# Electrolytic Reduction of *p*-Bromobenzophenone in the Presence of Benzenethiolate: an Electrochemically Catalysed Aromatic Nucleophilic Substitution

By JEAN PINSON and JEAN-MICHEL SAVÉANT*

(*Laboratoire d'Electrochimie de l'Université de Paris VII, 2, Place Jussieu* 75221 *Paris Cedex* 05)

*Summary* Electrolysis of *p*-bromobenzophenone in the presence of benzenethiolate anion leads to *p*-phenylthiobenzophenone *via* a substitution catalysed by the electrochemical injection of electrons.

THE electrochemical reduction of *p*-bromobenzophenone (I) in MeCN and dimethylformamide (DMF) involves cleavage of the C–Br bond and formation of benzophenone.[1] Decomposition of the initial anion-radical $Ph\text{–}\dot{C}(O^-)\text{–}C_6H_4Br$ into the aryl radical $Ph\text{–}CO\text{–}C_6H_4\cdot$ is a probable intermediary step in the reaction.[1] Trapping the latter radical by a nucleophilic reagent during the course of electrolysis thus appears as as possible means of inducing an $S_NR1$ type substitution[2] based on the well documented reactivity of aryl radicals towards nucleophilic anions.[3]

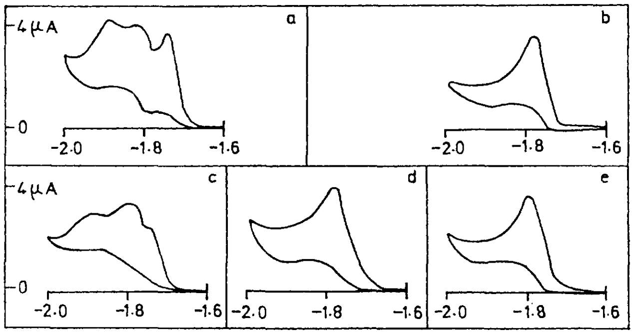


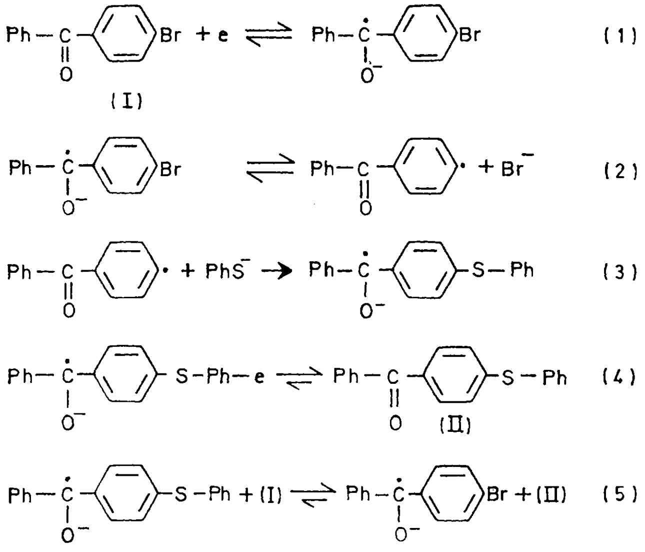
FIGURE. Cyclic voltammograms in MeCN-0·1N-$Et_4NClO_4$-1·5% $H_2O$ of *p*-bromobenzophenone, 1 mmol $l^{-1}$ (a), without $PhS^-$; (c)—(e) with $PhS^-$: (c) 3 mmol $l^{-1}$; (d) 8 mmol $l^{-1}$; (e) 50 mmol $l^{-1}$; and (b) of *p*-phenylthiobenzophenone, 1 mmol $l^{-1}$. Sweep rate 0·4 V $s^{-1}$. All potentials refer to the Ag–0·01N-$AgClO_4$ electrode in MeCN and are expressed in V.

TABLE

| Electrolysis potential/V | F/mol | Yields (%)<br>(II) | <br>$PhCHOHC_6H_4SPh$ | <br>$Ph_2CO$ |
|---|---|---|---|---|
| −1·8 | 0·2 | 80 | 0 | 3 |
| −1·9 | 2·0 | 30 | 65 | 0 |

Evidence that such a reaction actually occurs with $PhS^-$ as the nucleophile is presented in the Figure which shows the change in the cyclic voltammogram of (I) upon addition of increasing amounts of an equimolar mixture of benzenethiol and $Bu^n{}_4NOH$ (traces c, d, and e). The two waves of benzophenone [2nd and 3rd waves in Figure (a)] are gradually replaced by the wave system of *p*-phenylthiobenzophenone (II) [Figure (b)] while the first wave disappears. The final pattern at 50 mmol $l^{-1}$ of $PhS^-$ is almost identical to the cyclic voltammogram of pure (II) under the same conditions; variation of the time elapsed between the mixing of the reagents and the recording of voltammograms does not result in any modification. Additional evidence that spontaneous substitution does not occur was obtained by recovery of starting materials after 2 days contact [(I): 10 mmol $l^{-1}$; $PhS^-$: 100 mmol $l^{-1}$], as checked by g.l.c. after ether extraction.

These observations support the occurence of an $\overset{\rightarrow\leftarrow}{ECE}$ type process,[4] (Scheme) in which the electrons provided by the electrode merely play a catalytic role as shown by the disappearance of the first wave of (I). The standard potential of reaction (2) is $-2{\cdot}00$ V as determined by cyclic voltammetry at high sweep rates where the kinetic effect of follow-up reactions is eliminated. At the potential where (I) is reduced $\text{Ph-}\dot{\text{C}}(\text{O}^-)\text{-C}_6\text{H}_4\text{-S-Ph}$ is oxidizable into the parent ketone either at the electrode or through the solution electron-transfer reaction (5). The overall reaction thus appears to belong to a special field of electrochemistry, 'electrochemistry without current'.



SCHEME

The above deductions are further substantiated by preparative scale experiments. Typical runs [(I) : 10 mmol $l^{-1}$; $PhS^-$: 100 mmol $l^{-1}$] gave results in the Table.

The first experiment clearly shows the catalytic character of the electrochemical reduction. In the second experiment the substitution still occurs with a very good yield but the substituted anion-radical is further reduced into the alcohol, being only in part reoxidized into the ketone. This exemplifies the greater versatility offered by the electrochemical injection of electrons as compared to chemical means, the control of the electrode potential providing the equivalent of a continuous series of variable-strength reducing agents.

This work was supported in part by the CNRS (Equipe de Recherche Associée n° 309: "Electrochimie Organique").

(*Received*, 29*th July* 1974; *Com.* 947.)

[1] L. Nadjo and J. M. Savéant, *J. Electroanalyt. Chem.*, 1971, **30**, 41.

[2] N. Kornblum, Proceedings of the XXIII International Congress of Pure and Applied Chemistry, 4, 1971, 81.

[3] J. K. Kim and J. F. Bunnet, *J. Amer. Chem. Soc.*, 1970, **92**, 7463; 7464; R. A. Rossi and J. F. Bunnet, *ibid.*, 1972, **94**, 683; *J. Org. Chem.*, 1973, **38**, 1407; 3020; J. F. Bunnet and B. F. Gloor, *ibid.*, 1973, **38**, 4156; *ibid.*, 1974, **39**, 382; J. F. Wolfe, J. C. Greene, and T. Hudlicky, *ibid.*, 1972, **37**, 3199; D. E. Bartak, W. C. Danen, and M. D. Hawley, *ibid.*, 1970, **35**, 1206; R. Kumar and P. R. Singh, *Tetrahedron Letters*, 1972, 613.

[4] S. W. Feldberg and L. Jeftic, *J. Phys. Chem.*, 1972, **76**, 2439.