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Abstract

Full Text

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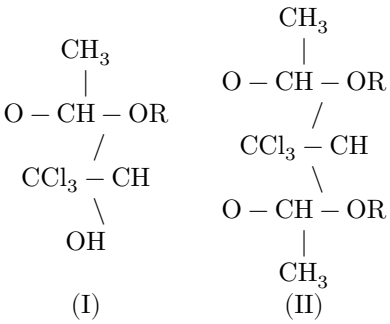
STUDY OF THE REACTIVITY OF HYDRATED FORMS OF ALDEHYDES

THE INTERACTION OF CHLORAL HYDRATE WITH CERTAIN VINYL ETHERS

The addition reaction of chloral hydrate to simple vinyl ethers is of great theoretical and practical importance, since it simultaneously addresses questions connected with the reactivity of hydrated forms of aldehydes and with the stability or instability of the corresponding derivatives. On the basis of a number of works ([1–6]), it has been established that compounds containing hydroxyl groups readily enter into reactions of nucleophilic addition at the double bond of simple vinyl ethers.

We undertook the present study with the aim of synthesizing new compounds on the basis of chloral hydrate and simple vinyl ethers. The reaction of chloral hydrate with vinyl ethers can lead to the formation of hemiacetals (I) and acetals (II):



(I)

(II)

Chloral hydrate readily reacts with vinyl ethers through either one or two hydroxyl groups. The reaction may proceed either with a catalyst (conc. HCl), with a yield of 25% (of theory), or without a catalyst but with heating to 60–65° for 1–1.5 hours, yield 50–60% (of theory). In addition, acetals may be obtained in a yield of 35% (of theory) when the reaction mixture is kept at room temperature for 4 days.

The addition reaction of chloral hydrate to vinyl ethers is carried out in two stages:

a) with an equimolecular ratio of the reactants, the principal reaction product is chloralalkoxyethylidene—a hemiacetal containing in its molecule a stable hemiacetal grouping

$$CCl_3 - CH(OH)_2 + CH_2 = CH - OR \rightarrow CCl_3 - CH(OH) - O - CH(CH_3) - OR$$

b) with a twofold (or greater) excess of vinyl ether, chloralbis(alkoxyethylidene) acetal is obtained

$$CCl_3 - CH(OH)_2 + 2\,CH_2 = CH - OR \rightarrow CCl_3 - CH(O - CH(CH_3) - OR)_2$$

The latter can also be obtained from chloral alkoxyethylidene hemiacetal by addition of one more molecule of vinyl ether

$$CCl_3 - CH(OH) - O - CH(CH_3) - OR + CH_2 = CH - OR \rightarrow CCl_3 - CH(O - CH(CH_3) - OR) - O - CH(C$$

An exception is vinyl phenyl ether, which, at any ratio of the reagents, gives only one derivative—chloral phenoxyethylidene hemiacetal

$$CCl_3 - CH(OH)_2 + CH_2 = CH - OC_6H_5 \rightarrow CCl_3 - CH(OH) - O - CH(CH_3) - OC_6H_5$$

This latter circumstance can apparently be explained by a strong decrease in the reactivity of the free hydroxyl as a result of the influence of the phenyl radical

$$CCl_3 - CH(O - CH(CH_3) - O - C_6H_5) - OH$$

Confirmation of the considerations expressed is provided by the instability of chloral phenoxyethylidene hemiacetal, which very readily decomposes into phenol, acetaldehyde, and chloral.

In our opinion, the decomposition of the hemiacetal proceeds in two stages: in the first stage the hemiacetal eliminates phenol with formation of an unstable tetrachlorinated cyclic acetal; in the second stage its further decomposition occurs. If an excess of vinyl phenyl ether is taken in the reaction, then the phenol formed as a result of decomposition of the hemiacetal reacts with vinyl phenyl ether to form diphenyl acetal.

$$CCl_3 - CH(OH) - O - CH(CH_3) - OC_6H_5 \rightarrow C_6H_5OH + CCl_3 - CH - O - CH(CH_3) - O$$

$$C_6H_5OH + CH_2 = CH - OC_6H_5 \rightarrow CH_3 - CH(OC_6H_5)_2$$

The chloral alkoxyethylidene hemiacetals obtained are stable compounds. They eliminate alcohol only on heating with alcoholic alkali

$$CCl_3 - CH(OH) - O - CH(CH_3) - OR \xrightarrow[C_2H_5OH]{KOH,\ t^\circ} ROH + CCl_3 - CH - O - CH(CH_3) - O$$

where R = C_3H_7; C_4H_9.

Experimental Part

The starting substances for the present investigation were: chloral hydrate (m.p. 53°) and vinyl ethers:

vinyl ethyl ether, b.p. 35-36°, n_D^{20} –1.3782;

vinyl *n*-propyl ether, b.p. 65°, n_D^{20} –1.3922;

vinyl *n*-butyl ether, b.p. 92-93°, n_D^{20} –1.4026;

vinyl phenyl ether, b.p. 155-156°, n_D^{20} –1.5224.

1. **Synthesis of chloralpropoxyethylidene hemiacetal.**
   Into a three-necked flask equipped with a stirrer, thermometer, reflux condenser, and dropping funnel, 20.6 g (0.12 mole) of chloral hydrate was charged. At room temperature, from the dropping funnel, with continuous stirring over the course of 1 hour, vinyl *n*-propyl ether was added in an amount of 10.7 g (0.12 mole). The temperature of the reaction mixture rose to 50°C.

After distillation under vacuum, a liquid product was isolated (18.6 g; 59.9% of theoretical) with b.p. 36°/1 mm, n_D^{20} –1.4660, d_4^{20} 1.3035. For $C_7H_{13}Cl_3O_3$, MR_D found 53.43, calculated 53.76.

2. **Synthesis of chloralbutoxyethylidene hemiacetal.**
   The synthesis was carried out analogously to that described above. 20.6 g (0.12 mole) of chloral hydrate and 12.5 g (0.12 mole) of vinyl *n*-butyl ether were taken. As a result of vacuum distillation, a liquid product was isolated (19.2 g; 58% of theoretical) with b.p. 41°/8 mm, n_D^{20} 1.4612, d_4^{20} 1.2296. Found MR_D 59.28, $C_8H_{15}Cl_3O_3$. Calculated 58.41. After two days the liquid product crystallized. The crystals were needle-like, m.p. 50°, readily soluble in alcohol, ether, benzene, and carbon tetrachloride, and poorly soluble in cold water.

3. **Synthesis of chloralphenoxyethylidene hemiacetal.**
To 20.6 g (0.12 mole) of chloral hydrate, 15 g (0.12 mole) of vinyl phenyl ether was added dropwise with continuous stirring. The mixture was then heated for 5 h at 55-56° and, after cooling, distilled under vacuum. A liquid product was isolated (4.6 g; 13% of theoretical) with b.p. 139°/9 mm –141°/9 mm; n_D^{20} 1.5258; d_4^{20} 1.3737. Found MR_D 63.79, $C_{10}H_{11}Cl_3O_3$, calculated 64.16.

Found %: C 42.09; H 4.17; Cl 36.92
Calculated %: C 42.02; H 3.88; Cl 37.24

4. **Synthesis of chloral-bis-(ethoxyethylidene)-acetal.**
To 20.6 g (0.12 mole) of chloral hydrate, at room temperature with stirring, 18.2 g (0.25 mole) of vinyl ethyl ether was added. The temperature of the reaction mixture rose to 45°. The mixture was heated for 1.5 h to 60-65°. After cooling it was distilled under vacuum. A liquid product was isolated (17.1 g; 45% of theoretical) with b.p. 30°/10 mm –32°/10 mm, n_D^{20} 1.4368, d_4^{20} 1.1718. Found MR_D 69.21, $C_{10}H_{19}Cl_3O_4$, calculated 69.40.

5. **Synthesis of chloral-bis-(propoxyethylidene)-acetal.**
Under the conditions of the preceding experiment, to 20.6 g (0.12 mole) of chloral hydrate was added 21.4 g (0.25 mole) of vinyl *n*-propyl ether. A liquid product was isolated (17.7 g; 42.1% of theoretical) with b.p. 34°/8 mm–35°/8 mm. n_D^{20} 1.4385, d_4^{20} 1.1142. Found MR_D 79.43, $C_{12}H_{23}Cl_3O_4$, calculated 78.69.

6. **Synthesis of chloral-bis-(butoxyethylidene)-acetal.**
Analogously to the two preceding experiments, from 20.6 g (0.12 mole) of chloral hydrate and 25 g (0.25 mole) of vinyl *n*-butyl ether, a liquid product was obtained.

(25.5 g; 56% of theoretical) n_D^{20} 1.4398, d_4^{20} 1.0885. Found MR_D 88.26; for $C_{14}H_{27}Cl_3O_4$, calculated 88.55.

Found, %: C 46.36; H 8.09; Cl 28.62
Calculated, %: C 46.12; H 7.46; Cl 29.18

A synthesis has been carried out of a new class of compounds containing mixed acetals of chloral and acetaldehyde. It has been established that chloral hydrate, which contains two hydroxyl groups in its composition, readily enters into nucleophilic addition reactions at the double bond of simple vinyl ethers.

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Note: Figure translations are in progress. See original paper for figures.