

SHORT
COMMUNICATIONS

2-Chlorovinyl 1,1-Dichloroethyl Ketone from 2-Chloropropionyl Chloride and 1,2-Dichloroethene

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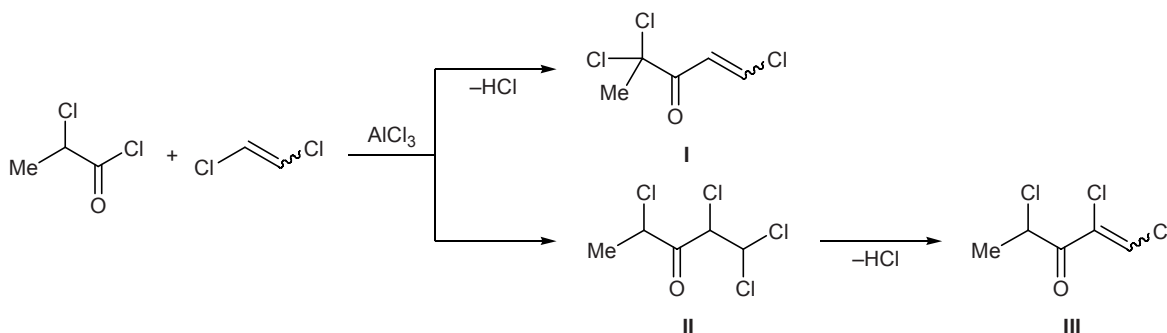
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We recently found [1, 2] that chloroacetyl chloride reacts with 1,2-dichloroethylene in the presence of AlCl_3 to give an unexpected product, dichloromethyl 2-chlorovinyl ketone. In contrast, aliphatic carboxylic acid chlorides and dichloroacetyl chloride were reported [3, 4] to react with 1,2-dichloroethylene under analogous conditions with formation of alkyl 1,2-dichlorovinyl ketones and 1,2-dichlorovinyl dichloromethyl ketone, respectively. In continuation of our studies on the chemistry of highly reactive 2,2-, 1,2-, and 2-chlorovinyl chloroalkyl ketones [5] we examined the reaction of 2-chloropropionyl chloride with 1,2-dichloroethylene with a view to elucidate the mechanism of reactions of α -chloroalkanoyl chlorides with 1,2-dichloroethylene. We found that 2-chloropropionyl chloride reacts with commercially available mixture of *cis*- and *trans*-1,2-dichloroethylenes (a large-scale chemical product) under the conditions described in [1–4] along two concurrent pathways. The first of these unexpectedly led to the formation of 49% of previously unknown 1,1-dichloroethyl 2-chlorovinyl ketone, while the second was the known process leading to diastereoisomeric 1-chloroethyl 1,2,2-trichloroethyl ketones **II** and 1-chloroethyl 1,2-dichlorovinyl

ketone (**III**) at a ratio of 69:13; here, compound **III** is formed as a result of thermal dehydrochlorination of ketone **II** [3, 4].

The mechanism of formation of 1,1-dichloroethyl 2-chlorovinyl ketone (**I**) from 1,2-dichloroethylene and 2-chloropropionyl chloride, which involves chlorotropic rearrangement, is not completely clear. The product structure suggests that the mechanism proposed by us previously for the formation of dichloromethyl 2-chlorovinyl ketone [2] from chloroacetyl chloride and 1,2-dichloroethylene is not operative here. Saturated ketone **II** failed to undergo transformation into 2-chlorovinyl ketone **I** on heating in the presence of aluminum chloride.

1,4,4-Trichloropent-1-en-3-one (I). A mixture of 18.7 g (0.14 mol) of AlCl_3 , 17.74 g (0.14 mol) of 2-chloropropionyl chloride, and 30 ml of 1,2-dichloroethylene was heated for 6–8 h at the boiling point. The mixture was then cooled and poured onto ice. The organic phase was separated, the aqueous phase was extracted with methylene chloride, the extracts were combined with the organic phase, dried over CaCl_2 , and filtered, the solvent was distilled off, and the residue was distilled under reduced pressure, a fraction



with bp 75–82°C (40 mm) being collected. Yield 12.81 g (49%). IR spectrum, ν , cm^{-1} : 1592 (C=C); 1707 (C=O); 2940, 2963, 3001 (CH_3); 3062, 3080 (=C–H). ^1H NMR spectrum (CDCl_3), δ , ppm: 2.19 s (3H, CH_3), 7.22 d (1H, =CHCO, $J = 13.3$ Hz), 7.53 d (1H, =CHCl). ^{13}C NMR spectrum, δ_{C} , ppm: 31.25 (CH_3), 83.74 (CCl_2), 125.41 (=CHCO), 140.61 (=CHCl), 184.19 (C=O). Found, %: C 32.33; H 2.76; Cl 56.30. $\text{C}_3\text{H}_5\text{Cl}_3\text{O}$. Calculated, %: C 32.04; H 2.69; Cl 56.74.

1,1,2,4-Tetrachloropentan-3-one (II). The procedure was the same as above. After distillation of ketone I, a fraction with bp 86–105°C (40 mm) was collected. Its amount was 6.93 g (60%), and it contained two diastereoisomers of ketone II, 15% of ketone III, and 25% of compound I. Compound II: IR spectrum, ν , cm^{-1} : 1592 (C=C); 1707 (C=O); 2940, 2963, 3001 (CH_3CH); 3062, 3080 (=C–H). ^1H NMR spectrum (CDCl_3), δ , ppm: major diastereoisomer: 1.70 d (3H, CH_3 , $J = 6.87$ Hz), 4.64 q (1H, CH_3CH), 5.02 d (1H, COCH, $J = 8.54$ Hz), 5.97 d (1H, CHCl_2); minor diastereoisomer: 1.63 d (3H, CH_3 , $J = 6.72$ Hz), 4.79 q (1H, CH_3CH), 5.11 d (1H, COCH, $J = 7.71$ Hz), 6.07 d (1H, CHCl_2). ^{13}C NMR spectrum, δ_{C} , ppm: major diastereoisomer: 20.25 (CH_3), 57.50 (CH_3CH), 61.37 (COCH), 70.29 (CCl_2), 195.41 (C=O); 18.93 (CH_3), 54.38 (CH_3CH), 61.55 (CHCl), 69.54 (Cl_2CH), 193.70 (C=O).

1,2,4-Trichloropent-1-en-3-one (III) was characterized by ^1H NMR data (from the spectrum of the product mixture, CDCl_3), δ , ppm: 1.71 d (3H, CH_3 , $J = 6.82$ Hz), 4.79 q (1H, CH_3CH), 7.67 s (1H, =CHCl).

REFERENCES

1. Bozhenkov, G.V., Savosik, V.A., Rudyakova, E.V., Mirskova, A.N., and Levkovskaya, G.G., *Russ. J. Org. Chem.*, 2008, vol. 44, p. 146.
2. Bozhenkov, G.V., Savosik, V.A., Rudyakova, E.V., Kha Kuok Khan', Albanov, A.I., Klyba, L.V., Mirskova, A.N., and Levkovskaya, G.G., *Russ. J. Org. Chem.*, 2008, vol. 44, p. 1745.
3. Bozhenkov, G.V., Levkovskaya, G.G., Larina, L.I., Ushakov, P.E., Dolgushin, G.V., and Mirskova, A.N., *Russ. J. Org. Chem.*, 2004, vol. 40, p. 1583.
4. Prins, H.J. and Haring, H.G., *Recl. Trav. Chim. Pays-Bas*, 1954, vol. 73, p. 479; *Chem. Abstr.*, 1955, vol. 49, p. 12265b.
5. Kochetkov, N.K., *Usp. Khim.*, 1955, vol. 24, p. 32; Pohland, A.E. and Benson, W.R., *Chem. Rev.*, 1966, vol. 66, p. 161; Levkovskaya, G.G., Bozhenkov, G.V., and Mirskova, A.N., *Izbrannye metody sinteza i modifikatsii geterotsiklov* (Selected Methods of Synthesis and Modification of Heterocycles), Kartsev, V.G., Ed., Moscow: IBS, 2003, vol. 2, p. 284; Moiseev, I.K., Makarova, N.V., and Zemtsova, M.N., *Izv. Vyssh. Uchebn. Zaved., Ser. Khim. Khim. Tekhnol.*, 2007, vol. 59, no. 8, p. 3.