of the d(GCGCGCGC)$_2$. Thermodynamic data obtained from UV melting transition of d(GCGCGCGC)$_2$ double helix and its complex with berenil also supported this result (Table 2, Figure 5). Basically, berenil is known to bind strongly to the 5'-AATT site in the minor-groove *via* two hydrogen bonds: one between amidino proton and thymine carbonyl oxygen, and the other between amidino proton at the other site and adenine N3.[20] Very recently, Pilch *et al.* reported that berenil could bind poly[d(G-C)]$_2$ *via* intercalation as well as complexation in the minor-groove,[21] but our NMR data did not show any evidence for intercalation. More detailed studies about the effect of berenil binding on the base-pair life time of the d(GCGCGCGC)$_2$ double helix is under progress by using 2-Dimensional NMR spectroscopy.

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[3,3]Sigmatropic Rearrangement of Dihydropyran Derivatives

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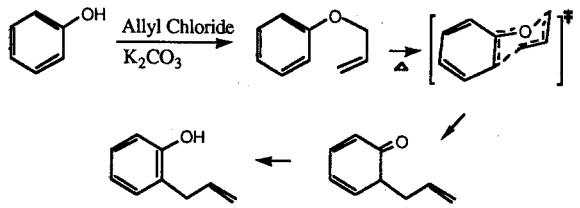
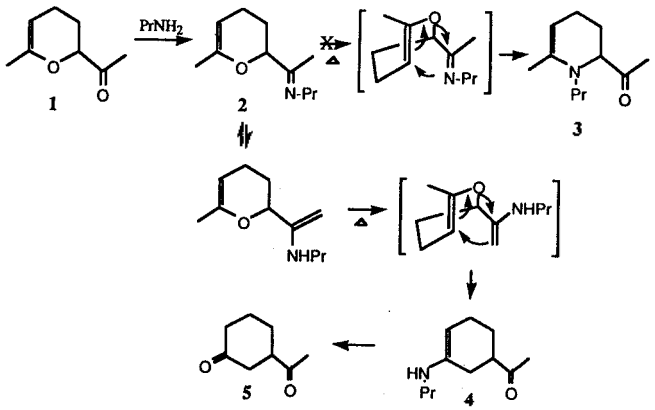
[3,3]sigmatropic shift, especially Claisen rearrangement, has been utilized for introduction of allyl group on benzene ring (Scheme 1).[1] This reaction has been known to proceed as stereoselective concerted mechanism *via* chair cyclohexane transition state.[2] Buchi has taken advantage of this [3,3]sigmatropic shift to gain entry into substituted cyclohexene system.[3] We now wish to introduce [3,3]sigmatropic rearrangement of dihydropyran derivatives to other structures, otherwise which are not readily available.

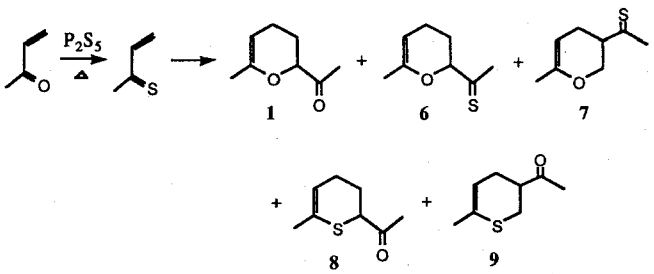
Dihydropyran **1**, was prepared from methyl vinyl ketone,[4] was converted to the imine **2** by mixing a slight excess of propylamine over molecular sieves in ether solution (Scheme 2). The propyl imine **2** could be purified by distillation, but because of rapid deterioration it had to be used within a few days after purification. Heating the imine at 250 ℃ re-



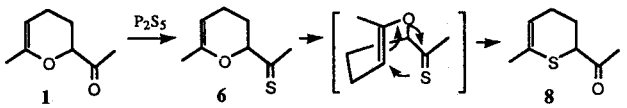
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

sulted in formation of a product which was an enamine (74 %). Spectral analysis of it was not consistent with enamine **3**, but showed enamine **4** through imine-enamine tautomerization[5]; ^{1}H NMR of enamine **4** showed only one methyl at δ 2.15 and NH shift at δ 3.38. Hydrolysis of enamine **4** yielded 3-acetylcyclohexanone **5**.[6]

To make thiocarbonyl hydropyran, methyl vinyl ketone was heated with phosphorus pentasulfide in autoclave. But the reaction resulted in the mixture of several products (Scheme 3).[7] The carbon-sulfur double bond can serve as either a diene or dienophile in Diels-Alder reaction, and produces a mixture of regioisomers whether acting as a dienophile to form **6** and **7** or as a diene to form **8** and **9**. The sulfur atom should be introduced as a thiocarbonyl function to methyl vinyl ketone dimer **1** instead of methyl vinyl ketone itself to prevent the formation of regioisomers (Scheme **4**).

To methyl vinyl ketone dimer **1**, which was heated to 90 ℃ in pyridine, phosphorus pentasulfide was added and the mixture was stirred overnight at the same temperature to give 64% of thiocarbonyl pyran **6**. The pyran **6** in neat was refluxed for 1 hour to give 80% of thiapyran **8**.[8] In this [3,3] sigmatropic rearrangement, sealded tube or quartz column thermolysis did not give any advantage and even worse using in solvent.

[3,3]Sigmatropic rearrangement is a reversible reaction in general and the equilibrium in this reaction depends upon the relative stability of product and starting material. In conclusion, the Claisen rearrangement of dihydropyran is a useful method for the preparation of cyclohexanone and thiapyran structures.

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Spectral data of **8**; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.53 (1H, br s), 3.77 (1H, t, J=5.5 Hz), 2.30-1.90 (4H, m), 2.27 (3H, s), 1.87 (3H, d, J=1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 206.1, 129.3, 126.3, 117.1, 50.0, 28.0, 23.4, 22.7; IR (neat) 1700, 1644, 1432, 1355, 1218, 1156, 1106 cm^{-1}; Ms (m/z): 156 (M^+, 49), 113 (66), 98 (56), 85 (14), 79 (27), 71 (10), 58 (14), 43 (100); Anal. calcd for $C_8H_{12}OS$: C, 61.54; H, 7.69; S 20.51. Found: C, 61.72; H, 7.79; S, 23.77.

Novel Migration of Aryl Group in Pyrazolyl Aryl Ether

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Pyrazolyl aryl ether derivatives **2** have been reported to exhibit a potent herbicidal activity[1] and also used as pesticidal intermediate materials.[2] To prepare their analogues,[2,3] the aryl group was usually introduced by the reaction of compound **1**[4-6] with an appropriate aryl halide under basic conditions. During the synthesis of their analogues, we reported that the pyrazolyl aryl ether derivatives **2** (R_1=H) underwent migration of aryl group from oxygen to nitrogen in pyrazole moiety.[7] Recently, another interesting aryl group migration from oxygen to carbon was also observed in the same process. We found that pyrazolyl aryl ether derivatives **2** (R_1=alkyl or aryl) with no substituent at 4-position in pyrazole moiety resulted in the formation of aryl-migrated compound **3** (Scheme 1). The progress of the reaction can be simply checked by TLC and the migrated compound **3** can