Tetrahedron Letters,Vol.22,No.51,pp 5157-5160,1981 0040-4039/81/515157-04$02.00/0
Printed in Great Britain

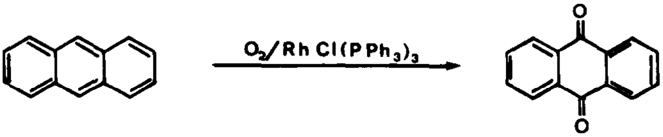
CATALYZED OXIDATION OF ANTHRACENE WITH OXYGEN AND *tert*-BUTYLHYDROPEROXIDE

Paul Müller* and Christiane Bobillier,
Département de Chimie Organique, Université de Genève, 1211 Genève 4, Suisse

Summary. Oxidation of anthracene to anthraquinone by oxygen/$RhCl(PPh_3)_3$ proceeds *via* solvent-derived hydroperoxides. *tert*-Butylhydroperoxide/$RhCl(PPh_3)_3$ effects the same transformation in up to 96% yield. Possible mechanisms for the TBHP-catalyzed reaction are discussed.

A variety of organic molecules are oxidized with molecular oxygen in the presence of transition metal catalysts.[1] In general these reactions proceed *via* hydroperoxides, and the catalyst intervenes mainly in hydroperoxide decomposition. Other mechanisms are however conceivable, for example substrate attack on coordinated oxygen, oxygen attack on coordinated substrate, etc.[1] or electron transfer from substrate to catalyst followed by oxygen attack on an intermediate radical cation.[2]

It is known that O_2 in conjunction with $RhCl(PPh_3)_3$ effects oxidation of anthracene to anthraquinone:[3]



We have reinvestigated this reaction in the hope of finding evidence for one of the unusual mechanisms. Our investigation showed however that anthracene oxidation with O_2/$RhCl(PPh_3)_3$ follows the general pathway.

The reaction was studied under a variety of conditions (Table 1). It was found that oxidation proceeds readily in ether solvents such as dioxane and dimethoxyethane to afford the quinone in 55 to 83% yield respectively. These reactions were accompanied by formation of high-boiling ether derived side-products showing NMR signals in the range of 3.5-4.5 δ. Oxygen consumption was 4 to 9 times the stoichiometric amount. In contrast, no oxidation took place when benzene or acetic acid were used as solvent, or when hydroquinone was added to the reaction in dioxane. Anthraquinone was also produced in dioxane containing no catalyst, but at a significantly slower yield. All these observations are consistent with a scheme where reaction is initiated by oxygen attack on the solvent to form hydroperoxides. The latter, in turn, could attack anthracene by a series of catalyzed oxidation steps. In order to test this hypothesis anthracene was exposed to 4.0 eq.

Table 1. Oxidation of anthracene with oxygen[a]

Catalyst	Solvent	Conditions	Anthraquinone
1% $RhCl(PPh_3)_3$	dioxane	70°/4 d	55%
"	dimethoxyethane	70°/2 d	83%
none	dioxane	70°/4 d	33%
1% $RhCl(PPh_3)_3$	benzene	70°/2 d	0[b]
"	AcOH	70°/2 d	0[b]
"	dioxane, 5% hydroquinone	70°/4 d	0[b]
"	benzene, 4 eq. TBHP	70°/4 d	96%[b]
none	"	70°/4 d	0[b]

[a] Conditions: 500 mg of anthracene in 100 ml of solvent under oxygen atmosphere. [b] No oxygen uptake.

of *tert*-butylhydroperoxide (TBHP)/$RhCl(PPh_3)_3$ in benzene. Anthraquinone was formed in 96% yield, while no oxidation occurred without catalyst. In both cases no oxygen was consumed during the reaction.

With the exception of two communications in the Russion literature,[4] oxidation of aromatic hydrocarbons with TBHP seems to have been overlooked so far. Catalysts which are efficient for TBHP epoxidation of alkenes,[5] such as $Mo(CO_6)$ or $VO(acac)_2$ are also effective with anthracene, but $RhCl(PPh_3)_3$ is superior (Table 2). Possible intermediates in the transformation of anthracene to the quinone, 9-anthrone and 9,10-dihydro-9,10-dihydroxyanthracene, but also 1,4-dihydroxynaphthalene and hydroquinone react with TBHP/$RhCl(PPh_3)_3$ to afford the respective quinones. Oxidation of hydroquinone to benzoquinone has already been reported in the literature.[6]

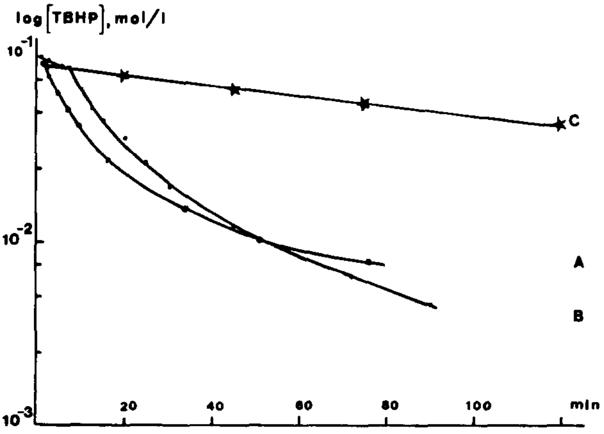


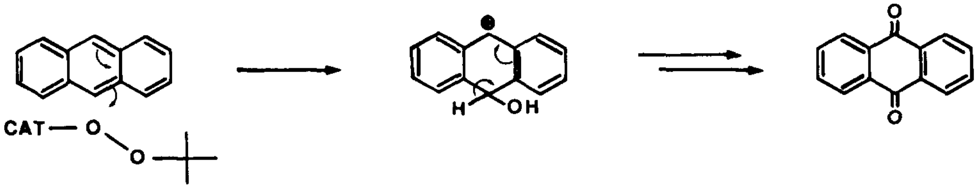
Figure: Decomposition of TBHP (benzene, 70°) by 0.3% $RhCl(PPh_3)_3$. A: no additive; B: with 5.3% DTBPC; C: with anthracene. Same conditions as in Table 2.

Table 2. Catalyzed oxidation of anthracene with TBHP[a]

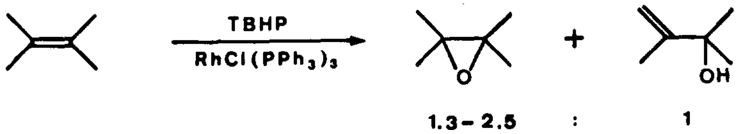
Substrate	Catalyst	Solvent	TBHP (eq)	Quinone
Anthracene	2.5% $Mo(CO)_6$	benzene	3	37%
"	2.5% $VO(acac)_2$	"	3	37%
"	1% $IrCl(CO)(PPh_3)_2$	"	3	15%
"	1% $RhClCO(PPh_3)_2$	"	3	40%
"	1% $RhCl(PPh_3)_3$	chlorobenzene	4	66%
"	"	tetrachloroethylene	4	0%
"	"	toluene		32%[b]
"	"	benzene	4[c]	96%
Anthrone	"	"	2	82-90%
9,10-Dihydro-9,10-dihydroxy-anthracene	"	"	3	87%
1,4-Dihydroxynaphthalene	"	"	4	60%
Hydroquinone	"	"	1.5	46%[d]

[a] Conditions: 500 mg of anthracene in 100 ml of solvent, T = 70°, 48 h. [b] Solvent attack. [c] 3.4 eq. consumed. [d] Unreacted material recovered.

The following observations concerning the reaction mechanism of these transformations were made: As other transition metal complexes,[7] $RhCl(PPh_3)_3$ decomposes TBHP to oxygen and *t*-butanol. This reaction is almost totally inhibited upon addition of anthracene (Figure). In fact, anthracene oxidation requires only a slight excess of TBHP (3.4 eq.). Similarly, addition of 2-5% of a radical scavenger, 2,6-di-*t*-butyl-*p*-cresol (2,6 DTBPC) retarded TBHP decomposition which, after scavenger consumption, proceeded normally.[8] The yield of anthraquinone was not affected by small amounts of DTBPC. Decomposition of TBHP to give oxygen is therefore probably not involved in the product-forming steps. Since catalysts like $Mo(CO)_6$ or $VO(acac)_2$ are effective in both alkene epoxidation and anthracene oxidation an analogous mechanism[9] should be involved:



In general, epoxidations with TBHP are stereospecific, and therefore do not involve free radical intermediates. With $RhCl(PPh_3)_3$/TBHP the situation is however more involved. For example, it was found that epoxidation of tetramethylethylene afforded the expected epoxide and the allylic alcohol 2,3-dimethyl-3-hydroxybutene in proportion of 1.3-2.5:1. This ratio changes slightly upon addition of 2,6-DTBPC, but no significant trend was produced. The same result was obtained with $RhCl(CO)(PPh_3)_2$.[10] The alcohol is most likely formed *via* a radical pathway, *i.e.* hydrogen abstraction at one of the allylic positions. Further it was found that epoxidation of stilbene with $TBHP/RhCl(PPh_3)_3$ lacks stereospecificity. *Trans*-stilbene afforded 28% of *trans*-epoxide (5 eq. of TBHP, 0.5% catalyst, in benzene, 70^0) and 16% of unreacted stilbene, but *cis*-stilbene gave 14% of *trans*-epoxide while 76% of *cis*-stilbene were recovered. The significance of these results is not entirely clear, since epoxidation of *cis*-stilbene with $TBHP/Mo(CO)_6$ gives a 9:1 mixture of *cis*- and *trans*-stilbene oxide (93% conversion). A similar lack of stereospecificity in catalyzed oxidation of stilbenes with hydrogen peroxide has been reported.[11] Although we believe that with $Mo(CO)_6$ and $VO(acac)_2$ oxygen transfer to anthracene should proceed in a single step in analogy to alkene epoxidation, it appears that with $RhCl(PPh_3)_3$ radical pathways could occur competitively.



Acknowledgment. We are indebted to the Swiss National Science Foundation (grant No 2.420-79) for financial support.

REFERENCES

1) J.E. Lyons, in R. Ugo, ed., Aspects of Homogeneous Catalysis, Vol. 3, D. Reidel, Dordrecht, chapter 1.

2) D.H.R. Barton & R.K. Hayeres, J. Chem. Soc., Perkin I, 1975, 2065, Chem. Commun. 511 (1974).

3) A. Fusi, R. Ugo, F. Fox, A. Pasini & S. Cenini, J. Organometal. Chem. 26, 417 (1971).

4) V.S. Markevich & N. Kh. Shtivel', Kinetika i Kataliz 17, 357 (1976); V.P. Yur'ev, I.A. Gailyunas & G.A. Tolstikov, Zhur. Obshch. Khim. 43, 215 (1973).

5) K.B. Sharpless & T.R. Verhoeven, Aldrichimica Acta 12, 63 (1979).

6) G.A. Tolstikov, V.P. Yur'ev & U.M. Dzhemilev, Russian Chemical Reviews 44, 319 (1975).

7) H. Kropf, J. Spangenberg, A. Gunst & J. Hinrichsen, Liebigs Ann. Chem. 1980, 1923; S.K. Ivanov, J. Kateva, J. Dahlmann & E. Höft, J. Prakt. Chem. 322, 529 (1980); B. Bierling, K. Kirschke, H. Oberender & M. Schulz, Z. Chem. 9, 105 (1969).

8) B.L. Booth, R.N. Haszeldine & G.R.H. Neuss, J. Chem. Soc., Perkin I, 1975, 209.

9) R.A. Sheldon, J. Molecular Catalysis 7, 107 (1980); F. Di Furia, G. Modena, R. Curci & J.O. Edwards, Gazzetta Chimica Italiana 109, 571 (1979).

10) J.E. Lyons & J.O. Turner, J. Org. Chem. 37, 2881 (1972).

11) Y. Kobayashi, quoted by J.T. Groves, T.E. Nemo & R.S. Myers, J. Am. Chem. Soc. 101, 1032 (1979).

(Received in Germany 26 August 1981)