pyridine (0.5 ml) for 2 hr. After work-up, the crude product was crystallized from benzene–petroleum ether to give the acetate **16** (35 mg) in needles: mp 148–149°; ir 1680, 1650 sh cm^{-1}; nmr (100 MHz) δ 1.68 (d, 3, $CH-CH_3$, J = 5.5 Hz), 1.74 (s, 3, $-CH_3$), 2.34 (s, 3, $N-CO-CH_3$), 5.4 (q, 1, $CH-CH_3$, J = 5.5 Hz), 6.5–7.5 (m, 14, ArH); *m/e* (rel intensity) 384 (M^+, 51), 342 (2), 327 (2), 297 (9), 280 (3), 210 (92), 209 (94), 202 (3), 194 (8), 182 (2), 175 (3), 166 (100), 165 (95), 159 (30), 152 (3), 132 (4), 118 (8), 116 (31), 105 (34), 91 (25), 77 (24).

Anal. Calcd for $C_{25}H_{24}N_2O_2$: mol wt, 384.18376. Found by high resolution mass spectrometry: mol wt, 384.18229.

Attempted Hydrolysis of 13 and 14. Compounds **13** and **14** were recovered unchanged after refluxing with 5% ethanolic HCl or KOH for 2 hr.

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Registry No.—**1**, 18963-82-1; **2**, 18963-83-2; **3**, 52827-39-1; **5**, 52827-40-4; **6**, 52827-41-5; **7**, 13182-44-0; **8**, 52827-42-6; **9**, 13182-40-6; **10**, 52827-43-7; **13**, 52827-44-8; **14**, 52827-45-9; **15**, 52827-46-0; **16**, 52827-47-1; *N*-acetylanthranilic acid, 89-52-1.

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Electrochemical Reductive Acylation of Benzophenone[1]

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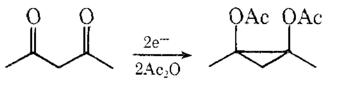
Polarographic and cyclic voltammetric studies of benzophenone in acetonitrile were carried out in the presence and absence of acetic anhydride, using tetraethylammonium bromide or perchlorate as supporting electrolytes. From the variation of pertinent parameters in these studies and from the known electrochemical behavior of benzophenone, a mechanism is proposed for the reduction of benzophenone in the presence of acetic anhydride. The results of controlled potential electrolysis substantiate the proposed mechanism.

There are many examples in the literature of electroorganic synthesis, defined as the transformation of one organic molecule into another by the action of an electric current.[2] In a number of cases involving cathodic processes, a radical anion produced by initial electron transfer undergoes followup chemical reactions in which one or more protons are abstracted from the reaction medium. We have for some time been interested in generating reactive species electrochemically and in studying their reactions with reagents other than proton donors. Our initial foray into this area[3] involved the reduction of 1,3-diketones in aprotic solvents in the presence of acetic anhydride, which led ultimately to the formation of 1,2-cyclopropanediol diacetates (eq 1), the products of intramolecular pinacol reduction. It was of some interest to examine the behavior of monoketones under similar conditions, and this paper reports the results of our investigation of benzophenone.



(1)

Electrochemical reduction of aromatic carbonyl compounds in aqueous and aprotic media has been extensively studied.[4-16] In particular there have been studies of the electrochemical reduction of benzophenone in dimethylformamide[12-14,16] and in pyridine.[15] These studies have shown that in aprotic solvents benzophenone undergoes an initial one electron reduction to form an anion radical intermediate **1**. Further reduction results in the formation of dianion **2**. Utilizing the techniques of polarography, cyclic voltammetry (CV), and large-scale controlled potential electrolysis, we have now studied the electrochemical behavior of benzophenone in acetonitrile containing acetic anhydride with tetraethylammonium bromide (TB) or perchlorate (TP) as the supporting electrolyte. As a result of these studies, we propose the following reaction scheme for the reduction of benzophenone under these conditions.

$$Ph_2C{=}O + e^- \longrightarrow [Ph_2C\text{-}O]^{\cdot -}$$

1

$$\mathbf{1} + e^- \longrightarrow Ph_2\bar{C}\text{-}\bar{O}$$

2

$$Ph_2C{=}O + e^- \longrightarrow \mathbf{1} \xrightarrow{Ac_2O} Ph_2\dot{C}\text{-}OAc$$

3

$$\mathbf{3} + e^- \longrightarrow \underset{\mathbf{4}}{Ph_2\bar{C}\text{-}OAc} \xrightarrow{Ac_2O} Ph_2C(COCH_3)\text{-}OAc$$

5

Table I
Polarographic Behavior of Benzophenone in the Presence of Acetic Anhydride in 0.1 M TP–Acetonitrile

Benzophenone concn, mM	Acetic anhydride concn, mM	Wave I			Wave II			
		$-E_{1/2}$, V	i_d, μA	Slope, mV	$-E_{1/2}$, V	i_d, μA	Slope, mV	$i_I + i_{II}$
2.0	0	1.83	7.78	61	2.09	6.48	120	14.26
2.0	2.0	1.81	12.3	65	2.09	1.48		13.8
2.0	4.0	1.79	13.8	72				13.8
2.0	10.0	1.77	15.3	80				15.3

Table II
Cyclic Voltammetry of Benzophenone in 0.1 M TB–Acetonitrile Containing Acetic Anhydride

Benzophenone concn, mM	Acetic anhydride concn, mM	Wave I					Wave II	
		$-E_{p_c}$, V	$-E_{p_a}$, V	ΔE_p, mV	i_{p_c}, μA	i_{p_a}, μA	$-E_{p_c}$, V	i_{p_c}, μA
2.0	0	1.86	1.79	70	13.62	10.65	2.26	6.24
2.0	1.0	1.85	1.79	60	13.66	8.55	2.25	3.43
2.0	2.0	1.84	1.79	50	14.58	5.09	2.19	1.62
2.0	4.0	1.76			21.75			
2.0	10.0	1.75			23.17			

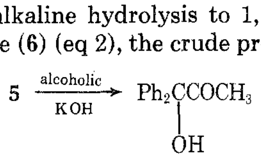
Results and Discussion

Polarography.[17] In acetonitrile with 0.1 M TP as supporting electrolyte, benzophenone shows two one-electron reduction waves, I and II, at $E_{1/2} = -1.83$ and -2.09 V. Acetic anhydride undergoes no reduction in this potential range. In the presence of acetic anhydride wave I grows in height (Table I) and wave II decreases until at a 2:1 ratio of anhydride to ketone the current due to wave II is immeasurably small. Further increase in the anhydride concentration then leads to relatively smaller increases in the height of wave I. Concurrently with its effect on the limiting currents, addition of acetic anhydride produces an anodic shift in the $E_{1/2}$ of wave I. These observations are consistent with the proposed mechanism. Wave I corresponds to the reduction of benzophenone to the radical anion **1**. In the absence of acetic anhydride **1** is then further reduced at a more cathodic potential to dianion **2**, giving rise to wave II. Addition of acetic anhydride diverts a fraction of the radical anion to **3**, decreasing the height of the second wave. The radical **3** is more reducible than benzophenone and immediately picks up a second electron to form acylated anion **4**. Addition of the second electron in the presence of acetic anhydride causes the first wave to increase in height and to shift to more cathodic potentials. At a sufficiently large anhydride concentration the net process occurring at the first wave will correspond to an overall transfer of two electrons, causing the limiting current to double. As indicated in Table I, the current does very nearly double for a 5:1 ratio of anhydride to ketone. The mechanism further requires that the total current for waves I and II remain constant, as is indeed observed (Table I, last column). The slopes observed for the two waves (Table I) suggest that wave I is nearly reversible in the absence of acetic anhydride (the theoretical slope for a reversible one electron process at 25° is 56 mV), but that wave II is irreversible. Further evidence bearing on the reversibility of the electron transfer steps was obtained by cyclic voltammetry.

Cyclic Voltammetry at the Hanging Mercury Drop Electrode.[18] Cyclic voltammetry data on benzophenone are given in Table II. In the absence of acetic anhydride, benzophenone shows two cathodic waves and one anodic wave. The two cathodic waves occur at potentials close to those observed polarographically and can be ascribed to successive reduction to **1** and **2**. By scanning the potential to a point midway between waves I and II, the single anodic wave at -1.76 V was established as arising from reoxidation of radical anion **1**. The resulting couple is not perfectly reversible, as both ΔE_p and i_{p_c}/i_{p_a} deviate from the theoretical values of 56 mV (for a one electron transfer) and unity, respectively. At the scan rate employed, the second wave, corresponding to formation of dianion **2**, is chemically and electrochemically irreversible. It is probable that **2** rapidly abstracts one or more protons, either from the solvent or from adventitious proton donors, to give nonreoxidizable products. Information on the reversibility of the two electron transfer steps obtained from cyclic voltammetry data agree well with the deductions made from polarographic studies.

When acetic anhydride is added to a solution in which benzophenone is undergoing reduction, trapping of radical anion **1** leads to an increase in the cathodic half of wave I as species **3** is generated and further reduced. Removal of **1** from solution means that less dianion **2** can be formed and explains the decrease with increasing anhydride concentration of i_{p_c} for wave II. The absence of any anodic waves at high anhydride concentration suggests that **4** undergoes a further rapid acylation to produce electroinactive ketoacetate **5**. Evidence for the ultimate formation of **5** is given below. It might be noted that much of the electrochemical behavior of benzophenone in acetonitrile in the presence of acetic anhydride parallels its behavior in pyridine and dimethylformamide containing proton donors.[12,15]

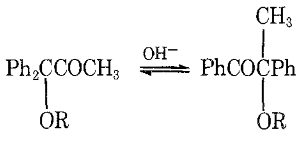
Large-Scale Controlled Potential Electrolysis. Further evidence supporting the proposed mechanism was provided by the large-scale electrolysis of benzophenone in the presence of acetic anhydride in acetonitrile at a potential slightly more cathodic than the first cathodic wave. At this potential the anion radical of benzophenone should be the primary product of the electrode reaction. The crude electrolysate, after removal of solvent and supporting electrolyte, was a dark brown viscous liquid. Gas chromatographic (gc) analysis revealed the presence of a single volatile product. While small amounts of this product could be separated by preparative gc, it was found more convenient to chromatograph the crude product on silica gel in order to obtain larger amounts. In this way, the electrolysis product was obtained as a colorless viscous liquid. A variety of evidence indicated that this was the postulated ketoacetate **5**. Infrared spectroscopy revealed the presence of two carbonyl groups absorbing at 1750 and 1725 cm^{-1}, positions typical of acetate esters and aliphatic ketones, respectively. Nmr also showed two slightly different C-methyl groups at 1.95 and 2.02 ppm, positions typical of methyl attached to carbonyl carbon. The aromatic hydrogens of **5** appeared as a complex multiplet centered near 7.2 ppm. As required by structure **5**, the integrated intensities of aryl and methyl hydrogens were very near the expected ratio of 5:3. Finally, elemental analysis of a carefully purified sample agreed well with structure **5**. The compound corresponding to **5**. 1,1-diphenyl-1-acetoxy-2-propanone, has been reported as a solid, mp 52.5–53.0,[19] and as a viscous oil.[20] The properties of our material are identical with those of the Italian workers.[20] In particular, the ir and nmr spectra of our **5** agree exactly with theirs. Prolonged efforts to cause our sample to crystallize were unavailing. The source of conflict between the two groups of workers is not known, but it may be related to the propensity of this system to undergo rearrangement.[21] Indeed, when we attempted to confirm the identity of **5** by alkaline hydrolysis to 1,1-diphenyl-1-hydroxy-2-propanone (**6**) (eq 2), the crude product showed its



$$\mathbf{5} \xrightarrow[\text{KOH}]{\text{alcoholic}} \underset{\text{OH}}{\text{Ph}_2\text{CCOCH}_3} \qquad (2)$$

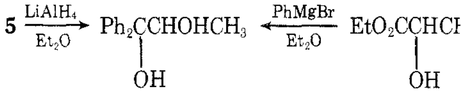
6

most prominent band in the ir at 1670 cm^{-1}, a position typical of aryl ketones. This suggests that either **5** or **6** or both underwent rearrangement in the course of the hydrolysis (eq 3). In fact, the transposition of groups represented by



$$\underset{\text{OR}}{\text{Ph}_2\text{CCOCH}_3} \underset{}{\overset{\text{OH}^-}{\rightleftharpoons}} \underset{\text{OR}}{\overset{\text{CH}_3}{\text{PhCOCPh}}} \qquad (3)$$

eq 3 has been reported previously by Elphimoff-Felkin.[21b] In order to secure structure **5**, the electrolysis product was reduced by lithium aluminum hydride to 1,1-diphenyl-1,2-propanediol (**7**), identical with material prepared[22] by an unambiguous route (eq 4). The yield of **5** from the bulk



$$\mathbf{5} \xrightarrow[\text{Et}_2\text{O}]{\text{LiAlH}_4} \underset{\text{OH}}{\text{Ph}_2\text{CCHOHCH}_3} \xleftarrow[\text{Et}_2\text{O}]{\text{PhMgBr}} \underset{\text{OH}}{\text{EtO}_2\text{CCHCH}_3} \qquad (4)$$

7

electrolysis was 66% of chromatographically pure material. The rest of the crude electrolysis product was a highly colored material which was not volatile at 230° (gc) and could not be eluted from a silica gel column with the usual solvent systems. No further attempts were made to characterize this material. It is noteworthy, however, that electrolysis of acetic anhydride alone under the same conditions yielded a substantial amount of a similar nonvolatile, highly colored material. Because of the formation of this product, reliable coulometric information could not be obtained.

Ketoacetate **5** can be regarded as a type of crossed acyloin or pinacol product. Such substances are often difficult to prepare by conventional synthetic techniques, and our electrochemical preparation could, in principle, be generalized to prepare other members of this class of compounds. Unfortunately, however, exploratory work with acetophenone and benzaldehyde has suggested that the electrochemical synthesis is probably limited to preparation of crossed acyloins derived from diaryl ketones only.

Experimental Section

Infrared spectra were measured on 10% solutions in carbon tetrachloride using a Beckmann IR-5A spectrometer. Nmr spectra were measured on carbon tetrachloride or deuteriochloroform solutions with a Varian A-60 spectrometer. Column chromatography was on Fisher silica gel (923) containing 15% added distilled water. An Aerograph A-90 P3 gas chromatograph equipped with an SF-96 column operated at 230° was used for gc analysis. Thin-layer chromatography was on microscope slides coated with silica gel G, using hexane–benzene mixtures for elution and iodine for spot visualization. A conventional saturated calomel electrode (sce) was employed as the reference electrode for all the electrochemical measurements.

Reagents and Chemicals. All chemicals were Fisher Certified reagents and except for acetonitrile were used without further purification. Acetonitrile was purified by the method of Forcier and Olver.[23] Tetraethylammonium bromide (TB) and tetraethylammonium perchlorate (TP) were used as supporting electrolytes. The bromide was commercially purchased. TP was prepared and purified as follows. TB (1 mol) and sodium perchlorate (1 mol) were separately dissolved in 1.5 l. of hot water. The solutions were mixed and allowed to cool. The TP which separated was repeatedly recrystallized from hot water until the filtrate gave no precipitate of silver bromide when tested with portions of silver nitrate solution. The resulting TP was dried over phosphorus pentoxide in a desiccator.

Polarography. A Sargent Polarograph Model XXI with Sargent IR Compensator Model A was used in a three-electrode system in a conventional H-type cell. The working electrode was a dropping mercury electrode and a platinum wire served as an auxiliary electrode. The benzophenone concentration was 2.0 mM and the acetic anhydride concentration was varied from 0 to 10.0 mM. Dry acetonitrile was used as the solvent with TP (0.1M) as supporting electrolyte. The solutions were deaerated with dry prepurified nitrogen for 20–30 min to remove oxygen, and an atmosphere of nitrogen was maintained over the solution throughout a particular experiment. The limiting or diffusion current i_d, the half-wave potential $E_{1/2}$, and the slope of the polarographic wave were all determined by standard procedures.[8]

Cyclic Triangular Wave Voltammetry (CV). The voltametric studies were carried out using standard techniques.[18] The triangular wave generator and the potentiostat were essentially the same as the instruments described by Chambers, *et al.*[24] The data were recorded on an X–Y recorder. A hanging mercury drop electrode (HDE) of approximately constant area was used as the stationary working electrode. The HDE was made by the method described by Enke and coworkers.[25] The constancy of the electrode area through a series of runs was checked by electrolyzing the initial solution at intervals in the series. As the CV studies were carried out to investigate qualitatively the follow-up reactions of the anion radical intermediate with acetic anhydride, the exact area of the electrode was not critical. A three-electrode system was employed with a sce and a platinum wire as the reference and the auxiliary electrodes, respectively. A conventional H-type cell with a total capacity of about 25 ml was used, the cathodic and anodic compartments being separated by a glass frit of medium porosity.

The CV measurements were made under aprotic conditions using dry acetonitrile as the solvent and 0.1M TB as the supporting electrolyte. The concentration of benzophenone was held at 2.0 mM and the anhydride concentration was varied from 0 to 10.0 mM. All solutions were thoroughly deaerated with dry prepurified nitrogen for 20–30 min to remove oxygen, and an atmosphere of nitrogen was maintained in the system. A scan rate of 230 mV/sec was used. That the working electrode was not contaminated by the products of electrolysis during the experiments with a particular series of solutions was shown by reproducing the voltammograms of the first solution of the series after the series had been completed.

Large-Scale Controlled Potential Electrolysis. Controlled potential electrolyses were carried out in a conventional three-electrode electrolysis cell constructed from a truncated 500-ml Pyrex erlenmeyer flask. A 200-ml Pyrex beaker was used as the anode compartment. The cathode and anode compartments as well as the cathode compartment and the sce were connected by bridges having fine porosity sintered glass frits. The bridges were filled with dry acetonitrile saturated with TB. A mercury pool was the working electrode (cathode), an sce the reference electrode, and a copper rod the auxiliary electrode (anode). The catholyte charge was 400 ml of 0.2 M TB in dry acetonitrile in which were dissolved 9.11 g of benzophenone and 38 ml of acetic anhydride. The entire system was purged with dry prepurified nitrogen for about 30 min before the start of the electrolysis, and the system was kept under a nitrogen atmosphere throughout the electrolysis. A high current, manually operated potentiostat was used to control the potential of the working electrode at a value slightly more cathodic than the E_{p_c} of the first benzophenone wave. The potential between working electrode and the sce was measured with a VTVM. The current was determined by measuring the potential drop across a precision resistor, either with a recorder or a potentiometer. Accurate coulometric measurements were not possible because the current efficiency was less than 100%. The electrolysis was continued until the current dropped almost to zero. The disappearance of ketone was also followed by CV. On completion of the electrolysis, the catholyte was diluted with a very large excess of distilled water (800–1000 ml) and extracted several times with a total of 500 ml of ether. The combined ether extract was washed with several portions of distilled water, saturated sodium bicarbonate solution, again with portions of distilled water, and finally with two portions of saturated sodium chloride solution. The extract was dried overnight over anhydrous magnesium sulfate. After filtration, the ether was removed by evaporation under reduced pressure until the crude product reached a constant weight. At this point the crude product weighed 10.5 g.

An aliquot of the crude product (1.05 g) was column chromatographed on 60 g of silica gel using hexane–benzene mixtures for elution. The material (0.89 g, 66%) eluting with 3:1 hexane–benzene showed a single spot on thin-layer chromatography and was the pure ketoacetate **5:** viscous oil; nmr (CCl_4, internal TMS) δ 1.95 (s, 3), 2.02 (s, 3), 7.2 ppm (m, 10); ir (10% in CCl_4) 3030 (m), 1750 (s), 1725 (s), 1490 (m), 1450 (m), 1430 (sh), 1370 (m), 1350 (sh), 1235 (s), 1180 (sh), 1160 (m), 1080 (w), 1020 (m), 950 (m), 920 (w), 890 (m), 695 cm^{-1} (s). An analytical sample was prepared by rechromatography over silica gel. *Anal.* Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 75.85; H, 6.22.

$LiAlH_4$ Reduction of Ketoacetate 5. To a suspension of $LiAlH_4$ (1.5 mmol) in anhydrous ether (5 ml), a solution of the ketoacetate **5** (300 mg, 1.1 mmol) in anhydrous ether (5 ml) was added dropwise with continuous stirring. After stirring for 1 hr at room temperature, excess $LiAlH_4$ was destroyed by dropwise addition of ethyl acetate, followed by 100 ml of 10% ammonium chloride solution. The mixture was then extracted with ether, the ether extract washed with portions of distilled water and saturated sodium chloride solution, and the extract dried overnight over anhydrous magnesium sulfate. Removal of the ether by vacuum evaporation left an oily liquid (220 mg) which solidified on standing. The crude solid had a mp of 90–92°. It was purified by recrystallization from hexane: mp 95–96°; nmr ($CDCl_3$, internal TMS) δ 1.05 (d, 3, CH_3CH), 2.00 (d, 1, CHOH), 3.12 (s, 1, COH), 4.75 (m, CH–O), 7.3 ppm (m, 10, ArH); ir (10% in CCl_4) 3550 (m), 3000 (b), 1595 (w), 1490 (m), 1450 (m), 1387 (m), 1350 (m), 1320 (w), 1260 (m), 1170 (m), 1130 (w), 1100 (m), 962 (m), 920 (w), 892 (m), 877 (m), 700 (s), 654 (m), 635 cm^{-1} (m).

Synthesis of 1,1-Diphenyl-1,2-propanediol.[22] In a three-necked 500-ml flask fitted with a separatory funnel, reflux condenser, and mechanical stirrer was prepared in the conventional manner a Grignard reagent from 27 g of magnesium turnings and 181 g of bromobenzene in 450 ml of ether. The reagent was cooled in an ice bath while freshly distilled ethyl lactate (29 ml) was added slowly. The excess Grignard reagent was decomposed by the addition of 150 ml of ammonium chloride solution (50 g in 150 ml). The ether layer was separated and washed with portions of distilled water and saturated sodium chloride solution. After drying over anhydrous magnesium sulfate, the ether was removed by vacuum evaporation. The crude white solid (mp 88–90°) was recrystallized several times from hexane to a constant melting point of 95–96°. The infrared and nmr spectra of this product were identical with that of the diol obtained by $LiAlH_4$ reduction of ketoacetate **5**. A mixture melting point of the two products was not depressed.

Registry No.—5, 13294-67-2; **7,** 52183-00-3; benzaphenone, 119-61-9.

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Selective Acylation of 2,4-Lutidine at Its 2- and 4-Methyl Groups

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2,4-Lutidine (1) has been acylated preferentially at its 2- or 4-methyl group depending on the condensing agent. It is suggested that if the metallic portion of the condensing agent can coordinate with the nitrogen atom of **1**, then the 2-methyl group of **1** is acylated; otherwise, the 4-methyl group is acylated. The acylation of **1** at its 2-methyl group has also been effected in high yields with three perfluorinated esters using phenyllithium as the condensing agent.

2,4-Lutidine (**1**) reacts selectively[1] with alkyl halides, aldehydes, and ketones at its 2- or 4-methyl group depending on the condensing agent.

We now report the selective lateral acylation of the 2- and 4-methyl groups of **1**. Earlier it was shown that 2-picoline[2] and 4-picoline[3] can be laterally metalated, the former by organolithium reagents and the latter by sodium amide in liquid ammonia.

Only one acylation of **1** could be found in the literature; its benzoylation using phenyllithium as the condensing agent[4,5] gave exclusively 4-methyl-2-phenacylpyridine in good yield. These results agree with a later study by Teague, *et al.*,[6] who showed that the reaction of **1** with benzaldehyde using phenyllithium gave exclusively 1-phenyl-2-(4-methyl-2-pyridyl)ethanol.

In the present study, **1** was acylated with ethyl benzoate