

Electrochemical Reduction of Trichloromethylbenzene

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The electrochemical reduction of trichloromethylbenzene (benzotrifluoride) has been investigated by cyclic voltammetry, pulse polarography, and preparative scale reductions. Depending on conditions, benzal chloride, benzyl chloride, 1,2-diphenyl-1,1,2,2-tetrachloroethane, *Z*- and *E*-1,2-dichloro-1,2-diphenylethylene, and diphenylacetylene may be obtained. At a mercury electrode at the potential of the prewave the main products are 1,2-diphenyl-1,1,2,2-tetrachloroethane (~60 %) and diphenylacetylene (~25 %); at a more negative potential benzal chloride is the main product with low yields of dimerized products. 1,2-Diphenyl-1,1,2,2-tetrachloroethane is reduced to a mixture of *Z*- and *E*-1,2-dichloro-1,2-diphenylethene which in turn is reduced to diphenylacetylene.

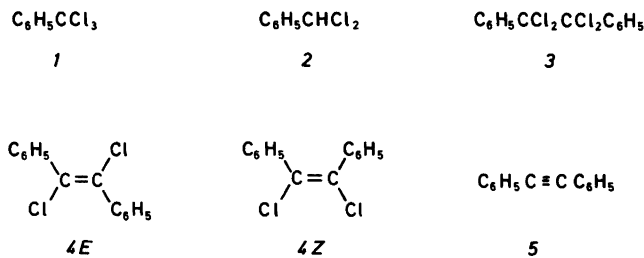
Electrochemical reduction of aromatic acids and their derivatives to aldehydes is in general not possible, either because the aldehyde is more easily reducible than the acid derivative or dimerizations to a diketone occurs; only if the aldehyde can be trapped as a non-reducible derivative, e.g. a hydrate, such a reduction is possible. Thus isonicotinic amide^{1a} or ethyl oxalate^{1b} may be reduced to the corresponding aldehyde hydrate in good yield; such a reduction is, however, possible only when the aldehyde group is activated by a strongly electron-attracting group. Salicylic acid may be reduced to the aldehyde at pH 6 in a two-phase system containing boric acid.²

Easily reducible acid derivatives such as an acid chloride would seem to be an attractive candidate for the reduction of an acid derivative to an aldehyde (an electrochemical Rosenmund reaction), but dimerization of the primarily formed radical followed by a reduction of the *vic.* diketone to an enedione which is acylated³ makes acid chlorides unsuitable for the desired reaction.

A method, possibly of more general applicability, for the reduction of a substituent in the oxidation state of an acid to that of an aldehyde might be the reduction of a trichloromethyl group to a dichloromethyl group which on hydrolysis could form the aldehyde.

2-Phenyl-4-trichloromethylpyrimidine⁴ has been reduced in high yield in DMF containing 0.5 % acetic acid to the corresponding dichloromethyl compound; in this particular case the dichloromethyl group proved very resistant to hydrolysis. Benzotrifluoride has been reduced stepwise in DMF to toluene,⁵ and 2-tribromomethylquinoline may be reduced in DMF to 2-dibromomethylquinoline.⁶ In order to investigate a more general case, trichloromethylbenzene (benzotrifluoride) (1) was chosen as a model compound, as benzal chloride (2) can be hydrolyzed to benzaldehyde.

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Benzotrichloride has been reduced polarographically in water–dioxane (1:3)⁷ with tetramethylammonium bromide as supporting electrolyte and in DMF and acetonitrile;⁸ a stepwise reduction with loss of chloride ion was reported, and in aprotic media⁸ a prewave was noted which was ascribed to a reaction of 1 with mercury with formation of mercury organic compounds. When an organic halide reacts with mercury under polarographic conditions it is often observed that a dimerization competes with the simple halide reduction under preparative conditions.

Reductive dimerization of 1 was observed during indirect reduction in DMF/LiClO₄ by means of Cr²⁺ electrogenerated at a glassy carbon cathode which gives diphenylacetylene (5) in fair yield (30 %).⁹

Besides 1 the reduction of dichloromethylbenzene (benzal chloride, 2), 1,2-diphenyl-1,1,2,2-tetrachloroethane (3), (Z)- and (E)-1,2-dichloro-1,2-diphenylethane (4Z, 4E), and diphenylacetylene (5) was investigated.

RESULTS AND DISCUSSION

Electroanalytical results. Some of the compounds, notably 1 and 1,2-diphenyl-1,1,2,2-tetrachloroethane (3), are not “well-behaved” compounds in many of the electroanalytical experiments; reaction with electrode material, film formation, slow, irreversible electrode reactions make the curves more dependent than usual on experimental conditions.

Classical polarography of 1 in 60 % aqueous DMF containing 0.3 M hydrochloric acid and 0.1 M tetrabutylammonium perchlorate (TBAP) gave a drawn-out prewave ($E_{1/2} \sim -0.7$ V vs. SCE) followed by a wave at ~ -1.2 V. The second wave was visible at concentrations of 1 higher than about 4×10^{-4} M.

The sum of the two waves was proportional to $h^{1/2}$ (h = height of mercury reservoir), whereas the height of the prewave grew approximately linearly with h . These results suggest a surface phenomenon, possibly an interaction of 1 with mercury; this is in accordance with the finding that 1 on stirring in DMF containing tetrabutylammonium fluoborate (TBABF) with mercury reacts with mercury with formation of 3 together with minor amounts of 2 and Z- and E-1,2-dichloro-1,2-diphenylethane (4Z, 4E).

Tast-polarography of 1 in DMF/TEAP (tetraethylammonium perchlorate) gives similar results as those described by Wawzonek and Duty;⁸ a stepwise reduction of 1 to 2 and further to benzyl chloride (6) and toluene is observed, and at the first wave a prewave is visible (Table 1).

Cyclic voltammetry (CV) of 1 in DMF/TEAP at a slowly dropping mercury electrode showed at 5 V s^{-1} three cathodic peaks at -1.25 , -1.96 and -2.27 V and an anodic one at -0.62 V; besides these peaks a small prepeak at -0.89 V was seen before the first cathodic

Table 1. Half-wave potentials (vs. aq. SCE) measured by tast-polarography (TastP) and pulse polarography (NPP) of trichloromethylbenzene (1), 1,2-diphenyl-1,1,2,2-tetrachloroethane (2), and (E)-1,2-dichloro-1,2-diphenylethene (4E), in DMF/TEAP.

Compound	Concentration Ml ⁻¹ × 10 ⁴	Method	1 wave		2 wave		3 wave	
			-E _{1/2} /V	i ₁ /μA	-E _{1/2} /V	i ₁ /μA	-E _{1/2} /V	i ₁ /μA
1	3.5	TastP	~1.0	1.5	1.72	1.5	2.08	1.5
1	3.5	NPP	1.1	8.0	1.84	8.0	2.20	8.0
3	4.6	TastP	1.0	1.2	1.56	1.2	2.35	1.4
3	4.6	NPP	1.22	6.0	1.62	6.0	2.35	5.0
4E	5.3	TastP	1.56	1.5	2.34	1.5		
4E	5.3	NPP	1.64	6.5	2.36	4.5		

peak. The cathodic peaks correspond to a stepwise reduction of 1 as also seen in classical polarography;⁸ the anodic peak is suggested to be caused by the oxidation of 2⁻ (PhCCl₂), as it is present if the sweep is reversed at -1.5 V (SCE) which is between the first and second peaks; reversal after the prepeak produces no anodic peak. If acetic anhydride is added to the solution no anodic peak is observed. An anodic peak about -0.6 V is also seen in CV of 2; this could be due either to C₆H₅CHCl⁻ (6⁻) or to 2⁻, the latter formed by proton abstraction by 6⁻ from 2. The oxidation of 2⁻ would be expected to give 3.

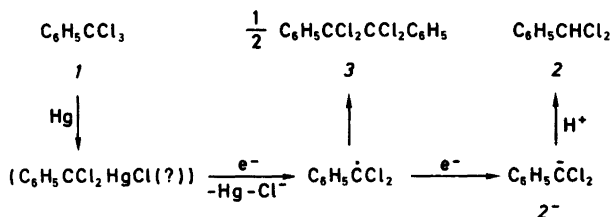
In tast-polarography of 3 in DMF/TEAP three waves are observed; the first one is drawn out (E₁ = -1.00 V (SCE); log i/i_d-i = 260 mV per log unit), the second one less so (E₂ = -1.56 V; log i/i_d-i = 77 mV per log unit), and the third one (E₃ = -2.35) is reversible; a fourth wave is barely visible close to the background. Tast-polarographic data of 4Z (or 4E) are similar to those of the second and third wave of 3 (Table 1).

CV of 3 in DMF/TEAP showed a drawn-out, irreversible peak or shoulder (E_p ~ -1.3 V), followed by an irreversible, more normally shaped peak (E_p = -1.69 V; v = 5 V s⁻¹), and a reversible system (E_p = -2.34 V). 4Z (or 4E) gives in CV an irreversible peak (E_p = -1.73 V; 5 V s⁻¹) followed by a reversible system (E_p = -2.35 V), closely resembling the second and third peaks of 3. The reversible system appears at the same potentials as diphenylacetylene (5). The electroanalytical data thus suggest that 3 is reduced to 4E+4Z, which in turn is reduced to 5 (Table 2).

Preparative reductions. In the reductions of 1, the anion of the supporting electrolyte must not be iodide, as iodide reduces 3 to 4, so perchlorate (P) or tetrafluoroborate (BF) was used. Reduction of 1 in DMF/0.1 M TBABF at a mercury cathode at -0.7 V (SCE) gave with the reaction run 90 % to completion a good yield of 3 (63 %) with 3 % 2, 7 % of 4Z and 4E and a rather high yield (25 %) of 5. The current density is low (about 100 mA dm⁻²).

Table 2. Peak potentials (vs. aq. SCE) from cyclic voltammetric investigation of 1, 3, and 4E in DMF/TBAP; scan rate 5 V s⁻¹.

Compound	Conc. Ml ⁻¹ × 10 ⁴	1. peak -E _p /V	2. peak -E _p /V	3. peak -E _p /V	Anod. peak -E _p /V
1	3.5	1.25	1.96	2.27	0.59
3	4.6	~1.33	1.69	2.34	
4E	5.3	1.73	2.35		2.28



Scheme 1.

and nearly constant during the reduction, if the stirring is kept constant; if the stirring rate is increased too much the mercury electrode has a tendency to disintegrate into small droplets which is often seen if radicals or formation of mercury compounds are involved in the reduction.

Dimeric compounds were also the main products even in a mixture of three parts acetic acid and one part 6 M aqueous hydrochloric acid containing 1 M sodium iodide; 4 (Z:E, 2:1) was obtained in 50 % yield together with 5 % 3 and 7 % 5. 3 is reduced to 4 by iodide under these conditions.

The dimerization reaction probably involves a "chemical" reaction between mercury and 1; this is made plausible by the fact that stirring 1 with mercury in DMF/0.1 M TBABF for 18 h yielded 13 % 3, 0.5 % 2, and 0.5 % 4Z+4E, together with 85 % unreacted 1. The further reduction is slow at metallic mercury, but fast at the cathode, which explains the relative low conversion at mercury compared to that at the cathode.

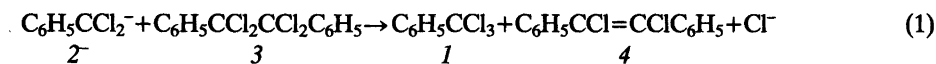
The anodic peak observed in CV of 1 with $E_p = -0.62$ V has been assumed to be caused by the oxidation of 2⁻ to 2', which would dimerize to 3. If that is correct, then any 1 reduced at -0.6 – -0.7 V would, after loss of Cl⁻ to 2', not be reduced further but would dimerize to 3 as observed. In that case it is not necessary to invoke the formation of mercury compounds, but they might still be involved.

The relatively high yield of 5 obtained at -0.7 V (SCE) is difficult to explain; 4 is reduced at about -1.6 V in CV and fast-polarography, and, contrary to 3, 4 does not show a very drawn-out wave. Any reducing agent, e.g. mercury, would be expected to attack 3 rather than 4; it seems that when 3 is reduced the reduction does in most cases not stop until 5 is formed; one could speculate that 3 first forms a mercury compound which then is reduced with loss of two chloride ions followed by a loss of mercuric chloride thus forming 5.

Under slightly different conditions (DMF/TBABF dried over molecular sieves, n-C₁₄H₃₀ as internal standard for GLC, $E = -1.3$ V (SCE) the product distribution changed dramatically in favour of 2 with less than 5 % 3 and similar yields of 4. The initial current density is higher (about 500 mA dm⁻²), but not as high as to make it limited by transportation of the electroactive compound to the electrode. Reductions at carbon or platinum resembles in the product distribution the just mentioned reduction; in some cases, however, inhibitions take place and the current drops to zero after very few coulombs have passed.

Apparently, two kinds of reactions take place, a reaction somehow involving the mercury surface and another not dependent on mercury. Mercury compounds have not been isolated.

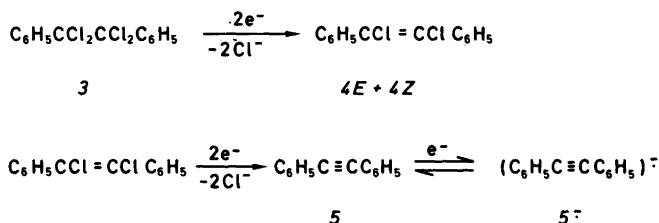
The situation is further complicated by atom-transfer reactions. The anion formed in a two-electron reduction of 1, C₆H₅CCl₂⁻, can react with 3 according to eqn. (1). When 2 is a major product, only little of 3 survives, and the dimerized products are mainly 4 and 5.



The reduction of 3 by 2^- can be demonstrated by stirring a solution of 2 and 3 in DMF with potassium *t*-butoxide. Such formal atom-transfer reactions have previously been observed for anions of polyhalogenated alkanes and has been described as a nucleophilic attack of the polyhalogenated anion on chlorine bound to carbon; also some other anions can react with e.g. carbon tetrachloride with transfer of chlorine.¹⁰⁻¹⁴ The reaction mechanism is not clear and might involve electron transfer from 2^- to 3.

Electrochemical reduction of 3 at -1.1 V in DMF/TBABF gave 4Z/4E in nearly quantitative yield; the ratio 4Z:4E was 5:3 whereas a ratio closer to 1:1 was found during the reduction of 1.

Reduction of either 4E or 4Z gives cleanly 5. 5 has also been obtained on reduction of other acid derivatives than 1; reduction of benzoate esters or dithioesters gives 1,2-dibenzoyloxy-1,2-diphenylethene¹⁵ (also obtained from benzoyl chloride³) and 1,2-diphenyl-1,2-di(thiobenzoylthio)ethene,¹⁶ respectively, which both on further reduction yield 5.



Scheme 2.

Reduction of 2 at the crest of the wave gave predominantly 6 together with small amounts of toluene, whereas reduction of 2 at the foot of the reduction wave with a low current density gave a 30 % yield of dimerized products consisting of a 5:3 mixture of diphenylacetylene (5) and *trans* stilbene (7). These products could be explained by a one-electron reduction of 2 followed by a loss of chloride ion and dimerization of the radical to 1,2-dichloro-1,2-diphenylethane (8). Base attack on 8 could give 5, whereas a two-electron reduction would produce 6. 8 was, however, not isolated from the product mixture.

EXPERIMENTAL

GLC-analysis: A Hewlett-Packard 5790 gaschromatograph was used with a 2 m column (5 % SE 30 on DMCS-glass) with injection and detector temperature at 250 °C, 5 min at 110 °C followed by a temperature increase of 5 °C min⁻¹ to 250 °C; *n*-C₁₄H₃₀ was used as internal standard. The chromatograms were recorded and integrated with a Hewlett-Packard integrator 3390.

The retention times for the compounds were under these conditions (min): Benzyl chloride 1.4; benzal chloride (2) 2.5; trichloromethylbenzene (1) 4.0; *n*-C₁₄H₃₀ 9.9; diphenylacetylene (5) 15.9; *Z*-1,2-dichloro-1,2-diphenylethene (4Z) 19.0; *E*-1,2-dichloro-1,2-diphenylethene (4E) 19.7; 1,2-diphenyl-1,1,2,2-tetrachloroethane (3) 26.0. 3, 4E, 4Z, and 5 were prepared according to known methods.¹⁷⁻¹⁹

Electroanalytical methods: The cell was a classical three electrode cell. The aqueous saturated calomel reference electrode (SCE) was connected to the cell by a bridge filled with DMF+0.1 M TEAP. The liquid junction potential corresponding to the H₂O/DMF interface is not known, but it was checked that it did not change with time for several weeks.

The electrochemical device was a multipurpose unit from SOLEA-TACUSSEL (Villeurbanne-France) - type PRG 4 - allowing measurements by dc and pulse polarography and by cyclic voltammetry on a tilted dropping mercury electrode. In our experiments the mercury flow $m=0.477$ mg/s and the imposed drop time 2.00 s. In normal pulse polarography the polarization delay was fixed to 1.95 s and the pulse duration to 40 ms. The current sampling was made between 80 and 90 % of the pulse duration.

Reduction of trichloromethylbenzene (at -0.7 V (SCE)). **1** (2.0 ml) was reduced in 150 ml DMF/0.2 M TBABF containing 1.0 ml n-C₁₄H₃₀ at -0.7 V (aq. SCE) at a mercury electrode (35 cm²); initial current 30 mA which gradually dropped to 20 mA. During the reduction samples (2 ml) were withdrawn, diluted with 5 ml of water, extracted with 4 ml of diethyl ether, which was washed with 5 ml of water, dried over molecular sieves (A 4), and analyzed by glc. The reaction was stopped when 90 % of **1** had been reduced, $n=2.8$; yield, calculated on the basis of consumed **1**, (GLC): **3** (63 %), **2** (3 %), **4Z+4E** (7 %), **5** (25 %).

Reduction of 1 at -1.3 V. **1** (2.0 ml) was reduced under similar conditions as above, except the cathode potential was -1.3 V (SCE); the initial current was 150-200 mA. Samples were withdrawn and analyzed as above during the reaction; at $n=2$ the reduction was discontinued; yield (GLC): unreacted **1** (4 %), **2** (85 %), **4E+4Z** (7 %), **3** (3 %).

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