

ELECTROCHEMICAL REDUCTIVE ACYLATION OF ACTIVATED OLEFINS

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Electrochemical reductive acetylation of aromatic¹ and heteroatomic² compounds, ketones³⁻⁵, nitrocompounds⁶, and disulfides⁷ has been described; in some cases^{1,4} acetylation at carbon takes place, but in most cases a heteroatom is attacked. Below is reported on electrolytic acetylation of activated olefins.

Ethyl cinnamate (1) (2 ml) was reduced at a mercury cathode in 150 ml of N,N-dimethylformamide (DMF) containing 10 ml of acetic anhydride and 10 g of Al₂O₃ at -1.85 V (SCE); after dilution of the catholyte with water, neutralization, and extraction with ether, the extracted products were separated on a column of silica using acetone/petrol ether (1:9) as eluent. Isolated were ethyl 3-phenyl-4-oxopentanoate⁸ (2) (75%), ethyl 2-benzyl-3-oxobutanoate (3) (2%) and different non-acylated products, mainly diethyl 3,4-diphenyladipate⁹ (4).

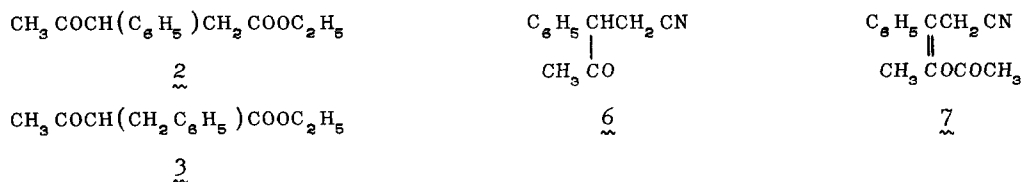
Similar results were obtained with other electron-deficient olefins. In the reduction of cinnamionitrile (5) at -1.80 V some 3-phenyl-4-oxovaleronitrile¹⁰ (6) was formed, but the major product (7) was the enol acetate of (6). ¹H NMR (CDCl₃) of (7): δ 1.84(3H,s), 2.21(3H,s), 3.31(2H,s), 6.8-7.8(5H,m). The stereochemistry (Z/E) of (7) has not yet been established. An enol acetate is also a major product in other cases, e.g. acenaphthylene.

The primarily formed product at the electrode is the radical anion of the olefin; the anion radical may dimerize or react with Ac₂O, and if the dimerization is very fast, little if any acylated product is obtained. The anion radical may react with Ac₂O either by a nucleophilic attack or by electron transfer¹; although the reaction formally is an addition of an acyl anion, the low reduction potential of Ac₂O makes the formation of Ac⁻ unlikely.

The enol acetate (7) may be formed from (6) by base and Ac₂O; basic conditions exist close to the electrode.

1,4-Addition of acyl anion equivalents to conjugated enones may be obtained with different reagents^{1,2-15}; the electrochemical reaction seems to be an attractive alternative to the chemical methods. The yield of methyl 3-phenyl-4-oxopentanoate (71%) from the addition of the lithium acylcarbonylnickelate reagent^{1,2} to methyl cinnamate is similar to that obtained (75%) by electrochemically acetylation of (1) to (2). It is noteworthy that one of the pathways suggested^{1,2} for the chemical reaction involves electron transfer to the conjugated enone with formation of its anion radical.

Preliminary results indicate a rather broad application of the electrochemical C-acylation, which will be reported on later.



REFERENCES

1. H.Lund, Acta Chem.Scand., B31 (1977) 424
2. H.Lund and J.Simonet, C.R.Acad.Sci.(Paris), 277 (1973) 1387.
3. T.J.Curphey, C.W.Amelotti, T.P.Layloff, R.L.McCartney, and J.H.Williams, J.Amer.Chem.Soc., 91 (1969) 2817.
4. T.J.Curphey, L.D.Trivedi and T.Layloff, J.Org.Chem., 39 (1974) 3831.
5. E.A.H.Hall, G.P.Moss, J.H.P.Utley, and B.C.L.Weedon, J.C.S.Chem.Comm., (1976) 586.
6. L.H.Klemm, P.E.Iversen, and H.Lund, Acta Chem.Scand., B28 (1974) 593.
7. P.E.Iversen and H.Lund, Acta Chem.Scand., B28 (1974) 827.
8. M.Julia, S.Julia, and C.Jeanmart, Bull.Soc.Chim.France, (1961) 1857.
9. J.P.Petrovich, M.M.Baizer, and M.R.Ort, J.Electrochem.Soc., 116 (1969) 749.
10. A.Oishi and H.Kugita, Japan Pat. 68 24 905 (CL 16 C 65); Chem.Abstr., 70 (1969) 87342.
11. P.E.Iversen and H.Lund, Tetrahedron Lett., 1969, 3523.
12. E.J.Corey and L.S.Hegedus, J.Amer.Chem.Soc., 91 (1969) 4926.
13. T.Mukaiyama, K.Narasaka, and M.Furusato, J.Amer.Chem.Soc., 94 (1972) 8641.
14. J.E.Richman, J.L.Herrmann, and R.H.Schlessinger, Tetrahedron Lett., 1973, 3267, 3271, 3275.
15. C.G.Chavdarian and C.H.Heathcock, J.Amer.Chem.Soc., 97 (1975) 3822.