Electroorganic Preparations.
XXXVI. Stepwise Reduction of Benzo trifluoride
HENNING LUND and NIELS J. JENSEN
Department of Chemistry, University of Aarhus,
DK-8000 Aarhus C, Denmark

Electrochemical reduction of trifluoromethyl compounds has been observed in some instances. In most cases reported the reduction has been performed in protic solvents, and under these conditions a complete reduction involving 6 F/mol to a methyl group is generally observed; the only exception seems to be the reduction of 2,2,2-trifluoroacetophenone to acetophenone in 80% aqueous ethanol during which monofluoroacetophenone was detected as an intermediate.

In N,N-dimethylformamide (DMF) some trifluoromethylbenzenesulphonamides have been investigated polarographically and a stepwise reduction was found in some cases; the electrode reaction corresponded to a reductive cleavage of the carbon-sulphur bonds, and the resulting benzo trifluoride was reported to give a single polarographic wave.

In the present work the electrochemical behaviour of benzo trifluoride and some other a-halogenated toluenes have been investigated by means of cyclic voltammetry (CV) and controlled potential electrolysis (CPE).

Results and discussion. In Table 1 are given the peak potentials of benzo trifluoride (I), a,a-difluorotoluene (II), a-fluorotoluene (III), benzo trichloride (IV), a,a-dichloro-a-fluorotoluene (V), a-chloro-a,a-difluorotoluene (VI), benzal chloride (VII), a-chloro-a-fluorotoluene (VIII), and benzyl chloride (IX). None of the electrode reactions are reversible on CV.

Whereas the peak potentials of II and III are very nearly equal, the potential of I is more than 200 mV less negative than that of II, and a reduction of I to II should be possible with a reasonable selectivity. The half-peak potential of II is about 0.05 V less negative than that of III which might indicate that the signal from II is a composite wave due to poorly separated peaks of the reduction of II to III and III to toluene. A reduction of II to III would thus be expected to be less selective than a reduction of I to II.

Cyclic voltammograms of I in DMF with added water showed that the peak potentials of the first and second peak were not affected by addition of up to 2% of water. The background current raised and at a water content higher than about 2% the waves merged with the background current.

The difference in reduction potential between that of the carbon-chlorine bond and that of the carbon-fluorine bonds in VI is about 0.7 V, sufficiently for a selective reduction; this was confirmed by a preparative reduction of VI to II in good yield. The potential difference between the reduction of the first and second carbon-chlorine bond in V is about 0.4 V; a selective reduction of V to VIII was shown to be possible.

The reduction of I was investigated in more detail; in Fig. 1 is shown the dependence of the concentrations of I, II, III, and toluene (X) on the electron consumption. The samples with...

---

Fig. 1. Dependence on concentration of benzo trifluoride (I), a,a-difluorotoluene (II), a-fluorotoluene (III), and toluene (X) on electron consumption during electrolytic reduction of I in DMF containing tetrabutylammonium iodide.
Table 1. Peak potentials (V vs. aq. SCE) at the hanging mercury drop electrode of α-halogen substituted tolenes in DMF containing 0.1 m tetrabutylammonium iodide. Sweep rate: 400 mV/sec.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E'_p$ (1)</th>
<th>$E'_p$ (2)</th>
<th>$E'_p$ (3)</th>
<th>V vs. aq. SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I C₂H₅CF₂</td>
<td>2.61</td>
<td>2.84</td>
<td>2.13</td>
<td>2.35</td>
</tr>
<tr>
<td>II C₂H₅CF₃</td>
<td>2.83</td>
<td>2.34</td>
<td>2.84</td>
<td></td>
</tr>
<tr>
<td>III C₂H₅CH₂F</td>
<td>2.84</td>
<td>2.36</td>
<td>2.36</td>
<td></td>
</tr>
<tr>
<td>IV C₂H₅CCL₂</td>
<td>1.77</td>
<td>2.36</td>
<td>2.36</td>
<td></td>
</tr>
<tr>
<td>V C₂H₅CH₂Cl</td>
<td>1.90</td>
<td>2.36</td>
<td>2.36</td>
<td></td>
</tr>
<tr>
<td>VI C₂H₅CCl₂</td>
<td>2.11</td>
<td>2.36</td>
<td>2.36</td>
<td></td>
</tr>
<tr>
<td>VII C₂H₅CH₂Cl</td>
<td>2.12</td>
<td>2.36</td>
<td>2.36</td>
<td></td>
</tr>
<tr>
<td>VIII C₂H₅CH₂Cl</td>
<td>2.36</td>
<td>2.36</td>
<td>2.36</td>
<td></td>
</tr>
<tr>
<td>IX C₂H₅CH₂Br</td>
<td>2.35</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The glassy carbon electrode was of the hanging mercury drop type; the platinum auxiliary electrode and the platinum indicator electrode were made from 0.050 mm and 0.025 mm wire, respectively. The counter electrode was a silver wire. The electrolyte was 0.1 M tetramethylammonium iodide in DMF. The cell was thermostated at 25°C. A voltage sweep rate of 50 mV/s was used.

The electrolytic solutions were prepared by dissolving the appropriate amount of halogenated tolenes in DMF and adding tetramethylammonium iodide to a concentration of 0.1 m. Before each experiment, the solutions were deaerated with argon for 30 min.

The cyclic voltammograms were obtained using a conventional three-electrode cell. The working electrode was a glassy carbon electrode of the hanging mercury drop type. The platinum auxiliary electrode and the platinum indicator electrode were made from 0.050 mm and 0.025 mm wire, respectively. The counter electrode was a silver wire. The electrolyte was 0.1 M tetramethylammonium iodide in DMF. The cell was thermostated at 25°C. A voltage sweep rate of 50 mV/s was used.

The electrolytic solutions were prepared by dissolving the appropriate amount of halogenated tolenes in DMF and adding tetramethylammonium iodide to a concentration of 0.1 m. Before each experiment, the solutions were deaerated with argon for 30 min.

The cyclic voltammograms were obtained using a conventional three-electrode cell. The working electrode was a glassy carbon electrode of the hanging mercury drop type. The platinum auxiliary electrode and the platinum indicator electrode were made from 0.050 mm and 0.025 mm wire, respectively. The counter electrode was a silver wire. The electrolyte was 0.1 M tetramethylammonium iodide in DMF. The cell was thermostated at 25°C. A voltage sweep rate of 50 mV/s was used.

The electrolytic solutions were prepared by dissolving the appropriate amount of halogenated tolenes in DMF and adding tetramethylammonium iodide to a concentration of 0.1 m. Before each experiment, the solutions were deaerated with argon for 30 min.

The cyclic voltammograms were obtained using a conventional three-electrode cell. The working electrode was a glassy carbon electrode of the hanging mercury drop type. The platinum auxiliary electrode and the platinum indicator electrode were made from 0.050 mm and 0.025 mm wire, respectively. The counter electrode was a silver wire. The electrolyte was 0.1 M tetramethylammonium iodide in DMF. The cell was thermostated at 25°C. A voltage sweep rate of 50 mV/s was used.

The electrolytic solutions were prepared by dissolving the appropriate amount of halogenated tolenes in DMF and adding tetramethylammonium iodide to a concentration of 0.1 m. Before each experiment, the solutions were deaerated with argon for 30 min.

The cyclic voltammograms were obtained using a conventional three-electrode cell. The working electrode was a glassy carbon electrode of the hanging mercury drop type. The platinum auxiliary electrode and the platinum indicator electrode were made from 0.050 mm and 0.025 mm wire, respectively. The counter electrode was a silver wire. The electrolyte was 0.1 M tetramethylammonium iodide in DMF. The cell was thermostated at 25°C. A voltage sweep rate of 50 mV/s was used.

The electrolytic solutions were prepared by dissolving the appropriate amount of halogenated tolenes in DMF and adding tetramethylammonium iodide to a concentration of 0.1 m. Before each experiment, the solutions were deaerated with argon for 30 min.

The cyclic voltammograms were obtained using a conventional three-electrode cell. The working electrode was a glassy carbon electrode of the hanging mercury drop type. The platinum auxiliary electrode and the platinum indicator electrode were made from 0.050 mm and 0.025 mm wire, respectively. The counter electrode was a silver wire. The electrolyte was 0.1 M tetramethylammonium iodide in DMF. The cell was thermostated at 25°C. A voltage sweep rate of 50 mV/s was used.

The electrolytic solutions were prepared by dissolving the appropriate amount of halogenated tolenes in DMF and adding tetramethylammonium iodide to a concentration of 0.1 m. Before each experiment, the solutions were deaerated with argon for 30 min.

The cyclic voltammograms were obtained using a conventional three-electrode cell. The working electrode was a glassy carbon electrode of the hanging mercury drop type. The platinum auxiliary electrode and the platinum indicator electrode were made from 0.050 mm and 0.025 mm wire, respectively. The counter electrode was a silver wire. The electrolyte was 0.1 M tetramethylammonium iodide in DMF. The cell was thermostated at 25°C. A voltage sweep rate of 50 mV/s was used.
analyzed by GLC on a 2.5 % diisodecylphthalate (DIDP)-column, programmed 4°/min from 40° to 150°, injection temperature 140°. The retention times (sec) were: I 470, toluene 603, II 900, III 967. The results are presented in Fig. 1.

B. I (2.0 ml) was reduced in 235 ml DMF containing 0.1 m TBAI at -1.95 Ag/AgI (DMF). After an electron consumption of 1.86 F/mol the reduction was stopped. Analysis by GLC gave I (11 %), II (52 %), and III (7 %). The catholyte was divided in two parts; one was treated as described above for the reduction of VI. Analysis of the residue showed a relative content of I, II, and III of 8:87:5.

The other part of the catholyte was reduced further at -2.1 V (the foot of the wave of II); after further 2 F/mol the catholyte was analyzed by GLC; II 13 %, III 72 %, and toluene 14 %.


Received December 19, 1973.

Fungal Extractives. VII.* A Formal Synthesis of (±)-Lactaral

J. FROBORG, G. MAGNUSSON and S. THOREN

Organic Chemistry 2, Chemical Center,
The Lund Institute of Technology, P.O. Box 740,
S-220 07 Lund, Sweden

The structure of lactaral (I), a new sesquiterpene furan-3-aldehyde from Lacktarius vellereus and L. pergamenus (Russulaceae), has been described.1 We now report a formal synthesis of lactaral confirming structure I.

A direct reductive cross-coupling of the allylic alcohol 3 and the 3-furyl alcohol 7 with TiCl4/butyllithium (or methylithium) in monoglyme 2 was unsuccessful. However, a lithium-promoted coupling reaction between the mesitate 8 of the furyl alcohol 7 and the allylic bromide 4 gave the tetrahydropranyl ether (THP) 9 of lactaral in low yield. Hydrolysis of compound 9 afforded racemic (±)-lactaral (2). This synthetic alcohol was spectroscopically identical with an authentic sample prepared from native lactaral by borohydride reduction (MS, IR and NMR). (−)Lactaral was reoxidized to lactaral with active manganese dioxide thus formally completing the total synthesis.

Experiment. The NMR spectra were recorded on a Varian T-60 spectrometer. Mass spectra were recorded on an LKB 1100 instrument.

4,4-Dimethyl-1-(1-bromo)ethylcyclopentene (4). The allylic alcohol 3 was brominated with triphenylphosphine-carbon tetrabromide in ether. After reflux for 24 h the reaction mixture was worked up to give the bromide 4 in 73 % yield. B.p. 78–81°C; nD 1.5250; λmax(neat) 3050, 1640, 1380, 820 cm⁻¹; NMR: δTMS(CDCl3) 5.62 (1 H, s broad), 4.83 (1 H, q, J = 7 Hz), 2.25 2.15 (2 H each, s broad), 1.80 (3 H, d, J = 7 Hz), 1.10 (6 H, s) ppm; MS: m/e 122 (24 %) (M⁺ – Br), 107 (100 %), 91 (31 %), 79 (19 %).

3,4-Bis(hydroxymethyl)furan (5). The diol 5 was prepared by lithium aluminium hydride reduction of the corresponding commercially available diethyl ester according to the literature.3 Yield 84 % (lit. 83 %). B.p. 100–102°C/0.2 mmHg (lit. 129–130°C/2 mmHg); nD 1.5103 (lit. nD 1.5080).

Reaction of diol 5 with 3,4-dihydro-2H-pyran. A mixture of diol 5 (1.28 g, 0.0100 mol), 3,4-