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A Convenient Synthesis of Substituted Pyrocatechols

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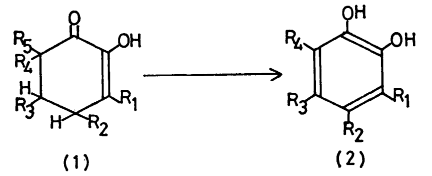
Synopsis. It was found that substituted pyrocatechol derivatives were formed by the reaction of polychlorinated cyclohexane-1,2-diones with lithium carbonate in DMF.

Substituted pyrocatechol derivatives have been reported to be formed from methyl substituted phenols and benzenes[1] in several steps. However, no report has appeared on their synthesis from cyclohexanone and methylcyclohexanones. In previous papers[2] we reported that polychlorinated cyclohexane-1,2-diones (**1a**—**1e**) were obtained in good yields from the reaction of cyclohexanones with a large excess of copper(II) chloride. The resulting products have a *gem*-dichloro functional group in the α-position with respect to the carbonyl group. It seems that this functional group would make them capable of leading to the following substituted pyrocatechol derivatives (**2a**—**2e**) by dehydrochlorination. We have studied the reaction of these polychlorinated compounds (**1a**—**1e**) with lithium carbonate in DMF.

The product obtained from **1a** showed no absorption of an α,β-unsaturated ketone, but showed the out-of-plane bending vibration of aromatic hydrogens in the IR spectrum (Table 1). In the NMR spectrum, there was no peak due to an aliphatic proton, but a peak at 5.71 ppm (broad, 2H) due to phenolic hydroxyl groups and a peak at 6.84 ppm (singlet, 2H) due to aromatic protons.



(1) (2)

1a: $R_1=R_4=R_5=Cl$, $R_2=R_3=H$ — **2a**: $R_1=R_4=Cl$, $R_2=R_3=H$

1b: $R_1=CH_3$, $R_2=R_3=H$, $R_4=R_5=Cl$ — **2b**: $R_1=CH_3$, $R_2=R_3=H$, $R_4=Cl$

1c: $R_1=R_4=R_5=Cl$, $R_2=CH_3$, $R_3=H$ — **2c**: $R_1=R_4=Cl$, $R_2=CH_3$, $R_3=H$

1d: $R_1=R_2=CH_3$, $R_3=H$, $R_4=R_5=Cl$ — **2d**: $R_1=R_2=CH_3$, $R_3=H$, $R_4=Cl$

1e: $R_1=R_3=CH_3$, $R_2=H$, $R_4=R_5=Cl$ — **2e**: $R_1=R_3=CH_3$, $R_2=H$, $R_4=Cl$

Fig. 1.

The results indicate that the product obtained is an *o,o'*-disubstituted pyrocatechol derivative, identified to be compound **2a**. In the same manner, the corresponding pyrocatechol derivatives **2b**, **2c**, **2d**, and **2e** were obtained from compounds **1b**, **1c**, **1d**, and **1e**, respectively. Physical properties of the products are given in Table 1.

The present work demonstrates that substituted pyrocatechol derivatives, which heretofore were prepar-

TABLE 1. PHYSICAL PROPERTIES AND ELEMENTAL ANALYSES OF PRODUCTS

Starting materials	Products	Mp (°C)	IR(KBr) (cm^{-1})	NMR($CDCl_3$) δ (ppm)	C (%) Found (Calcd)	H (%) Found (Calcd)	[Mol. formula]	Yields (%)
1a	**2a**	109—111	3478 3397 1605 1589	5.71(b, 2H) 6.84(s, 2H)	40.36 (40.26)	2.17 (2.25)	[$C_6H_4O_2Cl_2$]	60
1b	**2b**	66—67	3471 3370 1626 1590	2.21(s, 3H) 5.45(b, 2H) 6.60(d, *J*=8 Hz, 1H) 6.78(d, *J*=8 Hz, 1H)	52.98 (53.02)	4.33 (4.45)	[$C_7H_7O_2Cl$]	50
1c	**2c**	62—63	3527 3248 1626 1604	2.22(s, 3H) 5.47(b, 2H) 6.67(s, 1H)	43.48 (43.56)	3.20 (3.13)	[$C_7H_6O_2Cl_2$]	45
1d	**2d**	92.5—93.0	3497 3285 1629 1583	2.13(s, 3H) 2.16(s, 3H) 5.35(b, 1H) 5.55(b, 1H) 6.65(s, 1H)	55.51 (55.67)	5.57 (5.26)	[$C_8H_9O_2Cl$]	67
1e	**2e**	86.5—87.5	3460 3250 1625 1602	2.17(s, 3H) 2.22(s, 3H) 5.32(b, 2H) 6.49(s, 1H)	55.61 (55.67)	5.33 (5.26)	[$C_8H_9O_2Cl$]	70

ed with difficulty, can be synthesized readily from cyclohexanones *via* chlorination with copper(II) chloride followed by the above reaction.

Experimental

All melting points are uncorrected. Thin-layer chromatography was carried out on silica gel (Wakogel B-5), and detected with iodine. Column chromatography was carried out on silica gel (Wakogel C-100). The IR spectra were measured with a Hitachi 215 grating infrared spectrophotometer by the KBr disk method. The NMR spectra were recorded on $CDCl_3$ with TMS as an internal standard with a Hitachi R-20A nuclear magnetic resonance spectrometer. The chemical shifts are presented in terms of the δ value.

The general procedure was to reflux the polychlorocyclohexane-1,2-dione[2] (1 g) with 1.5 molar equiv. of Li_2CO_3 in DMF (20 ml) for 30 min in a nitrogen atmosphere. Ethereal extract of the reaction mixture was washed with 5% HCl. The product was chromatographed and crude material obtained from benzene–ether (9: 1) eluates was recrystallized from toluene.

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