CONDENSATION OF 5,5-DICHLORO-2,4-PENTADIENAL AND OF 7,7-DICHLORO-2,4,6-HEPTATRIENAL WITH SOME KETONES

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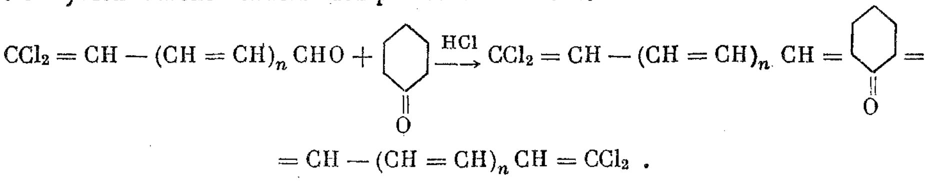
We have previously [1, 2] studied the condensation of 3, 3-dichloroacrolein with a series of ketones and investigated the conversion of the products into 2H-pyran-2-one derivatives in an acid medium. In the present work we carried out the condensation of vinylogs of 3, 3-dichloroacrolein [5, 5-dichloro-2, 4-pentadienal $CCl_2 = CH-CH = CH-CHO$ (I) and 7, 7-dichloro-2, 4, 6-heptatrienal $CCl_2 = CH-CH = CH-CHO$ (II)] with some ketones. The condensation of (I) and of (II) with acetophenone and with 4'-chloroacetophenone proceeds readily under cooling in presence of hydrogen chloride:

$$ArCOCH_3 + CCl_2 = CH - (CH = CH)_n CHO \xrightarrow{HCl} CCl_2 = CH - (CH = CH)_{n+1} COAr \ .$$
$$Ar = C_6H_5;\ p\text{-}Cl - C_6H_4;\ n = 1,2$$

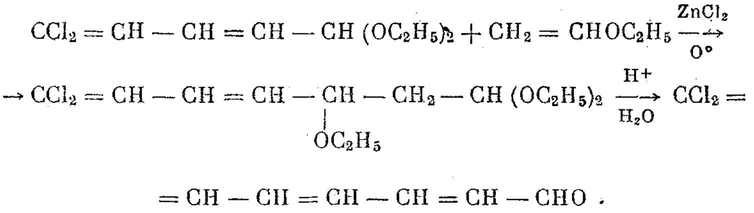
In the case of cyclohexanone condensation proceeds as follows:



In the reaction of (I) with acetone in methylene chloride solution in presence of sulfuric acid there is formed also a 2 : 1 condensation product $(CCl_2 = CH-CH-CH = CH = CH)_2CO$. With acetoacetic esters the compound (I) forms a product of composition $C_{11}H_{12}Cl_2O_3$. The ketones obtained are crystalline substances that are stable in air; the monocondensation products are yellow, and the dicondensation products are brown.

An attempt was made to hydrolyze the dichlorovinyl group in these polyenic ketones in order to obtain the corresponding acids, but on hydrolysis with sulfuric acid or alcoholic alkali the acids were not isolated. On hydrolyzing 7,7-dichloro-1-p-chlorophenyl-2,4,6-heptatrien-1-one with sulfuric acid or alcoholic alkali and 7,7-dichloro-1-phenyl-2,4,6-heptatrien-1-one with alcoholic alkali we obtained p-chlorobenzoic and benzoic acids respectively. The formation of these acids probably occurs as a result of the breakdown of the acids formed $ArCOCH = CH-CH = CH-CH_2-COOH$.

7,7-Dichloro-2,4,6-heptatrienal was synthesized by the condensation of 5,5-dichloro-2,4-pentadienal diethyl acetal with ethyl vinyl ether and subsequent hydrolysis of the 1,1-dichloro-5,7,7-triethoxy-1,3-heptadiene formed:



$$CCl_2 = CH - CH = CH - CH(OC_2H_5)_2 + CH_2 = CHOC_2H_5 \xrightarrow[0^\circ]{ZnCl_2}$$
$$\rightarrow CCl_2 = CH - CH = CH - \underset{\displaystyle OC_2H_5}{\underset{|}{CH}} - CH_2 - CH(OC_2H_5)_2 \xrightarrow[H_2O]{H^+} CCl_2 =$$
$$= CH - CH = CH - CH = CH - CHO \ .$$

5,5-Dichloro-2,4-pentadienal diethyl acetal was prepared from the aldehyde and tetraethoxysilane.

EXPERIMENTAL

7,7-Dichloro-1-p-chlorophenyl-2,4,6-heptatrien-1-one (III). A mixture of 11.5 g of 5,5-dichloro-2,4-pentadienal and 11.7 g of 4'-chloroacetophenone was saturated with dry hydrogen chloride over a period of 5-10 minutes with cooling to a temperature of from −10° to −20°. After one hour the reaction mixture had crystallized out completely. After crystallization from alcohol we obtained 16.6 g (72%) of the ketone (III), m. p. 112-114°. Found: C 54.26, 54.45; H 3.18, 3.15; Cl 36.77, 37.00%. $C_{13}H_9Cl_3O$. Calculated: C 54.26; H 3.15; Cl 37.01%.

2,6-Bis(5,5-dichloro-2,4-pentadienylidene)cyclohexanone (IV). A mixture of 16 g of 5,5-dichloro-2,4-pentadienal and 5.2 g of cyclohexanone was saturated with dry hydrogen chloride over a period of five minutes with cooling to a temperature of from −10° to −20°. After one hour the reaction mixture had crystallized out completely. After crystallization from butyl alcohol we obtained 13.5 g (70%) of the ketone (IV), m. p. 165-165.5°. Found: C 52.74, 52.67; H 3.88, 3.96; Cl 38.67, 38.93%. $C_{16}H_{14}Cl_4O$. Calculated: C 52.74; H 3.87; Cl 38.97%.

1,1,13,13-Tetrachloro-1,3,5,8,10,12-tridecahexaen-7-one (V). Two ml of concentrated sulfuric acid was added to a vigorously stirred mixture of 7 g of 5,5-dichloro-2,4-pentadienal and 3.3 g of acetone in 30 ml of methylene chloride at a temperature of from −65° to −60°. The temperature was maintained at this level for 90 minutes. Methylene chloride was removed in a vacuum. From the black resinous residue by crystallization from butyl alcohol we obtained 4.1 g (58%) of the ketone (V), m. p. 157-159°. Found: C 48.32, 48.32; H 3.35, 3.22%. $C_{13}H_{10}Cl_4O$. Calculated: C 48.15; H 3.10%.

Ethyl 2-acetyl-7,7-dichloro-2,4,6-heptatrienoate (VI). A mixture of 8 g of 5,5-dichloro-2,4-pentadienal and 7.5 g of acetoacetic ester was saturated with dry hydrogen chloride over a period of 20 minutes with cooling to from 0° to −5°; 25 ml of glacial acetic acid was added. The precipitate that separated was filtered off. We obtained 4.9 g (40%) of colorless crystals of the ketone (VI), m. p. 126-127° (from acetic acid). Found: C 50.14, 50.05; H 4.61, 4.66; Cl 27.45, 27.49%. $C_{11}H_{12}Cl_2O_3$. Calculated: C 50.00; H 4.96; Cl 26.87%.

9,9-Dichloro-1-phenyl-2,4,6,8-nonatetraen-1-one (VII). A mixture of 3 g of 7,7-dichloro-2,4,6-heptatrienal and 2 g of acetophenone was saturated with dry hydrogen chloride over a period of five minutes with cooling to a temperature of from −20° to −30°. After 1-2 hours the reaction mixture had crystallized out completely. After crystallization from butyl alcohol we obtained 3.3 g (71%) of the ketone (VII), m. p. 125-126°. Found: C 64.21, 64.28; H 4.35, 4.42; Cl 25.69, 25.89%. $C_{15}H_{12}Cl_2O$. Calculated: C 64.52; H 4.33; Cl 25.43%.

9,9-Dichloro-1-p-chlorophenyl-2,4,6,8-nonatetraen-1-one (VIII). A mixture of 3 g of 7,7-dichloro-2,4,6-heptatrienal and 2.8 g of 4'-chloroacetophenone was saturated with dry hydrogen chloride over a period of five minutes with cooling to a temperature of from −10° to −20°. After a few hours the reaction mixture had crystallized out completely. After crystallization from butyl alcohol we obtained 3.7 g (70%) of the ketone (VIII), m. p. 127-127.5°. Found: Cl 33.66, 33.60%. $C_{15}H_{11}Cl_3O$. Calculated: Cl 33.95%.

2,6-Bis(7,7-dichloro-2,4,6-heptatrienylidene)cyclohexanone (IX). A mixture of 2.5 g of 7,7-dichloro-2,4,6-heptatrienal and 1.4 g of cyclohexanone was saturated with hydrogen chloride over period of five minutes with cooling to from −50° to −60°. After a few hours the reaction mixture had crystallized out completely. After crystallization from butyl alcohol we obtained 2 g (66%) of the ketone (IX), m. p. 155.5-156.5°. Found: C 57.34, 57.17; H 4.35, 4.50; Cl 34.45, 34.26%. $C_{20}H_{18}Cl_4O$. Calculated: C 57.69; H 4.35; Cl 34.13%.

Acid hydrolysis of 7,7-dichloro-1-p-chlorophenyl-2,4,6-heptatrien-1-one (III). Five g of the ketone in 10 ml of concentrated sulfuric acid was heated to 120°; vigorous evolution of hydrogen chloride set in. The reaction mixture was then kept at 70-75° for 12 hours and poured into water. The thick resin that separated was dissolved in ether; the ether was extracted with dilute potassium hydroxide solution. The acid that was precipitated on acidification of the alkaline solution was filtered off, washed with water, and dried. We obtained 1.3 g of p-chlorobenzoic acid, m. p. 234-236°, undepressed by admixture of a known sample.

Alkaline hydrolysis of 7,7-dichloro-1-p-chlorophenyl-2,4,6-heptatrien-1-one (III). To a stirred suspension of 10 g of the ketone (III) in 100 ml of ethanol we added 9.6 g of potassium hydroxide in 50 ml of alcohol. The reaction mixture was heated at the boil for 30 minutes. The precipitate of KCl was filtered off, and water was added to the alcoholic solution; the precipitate formed was filtered off and dried, weight 6.3 g. Crystallization of the precipitate from ethanol gave the original ketone. The acid that separated on acidification of the alkaline solution was filtered off, washed with water, and dried in a desiccator; weight 1.6 g. After sublimation or crystallization from a mixture of ether and alcohol we isolated p-chlorobenzoic acid, m. p. 234-236°, undepressed by admixture of a known sample.

5,5-Dichloro-2,4-pentadienal diethyl acetal. A mixture of 15 g of 5,5-dichloro-2,4-pentadienal, 25.9 g (25% excess) of tetraethoxysilane 2.3 g of absolute ethanol, and 0.97 g of phosphoric acid was stirred in a closed flask for 15 days. After the addition of 30 ml of ether the reaction mixture was decomposed with 30% sodium hydroxide solution under cooling. The ethereal solution was separated from the aqueous layer, which was extracted with ether. The ethereal solution was washed with water and dried over calcined potassium carbonate. Ether was distilled off, and we obtained 15.3 g (70%) of 5,5-dichloro-2,4-pentadienal diethyl acetal; b. p. 60-62° (2 mm); $n^{20}D$ 1.4944. Found: C 47.72, 47.81; H 6.15, 6.23%. $C_9H_{14}Cl_2O_2$. Calculated: C 48.00; H 6.22%.

7,7-Dichloro-2,4,6-heptatrienal. 7.2 g of ethyl vinyl ether was added with stirring to 18.3 g of 5,5-dichloro-2,4-pentadienal diethyl acetal and 0.2 g of zinc chloride in 1.3 g of ethyl acetate at a temperature of from −2° to 0°. The reaction mixture was stirred until it reached room temperature (1 hour). 15 ml of concentrated hydrochloric acid and 10 ml of water were then added, and the whole was steam-distilled. The oil was extracted from the distillate with chloroform and dried over calcium chloride. Chloroform was distilled off, and we then obtained 11.5 g (80%) of 7,7-dichloro-2,4,6-heptatrienal, b. p. 90-92° (2 mm) and m. p. 30-32° (from petroleum ether). Found: C 47.05, 46.95; H 3.37, 3.50; Cl 39.81, 39.64%. $C_7H_6Cl_2O$. Calculated: C 47.47; H 3.41; Cl 40.09%.

SUMMARY

5,5-Dichloro-2,4-pentadienal and 7,7-dichloro-2,4,6-heptatrienal readily condense with various ketones in presence of acid catalysts with formation of the corresponding polyenic ketones.

LITERATURE CITED

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