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[a028]

Comparative study of classical and modified Clemmensen reduction of anthraquinone and alizarin with amalgamated and non-amalgamated zinc: what "hexahydroanthracene" Clemmensen have obtained?

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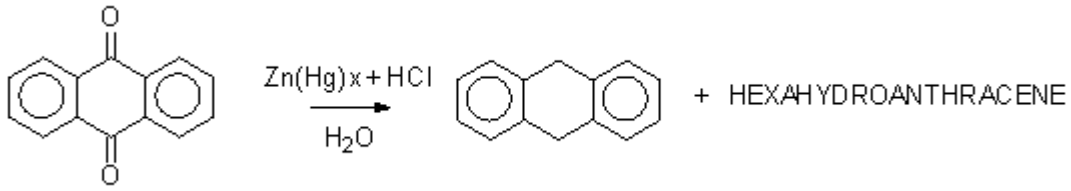
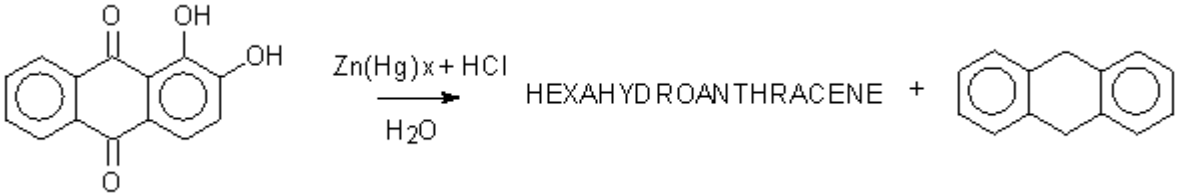
Abstract. The comparative study for reduction of anthraquinone and alizarin with zinc dust and zinc amalgam was conducted. Both reactions gives 9,10-dihydroanthracene, 1,2,3,4-tetrahydroanthracene, and 1,2,3,4,4a,9,9a,10-octahydroanthracene mixtures as reaction products. No any hexahydroanthracene isomers were detected by GC-MS.

The classical Clemmensen reduction of anthraquinone (**I**) with zinc amalgam gives 9,10-dihydroanthracene (**II**) as main product and some"hexahydroanthracene" (**III**), double bond site was not definied [1].



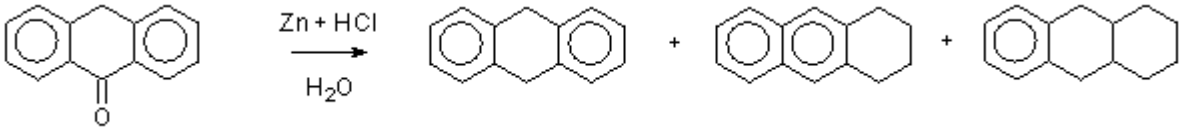
I **II** **III**

Alizarin (**IV**) on classical Clemmensen reduction with zinc amalgam gives **III** as main product and **II** as impurity [1].



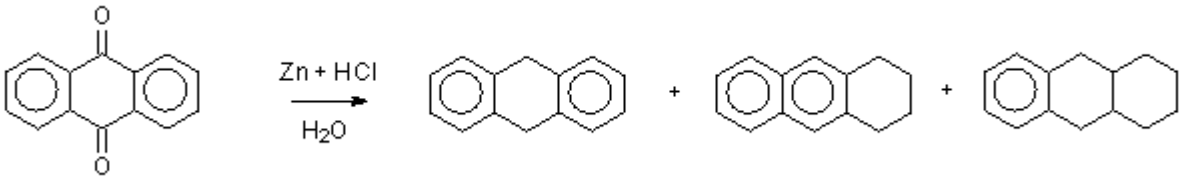
IV **III** **II**

Our study of anthrone (**V**) reduction with non-amalgamated zinc leads to **II** as sole product and as impurities traces of 1,2,3,4-tetrahydroanthracene (**VI**) and 1,2,3,4,4a,9,9a,10-octahydroanthracene (**VII**) were detected by GC-MS (probably, due to content some **I** in starting **V**) [2].



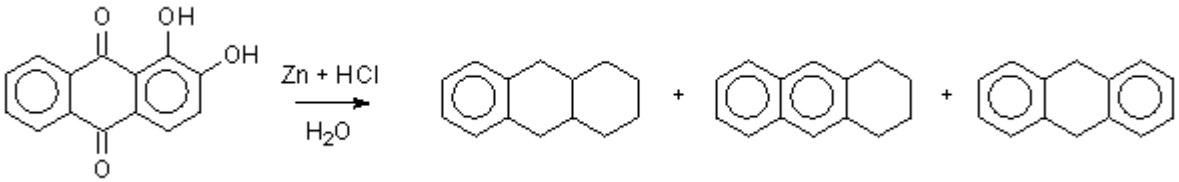
V **II** **VI** **VII**

Anthraquinone reduction by modified Clemmensen reaction with non-amalgamated zinc gives mainly **II**, whereas **VI** and **VII** as side products were obtained [3].



I **II** **VI** **VII**

In our study of alizarin reduction by modified Clemmensen reaction with non-amalgamated zinc mainly **VII** and **VI** mixture, also **II** as impurity were obtained [3].



IV **VII** **VI** **II**

No any isomers of hexahydroanthracene in above modified Clemmensen reduction of **I**, **IV**, and **V** we have detected. So, it became interesting, what hexahydroanthracene Clemmensen have obtained?

In our hands, re-investigation of **I** and **IV** reduction in classical Clemmensen conditions with zinc amalgam leads to **II**, **VI**, and **VII** mixtures in various proportions. Also, no any hexahydroanthracene were detected. As result, Clemmensen's "hexahydroanthracene" **III** proved to be an eutectic mixture of **VI** and **VII**.

Experimental.

General procedure for reduction of I and IV with zinc dust. To 9.68g (0.148mol) of zinc dust 20 ml of water and 20 ml of concentrated hydrochloric acid were added. Quinone (**I** or **IV**), 0.002 mol was grounded in a mortar with 5 ml of concentrated hydrochloric acid and resulting slurry was added to reaction mixture. After 12hr heating at reflux 10ml of toluene was added, reaction mixture was refluxed 1hr, cooled and excess of zinc was filtered with suction and washed with 5ml of toluene. Toluene layer was separated, dried over sodium sulphate and analyzed by TLC and GC-MS [4].

General procedure for reduction of I and IV with zinc amalgam. To 9.68g (0.148mol) of zinc dust 20 ml of 5% $HgCl_2$ in water and after 1hr 20 ml of concentrated hydrochloric acid were added. Quinone (**I** or **IV**), 0.002 mol was grounded in a mortar with 5 ml of concentrated hydrochloric acid and resulting slurry was added to reaction mixture. After 12hr heating at reflux 10ml of toluene was added, reaction mixture was refluxed 1hr, cooled and excess of zinc was filtered with suction and washed with 5ml of toluene. Toluene layer was separated, dried over sodium sulphate and analyzed by TLC and GC-MS [4].

References

1. E. Clemmensen. Uber eine allgemeine methode zur reduktion der carbonylgruppe in aldehyden und ketonen zur methylengruppe. (III Mitteilung). *Ber. Deutsch. Chem. Ges.* 1914, **47**, 681-687.

2. Vladimir N. Bulavka. Modified Clemmensen reduction of some diaryl ketones with non-amalgamated zinc. *Proceedings of ECSOC-10, The Tenth International Electronic Conference on Synthetic Organic Chemistry*, 1-30 November 2006. Editors: Julio A. Seijas, M. Pilar Vazquez Tato. http://www.usc.es/congresos/ecsoc/10/ECSOC10.htm & http://www.mdpi.org/ecsoc-10/ CD-ROM edition, ISBN 3-906980-18-9. Publisher MDPI, Basel, Switzerland. Poster A028.

3. V. N. Bulavka. Reduction of anthraquinones with non-amalgamated zinc by modified Clemmensen reaction. *9th Scientific School-conference on Organic Chemistry*. (Moscow – Zvenigorod, 11-15.12.2006). Abstracts of Reports. Moscow, 2006, Abstract C-39, p.92.

4. 1,2,3,4,4a,9,9a,10-octahydroanthracene, RT=13.71min, MS m/z (%): M+1 = 187 (7), M = 186 (46), 143 (7), 141 (6), 129 (13), 128 (12), 117 (8), 115 (11), 105 (27), 104 (100), 103 (7), 95 (13), 94 (12), 91 (11), 81 (18), 80 (14), 79 (8), 78 (8), 77 (8), 41 (8), 39 (6); 9,10-dihydroanthracene, RT=14.64min, MS m/z (%): M+1 = 181 (13), M = 180 (100), 179 (93), 178 (51), 177 (7), 176 (11), 165 (19), 152 (8), 151 (6), 90 (5), 89 (20), 88 (7), 76 (13), 63 (5); 1,2,3,4-tetrahydroanthracene, RT=15.60min, MS m/z (%): M+1 = 183 (14), M = 182 (100), 181 (18), 178 (8), 167(30), 166 (15), 165 (27), 155 (7), 154 (32), 153 (25), 152 (21), 151 (7), 142 (6), 141 (42), 139 (6), 128 (8), 115 (11), 91 (5), 90 (5), 89 (13), 88(5), 83 (12), 77 (8), 76 (17), 63 (8), 39 (5).