

New, optimized preparation of 1,2-dichlorocyclobuten-3,4-dione (C₄O₂Cl₂) from squaric acid and oxalyl chloride

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Received 2 October 2006; revised 14 March 2007; accepted 16 March 2007

Available online 21 March 2007

Abstract—1,2-Dichlorocyclobuten-3,4-dione, a key intermediate in the chemistry of cyclobutenes and their derivatives is obtained by the dimethylformamide catalyzed reaction of squaric acid and oxalyl chloride. The process was optimized by using guidelines from thermodynamics, transport properties, and experimental observations, and gives nearly quantitatively a product which can be easily brought to very high purity.

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1,2-Dichlorocyclobuten-3,4-dione (squaric acid dichloride, **1**) is one of the key substances in the rich chemistry of the cyclobutenes, and the products which start from them.¹ A number of its molecular properties in the solid, solution, and gas phase have been measured and analyzed.² **CAUTION:** dangerous by inhalation or penetration through the skin.³

It was first prepared by heating 1,2,3,3-tetrachlorocyclobuten-4-one (lachrymator, liquid at room temperature, mp 20 °C, nbp 176 °C, **2**) with oleum. The procedure had a rather low yield (40%) and the product contained unreacted **2**, which could be largely eliminated by extraction and crystallization from petroleum ether.⁴ We found that to get **1** with a purity of at least 99.9% from the product of this reaction the best procedure consisted of several crystallizations from cyclohexane, and then sublimation at reduced pressure, because **2** is less volatile than **1**.² This awkward process was used because the most logical precursor to **1**, the commercially available 1,2-dihydroxycyclobuten-3,4-dione or squaric acid **3**, does not react with the common reagents used for the preparation of acid chlorides in the absence of a catalyst.⁵ A detailed study on catalysts for the preparation of acid chlorides using SOCl₂ was overlooked.⁶

Indeed, such reaction channel could be opened by the basic catalyst dimethylformamide (henceforth DMF)⁷ and thionyl chloride SOCl₂, allowing an easy, higher yield preparation of **1**,⁸ but the product still contains a substantial fraction of **2**: To get pure **1** using this route it is necessary to follow the cumbersome purification indicated above. Overall, the procedure is very time consuming. Furthermore, a recent publication⁹ reports the formation of tarry material, which we did not find in the present procedure.

A long known¹⁰ alternative to SOCl₂ for the preparation of acid chlorides is oxalyl chloride (mp –16 °C, nbp 63.5 °C, *d*²⁰ 1.478, vapor pressure at 20 °C ≈ 150 Torr;¹¹ **CAUTION:** dangerous similarly to **1**, see above, easily and safely handled using a new container);¹² a cursory indication of reaction of **3** with oxalyl chloride is given in a patent.¹³

Having the need for gram quantities of pure **1** for an investigation of possible new oxocarbons, we decided to try the preparation of squaric acid chloride from squaric acid and oxalyl chloride, as an alternative to the optimization of the procedure using SOCl₂, which comprises at least two stoichiometrically independent reactions. Below some underpinnings and the results of the new process are given.

Squaric acid **3** is a monoclinic solid,¹⁴ mp >300 °C, vapor pressure at room temperature below 10^{–6} mbar,¹⁵ soluble only in more or less basic, hydrogen-bond forming solvents. If literature results concerning the reaction

Keywords: 1,2-Dichlorocyclobuten-3,4-dione; Oxalyl chloride; Cyclobutenes; Catalysis by dimethylformamide; Acyl halides; Reactive intermediates.

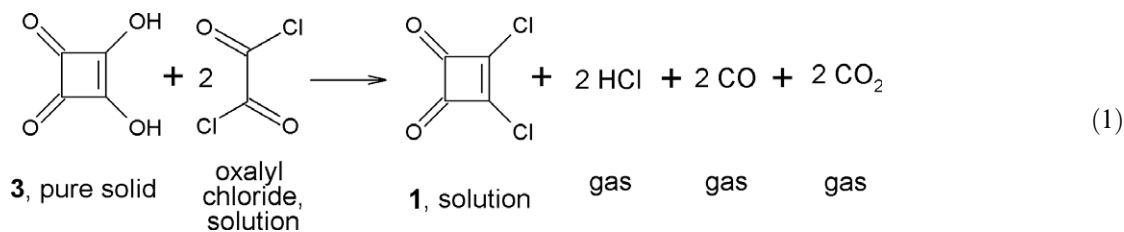
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of oxalyl chloride with phenols and/or monobasic carboxylic acids were applicable to the DMF catalyzed reaction of the peculiar, bibasic squaric acid, several products could be formed, among which are (1) squaric acid chloride **1**; (2) squaric acid monochloride; (3) squaric acid anhydrides; (4) mixed anhydrides of squaric and oxalic acid; (5) 1,2,3,3-tetrachlorocyclobuten-4-one **2**; (6) phosgene by decomposition of oxalyl chloride.¹⁶ But at temperatures slightly higher than room temperature, atmospheric pressure and in the presence of catalytic quantities of DMF preliminary experiments gave good yields of apparently only **1**. To try optimization of the procedure we then analyzed the gaseous, liquid and solid phases of several samples during and at the end of the reaction carried out under different conditions by means of IR spectrometry.

In the gas phase we detected only HCl, CO, CO₂, the solvent (when used), traces of **1** and oxalyl chloride; the latter disappeared in the last gases evolved. No phosgene was ever detected.

In the liquid phase after evolution of gas had ended only **1** and the solvent were found; no **2**, phosgene nor other species.

The solid phase at the end of the procedure consisted of **3** wetted by a weight slightly higher than that of the DMF of a yellow oil (soluble in CH₂Cl₂, water and acetonitrile) where squaric acid monochloride was not detected.¹⁷ These results indicated a very new convenient method to prepare pure squaric acid chloride, because under the above conditions the chemical reaction of **3** and oxalyl chloride is described to an approximation over 99% by the single stoichiometric equation



which shows that oxalyl chloride might be more efficient¹⁸ than SOCl₂, because each mole forms three rather than two moles of gaseous products and hence brings about a higher entropy increase. The necessity of heating to maintain the chosen, fixed reaction temperature is compatible with an endothermic or slightly exothermic process that did not show tendency to get out of control.

Thermodynamically, reaction (1) can be considered an heterogeneous reaction,¹⁹ where the gas and solid phases have substantially and, respectively, rigorously fixed composition from the beginning to the end of the reaction. Then an approximate equilibrium constant can

be given by the ratio of the mole fraction of **1** and the squared mole fraction of oxalyl chloride, $K_x \approx x(\mathbf{1})/x^2$ (oxalyl chloride).

The lack of oxalyl chloride in the final liquid phase further reveals that (1) is a substantially quantitative reaction. The reported yield of the preparation is lower than quantitative with respect to oxalyl chloride because part of it is carried away by the gases produced, especially initially, when its mole fraction in the liquid phase is high.

Temperature of the reaction: The reaction is slow at room temperature; a temperature of 50 °C allows a sufficient speed, is lower than the boiling point of oxalyl chloride and higher than the freezing point of **1** in the reacting system. This temperature reduces the quantity of oxalyl chloride in the unreactive gas phase and avoids hampering the contact between **3** and oxalyl chloride by possible separation of solid **1**.

Solvent: CCl₄, CH₂Cl₂, and the reagent oxalyl chloride were used.

CCl₄ (CAUTION: acutely and chronically toxic and possibly a carcinogen)²⁰ permits easy separation of the compounds originating from DMF and subsequently of **1** by evaporation. Room temperature evaporation of the solution under vacuum causes some transfer of **1** to the distillate, which can be minimized by first separating solid **1** from the solution by cooling²¹ and then evaporating under vacuum the cool solution.

CH₂Cl₂ keeps in solution the substances originating from DMF, hindering their separation and gives very

concentrated solutions of **1** from which the latter crystallizes with difficulty.

Oxalyl chloride is now solvent and reagent, whose concentration in this case is the highest possible, with potential advantages for the reaction speed and yield, which however were not observed. Using this variant, there is a larger removal of oxalyl chloride by the evolved gases and sublimations become necessary to remove the products presumably formed from DMF.

Analysis of the products by IR spectrometry: The spectra were recorded by means of a Bruker IFS 66v/S Fourier

transform vacuum spectrometer. Resolution 2 cm^{-1} , 16 scans, apodization function three-term Blackman–Harris. Using a demountable, variable thickness vacuum-tight cell with ZnSe windows for liquids and mulls of solids,²² and a 200 mm long cell with NaCl windows for gases. Concentrations and partial pressures were evaluated by comparison with archived or published spectra of the pure substances run under the same conditions.

Preparation of 1: Finely powdered **3** (1.140 g, 10 mmol), carbon tetrachloride (5 mL), DMF (40 μL), two magnetic stirring bars and four Pyrex glass balls of about 8 mm diameter were introduced into a 50 mL round-bottomed flask previously filled with nitrogen and connected to a reflux condenser²³ with exit-only gas valve. The mixture was frozen by immersion in liquid nitrogen vapors and oxalyl chloride (2.540 g = 1.720 mL, 20 mmol) was introduced at once through the condenser's outlet. Then the flask was allowed to warm to room temperature, agitation started at 300 rpm, and the flask was then lowered into an oil bath thermostatted to 50 °C. Regular gas evolution started immediately and was no more apparent after 50 min. After further 10 min, heating and agitation were discontinued, allowing cooling and decantation of the mixture.

The flask content was filtered through a sintered glass disk and washed two times with 1 mL of CCl_4 . The filtrate was cooled until it partially solidified and the liquid part evaporated in vacuum to a container cooled by liquid nitrogen. Then the pale yellow crystals were sublimed under vacuum, giving 1.300 g of product (mp 53 °C). The purity of this product was checked by comparing its IR spectrum in CCl_4 with that of the four-times sublimed squaric acid chloride used for the gas phase electron diffraction.^{2b} No differences were apparent.

The residue washed with methanol to remove substances presumably formed from DMF weighed about 20 mg and its IR spectrum as a paraffin oil mull showed it to be pure **3**.

Acknowledgments

The author gratefully acknowledges the contribution of two referees, one indicating redundant parts and the second proposing many language improvements. Financial support came from the ISMN of CNR, Sezione di Bologna; most of the IR measurements were carried out at the Laboratory of Infrared Spectrometry 'Fabio Roversi-Monaco' of the University of Bologna.

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