

ZINC REDUCTION OF CONJUGATED ALKENOIC ACIDS

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The essentially quantitative reduction of maleic to succinic acid by zinc was recently reported by the late Professor Emmett Reid.¹ We have studied both zinc and zinc-mercury couple (Clemmensen) reduction of a variety of conjugated unsaturated acids. The results are summarized in the following Table. These results show that reduction with zinc alone is

REDUCTION OF UNSATURATED CARBOXYLIC ACIDS			
with Zinc + HCl		with Zinc/Mercury + HCl	
Unsaturated Acid Used	% Yield of Reduced Acid	Unsaturated Acid Used	% Yield of Reduced Acid
Maleic	90	Cinnamic ^b	80
Fumaric	87	Glutaconic	65
Aconitic	88	Muconic ^c	82
Citraconic	92	Itaconic	81
Mesaconic	80	a) Required 2 equivalents of zinc, succinic produced.	
Dimethylmaleic	80	b) Layer of toluene to effect solubility	
Bromomaleic ^a	80	c) Hydromuconic acid produced by 1,4 addition	
Dibromomaleic ^a	80		
Acetylene di-COOH	89		

possible for both cis and trans butene-dicarboxylic acids, a variety of their derivatives, and acetylene dicarboxylic acid. With these conjugated diacids reduction to the corresponding succinic acid derivative is obtained in good yields (>80%). For the conjugated unsaturated monocarboxylic acids zinc mercury amalgam (Clemmensen reagent) was found to be necessary. Neither procedure reduced cis-1,2,3,6-tetrahydrophthalic acid or reacted with cis-1,2-cyclobutanedicarboxylic acid. Both methods gave essentially quantitative conversions of endo-5-norbornene - 2,3-dicarboxylic acid to the lactone or X-ester of Fieser.²

Replacement of zinc with chromium or cadmium resulted in no reduction of maleic acid. Reduction with zinc offers a quick, simple means of essentially quantitative reduction.

The general procedure used was to add unsaturated acid (0.05 moles) to 40 mesh zinc (0.055 moles) covered with boiling water (50 ml). After 10-30 minutes conc. HCl (10 ml) was added. Upon reaction of all the zinc the volume of solution was reduced 1/3 to 1/2 by evaporation and subsequent cooling produced crystalline saturated acid. Stirring, heating or length of reaction time had little effect in general on yield except with 2,3-dimethyl maleic where heating for 24 hours to form the zinc salt before HCl addition was necessary for good yield. For unsaturated monocarboxylic acids not reduced by this procedure the Clemmensen reagent as prepared by Poutsma and Wolthuis³ was found to give reduction. For the water insoluble cinnamic acid Martin's procedure⁴ using a layer of toluene to solublize was employed.

The reduction of dimethylmaleic acid in 80% yield was found to give the meso-2,3-dimethylsuccinic acid (literature⁵ for meso 195° and d,l 127°, found 195°). Formation of the meso acid indicates cis addition of the hydrogen. Further light was thrown on the mechanism of the reaction by the fact that the zinc can be completely reacted with organic acid, before the HCl is added and still essentially quantitative reduction obtained. This indicates that reduction can occur via the hydrogens of the carboxylic acid groups reacting with the zinc. As expected from the proposed mechanism the HCl can be replaced by H₂SO₄ or H₃PO₄ with essentially the same yield. Study of the reaction in a pneumatic gas collecting system showed that when reduction occurred less than 10% of the theoretical hydrogen was evolved while with nonreduced acids approximately 100% of the theoretical hydrogen was collected. At present no explanation is offered for the necessity of using the amalgam for reduction of the conjugated monoacids.

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