

Electrochemical Reduction of Trichloromethylbenzene II Reduction in the Presence of Electrophiles

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Electrochemical reduction of trichloromethylbenzene at a mercury electrode in DMF/TBABF₄ in the presence of acetic anhydride gives 1,2-diacetoxy-1-phenylpropene as major product; minor products are dichloromethylbenzene and dimerized products. During the reduction 1,1-dichloro-1-phenyl-2-propanone and 2-acetoxy-1-chloro-1-phenylpropene can be detected. With sodium perchlorate as supporting electrolyte 1-chloro-1-phenyl-2-propanone and 1-acetoxy-1-phenyl-2-propanone are formed; these products are also formed during the reduction of benzal chloride in the presence of acetic anhydride. Reductive carboxylation of trichloromethylbenzene gives 2,2-dichloro-2-phenylacetic acid.

Electrolytic reductive intermolecular coupling of halogen compounds has been widely investigated;¹ of special interest for this investigation are the reduction of trichloromethylbenzene (*I*) in THF/LiClO₄ in the presence of ketones to yield unsaturated ketones² and the reduction of benzyl halides in the presence of acyl halides to give benzyl ketones.³

This paper describes the reduction of *I* in the presence of acetic anhydride (*2*) and carbon dioxide (*3*). The reaction products, 1,1-dichloro-1-phenyl-2-propanone (*4*), 2-acetoxy-1-chloro-1-phenyl-1-propene (*5*), 1,2-diacetoxy-1-phenyl-1-propene (*6*), 1-acetoxy-1-phenyl-2-propanone (*7*), 1-phenyl-1-propyne (*8*), 2,2-dichloro-2-phenylacetic acid (*9*), and methyl 2,2-dichloro-2-phenylacetate (*10*), are also included.

RESULTS AND DISCUSSION

Polarography and Cyclic Voltammetry. The most noticeable change in the cyclic voltammetry in DMF/TEAP of *I*⁴ on addition of *2* is the disappearance of the anodic peak at about -0.6 V (SCE); the species responsible for the anodic peak thus reacts fast with *2*. It was previously⁴ suggested that the anion of benzal chloride (*II*) (C₆H₅CCl₂⁻) was responsible for the anodic peak; *II*⁻ would react with *2* to *4*. Compound *4* gives in classical polarography in DMF/TBABF₄ E_{1/2} = -0.6 V. (aq. SCE); *4* is thus reducible at the potential used for the reduction of *I* in the presence of *2*.

Compound *5*, however, is reduced at a much more negative potential (E_p = -2.40 V; SCE) and would not be reduced further at the potential used for reduction of *I*.

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and "dimerized products" (10–15 %); the "dimerized products" were the same as found in the absence of 2, that is 1,2-diphenyl-1,1,2,2-tetrachloroethane (12) *Z*- and *E*-1,2-diphenyl-1,2-dichloroethene (13), and diphenylacetylene (14). In the beginning of the electrolysis 1,1-dichloro-1-phenyl-2-propanone (4) could be detected, but the yield did not exceed 5–10 % as it was further reduced. 2-Acetoxy-1-chloro-1-phenyl-1-propene (5) was also detected but disappeared gradually on reaction with acetate ion with formation of 6, if the reduction mixture was allowed to stand for more than 12–15 h.

Reduction under similar conditions but with sodium perchlorate as supporting electrolyte gave 1-acetoxy-1-phenyl-2-propanone as the main coupling product and only traces of 6 might be formed but it was not detected; 1-chloro-1-phenyl-2-propanone (15) was present during the electrolysis and formed gradually 7 on reaction with acetate. Besides the coupled products, 11 (33 %) and dimerized products (12 (2 %), 13Z (9 %), 13E (12 %), 14 (4 %) were formed.

The "dimerized compounds" are formed in the same way as during the reduction in the absence of 2;⁴ the products coupled with 2 are suggested to be formed according to Scheme 1. The reduction current is not diffusion controlled, but may be limited by the rate of formation of mercury compounds.

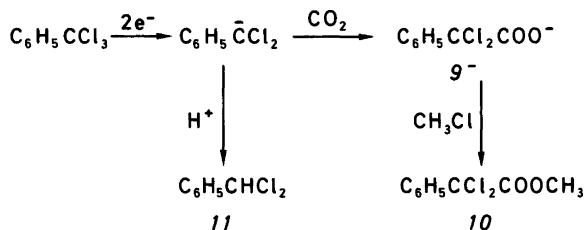
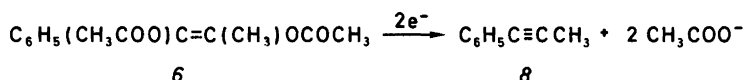
The potential (–1.2 V) is chosen so negative that the further reduction of the primarily formed radical is fast and 1 is reduced mainly to 11^{•-}. 11^{•-} may react with protons to form 11, with 12 to 1 and 13, and with 2 to 4.

4 is reducible at the applied potential and is reduced in a two-electron reaction to the enolate ion 15^{•-}. 15^{•-} may be protonated to 15 or acetylated to 5. In the presence of sodium ions the ion-pair is apparently so tight that the reaction with 2 is so slow that 5 or 6 are not detected as products. In that case protonation wins the competition and 15 which may react with acetate to 7 is formed.

With sodium perchlorate as supporting electrolyte 11^{•-} apparently also forms a relatively tight ion-pair with Na⁺, so more 11 and less 4 is formed compared with TBABF₄ as supporting electrolyte.

Reaction of 15^{•-} with 2 with TBABF present yields 5 by acylation of oxygen in 15^{•-}. The chlorine in 5 is vinylic, but also benzylic; in any case, it is rather reactive towards acetate, and 5 is transformed to 6 if the electrolysis is allowed to run to completion during the night.

The stereochemistry of 6 has not been determined; only one isomer was isolated and no significant peaks in GLC with retention time close to that of 6 was observed; a similar



situation is found for 5. Possibly the enolate in 15^- reacts so slowly with 2 that only the more stable isomer reacts, and the further reaction of 5 to 6 is stereospecific. Reduction of 6 at the potential of the first peak gave 1-phenyl-1-propyne (8) as the main product. This is analogous to the reduction of 1,2-dibenzoyloxy-1,2-diphenylethene to diphenylacetylene.⁶

8 is reducible at a potential about 200 mV more negative than 6. Reduction of 8 gave propylbenzene; the reduction consumed somewhat more than 4 F mol^{-1} , which must be due to reduction of supporting electrolyte and/or impurities.

Reduction of 1 in acetonitrile at -1.4 V at a platinum cathode in the presence of CO_2 , followed by methylation with methyl chloride produced a 2:1 mixture of methyl 2,2-dichloro-2-phenylacetate (10) and 11. Methylation cannot be performed during the reduction as 10 is reducible at about the same potential as 1; the anion of 2,2-dichloro-2-phenylacetic acid (9^-) requires a considerably more negative potential for a further reduction.

EXPERIMENTAL

The conditions and apparatus for GLC and electroanalytical measurements were the same as previously published.⁴ For MS a Micromass 7066 was used; 70 eV electron beam.

1-Chloro-1-phenyl-2-propanone 15,⁷ 2-acetoxy-1-phenyl-1-propene,⁸ and 1-acetoxy-1-phenyl-1-propene⁸ (reaction time 12 h was used) were prepared according to published procedures.

Reduction of 1 in the presence of 2: A solution of 1 (2 ml), 2 (10 ml), $n\text{-C}_{14}\text{H}_{30}$ (1 ml, internal standard for GLC) in DMF/0.2 M TBABF₄ was reduced at -1.2 V (SCE). Samples (2.0 ml) were withdrawn during the reduction, diluted with 5 ml of diethyl ether and washed twice with 5 ml of water; after drying (molecular sieves A4) the samples were analysed by GLC using standard conditions.⁴ The reduction stopped after $n \sim 3$; yields; 5+6 45–60 %, 11 15–20 %, 12+13+14 10–15 %. The catholyte was diluted with water, extracted twice with diethyl ether which was washed twice with water and dried (molecular sieves). The solvent was removed *in vacuo* and the residue separated on a column of silica with dichloromethane as eluent.

1,2-Diacetoxy-1-phenyl-1-propene 6: Retention time (standard conditions)⁴ 14.1 min. Mp. 43–45 °C (from light petroleum) (liquid, bp. 70 °C/0.2 mm).⁹ ¹H NMR (CDCl_3): δ 1.96 (3H,s); 2.00 (3H,s); 2.16 (3H,s); 7.1–7.4 (5H,m). MS (m/e (%)): 234(3), 192(15), 150(100), 105(10), 77(12), 43(50).

1,1-Dichloro-1-phenyl-2-propanone 4: 4 could be isolated if the reduction was stopped after $n=0.5$. Retention time 7.6 min. ¹H NMR (CDCl_3): δ 2.30 (3H,s), 7.3–7.7 (5H,m). MS (m/e (%)): 206(3.5), 204(20), 202(33), 169(4.5), 167(13), 103(50), 89(35), 43(100).

1-Chloro-1-phenyl-2-propanone 15: Retention time 3.5 min. ¹H NMR (CDCl_3): δ 2.11 (3H,s), 5.28 (1H,s), 7.1–7.3 (5H,s). MS (m/e (%)): 170(1), 168(3), 126(5), 124(12), 43(100).

2-Acetoxy-1-chloro-1-phenyl-1-propene 5: Retention time⁴ 7.7 min. ¹H NMR (CDCl_3): δ 1.90 (3H,s), 2.16 (3H,s), 7.1–7.4 (5H,m). Apparently only one isomer (*Z* or *E*) was formed, preparation of 4 using BuLi in THF yields both isomers¹⁰ (δ 2.15, 2.10, 1.89, 1.80).

1-Acetoxy-1-phenyl-2-propanone 7: Retention time⁴ 6.5 min. ¹H NMR (CDCl_3): δ 2.05 (3H,s), 2.17 (3H,s), 5.88 (1H,s), 7.1–7.4 (5H,m). MS (m/e (%)): 192(0.5), 176(8), 134(100), 91(20), 43(30). At lower electron beam energy m/e 192 increases and m/e 150 becomes a large peak.

Methyl 2,2-dichloro-2-phenylacetate 10: Retention time⁴ 10.1 min. ¹H NMR (CDCl_3): δ 3.75 (3H,s), 7.2–7.8 (5H,m). MS (m/e (%)): 222(2), 220(15), 218(20), 185(4), 183(13), 163(11), 161(66), 159(100), 89(28).

1-Phenyl-1-propyne 8: Retention time⁴ 1.3 min. ¹H NMR (CDCl_3): δ 1.84 (3H,s), 6.9–7.3 (5H,m). MS (m/e (%)): 116(50), 115(100).

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