RESEARCH ON UNSATURATED LACTONES

XXV.* REACTION OF 3-ACETYL-Δ^3-BUTENOLIDES WITH PHOSPHORUS PENTACHLORIDE

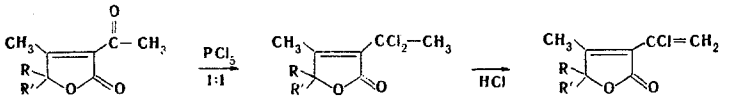
A. A. Avetisyan, A. N. Dzhandzhapanyan, L. E. Astsatryan, and M. T. Dangyan

UDC 547.722.724:542.944.1:543.422.4

Chloroalkenes are obtained in 55-70% yields in the reaction of equimolar amounts of 3-acyl-Δ^3-butenolides with phosphorous pentachloride; dichloroalkenes are formed in the presence of a twofold excess of phosphorus pentachloride. The ability of chloroalkenes to undergo polymerization is shown.

It is known that 2-chloroalkenylphosphorus tetrachlorides are formed in addition to gem-dichloroalkanes and chloroalkenes in the reactions of phosphorus pentachloride with ketones; this is explained by phosphorylation of the chloroalkenes obtained [2, 3].

A study of the reaction of 3-acetyl-Δ^3-butenolides with phosphorus pentachloride showed that the only reaction products in the presence of equimolar amounts of the starting components are chloroalkenes, which



I–III IV–VI

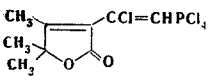
I, IV R=R′=CH$_3$ II, IV R=CH$_3$, R′=C$_2$H$_5$, III, VI R–R′=(CH$_2$)$_5$

are obtained in 55-70% yields. The chloroalkenes are not phosphorylated, apparently because of the absence of excess PCl_5.

3-(α,β-Dichlorovinyl)-4,5,5-trimethyl-Δ^3-butenolide (VII) is obtained in 56% yield in the reaction of I with a twofold excess of phosphorus pentachloride.

The characteristic frequencies of the absorption of the carbonyl group of an unsaturated γ-lactone at 1760 cm^{-1} and of a conjugated double bond at 1645-1650 cm^{-1} are found in the IR spectra of the compounds obtained (IV-VII).

The production of a dichloroalkene in the indicated reaction is evidently a consequence of destruction of the intermediate phosphorus-containing product (VIII); this was also previously noted by Fokin and coworkers [2].



VIII

Dichloro derivative VII is also obtained in the reaction of butenolide IV with an equimolar amount of phosphorus pentachloride.

*See [1] for communication XXIV.

Yerevan State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 310-311, March, 1974. Original article submitted March 26, 1973.

The 3-(α-chlorovinyl)-Δ^3-butenolides that we synthesized polymerize and undergo copolymerization reactions with vinyl monomers in the presence of free-radical initiators. Thus, for example, we subjected 3-(α-chlorovinyl)-4,5,5-trimethyl-Δ^3-butenolide to homopolymerization and copolymerization with acrylonitrile and methyl acrylate in the presence of 2,2'-azobisisobutyronitrile (AIBN). The resulting homopolymer and copolymers differ from one another with respect to their solubilities and appearance.

Bands of the absorption of the CO group of a five-membered lactone ring at 1745-1760 cm^{-1} and absorption at 1650-1660 cm^{-1} are found in the IR spectra of the polymers. The IR spectrum of the copolymer with acrylonitrile also contains an absorption band at 2244 cm^{-1}, which is characteristic for the C $\equiv$ N bond.

EXPERIMENTAL

The IR spectra of mineral oil suspensions were recorded with an IKS-14 spectrometer.

Reaction of 3-Acetyl-4,5,5-trimethyl-Δ^3-butenolide (I) with Phosphorus Pentachloride. A) An 11.9 g (0.06 mole) sample of PCl_5 was added in small portions with stirring to a solution of 10.08 g (0.06 mole) of butenolide I in 40 ml of absolute benzene, after which the reaction mixture was refluxed at 40-50° until the PCl_5 had dissolved completely (30 min). The benzene was removed by distillation, and the residue was vacuum distilled to give 7.75 g (70%) of butenolide IV with bp 116-119° (3 mm) and n_D^{20} 1.4990. Found: C 57.5; H 6.1; Cl 19.4%. $C_9H_{11}ClO_2$. Calculated: C 57.9; H 5.9; Cl 19.0%.

B) A 21 g (0.1 mole) sample of PCl_5 was added in small portions with stirring to a solution of 8.5 g (0.05 mole) of I in 40 ml of absolute benzene. The reaction mixture was then heated at 45° for 6-7 h. The benzene was removed by distillation, and the residue was vacuum distilled twice. The fraction with bp 86-92° (1 mm) was collected and recrystallized to give 4.9 g (44.5%) of butenolide VII with mp 62-63° (from petroleum ether). Found: C48.4; H 4.5; Cl 31.8%. $C_9H_{10}Cl_2O_2$. Calculated: C 49.0; H 4.6; Cl 32.1%.

3-(α-Chlorovinyl)-4,5-dimethyl-5-ethyl-Δ^3-butenolide (V). A 5.95 g (0.03 mole) sample of PCl_5 was added with stirring to a solution of 5.46 g (0.03 mole) of butenolide II in 20 ml of absolute benzene, after which the reaction mixture was heated at 50° for 45 min. The benzene was then removed by distillation, and the residue was washed with water to remove the phosphorus oxychloride and unchanged PCl_5. The reaction product was extracted with ether and dried with magnesium sulfate. The ether was removed, and the residue was vacuum distilled to give 3.28 g (55%) of V with bp 94-96° (1 mm) and n_D^{20} 1.4950. Found: C 59.9; H 6.9; Cl 17.1%. $C_{10}H_{13}ClO_2$. Calculated: C 59.8; H 6.5; Cl 17.7%.

3-(α-Chlorovinyl)-4-methyl-5,5-pentamethylene-Δ^3-butenolide (VI). Similarly, 6.24 g (0.03 mole) of III in 40 ml of absolute benzene and 5.95 g (0.03 mole) of PCl_5 gave 3.94 g (59%) of butenolide VI with mp 74° (from acetone). Found: C 63.1; H 4.1; Cl 16.0%. $C_{12}H_{15}ClO_2$. Calculated: C 63.5; H 4.4; Cl 16.1%.

3-(α,β-Dichlorovinyl)-4,5,5-trimethyl-Δ^3-butenolide (VII). A 5.95 g (0.03 mole) sample of PCl_5 was added to a solution of 5.04 g (0.03 mole) of IV in 30 ml of absolute benzene, after which the reaction mixture was heated at 60-70° for 6-7 h. The benzene was removed by distillation; the residue was vacuum distilled twice. The fraction with bp 86-90° (1 mm) was collected and recrystallized to give 3.85 g (58%) of a substance with mp 62-63° (from hexane); no melting-point depression was observed for a mixture of a sample of this product with dichloralkene VII.

Polymerization of 3-(α-Chlorovinyl)-4,5,5-trimethyl-Δ^3-butenolide. A 1 g (5.4 mmole) sample of butenolide I and 0.0088 g (1 mole %) of AIBN were placed in an ampule, and the mixture was heated in a thermostat at 80° for 10 h. The resulting polymer was purified by dissolving in chloroform and reprecipitation with ether. A viscous brown mass was obtained in 34.7% yield. Found: Cl 18.3%. $C_9H_{11}ClO_2$. Calculated: Cl 19.0%.

Copolymerization of I with Acrylonitrile and Methyl Acrylate. This reaction was also carried out in the presence of 1 mole % AIBN in sealed ampules at 80° for 10 h. The copolymers were taken in equimolar amounts. The copolymer with acrylonitrile was purified by reprecipitation with ether from acetone solutions to give a white powder with mp 228-232° (dec.) in 32.3% yield. The copolymer with methyl acrylate was precipitated by CCl_4 from dimethylformamide solutions and was obtained as yellow crystals with mp 220-225° (dec.) in 29% yield.

LITERATURE CITED

1. A. A. Avetisyan, K. G. Akopyan, and M. T. Dangyan, Khim. Geterotsikl. Soedin., 1604 (1973).
2. A. V. Fokin, A. M. Kolomiets, and V. S. Shchennikov, Zh. Obshch. Khim., 42, 801 (1972).
3. K. N. Anisimov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 803 (1954).