

A New Route to Polychlorinated Cyclohexanediones

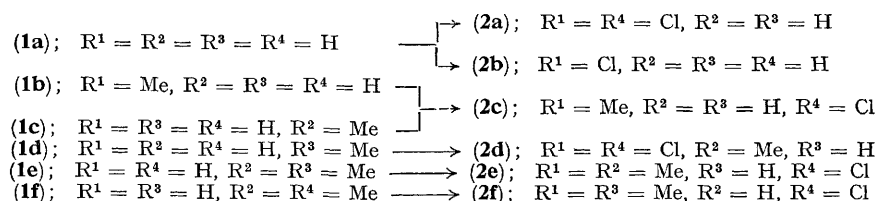
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Summary Cyclohexanone and its methyl derivatives react with a large excess of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to give polychlorinated cyclohexanediones in fairly good yields. **3,6,6-TRICHLOROCYCLOHEXANE-1,2-DIONE** has been synthesised from the reaction of cyclohexane-1,2-dione with chlorine,¹ but the direct synthesis of polychlorinated cyclo-

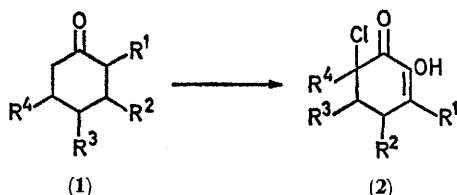
Starting materials

Products



M.p.s ($^{\circ}C$) and (isolated yields): (2a), 119—120 (53%); (2b), 98—100 (67%); (2c), 115—116 (70%); (2d) 119—121 (65%); (2e), 142—143 (61%); (2f) 107—109 (58%).

hexanedione derivatives from cyclohexanone and its methyl derivatives has not been reported.



We now report that cyclohexanone (1a) and its methyl derivatives (1b—f) react with a large excess of $CuCl_2 \cdot 2H_2O$ to give the dichloro- or trichloro-derivatives of cyclohexanone-1,2-diones.

¹ W. Sucrow and H. W. Wanzlick, *Chem. Ber.*, 1959, **92**, 2516.

Cyclohexanone (1 mol. equiv.) was heated under reflux with $CuCl_2 \cdot 2H_2O$ (30 mol. equiv.) in 50% acetic acid or 50% dioxan for 2 h. Ether extraction and recrystallization from CCl_4 gave the trichlorohydroxycyclohexenone (2a). Furthermore, treatment of cyclohexanone with 20 mol. equiv. of $CuCl_2 \cdot 2H_2O$ gave the dichloro-compound (2b).

For the methyl derivatives (1b—f), the reaction was carried out with 20 mol. equiv. of $CuCl_2 \cdot 2H_2O$ under the same conditions.

The expected analytical and spectral data were obtained for all compounds. We believe that this reaction is an improved method for the synthesis of polysubstituted cyclohexanones.

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