

7. Evidence is given for the following interpretation of the effect of the ferrous salt. The inactivity of the pure platinum black is due to the fact that it is deprived of the oxygen necessary for its activity by the readily oxidizable aldehyde. The iron salt specifically inhibits this reaction and so prolongs the active life of the catalyst.

8. Using appropriate amounts of ferrous chloride and 0.23 g. of catalyst, it is shown that 21.2 g. of benzaldehyde may be smoothly reduced to the alcohol in 20 to 25 minutes. The reaction then stops and no further reduction takes place. A method is described for reducing 100 g. of benzaldehyde in 4 hours with 0.025 g. of catalyst.

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NOTES

The Action of the Grignard Reagent on Keto Acids.—The action of the Grignard reagent on esters of γ -keto acids, where but 1 molecular proportion of the Grignard reagent is used to 1 of the ester, has been known for some time. This reaction involves the addition of the Grignard reagent to the keto group, which on hydrolysis of the reaction product gives a lactone of the hydroxy acid. Various yields have been reported depending on the type of reacting substances. In certain cases where the keto acid is difficult to prepare, or to esterify, it is desirable to use the Grignard reagent on the keto acid directly, thus eliminating not only the necessity of preparing the ester but also the probable loss of valuable material. In connection with other work which has led to the preparation of *iso*-campholactone from 3-keto-1,2-dimethyl-cyclopentane-carboxylic acid, the reaction of the Grignard reagent on levulinic acid was first studied.

*iso*Caprolactone was prepared by the action of methylmagnesium iodide on levulinic acid. Methylmagnesium iodide was slowly added to an ether solution of levulinic acid in the proportion of 2 moles of the former to 1 mole of the latter. On the addition of the first half of the Grignard reagent, an insoluble magnesium salt of levulinic acid was formed; but after the addition of the remainder, a slow reaction took place which continued for 4 hours, giving a second insoluble compound. After the reaction mixture had been cooled the addition compound was decomposed by 1:1 sulfuric acid and the *isocaprolactone* extracted with ether. The ether extract was washed with a solution of sodium bisulfite to remove free iodine. After the ether had been distilled, the residue was fractionated, and that portion boiling at 205–210° under atmospheric pressure was saved; yield, 31.5%. Noyes and Marvel¹ obtained a yield of 30–35% from ethyl levulinate.

The lactone of γ -methyl- γ -hydroxy-hexanoic acid was prepared in a similar manner by the action of 2 molecular proportions of ethyl magnesium

¹ Noyes and Marvel, *THIS JOURNAL*, **39**, 1269 (1917).

bromide on 1 of levulinic acid. The lactone distilled at 76–78° under 5 mm. pressure; yield, 35.1%. Grignard and Moissan² obtained the same compound from ethyl levulinate. Their product boiled at 105–106° under 18 mm. pressure, with a yield of 35%.

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Determination of Formic Acid.¹—Jones² has described a method for determining formic acid by oxidation with standard potassium permanganate in a solution made alkaline with sodium carbonate. The solution was made acid, excess of standard oxalic acid added and the excess titrated with standard permanganate. This method was tested by using solutions of known concentration, with the results shown in Table I.

TABLE I

Time allowed for oxidation, min. . . .	under under under									
	1	1	1	2	5	15	20	20	35	
0.05 N KMnO ₄ calc. consumed, cc. . . .	20.00	13.94	15.87	14.33	17.38	17.98	19.51	20.07	20.08	19.93

The results show that at least 20 minutes should be allowed for the completion of the oxidation. Jones probably allowed this time to elapse, but neglected to mention this detail in the description of his method.

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NEW BOOKS

The Theory of Emulsions and Emulsification. By WILLIAM CLAYTON, D.Sc. Foreword by Professor F. G. DONNAN, Ph.D., D.Sc. P. Blakiston's Son and Company, 1012 Walnut Street, Philadelphia, 1923. viii + 160 pp. 22 figs. 14 × 22.5 cm. Price \$3.00.

This is probably the most comprehensive book on emulsions available, although Bancroft and Fischer have written rather extensively on the subject. One of the most acceptable features of the book is the rather full bibliography of some two hundred references. Chapters are given on Emulsions and Emulsifying Agents; The Properties of Emulsions; Earlier Theories of Emulsions; Adsorption at Liquid-Liquid Interfaces; Dual

² Grignard and Moissan, *Compt. rend.*, **135**, 629 (1902).

¹ Published by permission of the Secretary of Agriculture.

² Jones, *Am. Chem. J.*, **17**, 540 (1895).