Alkali Metal and Electrochemical Reductions of Dibenzoylbenzenes[1]

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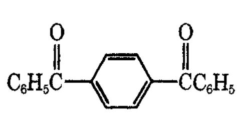
The three isomeric dibenzoylbenzenes **1**, **2**, and **3** have been found to react with 1 equiv of potassium in 1,2-dimethoxyethane (monoglyme) or ammonia to form radical anions **4**, **15**, and **22** as shown by comparison of their esr spectra with those of the radical anions produced from **1**, **2**, and **3** by controlled-potential electrolysis in monoglyme. Treatment of para isomer **1** with 2 equiv of potassium in monoglyme or ammonia affords the diamagnetic dianion **5**, as evidenced by protonation, alkylation, and carboxylation at one of the original carbonyl carbons. The chemical and electrochemical reversibility of this two-electron process has been demonstrated by controlled-potential redox experiments and aerial oxidation to regenerate **1**. Reaction of **1** with 2 equiv of lithium in ammonia produces a mixture of starting ketone **1** and the diastereomeric diols (**7**) resulting from reduction of both carbonyl groups. Treatment of ortho isomer **2** with 2 equiv of potassium in monoglyme or ammonia leads to predominant formation of 10-phenyl-10-hydroxy-9-anthrone (**16**), while similar reductions of **2** with potassium in monoglyme-*tert*-amyl alcohol or with lithium in ammonia afforded mainly 1,3-diphenylisobenzofuran (**17**). Exposure of meta isomer **3** to 2 equiv of potassium in monoglyme produces a paramagnetic intermediate, which appears to be the radical trianion resulting from reduction of a dimer of radical anion **22**.

Alkali metal reductions of ketones continue to be the subject of numerous synthetic and mechanistic studies.[2] In light of this, we have examined a series of alkali metal reductions of dibenzoylbenzenes **1–3** using the solvent systems liquid ammonia and 1,2-dimethoxyethane (monoglyme). For comparison purposes, electrochemical reductions of **1–3** were also carried out in monoglyme.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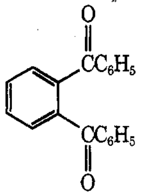
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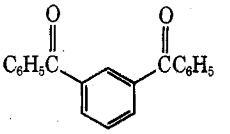
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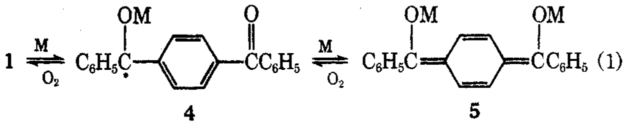
Previous studies dealing with alkali metal and electrochemical reductions of diketones **1–3** have been scattered, and no attempts have been made to compare the two processes under similar conditions. For example, Schlenk[3] has reported that para isomer **1** was converted into a dipotassio salt and meta isomer **3** afforded a monopotassio derivative upon treatment with the potassium ketyl of 4-phenylbenzophenone in ether. Using similar reduction conditions, Müller[4] obtained both the mono- and dipotassio salts of **1**. In the same study the monopotassio derivative of **3** was prepared and assigned a pinacolate structure on the basis of its diamagnetism. Further reduction of this material afforded a paramagnetic species, the structure of which was designated as a diketyl of the pinacolate, complexed with two molecules of neutral diketone. Recently, Szwarc and coworkers[5] found that reduction of **3** with sodium or sodium biphenylide in hexamethylphosphoramide (HMPA) afforded mainly the monomeric (paramagnetic) radical anion of **3**, while the dimeric (diamagnetic) radical anion of **3** was formed in tetrahydrofuran (THF). However, the chemistry of these intermediates was not investigated, nor have any reports concerning the chemistry of the presumed radical anion and dianion of **1** appeared to date. In contrast to this, products resulting from alkali metal reductions of ortho isomer **2** have been characterized by Herold,[6] but the spectral and magnetic properties of the intermediates presumably responsible for their formation have not been reported.

Electrochemical reductions of diketones **1–3** have been carried out in both protic[7–11] and aprotic solvents,[6,11] but no systematic study of all three isomers has been conducted under aprotic conditions. In a recent investigation,[12] it has been reported that polarographic reduction of para isomer **1** in anhydrous DMF was characterized by three waves, the first and second of which corresponded to reversible, one-electron processes, while the third corresponded to an irreversible two-electron step. Similar reduction of meta isomer **3** resulted in generation of two polarographic waves, the first of which represented a reversible one-electron step. The second was a three-electron wave, the initial portion of which supposedly corresponded to the reversible transfer of one electron. This study was not accompanied by spectral characterization of the postulated intermediates produced during reduction, and products of electrolysis were not identified.

Results and Discussion

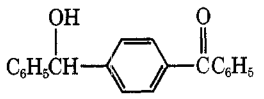
***p*-Dibenzoylbenzene (1).** Brief exposure of a 10^{-2} *M* solution of **1** in monoglyme to a potassium mirror under anaerobic conditions at 25° resulted in formation of an emerald-green solution, which exhibited an esr spectrum consisting of a broad envelope, and had absorption bands at 368, 400, and 790 nm (see paragraph at end of paper regarding supplementary material). Reexposure of this solution to the metallic mirror produced a deep blue solution. Development of the blue color was accompanied by gradual loss of the original esr signal and visible absorption bands, with a new maximum appearing at 575 nm.[13] The intensity of this band varied as the solution was diluted, but no new bands were evident. Slow addition of air to the green solution led to decoloration and regeneration of parent ketone **1**. Similar treatment of the diamagnetic blue solution resulted in initial production of the green species which, on continued admission of air, reverted to **1**. These results are consistent with the steps illustrated in eq 1 involving initial production of radical anion **4** followed by addition of a second electron to **4** to form dianion **5**.[14] Polarographic reduction of **1** in monoglyme revealed two well-defined waves at $E_{1/2}$ = −2.05 and −2.50 V, respectively. Cyclic voltammetry indicated that both waves were electrochemically reversible. Controlled-potential electrolysis and coulometry at −2.20 V demonstrated that the first wave corresponded to a one-electron process. The resulting green solution had esr and visible spectra identical with those observed during potassium reduction. Controlled-potential oxidation of this solution


4 **5** (1)

followed by polarographic and thin layer chromatography (tlc) analyses established the chemical reversibility of the initial reduction step. Exhaustive reduction and coulometry at −2.70 V was consistent with a two-electron process. When the resulting diamagnetic blue solution was oxidized at −0.60 V, polarographic and tlc analyses indicated that addition of a second electron to 1 resulted in some loss of chemical reversibility.

Exposure of diketone 1 to 1 molar equiv of potassium in ammonia also produced radical anion 4, the esr spectrum of which was essentially identical with that observed in monoglyme. Radical anion 4 (M = K, Na, or Li) exhibited a low order of basicity toward ammonia as evidenced by persistence of the esr signal and the absence of appreciable amounts of reduced products after 12 hr in this solvent. Radical anion 4 could also be prepared by means of potassium in THF or HMPA, but attempted preparations of dianion 5 in these two solvents were less satisfactory than in monoglyme and ammonia.

Treatment of radical anion 4 (M = K) in monoglyme with anhydrous methanol afforded mainly starting ketone 1, accompanied by ketone alcohol 6 and diastereomeric diols 7. Reaction of 4 with benzyl chloride gave mostly recovered 1 along with traces of benzylation product **8.** Diketone 1 was recovered in nearly quantitative yields after treatment of 4 (M = K) with methyl iodide and carbon dioxide. Attempted reactions of 4 (M = K) with methyl iodide and benzyl chloride in liquid ammonia failed to yield isolable amounts of alkylation products.



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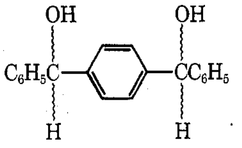

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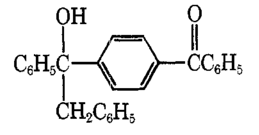

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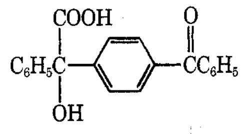

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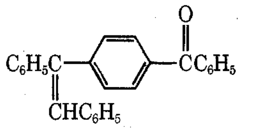

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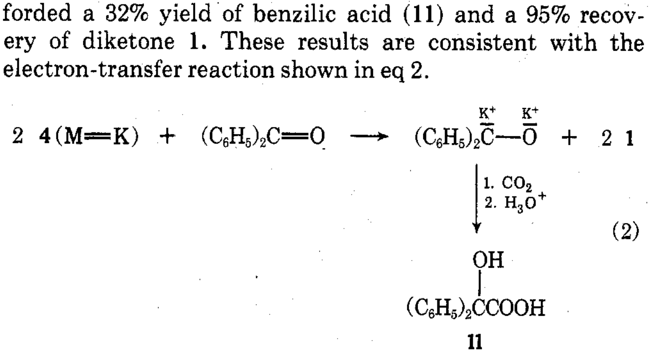
Treatment of 4 (M = K) with benzophenone in monoglyme, followed by carbonation of the reaction mixture, afforded a 32% yield of benzilic acid (11) and a 95% recovery of diketone 1. These results are consistent with the electron-transfer reaction shown in eq 2.



$$2\ \mathbf{4}(M{=}K) + (C_6H_5)_2C{=}O \longrightarrow (C_6H_5)_2\overset{K^+}{\bar{C}}-\overset{K^+}{\bar{O}} + 2\ \mathbf{1} \xrightarrow[2.\ H_3O^+]{1.\ CO_2} (C_6H_5)_2C(OH)COOH \quad (2)$$

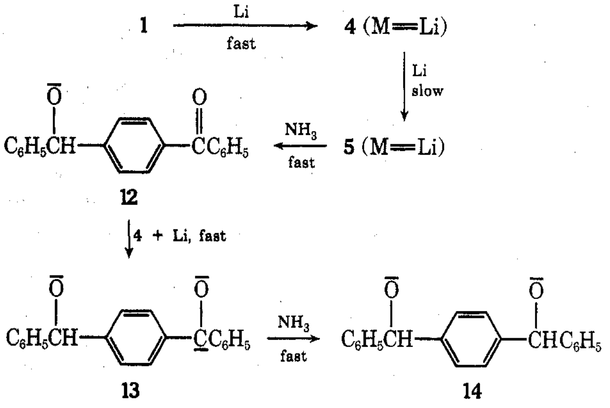
11

Failure of radical anion 4 to undergo significant alkylation with benzyl chloride and methyl iodide may result from its tendency to react with these halides, *via* a similar electron transfer mechanism,[15] which results in reduction of the electrophile and oxidation of 4 to starting diketone.

Although generation of dianion 5 proceeded smoothly with a potassium mirror at low ketone concentrations, more concentrated solutions of 5 were best prepared by refluxing 1 with 2 equiv of potassium or sodium-potassium alloy in monoglyme. Subsequent treatment of 5 with ethanol afforded keto alcohol 6 in 45–52% yield as its 2,4-dinitrophenylhydrazone. Alkylation of 5 with benzyl chloride gave tertiary carbinol 8 (53%), which was dehydrated to unsaturated ketone 10 in 95% yield. Carboxylation of 5 yielded acid 9 (55%). Dianion 5 (M = K) could also be formed by means of 2 molar equiv of potassium in ammonia, as shown by protonation and benzylation to afford 6 (41%) and 8 (57%), respectively. Recovery of starting diketone from the above reactions in yields of 15–25% indicated either that formation of 5 was incomplete or that this intermediate may have reacted to some extent with the added electrophiles by electron transfer.

Exposure of 1 to 2 equiv of lithium in ammonia gave a 44% recovery of 1 and a 47% yield of diols 7. None of the expected keto alcohol 6 could be detected. Treatment of the reaction mixture with methyl iodide or benzyl chloride failed to provide significant amounts of alkylation products; instead 1 and diols 7 were produced in approximately the same yields as in the absence of halide. A possible explanation of these results is presented in Scheme I.

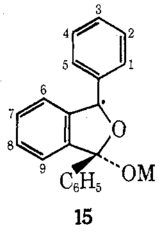
Scheme I



It is proposed that initial, rapid consumption of 1 equiv of lithium to form radical anion 4 is followed by somewhat slower formation of dianion 5. The relatively slow formation of 5, coupled with its rapid ammonolysis,[16] prevents accumulation of significant quantities of this intermediate during the reaction as shown by failure of the attempted alkylation reactions. Preferential reduction of 12 by residual metal and radical anion 4 (*cf.* the reduction of benzophenone by 4) to form trianion 13, ammolysis of this intermediate to yield dianion 14, and neutralization of 14 to give diols 7 completes the reduction process in a manner compatible with the observed stoichiometry. That the solvent does indeed serve as the source of the methine protons of diols 7 was verified by allowing diketone 1 to react with 4 equiv of lithium in ammonia, then removing the solvent, and quenching the residue with deuterium oxide. Pmr analysis of the resulting diols (97%) revealed no incorporation of methinyl deuterium. Although it seems likely that 12 should have a lower reduction potential than radical anion 4, and therefore accept an electron from either lithium or 4, it is not immediately obvious why the resulting radical dianion of 12 would be reduced to trianion 13 in preference to reduction of 4 to dianion **5.** However, this appears to be the case; otherwise keto alcohol 6 should have been the major product. In support of this mechanism it was also found that treatment of 1 with potassium in monoglyme containing *tert*-amyl alcohol as a proton source afforded diols 7 and recovered 1, accompanied by only traces of keto alcohol **6**. This indicates that reduction of the remaining carbonyl function of **6** proceeds more rapidly than initial reduction of the equivalent carbonyl groups of **1**.

***o*-Dibenzoylbenzene (2).** Initial contact of a 10^{-2} *M* solution of **2** in monoglyme with potassium gave rise to a burgundy solution which had a complex esr spectrum quite similar to the electrochemically generated spectrum (see supplementary material). The electronic spectrum of this solution was characterized by an intense band at 495 nm. Admission of air followed by quenching with absolute ethanol afforded starting diketone **2** in >90% purity as shown by uv analysis. Prolonged (6 hr) contact of a similar solution with potassium gave a dark blue, weakly paramagnetic solution. During development of the blue color the electronic spectrum gradually assumed the same general features as that obtained on treatment of 10-phenyl-10-hydroxy-9-anthrone (**16**) with potassium in monoglyme (intense bands at 380 and 400 nm). Aerial oxidation of the solution resulting from extended reduction of **2** yielded mainly **16**, along with traces of **2** and anthraquinone.[6b] Reaction of **2** with 1 equiv of potassium in ammonia produced a paramagnetic burgundy solution from which an esr spectrum similar to that observed in monoglyme was obtained.

Polarographic reduction of diketone **2** in monoglyme was characterized by two waves at $E_{1/2} = -2.30$ and -2.70 V. Cyclic voltammograms revealed that the first wave corresponded to an electrochemically reversible process, while the second wave exhibited nearly total irreversibility. Controlled potential reduction at -2.40 V gave a pink solution which gradually became burgundy as electrolysis continued. Coulometric analysis was consistent with a one-electron reduction, which proved to be chemically reversible. An esr spectrum of this solution was essentially identical with the spectra observed from potassium reductions.[17] Although the actual structure of the paramagnetic species must still be considered open to further study, we were able to obtain a reasonably good simulated spectrum of the electrochemically generated intermediate by assuming cyclic radical anion structure **15**[6d] with the following coupling constants: a_3^{H} or $a_8^{H} = 4.0$ or 3.8, $a_6^{H} = 3.75$, $a_1^{H} = a_5^{H} = 2.35$, and $a_2^{H} = a_4^{H} = a_7^{H} =$ $a_9^{H} = 0.8$ (all values given in gauss). Controlled-potential reduction of **2** at -2.75 V showed the uptake of nearly four electrons in a chemically irreversible process. The high electron count is attributed to formation and subsequent reduction of anthrone **16** and anthraquinone, both of which exhibit polarographic waves below -2.75 V and were detected as products of exhaustive electrolysis.



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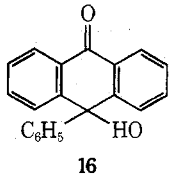

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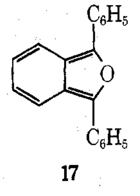
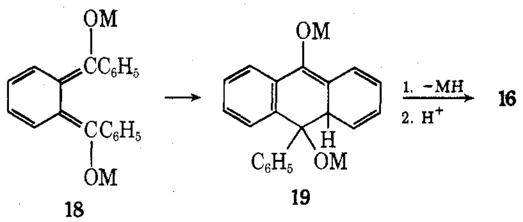


17

Reductions of **2** in ammonia were accompanied by an interesting metallic cation effect. Thus, 2 equiv of potassium produced anthrone **16** as the major product, while isobenzofuran **17** was the only product observed with 2 equiv of lithium. Reaction of **2** with 2 equiv of potassium in refluxing monoglyme followed by addition of ethanol produced anthrone **16**, while similar treatment of **2** with potassium in the presence of *tert*-amyl alcohol afforded isobenzofuran **17**. Attempts to trap a possible dianion intermediate by reduction of **2** with potassium or lithium in ammonia followed by addition of benzyl chloride gave **16** and **17**, respectively.

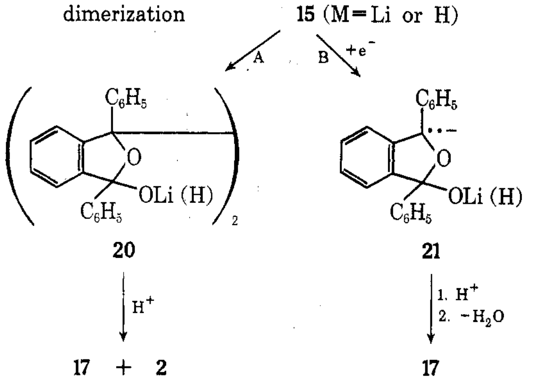
On the basis of the foregoing experiments it is suggested that diketone **2** initially accepts an electron from the reducing metal or mercury cathode to form cyclic radical anion **15**. Addition of a second electron to **15** in the absence of a proton source or lithium ions then yields an acyclic dianion such as **18**, which rapidly cyclizes to form anthrone **16**, possibly by loss of metal hydride from intermediate **19** (eq 3).[18]



(3)

Generation of **15** in the presence of a proton donor (*tert*-amyl alcohol) or lithium ions may effectively trap this intermediate in its cyclic form by O-protonation or formation of a highly covalent O–Li bond, respectively. Subsequent production of isobenzofuran **17** might then occur by either or both of the routes illustrated in Scheme II.

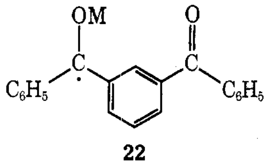
Scheme II



In route A, **15** dimerizes to afford **20**, the protonated form of which is known[6c] to disproportionate to yield equimolar amounts of **17** and **2** in the presence of mineral acid. Alternatively (route B) **15** could accept a second electron to form cyclic dianion **21**, which then undergoes C-protonation and subsequent acid-catalyzed, transannular dehydration[19] on work-up to produce **17**. We have now gained evidence that both of these mechanisms may be operating in the lithium–ammonia reductions. Thus, when **2** was subjected to such reduction and the reaction was processed with the careful exclusion of acid, two products, along with some unreacted starting material, were detected by tlc; however, **17** was not present in the crude mixture. The more mobile of these compounds was converted to a mixture of starting diketone **2** and isobenzofuran **17** on brief exposure to acid, while the less mobile component afforded only **17**. From this it is concluded that the first of these is the dimer **20** (H)[6c] and the second is the monomeric alcohol[19] resulting from C- and O-protonation of **21**. It was established that neither of these compounds was a diol resulting from reduction of both carbonyl groups of **2**, since independent synthesis of these diols followed by treatment with acid did not product **17**.

***m*-Dibenzoylbenzene (3).** Brief reaction of a 10^{-2} *M* monoglyme solution of **3** with potassium afforded a dark red solution with visible bands at 398 and 510 nm, characteristic of the "diamagnetic dimer" form of radical anion **22** (M = Na) in THF or HMPA.[5] Although the visible band at 760 nm attributed[5] to the monomeric form of **22**

was very weak, the red solution had an esr spectrum in agreement with that reported for the monomeric species in HMPA.[5] Treatment of 3 with 1 equiv of potassium in ammonia produced a red solution, the esr spectrum of which was characteristic of monomeric 22. This solution could be maintained for 24 hr in the absence of oxygen without appreciable loss of intensity of the original color or esr signal. Exposure of the liquid ammonia or monoglyme solutions of 22 to air resulted in rapid loss of color, and 3 was recovered in excellent yield. When the monoglyme solution of 22 was quenched with methanol prior to opening to the atmosphere, a mixture consisting of 3, diols 23, and a minor component possessing spectral properties consistent with keto alcohol structure 24 was obtained.



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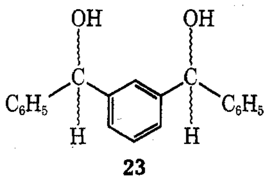
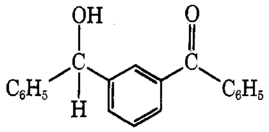


23



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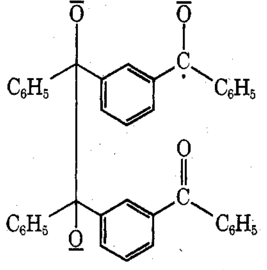
Repeated contact of the red solution of 22 in monoglyme with potassium resulted in eventual loss of the bands at 400 and 520 nm accompanied by appearance of an intense new band at 685 nm in the electronic spectrum of the resulting dark blue solution.[20] This solution retained a high degree of paramagnetic character as shown by the presence of a broad, intense esr singlet. Dilution and reconcentration of the solution resulted only in changes in the intensity of the 685-nm band; no new bands could be detected. Gradual admission of air into the blue solution caused it to regain the original red color and finally become colorless; diketone 3 was regenerated in a high state of purity. When the blue solution was quenched with methanol prior to exposure to air, starting ketone 3, diols 23, the presumed keto alcohol 24, and several minor components were produced.

Polarographic reduction of 3 in DME revealed two electrochemically reversible waves at $E_{1/2} = -2.30$ and -2.65 V. Controlled-potential electrolysis and coulometric measurements at -2.40 V were consistent with a one-electron process to form radical anion 22, the esr spectrum of which was practically the same as that produced by means of potassium in monoglyme or ammonia. A polarogram of the reoxidized solution coupled with tlc analysis demonstrated good chemical reversibility. Controlled-potential electrolyses of 3 at -2.80 V consistently resulted in uptake of *ca.* 1.5 electrons. Reoxidation of this weakly paramagnetic solution showed some loss of chemical reversibility, but 3 was still the major component of such reaction mixtures.

Attempted alkylations of radical anion 22 (M = K) in monoglyme or ammonia with benzyl chloride gave only recovered 3. Treatment of 3 with 2 equiv of potassium, sodium, or lithium in ammonia followed by ammonium chloride or benzyl chloride also afforded unchanged 3 in yields of >90%. Attempts to generate and trap a possible dianion intermediate by refluxing 3 with 2 equiv of potassium in monoglyme resulted in cleavage of 3 to form benzoic acid, benzhydrol, and several unidentified minor products. However, extended reaction of 3 with 4 equiv of sodium in ammonia afforded diols 23 in 81% yield.

On the basis of our results and those of Szwarc and coworkers,[5] it appears that diketone 3 is reduced by 1 equiv of potassium in monoglyme or liquid ammonia to form radical anion 22, which exists as a mixture of monomeric and dimeric forms with the latter predominating. However, the fate of 22 in the presence of a second equivalent of metal is less clear. Failure to produce significant amounts of alkylation products or the expected keto alcohol 24, coupled with the high degree of paramagnetism, appears to preclude the presence of appreciable amounts of a dianion such as that derived from para isomer 1. The absence of half-field transitions in the low-temperature esr spectra of the blue monoglyme solutions seems to rule out the possibility of triplet (diketyl) species arising from independent reduction of the carbonyl groups of 3. Since coulometric measurements conducted at -2.75 V ($n = 1.5$) can be rationalized by a one-electron reduction of a dimeric radical anion, we propose that the major species produced on further reaction of 22 may be the dimeric radical anion represented by structure 25. Although 25 is



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shown as having a formal C–C bond, the actual bonding may be of the π–π type[5] as evidenced by recovery of starting ketone 3 on exposure of such solutions to oxygen[21] or alkyl halides, and the predominant formation of monomeric reduction products with excess sodium in liquid ammonia.

Experimental Section

General. Melting points were determined on a Thomas-Hoover melting point apparatus in open capillary tubes and are corrected. Elemental analyses were performed by M-H-W Laboratories, Garden City, Mich., and in this laboratory by Miss Q. H. Tan using an F & M Model 185 C, H, and N analyzer. Infrared (ir) spectra were recorded on a Beckman IR-5A infrared spectrophotometer and are calibrated with a polystyrene spike at 6.24 μ. Potassium bromide pellets and chloroform solutions were employed for solids and neat samples between sodium chloride plates were used for liquids. Nuclear magnetic resonance (nmr) spectra were obtained on a Varian Associates A-60 spectrometer. Chemical shifts, relative to tetramethylsilane as the internal standard, were measured to the center of a singlet or multiplet. Peak areas were consistent with the assignments given. Mass spectra were obtained on an Hitachi Perkin-Elmer RMU-6E mass spectrometer at 50 eV. Electronic spectra were taken on a Cary 14 spectrophotometer. Thin layer chromatography (tlc) was conducted with an Eastman chromagram apparatus using chromagram sheets type K301R (silica gel) with fluorescent indicator and benzene as the developing solvent. Spots were detected with uv light and iodine.

All electrochemical studies were performed in a Vacuum Atmosphere Dry-Lab Train (argon atmosphere) drybox using 1,2-dimethoxyethane (freshly distilled from lithium aluminum hydride under argon) as solvent and tetrabutylammonium perchlorate as supporting electrolyte at 0.1 *M* concentrations. Substrate concentrations of 1×10^{-3} *M* were employed. Polarographic, cyclic voltammetric, and controlled-potential electrolysis experiments were run in a standard H-type cell employing procedures and circuity described elsewhere.[22] The general procedure used for studying electrochemical behavior is given in the supplementary material.

p-Dibenzoylbenzene (1) was prepared according to the procedure of Murray and Trozzolo.[23] *o*-Dibenzoylbenzene (2) was prepared as described by Jensen.[24] *m*-Dibenzoylbenzene (3) was synthesized by the procedure of Dischendorfer and Verdino.[25]

Simulation of the esr spectrum resulting from electrochemical reduction of 2 was accomplished using a program similar to SESR of Stone and Maki[26] suitably modified to permit its use on the VPI & SU IBM 360/50-40 with an associated Calcomp plotter.

Generation of Radical Anions 4, 15, and 22 and Dianion 5 on a Preparative Scale in Monoglyme and Liquid Ammonia. A. Radical Anions 4, 15, and 22. To a solution of 2.5 g (8.8 mmol) of the appropriate ketone in 150 ml of monoglyme contained in a 250-ml three-necked flask equipped with a sealed mechanical stirrer, a nitrogen inlet, and a 10-mm ball and socket stopcock at the bottom was added 0.35 g (9 mg-atoms) of freshly cut potassium. The reaction mixture was stirred at room temperature until metal could no longer be detected (2-3 hr) and the resulting colored solution was filtered through a glass wool plug into a second 250-ml three-necked flask containing a monoglyme solution of the reagent with which the radical anion was to be treated. Preparation of radical anions 4, 15, and 22 (M = K, Na, or Li) in ammonia was conducted similarly except that the ketone was added rapidly as a solid to a solution of the appropriate alkali metal in 150 ml of freshly distilled (from benzophenone potassium ketyl) liquid ammonia, and reagents were then introduced directly into the reaction mixture; a nitrogen atmosphere was maintained throughout.

B. Dianion 5. To a stirred solution of 6.87 g (24 mmol) of diketone 1 in 250 ml of monoglyme under nitrogen was added 1.75 g (49 mmol) of sodium-potassium alloy. The reaction mixture was allowed to reflux for 6 hr, after which time the resulting purple solution of 5 was used in the reactions described below. In the same manner 2.5 g (8.8 mmol) of 1 was refluxed for 6 hr with 0.77 g (19.7 mg-atoms) of potassium metal in 150 ml of anhydrous monoglyme to afford a purple solution of dianion 5. Dianion 5 (M = K or Na) was also prepared by adding 8.8 mmol of solid 1 to a solution of 19.5 mg-atoms of the appropriate alkali metal in 250 ml of anhydrous liquid ammonia. After 1 hr the resulting purple solution was used as described below.

Reactions of Radical Anion 4. A. With Methanol. A monoglyme solution of 4 (8.8 mmol) was added to excess methanol under nitrogen at 25°. The resulting solution was allowed to stir for 18 hr, then concentrated under vacuum, and 50 ml of water was added to the remaining pasty mass. The aqueous suspension was extracted with ether and the extracts were dried (Na_2SO_4). Concentration of the ethereal solution followed by tlc and nmr analysis revealed the presence of diketone 1, keto alcohol 6, and diols 7. Chromatography of the product mixture on silica gel (benzene-$CHCl_3$) afforded 1.75 g (70% recovery) of 1.

B. With Benzyl Chloride. A solution of 4 (8.8 mmol) in monoglyme was added to a solution of 1.11 g (8.8 mmol) of benzyl chloride in monoglyme. The reaction mixture was stirred for 1 hr at 25°, after which time absolute ethanol (5 ml) was added. The solvent was removed under vacuum and replaced with 500 ml of ether. The ethereal solution was washed with water, dried (Na_2SO_4), and concentrated. Analysis of the crude solid by tlc and nmr revealed the presence of starting ketone 1 as the major reaction component along with minor amounts of carbinol 8. Chromatography of the crude product mixture on neutral alumina (benzene) afforded a 73% recovery of 1. Similar treatment of 4 with methyl iodide resulted in nearly quantitative recovery of diketone 1.

C. With Carbon Dioxide. A freshly prepared solution of radical anion 4 in monoglyme was poured onto an excess of Dry Ice. The solvent was evaporated and the residue was diluted with 200 ml of water, after which the mixture was extracted with ether. The extracts was washed with water and dried (Na_2SO_4), and the solvent was removed to give a 90% recovery of starting diketone. After acidification, the aqueous solution was extracted with ether to give <1% of acid 9. Similar results were obtained on adding gaseous carbon dixoide to the reaction mixtures.

D. With Benzophenone. To a stirred monoglyme solution of 8.8 mmol of radical anion 4 was added 0.80 g (4.4 mmol) of benzophenone as a 5% w/v solution in anhydrous monoglyme. After 2 hr the purple reaction mixture was poured onto excess Dry Ice. The solvent was evaporated and the residue was diluted with 200 ml of water. The aqueous solution was extracted with ether and then acidified with 3 *N* HCl. The resulting suspension was extracted with ether, dried (Na_2SO_4), and concentrated to give a viscous yellow oil, which was crystallized from benzene-hexane to afford 0.32 g (32%) of benzilic acid (11), mp 151-153°. A mixture melting point with an authentic sample of 11 showed no depression; the ir spectra of the two samples were identical. The former ethereal extract was processed in the usual manner to afford a 95% recovery of starting diketone 1.

Reactions of Dianion 5. A. Protonation. A monoglyme solution of dianion 5 (24 mmol), prepared utilizing sodium-potassium alloy, was added dropwise to 50 ml of anhydrous ethanol. After 1 hr the solvent was distilled from the reaction mixture under reduced pressure and the residue was diluted with 250 ml of ether and 200 ml of water. The organic layer was separated and the aqueous solution was extracted with ether. The combined ethereal solution was dried (Na_2SO_4) and concentrated to give an oil, which was chromatographed on silica gel [benzene-hexane (1:2)] to give 1.76 g (26%) of starting diketone 1. Further elution with benzene gave 3.84 g of 4-benzoylbenzhydrol (6): nmr (DMSO-d_6) δ 7.93 (m, 14, aromatic), 6.42 (d, 1, OH), and 6.10 ppm (d, 1, CH); ir ($CHCl_3$) 2.77 and 6.93-7.15 (OH) and 6.03 μ (C=O). The 2,4-dinitrophenylhydrazone was prepared under mild conditions to give 5.86 g (52%) of orange crystals: mp 169-172°, and 171.5-172.5° after recrystallization from ethanol; nmr (DMSO-d_6, δ 11.05 (s, 1, NH), 7.99 (m, 17, aromatic), 6.19 (d, 1, OH), and 5.98 ppm (d, 1, CH); ir ($CHCl_3$) 2.76 and 6.92-7.03 (OH), 3.02 and 7.50-7.62 (NH), and 6.63 μ (NO_2); mass spectrum (50 eV) molecular ion peak at *m/e* 468 with abundant fragment peaks at *m/e* 374, 286, 165, 105, and 77.

Anal. Calcd for $C_{26}H_{20}N_4O_5$: C, 66.66; H, 4.30; N, 11.96. Found: C, 66.72; H, 4.58; N, 11.86.

Acidification of the aqueous solution after extraction with ether, followed by the usual work-up, afforded 0.24 g (8%) of benzoic acid, mp 120-122°, mmp 121-122°.

Similar protonation of 8.8 mmol of dianion 5 prepared from 1 and potassium metal in monoglyme afforded 1.86 g (45%) of the 2,4-dinitrophenylhydrazone of 6.

A solution of 8.8 mmol of dianion 5 (M = K) in ammonia was quenched with 2.81 g (0.0525 mol) of solid ammonium chloride. The ammonia was distilled from the reaction mixture as an equal volume of ether was added. Cold 3 *N* HCl was added to the ethereal solution and the layers were separated. After the aqueous solution was extracted with ether, the ethereal solution was washed with water, dried (Na_2SO_4), and concentrated to give a yellow oil, which was chromatographed on silica gel [benzene-hexane (1:2)] to give 1.12 g (45%) of diketone 1. Further elution with benzene afforded 1.28 g of 6; the 2,4-dinitrophenylhydrazone was prepared and gave 1.67 g (41%) of orange crystals, mp 170.5-172.5°, mmp 170-172°.

Similar treatment of 8.8 mmol of dianion 5 prepared by means of sodium in ammonia afforded 23% of 6 as its 2,4-dinitrophenylhydrazone. In this experiment, 1 was recovered in 61% yield.

B. Alkylation with Benzyl Chloride. A monoglyme solution of 24 mmol of dianion 5, prepared by means of sodium-potassium alloy, was added dropwise to a 10% v/v solution of 6.34 g (0.05 mol) of benzyl chloride in anhydrous monoglyme. The resulting mixture was allowed to stir for 2 hr before the dropwise addition of 50 ml of absolute ethanol. The solvent was distilled from the reaction mixture and replaced with an equal volume of ether. Cold water (250 ml) was added to the ethereal solution and the layers were separated. The aqueous solution was extracted with ether. The original ethereal solution and the extracts were combined, washed with water, and dried (Na_2SO_4), and the ether was evaporated to give a dark yellow oil. This oil was absorbed on a column of acid alumina which was eluted with benzene-hexane (1:2) to remove impurities. Further elution with chloroform gave 4.80 g (53%) of 4-benzoyl-α-benzylbenzhydrol (8) as a colorless oil: nmr (DMSO-d_6) δ 7.78 (m, 19, aromatic), 6.25 (s, 1, OH), and 3.87 ppm (s, 2, CH_2); ir (neat) 2.86 and 6.92-7.12 (OH) and 6.02 μ (C=O).

Anal. Calcd for $C_{27}H_{22}O_2$: C, 85.68; H, 5.86. Found: C, 85.77; H, 5.80.

A 2.00-g (53 mmol) sample of 8 was dehydrated by refluxing with a few crystals of *p*-toluenesulfonic acid in 200 ml of benzene. After 3 hr the mixture was cooled, washed with water, dried (Na_2SO_4), and concentrated to afford 1.82 g (95%) of 1,2-diphenyl-1-(4-benzoylphenyl)ethene (10) as a pale yellow oil. An analytical sample of 10, prepared by short-path distillation, had nmr (DMSO-d_6) δ 7.87 ppm (m, aromatic and vinyl CH); ir (neat) 6.00 μ (C=O).

Anal. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59. Found: C, 90.21; H, 5.76.

To a stirred solution of 8.8 mmol of dianion 5 (M = K) in ammonia was added 1.27 g (10 mmol) of benzyl chloride as a 10% v/v solution in anhydrous ether. The resulting mixture was stirred for 1 hr before addition of ammonium chloride. The reaction mixture was processed as in the protonation of dianion 5 to afford a pale yellow oil. Chromatography of this oil on acid alumina with benzene-hexane (1:2) gave a 25% recovery of diketone

1. Further elution with chloroform afforded 1.90 g (57%) of **8**. In a similar experiment employing 2 molar equiv of sodium, tlc analysis of the crude product revealed **8** as a minor product with recovered ketone **1** constituting the major component.

C. Carboxylation. Carbon dioxide gas was passed through a solution of 25 mmol of dianion **5**, prepared by means of sodium-potassium alloy in monoglyme. After decolorization had occurred (5 min), 50 ml of absolute ethanol was added. The solvent was evaporated and the residue was diluted with 250 ml of water. The aqueous solution was washed with ether and acidified with 3 *N* HCl. The resulting emulsion was extracted with ether. The ethereal extract was washed with water, dried (Na_2SO_4), and concentrated to give an oil which was passed through a column of silica gel (chloroform) to afford a pale yellow oil, which crystallized from benzene-hexane to give 4.38 g (55%) of 4-benzoylbenzilic acid (**9**), mp 160-161°. After recrystallization from benzene, **9** had mp 161-162°; nmr (DMSO-d_6) δ 7.59 ppm (m, 16, aromatic, OH, and COOH); ir ($CHCl_3$) 2.80-2.95 (OH and COOH), 5.82-5.90 (carboxyl C=O), and 6.04 μ (ketone C=O); mass spectrum (50 eV) molecular ion peak at *m/e* 332. The base peak was at *m/e* 287; abundant fragment peaks were also observed at *m/e* 209, 186, 105, and 77.

Anal. Calcd for $C_{21}H_{16}O_4$: C, 75.89; H, 4.85. Found: C, 76.08; H, 4.98.

Similar treatment of dianion **5**, prepared with potassium metal in monoglyme, afforded acid **9** in yields of 36 and 37%. Formation and carboxylation of dianion **5** were also attempted at room temperature in THF and in HMPA to give **9** in yields of 7 and 5%, respectively. In all reactions the recovery of starting ketone was excellent.

Reaction of 1 with 2 Equiv of Lithium in Liquid Ammonia. To a solution of 0.13 g (18.7 mg-atoms) of lithium in 250 ml of liquid ammonia under nitrogen was added 2.5 g (8.8 mmol) of **1** and the resulting purple solution was stirred for 1 hr. Solid ammonium chloride was added and the ammonia was distilled from the mixture and replaced with an equal volume of ether. Cold 3 *N* HCl was added to the ethereal solution and the layers were separated. The original ethereal solution and extracts were combined, washed with water, dried (Na_2SO_4), and concentrated. The solid residue was fractionally recrystallized from benzene-hexane to give 0.61 g of one diastereoisomer (**7a**) of 4,4′-bis(α-hydroxybenzyl)benzene as white needles: mp 170-172°; nmr (DMSO-d_6) δ 7.42 (m, 14, aromatic) and 5.76 ppm (broad s, OH and CH); ir (KBr) 2.79 and 6.90-7.05 (OH) and 8.94-9.28 μ (COH); mass spectrum (50 eV) molecular ion peak at *m/e* 290 with abundant fragment peaks at *m/e* 211, 183, 105, and 77.

Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.78; H, 6.25. Found: C, 82.84; H, 6.21.

The second diastereomer (**7b**) was obtained as 0.48 g of snowball-like crystals, mp 141-143°. After recrystallization from benzene-hexane, **7b** had mp 142.5-143.5°; nmr (DMSO-d_6) δ 7.28 (m, 14, aromatic), 5.80 (d, 2, OH), and 5.62 ppm (d, 2, CH) ir (KBr) 2.78 and 6.92-7.08 (OH) and 8.97-9.28 μ (COH); mass spectrum (50 eV) molecular ion peak at *m/e* 290 with abundant fragment peaks at *m/e* 211, 183, 105, and 77.

Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.78; H, 6.25. Found: C, 82.74; H, 6.22.

Further crystallization from benzene-hexane afforded a 41% recovery of diketone **1**.

In a similar experiment **1** was reduced with 4 equiv of lithium in ammonia. After the ammonia had been evaporated and replaced with an equal volume of ether, the reaction mixture was quenched with deuterium oxide. An nmr spectrum of a sample of the resulting dialcohol mixture revealed no incorporation of deuterium at the methinyl carbons. Attempted alkylation of a similar reaction mixture with methyl iodide gave only recovered **1** (40%) and diols **7a,b** (42%).

Reduction of 1 in the Presence of *tert*-Amyl Alcohol. A mixture of 8.8 mmol of **1**, 0.11 mol of *tert*-amyl alcohol, and 44 mg-atoms of potassium in 250 ml of monoglyme was refluxed for 4 hr. The reaction was processed in the same manner as when dianion **5** was protonated with ethanol. Tlc analysis of the crude product mixture revealed starting material and diols **7a,b**, but no keto alcohol **6**. Column chromatography afforded 0.74 g of the mixed diols and 0.80 g of **1**.

Reduction of 2 with Potassium in Monoglyme. A mixture of potassium (1.53 g, 38 mg-atoms), *o*-dibenzoylbenzene (**2**, 5.0 g, 17.5 mmol), and 250 ml of anhydrous monoglyme was stirred for 12 hr at reflux. The reaction mixtrue was then cooled in an ice bath and 25 ml of absolute ethanol was added dropwise. After the excess alkali metal had been destroyed, the solvent was removed and replaced with an equal volume of ether. Water was then added, the layers were separated, and the aqueous solution was extracted with three 150-ml portions of ether. The combined ethereal solution was washed with water and dried (Na_2SO_4), and the solvent was evaporated to give 2.81 g (56%) of 10-hydroxy-10-phenyl-9-anthrone (**16**): mp 212.5-215.5° (lit.[27] mp 207-208°); nmr (DMSO-d_6) δ 8.02 (m, 13, aromatic) and 7.34 ppm (s, 1, OH); ir ($CHCl_3$) 2.79 (OH) and 6.02 μ (C=O).

Reduction of 2 in the Presence of *tert*-Amyl Alcohol. To a mixture of 0.70 g (18 mg-atoms) of potassium, 3.97 g (45 mmol) of *tert*-amyl alcohol, and 200 ml of anhydrous monoglyme at room temperature was added 1.0 g (3.5 mmol) of **2**. The reaction mixture was refluxed for 4 hr and the solvent was removed under reduced pressure. The residue was diluted with 250 ml of ether and 150 ml of cold 3 *N* HCl. The layers were separated and the aqueous solution was extracted with two 100-ml portions of ether. The combined ethereal solution was washed with water, dried (Na_2SO_4), and concentrated to give a yellow oil. Tlc analysis revealed that 1,3-diphenylisobenzofuran (**17**) and the starting diketone were the only components present. The oil was chromatographed on acid alumina (hexane) to give 0.36 g (38%) of **17**, mp 131-132° (lit.[28] mp 127-128°). The ir spectrum of **17** was identical with that of an authentic sample. Further elution with chloroform gave a 39% recovery of diketone **2**.

Reduction of 2 in Liquid Ammonia. A. With Lithium. To a solution of 0.14 g (20 mg-atoms) of lithium in 250 ml of liquid ammonia was added 8.8 mmol of **2**. The resulting purple solution was allowed to stir for 1 hr and then neutralized with ammonium chloride. The ammonia was evaporated as an equal volume of ether was added. To this ethereal suspension was added 150 ml of cold 3 *N* HCl, and the layers were separated. After the aqueous solution was extracted with ether, the combined ethereal solution was washed with water, dried (Na_2SO_4), and concentrated to give a yellow oil, which was chromatographed on neutral alumina (hexane) to give 0.85 g (36%) of **17**. Further elution with chloroform gave a 35% recovery of **2**.

Similarly, diketone **2** was treated with 2 molar equiv of lithium. Following addition of ammonium chloride and removal of the ammonia, the reaction mixture was hydrolyzed with a 5% $NaHCO_3$ solution and extracted with ether. Tlc analysis of the ethereal extracts revealed, in order of decreasing R_f values, starting diketone **2**, two unidentified components, and traces of the diastereomeric diols resulting from reduction of both carbonyl groups of **2**. Chromatography on basic alumina allowed separation of unreacted **2** and the diols from the two unidentified components, but all attempts to separate these from one another failed. Therefore all fractions containing both unknown compounds were combined and an aliquot of their solution in ether was spotted on an analytical tlc sheet, which was developed with benzene. The sheet was turned to 90°, and authentic samples of starting ketone **2** and isobenzofuran **17** were applied. The sheet was exposed to HCl vapors for a few minutes and then developed in a direction perpendicular to the original solvent front. The more mobile of the two components was thus shown to be converted into a mixture of ketone **2** and isobenzofuran **17**, while the less mobile unknown afforded only **17**. Therefore the former is assigned dimeric structure **20** (H) and the latter is presumed to be monomer **21** (H).

B. With Potassium. To a solution of 0.77 g (19.7 mg-atoms) of potassium in 250 ml of liquid ammonia was added 2.5 g (8.8 mmol) of **2**. After stirring for 2 hr, the reaction was processed in the usual manner to afford an oil, which was shown by tlc analysis to consist of starting material, anthrone **16**, and traces of isobenzofuran **17**. Crystallization of the oil from benzene-hexane gave 0..47 g (19%) of anthrone **16**.

Sodium Borohydride Reduction of 2. A solution of sodium borohydride (0.68 g, 18 mmol) and sodium hydroxide (0.10 g, 2.5 mmol) in 50 ml of methanol was added slowly to a cooled suspension of **2** (2.5 g, 8.8 mmol) in 150 ml of methanol at 10-15°. The solution was then allowed to reflux with stirring for 30 min, after which it was stirred overnight at room temperature. The solvent was distilled from the reaction mixture and the residue was diluted with 100 ml of cold 3 *N* H_2SO_4. After this mixture was extracted with ether, the ethereal solution was washed with water, dried (Na_2SO_4), and concentrated. The resulting oil was chromatographed on silica gel to afford 1,2-bis(α-hydroxybenzyl)benzene as an oily mixture of diastereomers: nmr (DMSO-d_6) δ 7.99 (m, 14, aromatic), 6.63 (m, 2, CH), and 6.41 ppm (m, 2, OH); ir (neat) 2.79 and 6.90-7.15 (OH) and 9.10-9.30 μ (COH).

Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.78; H, 6.25. Found: C, 82.90; H, 6.07.

To a solution of the above diols (1.0 g, 3.4 mmol) in 250 ml of ether was added 150 ml of 3 N HCl. The reaction mixture was stirred at room temperature for 30 min, after which it was processed in the usual manner to afford a quantitative recovery of diols; no isobenzofuran **17** could be detected.

Protonation of Radical Anion 15. A solution of 0.8 mmol of radical anion **15** (M = K) in 25 ml of monoglyme was quenched with 25 ml of anhydrous methanol under vacuum. The resulting solution was allowed to stir for 12 hr before being opened to the atmosphere. One drop of 6 N HCl was added and the resulting yellow solution was subjected to tlc analysis to reveal the presence of starting diketone **2** and isobenzofuran **17**.

Protonation of Radical Anion 22. A methanol quench (under vacuum) of a solution of **22** (M = K) (8.8 mmol) in 150 ml of monoglyme afforded 2.5 g of crude solid. Tlc analysis of this material revealed, in order of decreasing R_f values, diketone **3**, the presumed keto alcohol **24**, and diols **23**. Elution chromatography of the crude product mixture on silica gel (benzene, benzene-chloroform, and chloroform) afforded 1.75 g of **3**, 200 mg of a mixture of diols **23**, and 150 mg of **24** as a colorless oil. This latter material had the following spectral properties: nmr ($CDCl_3$) δ 7.6 (m, aromatic), 5.92, (2, CH), and 2.66 ppm (s, OH); ir ($CHCl_3$) 2.89 (OH) and 6.1 μ (C=O); mass spectrum (50 eV) molecular ion peak at m/e 288 with abundant fragment peaks at m/e 209, 183, and 105.

Attempts to protonate radical anion **22** in liquid ammonia with ammonium chloride led to recovery of starting ketone **3** in >95% yield. Similarly, treatment of **3** with 2 equiv of sodium or potassium for 1-3 hr in liquid ammonia followed by attempted alkylation of a possible dianion intermediate with benzyl chloride, *p*-chlorobenzyl chloride, or allyl bromide gave nearly quantitative recoveries of **3**.

Reduction of 3 with 4 Equiv of Sodium. Addition of 5.0 g (17.5 mmol) of **3** to 77 mg-atoms of sodium in 250 ml of liquid ammonia was followed by a reaction period of 24 hr. Solid ammonium chloride was added and the reaction mixture was processed in the usual fashion to give a white solid. This residue was fractionally recrystallized from benzene to afford 2.35 g of one diastereomer (**23a**) of 1,3-bis(α-hydroxybenzyl)benzene as white needles: mp 161.5-162.5; nmr (DMSO-d_6) δ 7.46 (m, 14, aromatic), 6.04 (d, 2, OH), and 5.80 ppm (d, 2, CH); ir (KBr) 2.83 and 6.90-7.23 (OH) and 9.14-9.40 μ (COH); mass spectrum (50 eV) molecular ion peak at m/e 290 with abundant fragment peaks at m/e 211, 183, 105, and 77.

Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.78; H, 6.25. Found: C, 82.70; H, 6.20.

The second diastereomer (**23b**) of 1,3-bis(α-hydroxybenzyl)benzene was obtained as 1.76 g of white crystals, mp 94.0-96.5°, after chromatography of the mother liquor on silica gel (chloroform). Recrystallization of **23b** from benzene-hexane afforded white crystals: mp 95.0-96.5; nmr (DMSO-d_6) δ 7.51 (m, 14, aromatic), 6.03 (d, 2, OH), and 5.81 ppm (d, 2, CH); ir (KBr) 2.80 and 6.90-7.20 (OH) and 9.15-9.35 μ (COH); mass spectrum (50 eV) molecular ion peak at m/e 290 with abundant fragment peaks at m/e 211, 183, 105, and 77.

Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.78; H, 6.25. Found: C, 82.71; H, 6.37.

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Registry No. 1, 3016-97-5; **2**, 1159-86-0; **3**, 3770-82-9; **4**, 42908-48-5; **5**, 42908-49-6; **6**, 31020-20-9; **6** 2,4-DNP, 42991-62-8; **7a**, 42913-54-2; **7b**, 31024-90-5; **8**, 42908-51-0; **9**, 42908-52-1; **10**, 42908-53-2; **15**, 42908-54-3; **16**, 5146-30-5; **23a**, 42908-56-5; **23b**, 42908-57-6; methanol, 67-56-1; benzyl chloride, 100-44-7; carbon dioxide, 124-38-9; benzophenone, 119-61-9; lithium, 7439-93-2; *tert*-amyl alcohol, 75-84-3; sodium borohydride, 16940-66-2; 1,2-bis(α-hydroxybenzyl)benzene, 42908-58-7.

Supplementary Material Available. Esr spectra of radical anions **4** and **15**, electronic spectra of radical anion **4**, dianion **5**, and radical anion **15**, along with descriptions of procedures used for studying electrochemical behavior and for obtaining esr and electronic spectra, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-146.

References and Notes

(1) (a) Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, ORGN 138. (b) Abstracted in part from the Ph.D. Dissertation of J. A. C., Virginia Polytechnic Institute and State University, Aug 1970.

(2) For a recent comprehensive review see H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, New York, N. Y., 1972, pp 150-172.

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(13) Prolonged (16 hr) treatment of **1** with potassium afforded a diamagnetic, purple-blue solution possessing a weak visible absorption band at 437 nm and an intense band at 650 nm. A complex mixture of products including benzoic acid and benzhydrol was obtained on aerial oxidation of this solution in the presence of anhydrous methanol. Gradual admission of air failed to regenerate radical anion **4**.

(14) Although other resonance forms may contribute to the actual structure of this intermediate, the present representation is used for the sake of convenience.

(15) For examples of related electron-transfer reactions involving hydrocarbon radical anions and alkyl halides see D. F. Lindow, C. N. Cortez, and R. G. Harvey, *J. Amer. Chem. Soc.*, **94**, 5406 (1972), and references cited therein.

(16) Protonation of dianion **5** rather than radical anion **4** appears to be more likely based on our observations that **4** (M = Li) does not undergo appreciable ammonolysis in the absence of excess metal and that 1,2-dilithio, but not 1,2-disodio or 1,2-dipotassio salts of related aryl ketones are rapidly protonated by liquid ammonia; see W. S. Murphy and C. R. Hauser, *Chem. Ind.* (*London*), 832 (1969), and references cited therein.

(17) Well-resolved spectra were obtained on solutions taken for analysis just prior to complete reduction. However, some loss of fine structure was observed following exhaustive reduction at −2.40 V.

(18) It has been suggested[6a,b] that this cyclization involves a diradical intermediate, but a suitable rationale for ultimate loss of a hydrogen atom has not been presented. Although a short-lived diradical cannot be ruled out, the present results with para isomer **1** lead us to propose a dianion intermediate. The chemical and electrochemical irreversibility associated with electrolysis of **2** at −2.75 V support the hypothesis that addition of a second electron is a necessary prerequisite for cyclization to **16**. Loss of hydride ion from intermediate **19** is precedented in related cyclizations; for example, see G. Levin, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, **92**, 2269 (1970).

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(20) When this solution was allowed to remain in contact with potassium for 48 hr the band at 685 nm was replaced by a single maximum at 585 nm, which remained unchanged over a period of 48 hr and was unaffected by dilution. A methanol quench of this solution afforded a mixture of products including starting ketone **3**, diols **23**, and benzoic acid.

(21) For examples of similar oxidative cleavages of dimeric dianions, see J. Chaudhuri, S. Kume, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, **90**, 6421 (1968), and references cited therein.

(22) See R. E. Dessy and R. L. Pohl, *J. Amer. Chem. Soc.*, **90**, 1995 (1968).

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