

sulfur trioxide can bring about the conversion of **19** to **20**. Voltammetric measurements (Table VI and Figure 5) virtually rule out such oxidation mechanisms. For example, the proton adduct of DPA is oxidized at a platinum electrode with a peak potential of +2.73 V vs. the sce in dichloromethane containing FSO₃H (7%) while DPA⁺ is reduced irreversibly at +1.20 V to produce DPA which is immediately protonated. This would imply that the oxidation of unprotonated DPA should occur with a peak potential of about +1.26 V in the latter medium which compares favorably to the observed values of +1.23, +1.27, and +1.27 in neutral acetonitrile, nitrobenzene, and dichloromethane, respectively (Table II). Thus, the proton adduct is oxidized about 1.5 V more anodic than is DPA. Protonated forms of DTA and DEA are likewise much more difficultly oxidized than the corresponding substrates. These results suggest that oxidation of protonated aromatic compounds is a very unfavorable process and that oxidation of aromatic hydrocarbons on dissolving in strong acid proceeds by reaction of the unprotonated form (**18**) which exists in equilibrium with the proton adduct (**19**).

In dichloromethane containing FSO₃H (7%), the

proton adduct of DEA is stable at room temperature while the corresponding adducts of DPA and DTA are short lived, having half-lives of the order of 5 min. In the latter two cases, it was necessary to extrapolate to the time of mixing in order to obtain extinction coefficients. The instability appears to be connected with the aromatic groups substituted at the 9 and 10 positions and suggests sulfonation⁴⁸ as the substrate consuming reaction since FSO₃H has recently been shown to be a potent sulfonation agent.⁴⁹

In conclusion, it should be pointed out that the observation of oxidation of proton adducts, reversible cation radical-dication redox equilibria, the "elusive" monocations derived from ECE reactions, and the cathodic ECE reaction of the monocations which is the reverse of the ECE mechanism of anodic substitution has only been described for the "model" system, 9,10-disubstituted anthracenes. However, we feel that these "model" systems can be referred to with confidence in interpreting results of other anodic electrode processes.

(48) It is of interest to note that DPAH⁺ disappears according to a second-order rate law while the consumption of DTAH⁺ is cleanly first order. These reactions are being investigated.

(49) U. Svanholm and V. D. Parker, *J. Chem. Soc., Perkin Trans. 2*, 962 (1972).

Electrochemical Oxidation of the Enolate of Dibenzoylmethane

H. W. VandenBorn and Dennis H. Evans*

Contribution from the Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706. Received October 31, 1973

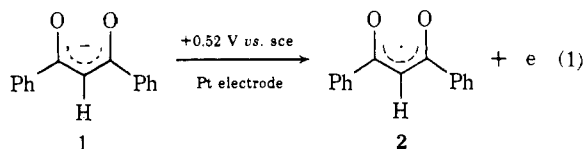
Abstract: The anodic oxidation of the enolate of dibenzoylmethane, **1**, at platinum anodes in dimethyl sulfoxide as solvent has been studied by cyclic voltammetry, controlled potential coulometry, and analysis of electrolytic products. The oxidation proceeds in an initial one-electron step forming the dibenzoylmethyl radical, **2**. Radical **2** is short-lived, reacting by dimerization to 1,1,2,2-tetrabenzoylthane (**4**) and by hydrogen atom abstraction forming dibenzoylmethane **3**. As expected, the fraction of **2** reacting by dimerization increases as the concentration of **1** is increased. Though **3** and **4** are the products formed at short times, complete electrolysis of the solution produces tetrabenzoylthylene (**7**) and additional **3**. **7** is formed from **4** by proton transfer from **4** to unreacted **1** followed by anodic oxidation of the resulting anion to **7**. The hydrogen abstraction reaction of **2** was suppressed when benzonitrile was used as solvent. The cathodic reduction of 2-bromo-1,3-diphenyl-1,3-propanedione was also studied. Both the two-electron product, **1**, and the 1,3-diketone, **3**, were formed. Radical **2** is probably an intermediate in this reduction.

The electrochemical oxidation of the anions of esters, 1,3-diketones, and nitroalkanes has been investigated by numerous workers.¹ Dimeric products are often formed in good yield but other products are also found.²⁻⁶ The relevant experimental conditions governing the type and distribution of products have not been established and very little information is available concerning the individual steps in the reaction sequence. In this paper we report a voltammetric

study of the anodic oxidation of the enolate of dibenzoylmethane, **1**, at platinum electrodes in dimethyl sulfoxide (DMSO) as solvent.

Results and Discussion

Cyclic Voltammetry. The electrochemical oxidation of **1** was studied using its tetra-*n*-butylammonium salt. The observed oxidation is consistent with a one-electron oxidation to the neutral radical, **2**, which reacts



very rapidly via two competing chemical reactions. One of these is hydrogen abstraction by the radical to

(1) (a) N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68**, 449 (1968); (b) K. Nyberg in "Organic Electrochemistry," M. M. Baizer, Ed., Marcel Dekker, New York, N. Y., 1973, pp 718-724.

(2) S. P. Mulliken, *Amer. Chem. J.*, **15**, 523 (1893).

(3) T. D. Binns and R. Brett, *J. Chem. Soc. C*, 336 (1966).

(4) R. G. Cooks, D. H. Williams, K. M. Johnston, and J. D. Stride, *J. Chem. Soc. C*, 2199 (1968).

(5) R. Brett and D. Seddon, *J. Chem. Soc. C*, 2175 (1970).

(6) T. E. Neal, Ph.D. Thesis, University of North Carolina, Chapel Hill, 1970.

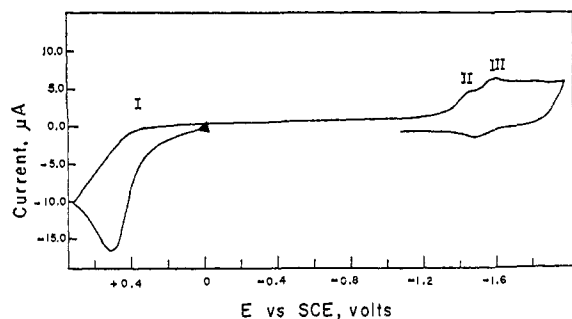
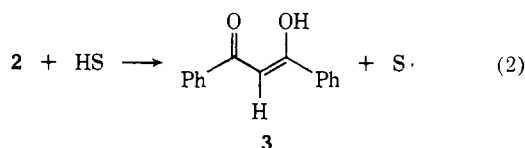


Figure 1. Cyclic voltammogram of 2.54 mM **1**. 0.10 M TEAP in DMSO. Scan rate: 0.200 V/sec. Scan initiated at arrowhead.

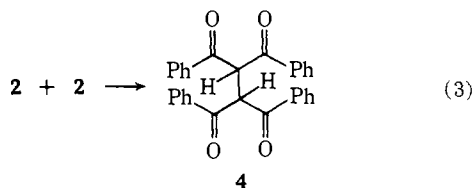
form dibenzoylmethane **3**. (The fate of **S** was not determined.) The more stable enol form of **3** is shown though it is not known whether this is the tautomer initially formed in reaction 2 (Scheme I). The other

Scheme I



reaction involves dimerization at the central carbon to form a dimer, 1,1,2,2-tetrabenzoylthane (**4**) (Scheme II).

Scheme II



The electrochemical oxidation of the enolate **1** to the radical **2** was studied using cyclic voltammetry. As shown in Figure 1, a single, irreversible oxidation wave, I, is observed with a peak potential of about +0.5 V. At scan rates up to 210 V/sec, no reduction peak for the radical **2** was observed. This indicates that the reactions consuming **2** are very rapid, having sub-millisecond half-lives.

The characteristics of oxidation peak I were studied as a function of scan rate over the range of 0.05–50 V/sec. The peak potentials and peak current functions are presented in Figure 2. When the peak current function is inserted in the theoretical expressions,^{7,8} the diffusion coefficient of the enolate **2** is computed to be $2\text{--}3 \times 10^{-6} \text{ cm}^2/\text{sec}$ if the process is assumed to involve the transfer of one electron. The value obtained depends on the overall mechanism chosen, e.g., a pseudo-first-order reaction⁷ or a dimerization⁸ following the electron transfer. The range of values obtained is similar to the diffusion coefficients of other molecules in this medium.^{9,10} Thus the peak current function is consistent with the postulated one-electron oxidation of **1**.

(7) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

(8) M. L. Olmstead, R. G. Hamilton, and R. S. Nicholson, *Anal. Chem.*, **41**, 260 (1969).

(9) R. C. Buchta and D. H. Evans, *J. Electrochem. Soc.*, **117**, 1494 (1970).

(10) J. P. Zimmer, J. A. Richards, J. C. Turner, and D. H. Evans, *Anal. Chem.*, **43**, 1000 (1971).

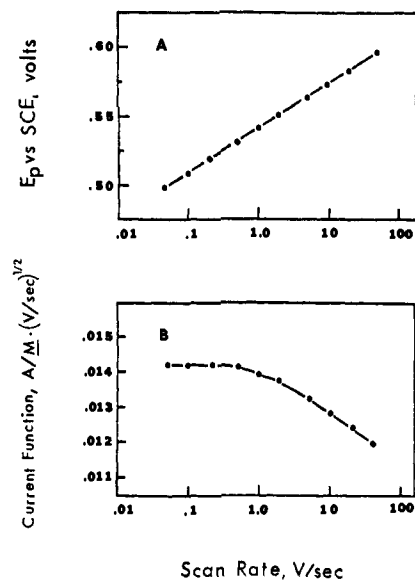


Figure 2. Peak potential (A) and peak current function (B) for oxidation of **1** as functions of scan rate; 1.97 mM **1**; 0.10 M TEAP in DMSO. Peak current function = $i_p/Cv^{1/2}$ where i is the peak current, C is the concentration of **1**, and v is the scan rate.

The products formed by the reactions of the radical **2** were postulated to be the 1,3-diketone **3** and the dimer **4**. These two products were tentatively identified from the two peaks, II and III, at -1.45 and -1.55 V on the return scan of Figure 1. The cyclic voltammetry of **3** has previously been studied in detail⁹ and the peak potential of -1.45 V agrees with that reported. The dimer **4** was found to give an irreversible reduction wave at -1.55 V vs. sce with a difference between the peak and half-peak potential of 70 mV.

The heights of peaks II and III might seem at first to be too small to correspond to 100% of the products formed at oxidation peak I. They are small because on the return scan a significant amount of time is required to change the potential from +0.2 V to the region of waves II and III. During this time, the formation of products has ceased and the **3** and **4** formed during wave I are able to diffuse away from the electrode causing II and III to be rather small peaks. Digital simulation¹¹ of this process shows that the observed peak heights are close to their theoretical values.

Controlled Potential Electrolysis. Controlled potential coulometry gave an average n value for three electrolyses of 0.98 ± 0.03 . The final electrolysis solutions were expected to contain a mixture of **3** and **4**. However, this was not the case.

In Figure 3 is shown a cyclic voltammogram of a solution of **1** that had previously been completely oxidized by controlled potential electrolysis at +0.7 V. From the peaks observed it is concluded that **3** is present as expected (cathodic peak at -1.45 V; anodic peak at -1.39 V) but no dimer **4** is observed. However, a new reduction peak is present at -0.7 V indicating that a new species has been formed during the coulometric experiment. This new peak is due to tetrabenzoylthylene.

The tetrabenzoylthylene (**7**) is formed in a series of reactions from the dimer **4**. The dimer is postulated to

(11) S. F. Feldberg in "Electroanalytical Chemistry," Vol. 3, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1969, pp 199–296.

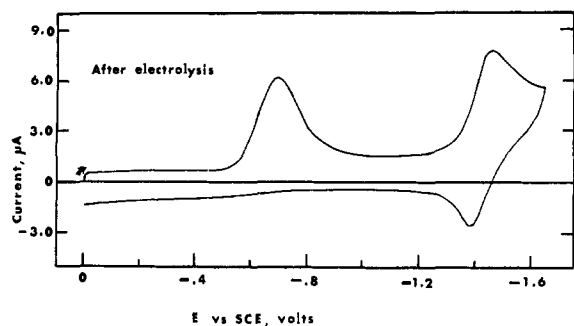
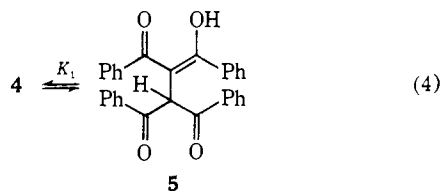
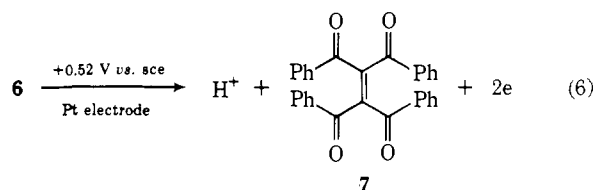
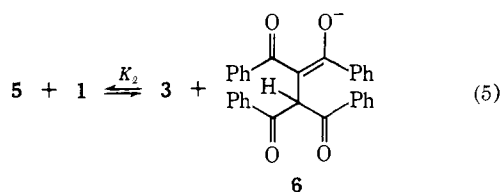


Figure 3. Cyclic voltammogram of solution after anodic oxidation of **1**; 2.24 mM **1** and 0.10 M TEAP in DMSO completely oxidized at +0.7 V. Cyclic voltammogram obtained after electrolysis. Scan rate: 0.200 V/sec. Scan initiated at arrowhead.

undergo tautomerism to its enol form, **5** (reaction 4).



This reaction is postulated to be quite slow to account for the fact that tetrabenzoyl ethylene is not detected in a cyclic voltammogram of **1**. Once the enol, **5**, is formed it can transfer a proton to the starting material, **1** (reaction 5), to form 1,3-diketone **3** and the enolate of the dimer, **6**. This enolate is quite similar in structure to the starting material and would also be expected to undergo oxidation. It oxidizes at the same potential as **1** in a two-electron step to form the final product, tetrabenzoyl ethylene (reaction 6). Overall, Scheme II



(reactions 1 and 3–7) can be written as



Thus, the overall stoichiometry (eq 8) is consistent with the coulometric experiments, *i.e.*, one electron is produced for each molecule of starting material. Thus coulometry cannot distinguish the relative importance of hydrogen abstraction reaction 2 and dimerization 3 as each scheme has an *n* value of 1. This question can be answered only through chemical analysis of the electrolysis solutions.

The curious fact that a formal two-electron oxidation product, tetrabenzoyl ethylene, is formed in an overall one-electron process finds its origin in reactions 5 and 7 where the enolate **1** is converted to neutral diketone **3**

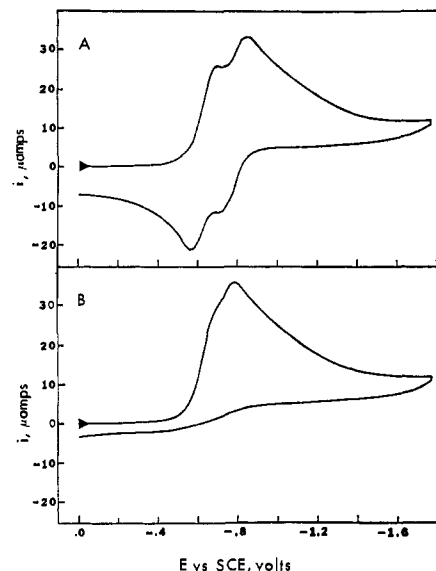


Figure 4. Cyclic voltammogram of 2.43 mM tetrabenzoyl ethylene. (A) Scan rate 0.50 V/sec; 0.10 M TEAP in DMSO. Scan initiated at arrowhead. (B) Same as A but 2.36 mM dibenzoylmethane added.

by the protons produced in the reaction. Product **3** is not oxidizable at the operating potential.

Characterization of the Products. The reactions outlined above were studied by a variety of techniques. A cyclic voltammogram of tetrabenzoyl ethylene (**7**) is presented in Figure 4A. The shape of this voltammogram corresponds to a stepwise reduction of **7** to its anion radical and dianion on the forward scan and stepwise oxidation of these species on the reverse scan.¹² The formal potentials of the neutral **7**/anion radical and anion radical/dianion couples are separated by about 150 mV. Though the reduction peaks in Figure 4A occur in the proper region of potential, the shape does not compare well with the reputed wave for **7** in Figure 3.

However, the cyclic voltammogram of tetrabenzoyl ethylene in Figure 3 was obtained in the presence of **3** which was produced during the coulometry. Therefore, a quantity of **3** equivalent to the amount of **7** present was added to the solution and the cyclic voltammogram under these conditions is shown in Figure 4B. There is a noticeable difference between Figures 4A and 4B. The effect of the **3** has been to cause the two peaks in Figure 4A to merge into one broad irreversible peak. The addition of more **3** caused the peaks to merge more completely so that the shoulder seen in Figure 4B disappeared. This broad peak is quite similar to the one shown in Figure 3 obtained after coulometry. The effect of **3** is probably due to its proton donor ability. Protonation of the radical anion and/or dianion of **7** by **3** causes the separate peaks of Figure 4A to merge and become irreversible. In the process, **3** is converted to **1** so a reduction peak for **3** at -1.45 V is not present in Figure 4B.

The voltammetric identification of **3** and **7** as products was confirmed by chromatographic analyses (see below).

To provide evidence for reactions 4 and 5, the relative *pK_a* values of **3** and **4** were determined by titration with tetra-*n*-butylammonium hydroxide in DMSO.

(12) D. S. Polcyn and I. Shain, *Anal. Chem.*, **38**, 370 (1966).

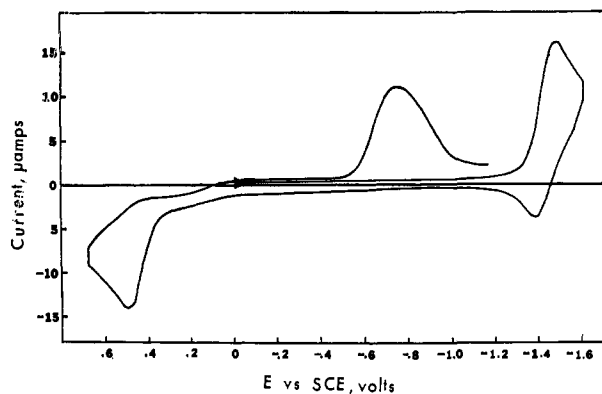


Figure 5. Cyclic voltammogram of a mixture of **1** and 1,1,2,2-tetrabenzoyl ethane. 2.25 mM **1** and 2.13 mM tetrabenzoyl ethane in DMSO, 0.20 M TEAP. Scan rate: 0.20 V/sec. Scan initiated at arrowhead.

Titration of **3** showed one sharp inflection point at 1 equiv of base. This is as expected because **3** has only one enolizable proton. Titration of the dimer **4** showed one sharp inflection point at 1 equiv of base and a second broad inflection point after the addition of 2 equiv of base. This indicates that two protons on **4** can be removed by hydroxide ion. The difference in the half-titration points for **3** and the first proton of **4** was 80 ± 5 mV in the direction indicating **3** to be less acidic than **4**.

As shown in the experimental section, **4** is principally in the keto form. Hence, its acidic properties may be thought of as a combination of equilibrium constants for tautomerization of **4** (reaction 4) and ionization of the resulting enol. The titration data reveal the relative acidities of **3** and **4** and permit the calculation of the product K_1K_2 from reactions 4 and 5. The experimental difference in half-titration potentials of 80 mV corresponds to $K_1K_2 = 23 \pm 5$. This value indicates that as **4** is produced during electrolysis it potentially can react with starting material giving enolate **6** and final product **3**.

Further evidence for this is provided by Figure 5 which shows a cyclic voltammogram of approximately equimolar **4** and **1**. These were allowed to equilibrate for 20 min. The initial scan toward negative potentials reveals a peak for the reduction of **3**. Upon returning the potential to positive values the normal⁹ oxidation peak for the anion radical of **3** is observed and an oxidation peak for enolate **6** (and any unreacted **1**) is seen at +0.5 V. Finally, on the second negative scan a peak for the reduction of the tetrabenzoyl ethylene formed by oxidation of **6** is seen at -0.7 V. This experiment provides further support for the importance of reactions 4 and 5 in that it shows that the dimer **4** can react with starting material **1** as indicated by the disappearance of the peak for **4** (-1.55 V) and the appearance of the peak of **3**.

The experiment also provided qualitative information concerning the rates of reactions 4 and 5. A cyclic voltammogram obtained immediately after the preparation of an equimolar mixture of **1** and **4** shows a large peak at -1.55 V for the reduction of **4** but only a small peak at -1.45 V for the reduction of **3**. After 10 min the reaction was complete. The peak for **4** had disappeared and that of **3** had reached the full height shown in Figure 5. Thus the overall rate of reactions

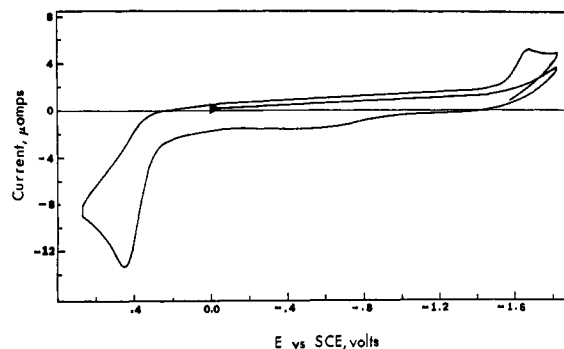


Figure 6. Cyclic voltammogram of **1** in benzonitrile. 1.65 mM **1** and 0.10 M TEAP. Scan rate: 0.25 V/sec. Scan initiated at arrowhead.

4 and **5** is not large explaining the fact that no tetrabenzoyl ethylene is formed on the time scale of a single cyclic voltammogram.

The oxidation of enolate **6** (reaction 6) was characterized by preparing a solution of **6** through treatment of **4** with 1 equiv of tetra-*n*-butylammonium hydroxide. The resulting solution showed an irreversible oxidation peak at +0.52 V due to the formation of tetrabenzoyl ethylene whose reduction peak was detected on the reverse scan.

The relative importance of the hydrogen atom abstraction reaction 2 and dimerization 3 was assessed by determining the concentrations of **3** and **7** in the final electrolysis solutions obtained by oxidation of enolate **1**. The results are presented in Table I. As expected, the

Table I. Percentage of **2** Reacting *via* Schemes I and II

[1], mM ^a	[3]/[7] ^b	Scheme I, % ^c	Scheme II, % ^c
0.95	7.2	72	28
2.24	4.8	58	42
2.33	5.0 ^d	60	40
5.55	2.4	17	83

^a Concentration of enolate of dibenzoylmethane at beginning of controlled potential electrolysis experiment. Solvent: DMSO with 0.10 M TEAP. Electrolysis performed using platinum electrode at +0.7 V *vs.* sce. ^b Ratio of concentration of dibenzoylmethane **3** to tetrabenzoyl ethylene (**7**) after electrolysis. Obtained from ratio of limiting currents in DME polarography. ^c Percentage of **2** consumed by reaction scheme. ^d Identical ratio obtained by liquid chromatography.

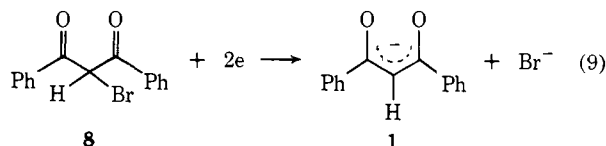
relative importance of the dimerization increased as the initial concentration of **1** was increased.

Reduction in Benzonitrile. The source of hydrogen atoms in reaction 2 could be residual water, tetraethylammonium ions, or the solvent, DMSO. Feeling that the solvent was the most probable hydrogen atom donor, a cyclic voltammogram of **1** was obtained in benzonitrile, a poor hydrogen atom donor. The result is presented in Figure 6. The initial scan in the negative direction shows a general increase in background current near -1.8 V and the return scan shows a flat peak near -0.6 V. These were detected in a cyclic voltammogram of benzonitrile and TEAP and they are attributed to impurities in the solvent. The main oxidation peak occurs at +0.45 V. Only a single reduction peak at -1.67 V is observed on the return scan. This peak is identical with that obtained with authentic

4. No peak for the product from hydrogen atom abstraction, **3**, was found. When **3** was added to the solution, a new reduction peak at -1.57 V was obtained. Clearly very little if any **3** is produced upon oxidation of **1** in benzonitrile containing 0.10 M tetraethylammonium perchlorate suggesting that DMSO is the source of hydrogen atoms in the earlier experiments.

Controlled potential coulometry of **1** in benzonitrile gave $n = 1.01$ and a ratio of **3/7** of 1.98 in the final electrolysis solution indicating 100% dimerization.

Other Experiments. As an alternative method of generating the reactive neutral radical, **2**, the reduction of 2-bromo-1,3-diphenyl-1,3-propanedione (**8**) was stud-



ied. The cyclic voltammogram of **8** features a broad, irreversible peak at -0.28 V. By analogy with other halogenated compounds,¹³ **8** might be expected to be reduced in a one-electron process to its radical anion which rapidly cleaves to produce radical **2** and bromide ion. **2** could then be reduced to the enolate **1**. The E^0 of the **2/1** couple could not be determined from the oxidation of **1** because **2** is never present in sufficient quantity (due to its reactivity) to observe its reduction peak. However, in view of the fact that the peak potential for the oxidation of **1** to **2** is about $+0.5$ V and the reduction of **8** occurs at -0.3 V, it is likely that any **2** formed during the reduction of **8** could be reduced to **1**. This represents an overall two-electron transfer.

From the known reactions of **2** observed during the oxidation **1**, two other reactions are likely, namely, hydrogen atom abstraction and dimerization as in Schemes I and II.

The cyclic voltammogram of **8** has a prominent reduction peak for **3** at -1.45 V and an oxidation peak for **1** on the return scan indicating that radical **2** undergoes competitive reduction to **1** and hydrogen abstraction producing **3**. No dimer **4** was detected.

Controlled potential coulometry of 2.13 mM **8** at -0.60 V yielded an n value of 1.54 . Polarographic analysis of the electrolysis solution yielded a ratio of **3/1** of 0.96 . This corresponds to an n value of 1.51 . Thus hydrogen atom abstraction and further reduction of **2** are about equally important in this reduction. The coulometric experiment was repeated at -1.10 V with the intention of causing the reduction of **2** to be predominant because of the more negative potential. The n value was 1.60 , far from the 2.0 expected for a reaction proceeding completely by overall reaction 9. Similarly, at -0.25 V an n value of 1.40 was obtained. Thus the product distribution is not strongly dependent on potential.

The data obtained in this research show that the oxidation of **1** produces a radical which undergoes hydrogen atom abstraction and dimerization. The dimer is susceptible to tautomerization, loss of a proton, and further oxidation to tetrabenzoyl ethylene. Thus the distribution of products in the anodic oxidation of **1** and other anions will depend not only on the reactions of the initially formed radicals but also on the acid-

(13) M. R. Rifi in ref 1b, pp 279-314.

base and redox properties of the dimer formed by radical coupling.

Experimental Section

Cyclic voltammetric experiments were performed with a Princeton Applied Research (PAR) Model 170 electrochemistry system, an instrument described by Whitson,¹⁴ or a computer-based system described earlier.¹⁵ The computer system was used in all rapid scan rate studies and the effects of solution resistance were compensated electronically.¹⁵ The PAR 170 was used for dropping mercury electrode polarography.

Controlled potential coulometric experiments were performed using a PAR Model 173 potentiostat or the PAR 170 electrochemistry system. Current-time data were recorded on a Sargent SR Y-T recorder (5 min/in.) when using the PAR 173 potentiostat. Areas under the current-time curves were measured using a Gelman Model 39321 planimeter.

The proton nmr spectrum of the dimer, tetrabenzoyl ethane, was obtained on a Varian XL100 spectrometer equipped with Fourier transform and signal averaging capabilities. The uv spectra were obtained on a Cary 14 spectrophotometer.

Liquid chromatography data were obtained on a Varian series 4000 liquid chromatograph with a Varian 4000-01 uv detector. The pressure on the solvent was maintained constant at about 100 psi. For the case of the controlled potential electrolysis mixture containing TEAP, DMSO, dibenzoylmethane **3**, and tetrabenzoyl ethylene (**7**), the mobile phase used was a 65:35% (v/v) mixture of water-acetonitrile. The column packing was Corasil II (Waters). Under these conditions, three peaks, corresponding (in order of elution) to DMSO, **7**, and **3**, were observed. The TEAP was not detected. Quantitative analysis was achieved by comparison of the areas of the **3** and **7** peaks to those of a standard solution containing **3**, **7**, and 0.10 M TEAP in DMSO.

The voltammetric cell has been described.¹⁶ An aqueous saturated calomel electrode (sce) was used as a reference electrode. The cell used for controlled potential electrolysis was a 250-ml lipless beaker fitted with a Teflon lid. The Teflon lid had a number of holes which allowed insertion of electrodes and a glass deaeration tube. The counter electrode was in a separate compartment and made contact with the working electrode compartment through a fine porosity fritted glass disk. The platinum working electrode for controlled potential electrolysis was a circular platinum disk with a radius of 2.5 cm and thickness of about 0.1 mm. Contact to the disk was made *via* a stout platinum wire spot welded to the disk. Both sides of the disk were exposed to the solution.

For cyclic voltammetric studies a Beckman type 39281 planar platinum electrode was used. Its area was determined to be 0.030 cm² by comparison of the cyclic voltammetric peak currents obtained for *p*-nitrotoluene reduction using both the platinum working electrode and a hanging mercury drop electrode of known area. In this work no fouling of the platinum electrode surface was noted so that cleaning of the surface between experiments was unnecessary.

Analysis of electrolysis solutions by dropping mercury electrode polarography was performed by comparing the limiting diffusion currents for the reduction of **7** and **3** with the diffusion currents obtained with a standard solution. The polarographic determination of **1** was based on its anodic wave. Identification of the electrolysis products was based on the agreement of the half-wave potentials with those of the standard solution and agreement between the liquid chromatographic retention times of the peaks for the electrolysis solution with the retention times of authentic samples.

Spectroquality DMSO (Matheson Coleman and Bell) was used as received. The residual water in the DMSO was approximately 30 mM as determined by gas chromatography. Deuterated DMSO (Stohler Isotope Chemicals) was used as received. Benzonitrile (Aldrich) was vacuum distilled once from phosphorus pentoxide as recommended by Adams.¹⁷

The supporting electrolyte, tetraethylammonium perchlorate (TEAP), was prepared as described¹⁸ from tetraethylammonium bromide (Eastman) and reagent grade sodium perchlorate. The

(14) P. E. Whitson, Ph.D. Thesis, University of Wisconsin, Madison, 1974.

(15) P. E. Whitson, H. W. VandenBorn, and D. H. Evans, *Anal. Chem.*, **45**, 1298 (1973).

(16) R. C. Buchta and D. H. Evans, *Anal. Chem.*, **40**, 2181 (1968).

(17) R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969, p 31.

(18) I. M. Kolthoff and J. F. Coetzee, *J. Amer. Chem. Soc.*, **79**, 870 (1957).

TEAP was recrystallized three times from triply distilled water and dried at 100°.

The tetra-*n*-butylammonium salt of the enolate of dibenzoylmethane was prepared as described¹⁶ by the reaction of tetra-*n*-butylammonium hydroxide (Matheson Coleman and Bell) and dibenzoylmethane.

1,1,2,2-Tetrabenzoylthane (**4**) was prepared as described¹⁹ by the addition of 2-bromo-1,3-diphenyl-1,3-propanedione (Eastman) to a solution of sodium iodide in acetone. The crystals that formed were washed with water and methanol. The white crystals (yield: 20%) had mp 208–211° (lit.¹⁹ 204–208°). High-resolution mass spectrometry gave *m/e* 446.152 for the parent peak (calcd for C₃₀H₂₂O₄, 446.152).

Though **4** is quite insoluble, a suitable nmr spectrum was obtained from a 2 mM solution in DMSO-*d*₆. The spectrum showed two broad multiplets at δ 7.95 and 7.69 ppm corresponding to the phenyl protons. A singlet for the central methine protons was found at δ 6.70. Integration gave a value of 0.081 for the ratio of the area of the singlet to the total area for all the protons. For **4** in the keto form the ratio should be 2:22 or 0.091. The region of 14–17 ppm was searched for a possible enol proton resonance^{9,20} but none was found. On this basis, it is quite certain that the dimer is predominantly (> 80%) in the keto form.

Qualitative interpretation of the uv spectrum of **4** (in acetonitrile) in comparison to the uv spectrum of dibenzoylmethane and 2,2-dimethyl-1,3-diphenyl-1,3-propanedione also supported the above conclusion. Dibenzoylmethane is known⁹ to be predominantly in

the enol form while the dimethyl derivative can only exist in the keto form. Dibenzoylmethane has a relatively strong uv absorption band centered at 340 nm while the dimethyl derivative has a band at 247 nm and none at 340 nm. The spectrum of **4** shows a band at 250 nm but none at 340 nm supporting the conclusion that **4** exists in the keto form.

Tetrabenzoylthane (**7**) was prepared by the oxidation of **4** with chlorine.²¹ Chlorine gas was bubbled for approximately 2 hr through a solution of 0.2 g of **4** in 10–15 ml of chloroform containing an equivalent amount of tetra-*n*-butylammonium hydroxide. The solution was then washed with aqueous solutions of Na₂CO₃, Na₂SO₄, and finally with water, and then dried over MgSO₄. Most of the chloroform was removed by evaporation and white crystals of **7** formed overnight, mp 183–185° (lit.²¹ 184°). The infrared spectrum corresponded to that reported.²² Tetrabenzoylthane is fluorescent and light sensitive, turning yellow in 1–2 days time.^{21,22} The 2,2-dimethyl-1,3-diphenyl-1,3-propanedione was prepared earlier.²³

Solutions were deaerated with nitrogen. The solution temperature was 24 ± 1° for all electrochemical experiments.

Acknowledgment. This research was supported by the National Science Foundation, Grant No. GP-19579. Most of the computer equipment was obtained through National Science Foundation Grant No. GP-12221. H. W. V. was an American Oil Foundation Fellow (1972–1973).

(19) H. von Halban and H. Geigel, *Z. Physik. Chem.*, **96**, 233 (1920).

(20) H. Schmid, M. Hochweber, and H. von Halban, *Helv. Chim. Acta*, **31**, 1899 (1948).

(21) R. C. Buchta and D. H. Evans, *J. Org. Chem.*, **35**, 2844 (1970).

(19) Von Leopold Wolf and C. Tröltzsch, *J. Prakt. Chem.*, [4] **17**, 69 (1962).

(20) J. L. Burdett and M. T. Rogers, *J. Amer. Chem. Soc.*, **86**, 2105 (1964).

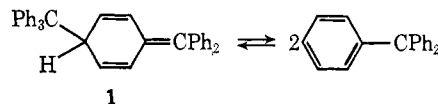
o- and *p*-Semibenzene Dimers of Benzylic Radicals. Autoxidation of Quinoid Dimers¹

Karen J. Skinner,^{2a} Howard S. Hochster, and J. M. McBride*^{2b}

Contribution from the Department of Chemistry, Yale University,
New Haven, Connecticut 06520. Received December 21, 1973

Abstract: Dimerization of benzyl radicals substituted at the α position with (a) two methyl groups, (b) two ethyl groups, or (c) one methyl and one isopropyl group gave the following distribution of isomers: α - α (1,2-diphenylethane): α -ortho (*o*-semibenzene): α -para (*p*-semibenzene) = (a) 1:0.1:0.2, (b) 1:0.04:0.6, (c) 1:0.02:0.6. The radicals were generated by photolysis or thermolysis of the related azoalkanes. The order of increasing stability to homolysis is *o*-semibenzene < *p*-semibenzene \approx azoalkane. The *o*-semibenzenes were identified by uv ($\lambda_{\max} \sim 315$ nm), the *p*-semibenzenes by uv ($\lambda_{\max} \sim 265$) and pmr and by autoxidation to an aromatized hydroperoxide. The proposed radical chain mechanism explains high hydroperoxide yield from autoxidation of triphenylmethyl dimer when termination is slow. In ether solution the triphenylmethyl dimer has $\lambda_{\max} 318$.

Within 5 years of Gomberg's discovery of organic free radicals Flürscheim suggested that benzylic radicals should show "free affinity" at the ortho and para positions of the phenyl ring as well as at the α position.³ His proposal of an equilibrium between triphenylmethyl and its α - α coupling product hexaphenylethane was, however, accepted for Gomberg's hydrocarbon until 1968.⁴ Jacobson's quinoid or *p*-semibenzene structure (**1**), an α -para coupling product,



has now been established for the triphenylmethyl dimer,⁵ and analogous structures have been proposed or demonstrated for coupling products of other radicals with triphenylmethyl radicals.⁶ There is fragmentary

(1) Taken in part from the Ph.D. Thesis of K. J. Skinner, Yale University, 1973. This work was supported in part by a grant from The Research Corporation.

(2) (a) National Institutes of Health Predoctoral Fellow 1968–1971; (b) Alfred P. Sloan Research Fellow 1971–1973; recipient of a Camille and Henry Dreyfus Teacher–Scholar Grant.

(3) B. Flürscheim, *J. Prakt. Chem.*, [2] **71**, 497 (1905).

(4) For references and discussion, see J. M. McBride, *Tetrahedron*, in press.

(5) H. Lankamp, W. Th. Nauta, and C. MacLean, *Tetrahedron Lett.*, 249 (1968); H. A. Staab, H. Brettschneider, and H. Brunner, *Chem. Ber.*, **103**, 1101 (1970); R. D. Guthrie and G. R. Weisman, *Tetrahedron Lett.*, 1316 (1969).

(6) For references, see (a) J. A. Kampmeier, R. R. Geer, A. J. Meskin, and R. M. D'Silva, *J. Amer. Chem. Soc.*, **88**, 1257 (1966); (b) J. P. Lorand and P. D. Bartlett, *ibid.*, **88**, 3294 (1966); (c) W. A. Pryor, K. Smith, J. T. Echols, Jr., and D. L. Fuiler, *J. Org. Chem.*, **37**, 1753 (1972); (d) J.-J. L. Fu and W. G. Bentrude, *J. Amer. Chem. Soc.*, **94**, 7710 (1972).