693. *Anodic Syntheses. Part VII.* Electrolyses of Mono-, Di-, and Tri-phenylacetic Acids in Non-aqueous Solutions.*

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The work of previous authors on the electrolyses of mono-, di-, and tri-phenylacetic acids in non-aqueous solutions has been extended.

Phenyl-substitution of acetic acid hinders the normal Kolbe coupling reaction and favours anodic methoxylation and acetoxylation in methanol and acetic acid, respectively.

As part of an exploratory investigation of the anodic reactions of substituted fatty acids (see Part V, Linstead, Shephard, and Weedon, *J.*, 1951, 2854) the electrolysis of mono-, di-, and tri-phenylacetic acids in non-aqueous solvents has been studied.

Previous work on this subject has been largely confined to experiments carried out in a mixture of methanol and pyridine, the latter being added to limit the deposition of polymeric materials which otherwise tend to coat the anode. In this mixture of solvents electrolysis of monophenylacetic acid gives dibenzyl in 50% yield by the normal Kolbe coupling reaction (Fichter and Stenzl, *Helv. Chim. Acta*, 1939, **22**, 976). Very similar yields have now been obtained by using methanol alone as solvent, and by electrolysing fused phenylacetic acid without added solvent.

With diphenylacetic acid the Kolbe reaction is largely suppressed, the main product (35%) in methanol–pyridine being diphenylmethyl methyl ether (van der Hoek and Nauta, *Rec. Trav. chim.*, 1942, **61**, 845). Under similar conditions triphenylacetic acid is reported to give (18%) triphenylmethyl peroxide (Riccoboni, *Gazzetta*, 1940, **70**, 748). In our hands the electrolysis of triphenylacetic acid in methanol alone has led to the formation of methyl triphenylmethyl ether, in 60% yield.

The anodic methoxylations observed with di- and tri-phenylacetic acids are analogous to the alkoxylation and acetoxylation reactions encountered on electrolysis of *N*-acyl-α-

* Part VI, preceding paper.

amino-acids in alcohols and acetic acid, respectively (Part V). It therefore seemed of interest to extend the present investigation to the use of the latter solvent. Electrolysis of mono- and di-phenylacetic acids in acetic acid solution gave benzyl and diphenylmethyl acetates, the yield of isolated ester being about 40%. By hydrolysing the crude product of the electrolysis of diphenylacetic acid the considerable loss involved in the purification of diphenylmethyl acetate was avoided and diphenylmethanol was obtained in 73% overall yield.

Electrolysis of triphenylacetic acid in acetic acid, and isolation of the product in the usual manner, gave triphenylmethanol directly, and not the acetate, in 50% yield. Most probably triphenylmethyl acetate was formed initially but was hydrolysed during isolation. The extreme ease of hydrolysis of this acetate is well known (Gomberg and Davis, *Ber.*, 1903, **36**, 3926).

To summarise the results described above, phenyl-substitution of acetic acid hinders the normal Kolbe coupling reaction and favours methoxylation and acetoxylation in methanol and acetic acid, respectively. Van der Hoek and Nauta (*loc. cit.*) have suggested that the initial products in the electrolyses of aryl substituted acetic acids are arylmethyl free-radicals which may then react further with the intermediate formation of aryl-substituted methyl peroxides. In our view, however, there is insufficient evidence for the assumption that substituted methyl peroxides are intermediates in the formation of other anodic products.

We do not think the evidence on anodic reactions is as yet sufficiently clear cut to justify any general discussion of mechanism. A good case can, however, be made for the intervention of acetoxyl free-radicals ($CH_3{\cdot}CO_2{\cdot}$) in the anodic acetoxylations described above. In support of this hypothesis it was found that lead tetra-acetate, which can also furnish acetoxy-radicals (*cf.* Waters, "The Chemistry of Free Radicals," Oxford Univ. Press, 1946), attacks both di- and tri-phenylacetic acid to give, after hydrolysis of the initial products, diphenyl- and triphenyl-methanol respectively in *ca.* 25% overall yields. The anodic reaction can thus be simulated by purely chemical means.

Since toluene and di- and tri-phenylmethane on treatment with lead tetra-acetate in acetic acid give benzyl and diphenyl- and triphenyl-methyl acetates, respectively (Dimroth and Schweizer, *Ber.*, 1923, **56**, 1375), the substitution of these hydrocarbons for the phenylacetic acids in the acetic acid electrolyses has also been examined. In all cases a complex mixture was obtained, possibly owing to occurrence of anodic methylation (*cf.* Fieser, Clapp, and Daubt, *J. Amer. Chem. Soc.*, 1942, **64**, 2002) in addition to acetoxylation. After hydrolysis of the crude products from di- and tri-phenylmethane small amounts of diphenyl- and triphenyl-methanol were isolated. Some alkali-soluble products were also formed on hydrolysis, suggesting that partial acetoxylation of the phenyl groups had occurred during electrolysis. Anodic acetoxylation of an aromatic nucleus, not previously reported, has now been definitely established. We find that when a solution of sodium acetate and naphthalene in acetic acid is electrolysed and the crude product hydrolysed, a 24% yield of α-naphthol is isolated. This recalls the conversion of naphthalene into 1-acetoxynaphthalene in 26% yield on treatment with lead tetra-acetate (*idem, loc. cit.*).

EXPERIMENTAL

In those experiments for which a recovery of starting material is given, allowance for this has been made in calculating the yields of products. In electrolyses in methanol, technical absolute methanol was used as solvent.

Apparatus.—Three cells, "A," "B," and "C," were employed. These consisted of cylindrical glass vessels containing two parallel platinum plates, placed 1—2 mm. apart, as electrodes. In cell "A" the electrodes measured 2·5 × 2·5 cm., in cell "B" 4 × 2·5 cm., and in cell "C" 8 × 5 cm.

Dibenzyl.—(*a*) Phenylacetic acid (13·6 g.) was added to sodium methoxide (from 0·046 g. of sodium) in methanol (30 c.c.), and the solution was electrolysed in cell "A," a current of 0·8 amp. being used, until the electrolyte became slightly alkaline. (During the electrolysis an insoluble material was deposited on the anode and was removed periodically.) The cell contents were neutralised by the addition of acetic acid, and the solvent was then evaporated under reduced pressure. Isolation of the neutral product in the usual way gave dibenzyl (5 g., 55%), b. p.

280—285°, m. p. 51° undepressed on admixture with an authentic specimen, m. p. 51° (Fichter, *Helv. Chim. Acta*, 1939, **22**, 970, gives m. p. 52°).

(*b*) A molten mixture of phenylacetic acid (54·4 g.) and potassium phenylacetate (from 5·44 g. of phenylacetic acid) was electrolysed in cell " B," a current of *ca.* 1 amp. being used, for 12 hours (total amount of electricity passed *ca.* 1 faraday/mole of aryl-acid). This current sufficed to maintain the temperature of the melt at 170—200° without the use of external heating. The cell contents were cooled and extracted with ether. The ethereal solution was washed thoroughly with saturated sodium carbonate solution and dried. On acidification of the alkaline extract, phenylacetic acid (21·0 g.) was recovered. The ethereal solution was evaporated, the residue was hydrolysed, and the product separated into acidic and neutral fractions in the usual way. The acidic fraction gave phenylacetic acid (3·0 g.), m. p. 73° (Found : equiv., 138. Calc. for $C_8H_8O_2$: equiv., 136). Distillation of the neutral fraction gave : (i) Crude benzyl alcohol, b. p. 90—100°/10 mm. The phenylurethane crystallised from light petroleum (b. p. 100—120°) in needles, m. p. 76·5° undepressed on admixture with an authentic specimen, m. p. 76·5°, of the derivative of benzyl alcohol (von Soden and Rojahn, *Ber.*, 1901, **34**, 2809, give m. p. 78°). (ii) Dibenzyl (14 g., 54%), b. p. 100°/0·1 mm., m. p. 51° undepressed on admixture with an authentic specimen.

Methyl Triphenylmethyl Ether.—Triphenylacetic acid (8·64 g.) was added to sodium methoxide (from 46 mg. of sodium) in methanol (300 c.c.), and the solution was electrolysed in cell " B," a current of 1·5 amp. being used, until alkaline. The solvent was evaporated under reduced pressure, the residue was dissolved in ether, and the solution was washed with N-sodium hydroxide solution, dried, and evaporated. Crystallisation of the residue from methanol gave methyl triphenylmethyl ether (5·0 g.) as plates, m. p. 82·5° undepressed on admixture with an authentic specimen (Friedel and Crafts, *Ann. Chim.*, 1884, **1**, 503, give m. p. 82°).

Benzyl Acetate.—A solution of phenylacetic acid (20·0 g.) and sodium acetate (8·2 g.) in glacial acetic acid (180 g.) was electrolysed in cell " B " for 19·5 hours, a current of 2 amp. being used (electricity passed *ca.* 10 faradays/mole of aryl acid). The solvent was evaporated under reduced pressure, the residue was dissolved in ether, and the ethereal solution was washed with saturated sodium carbonate solution and dried. On acidification of the alkaline extract, phenylacetic acid (8·6 g.) was recovered. The ethereal solution was evaporated and the residue distilled giving benzyl acetate (5·3 g.), b. p. 130—135°/64 mm., n_D^{21} 1·4975 (Found : sap. equiv., 152. Calc. for $C_9H_{10}O_2$: sap. equiv., 150). Hydrolysis of the ester (2·0 g.) gave benzyl alcohol (1·0 g.), n_D^{21} 1·5386 (Brühl, *Annalen*, 1888, **200**, 190, gives n_D^{20} 1·5396). The phenylurethane, prepared in 80% yield, had m. p. 76·5° undepressed on admixture with an authentic specimen.

Diphenylmethyl Acetate and Diphenylmethanol.—(*a*) A solution of diphenylacetic acid (10·6 g.) and anhydrous sodium acetate (4·1 g.) in glacial acetic (60 g.) was electrolysed in cell " B " for 3·5 hours a current of 2 amp. being used (electricity passed *ca.* 5 faradays/mole of aryl acid). Evaporation of the solvent and isolation of the neutral product gave diphenylmethyl acetate, which crystallised from light petroleum (b. p. 40—60°) at −30° in prisms (4·2 g.), m. p. 40° (Found : sap. equiv., 227. Calc. for $C_{15}H_{14}O_2$: sap. equiv., 226) (Bodroux, *Bull. Soc. chim.*, 1899, **21**, 290, gives m. p. 40°). Hydrolysis of the acetate (3·0 g.) gave diphenylmethanol which crystallised from light petroleum (b. p. 40—60°) in needles (2·6 g.), m. p. 67° undepressed on admixture with an authentic specimen (Linnemann, *Annalen*, 1865, **133**, 9, gives m. p. 68°).

(*b*) A solution of diphenylacetic acid (53·0 g.) and anhydrous sodium acetate (20·5 g.) in glacial acetic acid (300 g.) was electrolysed in cell " C " for 4 hours, a current of 8·0 amp. being used (electricity passed *ca.* 5 faradays/mole of aryl acid). Isolation of the product in the usual manner gave (i) recovered diphenylacetic acid (16·0 g.) and (ii) crude diphenylmethyl acetate, which was heated under reflux for 1 hour with excess of aqueous-alcoholic potassium hydroxide solution (10% w/v). Isolation of the neutral product and crystallisation from light petroleum (b. p. 40—60°) gave diphenylmethanol (25 g.) as needles, m. p. and mixed m. p. 67°.

(*c*) A solution of diphenylacetic acid (2·12 g.) and lead tetra-acetate (11·1 g.) in glacial acetic acid (25 c.c.) was heated on a steam-bath for 3 hours. The mixture was then cooled and diluted with ether. The ethereal layer was washed successively with water, 2N-nitric acid, and saturated sodium carbonate solution, dried, and evaporated. The residue was hydrolysed. Isolation of the crude product (1·0 g.) with ether and crystallisation from light petroleum (b. p. 60—80°)–carbon tetrachloride gave diphenylmethanol (0·5 g., 27%) as needles, m. p. 67° undepressed on admixture with an authentic specimen.

Triphenylmethanol.—(*a*) A solution of triphenylacetic acid (14·4 g.) and anhydrous sodium acetate (24·6 g.) in glacial acetic acid (360 g.) was electrolysed in cell " C " for 1·5 hours with a current of 7·0 amp. (*ca.* 8 faradays/mole of aryl acid). The solution was evaporated under reduced pressure, the residue was extracted with ether, and the extract was washed with aqueous sodium hydroxide solution (10% w/v). On acidification of the alkaline washing triphenylacetic acid (3·7 g.) was recovered. The ethereal solution was dried and evaporated, and the residue was crystallised from carbon tetrachloride, giving triphenylmethanol (4·8 g.), m. p. 161° undepressed on admixture with an authentic specimen, m. p. 161°. The carbon tetrachloride mother-liquors were evaporated and the residue was hydrolysed. Separation of the neutral fraction and crystallisation from carbon tetrachloride gave a further small quantity (1·0 g.) of triphenylmethanol. Evaporation of the mother-liquors gave an oil which with Brady's reagent yielded benzophenone 2 : 4-dinitrophenylhydrazone (0·8 g.), m. p. 238° undepressed on admixture with an authentic specimen.

An authentic specimen of triphenylmethyl acetate on treatment with water and with alcohol gave triphenylmethanol and ethyl triphenylmethyl ether, respectively, in almost quantitative yields (*cf.* Gomberg and Davis, *Ber.*, 1903, **36**, 3926).

(*b*) A solution of triphenylacetic acid (1·44 g.) and lead tetra-acetate (10 g.) in acetic acid (20 c.c.) was heated on a steam-bath for 4 hours. 2N-Nitric acid was added and the mixture was extracted with ether. The extract was washed successively with 2N-nitric acid, 2N-sodium hydroxide, and water, dried, and evaporated. Crystallisation of the residue from alcohol and then from carbon tetrachloride gave triphenylmethanol (0·3 g., 23%), m. p. 159—160° undepressed on admixture with an authentic specimen.

Electrolyses of Acetic Acid in the Presence of Toluene and Di- and Tri-phenylmethane.—Solutions of anhydrous sodium acetate (0·05M) in glacial acetic acid were electrolysed in cell " C " in the presence of toluene (0·05M), diphenylmethane (0·05M), and triphenylmethane (0·02M) severally. The electrolyses were continued until *ca.* 15 faradays/mole of hydrocarbon had been passed. Isolation and hydrolysis of the products in the usual way (sap. equiv., 170, 220—250, and 358, respectively) and separation of the neutral fractions (*ca.* 16, 55, and 40% yields, respectively, based on hydrocarbon) gave complex intractable mixtures from which, in the experiments with di- and tri-phenylmethane, small amounts of diphenyl- and triphenyl-methanol, respectively, were isolated. Hydrolysis of the crude products from these two hydrocarbons also gave small amounts (*ca.* 5 and 20%, respectively, based on hydrocarbon) of dark brown alkali-soluble materials.

α-Naphthol.—A solution of naphthalene (6·4 g.) and anhydrous sodium acetate (0·9 g.) in glacial acetic acid (30 g.) was electrolysed in cell " A " for 8·0 hours, a current of 0·5 amp. being used (3 faradays/mole of naphthalene). The dark brown contents of the cell were extracted with ether, and the extract was washed with sodium carbonate solution, dried, and evaporated. The residue was hydrolysed with aqueous alcoholic alkali. From the non-hydrolysable fraction naphthalene (0·5 g.), m. p. and mixed m. p. 80°, was recovered by chromatographic adsorption on alumina from benzene solution. The alkali-soluble product (4·7 g.) was distilled, giving crude α-naphthol (1·6 g., 24%), m. p. 80—85°. Sublimation under reduced pressure, followed by two crystallisations from light petroleum (b. p. 40—60°), containing a trace of ether, gave α-naphthol as needles, m. p. 95·5° undepressed on admixture with an authentic specimen.

Chromatographic purification of a small portion of the crude α-naphthol, m. p. 80—85°, on alumina from benzene solution, followed by treatment of the chromatogram with diazotised sulphanilic acid (*cf.* Zechmeister and Cholnoky, " The Principles and Practice of Chromatography," London, 1941, p. 87), indicated the presence of some β-naphthol in addition to the α-isomer.

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