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ON STEREOCHEMISTRY OF OSMIUM TETROXIDE OXIDATION OF ALLYLIC ALCOHOL SYSTEMS: EXAMPLES

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Abstract: Forty-two examples are presented to demonstrate the consistency of the empirical formulation proposed in the preceding paper.

In the preceding paper, we have presented an empirical formulation of the stereochemical outcome of osmium tetroxide oxidation of allylic alcohols and their derivatives.[1,2] This formulation is consistent with unpublished examples from this laboratory as well as examples known in the literature. Some selected examples are listed in the Table with classification of (A) acyclic and (B) cyclic systems. Acyclic systems are further divided into (a) nonconjugated compounds and (b) conjugated carbonyl compounds. Finally, nonconjugated compounds are classified into (1) the cases where a chiral center due to a hydroxyl or alkoxyl group is present at only one end of the olefinic bond, and (2) the cases where a chiral center due to a hydroxyl or alkoxyl group is present at both ends of the olefinic bond. The ratio indicated for each compound represents the ratio of the major and minor stereoisomers, predicted by this empirical formulation.

Seventeen examples under A-a-1 do not require further explanation except to point out the fact that, as mentioned in the preceding paper, acyl groups are poor in directing stereoselective osmylation (examples 3 and 17). For the cases where a chiral center due to a hydroxyl or alkoxyl group is present at both ends of the olefinic bond (examples under A-a-2), their effects seem to be additive; that is, the effects of two groups complement one another in compounds 18, 19, 20, 21, 23 and 25, while they counteract each other in compounds 22, 24 and 26.

This formulation seems to be applicable also for conjugated carbonyl compounds (examples under A-b). However, application to these systems must be made carefully, since at least two exceptions are known (examples 35 and 36).[3,4]

Related to the empirical formulation for osmylation, it would be interesting to examine the stereochemical outcome of permanganate oxidation of allylic alcohols and their derivatives. Preliminary experiments on permanganate oxidation of the olefins described in the preceding paper have shown that the stereochemistry of the major product corresponds to that of the major product obtained by osmium tetroxide oxidation.[5]

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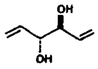
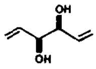
Table

A. Acyclic Systems

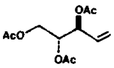
a. Nonconjugated Compounds - 1



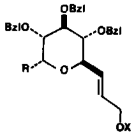
1[6] : Ratio = 1:0[7]



2[6] : Ratio = 1:0[7]



3[6] : Ratio = 1:1[7]



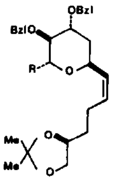
4[8] : Ratio = 6:1
R = X = H

5[8] : Ratio = 8:1
R = OMe, X = $\mathrm{COC(Me)_3}$

6[8] : Ratio = 4:1
R = $\mathrm{(CH_2)_2OCH_2OMe}$, X = H

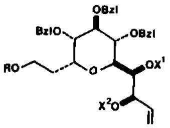
7[8] : Ratio = 4:1
R = $\mathrm{(CH_2)_2OCH_2OMe}$,
X = $\mathrm{Si(Ph)_2(t\text{-}Bu)}$

8[8] : Ratio = 8:1
R = $\mathrm{(CH_2)_2OCH_2OMe}$,
X = $\mathrm{COC(Me)_3}$



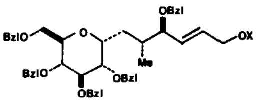
9[9] : Ratio = 11:1
R = $\mathrm{CH_2OSi(Ph)_2(t\text{-}Bu)}$

10[10]: Ratio = 7:1
R = $\mathrm{(CH_2)_2OSi(Ph)_2(t\text{-}Bu)}$

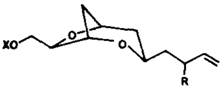


11[8] : Ratio = 1:0
R = X^2 = H, X^1 = $\mathrm{CH_2OMe}$

12[8] : Ratio = 2:1
R = $\mathrm{CH_2OMe}$, X^1 = X^2 = acetonide



13[11] : Ratio = 1:0
X = $\mathrm{Si(Me)_2(t\text{-}Bu)}$



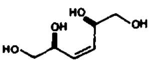
14[11] : Ratio = 1:0
X = $\mathrm{Si(Ph)_2(t\text{-}Bu)}$, R = β-OH

15[11] : Ratio = 4:1
X = $\mathrm{Si(Ph)_2(t\text{-}Bu)}$, R = β-OBzl

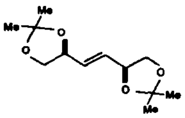
16[11] : Ratio = 10:1
X = $\mathrm{Si(Ph)_2(t\text{-}Bu)}$, R = α-OBzl

17[11] : Ratio = 1:1
X = $\mathrm{Si(Ph)_2(t\text{-}Bu)}$, R = α-OCOPh

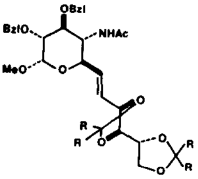
a. Nonconjugated Compounds - 2



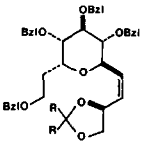
18[6] : Ratio = 1:0[7]



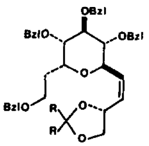
19[8] : Ratio = 10:1



20[12] : Ratio = 1:0
R = $\mathrm{-(CH_2)_5-}$



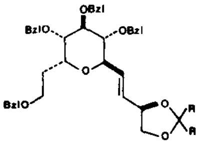
21[8] : Ratio = >10:1
R = $\mathrm{-(CH_2)_5-}$



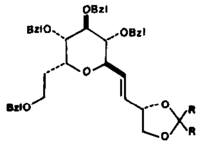
22[8] : Ratio (β:α) = 3:1
R = $\mathrm{-(CH_2)_5-}$

Table (Continued)

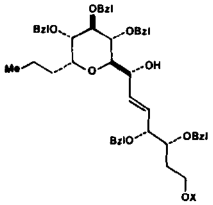
A. a. Nonconjugated Compounds - 2 (Continued)



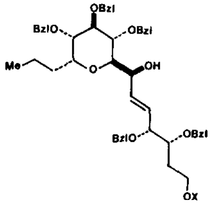
23[8] : Ratio = 1:0
R = -(CH$_2$)$_5$-



24[8] : Ratio = 1:1
R = -(CH$_2$)$_5$-



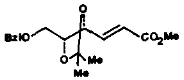
25[8] : Ratio = >10:1
X = Si(Ph)$_2$(t-Bu)



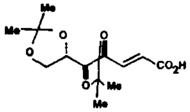
26[8] : Ratio (α:β) = 2:1
X = Si(Ph)$_2$(t-Bu)

A. Acyclic Systems

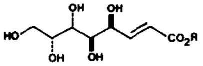
b. Conjugated Carbonyl Compounds



27[13] : Ratio = 8:1

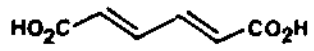


28[14] : Ratio = 1.8:1

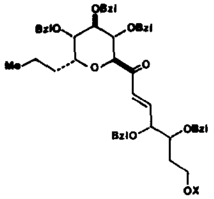


29[14] : Ratio = 2.2:1
R = H

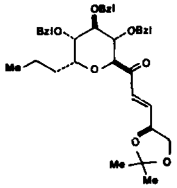
30[14] : Ratio = 1.8:1
R = Et



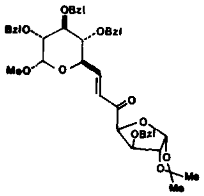
31[15] : Ratio = 16:1



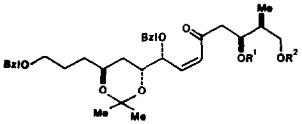
32[8] : Ratio = 10:1
X = Si(Ph)$_2$(t-Bu)



33[8] : Ratio = 4:1



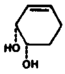
34[8] : Ratio = 2:1



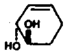
35[16] : Ratio = 1 : 4
R^1 = R^2 = Bzl

36[3] : Ratio = 1:2
R^1 = R^2 = acetonide

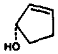
B. Cyclic Systems



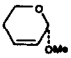
37[17] : Ratio = 1:0



38[17] : Ratio = 50:1

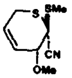


39[8,18] : Ratio = 4:1



40[19] : Ratio = 1:0

41[19] : Ratio = 1:0



42[20] : Ratio = 1:0

References and Footnotes

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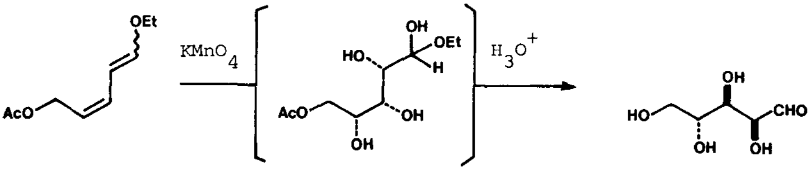
3. H. Fujioka, W. J. Christ, J. K. Cha, J. Leder, Y. Kishi, D. Uemura, and Y. Hirata, J. Am. Chem. Soc., 104, 7367 (1982).
4. This might be attributed to the differences in the preferred conformation between α,β-unsaturated carbonyl and isolated olefinic compounds. Namely, unsaturated carbonyl compounds may take the preferred conformation somewhat resembling the dipole model for the Cram's rule. See, J. W. Cornforth, R. H. Cornforth, and K. K. Mathew, J. Chem. Soc., 112 (1959). In the organic colloquium on March 14, 1983, at Harvard University, Professor Gilbert Stork at Columbia University discussed OsO_4 oxidation of trisubstituted α,β-unsaturated esters. The stereochemical outcome of his example was also opposite to the one expected from this formulation.
5. The experiment reported by Iwai and Tomita [Chem. Pharm. Bull. Japan, 9, 976 (1961)] is interesting to add. Potassium permanganate oxidation of diene 43 yielded arabinose, but not ribose. Assuming permanganate oxidation takes place on the diene system in a stepwise fashion, the stereochemical outcome of permanganate oxidation was opposite to that predicted for osmium tetroxide oxidation.



43 44 45 : arabinose

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7. This ratio is based on the amount of product(s) isolated by crystallization.
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17. Th. Posternak and H. Friedli, Helv. Chim. Acta, 36, 251 (1953).
18. Wolczunowicz, Bors, Cocu, and Posternak pointed out the importance of homoallylic hydroxyl groups in directing the stereochemistry of OsO_4 oxidation of polyhydroxycyclopentenes [Helv. Chim. Acta, 53, 2288 (1970) and references cited therein].
19. R. M. Srivastava and R. K. Brown, Can. J. Chem., 49, 1339 (1971).
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