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## Abstract

## Full Text

## Chemistry

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# Synthesis of Acetyl-2-chlorocycloalkenes

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Recently, in our laboratory, methods have been developed for the synthesis of $\beta$-chlorovinyl ketones of the aliphatic and aromatic series [1,2], and their transformations, widely used for synthetic purposes, have also been studied [3]. In order to broaden our knowledge of this important class of compounds, it seemed of interest to obtain $\beta$-chlorovinyl ketones, or closely related compounds, of the alicyclic series. In the patent literature [4] there is an indication that, on interaction of cyclohexanone with chloroacetyl chloride, acetyl-2-chlorocyclohexene-1 is formed. In another, recently published, brief note, Jacques [5] states, without any experimental details, that the only product of this reaction is acetyl-2-chlorocyclohexene-2; the author further asserts that the latter, on boiling with dimethylaniline, isomerizes into acetyl-2-chlorocyclohexene-1.

We studied this reaction in detail and found that its product is in fact a mixture of substances (yield 82%), consisting mainly of acetyl-2-chlorocyclohexene-2. This conclusion was drawn from the fact that the reaction product, on treatment with semicarbazide, gives a mixture of two semicarbazones, from which, as the main product, there is readily isolated a semicarbazone with m.p. 158°, readily soluble in benzene and completely identical in properties with the semicarbazone of acetyl-2-chlorocyclohexene-2 described by Mousseron [6]. The second semicarbazone is formed in small amounts and is insoluble in benzene; it cannot be isolated in pure form and melts indistinctly with decomposition, which makes it possible to regard it as the semicarbazone of acetyl-2-chlorocyclohexene-1, since it is known that semicarbazones of $\beta$-chlorovinyl ketones change their melting points as a result of cyclization into pyrazole derivatives [1].

In accordance with Jacques' indication [5], we attempted to carry out the rearrangement of acetyl-2-chlorocyclohexene-2 into the corresponding $\alpha,\beta$-unsaturated isomer by boiling with dimethylaniline; however, we were convinced that such an isomerization does not occur.

We were able to draw some conclusions also about the mechanism of the reaction of cyclohexanone with chloroacetyl chloride. Taking into account the fact that good yields are obtained only when the molar ratio of cyclohexanone to chloroacetyl chloride is 1:2 or higher, we assumed that under the reaction conditions the enol acetate of cyclohexanone is first formed (the formation of which under these conditions is quite probable [7,8]), which then adds a molecule of chloroacetyl chloride by the Kondakov–Krapivin reaction, common for unsaturated compounds.

This assumption was confirmed by the fact that, on interaction of equimolecular amounts of the enol acetate and chloroacetyl chloride under analogous conditions, acetyl-2-chlorocyclohexene-2 was likewise obtained in high yield. The supposition that the latter is formed simply by rearrangement of the enol acetate with subsequent enolization

and replacement of hydroxyl by chlorine under the action of aluminum chloride must be rejected, since, when the enol acetate of cyclohexanone was treated with aluminum chloride under the conditions used by us, acetyl-2-chlorocyclohexene-2 was not isolated. Thus, the reaction of cyclohexanone with acetyl chloride may be represented as follows:

$$\text{cyclohexanone} \xrightarrow[\text{AlCl}_3]{\text{CH}_3\text{COCl}} \text{enol acetate} \xrightarrow[\text{AlCl}_3]{\text{CH}_3\text{COCl}} \left[\begin{array}{c}\text{chloroacetate intermediate}\\ \text{bearing COCH}_3\end{array}\right] \longrightarrow \text{acetyl-2-chlorocycloh}$$

We succeeded in extending the reaction studied to the cyclopentanone series as well. The product of the reaction of cyclopentanone with acetyl chloride under analogous conditions is acetyl-2-chlorocyclopentene-1—the first representative of cyclic $\beta$-chlorovinyl ketones. This is indicated by the high lability of the substance obtained, exaltation of the molecular refraction, and formation of a salt with triethylamine and a pyridinium salt—features characteristic of $\beta$-chlorovinyl ketones ([1,9])*.

$$\text{cyclopentanone} \xrightarrow[\text{AlCl}_3]{\text{CH}_3\text{COCl}} \text{acetyl-2-chlorocyclopentene-1}$$

Thus, the reaction of acetyl chloride with cyclohexanone gives a $\beta$,$\gamma$-unsaturated chloroketone, whereas with cyclopentanone it gives the $\alpha$,$\beta$-unsaturated isomer; this difference is probably directly connected with the conformational features of the cyclohexanone and cyclopentanone rings.

For a final conclusion, the ultraviolet absorption spectra of the 2,4-dinitrophenylhydrazones of the acetyl-2-chlorocyclohexene-2 and acetyl-2-chlorocyclopentene-1 obtained were compared**. As is known ([10]), the UV spectra (in the region 300–400 m$\mu$) of 2,4-dinitrophenylhydrazones of $\alpha$,$\beta$-unsaturated ketones in isooctane solution are characterized by a shift of the maximum by approximately 17 m$\mu$ in comparison with the maximum in the spectrum of the derivative of a $\beta$,$\gamma$-unsaturated ketone. The 2,4-dinitrophenylhydrazone of acetyl-2-chlorocyclohexene-2 has $\lambda_{\text{max}}$344 m$\mu$, while the 2,4-dinitrophenylhydrazone of acetyl-2-chlorocyclopentene-1 has 362 m$\mu$. Analogous shifts are also observed in the spectra of alcoholic solutions (365 and 394 m$\mu$, respectively).

We are currently investigating the indicated reaction as applied to other ketones.

## Experimental Part

1. **Interaction of cyclohexanone with acetyl chloride.** In a three-necked flask equipped with a reflux condenser and a dropping funnel are placed 151 g (1.16 mole) of $AlCl_3$ and 75 $cm^3$ of dry dichloroethane. With vigorous stirring and cooling with water, a mixture of 36.5 g (0.39 mole) of cyclohexanone and 86 g (1.16 mole) of acetyl chloride is added; the mixture is stirred for a further 18 h and poured into a mixture of ice with concentrated hydrochloric acid. The oily layer is separated, and the aqueous layer is extracted with dichloroethane. The combined extracts are washed with water and dried over $CaCl_2$. The solvent is distilled off, and the residue is distilled under vacuum; the fraction 105–120°/20 mm is collected. After repeated distillation, 49.5 g (82%, calculated on cyclohexanone) of a substance with b.p. 124–129°/30 mm is obtained. After a third distillation, a fraction with b.p. 108–109°/15 mm was isolated; $n_D^{20}$ 1.4985; $d_4^{20}$ 1.1232; $MR_D$ 41.38, $C_8H_{11}OClF$. $MR_D$ calc. 41.35.

Found, %: C 60.33; 60.33; H 7.09; 7.09; Cl 22.29; 22.46
$C_8H_{11}ClO$. Calculated, %: C 60.56; H 7.00; Cl 22.35

The semicarbazone was obtained from the fraction 124–129°/30 mm, m.p. 136–138°. Of 22 g of semicarbazone, the greater part (20 g) dissolved in benzene and, after recrystallization from it, had m.p. 158°.

Found, %: N 19.73; 19.87
$C_9H_{14}ON_3Cl$. Calculated, %: N 19.48

Literature data (6): m.p. 158–159°.
The residue insoluble in benzene (2 g) melts indistinctly, with decomposition.

The 2,4-dinitrophenylhydrazone was obtained according to (10), m.p. 128–129° (from alcohol). Literature data (5): m.p. 128–129°.

2. Similarly, from 196 g (2 moles) of cyclohexanone, 314 g (4 moles) of acetyl chloride, and 534 g (4 moles) of aluminum chloride in 475 $cm^3$ of dichloroethane, 201 g (64%) of 2-chloro-1-acetylcyclohexene-2 (with an admixture of 2-chloro-1-acetylcyclohexane-1) was obtained, b.p. 110–120°/20

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* Mousseron (6) obtained a substance to which he assigns the structure acetyl-2-chlorocyclopentene-1; however, the article gives no analytical data for this substance, the nitrogen analysis of the semicarbazone differs by 5%, and the molecular refraction differs by several units; in connection with this one must think that the author did not have before him a pure compound of the indicated structure.

** The UV spectra were recorded in the laboratory directed by L. A. Kazitsyna, to whom the authors express their deep gratitude.

mm, $n_D^{20}$ 1.4961.

3. Similarly, from 49 g (0.5 mole) of cyclohexanone, 39 g (0.5 mole) of acetyl chloride, and 67 g (0.5 mole) of aluminum chloride, the following were obtained on distillation: 22.2 g of cyclohexanone, b.p. 58-59°/24 mm, $n_D^{20}$ 1.4515; 8.4 g of a fraction, b.p. 150-151°/21 mm, $n_D^{20}$ 1.5079, $d_4^{20}$ 1.0072: its constants are close to the constants of cyclohexylidenecyclohexanone (11): b.p. 148-150°/20 mm, $n_D^{20}$ 1.5062, $d_4^{20}$ 1.004.

4. **Attempted isomerization of acetylchlorocyclohexane-2 to acetyl-2-chlorocyclohexene-1.** 30 g of the substance from experiment No. 1, consisting mainly of acetylchlorocyclohexene-2, and 50 g of dimethylaniline are boiled for 24 hours with a reflux condenser. The reaction mixture is washed with dilute hydrochloric acid and with water. It is dried over $CaCl_2$. After distillation, 16.5 g of product with b.p. 93-100°/10 mm, $n_D^{20}$ 1.4990, is obtained; semicarbazone, m.p. 157.5-158°.

5. **Reaction of the enol acetate of cyclohexanone with acetyl chloride.** 30 g (0.215 mole) of the enol acetate of cyclohexanone in a mixture with 30.5 cm$^3$ (33.5 g, 0.43 mole) of acetyl chloride is added to a suspension of 57 g (0.43 mole) of aluminum chloride in 100 cm$^3$ of dichloroethane. After 5-hour stirring, the mixture is worked up as in experiment No. 1. 14.6 g of acetyl-2-chlorocyclohexene-1 is obtained. B.p. 115-125°/25 mm, $n_D^{20}$ 1.5000; semicarbazone, m.p. 158.5-159°, gives no depression with the semicarbazone from experiment No. 1.

6. **Reaction of cyclopentanone with acetyl chloride.**

a) **In dichloroethane solution.** To 134 g (0.5 mole) of $AlCl_3$ in 250 cm$^3$ of dichloroethane, under cooling with ice, (78.5 g) (1 mole) of acetyl chloride is added, and then 42 g (0.5 mole) of cyclopentanone. After 2-hour stirring, the mixture is worked up in the usual manner.

On distillation there were obtained: 21.7 g of cyclopentanone, b.p. 38-40°/25 mm; 10.6 g (15%, calculated on the cyclopentanone taken, 31%, calculated on that which entered into the reaction) of acetyl-2-chlorocyclopentene-1. B.p. 91-92°/22 mm, $n_D^{20}$ 1.5045, $d_4^{20}$ 1.1429, $MR_D$ 37.45, $C_7H_9ClOF$. $MR_D$ calculated 35.74.

Found, %: C 58.18; 58.35; H 6.50; 6.35
$C_7H_9ClO$. Calculated, %: C 58.20; H 6.28

The semicarbazone decomposes without melting. 2,4-Dinitrophenylhydrazone, m.p. 174-175° (from glacial $CH_3COOH$).

b) **In a carbon disulfide solution.** From 21 g of cyclopentanone, 35.5 cm$^3$ of acetyl chloride, and 67 g of $AlCl_3$ in 100 cm$^3$ of carbon disulfide, 7.9 g (22% of theoretical) of acetyl-2-chlorocyclopentene-1 was obtained analogously; b.p. 100-101°/30 mm, $n_D^{20}$ 1.5061.

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named after M. V. Lomonosov

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