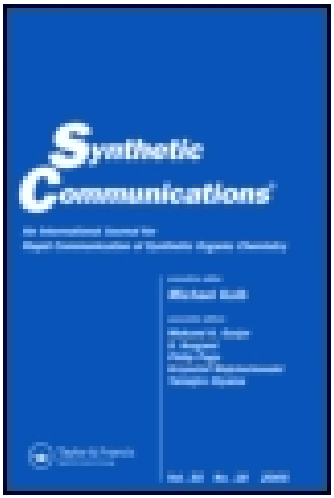

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A Convenient Synthesis of 4-Arylidene- 2-Phenyloxazol-5-Ones Catalyzed by KF-Alumina

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A CONVENIENT SYNTHESIS OF 4-ARYLIDENE- 2-PHENYLOXAZOL-5-ONES CATALYZED BY KF-ALUMINA

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ABSTRACT: A series of 4-arylidene-2-phenyloxzol-5-ones were synthesized by cyclodehydration-condensation of hippuric acid, aromatic aldehydes and acetic anhydride catalyzed by KF-Alumina.

4-Arylidene-2-phenyloxazol-5-ones are intermediates for the syntheses of non-proteinous amino acids[1~3] and homologation of carboxylic acids[4]. Usual method for their syntheses is the cyclodehydration-condensation of hippuric acid, aromatic aldehyde and acetic anhydride catalyzed by fused sodium acetate[5]. The yield, however, is generally low and their isolation requires elaborate

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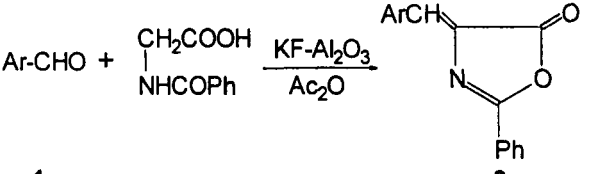
workup. The utility of fluoride salts as potential bases in a variety of synthetic reactions has been recongnized in recent years[6,7]. However, low solubilities of fluoride salts in ordinary solvents hamper their wide applications in organic synthesis. On the other hand, there has been increasing use of inorganic solid support as reagents in recent years[8,9]. In our previous papers[10,11], we reported that alumina coated with potassium fluoride (KF-alumina) is a versatile solid-supported reagent for Knoevenagel reaction and Michael reaction. In this paper, we describe the syntheses of 4-arylidene-2-phenyloxazol-5-ones catalyzed by KF-alumina.

When aromatic aldehydes (**1**), hippuric acid (**2**) and acetic anhydride were treatment with KF-alumina at 60℃ for 1h, the reaction product 4-arylidene-2-phenyloxazol-5-ones (**3**) was obtained.



1 **2** **3**

Entry	Ar	Isolated Yield(%)	m.p.(℃)
3a	C_6H_5	74	168~169
3b	4-ClC_6H_4	93	186~187
3c	2-ClC_6H_4	93	159~160
3d	3,4-$OCH_2OC_6H_3$	73	198~199
3e	4-$CH_3C_6H_4$	61	141~143
3f	4-OH-3-$OCH_3C_6H_3$	90	187~189
3g	4-OHC_6H_4	90	163~165
3h	4-$NO_2C_6H_4$	95	246~247
3i	4-$(CH_3)_2NC_6H_4$	85	210~212

In conclusion, with high yields and mild conditions, we think that the present work described herein provide a useful method for the preparation of 4-arylidene-2-phenyloxazol-5-ones.

EXPERIMENTAL

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a FT IR-8101 spectrometer. ^{1}H NMR spectra were measured on a JEOL FX-90Q spectrometer using TMS as internal standard. Elemental analysis were determined using Perkin-Elmer 240C elemental analyser.

General procedure:

A dry 50-mL flask was charged with aromatic aldehyde (10 mmol), hippuric acid (10 mmol), acetic anhydride (30mmol) and KF-alumina (250 mg). The mixture was stirred at 60℃ for 1h. To the hot solution was added 5mL of EtOH and filtered to remove the KF-Al_2O_3, the filtrate was cooled to room temperature. The yellow solid was filtered off, then washed with water. The crude solide was purified by recrystallization from 95% EtOH to give 4-arylidene-2-phenyloxazol-5-ones (**3**).

3a: m.p. 168~169℃(Lit.[12] m.p. 168℃), IR(KBr, ν, cm^{-1}): 3075, 1790, 1650, 1160, 760, 690; ^{1}H NMR($CDCl_3$, δ, ppm): 7.22(1H, s, -CH=), 7.36~7.70(6H, m, ArH), 8.00~8.35(4H, m, ArH).

3b: m.p. 186~187℃(Lit.[13] m.p. 185℃), IR(KBr, ν, cm^{-1}): 3080, 1800, 1650, 1480, 1160, 860, 825, 695; ^{1}H NMR($CDCl_3$, δ, ppm): 7.16(1H, s, -CH=), 7.38~7.65(5H, m, ArH), 8.07~8.16(4H, m, ArH).

3c: m.p. 159~160℃, IR(KBr, ν, cm^{-1}): 3060, 1790, 1650, 1160, 815, 760, 695; ^1H NMR($CDCl_3$, δ, ppm): 7.28~ 7.80(7H, m, ArH and -CH=), 8.05~8.25(2H, m, ArH), 8.84~9.02(1H, m, ArH); Elemental analysis: found(%): C, 68.03; H, 3.46; N, 4.75; Calcd. For $C_{16}H_{10}ClNO_2$: C, 67.74; H, 3.55; N, 4.94.

3d: m.p. 198~199℃, IR(KBr, ν, cm^{-1}): 3060, 2925, 1780, 1650, 1480, 1450, 1260, 1160; ^1H NMR($CDCl_3$, δ, ppm): 6.04(2H, s OCH_2O), 6.80~6.92(1H, d, ArH), 7.11(1H, s, -CH=), 7.38~7.64(4H, m, ArH), 8.05~8.23(3H, m, ArH); Elemental analysis: found(%): C, 69.91; H, 3.58; N, 4.93; Calcd. For $C_{17}H_{11}NO_4$: C, 69.62; H, 3.78; N, 4.77.

3e: m.p. 141~143℃, IR(KBr, ν, cm^{-1}): 3060, 2925, 1795, 1650, 1600, 1160, 860, 820, 695; ^1H NMR($CDCl_3$, δ, ppm): 2.42(3H, s, CH_3), 7.20~7.38(3H, m, ArH and -CH=), 7.43~7.65(3H, m, ArH), 8.04~8.25(4H, m, ArH); Elemental analysis: found(%): C, 77.48; H, 5.07; N, 5.59; Calcd. For $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32.

3f: m.p. 187~189℃, IR(KBr, ν, cm^{-1}): 3300, 3090, 1800, 1760, 1650, 1270, 1210, 1150, 700; ^1H NMR($CDCl_3$, δ, ppm): 3.95(3H, s, CH_3), 7.05~7.23(2H, m, ArH and -CH=), 7.40~7.72(4H, m, ArH), 8.00~8.25(3H, m, ArH); Elemental analysis: found(%): C, 69.42; H, 4.18; N, 4.52; Calcd. For $C_{17}H_{13}NO_4$: C, 69.15; H, 4.44; N, 4.74.

3g: m.p. 163~165℃, IR(KBr, ν, cm^{-1}): 3300, 3075, 1795, 1760, 1655, 1220, 1160, 980, 860, 700; ^1H NMR($CDCl_3$, δ, ppm): 7.15~7.34(3H, m, -CH= and ArH), 7.42~7.65(3H, m, ArH), 8.10~8.30(4H, m, ArH); Elemental analysis: found(%): C, 72.83; H, 3.96; N, 5.02; Calcd. For $C_{16}H_{11}NO_3$: C, 72.45; H, 4.18; N, 5.28.

3h: m.p. 246~247℃(Lit.[13] m.p. 245℃), IR(KBr, ν, cm^{-1}): 3100, 1795, 1650, 1600, 1560, 1520, 1340, 1330, 1295, 1160, 860, 700, 690; ^1H NMR($CDCl_3$, δ, ppm): 7.24(1H, s, -CH=), 7.45~7.74(3H, m, ArH), 8.10~8.55(6H, m, ArH).

3i: m.p. 210~212℃(Lit.[14] m.p. 213~214℃), IR(KBr, ν, cm^{-1}): 3060, 2920, 1760, 1650, 1600, 1530, 1370, 1160, 810, 690; ^1H NMR($CDCl_3$, δ, ppm): 3.08(6H, s, $(CH_3)_2N$), 6.74(2H, d, ArH), 7.20(1H, s, -CH=), 7.35~7.55(3H, m, ArH), 8.06~8.23(4H, m, ArH).

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