

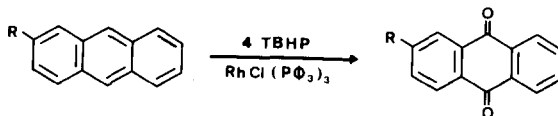
Rh-CATALYZED OXIDATION OF ANTHRACENES TO ANTHRAQUINONES USING *t*-BUTYLHYDROPEROXIDE

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Summary. Rh-catalyzed oxidation of 2-substituted anthracene with *t*-butylhydroperoxide affords anthraquinones in yields up to 90%, while V-catalyzed oxidation and stoichiometric oxidation with CrO₃ are less efficient.

Oxidation of anthracenes to anthraquinones can be achieved by a wide variety of oxidating agents, but requires vigorous conditions in order to prevent formation of bianthrone.¹ For some time there has been considerable interest in catalytic oxidations² which should be more efficient, more economical and would not produce vast amounts of polluting inorganic effluents as is the case with traditional oxidants such as chromium trioxide or potassium permanganate. One of the most convenient sources of oxygen atoms for a variety of organic oxidations is *t*-butylhydroperoxide (TBHP) in conjunction with a transition metal catalyst in a high oxidation state.³ It is particularly useful for oxidation of double bonds, for allylic oxidations and for sulfide oxidations.^{3,4} However, only poor yields are obtained when the system is applied to aromatics.⁵ On the other hand, low-valent transition metal complexes (Ir(I), Rh(I)) catalyze decomposition of TBHP to oxygen and *t*-butanol.⁶ We have recently reported that in the presence of anthracenes O₂ production from TBHP/RhCl(PPh₃)₃ is inhibited and anthraquinone is produced in up to 96% yield.⁷ This communication reports the preparative application of the system. Reactions are carried out at 70° with a 25% excess of TBHP in presence of 1% (with respect to anthracene RhCl(PPh₃)₃).



Results are summarized in the Table, which also contains yields obtained with TBHP/VO(acac)₂ and chromium trioxide for comparison. The procedure gives satisfactory results for all anthracenes investigated, yields being considerably higher than with VO(acac)₂ or CrO₃, but it fails for naphthalene and benzene derivatives with exception of hydroquinones. Oxidation of phenols and naphthols was also investigated but no positive results were obtained, TBHP being decomposed without attack of the substrate. It appears that the prerequisite for success of the method is catalyst complexation by the substrates which inhibits non-productive TBHP decomposition.

Table. Oxidation of Anthracenes (1) to Anthraquinones (2)

Anthracene R =	TBHP/RhCl(PPh ₃) ₃ ^{a)}		TBHP/VO(acac) ₂ ^{b)}		CrO ₃ Yield [%]
	Time [h]	Yield [%] ^{d)}	Time [h]	Yield [%] ^{d)}	
H	48	91	24	48 (27)	70
CH ₃	16	87	24	64 (14)	54
Cl	11	91	47	58 (15)	45
OCH ₃	36	82	39	55 (10)	41
OCOCH ₃	24	50 (15)	24	38 (27)	45
NO ₂	24	73 (11)	-	-	-
CN	24	76	-	-	-
Anthrone	48/3 eq. TBHP	82-90	-	-	-
9,10-Dihydroxy-9,10-dihydroanthracene	48/3 eq. TBHP	87			-
1,4-Dihydroxynaphthalene	48/4 eq. TBHP	68	(with or without catalyst)		
Naphthalene	48/4 eq. TBHP	0			
Hydroquinone	48/1.5 eq. TBHP	47 ⁷⁾			

^{a)} See general procedure. ^{b)} Conditions: 3% of VO(acac)₂, otherwise identical to ^{a)}. ^{c)} Conditions: 0.8 mmol of anthracene, 2.2 to 4 mol eq. (NH₄)₂Cr₂O₇, 100 ml AcOH 95%, 4.7-9.4 mmol H₂SO₄, 30-40°, 30 min. ^{d)} Numbers in parentheses refer to recovered anthracene.

Oxidation of 1 with TBHP/RhCl(PPh₃)₃ - General procedure. To a solution of anthracene (1) (0.56 mmol) and 5.4 mg (0.01 mol eq.) of catalyst in benzene (9.0 ml) at 70° is added under nitrogen atmosphere 2.3 mmol of TBHP (4 eq.) in benzene (1.1 ml). After the time indicated in the Table, the solvent is evaporated, the crude product purified by column chromatography and recrystallized. IR, NMR and MS spectra of the anthraquinones (2) are identical with those obtained from oxidation with CrO₃.

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