UDC 542.951.2

PREPARATION OF 6-SUBSTITUTED 2H-PYRAN-2-ONES VIA 3,3-DICHLOROACROLEIN AND ITS CHLOROACETALS*

L. P. Sorokina and L. I. Zakharkin

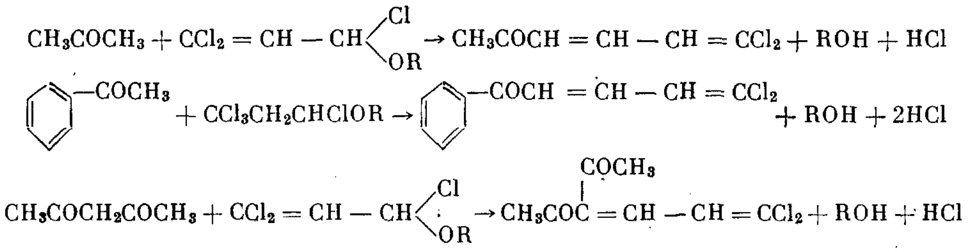
Institute of Heteroorganic Compounds, Academy of Sciences, USSR

Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1,
pp. 73-77, January, 1964
Original article submitted April 25, 1963

We have previously reported [1-3] on a method of synthesizing substituted 2H-pyran-2-ones by the cyclization of the dichloro dienic ketones $RCOCR' = CH - CH = CCl_2$ formed by the condensation of 3,3-dichloroacrolein with carbonyl compounds in presence of acid catalysts. The necessary 3,3-dichloroacrolein is obtained from the product of the addition of carbon tetrachloride to an alkyl vinyl ether in the following way [4]:

$$CCl_4 + CH_2 = CHOR \rightarrow \underset{(I)}{CCl_3CH_2CHClOR} \xrightarrow{-HCl} \underset{(II)}{CCl_2 = CH - CHClOR} \xrightarrow{\Delta}$$
$$\rightarrow CCl_2 = CH - CHO + RCl;\ (R = C_4H_9)$$

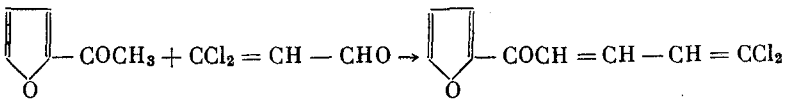
We have now found that the method of preparing 2H-pyran-2-ones can be simplified in some respects. It was found that, instead of 3,3-dichloroacrolein, in the condensation with carbonyl compounds it is possible to use "chloroacetals" of 3,3-dichloroacrolein [3-alkoxy-1,1,3-trichloropropenes] (II, $R = C_2H_5$; $R = C_4H_9$) and the products of the addition of carbon tetrachloride to alkyl vinyl ethers, 3-alkoxy-1,1,1,3-tetrachloropropanes (I, $R = C_2H_5$, $R = C_4H_9$). The reactions were carried out in acetic acid solution, and the yields of dichloro dienic ketones were the same as those obtained in condensations with 3,3-dichloroacrolein. In this way, we prepared products of condensation with acetone, acetophenone, 4'-chloroacetophenone, 4'- and 3'-nitroacetophenones, methyl 2-thienyl ketone, 2'-acetonaphthone, and 2,4-pentanedion



$$CH_3COCH_3 + CCl_2 = CH - CH\begin{matrix}Cl \\ OR\end{matrix} \rightarrow CH_3COCH = CH - CH = CCl_2 + ROH + HCl$$

$$CH_3COCH_2COCH_3 + CCl_2 = CH - CH\begin{matrix}Cl \\ OR\end{matrix} \rightarrow CH_3CO\overset{COCH_3}{\overset{|}{C}} = CH - CH = CCl_2 + ROH + HCl$$

It must be supposed that in acetic acid the conversion of (I) and (II) into 3,3-dichloroacrolein occurs by the hydrolysis of the "chloroacetal" grouping with, in the case of (I), the subsequent elimination of hydrogen chloride from unstable 3,3,3-trichloropropionaldehyde. It was found also that 3,3-dichloroacrolein condenses with some carbonyl compounds in absence of catalysts. In this way we carried out the condensation of 3,3-dichloroacrolein with 2-furyl methyl ketone:

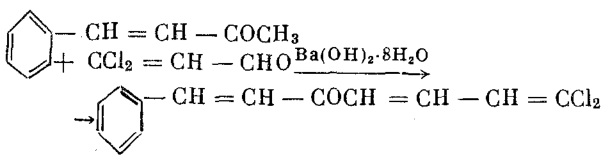


We were unable to bring about the condensation of 3,3-dichloroacrolein with 4-phenyl-3-buten-2-one under

---

*This article is published in accordance with a resolution of the Conference of Chief Editors of Journals of the Academy of Sciences of the USSR, July 12, 1962, as a dissertation paper by L. P. Sorokina.

the action of acidic catalysts; only in presence of barium hydroxide did we isolate the corresponding condensation product:



By the method that we have developed from the previously undescribed dichloro dienic ketones we prepared the following 2H-pyran-2-ones: 6-methyl-, 6-p-nitrophenyl-, 6-m-nitrophenyl-, 6-(2-thienyl)-, 6-(2-naphthyl)-, 5-acetyl-6-methyl-, 6-(2-furyl)-, and 6-styryl-2H-pyran-2-ones. We showed also that the 2H-pyran-2-ones may be obtained in one stage without the isolation of the ketone. The reaction was carried out in acetic acid solution in presence of phosphoric acid. In this way we prepared 6-phenyl-2H-pyran-2-one from acetophenone and 6-p-nitrophenyl-2H-pyran-2-one from 4'-nitroacetophenone and 3,3-dichloroacrolein or its chloroacetal.

EXPERIMENTAL

6,6-Dichloro-3,5-hexadien-2-one. A mixture of 20 g of 1,1,3-trichloro-3-ethoxypropene, 80 ml of acetone, and 3 ml of water was left at room temperature. After 72 h, the excess of acetone was vacuum-distilled off, and the residue was steam-distilled. The oil was extracted from the distillate with ether. The ether extract was dried over magnesium sulfate. Ether was vacuum-distilled off, and the residue was distilled in presence of hydroquinone. We obtained 3.8 g of 6,6-dichloro-3,5-hexadien-2-one, b.p. 65-67° (1 mm), n_D^{20} 1.5640, and m.p. 14-16° (from pentane). The literature [5] gives n_D^{19} 1.5650. The 2,4-dinitrophenylhydrazone had m.p. 196-197° (from acetic acid). The literature [5] gives m.p. 193-194°. Found: C 41.65, 41.74; H 2.78, 2.98%. $C_{12}H_{10}O_4N_4Cl_2$. Calculated: C 41.75; H 2.92%.

5,5-Dichloro-2,4-pentadienophenone. A mixture of 10 g of 1,1,3-trichloro-3-ethoxypropene, 6.4 g of acetophenone, and 15 ml of aqueous acetic acid was left at room temperature. After 10-12 h, crystals came down in the reaction mixture, and after five days the crystals were filtered off. We obtained 9.3 g (76%) of 5,5-dichloro-2,4-pentadienophenone, m.p. 76-77° (from alcohol). The literature [1] gives m.p. 76-77°.

A mixture of 10 g of 3-butoxy-1,1,1,3-tetrachloropropane, 4 g of acetophenone, and 15 ml of aqueous acetic acid was left at room temperature. After three days, the precipitated crystals were filtered off. We obtained 48 g (66%) of 5,5-dichloro-2,4-pentadienophenone, m.p. 76-77° (from alcohol).

4',5,5-Trichloro-2,4-pentadienophenone. A mixture of 40 g of 1,1,3-trichloro-3-ethoxypropene, 32 g of 4'-chloroacetophenone, and 80 ml of aqueous acetic acid was left at room temperature. After a few hours, crystals came down in the reaction mixture, and after 20-24 h they were filtered off. We obtained 42.1 g (78%) of 4',5,5-trichloro-2,4-pentadienophenone, m.p. 122° (from alcohol). The literature [1] gives m.p. 122°.

5,5-Dichloro-4'-nitro-2,4-pentadienophenone. A mixture of 10 g of 1,1,3-trichloro-3-ethoxypropene, 8.7 g of 4'-nitroacetophenone, and 15 ml of aqueous acetic acid was left at room temperature. After 10-12 h a yellow crystalline precipitate formed in the reaction mixture and was filtered off and dried. We obtained 13.3 g (93%) of 5,5-dichloro-4'-nitro-2,4-pentadienophenone, m.p. 107.5-108° (from alcohol). Found: C 48.80, 48.53; H 2.70, 2.72; Cl 25.85, 25.55%. $C_{11}H_7Cl_2NO_3$. Calculated: C 48.54, H 2.58, Cl 26.08%.

5,5-Dichloro-3'-nitro-2,4-pentadienophenone. A mixture of 10 g of 1,1,3-trichloro-3-ethoxypropene, 8.7 g of 3'-nitroacetophenone, and 15 ml of aqueous acetic acid was left at room temperature. After 10-12 h, a yellow crystalline precipitate formed and was filtered off and dried. We obtained 8.9 g (62%) of 5,5-dichloro-3'-nitro-2,4-pentadienophenone, m.p. 148-150° (decomp.) (from alcohol). Found: C 48.72, 48.70; H 2.57, 2.59; Cl 26.40%. $C_{11}H_7Cl_2NO_3$. Calculated: C 48.54, H 2.58, Cl 26.08%.

5,5-Dichloro-1-(2-thienyl)-2,4-pentadien-1-one. A mixture of 10 g of 1,1,3-trichloro-3-ethoxypropene and 6.6 g of methyl 2-thienyl ketone was left at room temperature. After 12 h, the reaction mixture crystallized out. After crystallization from methanol we obtained 7.1 g (60%) of 5,5-dichloro-1-(2-thienyl)-2,4-pentadien-1-one, m.p. 114.5-115.5°. Found: C 46.20, 46.03, 2.54, 2.56; Cl 30.90%. $C_9H_6Cl_2OS$. Calculated: C 46.36; H 2.59; Cl30.45%.

5,5-Dichloro-2,4-pentadieno-2'-acetonaphthone. A mixture of 5 g of 1,1,3-trichloro-3-ethoxypropene, 4.5 g of 2'-acetonaphthone, and 15 ml of aqueous acetic acid was left at room temperature. After 24 h, the precipitated crystals were filtered off. We obtained 1.58 g (23%) of 5,5-dichloro-2,4-pentadieno-2'-acetonaphtone, m.p. 122-123° (from alcohol). The literature [6] gives m.p. 122.5-123°.

3-Acetyl-6,6-dichloro-3,5-hexadien-2-one. A mixture of 17.9 g of 1,1,3-trichloro-3-ethoxypropene, 9.5 g of 2,4-pentanedione, and 10 ml of aqueous acetic acid was left at room temperature. After 72 h, the precipitated crystals were filtered off. We obtained 13.4 g (68%) of 3-acetyl-6,6-dichloro-3,5-hexadien-2-one [3-(3,3-dichloroallylidene)-2,4-pentanedione], m.p. 43.5-44.5° (from heptane). Found: C 46.46, 46.32; H 4.01, 3.86; Cl 34.18%. $C_8H_8Cl_2O_2$. Calculated: C 46.39; H 3.89; Cl 34.28%.

5,5-Dichloro-1-(2-furyl)-2,4-pentadien-1-one. A mixture of 3 g of 2-furyl methyl ketone and 3.4 g of 3,3-dichloroacrolein was left at room temperature. After two days crystals came down in the reaction mixture, and after six days' standing at room temperature they were filtered off. We obtained 1.7 g of 5,5-dichloro-1-(2-furyl)-2,4-pentadien-1-one, m.p. 128-129° (from methanol). Found: C 49.97, 49.83; H 2.88, 2.84; Cl 33.44%. $C_9H_6Cl_2O_2$. Calculated: C 49.78; H 2.79; Cl 32.70%.

7,7-Dichloro-1-phenyl-1,4,6-heptatrien-3-one. 12 g of 3,3-dichloroacrolein was added to a suspension of 12 g of 4-phenyl-3-buten-2-one and 8 g of barium hydroxide octahydrate in 75 ml of ethanol at -10°. The reaction mixture was then left for 2.5 h at -10° and for 12 h at 0°, after which it was decomposed with 2 N H_2SO_4. Water was added, the aqueous solution was saturated with sodium chloride, and the oil was extracted with ether. The ether extracts were washed with sodium bicarbonate solution and water and dried over calcium chloride. Ether was driven off leaving 13.5 g of oily residue. Dilution of the oil with methanol and cooling gave 2.3 g of yellow crystals of 7,7-dichloro-1-phenyl-1,4,6-heptatrien-3-one, m.p. 80-82° (from methanol). Found: C 61.65, 61.72; H 4.09, 4.11; Cl 27.87, 27.63%. $C_{13}H_{10}Cl_2O$. Calculated: C 61.66; H 3.98; Cl 28.03%.

6-Methyl-2H-pyran-2-one. 4 g of 6,6-dichloro-3,5-hexadien-2-one was boiled in 15 ml of glacial acetic acid for 18.5 h. Acetic acid was vacuum-distilled off, and from the residue we obtained 2.6 g (96%) of 6-methyl-2H-pyran-2-one; b.p. 102-104° (15 mm); n_D^{20} 1.5324; m.p. 30-31° (from pentane). Found: C 64.83, 64.99; H 5.57, 5.41%. $C_6H_6O_2$. Calculated: C 65.45; H 5.45%.

6-p-Nitrophenyl-2H-pyran-2-one. A mixture of 2 g of 5,5-dichloro-4'-nitro-2,4-pentadienophenone, 15 ml of glacial acetic acid, and 1 ml of concentrated phosphoric acid was boiled for 17 h. It was then poured into water, and the precipitate formed was filtered off, washed with water, and dried. We obtained 1.51 g of 6-p-nitrophenyl-2H-pyran-2-one, m.p. 190-191° (from alcohol). Found: C 61.01, 61.08; H 3.22, 3.24%. $C_{11}H_7O_4$. Calculated: C 60.83; H 3.25%.

6-m-Nitrophenyl-2H-pyran-2-one. A mixture of 2 g of 5,5-dichloro-3'-nitro-2,4-pentadienophenone, 25 ml of glacial acetic acid, and 1.5 ml of concentrated phosphoric acid was boiled for 17.5 h. It was then poured into water, and the precipitate formed was filtered off, washed with water, and dried. We obtained 1.5 g (93%) of 6-m-nitrophenyl-2H-pyran-2-one, m.p. 160-161.5° (from alcohol). Found: C 60.79, 60.80; H 3.24, 3.29%. $C_{11}H_7O_4$. Calculated: C 60.83; H 3.25%.

6-(2-Thienyl)-2H-pyran-2-one. A mixture of 1 g of 5,5-dichloro-1-(2-thienyl)-2,4-pentadien-1-one, 15 ml of glacial acetic acid, and 1 ml of concentrated phosphoric acid was boiled for 14 h. It was then poured into water, and the precipitate formed was filtered off, washed with water, and dried. We obtained 0.6 g (80%) of 6-(2-thienyl)-2H-pyran-2-one, m.p. 79.5-80° (from a mixture of petroleum ether and heptane). Found: C 60.91, 61.18; H 3.28, 3.39%. $C_9H_6O_2S$. Calculated: C 60.68; H 3.39%.

6-(2-Naphthyl)-2H-pyran-2-one. A mixture of 1 g of 5,5-dichloro-2,4-pentadieno-2'-acetonaphthone, 15 ml of acetic acid, and 1 ml of concentrated phosphoric acid was boiled for 15 h. It was then poured into water, and the precipitate formed was filtered off, washed with water, and dried. We obtained 0.8 g of 6-(2-naphthyl)-2H-pyran-2-one, m.p. 133.5-134° (from alcohol). The literature [6] gives m.p. 133.5-134.5°. Found: C 80.56, 80.52; H 4.53, 4.56%. $C_{15}H_{10}O_2$. Calculated: C 81.07; H 4.53%.

5-Acetyl-6-methyl-2H-pyran-2-one. 1.15 g of 3-acetyl-6,6-dichloro-3,5-hexadien-2-one was boiled in 10 ml of glacial acetic acid for 18 h. Acetic acid was vacuum-distilled off and we obtained 0.84 g of 5-acetyl-6-methyl-2H-pyran-2-one, m.p. 87-88° (from heptane). Found: C 62.96, 63.22; H 5.21, 5.21%. $C_8H_8O_3$. Calculated: C 63.15; H 5.30%.

We prepared the 2,4-dinitrophenylhydrazone of 5-acetyl-6-methyl-2H-pyran-2-one, m.p. 228-229° (from glacial acetic acid). Found: N 17.04, 16.88%. $C_{14}H_{12}N_4O_6$. Calculated: N 16.85%.

6-(2-Furyl)-2H-pyran-2-one. A mixture of 0.9 g of 5,5-dichloro-1-(2-furyl)-2,4-pentadien-1-one, 15 ml of acetic acid, and 1 ml of concentrated phosphoric acid was boiled for 15 h. We obtained 0.5 g of 6-(2-furyl)-2Hpyran-2-one, m.p. 92-93° (from heptane). Found: C 66.16, 66.41; H 3.71, 3.64%. $C_9H_6O_3$. Calculated: C 66.66; H 3.72%.

6-Styryl-2H-pyran-2-one. A mixture of 1.1 g of 7,7-dichloro-1-phenyl-1,4,6-heptatrien-3-one, 25 ml of glacial acetic acid, and 1 ml of concentrated phosphoric acid was boiled for 10 min. We obtained 0.85 g of 6-styryl-2H-pyran-2-one, m.p. 113.5-114.5° (from aqueous alcohol). Found: C 78.46, 78.69; H 5.04, 5.07%. $C_{13}H_{10}O_2$. Calculated: C 78.77; H 5.08%.

6-Phenyl-2H-pyran-2-one. a) A mixture of 5 g of 3,3-dichloroacrolein, 5.8 g of acetophenone, and 15 ml of glacial acetic acid was saturated with dry hydrogen chloride for 45 min at 0° and then left for 12 h at room temperature. 1 ml of concentrated phosphoric acid was added, and the reaction mixture was boiled for 14 h and then poured into water. The oil that separated was extracted with ether, and the ether extract was washed with sodium bicarbonate solution and with water. The extract was dried over sodium sulfate; ether was driven off; and from the residue we obtained 4.1 g (60%) of 6-phenyl-2H-pyran-2-one, m.p. 67° (from heptane).

b) A mixture of 10 g of 1,1,3-trichloro-3-ethoxypropene, 6.4 g of acetophenone, and 15 ml of aqueous acetic acid was left for 48 h at room temperature. 2 ml of concentrated phosphoric acid was added, and the reaction mixture was boiled for 13 h. We obtained 4 g (44%) of 6-phenyl-2H-pyran-2-one, m.p. 67° (from heptane).

6-p-Nitrophenyl-2H-pyran-2-one. A mixture of 5 g of 1,1,3-trichloro-3-ethoxypropene, 4.3 g of 4'nitroacetophenone, 15 ml of aqueous acetic acid, and 1 ml of concentrated phosphoric acid was boiled for 16 h. We obtained 2.1 g of 6-p-nitrophenyl-2H-pyran-2-one, m.p. 190-191° (from alcohol).

SUMMARY

1. For the preparation of the dichloro dienic ketones $RCOC(R') = CH - CH = CCl_2$, instead of 3,3-dichloroacrolein, a 3-alkoxy-1,1,3-trichloropropene or 3-alkoxy-1,1,1,3-tetrachloropropane can be used.

2. 6-Substituted 2H-pyran-2-ones can be prepared from 3,3-dichloroacrolein or its "chloroacetals" in one stage without isolation of the corresponding dichlorodienic ketones.

LITERATURE CITED

1. L. I. Zakharkin and L. P. Sorokina, Izv. AN SSSR. Otd. khim. n. 1958, 1445.
2. L. I. Zakharkin and L. P. Sorokina, Izv. AN SSSR. Otd. khim. n. 1962, 287.
3. L. I. Zakharkin and L. P. Sorokina, Izv. AN SSSR. Otd. khim. n. 1962, 2096.
4. A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, Dokl. AN SSSR 97, 91 (1954).
5. M. Julia and J. Bullot, Bull. Soc. Chim. 1960, 28.
6. M. Julia and J. Bullot, Bull. Soc. Chim. 1960, 23.
