Electrochemical Reactions. Part VI.[1] Application of the Hammett Relationship to the Polarographic Reduction of Substituted 9-Benzylidenefluorenes and 3-Phenylcoumarins

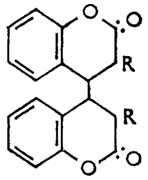
By **J. F. Archer** and **J. Grimshaw**,*† Department of Chemistry, Queen's University, Belfast

The influence of substituents on the half-wave potentials for the polarography of 9-benzylidenefluorenes in 68·1% methanol has been examined. The same linear correlation with Hammett σ-values and $\rho = +0{\cdot}23$ volt is found for substituents on both the benzyl group and the fluorene ring. The half-wave potentials for substituted 3-phenylcoumarins in 68·1% methanol show two linear correlations with Hammett σ-values. Substituents on the phenyl group have $\rho = +0{\cdot}11$ volt and substituents on the coumarin ring have $\rho = +0{\cdot}33$ volt.

THE existence[2] of a linear relationship between the Hammett σ-constant for a substituent and the half-wave potential for the electrochemical reaction under polarographic conditions of a group attached to the benzene ring has been demonstrated for a large number of reducible and oxidisable groups. The olefin bond in stilbene is reduced at a mercury cathode only at very negative potentials.[3] When this bond is conjugated to other groups the potential for reduction becomes less negative and in 9-benzylidenefluorene[4] and 3-phenylcoumarin[5] the olefin bond is reduced within a potential range where accurate polarographic measurements are possible. We have examined the reduction of substituted 9-benzylidenefluorenes and 3-phenylcoumarins in order to compare the Hammett ρ-values for substituent effects applied successively to either end of the bond being reduced. These substituent effects can then be used as a probe to measure the electron distribution in the transition state for the reduction process. A similar study of the reduction of substituted chalcones has been made by other workers[6] and this is relevant to the discussion of our results from 3-phenylcoumarins.

Preparative scale electrochemical reduction of 9-benzylidenefluorene was carried out at a mercury cathode in order to establish the products of this reaction. A good yield of 9-benzylfluorene was obtained as expected since this is also the product from reduction with aluminium amalgam.[7] The corresponding preparative scale electrochemical reduction of coumarins has been well examined. Coumarin[8] yields a mixture of the *meso*- and (±)-forms of (I; R = H), and other substituted coumarins react similarly.[9] Reduction of 3-phenylcoumarin gave a mixture from which one stereochemical form of the bimolecular product (I; R = Ph) was obtained.

Polarography of Substituted 9-*Benzylidenefluorenes*.—Latinen, Wawzonek, and Fan[4] have examined the polarography of a number of phenylated ethylenes including 9-benzylidenefluorene. They showed that the half-wave potentials for reduction were independent of pH and that two electrons were involved per molecule reduced. Their suggestion that the reduction of 9-benzylidenefluorene involves a slow reversible potential-determining addition of one electron followed by rapid irreversible addition of the second electron has subsequently been considered[10] to be indistinguishable theoretically from the irreversible addition of two electrons. These substances are reduced at such negative potentials at a dropping mercury electrode that it is necessary to use tetramethylammonium salts as supporting electrolyte. The polarographic wave then becomes well separated from the current rise owing to electrolyte decomposition at negative potentials.



(I)

The independence of the polarographic half-wave potential of 9-benzylidenefluorene with pH was confirmed using Bates's buffer solutions[11] as supporting electrolyte. The buffers were made up replacing any alkali-metal salts with the corresponding tetramethylammonium salt. The results for $E_{\frac{1}{2}}$ are given in Table 2 calculated *versus* the standard hydrogen electrode so as to eliminate any change in anode potential which results from a change in chloride ion activity. Since pH has no significant influence, subsequent polarograms were carried out in unbuffered 0·1 molal tetramethylammonium chloride solution.

The polarographic results (Table 1) are plotted in Figure 1 using σ-values taken from the compilation of

---

† *Present address:* Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. 02139, U.S.A.

[1] Part V, R. N. Gourley and J. Grimshaw, *J. Chem. Soc.* (*C*), 1968, 2388.

[2] For summaries of the literature see P. Zuman, *Coll. Czech. Chem. Comm.*, 1960, **25**, 3225; P. Zuman, 'Substituent Effects in Organic Polarography,' Plenum Press, New York, 1967.

[3] F. Goulden and F. L. Warren, *Biochem. J.*, 1948, **42**, 420.

[4] H. A. Latinen and S. Wawzonek, *J. Amer. Chem. Soc.*, 1942, **64**, 1765; 2365; S. Wawzonek and J. W. Fan, *ibid.*, 1946, **68**, 2541.

[5] R. Patzak and L. Neugebauer, *Monatsh.*, 1952, **83**, 776.

[6] V. D. Bezuglyi, V. F. Lavrushin, and G. G. Belons, *J. Gen. Chem.* (*U.S.S.R.*), 1965, **35**, 609.

[7] J. Thiele and F. Henle, *Annalen*, 1906, **347**, 298.

[8] A. J. Harle and L. E. Lyons, *J. Chem. Soc.*, 1950, 1575.

[9] R. N. Gourley, J. Grimshaw, and P. G. Millar, *Chem. Comm.*, 1967, 1278.

[10] P. Delahey, *J. Amer. Chem. Soc.*, 1953, **75**, 5716; S. Wawzonek, E. W. Berkey, and M. E. Runner, *J. Electrochem. Soc.*, 1955, **102**, 235.

[11] R. G. Bates, M. Paabo, and R. A. Robinson, *J. Phys. Chem.*, 1963, **67**, 1833.

TABLE 1

Polarography of substituted 9-benzylidenefluorenes

Subst.[a]	$-E_{\frac{1}{2}}$ ±0·005 [a]	αn ±0·03	Subst.[a]	$-E_{\frac{1}{2}}$ ±0·005 [b]	αn ±0·03
4′-OMe	1·730	0·85	3′-Cl	1·592	1·17
4′-CH_3	1·712	0·89	2-Br	1·567	0·67
3′,4′-$(OMe)_2$	1·705	0·88	2,7-I_2......	1·473	0·40
4′-Pr^i	1·711	0·81	2,7-Br_2 ...	1·501	1·10
H	1·671	0·99	2,7-Cl_2 ...	1·542	1·03
3′-OMe	1·653	1·07			
4′-Cl	1·632	0·97			

[a] Primes refer to positions on the benzylidene group. [b] Volts *versus* Ag/AgCl wire in 0·1 molal Me_4NCl; solvent 68·1% MeOH.

TABLE 2

Polarography of 9-benzylidenefluorene

Buffer soln.	pH	$-E_{\frac{1}{2}}$ ±0·005 [a]	$M(Cl^-)$	$-0·059 \log\gamma(Cl^-)$	$-E_{\frac{1}{2}}$ standardised [b]
Bates's *F* [11]	7·21	1·751	0·012	0·007	1·461
Bates's H [11]	9·52	1·774	0·010	0·006	1·479
0·01 molal Me_4NOH, ±0·01 molal Me_4NCl	13	1·773	0·010	0·006	1·479
0·01 molal Me_4NCl	—	1·771	0·010	0·005	1·478

[a] Volts *versus* internal Ag/AgCl anode. Volts *versus* standard hydrogen electrode.

McDaniel and Brown.[12] Other workers [13] have shown that substituent effects are transmitted from the 2-position through one ring of fluorene to the 9-position, and any mesomeric effect transmitted through the second benzene ring can be neglected in most cases. Accordingly, Hammett σ-values for the fluorene 2-substituents were taken as those of the corresponding benzene *meta*-substituent. All the data can be accommodated by the one linear relationship with ρ = 0·23 ± 0·01 v, the correlation coefficient being 0·982. Taking αn = 0·98 ± 0·04, the dimensionless Hammett ρ = 3·8 ± 0·2.[14] Computing the data from 9-benzylidenefluorene and the four derivatives with substituents in the fluorene ring gives ρ = 0·22 ± 0·05 v, correlation coefficient 0·935. The data from 9-benzylidenefluorene and the seven derivatives with substituents in the benzylidene group give ρ = 0·212 ± 0·001 v, correlation coefficient 1·00.

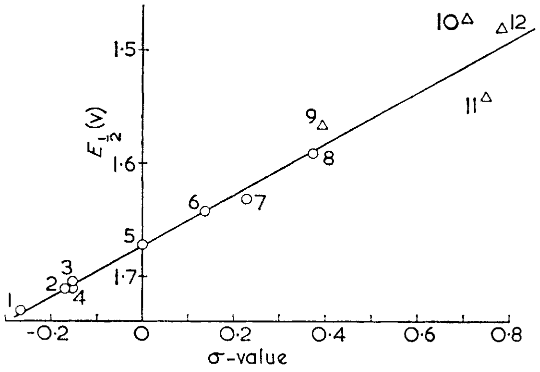


FIGURE 1 Hammett plot of substituted 9-benzylidenefluorenes; $E_{\frac{1}{2}}$ values (volts *versus* internal Ag/AgCl anode) in 68·1% methanolic 0·1 molal Me_4NCl; 1, 4′-OMe; 2, 4′-Me; 3, 3′,4′-$(OMe)_2$; 4, 4′-Pr^i; 5, unsubst.; 6, 3′-OMe; 7, 4′-Cl; 8, 3′-Cl; 9, 2-Br; 10, 2,7-I_2; 11, 2,7-Cl_2; 12, 2,7-Br_2

These results suggest that the transition state for the reduction of 9-benzylidenefluorene has, in the olefinic bond being reduced, a distribution of electrons that is essentially equally dense around each of the two carbon atoms of the bond.

Polarography of Substituted 3-*Phenylcoumarins*.—The polarography of coumarin and some of its derivatives, including 3-phenylcoumarin, has been examined in detail by other workers.[5,8] The half-wave potentials for these substances are pH-independent but in solutions more alkaline than pH 9 the situation is complicated by hydrolysis of coumarin to the *cis*-coumarate ion which also shows a polarographic wave at more negative potentials. Experiment showed an unbuffered electrolyte to be unsuitable for the polarography of 3-phenylcoumarin because waves due to both the coumarin and the coumarate ion were present. Finally, an electrolyte of 0·1 molal potassium chloride buffered with phosphate salts was chosen. The polarographic waves occur at less negative potentials than in the previous case and this permits the use of alkali-metal salts for the supporting electrolyte.

A series of substituted 3-phenylcoumarins was prepared by condensing together the appropriate 2-hydroxybenzaldehyde and phenylacetic acid. Reduction involves overall addition of one electron and one proton to give a radical species which subsequently dimerises. The polarography results (Table 3) are plotted in Figure 2.

TABLE 3

Polarography of substituted 3-phenylcoumarins

Subst.	$-E_{\frac{1}{2}}$ ±0·005 [a]	αn ±0·03	Subst.[b]	$-E_{\frac{1}{2}}$ ±0·005 [a]	αn ±0·03
7-OMe ...	1·641	0·86	6,8-Br_2	1·286	0·744
7-Bu^t	1·599	0·99	4′-OMe	1·585	0·96
6-Me	1·567	0·94	3′,4′-$(OMe)_2$	1·563	0·87
H	1·552	1·00	4′-Pr^i	1·573	0·93
8-OMe ...	1·542	0·97	3′-OMe	1·540	0·94
7-Cl	1·417	0·99	3′-Cl	1·511	1·00
6-Br	1·443	0·98			

[a] Volts *versus* Ag/AgCl wire in 0·1 molal KCl; solvent 68·1% MeOH. [b] Primes refer to positions on the phenyl group.

Substituents on the 3-phenyl group gave a Hammett plot with ρ = 0·112 ± 0·007 v, correlation coefficient 0·991 with six experimental points; αn = 0·96 ± 0·02 and so the dimensionless Hammett ρ = 1·8 ± 0·1. Substituents on the coumarin ring gave a Hammett plot with ρ = 0·33 ± 0·03 v, correlation coefficient 0·97 with eight experimental points; αn = 0·96 ± 0·02 and so the dimensionless Hammett ρ = 5·4 ± 0·5.

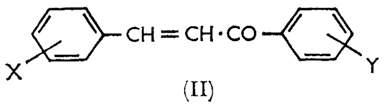
---

[12] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

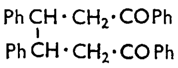
[13] J. D. Dickinson and C. Eaborn, *J. Chem. Soc.*, 1959, 3574; C. Eaborn, R. C. Golesworthy, and M. N. Lilly, *ibid.*, 1961, 3052; J. A. Parry and K. D. Warren, *ibid.*, 1965, 4049; K. D. Warren and J. R. Yandle, *ibid.*, 1965, 5518.

[14] L. Meites, in 'Treatise on Analytical Chemistry,' ed. I. M. Kolthoff and P. J. Elving, Interscience, New York, 1963, part I, vol. 4, p. 2333; P. Delahay, 'New Instrumental Methods in Electrochemistry,' Interscience, New York, 1954, p. 74; J. Koutecky, *Coll. Czech. Chem. Comm.*, 1953, **18**, 597.

These results can be compared with the Hammett plot[6] for the reduction of substituted chalcones (II).



(II)



$$\begin{matrix}\text{PhCH}\cdot\text{CH}_2\cdot\text{COPh}\\ |\\ \text{PhCH}\cdot\text{CH}_2\cdot\text{COPh}\end{matrix}$$

(III)

Here also, reduction involves overall addition of one electron and one proton, but proton addition must be involved in the electrochemical rate-determining step since the half-wave potentials are pH-dependent. Dissolving metal reduction of chalcone in acetic acid yields the *meso*- and (±)-forms of (III)[15] by dimerisation of the radical initially formed. At pH 2·93 $\rho_X = 0{\cdot}17$ v and $\rho_Y = 0{\cdot}26$ v, and at pH 6·97 $\rho_X = 0{\cdot}20$ v and $\rho_Y = 0{\cdot}50$ v in 50% methanol as solvent.

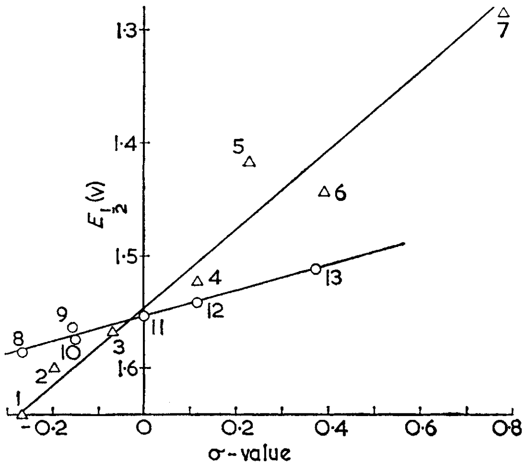


FIGURE 2 Hammett plot of substituted 3-phenylcoumarins; $E_{\frac{1}{2}}$ values (volts *versus* internal Ag/AgCl anode) in 68·1% methanolic 0·1 molal KCl: 1, 7-OMe; 2, 7-Bu^t; 3, 6-Me; 4, 8-OMe; 5, 7-Cl; 6, 6-Br; 7, 6,8-Br$_2$; 8, 4′-OMe; 9, 3′,4′-(OMe)$_2$; 10, 4′-Pr^i; 11, unsubst.; 12, 3′-OMe; 13, 3′-Cl

In both cases the transition state possesses anion-radical character stabilised by resonance over the conjugated carbonyl system and, if this resembles the radical intermediary produced, the oxygen end of the αβ-unsaturated carbonyl system will possess more anion character and the carbon end less anion, but more radical character. This is in accord for the chalcone system with the relative magnitudes of ρ_X and ρ_Y, which result from stabilisation of the transition state by electron withdrawal. For the 3-phenylcoumarin system, substituents exert a relatively small effect ($\rho = 0{\cdot}11$) probably because the phenyl group is attached to a carbon atom whose electron density changes little in forming to the transition state. Substituents on the coumarin ring could influence the reaction by effects transmitted to both the 4- and the 2-positions. Since a good correlation is observed between half-wave potentials with *meta*-σ-constants used for 6- and 8-substituents and *para*-σ-constants used for 7-substituents, these must influence the reaction principally by effects transmitted to the 4-position. The Hammett ρ-value (0·33) indicates a higher degree of electron density, in the transition state, on the 4-position than the 3-position. This is to be expected if the transition state resembles the radical which is the electrochemical product and which subsequently dimerises to give (I).

EXPERIMENTAL

Molecular weights were determined using a Mechrolab vapour pressure osmometer, model 301A, with dichloromethane as solvent.

Polarography. General Procedure.—A Southern Analytical model A1650 manual polarograph was used and time-averaged currents were recorded. Solutions were prepared by weight and concentration expressed in molal terms. The solvent was aqueous methanol (68·1%). The supporting electrolyte contained chloride ions and an Ag/AgCl wire was used as both anode and reference electrode; it was bent around the capilliary inserted into the lid of the polarographic vessel and sealed with paraffin wax. The vessel had a volume of about 10 ml., and could be flushed with a stream of nitrogen pre-saturated with solvent and with the outlet connected to a trap to prevent ingress of air. Measurements were made at 25° ± 0·1° with the mercury height adjusted to give a drop time of around 4 sec., the same capilliary and mercury height being used throughout. Bulk amounts of electrolyte, sufficient for all polarograms, were prepared and each group of results given in the Tables was obtained with a minimum of delay between individual polarograms.

9-Benzylidenefluorene, 3-phenylcoumarin, and their derivatives each gave a single polarographic wave similar to those described for the parent compounds in other aqueous-organic solvent mixtures.[4,5] $E_{\frac{1}{2}}$ values were read off from the polarograms and also checked from the intercept of the graph of E *versus* log $(i/i_d - i)$ where i_d is the diffusion current and i the current at potential E. The slope of the graph, which was linear, is $\boldsymbol{R}T/2{\cdot}303\alpha nF$ and hence αn was calculated where α is the transfer coefficient and n the number of electrons transferred in the electrochemical step.[14]

Electrochemical Reductions. General Procedure.—The electrolysis vessel[16] and potentiostat[17] have been described previously, and the general procedure has been described in other papers of this series. A mercury cathode was used throughout and nitrogen passed through the catholyte. The reference half-cell for cathode potentials was an Ag/AgCl wire immersed in the supporting electrolyte used for polarographic measurements. Cathode potentials were set to correspond to the polarographic diffusion plateau.

2,7-*Di-iodofluorene*.—2,7-Diaminofluorene (5·0 g.) was dissolved in hydrochloric acid (25 ml.; 5N) and the solution cooled to 0° when sodium nitrite (3·5 g.) in water was slowly added. When diazotisation was completed, a solution of potassium iodide (8·3 g.) in water was added, causing a vigorous evolution of nitrogen. The solution was warmed to 60°, extracted with benzene, and the benzene layer washed with sodium thiosulphate solution and water. The benzene solution was dried (Na_2SO_4) and filtered through a short column of active alumina which was washed with

---

[15] R. L. Finch and D. E. White, *J. Chem. Soc.*, 1940, 3367.
[16] R. Pasternak, *Helv. Chim. Acta*, 1948, **31**, 772.
[17] J. Grimshaw and R. K. Quigg, *Analyst*, 1966, 667.

more benzene. Evaporation of the eluent left 2,7-*di-iodofluorene* as a cream solid recrystallized from benzene, m.p. 195° (5·0 g., 48%) (Found: C, 37·6; H, 2·0. $C_{13}H_8I_2$ requires C, 37·4; H, 1·9%).

Substituted 9-*Benzylidenefluorenes*.—Most of the substituted 9-benzylidenefluorenes were prepared by refluxing the appropriate benzaldehyde and fluorene in xylene containing a little piperidine over potassium hydroxide in a Dean–Stark apparatus. Elimination of unreacted fluorene from 9-benzylidene-2-bromofluorene proved troublesome and this compound was prepared by an alternative route. Compounds not previously described in the literature are as follows. 9-(3-*Methoxybenzylidene*)*fluorene*, b.p. 240°/1·0 mm., crystallised from ethanol as a colourless solid, m.p. 111—112° (Found: C, 88·2; H, 5·9. $C_{12}H_{16}O$ requires C, 88·7; H, 5·6%); 9-(3,4-*dimethoxybenzylidene*)*fluorene*, yellow needles from ethanol, m.p. 112—113° (Found: C, 84·0; H, 5·7. $C_{22}H_{18}O_2$ requires C, 84·1; H, 5·7%); 9-benzylidene-2,7-di-iodofluorene crystallised from acetic acid as a cream solid, m.p. 143—144° (Found: C, 47·5; H, 2·4. $C_{20}H_{12}I_2$ requires C, 47·4; H, 2·4%).

9-*Benzyl*-2-*bromo*-9-*hydroxyfluorene*.—A solution of 2-bromofluoreneone (1·15 g.) in ether (20 ml.) was added to the Grignard reagent from benzyl chloride (4·24 g.) and magnesium (0·54 g.) in ether (20 ml.). The mixture was refluxed for 30 min., poured into iced ammonium chloride solution, and the organic layer separated, washed with water, and dried. Evaporation of the solvent left an oil which was chromatographed on alumina. Elution with ether and evaporation of the solvent afforded 9-*benzyl*-2-*bromo*-9-*hydroxyfluorene* (8·0 g.) which crystallised from light petroleum (b.p. 60—80°) as needles, m.p. 114—115° (Found: C, 68·2; H, 4·6. $C_{20}H_{15}BrO$ requires C, 68·4; H, 4·4%).

9-*Benzylidene*-2-*bromofluorene*.— 9-Benzyl-2-bromo-9-hydroxyfluorene (0·59 g.) was refluxed with formic acid (12 ml.) for 1 hr. Water was then added and the product extracted with benzene, washed with water, and dried (Na_2SO_4). Chromatography of the extract on alumina and elution with benzene followed by evaporation of the solvent yielded 9-*benzylidene*-2-*bromofluorene* as a yellow resin (0·45 g., 80%) (Found: C, 72·5; H, 3·75. $C_{20}H_{13}Br$ requires C, 72·1; H, 3·9%), probably a mixture of *cis*- and *trans*-forms.

Polarography of Benzylidenefluorenes.—Solutions of each benzylidenefluorene (6×10^{-4} molal) and tetramethylammonium chloride (0·1 molal) were prepared in aqueous methanol (68·1%) and placed in the polarographic vessel fitted with an internal silver/silver chloride anode and the polarograms recorded.

Influence of pH *on* $E_{\frac{1}{2}}$ *of Benzylidenefluorene*.—The buffer solutions required were prepared according to Bates's directions [11] but all cations were replaced by the tetramethylammonium ion. We prepared an aqueous solution of tetramethylammonium chloride, converted this into the hydroxide as required by passage through a column of Amberlite IRA-400 (hydroxide form),[18] and diluted the effluent to 0·1N, estimated by titration with standard acid. The required weights of this solution, 0·1N-tetramethylammonium chloride, the acid component of the buffer, water, and methanol were then mixed to give 68·1% methanol and made 3×10^{-4} molal in benzylidenefluorene. $E_{\frac{1}{2}}$ values are calculated *versus* the standard hydrogen electrode taking $E°(Ag/AgCl) = 0·170$ [19] and values of log $\gamma(Cl^-)$ from the mean ionic activity coefficient of potassium chloride in aqueous methanol.[20]

Electrochemical Reduction of 9-*Benzylidenefluorene*.—The catholyte was a solution of 9-benzylidenefluorene (0·30 g.) in 1·0 molal potassium hydroxide in aqueous methanol (150 ml.; 68%). The anolyte was 1·0 molal aqueous methanolic (68%) potassium hydroxide with a lead anode. Electrolysis was continued at 50° with a cathode potential of −1·86 v and was complete after 4 hr. when the catholyte was separated and cooled. 9-Benzylfluorene (0·27 g., 90%) crystallised out and was recrystallised from methanol as needles, m.p. 133—134° (lit.,[7] 130—131°) undepressed on admixture with authentic material.[7]

Preparation of Substituted 3-*Phenylcoumarins*.—The appropriate 2-hydroxybenzaldehyde (7 mmoles) and potassium phenylacetate (7 mmoles) were refluxed with acetic anhydride (4 ml.) for 10 hr. Water was then added and the product extracted with dichloromethane, washed with potassium hydrogen carbonate solution and water, dried ($MgSO_4$), and the solvent removed. The residual coumarin was crystallised from ethanol. Compounds not previously described in the literature: 7-*t*-*butyl*-3-*phenylcoumarin*, colourless needles from ethanol, m.p. 147—148° (Found: C, 81·9; H, 6·6. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%); 7-*chloro*-3-*phenylcoumarin*, colourless needles from ethanol, m.p. 150—151° (Found: C, 70·2; H, 3·8. $C_{15}H_9ClO_2$ requires C, 70·1; H, 3·5%); 3-(4-*isopropylphenyl*)*coumarin*, colourless needles from ethanol, m.p. 145—146° (Found: C, 81·4; H, 6·1. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%); 3-(3-*methoxyphenyl*)*coumarin*, colourless needles from ethanol, m.p. 103—104° (Found: C, 76·0; H, 4·8. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%).

4-*t*-*Butyl*-2-*hydroxybenzaldehyde*.—3-t-Butylphenol (38 g.) was dissolved in a solution of potassium hydroxide (140 g.) in water (175 ml.) when trichloroacetic acid (51 g.) dissolved in water (50 ml.) was added. The mixture was heated cautiously and when the initial violent reaction had subsided, the whole was refluxed for 1 hr., acidified with sulphuric acid (50 ml.) and water (60 ml.), and steam-distilled. The oily distillate was collected in ether and shaken overnight with a saturated solution of sodium hydrogen sulphite. The crystalline precipitate of bisulphite compound which separated was collected and decomposed with dilute sulphuric acid to yield 4-t-butyl-2-hydroxybenzaldehyde as an oil (4·0 g.) which was characterised as its 2,4-*dinitrophenylhydrazone*, red needles from ethanol, m.p. 266—267° (Found: C, 78·3; H, 5·9; N, 5·0. $C_{19}H_{17}NO_2$ requires C, 78·3; H, 5·9; N, 4·8%).

Polarography of Substituted 3-*Phenylcoumarins*.—Solutions of each coumarin (3×10^{-4} molal) were prepared in a supporting electrolyte of potassium chloride (0·1 molal), disodium hydrogen phosphate (0·01 molal), and potassium dihydrogen phosphate (0·01 molal) dissolved in aqueous methanol (68%). An internal Ag/AgCl anode was used and polarograms were obtained as previously described.

Electrochemical Reduction of 3-*Phenylcoumarin*.—The electrolyte contained lithium chloride (16·6 g.), hydrochloric acid (61·5 ml.; 0·1N), trisodium citrate (9·75 g.), water (66 g.), and methanol (274 g.). This solution was used as

---

[18] G. A. Harlow, C. M. Noble, and G. E. A. Wylde, *Analyt. Chem.*, 1956, **28**, 787.

[19] D. J. G. Ives and G. J. Janz, 'Reference Electrodes; Theory and Practice,' Academic Press, New York, 1961.

[20] G. Akerlöf, *J. Amer. Chem. Soc.*, 1930, **52**, 2353; C. L. de Ligny, P. F. M. Luykx, M. Rehbach, and A. A. Wieneke, *Rec. Trav. chim.*, 1960, **79**, 699.

anolyte with a silver anode. The catholyte was a solution of 3-phenylcoumarin (0·20 g.) in the electrolyte (150 ml.). Reduction was carried out at a cathode potential of −1·65 v and was complete after 9 hr. when the catholyte was separated, evaporated to a small volume, and diluted with water. The product was extracted with ether, washed with water, dried ($MgSO_4$), and the solvent removed, leaving a solid (0·17 g.) which crystallised from ether as colourless needles, m.p. 292—293° (Found: *M*, 442. $C_{30}H_{22}O_4$ requires *M*, 446).

Thanks are given to Queen's University for the award of a Musgrave Studentship to J. F. A.

[8/1215 *Received, August 20th,* 1968]