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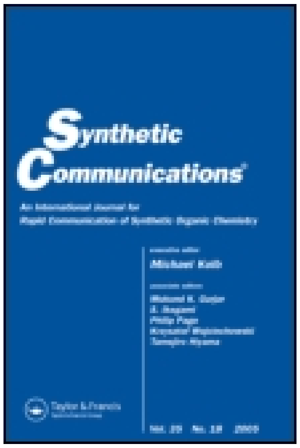

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ABSTRACT

The condensation of aromatic aldehyde with 5,5-dimethyl-1,3-cyclohexanedione is carried out in ethylene glycol as solvent without catalyst.

Key Words: Aromatic aldehydes; 5,5-Dimethyl-1,3-cyclohexanedione; Condensation reaction

Condensation reaction of carbonyl compounds with active methylene compounds is one of the most important synthetic methods of substituted alkenes. The reactions are generally catalyzed by bases or Lewis acids.[1] Recently, inorganic solid supports as catalysts, resulting in higher selectivity, milder conditions and easier work-up, has been reported as useful catalysts for Knoevenagel reaction. Thus, aluminium oxide,[2] xonotlite,[3] $AlPO_4$–Al_2O_3,[4] KF–Al_2O_3,[5] K10–$ZnCl_2$[6] and cadmium iodide[7] have been

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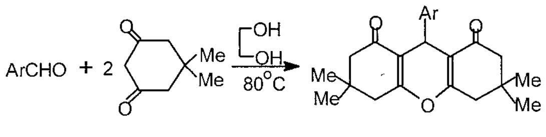
reported. In our previous paper,[8] we reported that 2,2′-arylmethylene-*bis*(3-hydroxyl-5,5-dimethyl-2-cyclohexen-1-one) was obtained by reaction of aromatic aldehyde with 5,5-dimethyl-1,3-cyclohexanedione in DMF as solvent without catalyst. However, treatment of aromatic aldehyde with 5,5-dimethyl-1,3-cyclohexanedione in ethylene glycol as solvent without catalyst, Knoevenagel condensation, Michael addition, cyclodehydration have taken place and 3,3,6,6-tetramethyl-9-aryl-1,8-dioxo-2,3,4,5,6,7-hexahydroanthene are obtained in excellent yield. In this paper, we would like to report that the condensation of aromatic aldehyde with 5,5-dimethyl-1,3-cyclohexanedione is carried out in ethylene glycol as solvent without catalyst. We also present the crystal structure of **3e**.



1 **2** **3**

The results were listed in Table 1.

All the compounds obtained gave analysis for C, H, N in good agreement to calculated values. The structures were established on the basis of spectroscopic data and confirmed by X-ray diffraction studies on monocrystal of **3e** (Fig. 1).[9]

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. X-ray diffraction were measured on a Rigaku 7R CAD4 diffractometer.

General Procedure

A dry 50 mL flask was charged with aromatic aldehyde (5 mmol), 5,5-dimethyl-1,3-cyclohexanedione (10 mmol) and ethylene glycol (15 mL). The mixture was kept at 80°C for 1.5 h, then cooled to room temperature.

Table 1. Condensation of Aromatic Aldehydes **1a–j** with **2**

Entry	Ar	Yield (%)	M.P. (°C)
3a	C_6H_5	94	198–200
3b	$4\text{-}CH_3C_6H_4$	92	218–220
3c	$2\text{-}NO_2C_6H_4$	90	246–248
3d	$4\text{-}NO_2C_6H_4$	99	222–224
3e	$4\text{-}ClC_6H_4$	96	230–231
3f	$2\text{-}ClC_6H_4$	95	228–229
3g	$4\text{-}HOC_6H_4$	97	246–248
3h	$3,4\text{-}OCH_2OC_6H_3$	98	216–218
3i	$4\text{-}CH_3OC_6H_4$	96	224–226
3j	$3,4\text{-}(CH_3O)_2\text{-}C_6H_3$	93	170–172

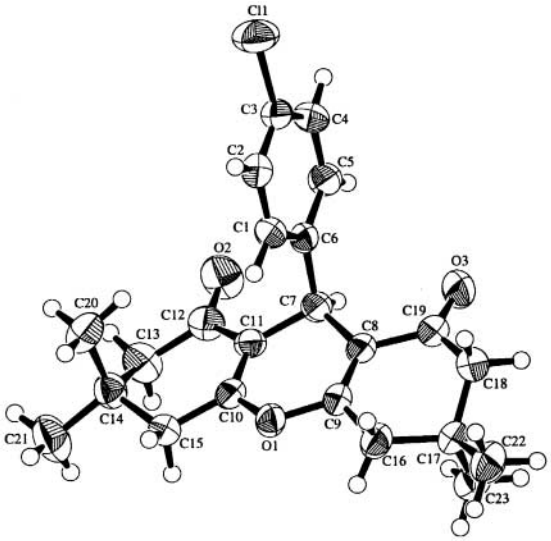


Figure 1. X-ray crystal structure of **3e**.

The reaction mixture was poured into 150 mL water. The solid was filtered off, then washed with water. The crude solid was purified by recrystallization from 95% EtOH to give **3a–j**.

3a: M.p. 198–200°C (Lit.[10] 204–205°C); IR (KBr, ν, cm^{-1}): 2980, 1680, 1665, 1625, 1470, 1360, 1200, 1170, 1140, 1000, 745, 700; ^1H NMR ($CDCl_3$, δ, ppm): 0.98 (6H, s, $2\times CH_3$), 1.10 (6H, s, $2\times CH_3$), 2.06–2.18

(8H, m, 4 × CH_2), 4.66 (1H, s, CH), 7.21 (5H, s, ArH); Elemental analysis: Found (%): C, 79.01; H, 7.33; Calcd. for $C_{23}H_{26}O_3$: C, 78.83; H, 7.47.

3b: M.p. 218–220°C; IR (KBr, ν, cm^{-1}): 2980, 1680, 1665, 1630, 1510, 1470, 1360, 1200, 1170, 1140, 790, 770; ^1H NMR ($CDCl_3$, δ, ppm): 0.98 (6H, s, 2 × CH_3), 1.10 (6H, s, 2 × CH_3), 2.07–2.20 (8H, m, 4 × CH_2), 2.42 (3H, s, CH_3–Ar), 4.69 (1H, s, CH), 6.80–7.28 (4H, m, ArH); Elemental analysis: Found (%): C, 79.28; H, 7.53; Calcd. for $C_{24}H_{28}O_3$: C, 79.08; H, 7.74.

3c: M.p. 246–248°C; IR (KBr, ν, cm^{-1}): 2980, 1680, 1670, 1620, 1530, 1360, 1210, 1170, 1150, 1010, 860, 800, 780, 740, 700; ^1H NMR ($CDCl_3$, δ, ppm): 0.98 (6H, s, 2 × CH_3), 1.10 (6H, s, 2 × CH_3), 2.03–2.18 (8H, m, 4 × CH_2), 5.61 (1H, s, CH), 7.36–7.44 (4H, m, ArH); Elemental analysis: Found (%): C, 69.96; H, 6.43; N, 3.31; Calcd. for $C_{23}H_{25}NO_5$: C, 69.85; H, 6.37; N, 3.54.

3d: M.p. 222–224°C; (Lit.[10] 222°C) IR (KBr, ν, cm^{-1}): 2980, 1660, 1650, 1620, 1520, 1360, 1340, 1200, 1070, 1040, 1000, 870, 830; ^1H NMR ($CDCl_3$, δ, ppm): 0.99 (6H, s, 2 × CH_3), 1.12 (6H, s, 2 × CH_3), 2.06–2.21 (8H, m, 4 × CH_2), 4.76 (1H, s, CH), 7.50–7.63 (2H, m, ArH), 8.06–8.18 (2H, m, ArH); Elemental analysis: Found (%): C, 69.91; H, 6.60; N, 3.29; Calcd. for $C_{23}H_{25}NO_5$: C, 69.85; H, 6.37; N, 3.54.

3e: M.p. 230–231°C; IR (KBr, ν, cm^{-1}): 2980, 1680, 1660, 1620, 1490, 1480, 1360, 1200, 1170, 1140, 1090, 1010, 1000, 850, 840; ^1H NMR ($CDCl_3$, δ, ppm): 0.98 (6H, s, 2 × CH_3), 1.10 (6H, s, 2 × CH_3), 2.03–2.14 (8H, m, 4 × CH_2), 4.64 (1H, s, CH), 7.26 (4H, s, ArH); Elemental analysis: Found (%): C, 71.92; H, 6.32; Calcd. for $C_{23}H_{25}ClO_3$: C, 71.77; H, 6.54.

3f: M.p. 228–229°C (Lit.[10] 224–226°C); IR (KBr, ν, cm^{-1}): 2980, 1680, 1660, 1620, 1490, 1470, 1360, 1200, 1170, 1140, 1100, 1000, 850, 840; ^1H NMR ($CDCl_3$, δ, ppm): 0.98 (6H, s, 2 × CH_3), 1.10 (6H, s, 2 × CH_3), 2.06–2.19 (8H, m, 4 × CH_2), 4.64 (1H, s, CH), 7.26 (4H, s, ArH); Elemental analysis: Found (%): C, 71.98; H, 6.39; Calcd. for $C_{23}H_{25}ClO_3$: C, 71.77; H, 6.54.

3g: M.p. 246–248°C (Lit.[10] 246°C); IR (KBr, ν, cm^{-1}): 3360, 2980, 1790, 1720, 1700, 1630, 1610, 1520, 1390, 1370, 1260, 1230, 1200, 1190, 850, 840; ^1H NMR ($CDCl_3$, δ, ppm): 0.99 (6H, s, 2 × CH_3), 1.10 (6H, s, 2 × CH_3), 2.03–2.31 (8H, m, 4 × CH_2), 4.62 (1H, s, CH), 6.77 (2H, d, $J = 8$ Hz, ArH), 6.98 (2H, d, $J = 8$ Hz, ArH); Elemental analysis: Found (%): C, 75.24; H, 7.06; Calcd. for $C_{23}H_{26}O_4$: C, 75.38; H, 7.15.

3h: M.p. 216–218°C; IR (KBr, ν, cm^{-1}): 2980, 1720, 1630, 1565, 1510, 1490, 1440, 1380, 1360, 1320, 1270, 1230, 1040, 940, 920, 890, 810, 790; ^1H NMR ($CDCl_3$, δ, ppm): 1.00 (6H, s, 2 × CH_3), 1.10 (6H, s, 2 × CH_3), 2.06–2.30 (8H, m, 4 × CH_2), 4.58 (1H, s, CH), 5.90 (2H, s, OCH_2O), 6.69–6.78 (3H, m, ArH); Elemental analysis: Found (%): C, 73.18; H, 6.76; Calcd. for $C_{24}H_{26}O_5$: C, 73.07; H, 6.64.

3i: M.p. 224–226°C; IR (KBr, ν, cm^{-1}): 2980, 1680, 1660, 1620, 1510, 1450, 1370, 1360, 1260, 1230, 1190, 1170, 1140, 1030, 1000, 840; ^{1}H NMR (CDCl$_3$, δ, ppm): 1.01 (6H, s, $2 \times CH_3$), 1.09 (6H, s, $2 \times CH_3$), 2.20 (4H, s, $2 \times CH_2$), 2.46 (4H, s, $2 \times CH_2$), 3.73 (3H, s, CH_3O), 4.70 (1H, s, CH), 6.67–7.28 (4H, m, ArH); Elemental analysis: Found (%): C, 75.84; H, 7.22; Calcd. for $C_{24}H_{28}O_4$: C, 75.76; H, 7.41.

3j: M.p. 170–172°C; IR (KBr, ν, cm^{-1}): 2980, 1580, 1520, 1470, 1420, 1380, 1360, 1255, 1240, 1150, 1030, 890, 870, 800, 760; ^{1}H NMR (CDCl$_3$, δ, ppm): 0.99 (6H, s, $2 \times CH_3$), 1.10 (6H, s, $2 \times CH_3$), 2.19 (4H, s, $2 \times CH_2$), 2.45 (4H, s, $2 \times CH_2$), 3.80 (6H, s, $2 \times CH_3O$), 4.70 (1H, s, CH), 6.76–6.90 (3H, m, ArH); Elemental analysis: Found (%): C, 73.30; H, 7.45; Calcd. for $C_{25}H_{30}O_5$: C, 73.14; H, 7.36.

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