

200. *The Electrolysis of some Nitro-substituted Mono- and Di-phenylacetic Acids.*

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The electrolysis of a series of five nitro-substituted mono- and di-phenylacetic acids in methanol has been investigated. Anodic methoxylation and the total suppression of the Kolbe coupling were observed with 4,4'-dinitrodiphenylacetic acid. With 2- and with 4-nitrophenylacetic acid, anodic methoxylation and partial suppression of the Kolbe coupling were observed. No methoxylation was noted with 3-nitro- and 2,4-dinitro-phenylacetic acid. With the exception of 4,4'-dinitrodiphenylacetic acid, all the nitrophenylacetic acids gave the corresponding nitrobenzaldehydes and nitrobenzyl alcohols.

PREVIOUS reports^{1,2} from this laboratory have described the electrolysis of some α -substituted phenylacetic acids. On electrolysis in methanol, α -alkoxy-phenyl- and -diphenyl-acetic acid failed to undergo the normal Kolbe reaction. Instead of the dimers, the acetals of benzaldehyde and benzophenone were obtained. α -Arylthiodiphenylacetic acids gave mixtures of benzophenone dimethyl acetal and disulphides. The acetals are not the expected products from the attack of free radicals on the solvent alcohol, and were shown to arise from the further oxidation of the electrolytically produced radicals to carbonium ions, which then attack the solvent.

In order to determine the type of structure which favours anodic methoxylation, an exploratory investigation of the electrolysis of ring-substituted phenylacetic acids has

¹ Wladislaw and Ayres, *J. Org. Chem.*, 1962, **27**, 281.

² Wladislaw, *Chem. and Ind.*, 1962, 1868.

been undertaken. The electrolysis of some nitro-substituted mono- and di-phenylacetic acids, in methanol, is here described.

RESULTS AND DISCUSSION

The results obtained with the nitrophenylacetic acids are summarized in the Table. Percentage yields are given for those products which were isolated quantitatively.

Yields of products obtained from the electrolysis of nitrophenylacetic acids in methanol.

Phenylacetic acids	Nitrobenzyl methyl ethers (%)	Nitrobenzyls (%)	Nitrobenzyl alcohols (%)	Nitrobenzaldehydes (%)
4-Nitro	16.0	32.6	7.0	trace
2-Nitro	16.7	0.0	trace	trace
2,4-Dinitro	0.0	0.0	trace	21.0
3-Nitro	0.0	0.0	0.0	7.9

When 4,4'-dinitrodiphenylacetic acid was electrolysed, 4,4'-dinitrodiphenylmethyl ether (63% yield) was obtained as the only product.

In all the electrolyses, large quantities of polymer were isolated: 4,4'-dinitrodiphenylacetic acid gave 26.0%; 4-nitrophenylacetic acid, 53.0%; 2-nitrophenylacetic acid, 63.0%; 2,4-dinitrophenylacetic acid, 78.0%; and 3-nitrophenylacetic acid, 90.0% of polymer. These yields are based on the weights of polymer and starting acid.

Thus, nitro-groups in the 4- or 2-position of the phenyl- and diphenyl-acetic acid ring favour methoxylation and suppress completely, or partially, the Kolbe coupling. Under similar conditions, diphenylacetic acid was reported to give tetraphenylethane in 8.1% yield, and only 35.0% of the diphenylmethyl methyl ether.³ However, no methoxylation at all was observed in the electrolysis of phenylacetic acid, and bibenzyl was isolated, as the only product, in 50.0% yield.⁴

The nitro-groups in the 3- and in the 2,4-positions of the phenylacetic acid ring hinder both methoxylation and the normal Kolbe coupling.

The assumption of van der Hoek and Nauta,³ that, in the electrolysis of phenyl-substituted acetic acids, the intermediate arylmethyl free radicals give, in the presence of oxygen, the unstable phenylmethyl peroxides which are responsible for aldehyde and alcohol formation, provides a reasonable explanation for the formation of the nitrobenzaldehydes and nitrobenzyl alcohols. The absence of these compounds in the electrolysis of 4,4'-dinitrodiphenylacetic acid indicates that, in this case, the anodic reaction does not involve the intermediate free radical.

We do not think there is at present sufficient information to justify a general discussion of the influence of nitro-groups, in different positions of the ring, on the mechanism of anodic reactions. Consequently, electrolyses with other ring-substituted phenylacetic acids are being carried out.

EXPERIMENTAL

Reagents.—4,4'-Dinitrodiphenylacetic acid, m. p. 169—172°, was prepared by reaction of methyl diphenylacetate with fuming nitric acid followed by acid hydrolysis of the 4,4'-dinitro compound using the procedure described by Haskelberg and Lavie⁵ and Hunsberger and Amstutz.⁶ 2-Nitrophenylacetic acid, m. p. 119—121°, was prepared from 2-nitrophenylpyruvic acid, by the method of Reissert.⁷ 2,4-Dinitrophenylacetic acid, m. p. 183—185°, was

³ van der Hoek and Nauta, *Rec. Trav. chim.*, 1942, **61**, 845.

⁴ Fichter and Stenzl, *Helv. Chim. Acta*, 1939, **22**, 976; Linstead, Shephard, and Weedon, *J.*, 1952, 3624.

⁵ Haskelberg and Lavie, *J. Amer. Chem. Soc.*, 1949, **71**, 2580.

⁶ Hunsberger and Amstutz, *J. Amer. Chem. Soc.*, 1949, **71**, 2635.

⁷ Reissert, *Ber.*, 1897, **30**, 1041.

prepared as described by Vogel.⁸ 3-Nitrophenylacetic acid, m. p. 119—120°, was prepared from 3-nitrotoluene, as described by Yabroff and Porter.⁹

Electrolysis Procedure.—Both the electrolysis cell and the method used were as previously described.¹

4-Nitrophenylacetic acid. The acid (5.0 g., 0.043 mole), in methanol (130 ml.) containing sodium (0.03 g.), was electrolysed by passage of a current of 1.2 A for 3 hr. During the electrolysis an insoluble material was deposited on the anode and was periodically removed. The cell contents were neutralized with acetic acid, and the solvent was then evaporated under reduced pressure. The residual oil was extracted with boiling ether, remaining an insoluble, brown, viscous oil, which slowly solidified. The ethereal extract was washed with saturated potassium hydrogen carbonate solution and then dried. On acidification of the alkaline extract, 4-nitrophenylacetic acid (0.02 g.) was recovered. The ethereal solution was evaporated and to the residual oil (3.85 g.), ice-cold ether was added; 4,4'-dinitrobenzyl (1.23 g., 32.6%), m. p. and mixed m. p. 180—182°, separated. The ether-soluble product was distilled giving: (i) a liquid (0.10 g.) boiling below 113°/1 mm., from which traces of 4-nitrobenzaldehyde (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 318°) were isolated; (ii) methyl 4-nitrobenzyl ether (0.75 g., 16.0%), b. p. 114°/1 mm. (lit.,¹⁰ 145—147/15 mm.) (Found: C, 57.5; H, 5.4; N, 9.4. Calc. for C₈H₉O₃N: C, 57.4; H, 5.6; N, 9.5%); (The identity of these products was confirmed by infrared spectroscopy.) (iii) 4-Nitrobenzyl alcohol (0.30 g., 7.0%), b. p. 154—155°/1 mm., m. p. and mixed m. p. 92—93°. (iv) A residue (1.57 g.). The total residue weighed 2.69 g.; it was insoluble in ethanol and had m. p. > 350°.

4,4'-Dinitrodiphenylacetic acid. The acid (5.0 g., 0.016 mole), in methanol (130 ml.) containing sodium (0.02 g.), was electrolysed by passage of a current of 1.2 A for 1 hr. A very small amount of polymer collected at the anode. Isolation of the ether-soluble product, as described in the preceding experiment, gave 4,4'-dinitrodiphenylmethyl ether (3.0 g., 63.0%), m. p. 114—116° (Found: C, 58.6; H, 4.4. Calc. for C₁₄H₁₂O₅N₂: C, 58.3; H, 4.2%), which absorbed strongly at 9.2 and 11.3 μ in the infrared region (methoxyl group). The total weight of polymer (the product which covered the anode, in addition to the ether-insoluble product) was 1.32 g.

2-Nitrophenylacetic acid. The acid (10.0 g., 0.086 mole), in methanol (260 ml.) containing sodium (0.06 g.), was electrolysed by passage of a current of 1.2 A for 2 hr. 22 min. Much polymeric material had to be periodically removed. Isolation of the ether-soluble product, in the usual way, gave an oil which, by addition of ethanol, was freed of a large amount of polymer and then distilled, giving: (i) a liquid (0.10 g.), boiling below 117°/1 mm., from which traces of 2-nitrobenzaldehyde (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 252°) and of 2-nitrobenzyl alcohol [benzoyl derivative, m. p. 100° (lit.,¹¹ 102°)] were isolated; and (ii) methyl 2-nitrobenzyl ether (1.6 g., 17.4%), b. p. 118°/1 mm. (lit.,¹² 130—132°/15 mm.) (Found: C, 57.8; H, 5.7; N, 8.3. Calc. for C₈H₉O₃N: C, 57.5; H, 5.4; N, 8.4%), which showed methoxyl absorption at 9.2 and 11.7 μ in the infrared spectrum. The total weight of polymeric material was 6.25 g.

2,4-Dinitrophenylacetic acid. The acid (10.5 g., 0.039 mole), in methanol (260 ml.) containing sodium (0.04 g.), was electrolysed by passage of a current of 1.2 A for 2 hr. 25 min. A large amount of polymeric material was deposited on the electrodes. Work up, as in the preceding experiment, gave a residue free from polymer. Distillation yielded: (i) a liquid (0.10 g.), boiling below 135°/1 mm., from which a trace of 2,4-dinitrobenzyl alcohol [benzoyl derivative, m. p. 137° (lit.,¹³ 141°)] was isolated; and (ii) 2,4-dinitrobenzaldehyde (1.8 g., 21.0%), b. p. 136°/1 mm., m. p. 70° (lit.,¹⁴ 72°) (Found: N, 14.0. Calc. for C₇H₄O₅N₂: N, 14.3%). [2,4-Dinitrophenylhydrazone, m. p. 258° (lit.,¹⁵ 258°); oxime, m. p. 127—128° (lit.,¹⁶ 127—128°)]. The total weight of polymeric material was 8.2 g.

3-Nitrophenylacetic acid. The acid (7.2 g., 0.06 mole), in methanol (215 ml.) containing

⁸ Vogel, "A Textbook of Practical Organic Chemistry," Longmans, London, 1951, p. 719.

⁹ Yabroff and Porter, *J.*, 1932, 1201.

¹⁰ Bergmann and Harvey, *Ber.*, 1929, 62, 907.

¹¹ Ref. 8, p. 776.

¹² Thiele and Dimroth, *Annalen*, 1899, 305, 108.

¹³ Krassuski and Pliisov, *Ukrain. khim. Zhur.*, 1952, 1, 638 (*Chem. Abs.*, 1927, 21, 2457).

¹⁴ Bennett and Pratt, *J.*, 1924, 1465.

¹⁵ Chattaway and Clemo, *J.*, 1923, 3061.

¹⁶ Friedländer and Cohn, *Ber.*, 1902, 1266.

sodium (0.04 g.), was electrolysed by passage of a current of 1.2 A for 1 hr. 50 min. Large amounts of polymer were deposited on the electrodes. Work up, as in the two preceding experiments, gave a residue free from polymer. Distillation gave 3-nitrobenzaldehyde (0.52 g., 8.9%), b. p. 101/1 mm. (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 290—293°). The weight of polymeric material was 6.58 g.

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