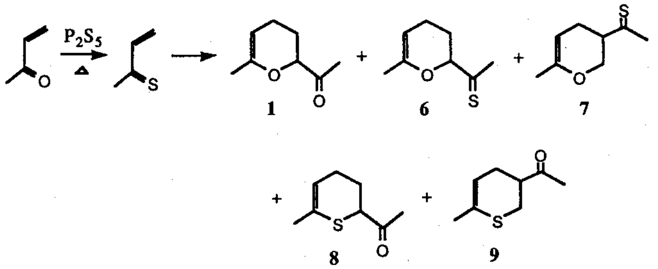
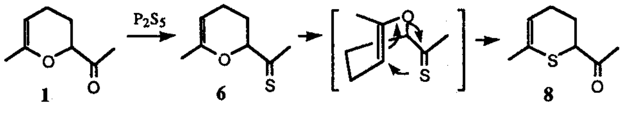


Scheme 3.



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.

Acknowledgment. Financial support of the Basic Science Research Institute Program of Ministry of Education (BSRI-94-3401) and the Research Center for New Bio-Materials in Agriculture (KOSEF) are gratefully acknowledged.

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8. Spectral data of **6**; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.91 (1H, d, $J=3$ Hz), 2.09 (1H, m), 1.85-1.50 (4H, m), 1.69 (3H, s), 1.65 (3H, s); ^{13}C NMR ($CDCl_3$) δ 254.4, 152.2, 98.9, 84.2, 38.5, 30.6, 27.2, 17.5; IR (neat) 1629, 1452, 1374, 1218, 1151, 1124, 1031 cm^{-1}; Ms (m/z): 156 (M^+, 1.3), 154 (24), 111 (100), 77 (11), 67 (8), 59 (6), 43 (20); Anal. calcd for $C_8H_{12}OS$: C, 61.54; H, 7.69; S 20.51. Found: C, 61.71; H, 7.70; S, 20.73.
   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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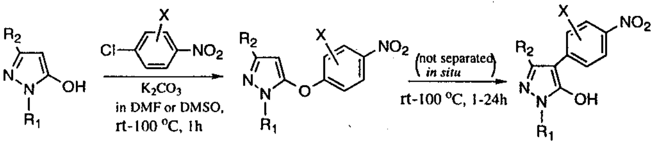
Received October 30, 1995

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



1 **2** **3**

Scheme 1.

Table 1. Aryl migration products **3** in pyrazolyl aryl ether derivatives

No.	R_1	R_2	X	**3** [Yield; mp(℃); MS (m/z); ^{1}H NMR^a]
1	Ph	CH_3	2-Cl	70%; 246-248 (dec.); 329 (M^+); (DMSO-d_6) δ 2.21 (s, 3H), 7.31-8.49 (m, 8H).
2	Ph	CH_3	2,6-Cl_2	62%; 262 (dec.); 364 (M^+); (DMSO-d_6) δ 2.22 (s, 3H), 7.29-7.93 (m, 5H), 8.30 (s, 2H), 11.81 (brs, 1H).
3	CH_3	CH_3	2-Cl	68%; 253 (dec.); 226 (M^+); (DMSO-d_6) δ 2.19 (s, 3H), 3.56 (s, 3H), 7.69 (d, *J*=8.5, 1H), 8.21-8.42 (m, 2H), 11.22 (brs, 1H).
4	CH_3	CH_3	2,6-Cl_2	69%; 288 (dec.); 302 (M^+); (DMSO-d_6) δ 2.20 (s, 3H), 3.61 (s, 3H), 8.31 (s, 2H).
5	CF_3CH_2	Ph	2,6-Cl_2	56%; 222-224 (dec.); 432 (M^+); (DMSO-d_6) δ 4.60-4.99 (m, 2H), 7.31 (s, 5H), 8.22 (s, 2H).
6	*t*-butyl	CF_3	2,6-Cl_2	62%; 158; 398 (M^+); (Aceton-d_6) δ 1.80 (s, 9H), 8.33 (s, 2H), 10.29 (s, 1H).

[a] Spectra were recorded on either Varian Gemini 200 or JEOL JUM-PMX 60 instrument with TMS as reference.

be easily identified from the disappearence of ^{1}H NMR peak[8] at 4-position in pyrazole moiety of derivatives **2**. The results of aryl migration in pyrazolyl aryl ethers are summarized in Table 1.

It is noteworthy that the intermediate *O*-arylated pyrazole derivatives **2** alone, did not effect the desired rearrangement to migrated products **3** under refluxing condition without using base. However, the migration was occurred by addition of base (K_2CO_3 or $KHCO_3$) to the reaction mixtures smoothly.

So far, we have introduced some alkyl groups at 4-position in pyrazole through Claisen rearrangement[9] under high temperature. Now it is possible to introduce some aryl groups to 4-position in pyrazole in this system under mild reaction conditions.

In summary, when the pyrazole aryl ether had no substituent at 4-position in pyrazole moiety, the novel migration of aryl group from oxygen to carbon atom was observed in the presence of base. The synthetic method can be applied to the synthesis of various pyrazole derivatives which have potential insecticides and agricultural chemicals.

Typical procedure:

Synthesis of intermediate 2 (R_1=Ph, R_2=CH_3, X=2,6-Cl_2). A solution of 5-hydroxy-3-methyl-1-phenyl pyrazole **1** (0.46 g, 2.65 mmol), 3,4,5-trichloronitrobenzene (0.6 g, 2.65 mmol) and potassium carbonate (0.54 g, 3.97 mmol) in DMF (5 mL) was stirred at 70 ℃ for 1 hr. After cooling to room temperature, ethyl acetate (50 mL) was added to the reaction mixture, and then organic layer was washed with water (20 mL×2), and dried over $MgSO_4$. The solvent was evaporated to leave the pyrazolyl aryl ether, which was purified by chromatography on silica gel (ethyl acetate-hexane, 1 : 9) to give **2** (0.51 g, 53% yield): mp 151-152 ℃; MS(EI) m/z 364 (M^+); ^{1}H NMR ($CDCl_3$) δ 2.31 (s, 3H), 5.29 (s,1H), 7.24-8.02 (m, 5H), 8.38 (s, 2H).

Synthesis of aryl-migrated product 3 (R_1=Ph, R_2=CH_3, X=2,6-Cl_2) by *in situ* method. The same scale reaction as described above was carried out at 70 ℃ for 1 h. At this stage of reaction the formation of intermediate **2** (R=H, X=2,6-Cl_2) was detected by TLC (ethyl acetate-hexane, 1 : 3). Further reaction at 70 ℃ for 10 h allowed totally to consume the intermediate **2** and to produce **3** which was detected in TLC (ethyl acetate-hexane, 1 : 3). Ethyl acetate (50 mL) was added to the reaction mixture at room temperature, and the solution was washed with water (20 mL×2). The aqueous layer was acidified by 5% HCl (10 mL) and extracted with ethyl acetate (50 mL). The combined organic layer was dried over $MgSO_4$, evaporated, and purified by chromatography on silica gel (ethyl acetate-hexane, 1 : 3) to give **3** (0.6 g, 62% yield): mp 262 (dec); MS (EI) m/z 364 (M^+); ^{1}H NMR (DMSO-d_6) δ 2.22 (s, 3H), 7.29-7.93 (m, 5H), 8.30 (s, 2H), 11.81 (br s, 1H).

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