to obtain crystallization was unsuccessful. IR (KBr) 3330 (NH_2), 1560 (NH), 1470, 1380, 1150, 1020 cm^{-1}.

2-Bis(2-chloroethyl)amino-2-oxo-6-(5α-cholestanyl)-1,3,2-oxazaphosphorinane (1a and 1b). A crude 1.7 g (3.9 mmol) of **4** and 1.0 g (3.9 mmol) of bis(2-chloroethyl) phosphoramidic dichloride (**5**) was dissolved in 160 m*l* of anhydrous THF, and added 0.79 m*l* (7.8 mmol) of anhydrous Et_3N. The reaction mixture was vigorously stirried for 24 hrs, and the $Et_3N \cdot HCl$ formed was filtered. The filtrate was evaporated in vaccuo and the residue was chromatographed on silica gel using EtOAc : CH_2Cl_2 : Hexane (2 : 2 : 1) to give fractions containing faster eluting **1a** and slower eluting **1b** (**1a** : **1b** = 1 : 1.2; 1.2 g; 58% yield). For **1a**: mp. 192-194℃; ^{1}H-NMR ($CDCl_3$) δ 3.61 (t, J=7.40, 4H, 2 x $-NCH_2\underline{CH_2}Cl$), 3.25-3.50 (m, 4H, 2 x $-N\underline{CH_2}CH_2Cl$), 3.19 (m, 2H, $-NH\underline{CH_2}-CH_2-$), 2.73 (br s, 1H, NH), 2.12 (m, 2H, $-NHCH_2\underline{CH_2}-$), 0.6-2.0 (m, H steroid); ^{13}C-NMR ($CDCl_3$) δ 84.9 (d, $J_{C.P.}$=7.8, spiro carbon), 49.3 (d, $J_{C.P.}$=3.0, 2 x $-N\underline{CH_2}CH_2Cl$), 42.5 (2 x $-NCH_2-\underline{CH_2}Cl$), 41.9 (d, $J_{C.P.}$=8.5, $-NH\underline{CH_2}CH_2-$), 36.0 ($-NHCH_2\underline{CH_2}-$), 12.0, 12.1, 18.7, 21.3, 22.5, 22.8, 23.8, 24.2, 28.0, 28.2, 28.5, 31.9, 32.0, 35.5, 35.8, 36.0, 36.2, 38.1, 39.5, 40.0, 42.5, 42.6, 43.7, 54.5, 56.3, and 56.5 (steroid carbons); ^{31}P-NMR ($CDCl_3$) δ 10.25; Mass (FAB) (m/z) 618 (M+1); Anal. Calcd. for $C_{33}H_{59}N_2O_2PCl_2$: C, 64.17; H, 9.62; N, 4.53. Found: C, 64.09; H, 9.79; N, 4.32. For **1b**: mp. 178-180℃; ^{1}H-NMR ($CDCl_3$) δ 3.60 (t, J=6.9, 4H, 2 x $-NCH_2\underline{CH_2}Cl$), 3.28-3.54 (m, 4H, 2 x $-N\underline{CH_2}CH_2Cl$), 3.19 (m, 2H, $-NH\underline{CH_2}CH_2-$), 2.50 (br d, 1H, NH), 2.13 (m, 2H, $-NHCH_2\underline{CH_2}-$), 0.6-2.0 (m, H steroid); ^{13}C-NMR ($CDCl_3$) δ 84.7 (d, $J_{C.P.}$= 7.8, spiro carbon), 49.4 (d, $J_{C.P.}$=4.3, 2 x $-N\underline{CH_2}CH_2Cl$), 42.5 (2 x $-NCH_2\underline{CH_2}Cl$), 35.0 (d, $J_{C.P.}$=7.4, $-NH\underline{CH_2}CH_2-$), 35.8 ($-NHCH_2\underline{CH_2}-$), 12.0, 12.1, 18.7, 21.1, 22.5, 22.8, 23.8, 24.2, 28.0, 28.5, 32.0, 35.4, 35.7, 35.9, 36.2, 38.7, 39.4, 40.0, 42.5, 42.6, 43.9, 54.5, 56.3, and 56.5 (steroid carbons); ^{31}P-NMR ($CDCl_3$) δ 10.48; Mass (FAB) (m/z) 618 (M+1); Anal. Calcd. for $C_{33}H_{59}N_2O_2PCl_2$: C, 64.17; H, 9.62; N, 4.53. Found: C, 64.32; H, 9.98; N, 4.49.

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Transformation Mechanism of Bicyclic Ketal Compound to 1,5-Diketone

Sung Hoon Kim[†] and Jong-Gab Jun*

Department of Chemistry, Hallym University, Chunchon 200-702

[†]Department of Chemistry, Konkuk University, Seoul 133-701

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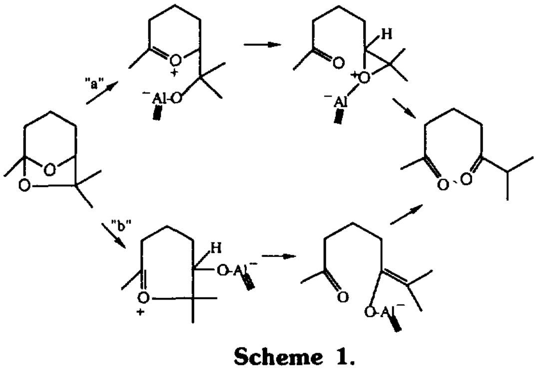
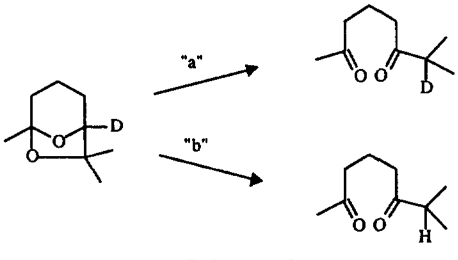
The chemistry of bicyclic ketals in the 6,8-dioxabicyclo[3.2.1]octane series are very unique and interesting. Our initial success in the preparation of 1,5-diketone from bicyclic ketal[1] expanded the utilities of this bicyclic ketal system to the direct syntheses of 2,6-disubstituted pyridines,[2] 2,3,6-trisubstituted pyridines,[3] cyclohexenones[4] and cyclopentanediol derivatives.[5] The 1,5-diketone is thought to be an active intermediate for these transformation reactions.

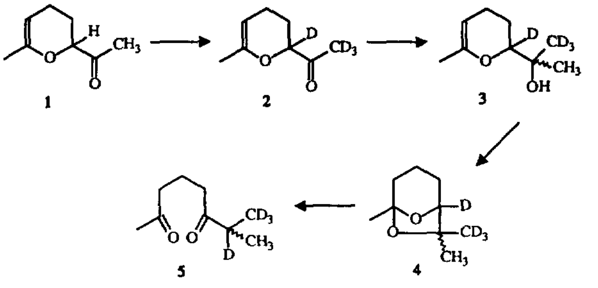
We proposed two possible mechanisms for the formation of 1,5-diketone from bicyclic ketal using aluminium chloride-sodium iodide in methylene dichloride.[1] The mechanism "a" in Scheme 1 involves O(6)-C(5) bond cleavage followed by 1,2-hydride shift *via* an epoxide intermediate, whereas the alternative mechanism "b" involves O(8)-C(5) bond cleavage followed by proton abstraction.



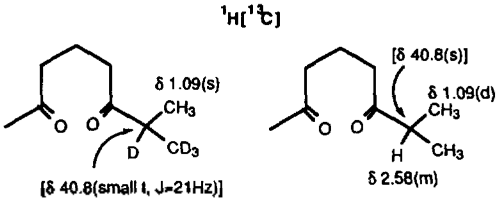
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

Now we wish to prove the mechanism for this novel skeletal transformation of bicyclic ketal to 1,5-diketone *via* deuterium labelling study.

If we have deuterium labelling at C-1 of bicyclic ketal, it will be easy to choose the correct mechanism between "a" and "b" as shown in Scheme 2. The deuterated diketone must result from path "a", whereas the protonated diketone must result from path "b".

To make deuterium labelled bicyclic ketal at C-1, MVK dimer **1** was deuterated with D_2O using NaOD as a catalyst (Scheme 3). We found that the less substituted site of the ketone (methyl group) is more reactive for deuterium exchange even in the thermodynamic conditions. So we deuterated all α and α′ protons to give compound **2** which was methylated with MeLi to carbinol **3** and cyclized to give expected deuterated bicyclic ketal **4**.

Finally, bicyclic ketal **4** was reacted with aluminium chloride-sodium iodide in methylene dichloride. The proton NMR spectrum indicated that deuterated diketone **5** was the only product; A multiplet at δ 2.58 of the methine proton disappeared and methyl group at δ 1.09 showed singlet. Also proton-decoupled carbon NMR spectrum showed that a singlet at δ 40.8 of the methine carbon turned to small triplet (J=21 Hz) (Scheme 4).

In conclusion, the mechanism for the transformation of bicyclic ketal to 1,5-diketone must be involved O(6)-C(5) bond cleavage followed by 1,2-hydride shift as shown in path "a" of Scheme 1.

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   Spectral data for (**3**): ^{1}H-NMR (200 MHZ, $CDCl_3$) δ 4.44 (1H, m, CH=), 2.46 (1H, br s, OH), 2.09-1.75 (4H, m, CH_2 CH_2), 1.73 (3H, br s, $CH_3C=$), 1.21 (1H, s, CH_3) and 1.18 (2H, s, CH_3) indicates 1 : 2 ratio of diastereomer (threo : erythro); ^{13}C-NMR ($CDCl_3$) δ 151.2 (MeC=), 96.0 (CH=), 81.9 (small t, J=22 Hz, OCD), 26.2 and 24.5 (1 : 2 ratio of diastereomer for CH_3, small septet of CD_3 buried in this region), 22.5 (CH_2), 21.4 ($\underline{C}H_3C=$), 20.4 (CH_2).
   Spectral data for (**4**): ^{1}H-NMR (200 MHZ, $CDCl_3$) δ 2.00-1.45 (6H, m, $CH_2CH_2CH_2$), 1.40 (3H, s, CH_3), 1.36 (2H, s, *endo*-CH_3); 1.26 (1H, s, *exo*-CH_3); ^{13}C-NMR ($CDCl_3$) δ 107.2 (s, OCO), 81.1 (small t, J=26 Hz, OCD), 80.8 (s, $O\underline{C}Me_2$), 34.2 (t, CH_2), 29.2 (q, CH_3), 24.2 (t, CH_2), 17.2 (t, CH_2), 25.8 and 20.9 (1 : 2 ratio of *exo* and *endo* CH_3, small septet for CD_3 also buried in the region).
   Spectral data for (**5**): ^{1}H-NMR (200 MHZ, $CDCl_3$) δ 2.49 (2H, t, J=7 Hz, CH_2CO), 2.46 (2H, t, J=7 Hz, CH_2CO), 2.13 (3H, s, CH_3CO), 1.83 (2H, pent, J=7 Hz, CH_2), 1.09 (3H, s); ^{13}C-NMR ($CDCl_3$) δ 214.2 (s, C=O), 208.4 (s, C=O), 42.6 (t, $\underline{C}H_2CO$), 40.8 (small t, J=21 Hz, $CDMe_2$), 39.0 (t, $\underline{C}H_2CO$), 29.8 (q, $\underline{C}H_3CO$), 18.2 (q, CH_3, CD_3, also buried as small multiplet in this region), 17.8 (t, CH_2).

The Mechanism for Cyclooligomerization of Acetylene: The Structures of $CpCo(C_4H_4)$ and $CpCo(\eta^2\text{-}C_2H_2)_2$ as Intermediates

Gab Yong Lee*, John B. Koerner†, and Thomas A. Albright†

Department of Chemistry, Hyosung Women's University, Kyungsan 713-702
†Department of Chemistry, University of Houston, Tx 77204-5641, U.S.A.

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A reaction of long-standing interest to the organometallic chemistry has been the trimerization of acetylene to give benzene *via* a number of transition metal catalysts. Despite its commercial and academic importance, there has been no prior theoretical work and several important issues are not yet resolved.

The basic mechanism[1-3] is outlined in Scheme 1. An acetylene-ML_n adduct, **1**, adds a second acetylene ligand to give