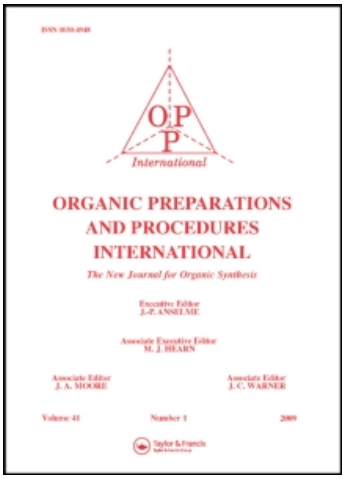

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IMPROVED PREPARATION OF 5,6-DICHLOROCYCLOHEX-2-ENE-1,4-DIONE

Vitor Francisco Ferreira[a]; Francis J. Schmitz[b]
[a] Departamento de Quimica Organica, Universidade Federal Fluminense, Rio de Janeiro, BRAZIL [b] Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK, USA

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IMPROVED PREPARATION OF 5,6-DICHLOROCYCLOHEX-2-ENE-1,4-DIONE

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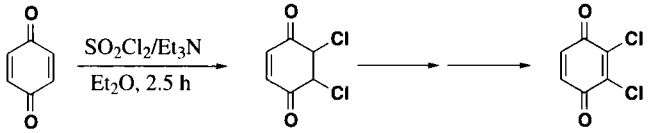
Vitor Francisco Ferreira[†] and Francis J. Schmitz[*††]

[†] *Departamento de Quimica Organica, Universidade Federal Fluminense Rio de Janeiro, 24020-150, BRAZIL*

[††] *Department of Chemistry and Biochemistry, University of Oklahoma Norman, OK 73072, USA*

5,6-dichlorocyclohex-2-ene-1,4-dione (**2**) is an intermediate used for the preparation of 2,3-dichlorobenzoquinone (**3**) which is an important dienophile[1,2] for the Diels-Alder reaction and has been used in the total synthesis of some important natural products.[3,4] The general procedures for the synthesis of **2** involve addition of either chlorine gas or sulfuryl chloride to benzoquinone (**1**).[5] Despite the convenience of using sulfuryl chloride, this procedure is reported to give poor yields,[3,5] and there are difficulties in reproducing the experimental results and controlling formation of the desired product.[6]

We have found that **2** can be obtained in quantitative yield and short reaction time from the reaction of benzoquinone (**1**) and sulfuryl chloride if the latter compound is treated with triethylamine immediately preceeding use. We speculate that the low yields and irreproducibility reported for this reaction earlier might be caused by the presence of traces of hydrochloric or chlorosulfonic acid in the sulfuryl chloride which promote tautomerization of **2** to 2,3-dichlorohydroquinol. Treatment of sulfuryl chloride with triethylamine removes any acids present.



1 **2** **3**

EXPERIMENTAL SECTION

^{1}H NMR spectra were recorded on a 300 MHz Varian Spectrometer. Chemical shifts are expressed in δ (ppm) downfield from TMS as internal standard. Reactions were carried out under positive pressure of dry nitrogen. Sulfuryl chloride, triethylamine and ether were freshly distilled.

Sulfuryl Chloride Treatment.- In a typical experiment, ether (6 mL) and then sulfuryl chloride (1 mL, 13.24 mmoles) were added *via* a syringe to a septum-capped centrifuge tube which had previously been flushed with nitrogen. Triethylamine [0.08 mL, 0.28 mmole (~2 mole%)] was added slowly to this mixture. After the addition was completed, the cloudy mixture was centrifuged for 1-2 minutes at high speed. The liquid phase was removed with a syringe and used in the reaction as described below.

5,6-Dichlorocyclohex-2-ene-1,4-dione (2).- To a stirred solution of benzoquinone (**1**, 600 mg, 5.56 mmole) in dry ether (14 mL) was added slowly with a syringe pump (3 mL/h) a solution of sulfuryl

chloride (1.0 mL, 13.24 mmoles) in ether (6 mL) which had previously been treated with triethylamine (0.08 mL, 0.28 mmole, see above). After the addition the mixture was stirred for an additional 30 min and the solvent was evaporated on a rotatory evaporator using first aspirator pressure and then a high vacuum to produce **2** as a very pale yellow solid in quantitative yield, mp. (crude) 143-145°, lit.,[5] 146.0-146.5°. The reaction was repeated several times starting with 300 mg, 600 mg and 1 g quantities of benzoquinone with proportionate changes in the other reagents and solvent; quantitative yields of essentially pure (NMR analysis) product were routinely obtained. The product was used in subsequent reactions without further purification. ^{1}H NMR ($CDCl_3$): δ 6.81 (s, 2H), 4.63 (s, 2H); ^{13}C NMR ($CDCl_3$); δ 187.0 (C=O), 137.4 (C=C), 57.9 (CHCl); LRMS (relative intensity) 180 (M^+ + 2; 5), 178 (M^+, 10), 143 (100), 145 (32), 89 (26), 82 (31), 87 (12), 54 (16).

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