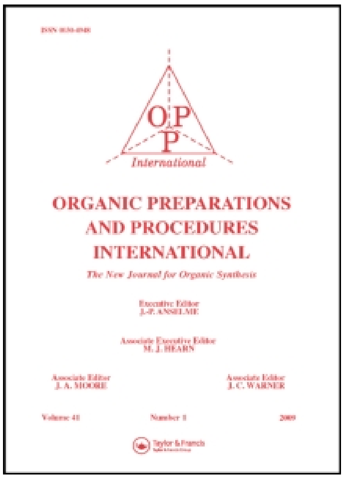

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A CONVENIENT SYNTHESIS OF SUBSTITUTED PHENOLS BY THE YATES-HYRE PROCEDURE

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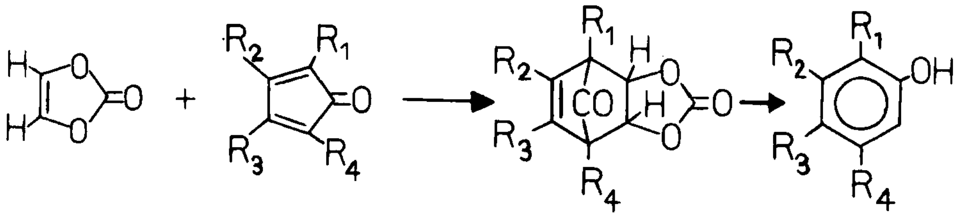
Utilizing a two-step procedure in which the intermediate Diels-Alder adduct IIIa was isolated and subsequently thermolyzed, Yates and Hyre[1] prepared 2,3,4,5-tetraphenylphenol (IVa) in 57% overall yield from vinylene carbonate (I) and tetracyclone (IIa). Although this procedure appears to offer a facile method for the preparation of various substituted phenols, no further examples of its use have appeared in the literature since the initial publication. Accordingly, we recently began an investigation of the scope of this thermal aromatization reaction and our findings from the basis of this communication.



I II III IV

a) $R_1 = R_2 = R_3 = R_4 = Ph$

b) $R_1 = R_4 = CH_3$; $R_2 = R_3 = Ph$

c) $R_1 = R_2 = R_3 = Ph$; $R_4 = CH_3$

d) $R_1 = R_4 =$ p - $CH_3C_6H_4$, $R_2 = R_3 = Ph$

e) $R_1 = R_4 = C_2H_5$; $R_2 = R_3 = Ph$

f) $R_1 = R_4 = Ph$; R_2, R_3 = o, o'-biphenylene

By carrying out the reaction I with IIa in a high-boiling solvent (bromobenzene) for an extended period of time (24 hours), we have obtained IVa in a yield of 90%. In addition, we have demonstrated that the reaction of I with other substituted cyclopentadienones (IIb-e) under identical conditions produces the phenols (IVb-e) in good to excellent yields.

The new compounds IVb-e (Table 1) were characterized by

Table 1. - Substituted Phenols (IV)

Compound	Yield[1] (%)	mp. (solvent)	IR(CCl_4) (OH) cm^{-1}	^{1}H-N.M.R.($CDCl_3$)
IVa	90	188-190°[2]	3560	5.06(s,1H,O$\underline{H}$), 6.98 (m,21H,arom.)
IVb	93	135-136° (petroleum ether)	3620	1.97 & 2.03(2s, 6H,-C$\underline{H}_3$,4.87(s, 1H,O$\underline{H}$)$_3$,6.87(m, 11H,arom.)
IVc	92	161-162° (cyclohexane)	3565 & 3625	2.05(s,3H,-C$\underline{H}_3$), 4.93(s,1H,O$\underline{H}$), 6.94(m,16H,arom.)[3]
IVd	80	196-198° (hexane)	3550	2.23(s,6H,-C$\underline{H}_3$), 5.10(s,1H,O$\underline{H}$), 7.06(m,19H,arom.)
IVe	70	123-125° (petroleum ether)	3620	1.03(t,6H,C$\underline{H}_3$ CH_2-),2.39(m,4H, $CH_3C\underline{H}_2$-),4.92(s, 1H,O$\underline{H}$),6.90(m, 11H,arom.)

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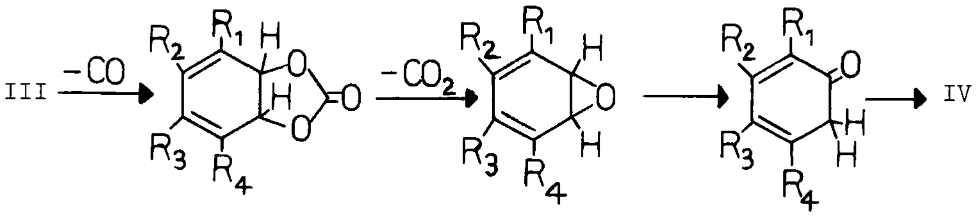
1) Isolated yields. 2) Lit. [1]mp. 183-184°; however a sample of IVa prepared by the literature[1] procedure melted at 187-188.5°. 3) Acetone-d_6 solvent.

I.R., ^{1}H-N.M.R. and mass spectral data. In the case of the reaction of I with IIc where two isomeric phenols could be produced, only a single product was obtained which was identified as the 2-phenyl-isomer IVe, (rather than the 2-methyl-) on the basis of ^{13}C-N.M.R. and I.R. spectral analysis. It should be pointed out that the phencyclone (IIf) is converted in high yield to a carbonyl compound rather than a phenol when reacted with I in refluxing bromobenzene. However, recent results indicate that thermolysis of Diels-Alder adduct IIIf does yield phenol IVf, albeit in moderate yield.

In all cases the intermediacy of the adduct III could be demonstrated by I.R. monitoring of the reaction. Dissapearance of the C=O peak of the cyclone II (about 1700 cm^{-1}) was accompanied by appearance of the characteristic twin peaks of III (about 1770 and 1810 cm^{-1}); ultimately, the phenolic -OH peak (about 3540 cm^{-1}) could be observed increasing in intensity at the expense of the carbonyl peaks of II and III. This information coupled with the fact that carbon monoxide and carbon dioxide are evolved in the course of the reaction, suggests the following as a possible sequence.



EXPERIMENTAL

General Procedure.- A mixture of the appropriate cyclopentadienone[2,3] (0.005 mole), vinylene carbonate[4] (0.012 mole) and bromobenzene (20 ml) was heated at reflux for twenty-four hours with stirring. The hot solution was filtered to remove any insoluble material and the solvent was evaporated *in vacuo* to yield an oil which crystallized on trituration with petroleum ether or benzene-petroleum ether. One recrystallization produced the pure compounds.

Acknowledgement is made to Professor J. Villafranca for obtaining and interpreting the ^{13}C-N.M.R. spectra and to Mr. William Grove for valuable technical assistance.

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