SYNTHESIS OF 5,5-DICHLORO-2,4-PENTADIENAL AND SOME

OF ITS TRANSFORMATIONS

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By condensation of β , β -dichloroacrolein with carbonyl compounds we previously [1] obtained a series of dichlorodienic ketones with the structure RCOCR' = CH - CH = CCl₂. 5,5-Dichloro-2,4-pentadienal,CCl₂ = CH - CH =CH - CHO, the vinylog of β , β -dichloroacrolein could not be synthesized by this method. In the present work we found that 5,5-dichloro-2,4-pentadienal is obtained in high yield by the following route:

$$CCl_{2} = CH - CHClOC_{2}H_{5} + CH_{2} = CHOC_{2}H_{5} \xrightarrow{ZnCl_{3}}$$
$$OC_{2}H_{5} \xrightarrow{I} OC_{2}H_{5} \xrightarrow{H_{3}O} CCl_{2} = CH - CH - CH_{2}CHClOC_{2}H_{5} \xrightarrow{H_{3}O} CCl_{2} = CH - CH = CH - CHO$$

Condensation of the easily accessible 1,1,3-trichloro-3-ethoxy-1-propene [2] with ethyl vinyl ether in presence of a small quantity of zinc chloride at temperatures below zero gives 1,1,5-trichloro-3,5-diethoxy-1-pentene in high yield. Without separation from the reaction medium, the latter is subjected to hydrolysis with dilute hydrochloric acid and the resulting dichloropentadienal is distilled with steam at the same time. Condensa-tion of β , β -dichloroacrolein diethylacetal with ethyl vinyl ether in presence of zinc chloride leads to 1,1-dichloro-3,5,5-triethoxy-1-pentene. In this case the yield is lower than for 1,1,3-trichloro-3-ethoxy-1-propene. Hydrolysis of 1,1-dichloro-3,5,5-triethoxy-1-pentene with dilute hydrochloric acid gives the dichloropentadienal in good yield:

$$CCl_2 = CH - CH (OC_2H_5)_2 + CH_2 = CHOC_2H_5 \xrightarrow{ZnCl_2}$$

$$\rightarrow CCl_2 = CH - CH (OC_2H_5) CH_2CH (OC_2H_5)_2 \xrightarrow{H_2O} CCl_2 = CH - CH = CH - CHO$$

An attempt was also made to prepare dichloropentadienal by another route. Carbon tetrachloride reacts with vinyl acetate in presence of benzoyl peroxide to give, according to the patent literature [3], a mixture of telomers with the structure $CCl_3(CH_2CHOCOCH_3)_nCl$. When this reaction was carried out in presence of azodiisobutyronitle and with a 4:1 molar ratio of CCl_4 : to vinyl acetate, the main products were found to be telomers with n=1 and 2. Hydrolysis of 1,1,1,5-tetrachloro-3,5-diacetoxypentane with hydrochloric acid and distillation with steam gives 5,5,5-trichloro-2-pentenal in admixture with dichloropentadienal.

$$CCl_{3}CH_{2}CH (OCOCH_{3}) CH_{2}CHCIOCOCH_{3} \xrightarrow{H_{2}O}_{H+}$$

$$\rightarrow CCl_{3}GH_{2}CH = CH - CHO + CCl_{2} = CH - CH = CH - CHO$$

Under these conditions 1,1,1,3-tetrachloro-3-acetoxypropane is entirely converted into β , β -dichloroacrolein.

2,4-Dinitrophenylhydrazine acts on tetrachlorodiacetoxypentane in an acid medium to form 5,5,5-trichloro-2-pentenal. 5,5-Dichloro-2,4-pentadienal is a light-yellow liquid, easily oxidized in the air to 5,5-dichloro-2,4pentadienic acid

$$CCl_2 = CH - CH = CH - CHO \xrightarrow{O_2} CCl_2 = CH - CH = CH - COOH$$

In carbon tetrachloride one molecule of bromine smoothly adds on to dichloropentadienal. The resulting 2,3-dibromo-5,5-dichloro-4-pentenal loses hydrogen bromide on standing to form the crystalline 2-bromo-5,5-dichloro-1,4-pentadienal

$$CCl_2 = CH - CH = CH - CHO + Br_2 \rightarrow CCl_2 = CH - CHBr - CHBrCHO \rightarrow$$
$$\rightarrow CCl_2 = CH - CH = CBr - CHO$$

Dichloropentadienal readily condenses with acetophenone in presence of hydrogen chloride to give the corresponding trienic ketone

$$C_{6}H_{5}COCH_{3} + CCl_{2} = CH - CH = CH - CHO \xrightarrow{H^{+}} C_{6}H_{5}COCH = CH - CH = CH - CH = CCl_{2}$$

Heating of dichloropentadienal in acetic acid solution leads to α -pyrone

Dichloropentadienal can be employed for synthesis of dienic acids according to the following scheme:

$$CCl_2 = CH - CH = CH - CHO + RMgX \rightarrow RCH (OH) CH = CH - CH = CCl_2 \rightarrow$$

 $\rightarrow RCH = CH - CH = CH - COOH$

When R = Ar the conversion of the dichlorodienic alcohol to the corresponding dienic acid takes place, as we showed earlier [4], under the action of acids due to an anionic allyl rearrangement. When R = alkyl the dichlorodienic alcohol does not undergo the anionic allyl rearrangement but splits off water to give the dichlorotriene. Heating of 1,1-dichloro-5-hydroxy-1,3-heptadiene in aqueous dioxanic solution in presence of sulfuric acid thus gave only 1,1-dichloro-1,3,5-heptatriene

$$CCl_{2} = CH - CH = CH - CHO + C_{2}H_{5}MgBr \rightarrow C_{2}H_{5}CH (OH) CH = CH - CH = CCl_{2} \xrightarrow{H^{+}} OH_{3}CH = CH - CH = CH - CH = CCl_{2}$$

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When R = alkyl the conversion to the dienic acid is effected by alkaline hydrolysis of the dichlorovinyl group with simultaneous removal of water. In this way the heating of 1,1-dichloro-5-hydroxy-1,3-octadiene with potassium hydroxide solution in diethyleneglycol gives 2,4-octadienic acid

$$CCl_2 = CH - CH = CH - CHO + C_2H_7MgBr \rightarrow C_3H_7CH (OH) CH = CH - CH = CCl_2 \xrightarrow{KOH}_{H_2O} \rightarrow C_3H_7CH = CH - CH = CH - COOH$$

Reaction of hexynemagnesium bromide with dichloropentadienal gave the acetylenic alcohol. On heating in aqueous dioxanic solution in presence of sulfuric acid, this alcohol undergoes both the anionotropic allylic rearrangement with formation of acetylenedienic acid and rearrangement to the dichlorotrienic ketone:

$$C_{4}H_{9}C \equiv CMgBr + CCl_{2} = CH - CH = CH - CHO \rightarrow C_{4}H_{9}C \equiv C - CH (OH) CH =$$
$$= CH - CH = CCl_{2} \xrightarrow{H^{+}} C_{4}H_{9}COCH = CH - CH = CH - CH = CCl_{2} + C_{4}H_{9}C \equiv$$
$$\equiv C - CH = CH - CH = CH - COOH$$

The ketone is formed in larger quantity than the acid.

Dichloropentadienal is prepared by cleavage of a molecule of alcohol from 1,1-dichloro-3,5,5-triethoxy-1-pentene on heating with KHSO₄. Heating with potassium hydroxide results in loss of hydrogen chloride with formation of the chloroacetyl compound

$$CCl_{2} = CH - CH - CH_{2} - CH (OC_{2}H_{5})_{2} \xrightarrow{KHSO_{4}} CCl_{2} = CH - CH - CH (OC_{2}H_{5})_{2} \xrightarrow{KHSO_{4}} CCl_{2} = CH - CH - CH (OC_{2}H_{5})_{2} \xrightarrow{KOH} CIC \equiv C - CH = CH - CH (OC_{2}H_{5})_{2}$$

Treatment of 1,1-dichloro-3,5,5-triethoxy-1-pentene with sodium, followed by decomposition of the reaction product with water, gives 1,1,3-triethoxy-4-pentyne in high yield

$$\begin{array}{c} & \text{OC}_2\text{H}_5 \\ \downarrow \\ \text{CCl}_2 = \text{CH} - \overset{|}{\text{CH}} - \text{CH}_2\text{CH} (\text{OC}_2\text{H}_5)_2 \xrightarrow[H_2O]{Na} \\ H_2O \end{array} \rightarrow \text{HC} \equiv \text{C} - \overset{|}{\text{CH}} - \text{CH}_2 - \text{CH} (\text{OC}_2\text{H}_5)_2 \end{array}$$

EXPERIMENTAL

<u>1,1,5-Trichloro-3,5-diethoxy-1-pentene</u>. At a temperature of -5 to 3°, 20 g of vinyl ethyl ether was gradually stirred into 50 g of 1,1,3-trichloro-3-ethoxy-1-propene to which a solution of 0.3 g of zinc chloride in 2 g of ethyl acetate had been added. The solution was then allowed to stand for half an hour. After addition of 2 g of finely pulverized, calcined potassium carbonate, the mixture was stirred for 20 min. The precipitate was filtered, and the filtrate distilled in vacuo. Yield 62.2 g of 1,1,5-trichloro-3,5-diethoxy-1-pentene with b.p. 85-86° (2 mm); nD^{20} 1.4672, d_4^{20} 1.1677. Found C 41.58; 41.60; H 5.89; 5.84%. C₉H₁₅Cl₃O₂. Calculated: C 41.30; H 5.73%.

<u>1,1-Dichloro-3,5,5-triethoxy-1-pentene</u>. Into 59 g of 1,1-dichloro-3,3-diethoxy-1-propene and 8.5 ml of 10% solution of zinc chloride in ethyl acetate was gradually stirred 27 g of vinyl ethyl ether at such a rate that the temperature did not rise above 45°. After addition of the whole of the vinyl ethyl ether, the reaction mixture was stirred for an hour at 45° and 1.5 hr at 50-60°. The cooled reaction mixture was diluted with an equal volume of ether, washed with 5% sodium hydroxide solution, and dried over potassium carbonate. Distillation in vacuo gave 20.3 g of the original dichlorodiethoxypropene and 37.2 g (70.5% of theory on the reacted dichlorodiethoxypropene) of 1,1-dichloro-3,5,5-triethoxy-1-pentene with b.p. 96-98° (2 mm); n_D^{20} 1.4480; d_4^{20} 1.0752; Found : MR 67.49; calculated MR 67.20. Found: C 48.78; 48.76; H 7.31; 7.31%. C₁₁H₂₀Cl₂O₃. Calculated: C 48.70; H 7.38%.

<u>5,5-Dichloro-2,4-pentadienal.</u> To the product of reaction of 50 g of trichloroethoxypropene with 19 g of vinyl ethyl ether was added 20 ml of concentrated hydrochloric acid and 20 ml of water, and the mixture was distilled with steam. The oil in the distillate was extracted with chloroform and dried over calcium chloride. Yield 30 g (67.8% of the theoretical) of 5,5-dichloro-2,4-pentadienal with b.p. 76-77° (8 mm); n_D^{20} 1.5949; d_4^{20} 1.3124. Found: C 39.77; 39.58; H 2.84; 2.78%. C₅H₄Cl₂O. Calculated: C 39.73; H 2.64%

<u>The 2,4-dinitrophenylhydrazone</u> had m.p. 174-175° (from the acetic acid). Found: N 16.98; 17.06%. $C_{11}H_8Cl_2N_4O_4$. Calculated: N 16.98%. The semicarbazone had m.p. 189-190° (from alcohol). Found: N 20.02; 19.84%. $C_6H_7Cl_2N_3O$. Calculated: N 20.18%.

To 20 g of 1,1-dichloro-3,5,5-triethoxypentene was added 15 ml of concentrated hydrochloric acid and 10 ml of water, and the mixture distilled with steam. The oil in the distillate was extracted with chloroform. Distillation gave 8.1 g (78% of the theoretical) of 5,5-dichloropentadienal with b.p. 76-77° (8 mm); n_{D}^{20} 1.5945.

1,1,1,5-Tetrachloro-3,5-diacetoxypentane. To 450 g of dry carbon tetrachloride and 0.5 g of azodiisobutyronitrile was added, in the course of an hour at 75-76°, 120 g of vinyl acetate containing 0.5 g of azodiisobutyronitrile. The solution was then boiled for 2.5 hr. Excess of carbon tetrachloride was taken off in vacuo and the residue distilled. Yield 60.3 g of 1,1,1,3-tetrachloro-3-acetoxypropane and 121 g of 1,1,1,5-tetrachloro-3,5-diacetoxypentane with b.p. 123-125° (2 mm); n_D^{20} 1.4770; d_4^{20} 1.3814; Found MR 66.68; calculated MR 66.84. Found: C 33.13; 33.23; H 3.73; 3.73%. C₉H₁₂Cl₄O₄. Calculated: C 32.92; H 3.66%.

Treatment with 2,4-dinitrophenylhydrazine in an alcoholic medium in presence of sulfuric acid gave the 2,4-dinitrophenylhydrazone of 5,5,5-trichloropenten-2-al with m.p. 147-148° (from acetic acid). Found: N 15.52; 15.31%. $C_{11}H_9Cl_3N_4O_4$. Calculated N 15.24%.

<u>Hydrolysis of 1,1,1,5-tetrachloro-3,5-diacetoxypropane</u> (from an experiment with 200 g of vinyl acetate). 75 ml of concentrated hydrochloric acid and 35 ml of water were added to the residue (250 g), and the mixture was distilled with steam. The distillate was extracted with chloroform. The extract was dried over calcium chloride, the solvent removed, and the residue distilled in vacuo. There was obtained 61.2 g of a mixture of 5,5,5-trichloropenten-2-al and dichloropentadienal with b.p. 78-80° (8 mm); n_D^{20} 1.5742; d_4^{20} 1.3278. Found: C 37.31; H 2.66; Cl 50.02%.

Treatment of the mixture with 2,4-dinitrophenylhydrazine gave the hydrazone of dichloropentadienal with m.p. 174-175°. Hydrolysis under similar conditions of 150 g of 1,1,1,3-tetrachloro-3-acetoxypropane gave 61 g (78% of theory) of β , β -dichloroacrolein with b.p. 125-126°; n_D^{20} 1.5080. Literature data [5]: b.p. 124-125°; n_D^{20} 1.5090.

5,5-Dichloro-2,4-pentadienic acid. The acid was obtained (yield 24% of theory) when dichloropentadienal was left to stand in the air. M.p. 120-122° (from ligroine). A mixture with the acid obtained by oxidation of dichloropentadienal with moist silver oxide melted at 120-122°. Found: C 36.16; 36.28; H 2.43; 2.55%. $C_5H_4Cl_2O_2$. Calculated: C 35.92; H 2.39%.

2,3-Dibromo-5,5-dichloropenten-4-a1. To a solution of 44 g of dichloropentadienal in 100 ml of carbon tetrachloride was slowly added 45 g of bromine at 5-10°. The solvent was removed in vacuo, and the residue distilled in vacuo. Yield 86.3 g of 2,3-dibromo-5,5-dichloropenten-4-al with b.p. 90-91° (1 mm); n_D^{20} 1.5823; d_4^{20} 2.0135. Found: C 19.74; 19.64; H 1.33; 1.30%. C₅H₄Br₂Cl₂O. Calculated: C 19.30; H 1.28%.

The product easily splits off hydrogen bromide on standing and gives 2-bromo-5,5-dichloropentienal; m.p. 97-98° (from alcohol). Found: C 26.53; 26.23; H 1.47; 1.26%. C₅H₃BrCl₂O. Calculated: C 26.12; H 1.30%.

2,4-Dinitrophenylhydrazine acts on 2,3-dibromo-5,5-dichloropentenal and 2-bromo-5,5-dichloropentadienal to form the same hydrazone with m.p. 215-216° (from acetic acid). Found: N 13.76; 13.76%. $C_{11}H_4BrClN_4O_4$. Calculated N 13.72%.

 α -Pyrone. A solution of 7 g of dichloropentadienal in 15 ml of acetic acid was boiled for 6 hr. Distillation of the acetic acid in vacuo left 1.8 g (38% of theory) of α -pyrone with m.p. 78-80° (7 mm); n_D^{20} 1.5280; d_4^{20} 1.2039, Literature [6]: $d_4^{19,5}$ 1.2006.

Heating of α -pyrone with maleic anhydride gave a crystalline adduct with m.p. 187° (from acetonitrile). Literature data [7]: m.p. of adduct 187°. Found: C 55.64, 55.64; H 3.18; 3.05%. C₉H₆O₅. Calculated: C 55.67; H 3.11%.

In addition to the α -pyrone there was obtained 1.5 g of a product with b.p. 124-125° (7 mm); n_D^{20} 1.5080; d_4^{20} 1.2733, which with 2,4-dinitrophenylhydrazine forms a hydrazone with m.p. 174-175°. This did not give a depression in admixture with the 2,4-dinitrophenylhydrazone of 5,5-dichloropentadienal.

<u>1,1-Dichloro-7-phenyl-1,3,5-heptatrien-6-one</u>. A mixture of 10 g of dichloropentadienal and 8 g of acetophenone was saturated with dry hydrogen chloride for 20 min while cooling with ice water. The resulting solid product was recrystallized from alcohol; yield 14 g, m.p. 119-120°. Found: C 61.60, 61.71; H 4.04; 4.09%. $C_{12}H_{10}Cl_2O$. Calculated: C 61.65; H 3.95%. <u>1,1-Dichloro-5-hydroxy-1,3-heptadiene</u>. To ethylmagnesium bromide (from 35 g of ethyl bromide and 8 g of magnesium) in 80 ml of ether was gradually added 38 g of dichloropentadienal. There was obtained 42.1 g of 1,1-dichloro-5-hydroxy-1,3-heptadiene with b.p. 101-102° (3 mm); n_D^{20} 1.5312; d_4^{20} 1.1886. Found C 46.21; 46.18; H 5.34; 5.43%. C₇H₁₀Cl₂O. Calculated: C 46.40; H 5.52%.

No acidic reaction products were obtained after heating for four hr of a solution of 10 g of dichlorohydroxyheptadiene in 70 ml of dioxane and 3 ml of water containing 0.5 ml of concentrated sulfuric acid. The sole neutral product of the reaction was 1,1-dichloro-1,3,5-heptatriene with b.p. 74-75° (7 mm); n_D^{20} 1.5766; d_4^{20} 1.1133. Found: C 51.34; 51.41; H 4.82; 4.70%. C₇H₈Cl₂. Calculated: C 51.53; H 6.15%.

<u>1,1-Dichloro-5-hydroxy-1,3-octadiene</u>. To propylmagnesium bromide (from 28 g of n-propyl bromide and 3.4 of magnesium) in 60 ml of ether at room temperature was added 26 g of dichloropentadienal in 20 ml of ether. After heating for 15 min, the mixture was cooled and poured into acidified water. There was obtained 26.8 g of 1,1-dichloro-5-hydroxy-1,3-octadiene with b.p. 102-103° (3 mm); n_D^{20} 1.5240; d_4^{20} 1.1547. Found: C 49.34; 49.01; H 5.86; 5.96%. C₈H₁₂Cl₂O. Calculated: C 49.23; H 6.15%.

<u>2,4-Octadienic acid</u>. To a stirred solution of 43 g of potassium hydroxide in 86 ml of diethyleneglycol and 8.6 ml of water at 100° was gradually added 26 g of dichlorohydroxyoctadiene. The mixture was then heated at 120-125° for 5 hr. After cooling, water was added and the mixture extracted with ether. The alkaline solution was separated, acidified with hydrochloric acid, and carefully extracted with ether. The ethereal extract was dried over sodium sulfate. There was obtained 8.1 g of a mixture of octadienic acids (liquid and crystalline) with b. r. 130-180° (4 mm). The crystalline acid had m.p. 75.5-76° (from ligroine). Found: C 68.85; 68.66; H 8.31; 8.54%. CgH₁₂O₂. Calculated: C 68.57; H 8.57%.

The liquid acid had b.p. 114-115° (2 mm); n_D^{20} 1.5057; d_4^{20} 0.9767. Found: C 68.35; 68.21; H 8.65; 8.72%. C₃H₁₂O₂. Calculated: C 68.57; H 8.57%.

Hydrogenation of the liquid and crystalline octadienic acid gave caprylic acid which was identified through its amide; m.p. 105-106°. A mixture of the amide with an authentic specimen of carylamide melted at 105-106°.

<u>1,1-Dichloro-5-hydroxy-1,2-undecadien-6-yne</u>. To hexynemagnesium bromide (from 14 g of butylacetylene) in 50 ml of ether was gradually added 18 g of dichloropentadienal at the boiling point of ether. After boiling for 3 hr, the solution was cooled and decomposed with acidified water. The ethereal solution was separated and dried over potassium carbonate. There was obtained 20.3 g of 1,1-dichloro-5-hydroxy-1,2-undecadien-6-yne with b.p. 145-146° (3 mm); n_D^{20} 1.5370; d_4^{20} 1.1264. Found: C 56.45; 56.42; H 5.98; 6.00%. C₁₁H₁₄Cl₂O. Calculated: C 56.65; H 6.00%.

Isomerization of 1, 1-dichloro-5-hydroxy-1, 2-undecadien-6-yne. A solution of 14 g of dichloroundecadienyne in 70 ml of dioxane and 4 ml of water was boiled in presence of 0.5 ml of concentrated sulfuric acid for 6 hr. After cooling of the reaction mixture, water was added and the oil extracted with ether. The ethereal solution was washed with 10% potassium hydroxide solution and dried over calcium chloride. The alkaline solution was acidified with hydrochloric acid and extracted with chloroform. Removal of the ether left 10 g of neutral product which crystallized on standing. Melting point of 1, 1-dichloro-1,3,5-undecatrien-6-one 58-59° (from ligroine). Found: C 56.44; 56.49; H 6.10; 6.13; Cl 30.26; 30.35%. $C_{11}H_{14}Cl_2O$. Calculated: C 56.65; H 6.00; Cl 30.44%.

2,4-Dinitrophenylhydrazone: m.p. 176-177° (from acetic acid). Found: N 13.23; 13.43%. $C_{17}H_{18}Cl_2N_4O_4$. Calculated: N 13.56%.

Removal of the chloroform left 2.5 g of 2,4-undecadien-6-ynic acid with m.p. 82-83° (from ligroine). Found: C 74.21; 74.09; H 7.80; 7.93%. $C_{11}H_{14}O_2$. Calculated: C 74.15; H 7.86%.

5,5-Dichloro-2,4-pentadienal diethylacetal. A mixture of 56 g of 1,1-dichloro-3,5,5-triethoxy-1-pentene and 0.3 g of potassium bisulfate was heated in a Claisen flask on an oil bath at 130-150°. Ethyl alcohol distilled off during the process. After 9.6 g of alcohol had been collected, the residue was distilled in vacuo to give 34.8 g of dichloropentadienal diethylacetal with b.p. 100-102° (7 mm); n_D^{20} 1.4920; d_4^{20} 1.1208. Found: C 48.15; 48.12; H 6.07; 6.07%. C₉H₁₄Cl₂O₂. Calculated: C 48.00; H 6.22%. <u>5-Chloro-2-penten-4-ynal.</u> A mixture of 30 g of dichloropentadienal diethylacetal and 50 g of potassium hydroxide powder was heated in a Claisen flask at a pressure of 10-20 mm. The dehydrochlorinated product was distilled. Ether was added to the distillate. The ethereal layer was separated from the water and dried over potassium carbonate. Yield 8.9 g of 5-chloro-2-penten-4-ynal with b.p. 89-90° (8 mm); n_D^{20} 1.4742; d_4^{20} 1.0360. Found: C 57.32; 57.48; H 6.92; 6.74; Cl 18.45; 18.53%. C₉H₁₃ClO₂. Calculated: C 57.29; H 6.89; Cl 18.83%.

2,4-Dinitrophenylhydrazone: m.p. 178-179° (from acetic acid). Found: N 18.88; 18.86%. $C_{11}H_7C1N_4O_4$ Calculated: N 19.02%.

<u>1,1,3-Triethoxy-4-pentyne</u>. Into 16.5 g of finely pulverized sodium in 100 ml of ether was gradually stirred 47 g of 1,1-dichloro-3,5,5-triethoxypentene at such a rate that the ether boiled gently. After completion of the addition, the mixture was heated for 4 hr, then cooled and carefully decomposed with water. The ethereal solution was dried over potassium carbonate. Yield 25.6 g (78%) of 1,1,3-triethoxypentyne with b.p. 82-83° (8 mm); n_D^{20} 1.4233; d_A^{20} 0.9142. Found: C 65.81; 65.91; H 10.03; 9.83%. C₁₁H₂₀O₃. Calculated: C 66.00; H 10.00%.

SUMMARY

1. A convenient method was found for the preparation of 5,5-dichloro-2,4-pentadienal from the product of condensation of β , β -dichloroacrolein diethylacetal with vinyl ethyl ether.

2. Some transformations of 5,5-dichloro-2,4-pentadienal, notably to α -pyrone and dienic acids, were investigated.

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