

A Convenient Synthesis of Substituted Pyrocatechols

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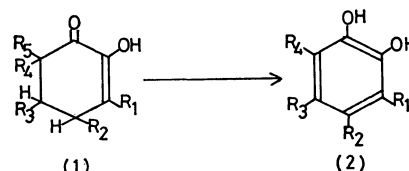
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Synopsis. It was found that substituted pyrocatechol derivatives were formed by the reaction of polychlorinated cyclohexane-1,2-diones with lithium carbonate in DMF.

Substituted pyrocatechol derivatives have been reported to be formed from methyl substituted phenols and benzenes¹⁾ in several steps. However, no report has appeared on their synthesis from cyclohexanone and methylcyclohexanones. In previous papers²⁾ 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.



- 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) [Mol. formula]	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) [C ₆ H ₄ O ₂ Cl ₂]	2.17 (2.25)	60
1b	2b	66—67	3471 3370 1626 1590	2.21(s, 3H) 5.45(b, 2H) 6.60(d, <i>J</i> =8 Hz, 1H) 6.78(d, <i>J</i> =8 Hz, 1H)	52.98 (53.02) [C ₇ H ₇ O ₂ Cl]	4.33 (4.45)	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) [C ₇ H ₆ O ₂ Cl ₂]	3.20 (3.13)	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) [C ₈ H ₉ O ₂ Cl]	5.57 (5.26)	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) [C ₈ H ₉ O ₂ Cl]	5.33 (5.26)	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 CDCl₃ 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-dione²⁾ (1 g) with 1.5 molar equiv. of Li₂CO₃ in DMF (20 ml) for 30 min in a nitrogen atmosphere. Etheral 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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