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Electroorganic Preparations. XXXVI. Stepwise Reduction of Benzotrifluoride

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Electrochemical reduction of trifluoromethyl compounds has been observed in some instances.¹⁻⁴ 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;¹⁻³ 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.³

In *N,N*-dimethylformamide (DMF) some trifluoromethylbenzenesulphonamides have been investigated polarographically⁴ 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 benzotrifluoride was reported to give a single polarographic wave.

In the present work the electrochemical behaviour of benzotrifluoride and some other α -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 benzotrifluoride (I), α,α -difluorotoluene (II), α -fluorotoluene (III), benzotrichloride (IV), α,α -dichloro- α -fluorotoluene (V), α -chloro- α,α -difluorotoluene (VI), benzal chloride (VII), α -chloro- α -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-

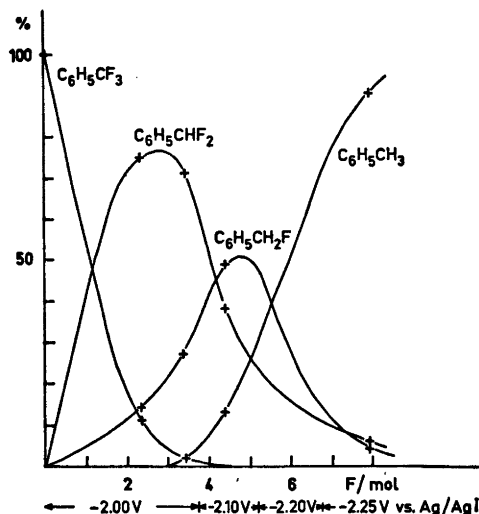


Fig. 1. Dependence on concentration of benzotrifluoride (I), α,α -difluorotoluene (II), α -fluorotoluene (III), and toluene (X) on electron consumption during electrolytic reduction of I in DMF containing tetrabutylammonium iodide.

Table 1. Peak potentials (V vs. aq. SCE) at the hanging mercury drop electrode of α -halogen substituted toluenes in DMF containing 0.1 M tetrabutylammonium iodide. Sweep rate: 400 mV/sec.

Compound	E_p (1)	E_p (2)	E_p (3)	V vs. aq. SCE
I $C_6H_5CF_3$	2.61	2.84		
II $C_6H_5CHF_2$	2.83 ₅			
III $C_6H_5CH_2F$	2.84			
IV $C_6H_5CCl_3$	1.77	2.13	2.35	
V $C_6H_5CCl_2F$	1.90	2.34	2.84	
VI $C_6H_5CClF_2$	2.11	2.84		
VII $C_6H_5CHCl_2$	2.12	2.36		
VIII C_6H_5CHClF	2.36	2.84		
IX $C_6H_5CH_2Cl$	2.35			

drawn during the electrolysis were analyzed by GLC; the retention times of the compounds were $I < X < II < III$. The electron consumption is somewhat higher ($\sim 20\%$) than the theoretical one reflecting a certain reduction of background components (e.g. supporting electrolyte) due to the very negative potential.

The cyclic voltammetry indicated the possibility of a reasonably selective reduction of I to II, but it seems somewhat more surprising that III is found in a rather high concentration during the latter part of the reduction, although the half-peak potential of III is only 0.05 V more negative than that of II. From the peak potentials a reduction of II to X could be expected.

Trifluoromethylbenzene (I) is thus in DMF reduced stepwise to toluene in a manner similar to other α, α, α -trihalotoluenes, although the differences in potential of the three steps are very small for I compared with the other trihalotoluenes. In protic media the trifluoromethyl compounds, when reducible, have mostly been found to be reduced to the toluenes without detection of any partly dehalogenated intermediates. The reason for this difference is not apparent, possibly the difference in ability of the fluoride ion to act as a leaving group in protic solvents, where it is highly solvated, and in DMF, where fluoride ions are less solvated, may play a role.

Reduction of I in protic solvents has not been attempted, as no voltammetric waves were observed; reduction of methyl *p*-trifluoromethylbenzoate in methanol produced the methyl toluate;² cyclic voltammetric and coulometric studies in DMF pointed, however, to a primary two-electron reduction.⁵

Cyclic voltammetric data in DMF of other substituted trifluoromethyl benzenes point to a stepwise reduction of these compounds; further studies with controlled potential reduction may show whether a stepwise reduction of the trifluoromethyl group is the general reduction mode in aprotic media.

Experimental. Apparatus. A Juul-electronics potentiostat, a F&M Research Chromatograph

Model 810 with a Hewlett-Packard 3370B electronic integrator, and a CEC 21-104 Mass Spectrometer were used.

Materials. Benzotrifluoride (I), benzyl fluoride (III), benzotrichloride (IV), benzal chloride (VII), and benzyl chloride (IX) were commercially available. α, α -Dichloro- α -fluorotoluene (V) and α -chloro- α, α -difluorotoluene (VI) were prepared according to Swarts,⁸ V (b.p. 178–180°C) was purified by preparative GLC on a 25% SE 52 column, $t = 80^\circ\text{C}$; $n_D^{25} = 1.5109$.

α, α -Difluorotoluene (II). 5 ml of α -chloro- α, α -difluorotoluene (VI) were reduced in 150 ml of DMF containing 5% of water and 0.1 M tetrabutylammonium iodide (TBAI) at -1.80 V vs. Ag/AgI (DMF), $n = 1.87$. The reduction completed the DMF was diluted with 1 l of water and extracted 3 times with 50 ml petrol ether. The petrol ether was washed 5 times with water to remove DMF and dried on "Sikkon Fluka". After removal of the petrol ether through a short column the residue, 3.6 g, was purified by preparative GLC on a 10% FFAP column at 50°C , 1.24 g. $n_D^{25} = 1.4550$. NMR-spectrum (neat): $\delta = 6.42$, 1 H, triplet, $J_{HF} = 57$ Hz; $\delta = 7.1$ –7.5, 5 H, multiplet. Mass spectrum, m/e (%): 39 (3), 41 (3), 43 (3), 50 (7), 51 (14), 55 (6), 57 (5), 63 (3), 69 (3), 74 (4), 75 (3), 77 (10), 78 (32), 79 (3), 81 (4), 83 (7), 101 (3), 107 (5), 109 (23), 126 (3), 127 (100), 128 (59), 129 (5).

α -Chloro- α -fluorotoluene (VIII). α, α -Dichloro- α -fluorotoluene (V) (2.7 g) was reduced in 150 ml of DMF containing 5 ml of water and 0.1 M TBAI at -1.3 V vs. Ag/AgI (DMF), $n = 2.03$. The catholyte was treated as described above for II, and the residue purified on a 10% FFAP-column at 70°C ; 1.34 g. NMR (CCl_4): $\delta = 5.30$, 1 H, doublet, $J_{HF} = 48$ Hz. $\delta = 7.28$, 5 H, singlet. Mass spectrum, m/e (%): 27 (7), 29 (9), 39 (7), 41 (21), 42 (16), 43 (27), 50 (8), 51 (8), 56 (23), 57 (38), 63 (8), 83 (17), 89 (6), 107 (9), 109 (100), 110 (13), 125 (2.4), 127 (0.9), 144 (29), 146 (11).

Reduction of benzotrifluoride (I). A. I (34 mg) was reduced in 45 ml DMF containing 0.1 M TBAI at -2.0 – -2.3 V vs. Ag/AgI. During the reduction samples were withdrawn, the electricity consumption noted, and the samples

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 (82 %), 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 %.

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

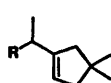
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The structure of lactaral (I), a new sesquiterpene furan-3-aldehyde from *Lactarius vellereus* and *L. pergamenus* (Russulaceae), has been described.¹ We now report a formal synthesis of lactaral confirming structure I.

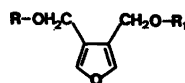
A direct reductive cross-coupling of the allylic alcohol 3 and the 3-furyl alcohol 7 with TiCl_4 /butyllithium (or methyllithium) in monoglyme² was unsuccessful. However, a lithium-promoted coupling reaction between the

mesitoate 8 of the furyl alcohol 7 and the allylic bromide 4³ gave the tetrahydropyranyl ether (THP) 9 of lactaral in low yield. Hydrolysis of compound 9 afforded racemic (±)-lactarol (2). This synthetic alcohol was spectroscopically identical with an authentic sample prepared from native lactaral by borohydride reduction (MS, IR and NMR). (-) Lactarol was reoxidized to lactaral with active manganese dioxide thus formally completing the total synthesis.



3. R = OH

4. R = Br

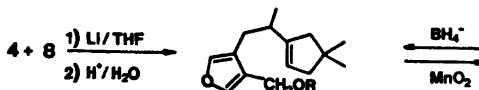


5. R, R₁ = H

6. R, R₁ = THP

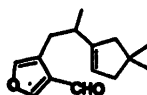
7. R = H; R₁ = THP

8. R = Mesitoyl; R₁ = THP



2. R = H

9. R = THP



1

Experimental. 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 3¹ was brominated with triphenylphosphine-carbon tetrabromide in ether.⁴ After reflux for 24 h the reaction mixture was worked up to give the bromide 4 in 73 % yield. B.p.₂₀ 78–81°; n_D^{26} 1.5250; ν_{\max} (neat) 3050, 1640, 1380, 1370, 820 cm^{-1} ; NMR: $\delta_{\text{TMS}}(\text{CDCl}_3)$ 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 %) ($\text{M}^+ - \text{HBr}$), 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.⁵ Yield 84 % (lit. 83 %). B.p. 100–102°/0.2 mmHg (lit. 129–130°/2 mmHg); n_D^{22} 1.5103 (lit. n_D^{20} 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-

* Part VI see Ref. 1.