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TANDEM RUTHENIUM-CATALYZED REARRANGEMENT/OXIDATION OF BICYCLIC [2.2.1] HEPTANE EPOXIDES

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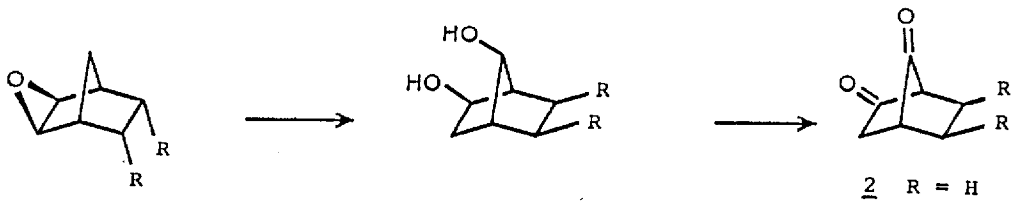
ABSTRACT : Ruthenium-catalyzed oxidation of variously substituted epoxides featuring the bicyclo [2.2.1] heptane skeleton affords β-diketones in fairly to good yields via a Wagner-Meerwein type rearrangement.

We have shown that RuO_4 obtained in situ is able to oxidize stereoselectively, bridged polycyclic derivatives in tertiary positions with retention of configuration (1). We now report that epoxides with the norbornane skeleton can be oxidized with the same reagent into β-diketones.

In a typical experiment sodium metaperiodate (877 mg ; 4.1 mmol) is added to a solution of exo-2,3-epoxynorbornane 1 (110 mg ; 1 mmol) in acetonitrile (2 ml), carbon tetrachloride (2 ml) and water (3 ml). Ruthenium(III) chloride trihydrate (5 mg ; 0.022 mmol) is then added and the reaction mixture is vigorously stirred at 60°C for 1.5 hours. After usual work-up, the diketone 2 is obtained in 48 % yield (entry 1). In a similar manner, oxidation of the epoxides 3 (entry 2) and 5 (entry 3) affords the diketones 4 and 6 respectively in 66 % and 80 % isolated yield. Oxidation of 5-acetoxymethyl, exo-2,3-epoxynorbornane 7 (entry 4) gives the expected diketone 8 in 35 % yield, along with the β-ketoacid 9 resulting from a retro-Claisen ring opening of the strained bicyclic β-diketone 8, by a stereoelectronically allowed process (2).

A possible route in the formation of diketones involves ring opening of the epoxide followed by a Wagner-Meerwein type rearrangement which leads to the corresponding diol (3). Further oxidation of these diols by RuO_4 affords the diketones (4). In order to verify this hypothesis, compound 5



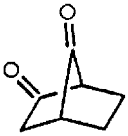
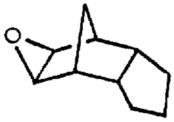
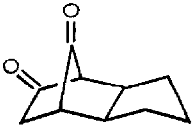
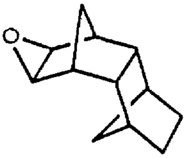
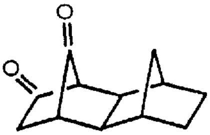
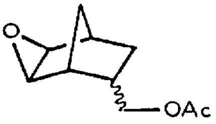
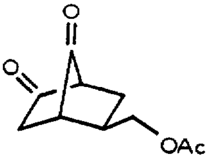
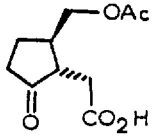
2 R = H

4 R R = $(CH_2)_3$

A R,R = 

6 R = 

Table : Ruthenium-Catalyzed Epoxide Oxidations[a]

Entry	Epoxide	Reaction Conditions	Product(s)[b]	Yield[c] (%)
1	 1	60°C, 1.5h	 2	48
2	 3	60°C, 1d	 4	66
3	 5	70°C, 1d	 6	80
4	 7 endo : exo = 4 : 1	60°C, 8.5h	 8  9	35[d] 10

a : All reactions were carried out on 1 mmol scale in CCl4/CH3CN/H2O (2/2/3 ml) with the following ratio: Epoxide : RuCl3 : NaIO4 : = 1 : 0.022 : 4.1
b : All new products have been fully characterized spectrally and elemental composition established by combustion analysis
c : Yields of isolated products obtained by flash chromatography
d : Minor products arised from 7 exo isomer have been detected but not fully characterized

was hydrolyzed into A (H_2O/THF, cat $HClO_4$, r.t., 2h, 87 % yield) which was further oxidized into 6 (PCC, CH_2Cl_2, r.t., 24h, 34 % yield).

The results of these catalytic oxidation reactions with RuO_4 using other reoxidizing reagents will be reported elsewhere.

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REFERENCES

1 - A.TENAGLIA, E.TERRANOVA, B.WAEGELL, preceding paper.
2 - P.DESLONGCHAMPS, "Stereoelectronic Effets in Organic Synthesis", J.E.BALDWIN Ed., Pergamon Press, Oxford, 1983.
3 - a) J.K.CRANDALL, J.Org.Chem., **29**, 2830 (1964).
    b) H.M.WALBORSKY and D.I.LONCRINI, J.Am.Chem.Soc., **76**, 5396 (1954).
    c) H.KWART and W.G.VOSBURGH, J.Am.Chem.Soc., **76**, 5400 (1954).
4 - P.E.MORRIS and D.E.KIELY, J.Org.Chem., **52**, 1149 (1987).

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