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[a028]

Modified Clemmensen reduction of some diaryl ketones with non-amalgamated zinc.

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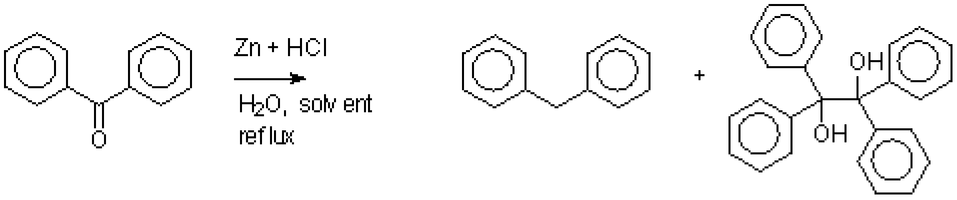
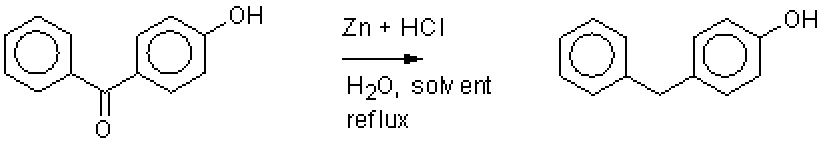
Abstract. The method for reduction of diaryl ketones to diphenylmethanes with zinc metal instead zinc amalgam was elaborated.

In course of our investigation directed to replace zinc amalgam for non-amalgamated zinc in Clemmensen reduction of carbonyl group to methylene group (preceeding poster [1]) we have investigated reduction of some diaryl ketones.



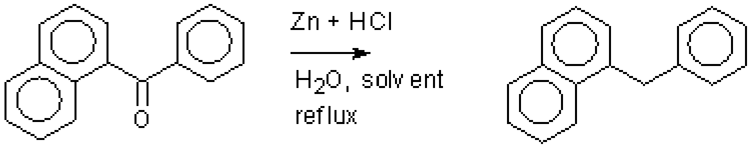
I **II** **III**

Unsubstituted benzophenone **I** was reduced with zinc dust without additional solvent to diphenylmethane **II** with low yield. Benzpinacone **III** was isolated as the main product. Reduction in ethanol-water medium proceeds with moderate yields of **II** and **III**.



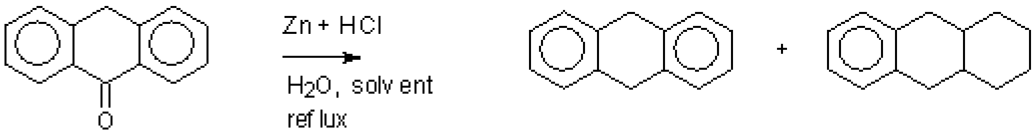
IV **V**

4-Hydroxybenzophenone **IV** was reduced to correspondent 4-hydroxydiphenylmethane **V** with zinc dust or with granulated zinc with high yield. Pinacone-type by-product was not detected.



VI **VII**

1-Benzoylnaphthalene **VI** was reduced to 1-benzylnaphthalene **VII** with moderate yield. Addition of ethanol co-solvent did not improve yield significantly.



VIII **IX** **X**

Reduction of anthrone **VIII** was proceeds to dihydroanthracene **IX** and hexahydroanthracene **X** mixture. Addition of solvent miscible with water also increases the yield of **IX**.

The results of reduction are summarised in Table.

No. of run	Starting compound	Co-solvent	Obtained compound	Yield, %	m. p., ^{o}C	m.p. [lit]), ^{o}C
1	**I**	-	**II** **III**	27 67	m.p. 22-24 m. p. 185-187	 m. p. 187 [2]
2	**I**	C_2H_5OH	**II** **III**	51 44	m.p. 22-24 m. p. 185-187	 m. p. 187 [2]
3	**IV**	-	**V**	95	m.p. 81-83	m.p. 83-84 [3]
4	**IV**	-	**V**	93*	m.p. 81-83	m.p. 83-84 [3]
5	**VI**	-	**VII**	60	m.p. 56-58	m.p. 58-59 [4]
6	**VI**	C_2H_5OH	**VII**	64	m.p. 56-58	m.p. 58-59 [4]
7	**VIII**	-	**IX** **X****	45 35	m. p. 105-107 m. p. 59-61	m.p. 106-107 [3] m.p. 60-62 [3]
8	**VIII**	C_2H_5OH	**IX** **X****	57 22	m. p. 105-107 m. p. 59-61	m.p. 106-107 [3] m.p. 60-62 [3]

* Granulated zinc instead zinc dust was used. **Compound **X** was isolated from ethanolic mother liquor after crystallisation of **IX**.

Experimental.

Diphenylmethane II and benzpinacone III.

1. To 0.1 mol of benzophenone and 0.3 mol of zinc dust 50 ml of water and 50 ml of concentrated hydrochloric acid were added. The reaction mixture was heated with reflux condenser at reflux during 24 hr. Each 6 hours 5 ml of concentrated hydrochloric acid was added. The reaction mixture was monitored with TLC. After the end of reaction from the reaction mixture **II** was separated by steam distillation. After cooling the residue was filered and extracted with ethanol. After removing of solvent the residue (**III**) was purified by crystallisation.
2. To 0.1 mol of benzophenone and 0.3 mol of zinc dust 50 ml of ethanol, 50 ml of water and 50 ml of concentrated hydrochloric acid were added. The reaction mixture was heated with reflux condenser at reflux during 24 hr. Each 6 hours 5 ml of concentrated hydrochloric acid was added. The reaction mixture was monitored with TLC. After the end of reaction ethanol was distilled and from the reaction mixture **II** was separated by steam distillation. After cooling the residue was filered and extracted with ethanol. After removing of solvent the residue (**III**) was purified by crystallisation.

General procedure for reduction of diaryketones IV, VI, VIII without additional solvent. To 0.1 mol of diarylketone and 0.3 mol of zinc dust (* granulated zinc, run 4), 50 ml of water and 50 ml of concentrated hydrochloric acid were added. The reaction mixture was heated with reflux condenser at reflux during 24 hours. Each 2 hours 5 ml of concentrated hydrochloric acid was added. The reaction mixture was monitored with TLC. After the end of reaction the reaction mixture was cooled, and extracted with ethyl ether. Combined organic solutions were dried with sodium sulphate, filtered, and solvents were removed at reduced pressure. The residue purified by crystallisaton.

General procedure for reduction of diaryketones VI, VIII with additional solvent miscible with water. To 0.3 mol of zinc dust 50 ml of water, 50 ml of solvent, and 50 ml of concentrated hydrochloric acid, heated to gentle boiling, 0.1 mol of alkylarylketone solution in 300 ml of solvent were added during 4 hours. The reaction mixture was heated with reflux condenser at reflux during 10-15 hours. Each 2 hours 5 ml of concentrated hydrochloric acid was added. The reaction mixture was monitored with TLC. After the end of reaction the co-solvent was distilled off, the reaction mixture was cooled and extracted with ethyl ether. Combined organic solutions were dried with sodium sulphate, filtered, and solvents were removed at reduced pressure. The residue purified by crystallisaton.

References

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