ther upon the mechanism of deposition, at this time.

There are, however, two or three additional points of interest which came out of these observations. The fact that during the whole growth of the disk the thickness remains the same makes it seem quite obvious that the deposition occurs only on the inner edge of the slowly closing ring. That being the case, it may be assumed then that the chain molecules have their active ends sticking out toward the center of the hollow disk where deposition takes place, and that growth occurs by addition of new residues on these ends. That conception of growth may be reinforced slightly by the commonly known fact that cell-wall formation is always associated with the presence of living protoplasm in contact with the growing wall. It is still further strengthened by the fact that only local activity may be seen in these growing walls. The protoplasm seems to be in contact with the side surfaces of the disk as well as with the inner edge yet it is only on the inner edge that deposition takes place. That the protoplasm takes an active part in the deposition seems evident, for the rate of deposition may be slowed down very materially or even stopped completely by very slight changes in the environment of the algal cells.

From what has been said above there appears to be a marked difference in the process of deposition between the animate and inanimate. In the former, for example, the surface may decrease rapidly as deposition occurs, while in the inorganic process such as crystallization the active surface usually becomes greater.

May we say in conclusion that in this report we have tried to make the conception of cell-wall growth, in at least one phase of its construction, somewhat less vague by introducing a molecular picture into the process.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Reaction of Diethylzinc on Acetoxime

BY DAVID F. MENARD AND JOHN G. ASTON

This paper describes a study of the reactions of diethylzinc on acetoxime in which it is shown that the products are analogous to those obtained by the action of dimethylzinc on methanol.[1]

When one mole of diethylzinc was added to an ether solution containing two moles of acetoxime, two moles of ethane was evolved and an insoluble zinc compound was formed, by the consecutive reactions A and B

$$Zn(C_2H_5)_2 + (CH_3)_2CNOH \longrightarrow (CH_3)_2CNOZnC_2H_5 + C_2H_6 \quad (A)$$

ethyl zinc acetoximate

$$(CH_3)_2CNOZnC_2H_5 + (CH_3)_2CNOH \longrightarrow [(CH_3)_2CNO]_2Zn + C_2H_6 \quad (B)$$

zinc diacetoximate

The reaction of one mole of diethylzinc with one mole of acetoxime formed a soluble zinc compound and one mole of ethane was evolved according to reaction (A). In each of these reactions the pure zinc compound was isolated and identified.

Upon hydrolysis of zinc diacetoximate acetoxime was formed, while hydrolysis of ethyl zinc acetoximate formed ethane and acetoxime.

Experimental

Apparatus and Manipulation.—The apparatus (Fig. 1) was tested for leaks and swept completely with dry carbon dioxide before each experiment. The acetoxime solution was introduced into the 250-cc. reaction flask, A, through tube, E, taking care to exclude air. The calculated amount of diethylzinc was added dropwise from the calibrated pipet, B. This pipet had been connected to the addition side arm by a ground glass joint covered with paraffined heavy rubber tubing.

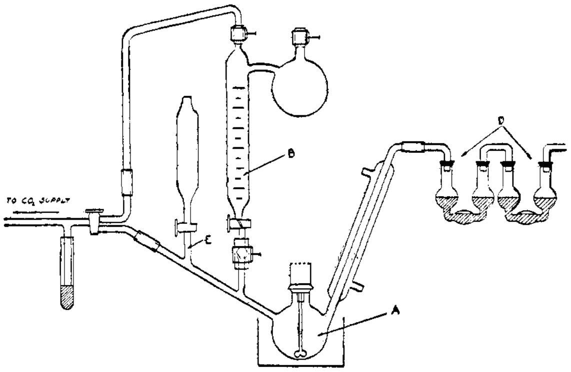

Fig. 1.—Apparatus for reactions with zinc alkyls.

The gas evolved passed through the condenser and the sulfuric acid traps, D, to remove ether vapor. It was collected in a gas holder over saturated salt solution.

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[1] Tolkätschew, *Chem. Zentr.*, II, 1200 (1901).

After all the diethylzinc had been added it was possible to withdraw safely the zinc alkyl pipet without exposing the system to air by unfastening the ground glass joint inside the rubber tubing and closing off the latter with a screw clamp before pulling the pipet out. Any excess of zinc ethyl was returned to the flask connected to the pipet, and the ends of the latter closed off with paraffined rubber tubing secured by screw clamps. Then to prevent the stopcock from "freezing," it was withdrawn and the barrel quickly stoppered with shellacked corks.

Zinc Diacetoximate.—Fifty-one grams (0.414 mole) of diethylzinc was added to a solution of 60.4 g. (0.828 mole) of acetoxime in 125 cc. of sodium dried ether. The apparatus was then brought to room temperature and swept with enough carbon dioxide to drive the residual ethane into the gas holder. The ether solution was poured off from the white solid remaining in the reaction flask. The solid was ground, and washed twice with dry ether on a Buchner funnel. These operations were all carried out in an atmosphere of carbon dioxide to prevent hydrolysis or oxidation. The solid, dried *in vacuo* at room temperature, weighed 86.5 g. (0.413 mole), a yield of 99.8% of the theoretical.

Anal. Calcd. for $C_6H_{12}N_2O_2Zn$: Zn, 31.20; N, 13.57. Found: Zn, 31.38, 31.48; N (Kjeldahl), 13.67, 13.53.

The gas was analyzed in an Orsat apparatus using 100 cc. samples. Carbon dioxide was absorbed by 40% potassium hydroxide, oxygen by potassium pyrogallate solution, and excess ether vapor by fuming sulfuric acid. Ethane was determined by slow combustion. The remaining gas was considered to be nitrogen, as it was nearly four times the amount of oxygen.

The average of two analyses was: 23.4% carbon dioxide, 0.0% ether vapor, 1.9% air and 74.7% ethane. Thus the total volume of wet gas, 27.75 liters at 23° and 737 mm., corresponded to 24.12 g. (0.804 mole) of ethane, a yield of 96.9% of the theoretical.

Sixty-two grams (0.296 mole) of zinc diacetoximate was hydrolyzed with dilute hydrochloric acid and the resulting solution continuously extracted with ether for fifteen hours. Forty and four-tenths grams (0.554 mole) of acetoxime (93.5% of the theoretical) was identified as acetoxime in the ether solution and as its hydrolysis products, acetone and hydroxylamine, in the aqueous portion.

Ethyl Zinc Acetoximate.—Fifty-three grams (0.431 mole) of diethylzinc was added to a solution of 32 g. (0.438 mole, 2% excess) of acetoxime in 125 cc. of anhydrous ether, 4.5 g. (0.0215 mole) of zinc diacetoximate was filtered off, corresponding almost exactly to the excess of acetoxime used. The original excess of acetoxime removed as zinc diacetoximate ensured the complete removal of all the zinc ethyl from the ether solution. After distilling off most of the ether from the solution, 60.5 g. (0.365 mole) (84.5% of the theoretical) of white crystals of ethyl zinc acetoximate was deposited. Ethyl zinc acetoximate hydrolyzes readily on exposure to moist air and decomposes at 190° when heated in a sealed tube.

Anal. Calcd. for $C_5H_{11}NOZn$: Zn, 39.28; N, 8.30. Found: Zn, 39.35, 39.39; N (Kjeldahl), 8.30. Samples were hydrolyzed in a Zerewitinoff apparatus: subs., 0.1567, 0.2170 g. C_2H_6 calcd.: 0.000940, 0.001275 mole; found: 0.000937, 0.001205 mole.

The average of two analyses of the gas evolved in the preparation reaction was: 29.5% carbon dioxide, 0.0% ether vapor, 2.0% air and 68.5% ethane. Thus the total volume of wet gas, 17.00 liters at 25° and 730 mm., corresponded to 13.40 g. (0.446 mole) of ethane, a yield of 103.9% of the theoretical.

Twenty-one and three-tenths grams (0.127 mole) of ethyl zinc acetoximate dissolved in 125 cc. of ether was hydrolyzed with dilute hydrochloric acid in the above apparatus (Fig. 1) and 8.7 g. (0.119 mole) of acetoxime (94% of the theoretical) was identified in the same manner as in the hydrolysis of zinc diacetoximate. The average of two analyses of the wet gas evolved was: 43.6% carbon dioxide, 1.6% ether vapor, 7.5% air and 47.3% ethane. Thus the total volume of wet gas, 6.80 liters at 26° and 732 mm., corresponded to 3.69 g. (0.123 mole) of ethane. a yield of 97.0% of the theoretical.

Summary

1. Two new zinc compounds, zinc diacetoximate and ethyl zinc acetoximate, have been prepared and some of their properties recorded.

2. The reaction of diethylzinc on acetoxime is analogous to that of dimethylzinc on methanol.

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