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RUTHENIUM-CATALYZED OXIDATION OF 2,3-EPOXYNORBORNANE. INFLUENCE OF THE NATURE OF THE REOXIDIZING REAGENT.

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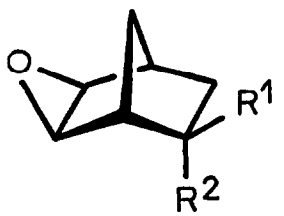
The nature of the reoxidizing reagent plays a decisive role in the outcome of the ruthenium-catalyzed oxidation of 2,3-epoxynorbornane.

Catalytic oxidations involving RuO_4* generated *in situ* strongly depend upon the reaction conditions (1) and upon the nature of the reoxidizing species (2). It was therefore of interest to analyze this influence on the tandem ruthenium-catalyzed rearrangement/oxidation of 2,3-epoxy bicyclo [2.2.1] heptane **1** which we have recently reported (3). We describe here our preliminary results (see Table) which are of particular interest in view of the fact that a Baeyer-Villiger type reaction (entry 1) occurs when NaOCl is used as reoxidizing species (4) ; the epoxide ring remains intact under the basic conditions of the reaction. Although the mechanistic studies are still under progress, the first intermediate in the process giving the epoxylactone **2** is likely to be the ketoepoxide **4**.

It is not clear yet, how the chloroepoxide **3** is formed although it probably results from a straightforward chlorination of **1** by sodium hypochlorite acting as a chlorine source (5). It is also interesting to note that the use of hydrogen peroxide (entry 2) or potassium persulfate (entry 3) allows the isolation of the glycol **5** previously postulated as an intermediate (3). Quite curiously, the other reoxidizing species currently used, such as $NaBrO_2$ (entry 4) [but also the N-oxide of N-methylmorpholine and tBuOOH (2)] leave the norbornane epoxide untouched. Finally it should be mentioned that the use of Oxone® (6) gives rise to the formation of product **8** (entry 5), resulting from a retro-Claisen (3) on the diketone **9** (entry 6).



1 $R^1 = R^2 = H$

4 $R^1, R^2 = O$

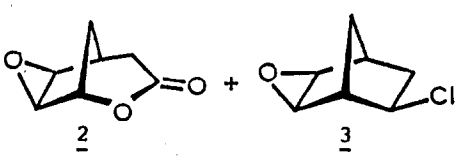
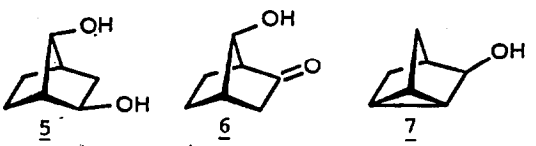
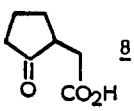
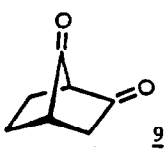
Entry	Reoxidizing Species (nb.equiv.)	Reaction time	Product(s) Yield(%)
1	NaOCl (20)	4h	 2 + 3 50 % (1:1)
2	H_2O_2 (4)	17h	 5 6 7 85.% (73:19:8)
3	$K_2S_2O_8$ (4)	2d	5 (86%)
4	$NaBrO_2$ (2)	1d	1 (recovered unchanged)
5	Oxone® (4)	2h	 8 37%
6	$NaIO_4$ (4) (see ref.3)	1,5h	 9 48%

TABLE. Ruthenium-Catalyzed Oxidation of 2,3-epoxynorbornane 1.

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REFERENCES

1 - By RuO_4* we mean the species which is the most likely to be formed under the following experimental conditions : $RuCl_3.3H_2O$ (0.022 mmol.) ; reoxidizing species [x equivalents -relatively to substrate- (see Table)] for 1 mmol. of epoxynorbornane 1 in CH_3CN / CCl_4 / H_2O (2 / 2 / 3 mL) at 60°C.
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2 - K.Takehura, T.Hayakawa, H.Orita, Bull.Chem.Soc.Japan, 1986, 59, 2637.
3 - A.Tenaglia, E.Terranova, B.Waegell, Tetrahedron Lett., 1989, 30, 5275.
4 - H.Nakata, Tetrahedron, 1963, 19, 1959.
5 - S.K.Chakrabartty in "Oxidation in Organic Chemistry", part C, Chap V, Ed. W.S.Trahanovsky, Academic Press, 1978.
6 - Potassium hydrogen persulfate, available from Janssen Chemica, under the trade name Oxone®, is a ternary mixture containing 2 moles $KHSO_5$, 1 mole $KHSO_4$, 1 mole K_2SO_4.

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