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OXIDATION OF PSEUDOCUMENE IN ACETIC ACID

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547.292

The oxidation of pseudocumene in the benzene nucleus can be effected in HOAc solution by using inorganic oxidizing agents containing oxygen, such as $NaNO_3$, heteropolyacids, O_2, $Na_2S_2O_8$ and H_2O_2, with $Pd(OAc)_2$ as catalyst. $Na_2S_2O_8$ and H_2O_2 are the most effective, being also active in the absence of Pd(II).

Pseudocumene (PC) is known to be oxidized into a mixture of phenols and trimethyl-p-benzoquinone (TMBQ) by organic peracids [1, 2] and by H_2O_2 [3]. The acetoxylation of arenes in the nucleus is catalyzed by Pd(II) acetate in the presence of a number of oxidants [4-6]. We have investigated the oxidation of PC by various inorganic oxidizing agents containing oxygen, and have also studied the catalytic effect of $Pd(OAc)_2$ in these reactions. Most attention was paid to the oxidation of PC by sodium persulfate.

EXPERIMENTAL

Pseudocumene of "pure" grade was purified by distillation. The salts of the heteropolyacids $H_2Na_3PMo_{10}V_2O_{40}$ (HPA-2) and $H_4Na_4PMo_7V_5O_{40}$ (HPA-5) were obtained by the reactions between stoichometric quantities of H_3PO_4, Na_2MoO_4 and $NaVO_3$ in aqueous solution with heating. $K_5CoW_{12}O_{40}$ was obtained as described by Eberson and Wistrand [7]. The remaining reactants (of "chemically pure" or "analytical" grade) were used without further purification. The concentrations of $Na_2S_2O_8$ and H_2O_2 were determined by permanganate titration. H_2O_2 was used as a 30% aqueous solution. $Na_2S_2O_8$ decomoses rapidly in HOAc at 115°C (with $[Na_2S_2O_8] = 1.0$ mole$\cdot$dm^{-3} 85% of the persulfate has decomposed after 2 h; Pd(II) does not affect the rate of decomposition).

The oxidation of PC was carried out in HOAc in sealed glass ampuls (without stirring), or in a flask with a reflex condenser with vigorous stirring. The products were separated by extraction with ether or ethyl acetate from the reaction mixture diluted with water.

The products were identified by chromato-mass spectrometery (LKB spectrometer with 2130 handling system, column with a mixed phase OV-1/Carbowax 20M in the proportions 3:1), GLC (LKhM-80, $\ell = 3$ m, 10% Carbowax 20M on Chromaton N-AW-HMDS, carrier gas He, DPI) and liquid chromatography (Varian 8500, Micro-pak Si-10 column (250 × 2 mm), mobile phase $n\text{-}C_6H_{14}$: $CHCl_3$ (93:7), $v = 30$ cm^3 h^{-1}, $p = 5\text{-}10$ atm, UV detector, $\lambda = 280$ nm). Identification employed standard samples of trimethyl-p-benzoquinone, trimethylhydroquinone, 2,3,5-, 2,3,6- and 2,4,6-trimethylphenols and their acetates. The benzyl acetates were obtained as described by Belli et al. [8]. The 2,3,5- and 2,4,5-trimethylphenol isomers were separated on a preparative column with Lichrosorb Si-60 (eluent C_5H_{12}—$CHCl_3$ 80:20) and identified by IR spectroscopy.

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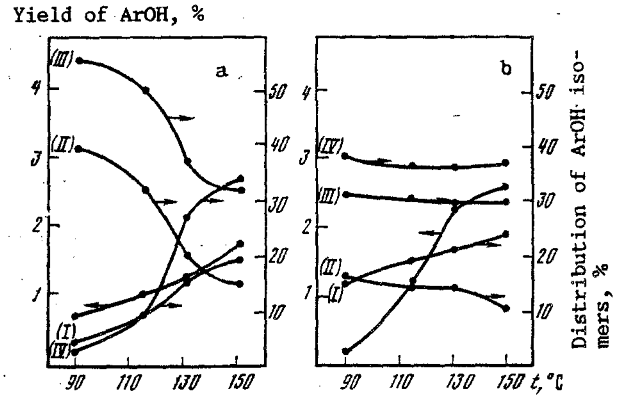


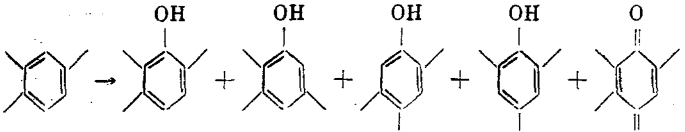
Fig. 1. Temperature dependence of the yield of ArOH (mole % of initial PC) and of the isomeric composition of ArOH ([PC] = 2.0, $[Na_2S_2O_8]$ = 1.0 mole dm^{-3}, 4 h, in ampuls): a) 0.005 mole dm^{-3} $Pd(OAc)_2$, b) without $Pd(OAc)_2$

The yields of the products and the proportions of the isomeric phenols were determined by GLC (ℓ = 3 m, 10% Carbowax 20M, 180°C, internal standard ionol) after hydrolyxing the phenylacetates with 5% alcoholic KOH (6-10 h, 80°C). The conversion of PC to products was estimated on the same column at 150°C (internal standard durene). The yield of TMBQ was determined by GLC before hydrolyzing the acetates (3 m, graphitized carbon black modified with 0.8% Carbowax 20M, 125°C, internal standard 2,6-dimethylphenol).

RESULTS AND DISCUSSION

The pseudocumene molecule can undergo oxidation both in the nucleus and in the CH_3 groups. We established that oxidation by $KMnO_4$, $K_2Cr_2O_7 + H_2SO_4$, $NaVO_3 + H_2SO_4$, $Cu(OAc)_2$, $NaClO_3$, $H_3PMo_{12}O_{40}$ in HOAc at 115°C, both with and without the addition of $Pd(OAc)_2$, gives only products of side-chain oxidation (benzyl alcohols, bezyl acetates, aldehydes, diarylmethanes). Pd(II) acetate hardly oxidizes PC at all under these conditions.

Products of the nuclear oxidation, trimethylphenols, their acetates (I)-(IV) and trimethylbenzoquinone (TMBQ) were observed in the reactions of PC with $NaNO_3$, heteropolyacids (HPA), O_2, $Na_2S_2O_8$ and H_2O_2



(I) (II) (III) (IV) TMBQ

Oxidation products of the CH_3 groups were also formed. With $NaNO_3$, HPA and O_2 oxidation of the nucleus occurs only in the presence of $Pd(OAc)_2$. In the absence of Pd(II) $NaNO_3$ and HPA give only oxidation products of the side chains, while with O_2 no reaction at all occurs.

The most effective systems are those with $Na_2S_2O_8$ and H_2O_2. They oxidize the side chains both with and without Pd(II), though Pd(II) catalyzes this reaction. The system $Na_2S_2O_8$ + HOAc is heterogeneous, since $Na_2S_2O_8$ is sparingly soluble in HOAc.

The composition of the oxidation products of PC are shown in Table 1. Most of the experiments were carried out with low concentrations of PC, in order to exclude subsequent oxidation of the reaction products. On increasing the concentration of PC the selectivity of the oxidation falls. Thus at 75% conversion of PC the yield of ArOH (ArOAc) (in terms of the amount of PC which has reacted) is 25% ($Na_2S_2O_8$ + Pd(II), 115°C, 3h).

Pd(II) has a marked influence on the composition of the products of oxidation of PC by $Na_2S_2O_8$. In the presence of Pd(II) the main oxidation products are phenyl acetates, phenols being hardly formed at all, but in the absence of Pd(II) phenols and TMBQ are formed predominantly. Pd(II) also affects the distribution of the isomeric trimethylphenols. In the presence of Pd(II) the isomers (II) and (III) are the main products. In the reactions without Pd(II) the yield of (I) increases and that of (II) falls, while mesitol (IV) appears.

TABLE 1. Oxidation of Pseudocumene by Various Oxidizing Agents in HOAc at 115°C

Oxidant, mole dm^{-3}	PC, mole dm^{-3}	τ, h	Composition of oxidation products, mole %						Conversion of PC, %	Isomeric composition of ArOH, %			
			ArCHO	ArCH$_2$OH	ArCH$_2$Ar′	TMBQ	ArOH[a]	Yield of ArOH[a,b]		(I)	(II)	(III)	(IV)
0,2NaNO$_3$, 0,005Pd(II)[c]	2,0	0,5	27	30	–	–	43	0,5		3	37	60	–
»	0,5	6	31	37	–	–	32	2	45	2	39	59	–
0,05 HPA-2, 0,005Pd(II)[d]	2,0	1	–	37	33	–	30	0,2		2	43	55	–
»	0,5	6	–	56	27	–	16	0,6	4	–	52	48	–
0,005Pd(II), O$_2$[e,f]	2,0	4	46	31	–	–	23	0,1		–	65	35	–
1,0Na$_2$S$_2$O$_8$, 0,005Pd(II)	2,0	1,5	–	15	32	–	53	3		9	43	46	2
»	2,0	3	–	9	40	–	51	3	31	9	37	51	4
»[g]	0,5	3	–	10	6	–	84	19	75	12	29	57	2
0,5Na$_2$S$_2$O$_8$, 0,005Pd(II)	0,5	3	–	11	18	–	71	8	52	9	36	54	1
1,0Na$_2$S$_2$O$_8$, 0,005Pd(II)[e]	2,0	4	–	10	20	–	70	1		9	32	50	9
»[e,h]	2,0	4	–	10	29	20	41	0,5		9	19	39	32
1,0Na$_2$S$_2$O$_8$[e,h]	2,0	4	–	4	16	23	58	1		14	12	35	39
1,0Na$_2$S$_2$O$_8$, 0,05AgNO$_3$[e,h]	2,0	4	–	11	37	45	7	0,1		6	15	26	53
1,0Na$_2$S$_2$O$_8$	2,0	1,5	–	7	1	27	66	1		19	12	34	35
»	2,0	3	–	7	3	32	58	2	25	13	11	27	48
»	0,5	1,5	–	6	–	–	94	7		19	12	32	38
»	0,5	3	–	4	–	–	96	12	51	20	10	36	34
1,0H$_2$O$_2$, 0,5H$_2$SO$_4$[e]	1,0	4	–	6	11	21	62	4		18	17	34	30
0,6H$_2$O$_2$, 0,005Pd(II)[e]	2,0	4	59	30	–	–	11	0,4		4	52	41	3
0,6H$_2$O$_2$[e]	2,0	4	34	32	2	–	32	0,6		16	20	45	20

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[a] Total quantity of ArOH and ArOAc, measured after alkayline hydrolysis of the reaction products,

[b] In mole % of the original PC.

[c] The composition and yield of the products hardly changes for [NaNO$_3$] = 0.1-0.6 mole dm^{-3}; an increase in τ leads to a decrease in the fraction of ArOH relative to ArCHO and ArCH$_2$OH.

[d] The composition and yield of the products are not appreciably affected by replacing HPA-2 by HPA-5 or by bubbling O$_2$ through the reaction mixture.

[e] Experiments in ampuls.

[f] There is no reaction in the absence of O$_2$.

[g] The result is similar with [Pd(OAc)$_2$] = 0.02 mole dm^{-3},

[h] 3 moles dm^{-3} H$_2$O added.

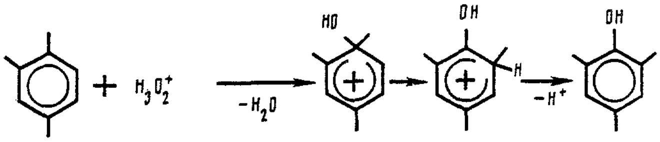
Pd(II) has less effect on the reaction of PC with $Na_2S_2O_8$ at higher temperatures, and also when water is added. With increase of temperature the yield of phenols (phenyl acetates) rises both in the presence and in the absence of Pd(II) (see Fig. 1). The distribution of the isomers in the catalyzed and uncatalyzed reactions is approximately the same. The addition of H_2O has a similar effect. In the reaction of PC with $Na_2S_2O_8$ additions of $AgNO_3$, $Cu(OAc)_2$ and $FeSO_4$ increase the yield of oxidation products of the methyl groups.

It is generally assumed that the oxidation of arenes by persulfate involves the intermediate formation of the radical $SO_4^{\overline{\cdot}}$, which reacts with the arene to form an aromatic cation-radical [9-11]. In HOAc such a mechanism leads to aryl and benzyl acetates. It appears that another mechanism operates in the oxidation of PC by $Na_2S_2O_8$ in HOAc, since the reaction products are phenols. Moreover, the additions of the salts $AgNO_3$, $FeSO_4$ and $Cu(OAc)_2$, which catalyze the homolytic cleavage of persulfate, promote the oxidation of the CH_3 groups, and not of the nucleus. The similarity between the product composition and the distribution of isomers in the reactions of PC with $Na_2S_2O_8$ and with $H_2O_2 + H_2SO_4$ (see Table 1) suggests that, as in aqueous acid solutions [12], $Na_2S_2O_8$ decomposes heterolytically rather than homolytically in HOAc

$$Na_2S_2O_8 + 2HOAc \rightleftarrows 2NaOAc + H_2S_2O_8$$
$$H_2S_2O_8 + 4HOAc \rightarrow H_2O_2 + 2H_2SO_4 + 2Ac_2O$$

Thus in HOAc the systems $Na_2S_2O_8$ and $H_2O_2 + H_2SO_4$ are probably equivalent. The formation of phenols in the reactions of arenes with H_2O_2 in acid media is generally regarded as electrophilic hydroxylation by the species $H_3O_2^+$ (or OH^+) [3, 13, 14]. It is also possible that the reaction involves peracetic acid, which can be formed from HOAc and H_2O_2. Peracids react with arenes by an electrophilic substitution mechanism, as does H_2O_2[13]. Thus the oxidation of PC by trifluoroperacetic acid gives the phenols (I) and (III) (43:57) and TMBQ [2].

An interesting feature of the reaction of PC with $Na_2S_2O_8$ and H_2O_2 is the migration of the CH_3 group to give mesitol (IV). On adding Pd(II) the yield of mesitol falls sharply. The migration of CH_3 groups in the hydroxylation of arenes has been observed previously only in strongly acid media ($CF_3CO_2H + BF_3$ [13], 98% $H_2O_2 + HSO_3F/SO_2ClF$ [14], 30% H_2O_2+ excess HF [3]). We have shown that the acid isomerization of PC and of trimethylphenols does not occur under our conditions. The migration of CH_3 groups in the cation-radical of PC can also be excluded, since neither mesitol nor other phenols have been observed in the oxidation of PC by $K_5CoW_{12}O_{40}$, which is an outer-sphere electron acceptor [7]. A mechanism has been proposed [3] to account for the migration of methyl groups which includes attack by $H_3O_2^+$ (or OH^+) on the substituted position of PC with the highest electron density, followed by isomerization of the cyclohexadienyl intermediate



Thus the observed migration of the CH_3 group supports a mechanism of electrophilic hydroxylation for the oxidation of the nucleus of PC by $Na_2S_2O_8$.

The catalyzed reaction in the presence of Pd(II) is characterized by another set of products, the acetates (I)-(III). The absence of TMBQ is apparently due to the higher stability of the acetates (I) and (II) towards further oxidation. Phenols, including (IV), and TMBQ are formed only in the presence of water, which hydrolyzes the acetates. The formation of (IV) can then be accounted for by an increase in the solubility of $Na_2S_2O_8$ and in the contribution of the uncatalyzed process.

The difference between the products of the catalyzed and uncatalyzed reactions shows that they have different mechanisms. In the presence of Pd(II) the acetoxylation of arenes probably occurs [4-6]. It is noteworthy that under the given conditions Pd(II) activates acetoxylation only in conjunction with oxidizing agents containing oxygen. Two mechanisms have been proposed for the nuclear acetoxylation of arenes [4, 15], involving the electrophilic palladization or the acetoxylation of the arene. The part played by the oxidant in promoting acetoxylation is not yet completely clear (see [15]). Attention has been called to the low regioselectivity of the attack by Pd(II) on the nucleus of arenes [16]. In the present instance this is shown by the relatively high yield of the isomer (II), which is "disfavored" from the point of view of orientation in electrophilic aromatic substitution. The low yield of the isomer (I) may be attributed to steric hindrance, since Pd(II) acetate is at least partially polymerized in HOAc [4].

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REACTION OF PERFLUOROPROPENYLBENZENE WITH SULFUR TRIOXIDE

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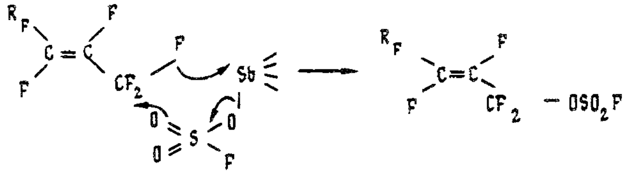
Depending on the ratio of the reagents and the reaction conditions, the reaction of perfluoropropenylbenzene with SO_3 in the presence of BF_3 or SbF_5 gives perfluoro-γ-phenylallyl fluorosulfate or perfluorocinnamoyl fluorosulfate; hydrolysis of the latter gives perfluorocinnamic acid.

The stereoisomeric composition of perfluoro-2-alkenyl fluorosulfates formed in the reaction of perfluoro-2-alkenes with SO_3 in the presence of SbF_5 corresponds completely to the stereoisomeric composition of the starting olefin [1]. On this basis, it was concluded that replacement of a fluorine atom by the FSO_3 group occurs via the cyclic intermediate state

$$SO_3 + SbF_5 \rightleftharpoons [(FSO_3)_nSbF_{5-n}]$$



Nevertheless, it was impossible to preclude the probability that when the molecule contains fragments capable of stabilization of a positive charge, especially of an aromatic ring system, and, therefore, which increase the allyl mobility of fluorine atoms, the re-

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