Chlorination with Sulfuryl Chlorofluoride and Mechanism of the Chlorination of Cyclohex-2-enones with Sulfuryl Chloride

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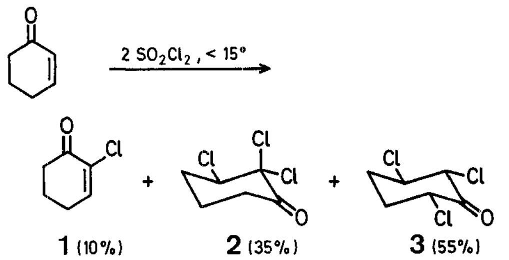
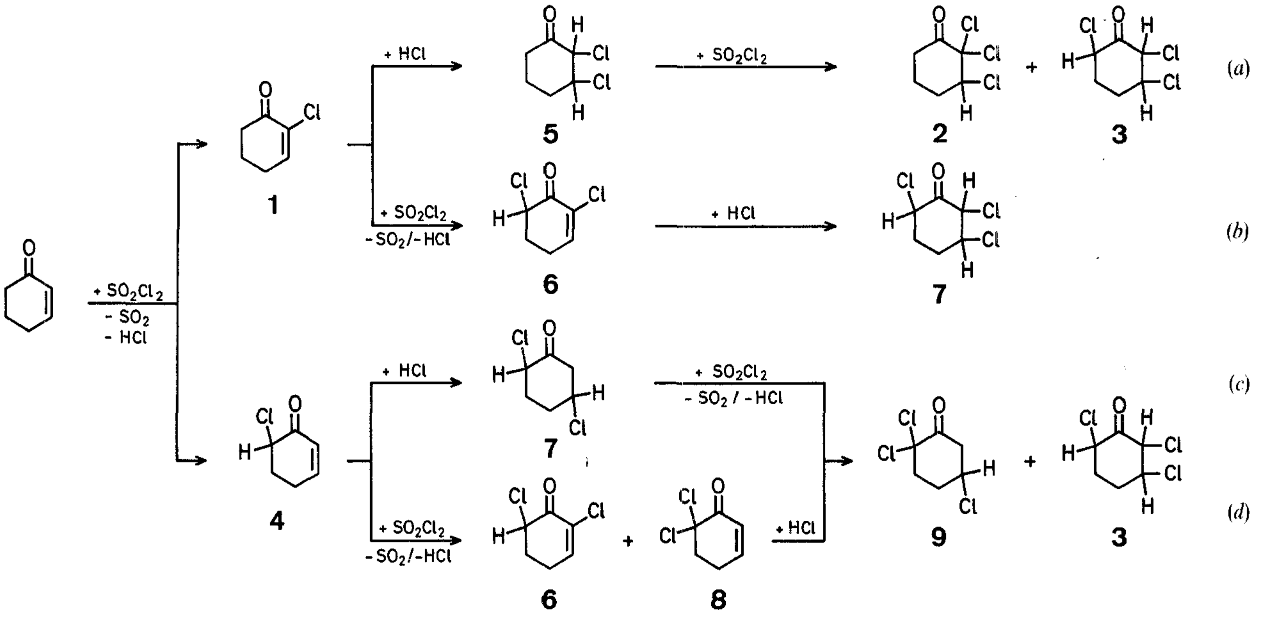
Cycloalkanones react with sulfuryl chloride to give almost exclusively α-chlorination products[1]. The reaction of cyclohexene with sulfuryl chloride proceeds, under appropriate conditions, with addition of chlorine to the C=C double bond[2]. In the present communication, we report the reaction of cyclohexen-2-ones with sulfuryl chloride and sulfuryl chlorofluoride. A mechanism is discussed.

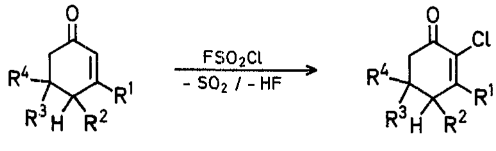
The overall reaction of unsubstituted cyclohex-2-enone with sulfuryl chloride (2 equiv) can be formulated as follows. The steric structure of the products has been established[3, 5].



Four reaction pathways (*a–c*) consisting of chlorination and HCl-addition steps may be discussed. Of these pathways, (*c*) and (*d*) can be excluded since compound **4** could not be isolated from the reaction of cyclohexenone with sulfuryl chlorofluoride (1 equiv); instead, compound **1** was obtained in high yield. Pathway (*b*) can be excluded since the only compound obtained from **1** and sulfuryl chloride (1 equiv) was **6**, and HCl addition to **6** failed. On the other hand, HCl addition to compound **1** gave **5**. Thus, the reaction may be assumed to proceed exclusively via pathway (*a*).



As mentioned above, cyclohexenone reacts with sulfuryl chlorofluoride to give exclusively 2-chloro-3-oxocyclohexene (**1**). The reaction was also carried out with substituted cyclohexenones and was found to represent a useful method for the preparation of compounds of the type **1**.



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The hydrogen fluoride formed in this reaction[4] did not add to the C=C double bond of **1**. Thus, sulfuryl chlorofluoride is an efficient chlorinating agent under the conditions described here.

Reaction of 3-Oxocyclohexenes with Sulfuryl Chlorofluoride; General Procedure:

Sulfuryl chlorofluoride (Research Inorganic Chemical; 17.7 g, < 1 equiv) is added dropwise to a stirred solution of the 3-oxocyclohexene (0.1 mol) in dichloromethane (100 ml) and dioxan (50 ml). During the addition, the temperature of the reaction mixture is kept at 15° by external cooling. The resultant mixture is washed with dilute aqueous sodium hydrogen carbonate and with water, the solvent is removed in vacuo, and the residue is distilled in vacuo. The product **1** is purified by column chromatography on silica gel using ether/petroleum ether as eluent.

Reaction of 3-Oxocyclohexenes with Sulfuryl chloride:

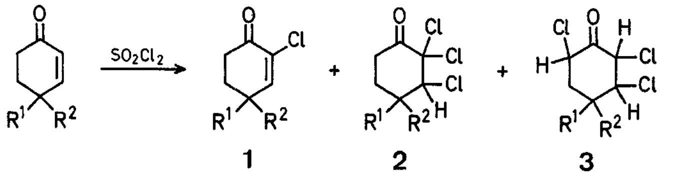
A solution of sulfuryl chloride (29.15 g, 0.245 mol) is added dropwise to a stirred solution of the cyclohexenone (0.125 mol) in dichloromethane (5 ml) and dioxan (9 ml). The temperature of the reaction mixture is held at 15° by external cooling. The resultant mixture is washed with dilute sodium hydrogen carbonate and with water, the solvent is removed in vacuo, and the residue is distilled in vacuo. The mixture of **1**, **2**, and **3** thus obtained is separated by column chromatography using ether/petroleum ether (1 : 1) as eluent.

Table 1. 2-Chloro-3-oxocyclohexenes (**1**) from 3-Oxocyclohexenes and Sulfuryl Chlorofluoride

R^1	R^2	R^3	R^4	Yield [%]	m.p.	Brutto formula[a]	I.R. (CCl_4) $\nu_{C=O}$ [cm^{-1}]
H	H	H	H	70	72°	C_6H_7ClO (130.6)	
H	CH_3	H	H	65	99°	C_7H_9ClO (144.6)	1701
CH_3	H	CH_3	CH_3	75	115°	$C_9H_{13}ClO$ (172.6)	1708
H	t-C_4H_9	H	H	50	122°	$C_{10}H_{15}ClO$ (186.7)	1705

[a] All compounds gave satisfactory elemental analyses (C, H, Cl).

Table 2. Chlorinated Cyclohexanones (**2**, **3**) from 3-Oxocyclohexenes and Sulfuryl Chloride



R^1	R^2	Total Yield [%]	Products	m.p.	Brutto formula[a]	I.R. (CCl_4) $\nu_{C=O}$ [cm^{-1}]	U.V. λ_{max} [nm]
H	H	45	10% **1**	72°	C_6H_7ClO (130.6)	1700	
			35% **2**	53°	$C_6H_7Cl_3O$ (201.5)	1752	294 (acetonitrile)
			55% **3**	112°	$C_6H_7Cl_3O$ (201.5)	1739–1753, 1792	276 (acetonitrile)
CH_3	H	35	2% **2**	53°	$C_7H_9Cl_3O$ (215.5)	1753	294 (CCl_4)
			95% **3**	84–85°	$C_7H_9Cl_3O$ (215.5)	1741	329 (CCl_4)
CH_3	CH_3	55	15% **2**	104–105°	$C_8H_{11}Cl_3O$ (227.5)	1753	293 (hexane)
			85% **3**	109–110°	$C_8H_{11}Cl_3O$ (227.5)	1810, 1783, 1757	286 (hexane)

[a] All compounds gave satisfactory elemental analyses (C, H, Cl).

2,3-Dichlorocyclohexanone (5):

Dry hydrogen chloride is bubbled through a solution of 3-oxocyclohexene (9.62 g, 0.1 mol) in chloroform (100 ml) at room temperature. After ~ 1 h, the mixture is saturated with hydrogen chloride. It is then washed with dilute aqueous sodium hydrogen carbonate, dried with magnesium sulfate, and concentrated while cooling (< 10°). The residue is chromatographed on silica gel (eluent: carbon tetrachloride) to separate 2,3-dichlorocyclohexanone from the starting ketone. The 2,3-dichlorocyclohexanone has to be stored in solution (carbon tetrachloride or chloroform) at −25°; yield: 35%; m.p. 35°.

Similarly was obtained:

3-Chlorocyclohexanone; yield: 82%.

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