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ELECTROCHEMICALLY INDUCED HYDROGEN-DEUTERIUM EXCHANGE

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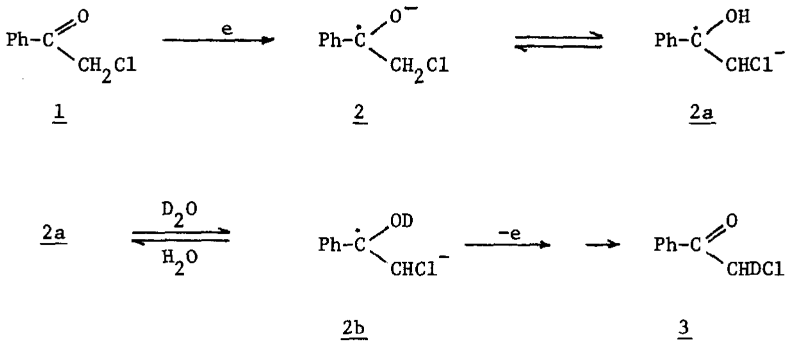
Recently, Diaz, Cheng and Ochoa were reporting electrochemical reductions of phenacyl chloride, 1, in non-aqueous DMF containing deuterium oxide, which were accompanied to a large extent by hydrogen-deuterium exchange in recovered starting material 1).
In the authors' opinion, the H/D exchange would occur at the stage of the electrochemically produced radical anion 2 which, on tautomerization and equilibration with D_2O would be reoxidized via electron transfer to the electrode or to another molecule species, giving exchanged starting material, 3 (Scheme 1). Thus, the observed H/D exchange is taken as an evidence for a new type of reversible formation of radical anions from organic halides which has not been established thus far by electroanalytical techniques.

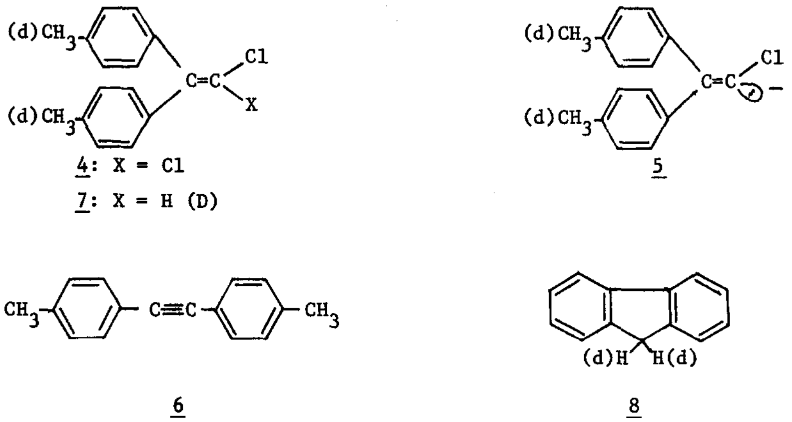
Scheme 1



This work prompts us to present our findings on a related electrochemical reaction, also accompanied by hydrogen-deuterium exchange, which has, however, led us to a different interpretation.

In the course of our investigations on the electrochemically induced [2] Fritsch-Buttenberg-Wiechell rearrangement [3] of 1,1-diaryl-2,2-dihaloethylenes yielding diarylethylenes, we studied the electrochemical reduction of 2,2-dichloro-1,1-bis(p-tolyl)-ethylene, 4, (Scheme 2)

Scheme 2



Under strictly aprotic conditions (0.5 M LiBr in DMF), the electrochemically produced intermediate, carbanion 5, rearranges to bis(p-tolyl)-acetylene, 6, the protonation product of 5, 2-chloro-1,1-bis(p-tolyl)-ethylene, 7, being a minor but persistent by-product.

In order to evaluate the relative importance of the possible proton sources (solvent, supporting electrolyte, residual water) causing the formation of 7, among other experiments, we carried out controlled potential electrolyses of 4 (0.2 M) in carefully dried DMF containing D_2O (0.2 M) and lithium bromide or tetra-n-butylammonium bromide (TBABr) (0.5 M in each case) as supporting electrolytes. A two compartment cell with a mercury pool cathode was used. Under these conditions, 7 is the only reduction product, the rearrangement 5 → 6 being totally suppressed. The deuterium content in the isolated product which serves as an indicator of the activity of D_2O as a deuteron source was determined by mass spectroscopical and ^1H-NMR analysis [4].

From the data listed in Table 1, the first significant observation is that D_2O is a far more powerful D^+ source when LiBr is employed as a supporting electrolyte as compared to TBABr. This may be interpreted with respect to the change in the double layer composition due to either supporting electrolyte cation [5]. Since the small Li^+ cation exhibits a strong tendency to establish a water (or D_2O) solvation shell, a high D_2O concentration is built up in the vicinity of the electrode, thus giving rise to a substantial amount of deuterium incorporation into 7. This principle has been used by other workers as a valuable synthetic tool for specific labelling of organic molecules with heavier hydrogen isotopes [6].

Contrary, the TBA^+ cation is poorly solvated by water (or D_2O), the H-bonding of water to the solvent, DMF, appearing to be stronger than the interaction with this cation [7].

Table 1 : Deuterium Incorporation into the Reaction Products upon Electrolysis of 0.2 M 2,2-Dichloro-1,1-bis(p-tolyl)-ethylene 4 in Non-aqueous DMF Containing 0.2 M Deuterium Oxide.

Support. Electrol.	Potential E,V vs SCE	Faraday per mole	Product	% Vinyl - D	% Methyl - D[a)]
LiBr	-2.00	2	7	68	0
TBABr[b)]	-2.00	2	7	8	24
TBABr	-2.00	1	7	12	12
			4	-	12
TBABr	-1.60	0	4	-	0

a) based on possible sixfold deuteration; b) tetra-n-butylammonium bromide

In fact, the TBA^+ cation itself serves as a proton source as is proved by the isolation of tri-n-butylamine, the Hofmann degradation product of the TBA^+ cation, from the reaction mixture. Thus, it turns out that, with tetra-n-butylammonium salts used as supporting electrolytes, water does not play a dominant role as a primary proton source even for highly reactive carbanions produced at the electrode surface.

The most surprising result of Table 1 is the fact that, in the TBABr case, 7 is additionally deuterated in the methyl groups attached to the aromatic rings. Moreover, on interruption of the electrolysis at half completion, the recovered starting material is likewise deuterated.

Since, from electroanalytical investigations [3,8)] there is not the least evidence of a possible regeneration of 4 from any intermediate on the electrochemical reaction path (the radical anion corresponding to 2, as well as the neutral radical precursor of 5 included), the H/D exchange in the methyl groups of 4 (and 7) is unlikely to be connected with the electrode reaction itself. Alternatively, the exchange could be base catalyzed, in which case, by estimation of relative p_Ka values, the only base capable of deprotonating an aromatic bound methyl group would be carbanion 5. Indeed, we found strong evidence for the latter interpretation from an independent experiment: co-electrolyses of 0.05 M bromobenzene ($E_{1/2}$ = -2.32 V) and 0.1 M fluorene ($E_{1/2}$ = -2.58 V) at cathode potentials around -2.3 V, at which 8 is not affected electrochemically, in non-aqueous DMF containing 0.4 M D_2O and 0.1 M TBABr, produced fluorene samples which contained 65-70 per cent deuterium in the 9,10-positions [9)].

Thus, the observed H/D exchange phenomena, to our opinion, must be regarded as further examples of "reactions of electrogenerated bases (EGBs)" like those previously reported in promoting Wittig olefination [10)] and hydrocarbon alkylation [11)]. The amazing fact that deprotonation of weak carbon acids is possible even in the presence of water (or D_2O) arises from the ability of the tetra-n-butylammonium cation to largely exclude water molecules from the double layer region where the protonation of highly reactive carbanions seems to proceed.

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