A New Route to Polychlorinated Cyclohexanediones

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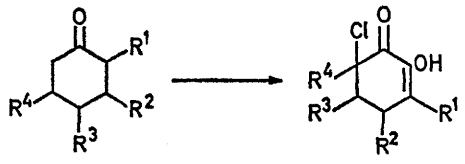
Summary Cyclohexanone and its methyl derivatives react with a large excess of $CuCl_2,2H_2O$ to give polychlorinated cyclohexanediones in fairly good yields.

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	
(**1a**); $R^1 = R^2 = R^3 = R^4 = H$	→	(**2a**);	$R^1 = R^4 = Cl$, $R^2 = R^3 = H$
	→	(**2b**);	$R^1 = Cl$, $R^2 = R^3 = R^4 = H$
(**1b**); $R^1 = Me$, $R^2 = R^3 = R^4 = H$	→	(**2c**);	$R^1 = Me$, $R^2 = R^3 = H$, $R^4 = Cl$
(**1c**); $R^1 = R^3 = R^4 = H$, $R^2 = Me$	→		
(**1d**); $R^1 = R^2 = R^4 = H$, $R^3 = Me$	→	(**2d**);	$R^1 = R^4 = Cl$, $R^2 = Me$, $R^3 = H$
(**1e**); $R^1 = R^4 = H$, $R^2 = R^3 = Me$	→	(**2e**);	$R^1 = R^2 = Me$, $R^3 = H$, $R^4 = Cl$
(**1f**); $R^1 = R^3 = H$, $R^2 = R^4 = Me$	→	(**2f**);	$R^1 = R^3 = Me$, $R^2 = H$, $R^4 = Cl$

M.p.s (°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.



(**1**) (**2**)

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

Cyclohexanone (1 mol. equiv.) was heated under reflux with $CuCl_2,2H_2O$ (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 $CuCl_2,2H_2O$ gave the dichloro-compound (**2b**).

For the methyl derivatives (**1b—f**), the reaction was carried out with 20 mol. equiv. of $CuCl_2,2H_2O$ 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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[1] W. Sucrow and H. W. Wanzlick, *Chem. Ber.*, 1959, **92**, 2516.