Some Reactions of 1,4-Dichlorobutanone-2

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Abstract

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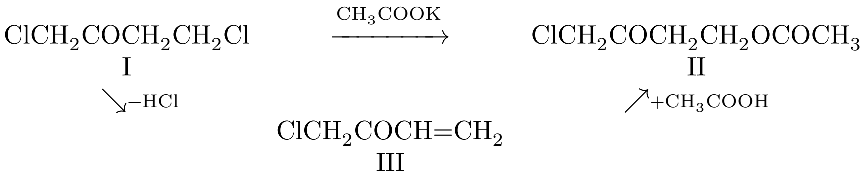
By the action of potassium acetate in glacial acetic acid on 1,4-dichlorobutanone-2 at room temperature, we obtained, in 72% yield, the product of replacement of one chlorine atom in the molecule of 1,4-dichlorobutanone-2 by an acetoxy group. On heating the substance obtained in vacuo with potassium bisulfate, chloromethyl vinyl ketone was obtained. It follows from this that the substance obtained by us through the action of potassium acetate on 1,4-dichlorobutanone-2 is 1-chloro-4-acetoxybutanone-2. It was of interest to us to determine whether the reaction forming 1-chloro-4-acetoxybutanone-2 (II) from 1,4-dichlorobutanone-2 (I) proceeds by double exchange or through the intermediate formation of chloromethyl vinyl ketone (III) with subsequent addition of acetic acid to III. For this purpose it was necessary to investigate whether potassium acetate eliminates hydrogen chloride from 1,4-dichlorobutanone-2 and whether acetic acid adds to chloromethyl vinyl ketone.



$$\begin{tikzcd} \underset{\mathrm{I}}{ClCH_2COCH_2CH_2Cl} \arrow[rr, "CH_3COOK"] \arrow[dr, "-HCl"] & & \underset{\mathrm{II}}{ClCH_2COCH_2CH_2OCOCH_3} \\ & \underset{\mathrm{III}}{ClCH_2COCH{=}CH_2} \arrow[ur, "+CH_3COOH"] & \end{tikzcd}$$

To determine whether potassium acetate eliminates hydrogen chloride from 1,4-dichlorobutanone-2, cyclopentadiene and 1,4-dichlorobutanone-2 were added at room temperature to a solution of potassium acetate in ethanol. From the reaction mixture there was isolated, in 81% yield, the product of addition of chloromethyl vinyl ketone to cyclopentadiene. Thus, it was shown that potassium acetate eliminates hydrogen chloride from 1,4-dichlorobutanone-2.

It was then necessary to establish whether acetic acid adds to chloromethyl vinyl ketone at room temperature. An attempt to add acetic acid to chloromethyl vinyl ketone in the absence of a catalyst was unsuccessful. However, when the reaction was carried out in the presence of potassium acetate, 1-chloro-4-acetoxybutanone-2 was obtained (in 67% yield). Thus, it was shown that the addition of acetic acid is catalyzed by potassium acetate.*

It follows from the results set forth that the reaction of 1,4-dichlorobutanone-2 with potassium acetate in acetic acid, leading to the formation of 1-chloro-4-acetoxybutanone-2, proceeds through the intermediate formation of chloromethyl vinyl ketone.

We further found that, on heating a mixture of 1-chloro-4-acetoxybutanone-2 with 1,1′-dicyclohexenyl in the presence of potassium acetate, a product is formed from the addition of chloromethyl vinyl ketone to 1,1′-dicyclohexe-

* We have found that formic acid adds to chloromethyl vinyl ketone on heating.

Thus it has been shown that, upon heating in the presence of potassium acetate, 1-chloro-4-acetoxybutanone-2 is capable of eliminating acetic acid.

By the action of potassium acetate in glacial acetic acid on chloromethyl vinyl ketone upon heating, we obtained acetoxymethyl vinyl ketone. Heating the latter with 1,1′-dicyclohexenyl gave 1-acetoxyacetyl-2,3,4,5-dicyclohexanocyclohexene-3.

Experimental Part

Interaction of 1,4-dichlorobutanone-2 with potassium acetate. To a solution of 19.3 g (0.2 mole) of anhydrous potassium acetate in 75 ml of glacial acetic acid, 28.2 g (0.2 mole) of 1,4-dichlorobutanone-2 was added. After one day, potassium chloride was filtered off, most of the acetic acid was distilled off in vacuo, the residue was poured into water, the mixture was neutralized with sodium bicarbonate and extracted with ether. Obtained: 23.9 g (72%) of 1-chloro-4-acetoxybutanone-2 with b.p. 93-95° at 2 mm, n_D^{20} 1.4565; d_4^{20} 1.2236; MR_D 36.60, calculated for $C_6H_9O_3Cl$ 36.44.

Found, %: C 44.16; 44.00; H 6.01; 5.81; Cl 21.48
$C_6H_9O_3Cl$. Calculated, %: C 43.68; H 5.64; Cl 21.54

Elimination of acetic acid from 1-chloro-4-acetoxybutanone-2. A mixture of 12.0 g (0.073 mole) of 1-chloro-4-acetoxybutanone-2 and 1.5 g of finely powdered potassium bisulfate was heated in vacuo. At a bath temperature of 145-150° and 30-35 mm, a distillate was collected, which was poured into water; the mixture was neutralized with sodium bicarbonate and extracted with ether. Obtained: 2.3 g (30%) of chloromethyl vinyl ketone with b.p. 57-60° at 32 mm, n_D^{20} 1.4690, d_4^{20} 1.1478; MR_D 25.36, calculated for C_4H_5OCl 25.08. Literature data (^{1}): b.p. 56.5-57° at 31 mm, n_D^{20} 1.4690, d_4^{20} 1.1451.

A mixture of 2.2 g (0.02 mole) of the chloromethyl vinyl ketone obtained in this experiment and 3.5 g (0.02 mole) of 1,1′-dicyclohexenyl was heated in the presence of hydroquinone on a boiling water bath for 3 hours. Obtained: 3.0 g (53%) of adduct with m.p. 101.5-103.5°. After recrystallization from ethanol, m.p. 104-104.5°. A mixed sample with an authentic specimen of 1-chloroacetyl-2,3,4,5-dicyclohexanocyclohexene-3 (m.p. 104.5-105°) melted without depression.

Literature data (^{1}): m.p. 104.5-105°.

Addition of acetic acid to chloromethyl vinyl ketone. To a solution of 5 g of anhydrous potassium acetate in 45 ml of glacial acetic acid, 26.5 g (0.255 mole) of chloromethyl vinyl ketone was added. The mixture was left at room temperature for $3^1/_2$ days, then poured into water, neutralized with sodium bicarbonate, and extracted with ether. Obtained: 28.0 g (67%) of 1-chloro-4-acetoxybutanone-2 with b.p. 97-100° at 4 mm. After repeated distillation, b.p. 92-93° at 1.5 mm, n_D^{20} 1.4560, d_4^{20} 1.2270; MR_D. 36.45, calculated for $C_6H_9O_3Cl$ 36.44.

Addition of formic acid to chloromethyl vinyl ketone. A mixture of 15.6 g (0.149 mole) of chloromethyl vinyl ketone and 50 ml of anhydrous formic acid was heated on a boiling water bath for $1^1/_2$ hours. The mixture was cooled, poured onto crushed ice, neutralized with sodium bicarbonate, and extracted with ether. Obtained: 11.8 g (53%) of 1-chloro-4-formoxybutanone-2 with b.p. 86-90° at 2 mm. After repeated distillation, b.p. 99-100° at 5 mm, n_D^{20} 1.4640, d_4^{20} 1.2955; MR_D 32.06, calculated for $C_5H_7O_3Cl$ 31.82.

Found, %: C 39.76; 39.88; H 5.03; 5.13
$C_5H_7O_3Cl$. Calculated, %: C 39.88; H 4.69

Interaction of chloromethyl vinyl ketone with potassium acetate. A mixture of 13.3 g (0.136 mole) of anhydrous potassium acetate, 37 ml glacial acetic acid and 14.0 g (0.136 mole) of chloromethyl vinyl ketone was heated on a boiling water bath for 6 hours. The mixture was then cooled, the potassium chloride was filtered off, and the filtrate was fractionated in vacuo. This gave 5.65 g (33%) of acetoxymethyl vinyl ketone with b.p. 73-74° at 8 mm, n_D^{20} 1.4452, d_4^{20} 1.0882; MR_D 31.34, calculated for $C_6H_8O_3 = 31.11$. Literature data (^{2}): b.p. 70-71° at 14 mm, n_D^{25} 1.4355, d_4^{25} 1.0788; (^{3}): b.p. 83° at 14 mm, n_D^{15} 1.4455; (^{4}): b.p. 81° at 12 mm.

A mixture of 1.8 g (0.014 mole) of acetoxymethyl vinyl ketone and 2.5 g (0.015 mole) of 1,1′-dicyclohexenyl was heated in the presence of hydroquinone on a boiling water bath for 3 hours. On cooling, the mixture solidified. The crystalline mass was triturated with petroleum ether; the crystals were filtered off and washed with cold ethanol. This gave 3.2 g (73%) of 1-acetoxyacetyl-2,3,4,5-dicyclohexanocyclohexene-3, m.p. 127-128.5°. After two recrystallizations from aqueous acetone, m.p. 134.5-135°. The adduct crystallizes in the form of very thin, threadlike crystals.

Found, %: C 74.82; 74.67; H 9.18; 9.25
$C_{18}H_{26}O_3$. Calculated, %: C 74.45; H 9.02

Preparation of 1-chloroacetyl-2,5-endomethylenecyclohexene-3 from 1,4-dichlorobutanone-2, potassium acetate, and cyclopentadiene. Into a flask equipped with a reflux condenser were placed a solution of 9.8 g (0.1 mole) of anhydrous potassium acetate in 40 ml of 95% ethanol and 9.9 g (0.15 mole) of cyclopentadiene. Then 14.1 g (0.1 mole) of 1,4-dichlorobutanone-2 was added.

Potassium chloride immediately began to precipitate, and the reaction mixture became very hot. The flask was cooled and left at room temperature for 12 hours. This gave 13.9 g (81%) of 1-chloroacetyl-2,5-endomethylenecyclohexene-3 with b.p. 98–100° at 7 mm. After redistillation, b.p. 94–95° at 5 mm, n_D^{20} 1.5138, d_4^{20} 1.1772; MR_D 43.61, calculated for $C_9H_{11}OCl = 43.77$. Literature data (1): b.p. 92° at 4 mm, n_D^{20} 1.5134, d_4^{20} 1.1747.

Preparation of 1-chloroacetyl-2,3,4,5-dicyclohexanocyclohexene-3 from 1-chloro-4-acetoxybutanone-2, potassium acetate, and 1,1′-dicyclohexenyl. A mixture of 1.6 g (0.01 mole) of 1-chloro-4-acetoxybutanone-2, 1.6 g (0.01 mole) of 1,1′-dicyclohexenyl, and a small amount of potassium acetate was heated on a boiling water bath for $2\frac{1}{2}$ hours. This gave 0.7 g (26%) of adduct with m.p. 104–105°. A mixed sample with an authentic specimen of 1-chloroacetyl-2,3,4,5-dicyclohexanocyclohexene-3 (m.p. 104.5–105°) melted without depression.

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