Polarography of Fluorenone, Anthrone and Benzophenone

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Some data on the polarographic reduction of fluorenone[1,2] anthrone[3] and benzophenone[1,4,5,6,7] have been reported in the literature. Fluorenone has been reported to reduce in two steps over a *p*H range of 1.8 to 12, but no half-wave potential data were given.[1] One value for the half-wave potential of −0.99 volt was reported for fluorenone in a solution of aqueous isopropyl alcohol containing tetramethylammonium hydroxide.[2] Anthrone has been found to reduce in two steps at *p*H 6 and 7 in a dioxane medium, but the wave form was poor in all cases.[3] More numerous studies of benzophenone have been made.[1,4,5,6,7]

In some recent studies involving aromatic ketones we had occasion to observe the polarographic behavior of fluorenone and anthrone in ethanol–water media at various hydrogen-ion concentrations. Since so few data have been published on these two compounds, it was thought of interest to report the half-wave potentials at various *p*H values. Some additional runs were made with benzophenone in the same media in order to have a comparison of the three ketones under comparable conditions. The data are given in Table I.

TABLE I

$E^{1/2}$ *vs.* THE SATURATED CALOMEL ELECTRODE (ALL $E^{1/2}$ VALUES ARE NEGATIVE)

Fluorenone				Anthrone				Benzophenone			
*p*H (aq.)	*p*H (alc.)	$E^1{}_{1/2}$	$E^2{}_{1/2}$	*p*H (aq.)	*p*H (alc.)	$E^1{}_{1/2}$	$E^2{}_{1/2}$	*p*H (aq.)	*p*H (alc.)	$E^1{}_{1/2}$	$E^2{}_{1/2}$
1.1	1.2	0.63	0.87	1.3	2.0	0.89	...	1.2	1.5	0.93	1.28
2.2	2.7	.69	0.95	2.3	3.1	0.99	1.23				
3.1	3.6	.76	1.03	2.8	3.6	1.03	1.22	3.2	3.7	1.06	1.30
4.1	4.5	.81	1.07	3.8	4.8	..	1.17	4.3	4.8	1.10	1.29
5.0	5.5	.86	1.08	5.2	6.0	..	1.21	5.3	5.8	..	1.24
6.2	6.8	.91	1.10	6.3	7.2	..	1.26				
7.1	7.8	.96	1.13	6.9	7.8	..	1.26	7.4	7.9	..	1.33
8.0	8.6	.99	1.16	8	8.9	..	1.29^a				
9.1	9.8	1.10	1.32	9	10.3	..	1.26^a	9.1	9.8	..	1.40^b
9.9	10.4	1.11	1.36	10	10.9	..	1.27	10.3	11.0	..	1.43^b
10.8	11.1	1.11	1.36	10.5	11.4	..	1.29				
11.6	11.6	1.10	1.35	11.8	12.6	..	1.27				
12.2	12.2	1.10	1.35	12.5	12.6	..	1.31	12.5	12.6	..	1.50^b

[a] Waves at higher potentials (1.48, 1.50, respectively) also present. [b] Waves at higher potentials (1.54, 1.57, 1.80, respectively) also present.

Two waves of approximately equal heights were observed with fluorenone over the entire *p*H range. In the more acid solutions the half-wave potentials of both waves are *p*H dependent, and the two waves do not merge at higher *p*H values as is frequently the case. There is a large increase in the half-wave potential of both waves at *p*H 9.[8] It should be noted that the type of buffer used was changed at this point.

The wave forms of anthrone were quite good in the ethanol–water media. Only one wave of half-height was observed at a *p*H of 1. At *p*H 2 and 3 two waves of about equal height were found, these merging at a *p*H of about 4. Only one wave of full height was observed at higher *p*H values. It was necessary to use freshly prepared solutions of anthrone since anthraquinone waves, as observed by Stone and Furman,[3] were found in solutions which had stood for some time. In addition, a wave at potentials between those of anthraquinone and anthrone was observed with the older solutions. In the highly alkaline region these additional waves were observed even with fresh solutions. The anthrone wave was still present, however, but the wave height was less than normal.

With benzophenone two waves of about equal height were found at *p*H values of 1 to 5. Above *p*H 5 the two waves merge. At *p*H values above 9, the height of the wave decreased and a second wave at more negative potentials was observed. This is apparently the same effect noted by Ashworth[1] which he attributed to the reduction of a metal ketyl. The same effect was found with anthrone at *p*H values of 8 and 9, but not in more alkaline solutions. The first wave in these cases was of greater height than the second, the total height being equal to that obtained at lower *p*H values.

Experimental

Apparatus.—The current-voltage curves were determined using a Leeds and Northrup Electrochemograph. The electrolysis cell was the H-type used by Lingane and Laitinen,[9] one arm (anode) containing a saturated calomel electrode. A single capillary of Corning marine barometer tubing was used in all the measurements. The

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(1) Ashworth, *Collection Czechoslov. Chem. Communs.*, **13**, 229 (1948).

(2) Baker and Schafer, THIS JOURNAL, **65**, 1675 (1943).

(3) Stone and Furman, *ibid.*, **70**, 3062 (1948).

(4) Schweitzer and Laqueur, *Rec. trav. chim.*, **55**, 959 (1936).

(5) Pasternak, *Helv. Chim. Acta*, **31**, 753 (1948).

(6) Adkins and Cox, THIS JOURNAL, **60**, 1151 (1938).

(7) Wawzonek, Laitinen and Kwiatkowski, *ibid.*, **66**, 827 (1944).

(8) *p*H values herein refer to aqueous solutions.

(9) Lingane and Laitinen, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 504 (1939).

characteristics were: droptime, t = 5.0 sec., m = 1.468 mg./sec., $m^{2/3}t^{1/6}$ = 1.69.

The electrolysis experiments were carried out in a thermostat at 25 ± 0.05°. All volumetric apparatus was calibrated.

Materials and Medium.—The three ketones were purified by recrystallization. Melting points (uncor.) were: anthrone 154°, fluorenone 83.5°, benzophenone 48.5°.

The cell solutions were 25% ethanol by volume in the cases of benzophenone and fluorenone, and 50% ethanol by volume in the case of anthrone. The cell solutions were also 0.1 M in potassium chloride.

To obtain the desired *p*H the following aqueous solutions were used: *p*H 1, hydrochloric acid; *p*H 2 to 8, McIlvaine's buffers (0.1 M citric acid, 0.2 M disodium phosphate); *p*H 9 and 10 Clark and Lubs' buffers (0.1 M sodium hydroxide, 0.1 M boric acid); *p*H 11, sodium carbonate; *p*H 12 and 13, sodium hyroxide. Equal volumes of aqueous buffer and alcoholic solution of the ketone were mixed to form the cell solutions. Both phthalate and acetate buffers were tried in the *p*H range 4 to 5, but the curves were not as well defined as in solutions containing citrate and phosphate. Some tests were also made with fluorenone to see if increased buffer concentration affected the number of reduction waves. No effect of this nature was found.

Assuming two electrons to be consumed in the total reduction of the carbonyl group, the diffusion current constants, $i_D/C\ m^{2/3}t^{1/6}$, were: fluorenone 2.48, anthrone, 2.54 (acid solution), and benzophenone 2.60. The diffusion currents were found to be fairly constant for all three ketones, the above constants being calculated from the average of a large number of measurements. The concentrations of ketones in the cell solutions were normally between 1×10^{-4} and 1×10^{-3} molar.

Measurements of *p*H were made using a glass electrode and a Beckman Model G *p*H meter. Measurements were recorded for both the aqueous solutions and the final cell solutions containing alcohol.

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Use of the Halogen–Metal Interconversion Reaction for the Preparation of an Aromatic Iodo Compound

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The halogen–metal interconversion reaction of organolithium compounds[2]

$$\mathrm{RLi} + \mathrm{R'X} \rightleftarrows \mathrm{R'Li} + \mathrm{RX}$$

(where R and R′ = alkyl or aryl, and X = preferably I or Br) has been applied to a variety of synthetic problems during the ten years since it was first described. In the applications recorded in the literature the interconversion has been used as a means of preparing organolithium compounds not otherwise readily available, and the RX compounds have represented simply by-products. In special cases, however, the halogen–metal interconversion may offer a convenient method for the laboratory preparation of RX compounds. In this Laboratory, in connection with studies concerned with the course of some organolead reactions, a need arose for *p*-iododimethylaniline. The present note describes its preparation from *p*-dimethylaminophenyllithium and iodobenzene.

p-Iododimethylaniline has been prepared from dimethylaniline by direct iodination, and from *p*-aminodimethylaniline by diazotization followed by treatment with potassium iodide. The direct iodination has been accomplished by various methods.[3] Yields are often not mentioned in the literature. The procedure most frequently cited is that of Baeyer,[3a] who used iodine in glacial acetic acid. By this method we obtained only 13% yield, and the crude product was very dark and difficult to decolorize.[4] The best procedure described would appear to be that of Reade and Sim,[3b] who used iodine and iodic acid in glacial acetic acid, and obtained a yield which we calculate as 48%. Ayling, Gorvin and Hinkel[5] diazotized *p*-aminodimethylaniline and obtained 33% yield of *p*-iododimethylaniline by addition of potassium iodide. They note, however, that the reaction with potassium iodide proceeds very slowly, and in our experience this is also true of the diazotization, so that this method of preparation is not convenient.

p-Dimethylaminophenyllithium is easily prepared, and reacts smoothly with iodobenzene to give 42–54% yields (after recrystallization) of *p*-iododimethylaniline. Since there is no free iodine present in this reaction, the crude product has none of the deep violet color characteristic of material prepared in the presence of excess iodine, and pure white plates are obtained by a simple recrystallization without charcoal treatment. *p*-Dimethylaminophenyllithium reacts also with iodine to yield the iodo derivative,

$$p\text{-}(\mathrm{CH_3})_2\mathrm{NC_6H_4Li} + \mathrm{I_2} \longrightarrow p\text{-}(\mathrm{CH_3})_2\mathrm{NC_6H_4I} + \mathrm{LiI}$$

and yields up to 48% have been obtained from this reaction.

Experimental

In each experiment described below, all operations up to the hydrolysis step were conducted in an atmosphere of pure dry nitrogen.

***p*-Dimethylaminophenyllithium and Iodobenzene.**—To 2 g. of lithium metal, cut into small pieces and stirred in 45 ml. of anhydrous ether, there was added a solution of 21.8 g. (0.109 mole) of *p*-bromodimethylaniline in 45 ml. of ether at such a rate that steady refluxing was maintained. After addition was complete the mixture was stirred fifteen minutes longer, then allowed to settle and decanted under nitrogen, through glass wool, into a separatory funnel. This solution of *p*-dimethylaminophenyllithium was added rapidly (without cooling, since there is very little heating effect) to a stirred solution of 44.5 g. (0.218 mole) of iodobenzene in 50 ml. of ether, and the solution was refluxed for one hour, then cooled in an ice-bath and hydrolyzed by the addition of ice-water. The ether layer was separated, washed once with water, and then extracted with

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[1] du Pont Postgraduate Fellow, 1948–1950.

[2] Gilman, Langham and Jacoby, THIS JOURNAL, **61**, 106 (1939); Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938); Wittig, Pockels and Dröge *Ber.*, **71**, 1908 (1938).

[3] (a) Baeyer, *ibid.*, **38**, 2759 (1905); (b) Reade and Sim, *J. Chem. Soc.*, **125**, 157 (1924); Sandin and Williams, THIS JOURNAL, **69**, 2747 (1947), (c) Weber, *Ber.*, **10**, 765 (1877), Merz and Weith, *ibid.*, **10**, 746 (1877); Samtleben, *ibid.*, **31**, 1141 (1898); Marsden and Sutton, *J. Chem. Soc.*, 599 (1936).

[4] Militzer, Smith and Evans, THIS JOURNAL, **63**, 436 (1941), studied the direct iodination of dimethylaniline with iodine in aqueous acetic acid, but report the yield only as "very small."

[5] Ayling, Gorvin and Hinkel, *J. Chem. Soc.*, 613 (1941).