

THE OXIDATION OF PHENOLS WITH LEADDIOXIDE

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The oxidation of phenols with metal oxides has been described by several investigators.

Oxidation in apolar solvents with Ag_2O ¹⁾, MnO_2 ^{2,3,4)} and PbO_2 ^{5,6,7)} gave mainly polymeric ethers. In contrast we have found that oxidation with PbO_2 in polar solvents, e.g. acetic acid and formic acid yielded diphenoquinones and p-benzoquinones almost exclusively. The results are summarized in the table. From our data a reaction-mechanism (Scheme I) can be visualized.

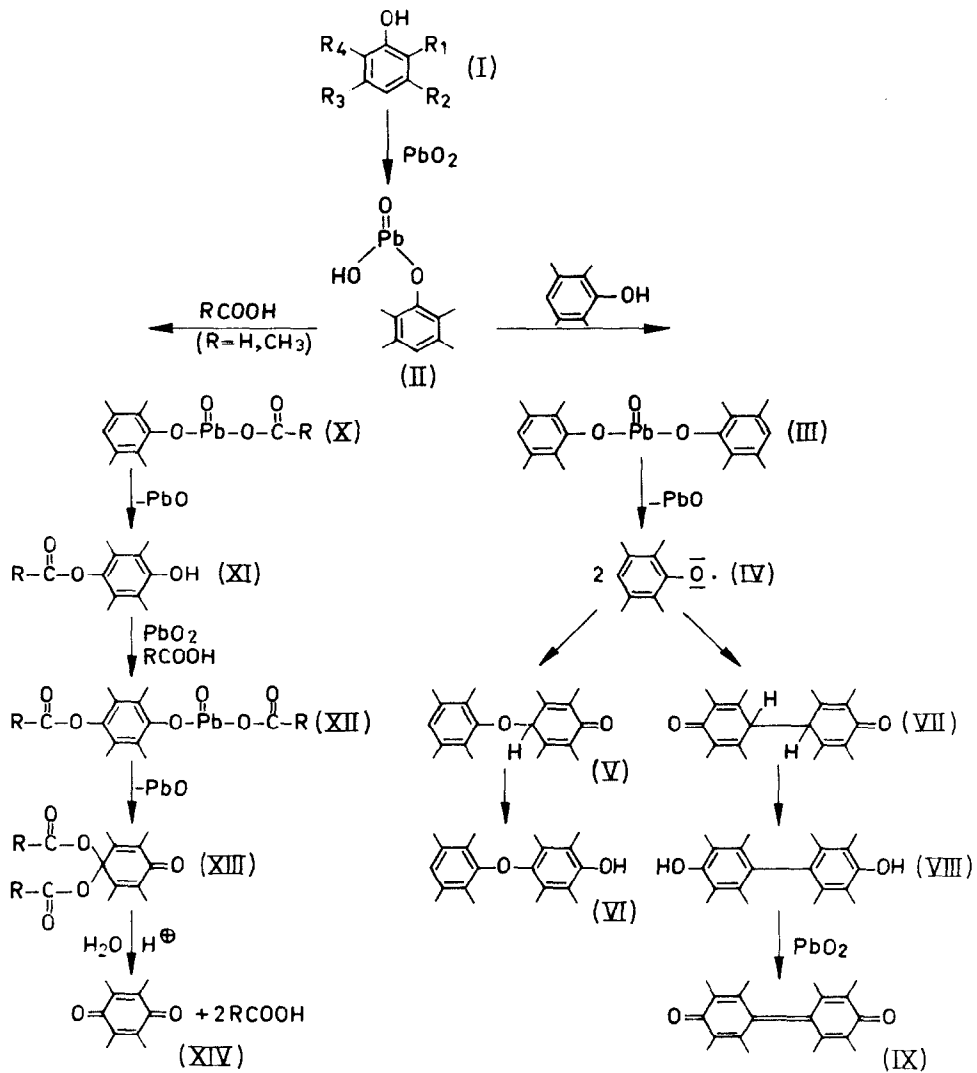
The formation of metal-phenolates is postulated as initial step⁷⁾ (cf. Scheme I). The oxidation of 2,6-dimethylphenol in acetic acid was followed by GLC, combined with two-dimensional TLC. Besides 3,3',5,5'-tetramethyldiphenoquinone and 2,6-dimethylbenzoquinone, the phenols (VI) and (XI) were detected. Oxidation of the phenol (VI) yielded (I), (IX) and (XI) and oligomers of 2,6-dimethylphenol. The mechanism of the formation of these oligomers has been well demonstrated⁸⁾.

From the oxidation of 2,6-diphenylphenol in acetic acid, 4-acetoxy-2,6-diphenylphenol (XI) was isolated, which exclusively yielded 2,6-diphenylbenzoquinone on further oxidation.

Noteworthy is the synthesis of (VIII) ($\text{R}_1=\text{R}_2=\text{R}_3=\text{R}_4=\text{CH}_3$), which is not easy to obtain in any other way⁹⁾. This compound proved to be incapable of further oxidation.

The reactions in acetic acid generally offer an efficient way for preparing diphenoquinones and p-benzoquinones. The PbO formed dissolves and the diphenoquinones are isolated by filtration. In formic acid, however, the working-up procedure is somewhat more difficult, due to the insolubility of Pb -formate^{II}.

SCHEME I



TABLE

Phenol	Mol. ratio phenol/PbO ₂	Solvent	Temp. (°C)	Reaction time (min.)	Yield	Yield	Other products
					p-benzo quinone (%)	dipheno quinone (%)	
2,6-dimethyl-	1 : 1	CH ₃ COOH	30	90		55 ^b	
"	1 : 2	"	30	15	22 ^a	70	
"	1 : 2	"	16	120	28	42	
"	1 : 2	"	117	15		90	
2,6-diaethyl-	1 : 1	"	30	20		52 ^c	
"	1 : 2	"	25	15		70	
2,6-di-iso-propyl-	1 : 1	"	20	30		65	
"	1 : 2	"	25	15	4	88	
2,6-di-t-butyl-	1 : 1	"	20	15		90	
"	1 : 2	"	20	15		92	
2,6-dimethoxy-	1 : 1	"	20	15		90 ^d	
"	1 : 2	"	20	15	5 ^e	88	
2,6-diphenyl-	1 : 1	"	35	45	25 ^f	45 ^d	A)
"	1 : 2	"	25	30	30	65	
"	1 : 2	HCOOH	30	60	71		
"	1 : 4	"	30	60	80		
2,3,5,6-tetra-methyl	1 : 0,5	CH ₃ COOH	30	30			B)
"	1 : 1	"	20	30	55 ^g		
"	1 : 2	HCOOH	20	20	50		

A) 15% 4-acetoxy-2,6-diphenylphenol. m.p. 166°C.

B) 51% Octamethyl-4,4'-dihydroxybiphenyl. m.p. 201-202, 5°C.

Recrystallisation data:

a) light petroleum (40-60) b) 1,2-dichloroethane c) light petroleum (60-80)

d) phenol-methanol 1:1 e) acetic acid f) aethanol g) acetic acid-water 8:2.

Oxidations (general procedure) : A solution of the phenol in acetic or formic acid was cooled to 20-30°C. Leaddioxide was added in small portions to the vigorously stirred solution. Since the reaction is rather exothermic, cooling in ice was necessary. When the temperature began to decrease stirring was continued during 10-15 min. Excess of leaddioxide (if any) was treated with a 3% hydrogen peroxide solution. The diphenoquinones were isolated by filtration. The p-benzoquinones were isolated by extraction of the filtrate with benzene and purified by recrystallisation.

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