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STEREOSELECTIVE ADDITION OF SINGLET OXYGEN TO 8-ISOPROPYLIDENE-TRICYCLO[3.2.1.$0^{2,4}$]OCTANE DERIVATIVES[1]

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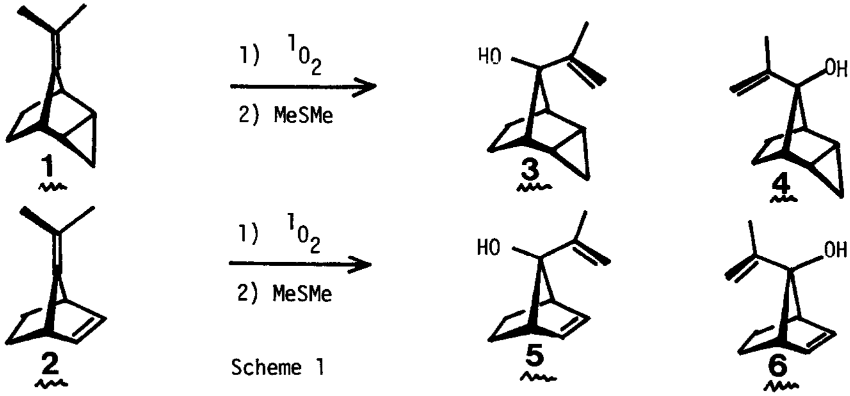
Summary: Singlet oxygen adds stereoselectively to 8-isopropylidenetricyclo[3.2.1.$0^{2,4}$]octane. The π-orbital distortion and the secondary orbital interaction are discussed in order to explain the observed stereoselectivity.

Recently it has been reported by two groups[2,3] that singlet oxygen adds stereoselectively to 7-isopropylidenenorbornene derivatives (2) where the π-orbital distortion of the exocyclic double bond seems to take an important role. In this connection, we wish to report the photooxidation of 8-isopropylidenetricyclo[3.2.1.$0^{2,4}$]octane (1), which contain a cyclopropane ring instead of the double bond of 2. When a solution of 1 in acetonitrile or acetone was photooxidized by irradiation with a 500W Tungsten-Brom lamp in the presence of methyleneblue as a sensitizer, followed by the reduction with dimethylsulfide in methanol[5], a pair of alcohols, anti-(3) and syn-one (4) were obtained in the yields, 56 % and 14 % in acetonitrile, and 72 % and 15 % in acetone, respectively (Scheme 1).[6,7] [3,oil,ν_{max}^{oil}(cm^{-1}) 3425,1650,897,$\delta_{ppm}^{CCl_4}$ 0.3-1.6(7H,m),1.83 (2H,m),1.91(3H,dd,J=1.5,1.0),2.05(2H,dddd,J=2.0,2.0,2.0,2.0),4.93(1H,m),5.01(1H,m), 4,oil,ν_{max}^{oil} (cm^{-1}) 3450,1650,897,$\delta_{ppm}^{CCl_4}$ 0.8-1.3(4H,m),1.3-1.7(4H,m),1.79(3H,dd,J=1.2,1.2),1.98(1H,br),2.01(2H,dddd,J=2.0,2.0,2.0,2.0),4.86(2H,m),] Table I shows the relationship between the product ra-



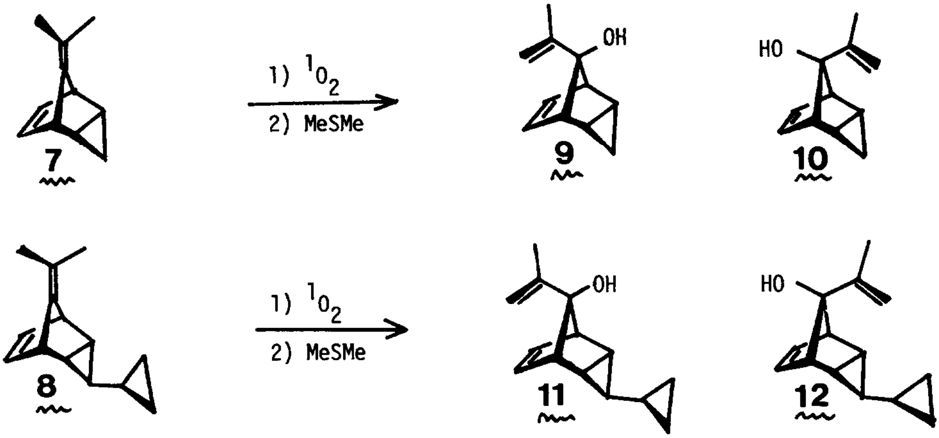
Scheme 1

tio and the degree of polarization of the exocyclic double bond which was learned from the difference in the ^{13}C-NMR values[8] at the two carbon atoms of the exocyclic double bond, as well as the resonance integral values which were estimated by Heilbronner and Martin[9] From Table I it is apparent that the endo-cyclopropane ring of **1** has a similar effect on the stereoselectivity as the double bond of **2**. It is also interesting to discuss the stereoselectivity from the viewpoint of the orbital interaction. The bigger polarization of the exocyclic double bond and resonance integral value in **1**, compared to that in **2**, indicate that the Walsh orbital interacts with π_{exo}-orbital(orbital of the exocyclic double bond) more strongly than the π_2-orbital(orbital of the endocyclic double bond of **2**) does. This is also in accord with solvolysis experiment of the related system[4] However, the singlet oxygen addition reaction in **1** is slightly less stereoselective than in **2**. In order to directly compare the effect of Walsh and π_2-orbitals, 8-isopropylidenetricyclo[3.2.1.0^{2,4}]octene (**7**)[10] and its derivative (**8**)[11] were photooxidized under the similar conditions. Thus, anti alcohols (**9** and **11**) in which the hydroxyl group is anti to the double bond and corresponding syn alcohols (**10** and **12**) were obtained in the ratio shown in Table I (Scheme 2). [**9**,oil,ν^{oil}_{max}(cm^{-1}) 3470,1650,890,$\delta^{CCl_4}_{ppm}$ 0.5-0.9(2H,m),1.43(2H,m),1.68(3H,dd,J=1.2,1.2),2.50(1H,br),2.68(2H,dddd,J=2.0,2.0,2.0,2.0),4.70(2H,m),5.58(2H,dd,J=2.0,2.0), **10**, oil,ν^{oil}_{max}(cm^{-1}) 3560,3460,1650,890,$\delta^{CCl_4}_{ppm}$ 0-0.6(2H,m),0.9-1.3(2H,m),1.82(3H,dd,J=1.2,1.2),2.53(1H,br),2.90(2H,dddd,J=2.0,2.0,2.0,2.0),4.96(2H,m),5.83(2H,dd,J=2.0,2.0), **11**,m.p 38-40°C,ν^{oil}_{max}(cm^{-1}) 3570,3470,1650,890,$\delta^{CCl_4}_{ppm}$ 0-0.9(6H,m),1.31(2H,ddd,J=2.0,2.0,2.0),1.69(3H,m),2.54(1H,br),2.70(2H,dddd,J=2.0,2.0,2.0,2.0),4.71(2H,m),5.58(2H,dd,J=2.0,2.0), **12**,oil,ν^{oil}_{max}(cm^{-1}) 3560,3475,1652,892,$\delta^{CCl_4}_{ppm}$ 0-0.7(6H,m),0.98(2H,ddd,J=2.0,2.0,2.0),1.82(3H,m),2.66(1H,br),2.90(2H,dddd,J=2.0,2.0,2.0,2.0),4.95(2H,m),5.82(2H,dd,J=2.0,2.0)]. As expected from the results with **1** and **2**, anti alcohol **9** was produced in a slightly better yield than syn alcohol **10**. The cyclopropane

Table I. The reaction selectivity and physical properties of **1**,**2**,**7**, and **8**.

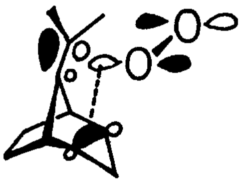
	product ratio(anti:syn)		Δ ppm	resonance integral values[9]	
1	80:20^a	82:18^b	47.3(C_8-C_9)	-0.44 eV	$\langle\pi_{exo}\vert H\vert Walsh\rangle$
2	83:17^a	86:14^b	41.7(C_7-C_8)	-0.24 eV	$\langle\pi_{exo}\vert H\vert\pi_2\rangle$
7	57:43^a	57:43^b	58.7(C_8-C_9)	-0.44 eV -0.45 eV	$\langle\pi_{exo}\vert H\vert Walsh\rangle$ $\langle\pi_{exo}\vert H\vert\pi_2\rangle$
8	50:50^a	55:45^b			

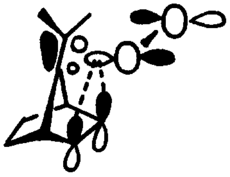
a; in acetonitrile b; in acetone



Scheme 2

attached to the endo-cyclopropane ring does not have a great influence on the stereoselectivity. Thus, the attack of singlet oxygen on the exocyclic double bond from the side anti to the Walsh orbital is not so predominant, contrary to the expectation from the ^{13}C-NMR values and resonance integral values. To clarify the point, we carried out the competition reactions between 1, 2 and 7 in acetonitrile, where the relative rate constants, k_{anti}=1.7 and k_{syn}=0.41 for 1, k_{anti}= 1.0 and k_{syn}=0.21 for 2, k_{anti}=0.32 and k_{syn}=0.24 for 7 were obtained.[12] With 1 and 2, the higher reactivity of anti-side in 1 is compatible with the ^{13}C-NMR values and resonance integral values, and can be interpreted by the π-orbital distortion and low ionization potential of 1. The observed smaller stereoselectivity in 1 could be ascribed to the increase of reactivity in the syn-side. Although the reason for the increase of reactivity in syn-side in 1 is not clear, the secondary orbital interaction[13] seems to be an attractive explanation. The repulsive effect due to the antibonding secondary orbital interaction between the coming singlet oxygen and Walsh orbital might be reduced in 1 (Fig. A), compared to that in 2 (Fig. B), because of the characteristic shape of the Walsh orbital. The low reactivity of 7 is likely to support the proposed secondary orbital interaction, although electron delocalization effect which will cause the decrease of electron density of the exocyclic double bond could not be neglected.

A


B


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6) Satisfactory elemental analyses were obtained for all new compounds appeared in this paper.

7) Stereochemistry of the alcohols was determined by use of NMR shift reagent Eu(fod)$_3$. Anisotropic upfield effect of isopropenyl group is also in accord with the assigned stereochemistry. Yield and product ratio were determined by NMR.

8) Chemical shifts, in parts per million to lower fields from Me$_4$Si, at the C$_8$ and C$_9$ positions for **1** are 154.3 and 107.0, respectively.

9) E. Heilbronner and H.D. Martin, *Helv. Chem. Acta*., **55**, 1490 (1972). Neglection of the mixing of the π^*_{exo}- and σ_{exo}-orbitals might cause the difference in the resonance integral values $\langle \pi_{exo} | H | \pi_2 \rangle$ between **2** and **7**.

10) Laticyclic charator of **7** was also confirmed from the ^{13}C-NMR data. Carbon chemical shift at exocyclic double bond are 158.8 (C$_8$) and 100.1 (C$_9$) for **7**, 143.1 (C$_7$) and 112.8 (C$_8$) for 7-isopropylidenenorbornane (standard compound).

11) **8** was obtained as a by-product in the Diels-Alder reaction of 6,6-dimethylfulvene with cyclopropene.

12) The values at the ca. 50 % and 80 % conversion of **2**. The error limit was within ±10 %.

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