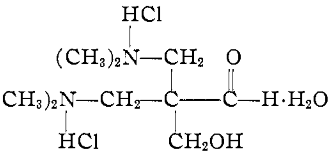
companied the Mannich condensation. Our preliminary work confirmed this conclusion.



$$(CH_3)_2\underset{HCl}{\underset{|}{N}}-CH_2-\underset{CH_2OH}{\underset{|}{\overset{\overset{(CH_3)_2\overset{\overset{HCl}{|}}{N}-CH_2}{|}}{C}}}-\overset{\overset{O}{\|}}{C}-H\cdot H_2O$$

I

We have studied the Mannich condensation of monochloro- and dichloroacetaldehyde in an effort to determine the type of condensation which predominates as the number of available hydrogen atoms on the α-carbon atom of the aldehyde is reduced.

Monochloroacetaldehyde reacts according to the equation

$$ClCH_2CHO + 2CH_2O + (CH_3)_2NH\cdot HCl \longrightarrow (CH_3)_2NCH_2CCl(CH_2OH)CHO\cdot HCl$$

II

The isomeric structure $(CH_3)_2NCH_2CHClCH(OH)CHO\cdot HCl$ was eliminated as a possibility by the failure of the product to undergo oxidation to an α-keto acid.

The dichloroacetaldehyde also reacted with two moles of formaldehyde to produce the α-hydroxyaldehyde $(CH_3)_2NCH_2CCl_2CH(OH)CHO\cdot HCl$ (III), which formed a 2,4-dinitrophenylhydrazone and yielded upon oxidation an α-keto acid. Qualitative evidence of the formation of a 1,2-glycol was observed after reduction of the ketoaldehyde with sodium amalgam.

From the products of the reactions, no generalization can be made as to the type of condensation favored by the number and degree of reactivity of the hydrogen atoms on the α-carbon atom. However, by the use of Hirschfelder models it was found that in those cases in which an aldol condensation had taken place, the introduction of a dimethylaminomethyl group in its place would give rise to steric hindrance.

In the case of dichloroacetaldehyde the one replaceable hydrogen atom is free to undergo either the Mannich or aldol condensation, but yields upwards of 80% of the Mannich base are obtained. Therefore, the Mannich reaction must take precedence over the aldol condensation as long as spacial relationships are favorable.

Experimental

α-Chloro-α-(dimethylaminomethyl)-β-hydroxypropionaldehyde Hydrochloride.—Monochloroacetaldehyde, prepared from its acetal (30.5 g.) by heating with anhydrous oxalic acid, was distilled (b.p. 85–87°) directly into a flask containing 16.8 g. (0.206 mole) of dimethylamine hydrochloride, 6.3 g. (0.21 mole) of paraformaldehyde and 20 ml. of acid. The reactants were heated under reflux for 1 to 1.5 hours. When a pale yellow color developed, the solution was cooled in an ice-bath. Crystals were formed in the cold solution but final crystallization was effected by adding 100 ml. of boiling ethyl acetate. The hygroscopic compound was purified by dissolving in warm methanol and reprecipitating by the addition of acetone. The yield of product melting at 122–124° was 31%. Qualitative tests for carbonyl, primary alcohol and amine were positive.

Anal. Calcd. for $C_6H_{13}NO_2Cl_2$: neut. equiv., 202.06; C, 35.66; H, 6.48; N, 6.96; total Cl, 35.10; ionizable Cl, 17.55. Found: neut. equiv., 202.1; C, 35.48; H, 6.48; N, 7.02; total Cl, 35.19; ionizable Cl, 17.51.

The free base was prepared by the same method as described above. The long colorless crystals of the base were hygroscopic and unstable; decomposition was complete within a few hours. No quantitative data were collected. Qualitative tests for functional groups were positive.

α-Hydroxy-β,β-dichloro-β-(dimethylaminomethyl)-propionaldehyde Hydrochloride.—Seventeen grams (0.15 mole) of dichloroacetaldehyde, 12.7 g. (0.156 mole) of dimethylamine hydrochloride and 9.3 g. (0.31 mole) of paraformaldehyde were dissolved in 25 ml. of glacial acetic acid. The solution was heated under reflux for 1 to 1.5 hours until a pale yellow color developed. Crystals formed when the solution was cooled; final crystallization was effected by the addition of 50 ml. of boiling ethyl acetate. The crude product was recrystallized from boiling acetic acid. Yields of pure product m.p. 178° dec., ranged from 72–80%. Tests for carbonyl, primary alcohol and amine were positive.

Anal. Calcd. for $C_6H_{12}NCl_3O_2$: neut. equiv., 236.5; C, 30.47; H, 5.11; N, 5.92; total Cl, 44.97; ionizable Cl, 14.99. Found: neut. equiv., 236.2; C, 30.40; H, 5.17; N, 5.98; total Cl, 45.11; ionizable Cl, 15.10.

The free base was prepared by neutralizing with 3 *N* sodium hydroxide 3 g. of the hydrochloride dissolved in 5 ml. of water. The neutralized solution was cooled in an ice-bath. Colorless cubic crystals of the base were formed. The compound m.p. 63° was found to be unstable after long standing but the crystals were not hygroscopic. It appears by analysis to be a monohydrate. Tests for the carbonyl group, primary alcohol and amine were positive.

Anal. Calcd. for $C_6H_{13}NCl_2O_3$: C, 33.04; H, 6.07. Found: C, 32.60; H, 5.90.

Oxidation of the Hydrochloride to α-Keto Acid.—One-half gram of the hydrochloride dissolved in 5 ml. of distilled water was treated with an excess of a saturated solution of potassium permanganate. The mixture was stirred and cooled until a reaction was complete. The solution was cleared by the addition of sodium bisulfite. The solution was made acid with hydrochloric acid, and 2,4-dinitrophenylhydrazine reagent added. The crystals of the derivative were removed and recrystallized from 95% alcohol, m.p. 204°.

Anal. Calcd. for $C_{12}H_{14}N_5O_6Cl_3$: C, 33.5; H, 3.28. Found: C, 33.70; H, 3.26.

Reduction of the Hydrochloride to 1,2-Glycol.—To 3 g. of the hydrochloride dissolved in 20 ml. of distilled water, containing 0.5 ml. of concd. hydrochloric acid, was added with vigorous stirring, 15 g. of 2% sodium amalgam. The solution was neutralized with dilute sodium hydroxide and evaporated to dryness under reduced pressure. The residue was extracted with chloroform. Long colorless needles were formed as the chloroform evaporated. The reduced product, m.p. 120° with sublimation, was stable at room temperature and non-hygroscopic. Tests made on the compound for carbonyl were negative, and the Denige test[4] proved the absence of formaldehyde. Crystals of the compound were placed in a dilute solution of periodic acid and allowed to stand for 12 hours. A positive test for formaldehyde was then obtained by the Denige method.

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[4] J. Walker, "Formaldehyde," Reinhold Publishing Corp., New York, N. Y., 1944, p. 244.

DEPARTMENT OF CHEMISTRY
OREGON STATE COLLEGE
CORVALLIS, OREGON

Calculated Approximate Values of the Free Energy Function for the OD Molecule

BY G. MCDONALD

RECEIVED JUNE 2, 1952

The values for the free energy function of the OD molecule as a harmonic oscillator have been calculated for the temperature range from 1000 to 3000°K. The values do not include the contribution due to nuclear spin. The values for the function are listed in Table I.

TABLE I

Temperature, °K.	1000	1200	1400	1600	1800	
$\frac{F^0 - H^0_0}{T}$, cal./deg. mole	−46.87	−48.15	−49.24	−50.20	−51.06	
Temperature, °K.	2000	2200	2400	2600	2800	3000
$\frac{F^0 - H^0_0}{T}$, cal./deg. mole	−51.83	−52.53	−53.18	−53.79	−54.35	−54.88

The values used in these calculations are: the moment of inertia, $I = 2.85 \times 10^{-40}$; and the characteristic frequency, $\omega = 3620$ calculated from the relationship

$$\rho = \frac{\omega_{OD}}{\omega_{OH}} \text{ and } \rho = \left[\frac{17.008}{18.014}\right]^{1/2}$$

A similar calculation for the OH molecule over the same temperature interval has an average deviation of 0.03 cal./deg. mole from the values given by the NBS.[1]

[1] Selected Values of Properties of Hydrocarbons, Circular C461 NBS Nov. 1947.

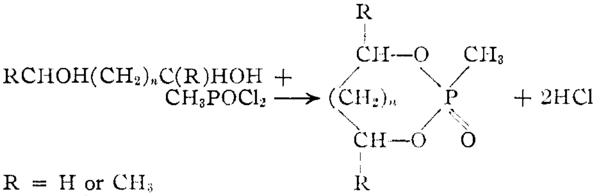
NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS
LEWIS FLIGHT PROPULSION LABORATORY
CLEVELAND AIRPORT
CLEVELAND, OHIO

Organic Phosphorus Compounds. I. Reactions of Methanephosphonyl Dichloride with Glycols[1]

BY A. F. MCKAY, R. O. BRAUN AND G. R. VAVASOUR

RECEIVED JUNE 25, 1952

Methanephosphonyl dichloride combines with glycols to give phosphorus-containing heterocyclics. The general reaction is



R = H or CH_3
n = 0–2

I

If no precautions are taken to remove the hydrogen chloride formed in this reaction, a mixture of methanephosphonic acid and methanephosphonic anhydride forms with a lowering of the yield of the cyclic product. When pyridine was used to remove the hydrogen chloride as formed, no methanephosphonic acid or its anhydride was present in the reaction mixture and the yield of cyclic product (I) was increased by 15%. This reaction does not appear to be general for all glycols because ethylene glycol and *meso*-2,3-butanediol have been observed to give linear products. These latter observations will be reported at a later date.

An attempt was made to hydrolyze the cyclic compound 2,4,5-trimethyl-2-oxo-1,3-dioxa-2-phosphacyclopentane into 2,3-butanediol and methanephosphonic acid in order to determine whether D-(−)-2,3-butanediol had retained its configuration in the cyclic product (I, R = CH_3, n = O). However, the conditions required for hydrolysis were too drastic to permit definite conclusions about the configuration of the cyclic product. The formal derivative of the resulting 2,3-butanediol possessed a specific rotation of −3.64° as compared with a value of −25.01°[2] given for the formal derivative of pure D-(−)-2,3-butanediol.

Experimental[3,4]

Methanephosphonyl Dichloride.—The methanephosphonyl dichloride used in this work had a melting point of 32.6°. Hofmann[5] reports a melting point of 32° for methanephosphonyl dichloride obtained by chlorination of methylphosphonic acid with two mole equivalents of phosphorus pentachloride.

D-(−)-2,3-Butanediol.—The D-(−)-2,3-butanediol[6] used in this work had a specific rotation of −13.0° at a temperature of 25°.

2,4,5-Trimethyl-2-oxo-1,3-dioxa-2-phosphacyclopentane. Method A.—D-(−)-2,3-Butanediol (90 g., 1.0 mole) was added dropwise to 121 g. (0.91 mole) of freshly distilled methanephosphonyl dichloride in absolute ether (200 cc.). The rate of addition of the butanediol was regulated to maintain the ether at a gentle reflux. After the addition of the glycol, which required 45 minutes, the stirred solution was refluxed for an additional hour. Then the ether was removed by distillation and the residue degassed at 100° and 17 mm. pressure. The residue on distillation *in vacuo* gave a water-white oil (b.p. 99–104° (1 mm.)) yield 85 g. (62.3%). This material was fractionated using a 6-inch Vigreux column equipped with a partial take-off head. The reflux ratio was held at 5:1. The main fraction (b.p. 86–88° (0.5 mm.)) solidified on standing, yield 82 g. (60.0%). The pure product had a setting point of 40.8° and it melted at 42–44° (capillary method). It was difficult to obtain a melting point by the capillary method because of the hygroscopic nature of the product.

Anal. Calcd. for $C_5H_{11}O_3P$: C, 40.00; H, 7.39; mol. wt., 150.12. Found: C, 40.04; H, 7.57; mol, wt., 152.4 and 159.0; $[\alpha]^{25}\text{D}$ −1.62 (11.226 g. in 25 cc. of $CHCl_3$).

The brown crystalline residue (21.6 g., 27.6%) from the first distillation melted at 141–141.5°. It gave analytical values in good agreement with methanephosphonic anhydride.

Anal. Calcd. for $C_2H_8O_5P_2$: C, 13.79; H, 4.63; P, 35.62. Found: C, 14.00; H, 4.73; P, 35.37.

A sample (5 g., 0.028 mole) of methanephosphonic anhydride was hydrolyzed by warming with 0.6 cc. of water until the mixture was homogeneous. A quantitative yield of methanephosphonic acid (m.p. 105°, soft 102°) was obtained. After crystallization from methyl ethyl ketone, it melted at 108–109°. It did not depress the melting point of an authentic sample of methanephosphonic acid (m.p. 108–109°) prepared by the hydrolysis of methanephosphonyl dichloride. The previously reported[7] melting point of methanephosphonic acid is 105°.

Method B.—In this procedure 42.6 g. (0.47 mole) of D-(−)-2,3-butanediol was added dropwise to a refluxing solution of 60 g. (0.452 mole) of methanephosphonyl dichloride in 150 cc. of methylene chloride. The products were separated and identified as in Method A. The yield of 2,4,5-trimethyl-2-oxo-1,3-dioxa-2-phosphacyclopentane was 47.8 g. (70.5%) while the yield of methanephosphonic anhydride–methanephosphonic acid mixture (m.p. 138–141°) was 10.5 g. These products were identified by comparison and mixed melting point determinations with the products obtained above in method A.

Method C.—D-(−)-2,3-Butanediol (90.0 g., 1.0 mole) was added dropwise over a period of 70 minutes to 133 g. (1 mole) of methanephosphonyl dichloride and 158.2 g. (2 moles) of pyridine in methylene chloride (400 cc.). This rate of addition of butanediol kept the mechanically stirred reaction mixture at a gentle reflux. The stirring was continued for three hours after which the reaction mixture was

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[1] Issued as D.R.C.L. Report No. 90.

[2] H. K. Garner and H. J. Lucas, THIS JOURNAL, **72**, 5497 (1950).

[3] All melting points and boiling points are uncorrected.

[4] Microanalysis by C. W. Beazley, Skokie, Illinois.

[5] A. W. Hofmann, *Ber.*, **6**, 303 (1873).

[6] D-(−)-2,3-Butanediol was obtained through the courtesy of Mr. J. Wheat, Department of Applied Biology, National Research Council, Ottawa, Canada.

[7] A. W. Hofmann, *Ber.*, **5**, 104 (1872).