

Deoxygenation of Aliphatic Acetate Derivatives Using Electrogenerated Organic Amalgams¹

Lizeth M. Fragoso-Luna, Bernardo A. Frontana-Uribe*, Jorge Cárdenas

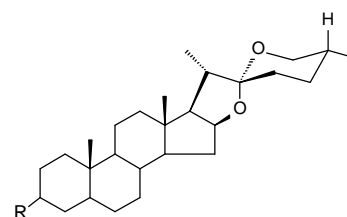
Laboratorio de Electroquímica y Electrosíntesis
Instituto de Química de la Universidad Nacional
Autónoma de México, Circuito Exterior, Ciudad
Universitaria, Coyoacán C.P. 04510, México D.F.

Reduction of aliphatic alcohols to the corresponding alkanes has acquired a great interest, mainly in the field of the sugar derivatives, due to the enhancement of the biological activity of some deoxygenated antibiotics. Radical processes have shown to be applicable to carry out this reductive transformation in the presence of sensitive functional groups. The possibility to produce rearranged products, frequently observed in ionic reactions are considerably reduced in the radical reactions. However, most of the radical reactions use tin hydrides as reducing agents and chain carriers. Toxicity of tin derivatives and the difficulties found in their adequate complete removal from the reaction mixtures, has prompted the search for alternative deoxygenating methods and reagents to find suitable hydrogen sources.²

Quaternary ammonium amalgams are known since the end of sixties.³ Lately, Kariv-Miller and coll. have demonstrated that during the electrochemical reduction of aromatic compounds on mercury cathode, if tetraalkylammonium ions are present, organic amalgams (R₄N-Hg) are involved in the electron transfer.⁴ The reactivity of these organomercuric compounds is similar to the reductions with alkaline metals (Li, Na, K). The utility of these organic amalgams to achieve difficult reductions (aromatics, ketones, conjugated dienes and fluoroaromatic compounds for example) has been well documented also⁵, but there are no references about their use in deoxygenation reactions.

We observed during our work that 3-acetyl-diosgenin (**1**) in the presence of electrogenerated tetrabutylammonium amalgam lost the acetoxy group, yielding the corresponding alkane and alcohol in a ratio *ca* 50:50 per cent. The chemical equivalent to this deoxygenation reaction is carried out by a dissolving metal (Li or K) reduction of esters to alkanes at -60°C using as solvents mixtures of dry *t*-BuNH₂ - THF or EtNH₂ - THF and crown ethers to dissolve the metal ions.⁶ We were interested in the electrochemical deoxygenation reaction, due to the easy access to the acetyl derivatives, the low cost of the reaction media compared with the chemical method and the possibility of work with wet organic solvents. In the literature some electrochemical deoxygenation methods are reported, but they are performed in dry organic solvents^{7,8,9} or they are useful only for specific functions.¹⁰ In this communication we report our findings in the reductive deoxygenation reaction of aliphatic acetate derivatives with electrogenerated tetrabutylammonium amalgams.

Examples using the acetates of sarsasapogenin, diosgenin, 16-dehydro-pregnanolone and argentinine A, show the applications and some limitations of this electrochemical reaction.



Starting Compound	Products (yield)
1a : R= AcO	1b : R= H (48%) + 1c : R= HO (32%)
1d : $\Delta^{5,6}$ R= AcO	1e : $\Delta^{5,6}$ R= H (53%) + 1f : $\Delta^{5,6}$ R= HO (45%)
1g : R= TBDMS	1g : R= TBDMS (90%)

Electrolysis conditions: WE= Hg, AuxE=Pt, Divided cell, 2.3 F/mol
5 mA/cm², THF/H₂O Bu₄NBF₄ 0.1M

Fig.1 Electrochemical deoxygenation of diosgenin acetate and sarsasapogenin acetate

¹ Fragoso-Luna L.M., Frontana-Uribe B.A., Cárdenas J., *Tetrahedron Lett.* In Press.

² Neumann, W. P.; Peterseim, M. *Synlett* **1992**, 801-802.

³ Littlehailes J. D., Woodhall B. J., *Discuss. Faraday Soc.* **1968**, 45 187-192.

⁴ Swenson, K. E.; Zemach, D.; Nanjundiah, C.; Kariv-Miller E. *J. Org. Chem.* **1983**, 48, 1777-1779.

⁵ Kariv-Miller, E.; Swenson, K. E.; Lehman, G. K.; Andruzzi, R. *J. Org. Chem.* **1985**, 50, 556-560.

⁶ Barrett, A. G. M.; Godfrey, C. R. A.; Hollinshead, D. M.; Prokopiou, P. A.; Barton, D. H. R.; Boar, R. B.; Joukhadar, L.; McGhie, J. F.; Misra, S. C. *J. Chem. Soc. Perkin I* **1981**, 1501-1509.

⁷ Shono, T.; Matsumura, Y.; Tsubata, K.; Sugihara, Y. *Tetrahedron Lett.* **1979**, 2157-2160.

⁸ Maeda, H.; Maki, T.; Eguchi, K.; Koide, T.; Ohmori, H. *Tetrahedron Lett.*, **1994**, 35, 4129-4132.

⁹ Rodríguez-Hahn, L.; Manríquez, M. E.; Frontana, B. A.; Cárdenas, J. *An. Quím. Int. Ed.* **1997**, 93, 291-294.

¹⁰ Mazur, D. J.; Kendall, P. M.; Murtiashaw, C. W.; Dunn, P.; Pezzullo, S. L.; Walinsky, S. W.; Zung, J. B. *J. Org. Chem.* **1996**, 61, 405-407.