly dependent on concentration as predicted by the Ilkovic equation, but the limiting current for the second wave departs rather severely from linearity. The limiting currents of both waves are diffusion controlled, since their magnitudes were found experimentally to be closely proportional to the square root of the mercury pressure. This is the generally accepted criterion for diffusion-controlled waves.[3] The two waves differ in shape; the values of αn_a calculated from the slope of the graph of E *vs.* $\ln[(i)/(i_D - i)]$ are 0.28 and 0.77 for the first and second waves, respectively.

Two waves are also observed in polarography of α,α'-dibromo-*o*-xylene (V), and both α,α'-dibromo-2-chloro-*p*-xylene and α,α'-dibromo-2,4-dichloro-*p*-xylene are reduced in at least two well-defined steps.



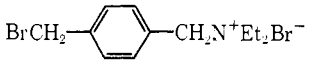
V



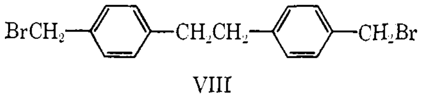
VI

The *meta* isomer VI, however, displays only a single wave, as does benzyl bromide.

The unsymmetrically substituted *p*-xylene, N,N,N-triethyl-N-(4-bromomethylbenzyl)ammonium bromide (VII) also displays two reduction waves, at $E_{1/2}$ = −0.79 v and at $E_{1/2}$ = −1.72 v. 4,4′-Bis(bromomethyl)bibenzyl (VIII) displays a single reduction wave at $E_{1/2}$ = −1.13 v. [2.2]Paracyclophane (X) is not reducible polarographically.



VII



VIII

All of the polarographic data has been summarized in Table I.

Controlled Potential Electrolysis. When α,α'-dibromo-*p*-xylene is electrolyzed at a cathode potential corresponding to the plateau region of either the first or second polarographic wave, the major product (*ca.* 90%) is the *p*-xylylene polymer IX. In addition, a

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(3) For example, see "Progress in Polarography," Vol. 2, P. Zuman and I. M. Kolthoff, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p 596.

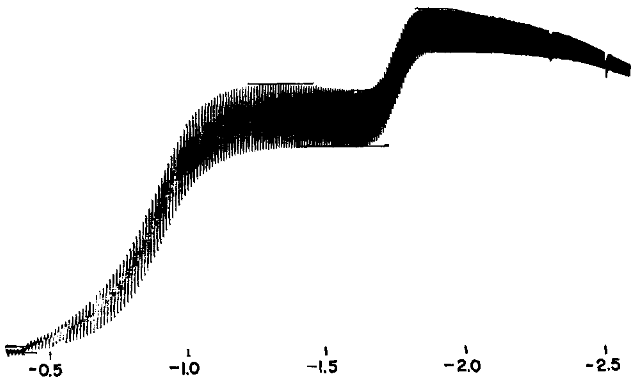


Figure 1. Polarogram of α,α'-dibromo-p-xylene.

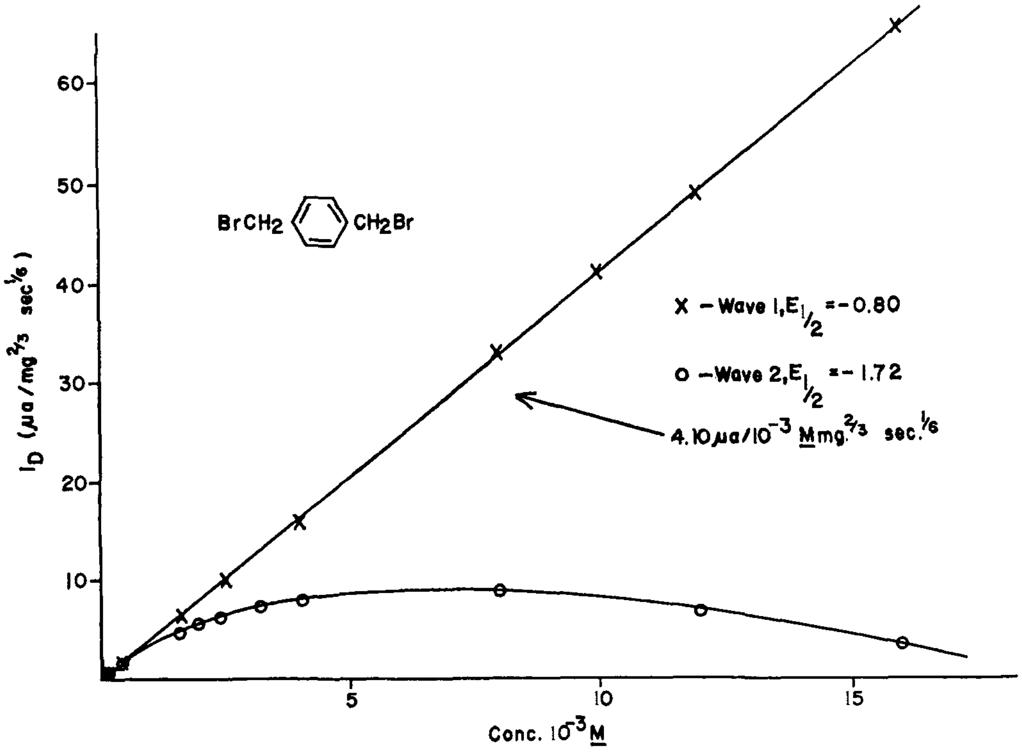
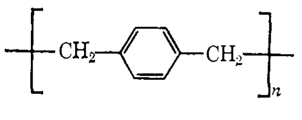
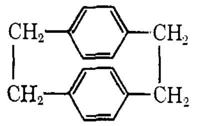


Figure 2. Polarographic data of α,α-dibromo-p-xylene.

small but significant amount (5–10%) of [2.2]paracyclophane (X) is also formed. 4,4′-Bis(bromomethyl)bibenzyl (VIII) was shown to be absent (<0.1%), nor could p-xylene be detected.

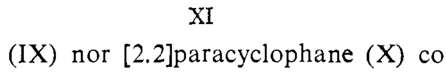


IX



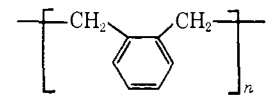
X

Controlled potential reduction of 4,4′-bis(bromomethyl)bibenzyl at a potential corresponding to its polarographic reduction wave gave 4,4′-dimethylbibenzyl (XI) as the major product. Neither poly-p-xylylene (IX) nor [2.2]paracyclophane (X) could be detected.



XI

Electrolysis of VI at potentials corresponding to its reduction wave produced m-xylene exclusively. In contrast, V gave a product consisting of 50% of poly-o-xylylene (XII) and 50% of an oil which was not characterized except that it was shown to contain neither o-xylene nor benzcyclobutene, when the electrolysis was conducted at a potential corresponding to the first polarographic reduction wave. When the electrolysis was conducted at a potential corresponding to the second wave, a small amount of o-xylene could be isolated, as well as the above-mentioned products.



XII

Coulometry. Measurement of the total number of coulombs required for electrolysis of α,α'-dibromo-p-xylene at potentials in the plateau region of the first polarographic wave demonstrated that 2 electron equiv/mole was consumed. When the electrolysis was conducted at −2.3 v, a potential corresponding to the plateau of the second wave, a total of 2 electron equiv/mole was also required. It should be pointed out, however, that at the concentration levels used in the electrolyses (~0.05 M), the height of the second polarographic wave would have been very small. Polarography of the partially electrolyzed solutions gave no indication that any electrochemically reducible material was forming.

Cyclic Voltammetry. Triangular wave cyclic voltammetry of III and V indicates that neither part of the two-step reduction is reversible at sweep rates up to 100 Hz. A typical oscilloscope tracing is shown in

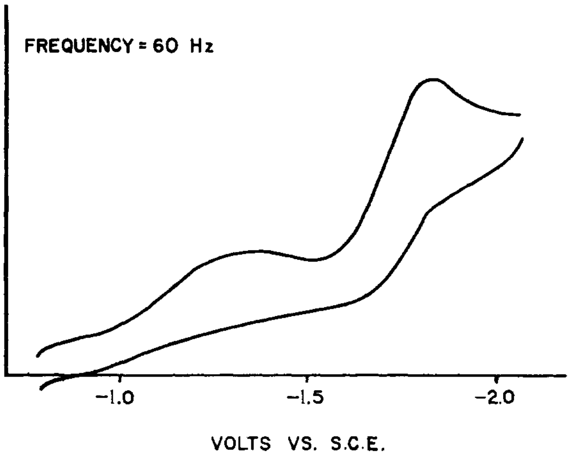


Figure 3. Cyclic voltammetry of α,α′-dibromo-*p*-xylene.

Figure 3. The second wave is much more sharply defined than the first, as expected from αn_a values calculated from dme polarography. Also, at these oscilloscopic sweep rates, it was observed qualitatively that the peak current of the second wave did not decrease markedly relative to that of the first wave as the concentration was increased, as was observed in conventional dme polarography of III. This may be an indication of an intervening chemical reaction which is slow compared to the oscilloscopic sweep rates but fast compared to the sweep rates used in dme polarography. This effect is being investigated further.

Discussion

***p*-Xylylene as the Product-Determining Intermediate.** The nature of the products of electrolysis of α,α′-dibromo-*p*-xylene strongly suggests that *p*-xylylene (IV) is the key intermediate. The major product of electrolysis is poly-*p*-xylylene (IX), which is known to form from homopolymerization of *p*-xylylene.[2,4] Moreover, it is well established[5] that *p*-xylylene can also dimerize to [2.2]paracyclophane, which is, in fact, observed as a minor product of electrolysis.

The possibility that 4,4′-bis(bromomethyl)bibenzyl (VIII) is the precursor to polymer and/or [2.2]paracyclophane is unlikely in view of the results of electrolysis of the former compound. The major product is 4,4′-dimethylbibenzyl (XI), and neither poly-*p*-xylylene nor [2.2]paracyclophane is observed. Also, VIII could not be detected polarographically at any time during the electrolysis of α,α′-dibromo-*p*-xylene.

The appearance of a second polarographic reduction wave is also apparently indicative of the xylylene intermediate, since only those compounds which can lead to a stabilized xylylene structure display two waves. Thus, three α,α′-dibromo-*p*-xylenes (see Table I) and a tetraalkylammonium derivative (VII) display two waves. The facts that electrolysis of α,α′-dibromo-*o*-xylene (V) yields some poly-*o*-xylylene (VII) and that polarography displays two waves suggest the formation of *o*-xylylene, which is known[6] to polymerize partially.

In contrast, α,α′-dibromo-*m*-xylene (VI) yields *m*-xylene exclusively as the product of electrolysis, and displays only a single polarographic reduction wave. Special resonance stabilization is not expected for *m*-xylyl diradical and the above data suggest that it is not formed.

Considerable resonance stabilization is predicted for *p*-xylylene by MO calculations.[7] Relative stability of *p*-xylylene is in fact shown by the observation that it has finite lifetime in the gas phase[8] and in solution.[9] The absence of an esr signal[10] suggests that it exists in the singlet state, as predicted by the MO theory, since the highest occupied orbital is not degenerate. A high degree of radical character at the 1 and 6 positions is expected from the free valence values calculated by Coulson,[11] and is demonstrated by its extreme reactivity.[10,12]

The Potential-Determining Step. At least two distinct mechanisms can be devised for the electrochemical generation of *p*-xylylene from α,α′-dibromo-*p*-xylene.

It has been shown by Gilch[13] that the α-halo-*p*-xylyl anion, proposed as an intermediate in mechanism A, rapidly loses halide ion to form *p*-xylylene. In either case, the *p*-xylylene reacts chemically to give the observed products, *ca.* 95% poly-*p*-xylylene (IX) and *ca.* 5% [2.2]paracyclophane (X). The intermediates of mechanism A have precedents in the analogous benzyl system. A radical anion has been postulated as the transition state for polarographic reduction of benzyl chlorides.[14] The isolation of bibenzyl from electrolysis of benzyl chloride[15] and of 4,4′-dinitrobibenzyl from electrolysis of *p*-nitrobenzyl bromide[16] has been taken to indicate the presence of radical intermediates. On the other hand, carbonation during electrolysis of benzyl bromide[17] produces small amounts of phenylacetic acid, suggesting the intermediacy of the benzyl anion. The major product (75%) in the latter case was, in fact, toluene, which also indicates an anionic intermediate. Mechanism A, therefore, is an extension to the *p*-xylyl dihalides of what has been considered[14] to be the mechanism for reduction of benzyl halides.

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(4) J. R. Schaefgen, *J. Polymer Sci.*, **15**, 203 (1965), and references cited therein.

(5) L. A. Errede, R. S. Gregorian, and J. M. Hoyt, *J. Am. Chem. Soc.*, **82**, 5218 (1960); L. A. Errede and J. P. Cassidy, *ibid.*, **82**, 3653 (1960); D. F. Pollart, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 12–17, 1965, p U24.

(6) L. A. Errede, *J. Am. Chem. Soc.*, **83**, 949 (1961).

(7) C. A. Coulson, *et al.*, *Discussion Faraday Soc.*, **2**, 35 (1947).

(8) M. Szwarc, *J. Polymer Sci.*, **6**, 319 (1951).

(9) L. A. Errede and B. F. Landrum, *J. Am. Chem. Soc.*, **79**, 4952 (1957).

(10) L. A. Errede and J. M. Hoyt, *ibid.*, **82**, 436 (1960).

(11) C. A. Coulson, *Discussions Faraday Soc.*, **2**, 9 (1947).

(12) J. R. Schaefgen, *J. Polymer Sci.*, **15**, 203 (1965).

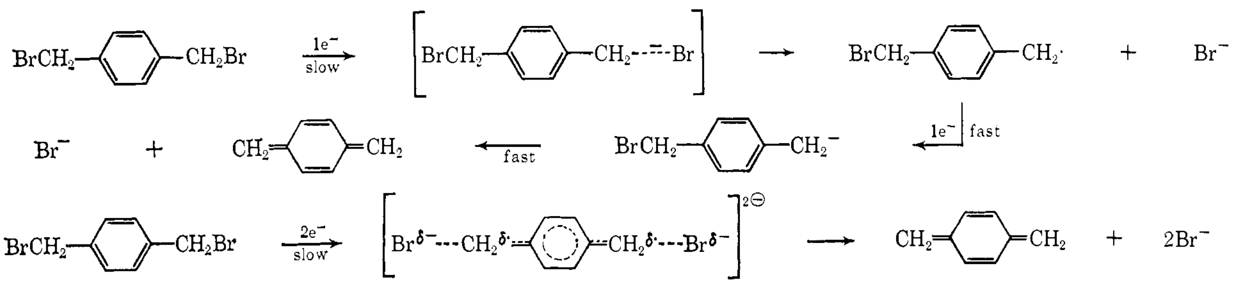
(13) H. G. Gilch and W. L. Wheelwright, Jr., *ibid.*, [A1] **4**, 1337 (1966).

(14) A. Streitweiser, Jr., and C. Perrin, *J. Am. Chem. Soc.*, **86**, 4938 (1964).

(15) (a) L. W. Marple, L. E. I. Hummelstadt, and L. B. Rodgers, *J. Electrochem. Soc.*, 107, 437 (1960). (b) It was pointed out by one of the referees that "the isolation of bibenzyl from the electrolysis of benzyl chloride[15a] is based on mass spectral data and is incorrect. Benzylmercuric bromide and dibenzylmercury formed in the electrolysis decompose while their mass spectra are being obtained to produce bibenzyl as the chief product." In the case of α,α′-dibromo-*p*-xylene, electrolysis at aluminum or copper cathodes was shown to produce the same products as at a mercury cathode, except that the polymer formed a coating on the surface of the solid electrode and thus prevented accurate measurement and control of the cathode potential. Also, preliminary voltammetric data obtained with a rotating platinum electrode indicate that the two-step reduction of α,α′-dibromo-*p*-xylene occurs at nearly the same potentials as measured at a mercury electrode. Therefore, the author believes that benzylmercuric intermediates are not formed in the electrochemical reduction of α,α′-dibromo-*p*-xylene at a mercury cathode.

(16) G. Klopman, *Helv. Chim. Acta*, **44**, 1908 (1961).

(17) S. Wawzonek, R. C. Duty, and J. H. Wagenknecht, *J. Electrochem. Soc.*, 107, 74 (1964).



(A)

(B)

Mechanism B differs fundamentally from A in that two electrons are involved in the transition state, generating p-xylylene in a concerted fashion, whereas mechanism A involves one electron. Both mechanisms correctly predict that a total of two electrons are consumed in the over-all process, and that p-xylylene is the key intermediate; therefore, analysis of polarographic wave height, identification of products, and measurement of the coulombic requirement, all of which indicate a two-electron over-all process, cannot distinguish between the two suggested mechanisms. Analysis of the polarographic wave form leads to a determination of αn_a as 0.28 for the first wave (α is the cathodic transfer coefficient; n_a is the number of electrons transferred in the slow, *i.e.*, potential-determining, step). However, since α values are relatively unpredictable for organic systems, the value of n_a cannot be assigned with confidence by this technique. Although the number of electrons transferred in the potential-determining step could not be directly measured, several factors, presented below, combine to suggest that mechanism B is operative in the first step of the electrochemical reduction of α,α'-dibromo-p-xylene.

The absence of 4,4′-bis(bromomethyl)bibenzyl (VIII) as either a product or an intermediate during the course of the electrolysis of α,α'-dibromo-p-xylene indicates that a benzyl-like radical cannot be present as a long-lived intermediate. Moreover, electrolysis of the title compound produces polymer predominantly, even when the electrolyte contains appreciable amounts of aqueous hydrochloric acid,[1] a fact which is difficult to reconcile with a carbanionic intermediate.

The most compelling argument in favor of mechanism B arises from consideration of half-wave potentials (Table I). The half-wave potential of α,α'-dibromo-p-xylene is 0.42 v more positive (*i.e.*, reduction is easier) than that of benzyl bromide, and 0.52 v more positive than that of α,α'-dibromo-m-xylene. A positive shift of this magnitude, corresponding to at least 10 kcal/mole of relative stabilization, is not surprising if the transition state for the former case possesses considerable xylylene character, as suggested by mechanism B. On the other hand, substituent effects, such as would be a factor in mechanism A, normally cause much less significant shifts. As an example, the half-wave potentials of p-chloro-, p-fluoro-, p-methoxy-, and p-methylbenzyl chlorides differ from that of benzyl chloride by only +0.124, +0.026, −0.025, and +0.01 v, respectively.[14]

A positive shift in half-wave potential has been taken to imply the occurrence of a concerted reaction in the reductive ring closure of bis-activated olefins.[18] Moreover, a xylylene-like intermediate has been proposed in the electrochemical reduction of p-diacetylbenzene[19a] and to account for the abnormally large positive shift (~0.4 v) in the polarographic reduction.[19b]

The conclusion, then, is that the observed large positive shift in half-wave potential for the first wave of α,α'-dibromo-p-xylene is a result of considerable xylylene character in the transition state of the electron transfer, thereby lowering the activation energy of the reduction. This implies that two electrons are transferred in a concerted fashion in the slow step, consistent only with mechanism B.

The transition state postulated for mechanism B does not imply that the electrons entered the molecule at opposite ends simultaneously, an occurrence which would undoubtedly be very unlikely. More probably, the electrons could be introduced by attack at a bromine or at a benzylic carbon or even at the aromatic ring. Distinctions between these alternatives cannot be made experimentally at present. However, since the starting material is symmetric and loses both bromine atoms to yield the symmetric product, p-xylylene, the author prefers to depict the transition state as a symmetric species, as shown.

The behavior of the unsymmetrically substituted p-xylene, N,N,N-triethyl-N-(4-bromomethyl)ammonium bromide (VII), indicates that it also reduces in a two-electron transfer to p-xylylene, as suggested by the fact that its half-wave potential is 0.43 v more positive than that of benzyl bromide and by the appearance of a second polarographic wave at $E_{1/2} = -1.72$ v. This latter value is equal to the half-wave potential of the second wave of α,α'-dibromo-p-xylene, the inference being that both compounds reduce *via* the same intermediate, p-xylylene, although the transition state for this case cannot be symmetric.

The Second Wave. Perhaps the most significant aspect of the polarographic behavior of α,α'-dibromo-p-xylene is the unexpected appearance of a second wave at −1.72 v. The wave is apparently related to the xylylene intermediate since only the *para*- and *ortho*-substituted xylenes display two waves. The *meta*-substituted compound, for which no stabilized xylylene structure is possible, reduces polarographically in the normal one-wave fashion to give m-xylene.

The concentration dependence of the limiting current of the second wave for α,α'-dibromo-p-xylene is also unusual. At low concentrations (*ca.* 0.3×10^{-3} M), the limiting current nearly equals that of the first wave, and hence must also represent an over-all two-electron transfer. At higher concentrations, the height of the second wave relative to that of the first decreases markedly. At 10^{-2} M, the height of the second wave is only about 5% of the height of the first wave. This

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(19) (a) R. H. Philp, Jr., R. L. Flurry, and R. A. Day, Jr., *J. Electrochem. Soc.*, 111, 328 (1964); (b) Y. Kargin, O. Mahousek, and P. Zuman, *J. Electroanal. Chem.*, 12, 443 (1966).

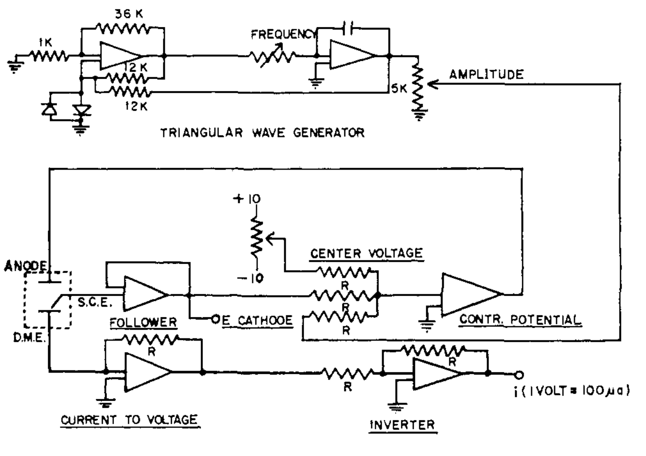
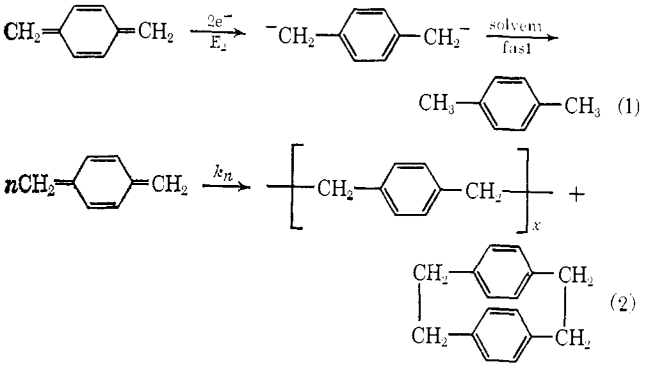


Figure 4. Apparatus for cyclic voltammetry.

type of behavior is generally explicable if the first intermediate is consumed rapidly in a parallel second- or higher order chemical reaction, so that it might compete effectively with the second electrochemical reaction only at high concentrations.

The above behavior can be explained qualitatively by the following mechanism.



The fate of the dianion, to the extent that it might be formed, would presumably be protonation by the solvent to yield *p*-xylene. At the concentration of the electrolyses (>0.05 *M*), the *p*-xylylene would be consumed by the chemical reaction (step 2) presumably faster than by the electrochemical reaction and, therefore, no detectable amount of *p*-xylene was formed. In fact, the second electrochemical reaction (step 1) which leads to *p*-xylene as the product could only be detected by polarography at low concentrations (<0.01 *M*), too dilute for preparative work.

It should also be pointed out that, in the case of α,α'-dibromo-*o*-xylene, reduction at highly negative potentials produced traces of *o*-xylene, presumably by protonation of the dianion. This fact supports the mechanism proposed above and suggests that *o*-xylylene is somewhat more stable chemically, *i.e.*, polymerizes more slowly, than *p*-xylylene, as indicated by the data of Errede.[6]

In addition to explaining qualitatively the concentration dependence of the second wave, the above mechanism also accounts for the higher value of αn_a calculated for the second wave, since bond cleavage is not involved in that step. In fact, one might expect some degree of reversibility for this electron transfer. Since the cyclic voltammetric data show that the second step is irreversible at sweep rates up to 100 Hz, this may imply that the dianion, formed only under polarographic conditions, is protonated extremely rapidly and irreversibly.

Experimental Section

Polarographic measurements were made using a Sargent Model XXI recording polarograph, modified for use as a three-electrode system by the standard operational amplifier technique. A Philbrick Model USA-3 amplifier was used for this purpose. The polarograph cell was the standard H type with the reference electrode in one isolated (fritted glass disk) compartment and the dme cathode and platinum wire anode in the other compartment. In all cases, a fiber-junction saturated calomel electrode (sce) was used as the reference. The electrolyte consisted of 0.1 *M* tetraethylammonium bromide (TEAB), purified by crystallization from ethanol-water and carefully dried, in N,N-dimethylformamide (DMF) as solvent, purified by distillation over anhydrous cupric sulfate. Prior to the addition of a weighed amount of the sample, dry nitrogen was purged through the electrolyte for at least 15 min. The measurements were carried out at an ambient temperature of 25 ± 2°. Most samples were commercially available and were purified by crystallization or distillation. Capillary characteristics were measured in the supporting electrolyte at several potentials by the usual technique of timing and weighing a fixed number of mercury drops.

Coulometric measurements were conducted in an H-type cell. The anode, a platinum wire or a graphite rod, was placed in an isolated compartment and further isolated by placing it within a ceramic thimble. A mercury pool, stirred by bubbling nitrogen just below the mercury surface, served as the cathode. A fiber-junction sce was used as the reference, and was positioned with its tip as close as possible to the cathode. Current was supplied through a cathode follower vacuum tube, driven by the control amplifier output of the polarograph. The number of coulombs passed was measured by integrating the voltage drop across a standard (0.1%) resistor placed in series with the anode. The integrator used a Philbrick Model P2A differential operational amplifier. With a low-leakage polystyrene capacitor in the feedback loop, the integrator was accurate to better than 1% at currents of less than 1 ma over periods as long as 5 hr. The progress of the electrolyses was followed polarographically.

Controlled potential electrolyses were performed with an Anotrol Model 4100 Research Controller. The electrolyte consisted of 0.1 *M* TEAB in DMF as solvent. The electrolysis cell consisted of a beaker containing a platinum insert at the bottom. A mercury pool, stirred with a magnetic stirring bar, served as the cathode. A fiber-junction sce, positioned with its tip as close as possible to the cathode surface, was used as the reference. The anode, either a platinum wire or a carbon rod, was isolated by placing it within a ceramic thimble. The initial currents for all the electrolyses were in the range 100–200 ma, requiring 20–40 v across the cell. The disappearance of starting material was followed polarographically, and the electrolyses were stopped when less than 5% of the starting material remained. The electrolyses lasted 5–10 hr.

The apparatus for triangular-wave cyclic voltammetry was constructed with operational amplifiers (Figure 4), a design which the author believes has not been previously reported. A slow dme (>15-sec drop time) was used and a fiber-junction sce was employed as the reference. Measurements of *i vs. E* were displayed on a Techtronix Model 561A oscilloscope using two Model 2A60 plug-in units as X and Y amplifiers. Polaroid photographs of the tracings were taken during the last part of the drop life.

Electrolysis of α,α'-Dibromo-*p*-xylene (III). A solution of 2.0 g (0.0076 mole) of α,α'-dibromo-*p*-xylene in 100 ml of DMF-0.1 *M* TEAB was exhaustively electrolyzed at −1.5 v. The precipitate was filtered and dried, leaving 0.82 g (92%) of polymer, identified as poly-*p*-xylylene by comparison of the infrared spectrum with that of an authentic sample prepared by D. D. Stewart of these laboratories by pyrolysis of [2.2]paracyclophane. The filtrate was diluted with 100 ml of methylene chloride and the resulting solution continuously extracted with water overnight. After evaporation of methylene chloride, a white solid remained. This was shown by vpc analysis (2 m, 10% silicone rubber on Chromasorb P) to consist mainly of [2.2]paracyclophane and some starting material. Traces of unidentified materials were also observed. The [2.2]-paracyclophane was isolated in pure form by preparative vpc and unambiguously identified by comparison of retention time, infrared spectrum, and melting point with the respective values of an authentic sample, obtained from D. D. Stewart of these laboratories by pyrolysis of *p*-xylene. Yield, based on vpc measurements, was 5%.

Electrolysis at −2.0 v gave essentially the same results as reported above, except that the polymer had a light green fluorescent color.

Electrolysis of α,α'-Dibromo-*m*-xylene (VI). With the apparatus described above, a solution of 2.0 g (0.0076 mole) of α,α'-dibromo-*m*-xylene was exhaustively electrolyzed at −2.0 v. The resulting solution was extracted with pentane. Evaporation of the pentane left a light yellow oil, which was shown to be a mixture of DMF and *m*-xylene by vpc and infrared analysis. Chromatography over alumina was quite effective in removing DMF, and 0.65 g (81%) of *m*-xylene was isolated.

Electrolysis of α,α'-Dibromo-*o*-xylene (V). Electrolysis of 2.0 g (0.0076 mole) of α,α'-dibromo-*o*-xylene was conducted in the apparatus described above and at a cathode potential of −0.9 v. A white solid formed during the electrolysis. Filtration yielded 0.41 g (51%) of poly-*o*-xylylene, which softened at 80° and had a nmr and infrared spectrum identical with that reported for poly-*o*-xylylene by Errede.[6] Extraction of the filtrate with pentane, followed by chromatography over alumina, left 0.3 g of an oil which could not be crystallized. Attempted distillation, vpc, and infrared analysis showed that the oil contained neither *o*-xylene nor benzcyclobutane.

Electrolysis of α,α'-dibromo-*o*-xylene at −2.0 v gave essentially the same results, except that a small amount (~4%) of *o*-xylene was isolated by distillation.

Electrolysis of 4,4'-Bis(bromomethyl)bibenzyl (IX). A solution of 2.0 g (0.0086 mole) of 4,4'-bis(bromomethyl)bibenzyl in 100 ml of 0.1 *M* TEAB–DMF was electrolyzed exhaustively at −2.0 v using a stirred mercury cathode. A small amount of white solid (~5 mg) separated as the electrolysis proceeded. The catholyte was diluted with 100 ml of methylene chloride; the resulting solution was continuously extracted with water for 10 hr. The methylene chloride was evaporated from the organic phase, leaving 1.1 g of light tan solid. Crystallization from heptane left 0.8 g (70%) of white solid, mp 78–80°. Infrared and nmr spectra confirmed the identity of this material as 4,4'-dimethylbibenzyl.

Preparation of N,N,N-Triethyl-N-(4-bromomethylbenzyl)ammonium bromide (VIII). To a stirred solution of 72.5 g (0.275 mole) of α,α'-dibromo-*p*-xylene in 1 l. of 3:1 v/v xylene–ethyl ether was added slowly (*ca.* 1 hr) 27.9 g (0.275 mole) of triethylamine. The suspension was stirred for *ca.* 0.5 hr at room temperature after the addition had been completed. The precipitate was filtered and washed with ether. The filtrate gave 43 g of starting material by recrystallization from heptane. The precipitate was triturated with hot heptane, refiltered, and dried. This left 40 g (90% based on reacted starting material) of amorphous white solid, mp 173–175°, and completely soluble in cold water.

Photoreduction of *p*-Dimethylaminobenzophenone. Effect of Acid[1,2]

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Abstract: *p*-Dimethylaminobenzophenone (DMABP) is photoreduced inefficiently in 2-propanol, $\varphi \sim 0.004$, and appears to be inert in 1:1 2-propanol–water. Its intense charge transfer absorption band at 352 mμ (ϵ ~24,000) in 2-propanol, is decreased with protonation by HCl, and is replaced by a weak n → π^* band of the protonated base at 344 mμ (ϵ ~190). Photoreduction increases with protonation to $\varphi \sim 0.5$–0.6 at 1–2 *N* HCl in 2-propanol. At low acidities rates appear proportional to the light absorbed by the protonated base. Photoreduction is less efficient in aqueous acidic 2-propanol. Photoreduction in acidic 2-propanol leads to an almost quantitative yield of the pinacol. The reaction proceeds by a normal free-radical mechanism and is strongly retarded by aromatic mercaptans, mesityl mercaptan, and *p*-dimethylaminothiophenol, present in low (10^{-3}–10^{-2} *M*) concentration.

The photoreduction by alcohols of benzophenone, acetophenone, and certain of their substitution products proceeds readily[3,4] *via* abstraction of hydrogen by the first excited n → π^* triplet of the ketone[5] (eq 1).

$$\mathrm{RR'C{=}O^* + R''_2CHOH \longrightarrow RR'\dot{C}OH + R''_2\dot{C}OH} \qquad (1)$$

Amino- and hydroxybenzophenones do not undergo photoreduction efficiently in alcohols,[6,7] their lowest lying triplet states in these solvents being chemically unreactive $\pi \rightarrow \pi^*$ or charge transfer[8] (CT) rather than n → π^*. Such ketones undergo photoreduction with low quantum yield in an aliphatic hydrocarbon in which the lowest lying triplet state may be n → π^* and chemically reactive.[8a,9] *p*-Aminobenzophenone may be photoreduced efficiently, $\varphi \sim 0.5$, by tertiary amines in hydrocarbon solvent, the amine providing heteroatom activation for abstraction of hydrogen and the nonpolar solvent permitting the n → π^* triplet state to be occupied.[9]

p-Dimethylaminobenzophenone (DMABP) has important contributions in the ground state from forms I and II. Similarly, electron donation by the amino group may cause the chemically unreactive CT excited state, related to II, to be of lower energy and favored in polar media. Photoreduction in aqueous and other polar media is of interest to us, intrinsically and in relation to our study of inhibition of photochemical and

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(1) We are pleased to acknowledge generous support of this work by the U. S. Atomic Energy Commission, AT(30-1)2499.

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