

Electrochemical Reduction of 1,3,5-Triphenylbenzene to 1,3,5-Triphenylcyclohexane.

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Electrochemical reduction of nitroalkenes has been investigated under varied conditions, and different products have been isolated. In acidic alcoholic solution ethylnitrobenzene (2'-nitrostyrene) (**1**) has been reduced to phenylacetaldoxime [1] and a reduction of nitroalkenes to oximes has been used to prepare carbonyl compounds with a longer carbon chain [2]. If the nitroalkenes are reduced in the presence of TiCl_4 nitriles are obtained [3].

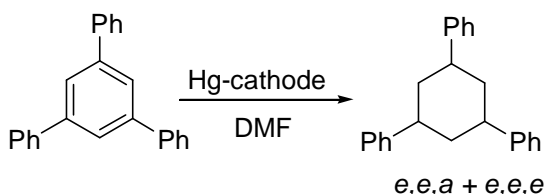
Bard and co-workers [4] have investigated β -nitrostyrene in DMF using polarography, cyclic voltammetry, and rotating ring disc voltammetry. Their experiments were in accordance with a one-electron reduction to the radical anion followed by a dimerization of two radical anions with a rate constant of $1.7 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$; the independence of the Lewich constant with rotation rate and the coulometric results with n close to 1 suggested the absence of base induced polymerization which is observed during the reduction of many activated olefins.

Preparative reduction of β -nitrostyrene in DMF gave $n = 0.2 - 0.3$, and besides polymerized material the main compound was transformed in GC-MS to 1,3,5-triphenylbenzene (**2**); trace amounts of 2,4,6-triphenylnitrobenzene and 2,4,6-triphenylaniline were also found [5]. 2-Nitro-1-phenylpropene (**3**) on reduction gave $n = 0.9$ and GC-MS showed a mixture of *d,l*-3,4-diphenylhexa-2,5-dione and 2,5-dimethyl-3,4-diphenylpyrrole and no trimerized product. As **3** does not trimerize the trimerization of **1** seems to be induced by the electrogenerated base and thus requires an acidic β -hydrogen [5]. A similar trimerization to a cyclohexane derivative has been observed during the reduction of 1,3-diphenylpropenone in DMF [6].

1,3,5-Triphenylbenzene is in cyclic voltammetry in DMF reduced reversibly to the radical anion at -2.35 V (SCE); preparative reduction in DMF at a mercury cathode gives a 3 : 2 mixture of *e,e,a*-triphenylcyclohexane (**4a**, m.p. $98 - 100^\circ\text{C}$) and *e,e,e*-triphenylcyclohexane (**4e**, m.p. $75 - 77^\circ\text{C}$). The assignment was made from the ^1H NMR spectra:

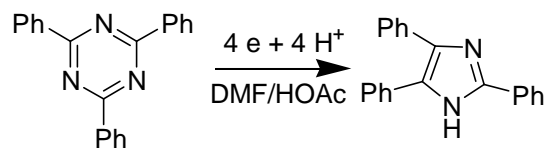
NMR (CDCl_3): *e,e,e*-1,3,5-Triphenylcyclohexane: $\text{H}(2,4,6)a$: $\delta = 1.64$, 3 H, quartet, $J = 12.4 \text{ Hz}$; $\text{H}(2,4,6)e$: $\delta = 2.18$, 3 H, broad doublet, $J = 12.0 \text{ Hz}$; $\text{H}(1,3,5)a$: $\delta = 2.93$, 3 H, triplet of triplets, $J_1 = 12.0 \text{ Hz}$, $J_2 = 3.1 \text{ Hz}$; phenyl groups, $\delta = 7.1 - 7.4$, 15 H, multiplet.

e,e,a-1,3,5-Triphenylcyclohexane (C_6D_6): $\text{H}(4)a$: $\delta = 1.63$, 1 H, "quartet" (double triplet), $J_1 \cong J_2 = 12.2 \text{ Hz}$; $\text{H}(2,6)a$: $\delta = 2.04$, 2 H, triplet of doublets, $J_1 = 13.2 \text{ Hz}$, $J_2 = 5.2 \text{ Hz}$; $\text{H}(4)e$: $\delta = 1.96$, 1 H, double multiplet, $J \cong 12.4 \text{ Hz}$; $\text{H}(2,6)$, broad doublet, $J_1 \cong 12.4 \text{ Hz}$; $\text{H}(2,6)e$: $\delta = 2.43$, 2 H, broad doublet, $J \cong 13.4 \text{ Hz}$; $\text{H}(3,5)a$: $\delta = 2.86$, 2 H, triplet of triplets, $J_1 = 12.4$, $J_2 = 3.2 \text{ Hz}$; $\text{H}(1)e$: 3.17, multiplet; phenyl; $\delta = 7.1 - 7.1 \text{ Hz}$, multiplet.



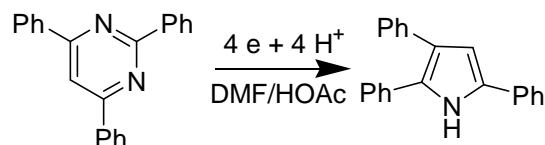
The reduction of a substituted benzene to the substituted cyclohexane at a non-catalytic electrode is probably possible, because any two-electron or four-electron reduction product would have a double bond conjugated to a benzene ring and thus be reducible at a potential close to that of styrene. Under the same conditions the reduction potentials of **2**, biphenyl, and styrene are, respectively: -2.32 , -2.46 , and 2.52 V vs SCE.

2,4,6-Triphenylnitrobenzene is reduced chemically reversible to the radical anion, but the heterogeneous rate constant for the electron transfer is rather low which is connected to the influence of the *ortho*-substituent. The esr-spectrum of the radical anion has been interpreted [7] to indicate that the radical anion exists in two forms. - Reduction under acidic conditions gives cleanly the 2,4,6-triphenylaniline.



2,4,6-Triphenylheteroaryls are reduced differently. 2,4,6-Triphenyl-1,3,5-triazine is thus reduced in DMF/HOAc 9 : 1 in a four-electron reduction to 2,4,5-triphenylimidazole, possible through an internal hydrodimerization of the initially formed 1,4-dihydro-2,4,6-triphenyl-1,3,5-triazine followed by loss of ammonia.

2,4,6-Triphenylpyrimidine is similarly reduced to 2,3,5-triphenylpyrrole in DMF/HOAc. 4,6-dimethyl-2-phenylpyrimidine has previously been shown to be reduced in aqueous/alcoholic acetate buffer to 3,5-dimethyl-2-phenylpyrrole [8] and a similar mechanism may be followed in DMF/HOAc.



References

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