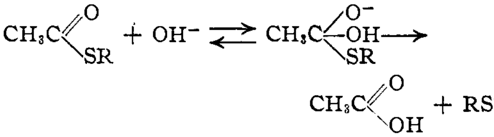
Therefore the preferred mechanism for alkaline thiolester hydrolysis is



$$CH_3C(=O)SR + OH^- \rightleftarrows CH_3C(O^-)(OH)SR \longrightarrow CH_3C(=O)OH + RS^- \qquad (6)$$

The activation energy for thiolester hydrolysis by mechanism (6) should be appreciably greater than for ester hydrolysis by mechanism (5) for two reasons: firstly, the coöperation of a water molecule lowers the energy necessary to add hydroxyl ion and to split off alcohol, as pointed out in the preceding paragraph; and secondly, the relatively greater polarization of the C–OR bond in esters compared to the C–SR linkage in thiolesters further lowers the energy necessary for hydroxyl ion addition and bond rupture. The latter reason alone, it should be noticed, is insufficient in itself to account for the large observed difference in activation energies (Table III), since its numerical value will amount to only about 1.6 kcal. as a comparison of acid catalyzed hydrolysis of ester and thiolester reveals (same Table). The steric hindrance to the hydrolysis reaction will be greater for esters (mechanism 5) than for thiolesters (mechanism 6) owing to the shielding effect of the water molecule, thus making the log *PZ* factor lower for ester than for thiolester hydrolysis, also in accord with observation. On the other hand, the alkaline hydrolyses of ester and of thiolester are similar in that *E* and log *PZ* for each reaction both increase with increase in acetone content of the reaction medium[10] (see Table II). The increase of activation energy with change in acetone concentration of the reaction medium is in the expected direction, since a decrease in the dielectric constant of the medium would be expected to decrease the ease of addition of hydroxyl ion at the carbonyl carbon atom.

Acknowledgment.—The author wishes to express his sincere thanks to Dr. Paul J. Flory for his valuable suggestions pertaining to this problem, and to Mr. Daniel Fouser for his assistance in part of the experimental work.

Summary

A kinetic study of the acid catalyzed and the alkaline hydrolysis of ethyl thiolacetate in aqueous acetone has been made. The acid catalyzed hydrolysis is first order with respect to thiolester and with respect to hydrogen ion concentration. The basic hydrolysis is second order. The activation energies are as follows: acid catalyzed hydrolysis 17,800 cal./mole; alkaline hydrolysis 13,000 cal./mole (24.6% acetone solution), 13,800 cal. (43.0% acetone), and 14,400 cal. (62.0% acetone).

A comparison of thiolester and ester hydrolysis has been made, and the mechanisms of hydrolysis have been discussed in view of the results obtained.

[10] R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, 538 (1937); C. N. Hinshelwood, K. J. Laidler and E. W. Timm, *ibid.*, 848 (1938); R. A. Harman, *Trans. Faraday Soc.*, **35**, 1336 (1939).

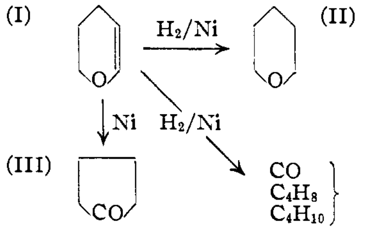
AKRON 16, OHIO RECEIVED NOVEMBER 22, 1947

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

Reactions of Furan Compounds. IX. Catalyzed Rearrangement of 2,3-Dihydropyran into Cyclopentanone[1]

BY CHRISTOPHER L. WILSON

Experiments described in the present paper have shown that 2,3-dihydropyran (I) can be reduced in good yield to tetrahydropyran (II) by passing the vapor with hydrogen over a nickel catalyst at 100°. This confirms an earlier observation.[2] When the temperature was raised to 200° or above, however, two other reactions were noticed. One was ring fission to butane, butene and carbon monoxide and the other rearrangement to cyclopentanone (III). These two reactions have not been recorded before although reference has been made[2] to the formation of unidentified materials of "high molecular weight." Catalysts of nickel or cobalt and mixtures of each of these with copper were effective. On the other hand, copper chromite failed to induce any change whatever.



The yield of cyclopentanone, calculated on consumed dihydropyran, under favorable circumstances attained almost 30% but the reaction was always accompanied by fission. Replacement of added hydrogen by nitrogen suppressed to some extent both fission and reduction but the rearrangement was only affected to a minor extent. Thus hydrogen does not appear to be essential for this reaction. On the other hand, the catalyst to be active must be so for all three processes and deterioration toward one reaction is accompanied

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[1] This paper was presented before the Organic Division at the New York meeting of the American Chemical Society in September, 1947.

[2] British Patent 565,175, Bremner, Jones and Taylor.

by inactivation in the other two. These features are illustrated by Tables I and II.

TABLE I

REACTION OF DIHYDROPYRAN VAPOR OVER A NICKEL CATALYST

Input: Dihydropyran, 84 g. for each experiment during two hours. Experiments consecutive without catalyst reactivation

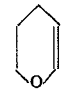
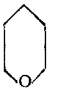
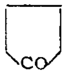
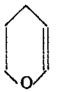
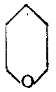
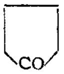
			Products (g.)		
Temp., °C.	Carrier and rate (l/hr.)	 Unchanged (g.)	n-C_4H_8 n-C_4H_{10}		
100	H_2 45	0	0	77	0
200	H_2 25	7.5	3.3	61	0.9
200	N_2 25	63	0.1	0	2.9
250	N_2 10	44	4.4	1.9	9.2
300	H_2 25	19	11.0	7.5	8.8
300	N_2 10	21	11.0	3.1	7.1

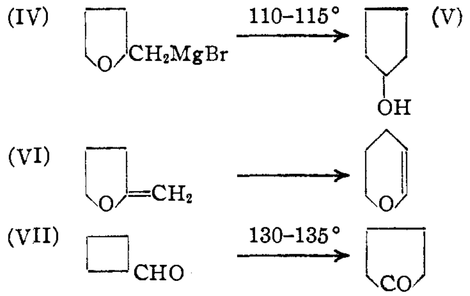
TABLE II

REACTION OF DIHYDROPYRAN VAPOR OVER A COBALT CATALYST

Input: Carrier: 10 l./hr., dihydropyran, 84 g. for each experiment during two hours. Experiments consecutive without catalyst reactivation

			Products (g.)			
Temp., °C.	Carrier	 Unchanged (g.)	n-C_4H_{10}	n-C_4H_8		
250	H_2	27	3.9	1.6	33	7.2
250	N_2	65	0.1	0.1	3.7	6.6
300	H_2	29	4.2	3.6	8.3	10.0
300	N_2	54	0.2	0.6	0.9	5.0
300	H_2	63	0.1	0.1	3.2	2.7

There appears to be no recorded parallel with the reaction leading to cyclopentanone, but certain observations of significance have been made previously. Cyclopentanone is present in the higher ketone fractions from the destructive distillation of wood or lignite which may suggest a connection with furan compounds. Furthermore Paul[3] obtained what he thought was a small amount of cyclopentanol (V) by heating the magnesium derivative of tetrahydrofurfuryl bromide (IV). Later[4] he drew attention to the fact that thermal rearrangement of methylenetetrahydrofuran (VI), which may be made by the elimination of hydrogen bromide from tetrahydrofurfuryl bromide, would be expected to give rise to cyclopentanone if the usual mode of vinyl ether rearrangement was followed.[5] His experiments gave, however, only a poor yield of dihydropyran. At temperatures higher than those Paul used, dihydropyran is known to split into acrolein and ethylene, and it has already been pointed out that if the usual mode of vinyl ether rearrangement obtained here the initial product would be cyclobutane aldehyde.[6] This compound, however, could not be detected but its intervention was not disproved. It has since been noted that cyclobutane aldehyde (VII) on heating in the presence of certain acidic substance rearranges to cyclopentanone.[7] Since this ketone was absent from the pyrolytic products from dihydropyran the intervention of the cyclic aldehyde would appear to be excluded. The catalysed rearrangement of course might proceed in quite another manner, and cyclobutane aldehyde might intervene here before being transformed into cyclopentanone.



The formation of cyclopentanone from dihydropyran offers an explanation of the hitherto unaccountable presence of the cyclic ketone in the products from the reaction of tetrahydrofurfuryl alcohol over a nickel catalyst.[8] It is, however, necessary to suppose the intermediate formation of some dihydropyran which although not detected with a nickel catalyst has since been shown to form using a cobalt catalyst.

The function of the catalyst in the rearrangement is obscure. Activated adsorption involving the C–O links, and particularly the weaker one remote from the carbon double bond, might be expected to be the first step in ring fission and loss of carbon monoxide. On the other hand, adsorption by attachment of the carbon double bond must be an important step in reduction. The type of activation necessary for rearrangement is not so clear but it may be that the second variety which leads to reduction, if hydrogen is also present, might also be responsible for a loosening of the α-hydrogen atom of the double bond. This kind of effect has been recognized ever since it was shown[9] that the rate of hydrogen-isotope exchange with an olefin under the influence of a metallic catalyst is much more rapid than the rate of hydrogen addition to the double bond. If this is so it should be possible to find a catalyst which will cause rearrangement and reduction rather than fission.

Experimental

Catalysts.—These were used in the form of granulated (4–16 mesh) sintered powders. They were placed in the

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[3] Paul, *Bull. soc. chim.*, **53**, 424 (1933).

[4] Paul, *ibid.*, **2**, 751 (1935).

[5] Part VII, THIS JOURNAL, **69**, 3002 (1947).

[6] Part VIII, *ibid.*, **69**, 3004 (1947).

[7] Venus-Danilova, *J. Gen. Chem.* (*U. S. S. R.*), **8**, 1179 (1938); *C. A.*, **33**, 4203 (1939).

[8] Part III, *J. Chem. Soc.*, 54 (1945).

[9] Farkas, Farkas and Rideal, *Proc. Roy. Soc.* (*London*), **A146**, 630 (1934).

catalyst chamber consisting of a Pyrex glass tube, 1.7 in. diameter, and heated electrically. The metal was activated by oxidation in a stream of air at 500° followed by slow reduction below 300° with hydrogen. The weight of each catalyst and the amount of water produced at the first reduction was as follows, pure nickel (2500 g., 250 cc.), pure cobalt (2300 g., 359 cc.), nickel–copper (50% of each, 2500 g., 607 cc.) and cobalt–copper (50% of each, 2500 g., 425 cc.). Copper chromite (750 g.) prepared by the usual precipitation method was inactive at 225° and 350°. The catalysts were reactivated by oxidation and reduction as above.

Isolation and Analysis of Products.—Dihydropyran was prepared by dehydration of tetrahydrofurfuryl alcohol over aluminum silicate at 350°. After drying over solid sodium hydroxide it had b. p. 86–88°.

The product issuing from the catalytic chamber containing the active metals was passed through a trap at −78° and the condensed portion distilled at atmospheric pressure. Material, b. p. below 20°, consisted of C_4-hydrocarbons. Bromine was added at −78° until addition was complete and the volatile unreacted butane distilled off into a graduated tube where its volume at 0° was measured. The involatile bromide was weighed and the amount of butene to which it corresponded was calculated. The bromide had b. p. 159–160° and would therefore appear to consist essentially of the symmetrical butene dibromide. The boiling point of the 1,2-compound is recorded as 166°.

The fraction of the products collected between 20 and 100° boiled mainly between 70 and 90°. It appeared to contain only di- and tetra-hydropyrans in addition to a little water. The organic substances were estimated in one of three ways depending on the accuracy desired, each method being checked using authentic mixtures. The most accurate was to weigh the precipitated δ-hydroxyvaleraldehyde 2,4-dinitrophenylhydrazone formed by adding a weighed sample to excess of a saturated solution of the hydrazine in hydrochloric acid (2 *N*); the accuracy was 1% with a mixture of equal amounts of the pyrans. A second method, accurate to 6% with the same mixture of pyrans, was to measure the reduction in weight of a sample (5 cc.) after shaking with hydrochloric acid (2 *N*) saturated with sodium chloride. Shaking and separation were carried out in a micro-separatory funnel. This method was only reliable when the pyrans were present in approximately equal amounts. The third method depended on titration of a sample with bromine (about *M*) dissolved in aqueous acetic acid (50%) containing sodium acetate (5%). The last method was the most rapid but least reliable.

Cyclopentanone was estimated in the material, b. p. above 100°, by measuring the reduction in weight after shaking with excess of saturated sodium bisulfite. The method was accurate to within 5% of the ketone which usually amounted to about half the material. A more accurate method for small quantities depended on precipitation with dinitrophenylhydrazine.

In the experiments with nickel, distillation of the material from the last fraction and insoluble in bisulfite gave a small quantity, b. p. 136–142°, which may have been cyclopentanol. It could not be induced to give a solid dinitrobenzoate and was therefore unidentified.

Experiments with cobalt–copper were carried out over a range of temperatures between 200 and 350°. Cyclopentanone was formed in all the experiments above 250° in amounts similar to those with the cobalt catalyst. Reduction and fission were also observed and the catalyst deteriorated in use.

The nickel–copper catalyst was investigated only at one temperature (275°). Dihydropyran (84 g.) was passed over the catalyst with hydrogen (24 l./hr.) during two hours. The product contained *n*-butane, b. p. 0–2° (6 g.), tetrahydropyran, b. p. 87–89° (44 g.), and cyclopentanone, b. p. 129.5–130.5° (7.5 g.), 2,4-dinitrophenylhydrazone, m. p. 142–143°, m. m. p. with an authentic specimen (m. p. 144–145°) was 142–143°. There was no unsaturated material.

Summary

2,3-Dihydropyran has been shown to undergo three simultaneous reactions when passed with hydrogen over catalysts containing nickel or cobalt at a temperature of 200° or above.

The reactions are (1) reduction to tetrahydropyran, (2) fission to butene, butane and carbon monoxide and (3) rearrangement into cyclopentanone.

The mechanism of the reactions is discussed.

NOTRE DAME, INDIANA RECEIVED AUGUST 18, 1947

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

Reactions of Furan Compounds. X. Catalytic Reduction of Methylfuran to 2-Pentanone

BY CHRISTOPHER L. WILSON

Reference was made some years ago[1] to the formation of small amounts of 2-pentanone (II) and 2-pentanol (III) during the gas phase reduction of methylfuran (I) to tetrahydromethylfuran (IV). Experiment has now shown that either tetrahydromethylfuran or 2-pentanone can be the major product depending on conditions. Results obtained using a nickel catalyst at various temperatures are shown in the diagram. At 100° the chief product (86% yield) was tetrahydromethylfuran but as the temperature was raised the quantity decreased and ketone appeared in increasing amounts attaining a maximum (yield 75%) at about 185°. Along with the ketone a small quantity of its reduction product, 2-pentanol, was also formed. Below 150° conversion of methylfuran was complete but surprisingly enough a proportion escaped reaction above this temperature. This coincided with the formation of quantities of gaseous products, with a slight increase in the amount of tetrahydromethylfuran and with a rapid drop in ketone production. No adequate explanation of these variations has yet been found but the reason is undoubtedly connected with complex surface conditions. Furthermore, nuclear hydrogenation of methylfuran might be reversible.

Other metallic catalysts such as cobalt and mixtures of nickel, cobalt or iron with copper as well as copper chromite also gave some ketone but a

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[1] French Patent 811,695 (1937).