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Volume 6

A Review of the Literature Published up to the End of 1976

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Preface

The responsibility for compiling these Specialist Periodical Reports leaves one very much indebted to the considerable efforts of the authors, who invariably are active scientists with a heavy commitment. At times pressure of work is so great that a deadline cannot be met and there is a resultant imbalance in the final volume.

The Senior Reporter apologizes for the fact that this has happened in the present volume, which is more heavily weighted towards theory and technique than was the original intention. Hopefully the balance may be redressed in subsequent volumes.

The interest in organic electrochemistry is still well sustained, and there would seem to be a continuing need for an annual review (Chapter 1). Professor Schmidt contributes the second part of the review on electron-transfer reactions, the first part having appeared in Volume 5 of this series (Chapter 4).

The interfacial tension of solid electrodes is a matter of considerable interest to electrochemists and a review of progress in this field seemed both useful and timely but of necessity covering a fairly long time-scale (Chapter 2). It is also hoped that the review of a.c. impedance methods (Chapter 3) will prove helpful to those electrochemists who are interested in the application of the technique to complex reactions and reactions involving intermediates at the interface, being supplementary to existing extensive reviews of studies more related to reactions in the solution.

JUNE 1977 H.R.T.

Contents

1

Organic Electrochemistry – Synthetic Aspects

BY O. R. BROWN

During 1974 the number of publications in this area of research was similar to that of the previous year. The incidence of completely new reactions being reported is quite small, and the rapid progress of the past decade may be giving way to a period of consolidation, emphasis being placed upon increased understanding of detailed reaction mechanisms. One major area for future work will clearly be concerned with transition-metal organic compounds; great interest and activity already exist in the application of electrochemical methods to various porphyrin compounds.

The material included here and the organization of the coverage will be the same as in Volume 5. New textbooks on organic electrochemistry continue to appear.[1—3] A particularly important collection of papers, too numerous to review here individually, has been published in the Soviet Union.[4] Several useful review articles should be mentioned. Morris has given a timely survey of organometallic electrochemistry,[5] and the physical parameters involved in the control of organic electrode processes have been discussed.[6] Intramolecular cyclizations, an important class of electrode reactions, have been reviewed,[7] as has the electrochemistry of carbohydrates and their derivatives.[8] An omission from previous Reports is Lund's survey of the electrochemistry of the hydroxy-group.[9] Other aspects of organic electrochemistry to have been reviewed include the use of redox systems in reductions,[10] amino-acid syntheses,[11] electrochemistry of dithiolylium salts,[12] and the polarography of heterocyclic compounds.[13]

[1] F. Beck, 'Principles and Applications of Electro-organic Chemistry', Verlag Chemie, Weinheim, 1974.
[2] 'Techniques of Electro-organic Synthesis', ed. N. L. Weinberg, Wiley, New York, 1973.
[3] M. Rifi and F. H. Covitz, 'Introduction to Organic Electrochemistry', Dekker, New York, 1974.
[4] Novosti Elektrokhim. Org. Soedin. Tezisy. Dokl. Vses. Soveshch, Elektrokhim. Org. Soedin. 8th, ed. L. G. Feoktistov, 1973, 'Zinatne', Riga, 1973.
[5] M. D. Morris, *Electroanalyt. Chem.*, 1974, **7**, 79.
[6] M. Fleischmann and D. Pletcher, *Adv. Phys. Org. Chem.*, 1973, **10**, 155.
[7] M. Lacan and I. Tabakovic, *Kem. Ind.*, 1974, **23**, 225.
[8] M. Fedoronko, *Adv. Carbohyd. Chem. Biochem.*, 1974, **29**, 107.
[9] H. Lund, in 'Chemistry of the Hydroxyl Group', ed. S. Patai, Wiley, London, 1971, Part 1, p. 253.
[10] P. N. Anantharaman and H. V. K. Udupa, *Trans. Soc. Adv. Electrochem. Sci. Technol.*, 1974, **9**, 108.
[11] I. A. Avrutskaya and M. Ya. Fioshin, *Itogi Nauki Tekh. Electrokhim.*, 1974, **9**, 228.
[12] C. T. Pederson, *Angew. Chem. Internat. Edn*, 1974, **13**, 349.
[13] J. Stradins, V. Kadis, and S. Hiller, *Khim. geterotsikl. Soedinenii*, 1974, 147.

An educational experiment combining organic synthesis and electrochemistry has been devised.[14]

Abbreviations used throughout this chapter are as follows: DMF, *NN*-dimethylformamide; DMSO, dimethyl sulphoxide; THF, tetrahydrofuran; HMPT, hexamethylphosphoramide; TFA, trifluoroacetic acid; MeCN, acetonitrile; HOAc, acetic acid; TEAB, tetraethylammonium bromide; TBAP, tetra-n-butylammonium perchlorate; TMAF, tetramethylammonium fluoroborate; TPAT, tetrapropylammonium tosylate.

1 Reductions

Hydrocarbons.—A further spate of patents has been taken out by Japanese workers for the reduction of benzenoids to the 1,4-dihydro-compounds. Various solvent systems have been suggested for use with quaternary ammonium salt electrolytes and either mercury or amalgam cathodes.[15—20]

It has been shown that rigorous removal of electrophiles from various aprotic solvents (DMF, THF, HMPT, pyridine and, to a lesser extent, MeCN) enables the dianions derived from anthracene, 9,10-diphenylanthracene, benzophenone, or nitrobenzene to remain stable on the time-scale of cyclic voltammetry.[21] These conditions were achieved by the addition of neutral alumina to the solution. Quaternary ammonium ions Et_4N^+ and Bu_4N^+ are not rapid proton donors for the anthracene dianion at −30 °C.

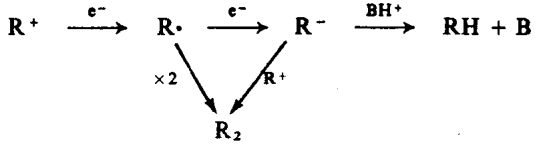
Electrochemical methods have been used to determine the rates of protonation of polynuclear aromatic radical anions generated in DMSO.[22] Substituted phenols and 9-phenylfluorene were used as donors. Protonation rates correlated with optimum electron densities in the anions.

The reduction of 9,10-diethylideneacenaphthene, in DMF containing phenol, consumes more than 4 F mol^{-1}, indicating that there is reduction of the olefinic bonds and of the naphthalene system.[23] The thermodyamics and kinetics of disproportionation and protonation of radical anions generated electrochemically from tetraphenylethylene, triphenylethylene, 1,1-diphenylethylene, α-methylstilbene, and *trans*-stilbene have been studied in DMF and in HMPT.[24]

Reductions of the cycloheptatrienyl and 1,2,3-triphenylcyclopropenyl cations in MeCN each give two amperometric peaks, corresponding to the formation of the radicals and anions respectively.[25] The products resulting from controlled-potential

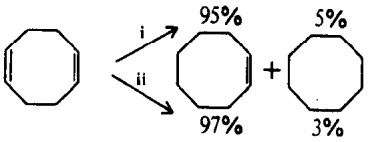
[14] P. E. Iverson, *J. Chem. Educ.*, 1974, **51**, 489.
[15] A. Misono and T. Osa, Ger. P. 1 668 471 (*Chem. Abs.*, 1974, **80**, 140 596).
[16] T. Hatayama and T. Yamamoto, Japan. P. 74 47 740 (*Chem. Abs.*, 1975, **82**, 155 576).
[17] T. Hatayama, Y. Hamano, K. Udo, and T. Yamamoto, Japan. P. 74 41 192 (*Chem. Abs.*, 1975, **82**, 147 142).
[18] T. Hatayama, K. Udo, Y. Hamano, and G. Inoue, Japan. P. 74 33 955 (*Chem. Abs.*, 1975, **82**, 117 890).
[19] M. Fujii, M. Moritake, and T. Okazaki, Japan. Kokai 74 56 952 (*Chem. Abs.*, 1974, **81**, 135 682).
[20] M. Fujii, M. Moritake, and T. Okazaki, Japan. Kokai 74 100 050 (*Chem. Abs.*, 1975, **82**, 86 181).
[21] B. S. Jensen and V. D. Parker, *J.C.S. Chem. Comm.*, 1974, 367.
[22] A. J. Fry and A. Schuttenberg, *J. Org. Chem.*, 1974, **39**, 2452.
[23] S. Valcher and A. M. Ghe, *J. Electroanalyt. Chem.*, 1974, **55**, 407.
[24] T. Troll and M. M. Baizer, *Electrochim. Acta*, 1974, **19**, 951.
[25] R. Breslow and R. F. Drury, *J. Amer. Chem. Soc.*, 1974, **96**, 4702.

electrolyses at each wave are the dimers. Even in the presence of hydroxylic solvents, *e.g.* HOAc, the anions react to form the dimer. The anion can in part be protonated, however, by the use of guanidinium perchlorate as supporting electrolyte (Scheme 1). The extraordinary appearance of the second cyclic voltammetric peak will clearly attract further investigation of this system.



Scheme 1

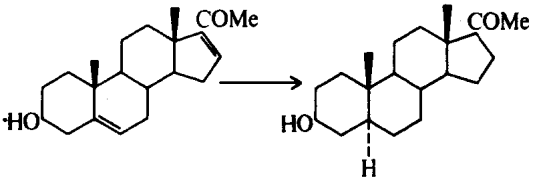
Alicyclic polyene compounds can be reduced in HMPT–alcohol solvents containing inorganic electrolytes[26] (*e.g.* see Scheme 2). Cyclododeca-1,5,9-triene yields 2% diene, 94% cyclododecene, and 4% cyclododecane.



Reagents: i, EtOH–HMPT–LiCl; ii, PrOH–HMPT–LiCl

Scheme 2

Cathodic hydrogenation of olefinic bonds of several steroids has been carried out at palladized cathodes in acidic ethanol.[27] Even isolated olefinic bonds were reduced, but carbonyl groups were unaffected. Some of the reductions were stereoselective;



Scheme 3

for example, 3β-hydroxypregna-5,16-dien-20-one gave 3β-hydroxy-5α-pregnan-20-one in 90% yield (33% when purified) (Scheme 3). The olefinic bond in 1-chloroacenaphthylene-2-carboxylic acid can be reduced polarographically in aqueous alcoholic solution; functional groups are left intact.[28]

Rates of reaction of electrogenerated polycyclic hydrocarbon radical anions with organic halides, azides, tosylates, and sulphonamides have been studied by the polarographic method of catalytic currents.[29]

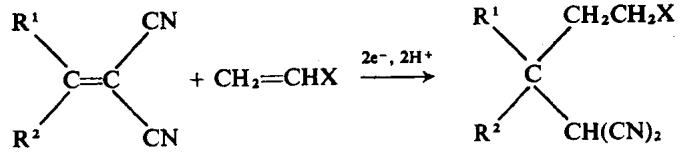
[26] S. Senoo and K. Saotome, Japan. P. 74 16 413 (*Chem. Abs.*, 1974, **81**, 169 220).
[27] K. Junghans, *Chem. Ber.*, 1974, **107**, 3191.
[28] A. M. Ghe and S. Valcher, *J. Electroanalyt. Chem.*, 1974, **55**, 417.
[29] H. Lund, M.-A. Michel, and J. Simonet, *Acta Chem. Scand.* (*B*), 1974, **28**, 900.

Activated Olefins.—The reduction of fumaric and maleic acids to succinic acid with 100% current yield at a rotating Pb cylinder in 5% H_2SO_4 has been patented.[30]

In 0.1N-H_2SO_4, acrylonitrile is converted into amines at a platinum electrode held at the reversible hydrogen potential.[31] At more positive potentials, propionaldehyde is produced in 56—7% yield.

The usual crop of patents concerned with electrohydrodimerization of acrylonitrile to adiponitrile appeared during 1974.[32—35] The reduction performed at a mercury cathode in liquid ammonia–ammonium perch orate electrolyte at −78 °C is claimed to give higher current efficiencies for adiponitrile than are obtained under aqueous conditions.[36] The monocarboxylation of acrylonitrile by its reduction at cadmium cathodes in the presence of CO_2 and water has been carried out with 48% current efficiency[37] (see below).

A crossed hydrocoupling of 1,1-dicyano-2-methylprop-1-ene and its analogues with acrylonitrile or methyl acrylate in a divided cell has been reported[38] (Scheme 4). Increased length and branching of the alkylidene chain caused current yields to fall.



(X = CN or CO_2Et)

(R^1 = Me, R^2 = Me, Et, Me_2CH, or Me_3C; $R^1 = R^2$ = Et; or R^1CR^2 = cyclopentylidene)

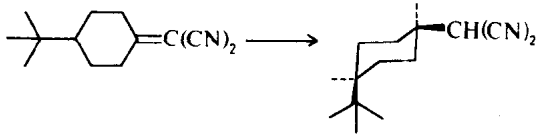
Scheme 4

A mechanistic study of the reductions of dimethyl maleate and dimethyl fumarate in DMF has shown that the *cis* radical anion reacts more rapidly than the *trans*-isomer in self-coupling and cross-coupling reactions, and it spontaneously isomerizes to the *trans* radical anion.[39] *cis*-1,2-Dibenzoylethylene is similarly more reactive than the *trans*-isomer. The effect of ion-pairing upon the dimerization rate of diethyl

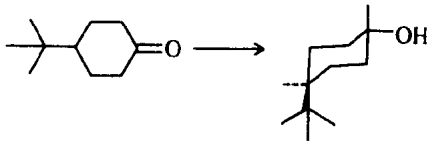
[30] H. V. Udupa, M. S. Venkatachalapathy, and R. I. Kanakam, Indian P. 102 485 (*Chem. Abs.*, 1974, **81**, 130 199).
[31] N. N. Gudeleva, N. A. Zakarina, and G. D. Zakumbaeva, *Izvest. Akad. Nauk Kazakh. S.S.R., Ser. khim.*, 1974, **24**, 75.
[32] C. R. Campbell, D. E. Danly, and W. H. Müller, Ger. Offen. 2 343 138 (*Chem. Abs.*, 1974, **81**, 49 287).
[33] D. L. Sadler and W. A. Heckel, Ger. Offen. 2 343 137 (*Chem. Abs.*, 1974, **81**, 49 288).
[34] F. N. Ruehlen, Ger. Offen. 2 338 341 (*Chem. Abs.*, 1974, **81**, 4347).
[35] J. H. Lester and J. S. Stewart, Ger. Offen. 2 344 294 (*Chem. Abs.*, 1974, **80**, 140 595).
[36] T. Chiba, Y. Takata, and A. Suzuki, *Chem. Letters*, 1974, 1241.
[37] D. A. Tyssee, Ger. Offen. 2 356 657 (*Chem. Abs.*, 1974, **81**, 44 737).
[38] Yu. D. Smirnov, S. K. Smirnov, and A. P. Tomilov, *Zhur. org. Khim.*, 1974, **10**, 1597.
[39] A. J. Bard, V. J. Puglisi, J. V. Kenkel, and A. Lomax, *Faraday Discuss. Chem. Soc.*, 1973, **56**, 353.

fumarate radical anions has been examined.[40] In MeCN the anion radicals are predominantly paired with sodium ions from the supporting electrolyte, but in DMSO a substantial number of the dimerizing anion radicals are unpaired. Radical anions derived from dimethyl fumarate, *trans*-stilbene, ethyl cinnamate, and anthracene all react with butyl bromide, in DMSO–TBAP.[41] In dry solvents, dialkylation occurs, but with added water monoalkylation takes place.

Stereoselective cathodic reductions of some compounds containing exocyclic double bonds have been investigated.[42] The less stable axial isomers are favoured,



67% axial, 33% equatorial
(relative yields)

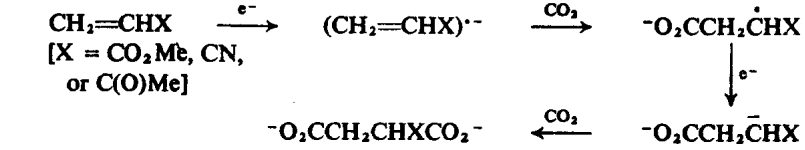


>98% axial (relative)

Scheme 5

but to different extents, according to the electrolytic medium (Scheme 5). Mercury and vitreous carbon cathodes gave similar results. Stereoselectivity was enhanced by the use of LiCl instead of TBAI and by the use of HOAc–DMF in place of ethanol.

The reduction of activated olefins at a mercury cathode in the presence of excess carbon dioxide has been examined in detail.[43] In MeCN–TEAT, disubstituted succinic acids were obtained, provided that the potential was held at a value corresponding to a two-electron wave (Scheme 6). A similar result is obtained even if

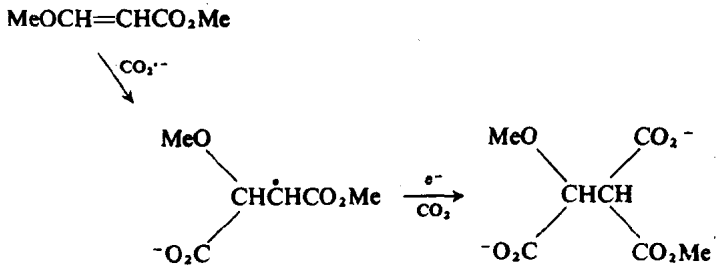


Scheme 6

carbon dioxide is reduced in preference to the olefin (Scheme 7). Monocarboxylation of the olefins to give β-substituted propionic acids proved to be possible in solutions containing water (~2.8 mol l^{-1}):

$$CH_2{=}CHCN + CO_2 + H_2O \xrightarrow{2e^-} OH^- + NCCH_2CH_2CO_2^-$$

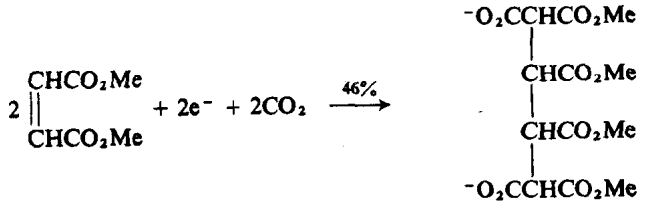
[40] M. D. Ryan and D. H. Evans, *J. Electrochem. Soc.*, 1974, **121**, 881.
[41] S. Margel and M. Levy, *J. Electroanalyt. Chem.*, 1974, **56**, 259.
[42] R. J. Holman and J. H. P. Utley, *Tetrahedron Letters*, 1974, 1553.
[43] D. A. Tyssee and M. M. Baizer, *J. Org. Chem.*, 1974, **39**, 2819.



Scheme 7

A flow system with continuous extraction and neutralization was developed to avoid evolution of hydrogen from the propionic acid.

The competitive reactions of radical anions formed by the reductions of activated olefins at potentials on their first ($1e^-$) reduction wave have been studied.[44] Reaction with a second activated olefin can compete effectively with carboxylation. Thus dimerization can accompany carboxylation during reduction in MeCN–0.25M-TEAT (*e.g.* Scheme 8). Analogous reactions occur with those activated olefins

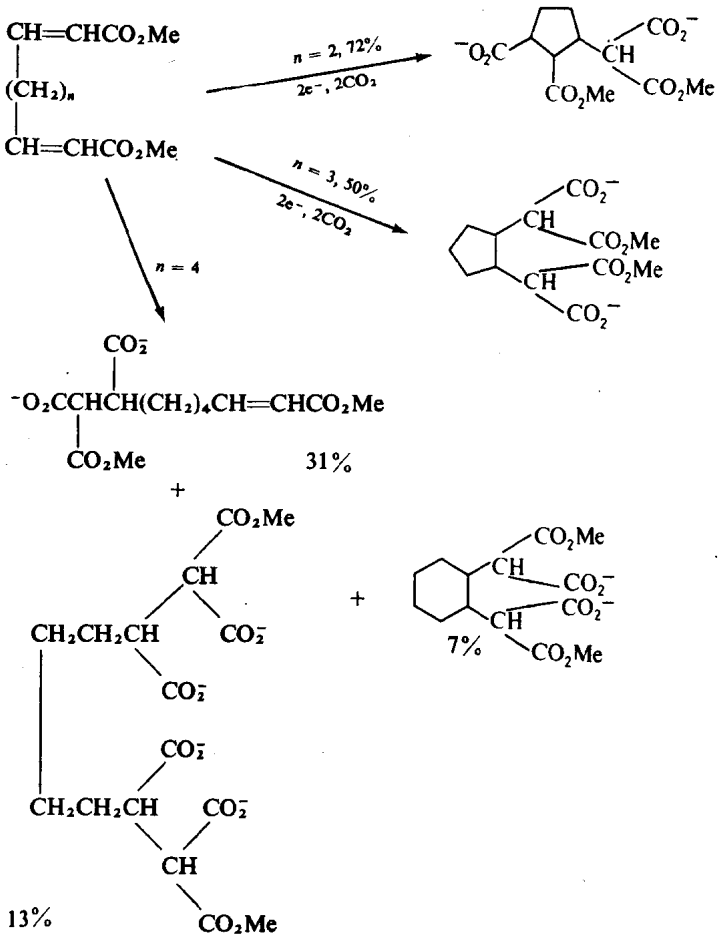


Scheme 8

which show only one two-electron reduction wave, provided that the olefin concentration is high. Bis-activated olefins, under similar conditions, can cyclize as they are carboxylated. Products obtained after treatment with methyl iodide indicated that reactions such as those shown in Scheme 9 are occurring.

αβ-Unsaturated Carbonyl Compounds.—Cathodic hydrogenations carried out at platinized platinum have included conversion of benzalacetone into benzylacetone and of chalcone into dihydrochalcone.[45, 46] On a mercury-poisoned electrode in H_2SO_4–aq. dioxan, the hydro-dimer was obtained from chalcone.[47] Chalcone in media of low acidity yields radical anions which dimerize.[48] Cinnamaldehyde, cinnamate esters, isophorone, *etc.* behave similarly.[49] The stability of radical anions

[44] D. A. Tyssee and M. M. Baizer, *J. Org. Chem.*, 1974, **39**, 2823.
[45] L. A. Taran, S. I. Berezina, L. G. Smolentseva, and V. A. Likhachev, *Soviet Electrochem.*, 1974, **10**, 749.
[46] L. A. Taran, S. I. Berezina, L. G. Smolentseva, and V. A. Likhachev, *Soviet Electrochem.*, 1973, **9**, 756.
[47] L. A. Taran, S. I. Berezina, L. G. Smolentseva, and Yu. P. Kitaev, *Izvest. Akad. Nauk. S.S.S.R., Ser. khim.*, 1974, 2611.
[48] V. N. Nikulin, N. M. Kargina, and Yu. M. Kargin, *Russ. J. Gen. Chem.*, 1974, **44**, 2479.
[49] E. Lamy, L. Nadjo, and J. M. Saveant, *J. Electroanalyt. Chem.*, 1974, **50**, 141.



Scheme 9

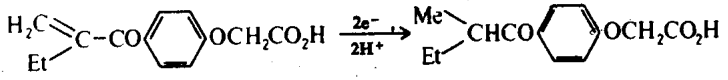
derived from furan-substituted chalcones depends upon the cation of the supporting electrolyte.[50]

4,5-Di(2-furyl)octane-2,7-dione has been prepared by hydrodimerization of 4-(2-furyl)but-3-en-2-one in aqueous organic solvents containing H_2SO_4 electrolyte.[51] In DMSO–TBAP incorporating 0.05M-H_2O, *trans*-4,4-dimethyl-1-phenylpent-1-en-3-one radical anions formed at a mercury cathode dimerize at the 1- and 1′-positions.[52]

[50] A. Rusina, J. Volke, J. Cernak, J. Kovac, and V. Kollar, *J. Electroanalyt. Chem.*, 1974, **50**, 351.
[51] H. Satonaka, Z. Saito, and T. Shimura, *Kanagawa-Ken Kogyo Shikensho Kenkyu Hokoku*, 1974, 29.
[52] S. C. Rifkin and D. H. Evans, *J. Electrochem. Soc.*, 1974, **121**, 769.

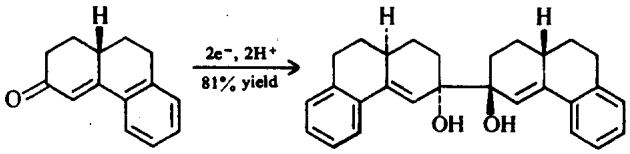
When the water content is increased, competition from a first-order reaction becomes significant.

Ethacrynic acid has been used as a model compound to study the reduction of $\alpha\beta$-unsaturated carbonyl compounds.[53] The olefinic bond was found to be reduced



Scheme 10

preferentially before the carbonyl group (Scheme 10). A remarkable case of stereoselectivity and enantioselectivity has been reported for a cathodic pinacolization.[54] The presence of an existing optical centre within the reacting molecule determines the geometry of the new optical centre created during the reduction, and in addition it discriminates between like and unlike radicals in the dimerization step. Thus at pH 6, 1,9,10,10a-tetrahydro-3-(2*H*)-phenanthrone, when optically pure, gives only the *cis-threo-cis*-isomer instead of the expected three diastereoisomers when reduced



Scheme 11

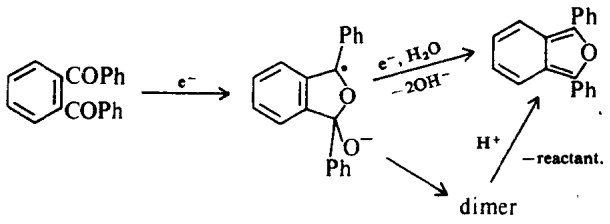
at controlled potential (Scheme 11). The same principle is followed when a racemic mixture of the ketones is reduced. The only products are a racemic mixture of glycols instead of the eight possible pinacols.

Other Carbonyl Compounds.—Intramolecular cyclization reactions occur in the reductions of some diketones. In acetonitrile, 1,3-dibenzoylpropane is reduced to *cis*-1,2-diphenylcyclopentane-1,2-diol through cyclization of the dianion which results from disproportionation of the dibenzoylpropane radical anion.[55] A nearly quantitative yield can be obtained provided either that lithium ions are present to ion-pair with the organic anions or that acid is added continuously, so as to avoid strongly basic conditions.

1,2-Dibenzoylbenzene is reduced in monoglyme containing lithium salts to a radical anion which dimerizes or is reduced further, under more severe conditions, to an isobenzofuran.[56] In mineral acid the dimer dissociates to the reactant and the isobenzofuran (Scheme 12).

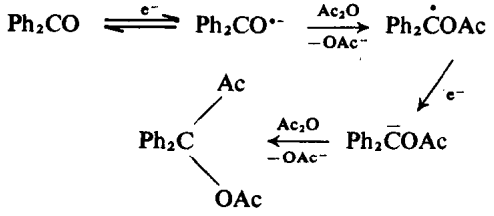
Reduction of benzophenone with TEA salts as supporting electrolytes in acetoni-

[53] L. Deshler and P. Zuman, *Analyt. Chim. Acta*, 1974, **73**, 337.
[54] E. Touboul and G. Dana, *Compt. rend.*, 1974, **278**, *C*, 1063.
[55] F. Ammar, C. P. Andrieux, and J. M. Saveant, *J. Electroanalyt. Chem.*, 1974, **53**, 407.
[56] J. A. Campbell, R. W. Koch, J. V. Hay, M. A. Ogliaruso, and J. F. Wolf, *J. Org. Chem.*, 1974. 39, 146.



Scheme 12

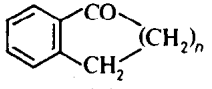
trile containing acetic anhydride as the added electrophile in place of the more familiar proton donor leads to an acylation reaction (Scheme 13).[57]



Scheme 13

Several papers have described the familiar cathodic reductions of aromatic carbonyl compounds to alcohols or pinacols. Thus acetylferrocene hydrodimerizes to 2,3-diferrocenylbutane-2,3-diol, which dehydrates in two stages to 2,3-diferrocenylbuta-1,3-diene.[58]

In the absence of added proton donors, 2-benzoylthiophen[59] and 2-acetylthiophen[60] are reduced to resins at mercury in MeCN–TEAP. However, in the presence of acetic or benzoic acids, the corresponding pinacols are formed. When the added proton donor is water or phenol, then 2-benzoylthiophen yields thienyl-2-phenylmethanol at the potential of the second wave.[61]



(1)

Reductions of three benzocyclenones (1) on mercury have been examined in aqueous methanol.[62] Indanone (n = 1) yields the secondary alcohol, tetralone (n = 2) produces the pinacol, and benzosuberone (n = 3) gives the pinacol under mild conditions and its alcohol at more negative potentials.

Dimerization rates of substituted benzaldehyde radical anions, electrogenerated at a platinum cathode in sulpholane–TBAP, have been measured by cyclic voltammetry.[63]

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Further work has been published on the reductions of alkyl phenyl ketones at mercury cathodes from methanolic solutions of optically active salts.[64] Product distributions of optically active carbinols and optically inactive pinacols have been explained in terms of adducts between the ketone radical anion and the electrolyte cation. Unfortunately, electrode potential and pH, known to be important factors in ketone reductions, were not controlled. The reduction of phenylglyoxylic acid to mandelic acid in the presence of various alkaloids (*e.g.* brucine, strychnine) has led to optical yields as high as 20%.[65] It is supposed that the inducing alkaloid forms an adsorbed complex with the carbanion, causing it to retain its configuration at least partially whilst undergoing protonation.

The electroreduction of aliphatic carbonyl compounds has also received attention. Various aliphatic ketones were reduced at Ni–Pd cathodes in 5% aqueous NaOH solution containing equal amounts of the ketone and ammonia.[66] High yields of the corresponding amine were obtained.

The β-keto-nitriles RCO—CHArCN (R = H or Me; Ar = Ph, 1-naphthyl, or 2-naphthyl) are reduced at a mercury cathode in H_2O–EtOH–LiCl to the corresponding β-hydroxy-nitriles in good yields, provided that acid is added progressively, so that decomposition of the irreducible enolate is avoided.[67] An exception is naphthyl-2′-α-formylacetonitrile, which is not reduced under these conditions. Propionaldehyde in an aqueous alkaline phosphate buffer solution is converted, at a lead cathode, into 2-methylpentane-1,3-diol.[68]

Some higher alkyl methyl ketones have been hydrocoupled with acrylonitrile or ethyl acrylate at a mercury cathode in acidic aqueous solutions.[69] Good yields of the γ-lactones are obtained from acrylonitrile with ketones up to 2-heptanone, whereas 2-undecanone does not couple at all. 2-Octanone gives moderate yields. Patents have been issued for the corresponding coupling reactions between acrylonitrile and lower aliphatic aldehydes.[70] Less acidic conditions and graphite cathodes can be used with these systems.[71]

Ketyl radicals derived from acetone have been successfully hydrocoupled with chlorotrifluoroethylene:[72]

$$Me_2CO + CF_2{=}CFCl + 2H^+ + 2e^- \longrightarrow Me_2C(OH)CF_2CHFCl$$

Mercury cathodes were used in acidic aqueous solutions. Several simple electrocatalytic hydrogenations of ketones and aldehydes to alcohols have been reported. The effects of electrode potential and Pt–Ir alloy catalyst composition upon acetone reduction were studied.[73] Non-aqueous solutions of TBAB have been used to reduce

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