Acta Chemica Scandinavica B 31 (1977) 424—438

Short Communications

Electrochemical Reductive Acetylation of Anthracene

HENNING LUND

Department of Organic Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

Electrochemical reductive acetylation of heteroaromatic compounds,[1] ketones,[2-4] nitro compounds,[5] and disulfides [6] has been described: in most of these examples the acetylation takes place at a hetero atom. Below is reported on an electrochemical reductive acetylation which involves formation of a carbon-carbon bond.

Results and discussion. Anthracene (*1*) in *N,N*-dimethylformamide (DMF) containing tetrabutylammonium iodide (TBAI) as supporting electrolyte is reduced more easily than acetic anhydride (*2*). Cyclic voltammograms of *1* in the absence and presence of *2* showed that the peak height of the first one-electron wave (formation of the anion radical) increased to approximately the height of a two-electron wave on addition of *2*; the peak potential of *1* was not affected by the addition of *2*.

Preparative reduction of *1* in the presence of excess of *2* gave a major product in good (66 – 75 %) yield together with small amounts of some side products. The major product was suggested to be the enol acetate of 9-acetyl-9,10-dihydroanthracene (*3*) from the mass spectrum, ^{1}H NMR and IR spectra. The MS indicated a molecular weight of 264, the ^{1}H NMR had singlets at δ 2.06 (3 H), 2.27 (3 H) and 3.84 (2 H), and the IR a carbonyl band at 1745 cm^{-1}. The compound was further characterized by acid hydrolysis to 9-acetyl-9,10-dihydroanthracene (*4*).

One of the minor products which was obtained in a small and variable yield (0 – 2 %) was suggested to be a mixture of the *cis* and *trans* forms of the diacetate of 9,10-diacetyl-9,10-dihydroanthracene (*5a*) and (*5b*) from the ^{1}H NMR spectrum and the mass spectrum. The reaction may be formulated as shown in Scheme 1.

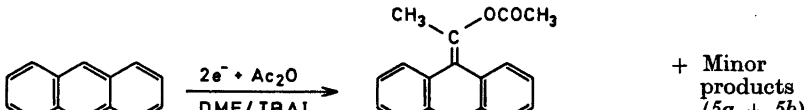
With lithium chloride as supporting electrolyte no *3* was formed but some *4* and 9,10-dihydroanthracene (*6*).

The reaction mechanism has not yet been established. A nucleophilic attack on acetic anhydride might occur, but attack by acetyl radicals formed by electron transfer from $1^{\cdot-}$ cannot be excluded. The nucleophile might be the anthracene anion radical, its dianion, or the monoanion of dihydroanthracene; the substrate for a radical attack might be anthracene or its anion radical.

The reductive acetylation is not limited to anthracene and similar aromatic hydrocarbons; an activated olefin, such as ethyl cinnamate (*7*), reacts similarly. *7* is thus reductively acetylated in good yield mainly to ethyl 3-phenyl-4-oxopentanoate which after reaction with hydrazine forms 4,5-dihydro-6-methyl-5-phenylpyridazin-3-(2*H*)-one.[7]

Experimental. Reductive acetylation of anthracene (1). 1 (2 g) was reduced at a mercury cathode in 150 ml of dry DMF/0.1 M TBAI containing 10 ml of acetic anhydride at – 2.0 V *vs.* aq. SCE. The acetic anhydride was, prior to the addition, purified by standing over activated alumina and 10 g of alumina were suspended in the catholyte. When the reduction was completed the catholyte was diluted with water and extracted three times with diethyl ether; the pooled ether extracts were washed with an aqueous sodium bicarbonate solution, dried with molecular sieves A4 and the solvent evaporated leaving 2.5 g of crude product. The crude product was separated on a column of silica using methylene chloride as eluent. *3* was eluted before *4a+b*.

3, Enolacetate of 9-acetyl-9,10-dihydroanthracene. Isolated was 1.92 – 2.20 g (66 – 75 %), m.p. 108 – 109 °C (ethanol). ^{1}H NMR



1 *3*

Scheme 1.

spectrum ($CDCl_3$): δ 2.06 (s, 3 H); 2.27 (s, 3 H); 3.84 (s, 2 H); 7.1 – 7.35 (m, 6 H); 7.40 – 7.65 (m, 2 H). IR spectrum (KBr) cm^{-1} (intensity): 2920 (w), 1745 (s), 1655 (m), 1445 (m), 1365 (ms), 1220 (s), 1155 (s), 1008 (m), 948 (m), 781 (s), 738 (s). Mass spectrum (*m/e* (%)): 264 (4), 222 (64), 179 (64), 178 (60), 43 (100).

4a+b, Enolacetate of 9,10-diacetyl-9,10-dihydroanthracene, 0 – 2 % yield, m.p. 152 – 158 °C (light petroleum), probably a mixture of the *cis* and *trans* forms. ^1H NMR spectrum ($CDCl_3$): δ 2.10 (s 6 H), 2.3 (two closely spaced singlets, 6 H), 7.1 – 7.6 (m 8 H). Mass spectrum (*m/e* (%)): 348 (1.5), 306 (10), 264 (28), 263 (38), 246 (17), 221 (16), 203 (17), 178 (22), 73 (68), 43 (100).

9-Acetyl-9,10-dihydroanthracene, (4). 3 was hydrolyzed in aqueous ethanolic 1 N HCl by boiling for 3 h under nitrogen. After cooling the mixture was diluted with water and extracted with ether, which was washed with an aqueous sodium bicarbonate solution and dried. Evaporation of the ether left a residue which was purified on a column of alumina using 5/95 ethyl acetate/light petroleum as eluent. *4* (liquid),[8,9] ^1H NMR (60 HMz, $CDCl_3$): δ 1.96 (3 H, s), 3.89 (1 H, d, *J* 18.5 Hz), 4.14 (1 H, d, *J* 18.5 Hz), 4.93 (1 H, broad s) 7.1 – 7.5 (8 H, m). Besides the couplings recorded, small unresolved long-range couplings between the 9 and 10 protons are found. *4* semicarbazone, m.p. 222 – 224 °C (224 – 226 °C).[9]

1. Lund, H. and Simonet, J. *C. R. Acad. Sci. 277* (1973) 1387.
2. Curphey, T. J., Amelotti, C. W., Layloff T. P., McCartney, R. L. and Williams, J. H. *J. Am. Chem. Soc. 91* (1969) 2817.
3. Curphey, T. J., Trivedi, L. D. and Layloff, T. P. *J. Org. Chem. 39* (1974) 3831.
4. Hall, E. A. H., Moss, G. P., Utley, J. H. P. and Weedom, B. C. L. *Chem. Commun.* (1976) 586.
5. Klemm, L. H., Iversen, P. E. and Lund, H. *Acta Chem. Scand. B 28* (1974) 593.
6. Iversen, P. E. and Lund, H. *Acta Chem. Scand. B 28* (1974) 827.
7. Lund, H. and Degrand, C. *To be published.*
8. Nenitzescu, C. D., Gavat, I. and Cocora, D. *Ber. Dtsch. Chem. Ges. B 72* (1939) 819.
9. May, E. L. and Mosettig, E. *J. Am. Chem. Soc. 70* (1948) 688.

Received February 10, 1977.

The Reaction of 2-Methylphenylmagnesium Bromide with Ethyl 3-Coumarincarboxylate. Addition of Three Reagent Molecules Followed by a Ring Opening

BILL GUSTAFSSON* and KAJ ÖSTMAN

Department of Organic Chemistry, Åbo Akademi, SF-20500 Åbo 50, Finland

The reaction of 2-methylphenylmagnesium bromide with ethyl 3-coumarincarboxylate (*1*) has recently been studied in this laboratory.[1] The reaction product proved to be ethyl 4-(2-methylphenyl)-3,4-dihydrocoumarin-3-carboxylate (*2*), formed by a fast conjugate addition.

It has earlier been established that phenylmagnesium bromide to some extent can react further with the primarily formed 1,4-adduct giving slowly 3-(2-hydroxyphenyl)3-phenylpropiophenone on saponification.[2]

When 2-methoxyphenylmagnesium iodide was allowed to react with ethyl 3-coumarincarboxylate, several higher boiling products appeared if the reaction time was extended.[3]

Because 2-methylphenylmagnesium bromide can be considered to have a reactivity between that of phenylmagnesium bromide and 2-methoxyphenylmagnesium iodide it seemed interesting to look more closely at the reaction between 2-methylphenylmagnesium bromide and ethyl 3-coumarincarboxylate.

When the ratio of reagent to substrate was raised to 5 in the reaction of 2-methylphenylmagnesium bromide with ethyl 3-coumarincarboxylate and the reaction time was prolonged to 48 h, mainly one new product (GLC yield *ca.* 25 %) appeared. This compound, which was isolated by column chromatography, was formed rather slowly. By spectroscopic methods it was shown to be 1,3-di(2-methylphenyl)-3-[2′-(2-methylbenzoyloxy)phenyl]propan-1-one (*3*).

This compound is obviously formed by addition of three molecules of the Grignard reagent followed by a ring opening reaction during and after hydrolysis of the primarily formed magnesium complexes (Scheme 1). The ring opening reaction can be considered as an example of the reverse aldol condensation, where the equilibrium lies far towards the free ester and ketone.

The missing reactivity of the magnesium complex, which is formed by the first 1,4-addition, is explained by the lack of a well-defined carbonyl group. The actual reagent in

* Present address: Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, Fack, S-40220 Göteborg 5, Sweden.