Summary

It is shown that the formation of macrocyclic ketones from salts of the dibasic acids probably involves first a linear polyketone which is subsequently cracked or decomposed. The ketones thus follow a course already established for esters and anhydrides. The characteristic analogies and differences in the three series can be explained by taking into account the nature of the reactions involved and the steric effects of peripheral atoms. Rings of more than 5 atoms cannot be regarded as entirely strainless. The probable nature of the strains in large rings is indicated.

WILMINGTON, DELAWARE RECEIVED SEPTEMBER 2, 1933
PUBLISHED DECEMBER 14, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Organic Reactions with Boron Fluoride. VI. The Reaction of Acetamide with Alcohols and Phenol

BY FRANK J. SOWA AND JULIUS A. NIEUWLAND

The purpose of this paper is to describe the formation of esters by the removal of ammonia, in the form of monoammino boron fluoride,[1] from the acetamide–boron fluoride compound[2] and a second compound of the type ROH. The reaction takes place according to the equation

$$CH_3CONH_2{\cdot}BF_3 + ROH — CH_3CO_2R + BF_3{\cdot}NH_3$$

By this method the acetates of methyl, ethyl, isopropyl, *n*-butyl and *tert*-butyl alcohols and of phenol have been prepared in yields of 71, 69, 32, 50, 38 and 50%, respectively. The percentage yield depends upon the amount of boron fluoride used (as long as the latter is not in excess). This seems to indicate that the formation of the monoammino boron fluoride is the driving force of the reaction. From the foregoing results it is predicted that the acetamide–boron fluoride compound should be a good acetylating agent.

Various amides and alcohols are being studied in connection with this reaction. The reaction of the acetamide–boron fluoride compound with amines, acids, esters and hydrocarbons is also being examined.

Experimental

One mole of the alcohol or phenol was introduced into a 500-cc. flask containing the acetamide–boron fluoride compound, prepared by passing a mole of boron fluoride into a mole of acetamide. In a few cases monoammino boron fluoride separated as a white solid almost immediately. The flask was fitted with a reflux condenser and the mixture was refluxed

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(1) Kraus and Brown, THIS JOURNAL, **51**, 2690 (1929); Mixter, *Am. Chem. J.*, **2**, 153 (1881); Pflaum and Wenzke, *Ind. Eng. Chem.*, *Anal. Ed.*, **4**, 392 (1932).

(2) Bowlus and Nieuwland, THIS JOURNAL, **53**, 3835 (1931).

from fifteen to forty-five minutes. The ester was then distilled directly from the flask through a fractionating column.

The solid residue, after organic matter had been removed, was shown by analysis to contain one mole of ammonia. When treated with concentrated sulfuric acid and heated, the residue gave a large amount of boron fluoride gas. It is possible to recover practically all of the boron fluoride by the treatment with sulfuric acid.

Summary

It has been shown that the addition compound formed between acetamide and boron fluoride reacts rapidly with alcohols and with phenol to form acetates and monoammino boron fluoride.

NOTRE DAME, INDIANA

RECEIVED OCTOBER 4, 1933
PUBLISHED DECEMBER 14, 1933

Notes

Note on the Oxidation Products of Benzophenone Oxime[1]

BY W. H. HUNTER AND W. S. DYER

The work presented in this paper was begun a number of years ago, but unfortunately it had to be interrupted before it was completed. Recently, v. Auwers and Wunderling[2] have published a paper under the above title, and it therefore seems advisable for us to present a summary of our own work in this field, even though it is still incomplete.

Oxidation with Ferricyanide.[3]—Twenty grams of benzophenone oxime was dissolved in 200 cc. of ethyl alcohol by adding a small amount of 1:1 aqueous sodium hydroxide. This solution was then added to one liter of ice cold alkaline ferricyanide (40 g. of ferricyanide, 40 g. total of sodium hydroxide). The temperature was kept at 0° and the mixture stirred for two hours. The floating blue mass was removed and boiled with 500 cc. of ethyl alcohol, filtered from the fine white precipitate, and the alcohol evaporated. The residue was stirred repeatedly with separate portions of petroleum ether, and was again boiled with ethyl alcohol and filtered. Several such alternations of solvents gave three products: (I) a compound soluble in alcohol and in petroleum ether; when "seeded" with benzophenone it gave crystals melting at 47°. When mixed with benzophenone the melting point was unchanged; yield, 11 g. (II) a compound soluble in alcohol and insoluble in petroleum ether. Recrystallized from hot alcohol, this gave 2 g. of yellow needles, m. p. 156–157°.

Anal. Calcd. for $C_{26}H_{20}ON_2$: C, 82.98; H, 5.32; N, 7.45; mol. wt., 348. Found: C, 82.98; H, 6.1; N, 7.51; mol. wt. by freezing point in benzene, 357.

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(1) Part of the work presented in this paper is taken from a thesis by Walter S. Dyer presented to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Master of Science, September, 1925.—L. I. SMITH.

(2) v. Auwers and Wunderling, *Ber.*, **66**, 538 (1933).

(3) Holleman, *Rec. trav. chim.*, **13**, 429 (1894).