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P_2O_5-Promoted Efficient and Diastereoselective Synthesis of Substituted 5-Methylene-dihydropyran-2,6-diones and 3-Methylene-3,4-dihydropyran-2-ones

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Abstract: A simple, efficient, and diastereoselective synthesis of 5-methylene-dihydropyran-2,6-diones and 3-methylene-3,4-dihydropyran-2-ones from substrates afforded by the S_N2 reaction between the acetyl derivatives of the Baylis–Hillman adducts and methylacetoacetate or acetylacetone or benzoyl acetone via saponification followed by P_2O_5-mediated cyclization is described.

Keywords: Baylis–Hillman; 5-methylene-dihydropyran-2,6-diones; 3-methylene-3,4-dihydropyran-2-ones; P_2O_5

Over the past couple of years, growth in synthetic applications of the Baylis–Hillman adducts and their derivatives for the construction of a variety of heterocycles is noteworthy.[1] Particularly, the derivatives of the S_N2 reaction between the acetyl derivatives and appropriately substituted carbon nucleophiles serve as appropriate substrates for the synthesis of a heterocyclic architecture incorporating an exocyclic methylene group. We have demonstrated the synthesis of a variety of such structural motifs including 3-methylene-δ-valerolactone, 3-methylene-2-pyrrolidinone, 3-methylene-pyrimidin-2,6-dione, and 3-methylene-1,3,4,5-tetrahydro-benzo[*b*][1,4] diazepin-2-ones.[2] In continuation of our efforts

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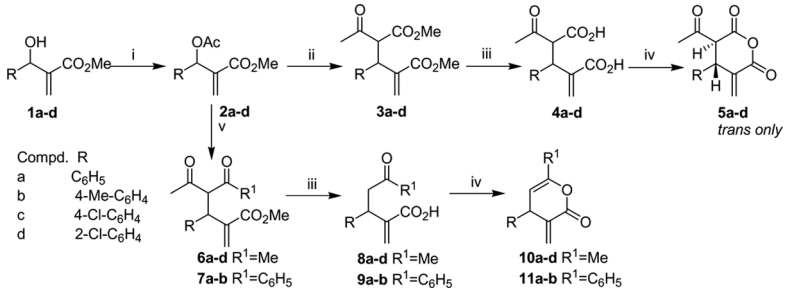
in this direction, we now report the synthesis of 5-methylene-dihydropyran-2,6-diones and 3-methylene-3,4-dihydropyran-2-ones.

Recently, we have achieved the synthesis of quinolines from the substrates derived from the S_N2 reaction between the acetate of the Baylis–Hillman adducts of 2-nitro benzaldehyde and an acetyl group containing carbon nucleophiles.[3] Based on these studies, it occurred to us that analogous compounds derived from other aldehydes could serve as substrates for the generation of a pyranone system. The presence of pyran-2,6-diones and pyran-2-ones as structural components of several complex natural products makes them attractive synthetic targets.[4] In addition, glutaric anhydride derivatives serve as useful synthetic intermediates,[5] whereas 3-methylene-pyran-2,6-diones have been useful in polymer chemistry.[6] But there exist only a few reports that describe the synthesis of pyranone systems containing an exocyclic double bond. In principle, the products afforded from S_N2 reaction of methylacetoacetate with the acetate of the Baylis–Hillman adduct of acrylate, upon saponification, would lead to a 1,5-pentane dicarboxylic acid that could be readily cyclized in the presence of a dehydrating agent to yield such pyranones. A careful literature survey revealed that several workers have reported the dehydaration of diacids in the presence of trifluoroacetic anhydride (TFAA).[7] In the context of Baylis–Hillman chemistry, Basavaiah and Satyanarayana reported the synthesis of [4.4.3] and [4.4.4] propellano-bislactones from the acetates of Baylis–Hillman adducts wherein the final dehydration was carried out in the presence of TFAA too.[8] More recently, Kim et al. also reported the synthesis of α-pyranone from the acetate of the Baylis–Hillman adducts via cyclization with TFAA.[9] However, to effect dehydration, we decided to examine other dehydrating agents because TFAA requires specialized handling procedures. Gratifyingly, treatment of 1,5-pentane dicarboxylic acid with P_2O_5, which happens to be one of the cheapest dehydrating agents in a chemical laboratory and was earlier utilized to effect anhydride formation,[10] successfully yielded the desired pyranones in excellent yields. This communication describes the results of this synthetic achievement.

Initially the Baylis–Hillman adducts **1a–d** were generated following literature procedure.[11] Acetylating **1a–d** with acetyl chloride in the presence of pyridine furnished the respective acetyl derivatives **2a–d** in good yields. The S_N2 reaction of methyl acetoacetate in the presence of DABCO in a THF–H_2O system yielded substituted 1,5-dipentanoate **3a–d** in 78–88% yields as diastereoisomeric mixtures. The saponification of **3a–d** with NaOH in the presence of methanol afforded the substituted 1,5-pentane dicarboxylic acid **4a–d** in quantitative yields. Although the formation of **4a** was confirmed by mass spectroscopy, these diacids were



Scheme 1. Reagents and conditions: (i) AcCl, pyridine, rt, 3 h; (ii) DABCO, methyl acetoacetate, THF–H_2O, rt, 3 h; (iii) NaOH, MeOH–H_2O, rt, 4 h; (iv) P_2O_5, dry toluene, rt, 1 h; (v) DABCO, acetyl acetone or benzoyl acetone, THF–H_2O, rt, 3 h.

not subjected to detailed spectral analysis and were used further without any purification. Notably the molecular ion peak corresponded to a product where the presence of an acetyl group was indicated. Generally, it was observed that during the saponification, the loss of the acetyl group takes place. Subsequent treatment of the 1,5-pentane dicarboxylic acid **4a–d** with P_2O_5 in anhydrous toluene at room temperature furnished the substituted 3-methylene-pyran-2,6-dione **5a–d** in excellent yields. Interestingly, the spectral data show the presence of single isomer. The nuclear overhauser effect spectroscopy (NOESY) experiment led us to assign the *trans* stereochemistry to these products. Significantly, this methodology worked very well even at a higher scale.

Once the objective to obtain the desired pyranones from the substrates of methyleacetoacetate was accomplished, to extend the utility of our strategy we directed our attention to similar substrates afforded from acetylacetone and benzoyl acetone. Thus, compounds **6a–d** were readily obtained via the S_N2 reaction between compounds **2a–d** and acetyl acetone, whereas **7a–b** were afforded from the reaction of **2a–b** with benzoyl acetone. Unlike **3a–d**, saponification of **6a–d** and **7a–b** in the presence of NaOH furnished the products **8a–d** and **9a–b**, respectively, where the acetyl group was lost. Without any purification, these products were treated with P_2O_5 in the presence of dry toluene to afford **10a–d** and **11a–b**. The formation of 3-methylene-3,4-dihydropyran-2-ones implies that mechanistically in the first step of this reaction keto-enol tautomerization occurs, followed by dehydration of the intermediate.

In summary, we have demonstrated an efficient and practical synthesis of substituted 5-methylene-dihydropyran-2,6-diones and 3-methylene-3,4-dihydropyran-2-ones in excellent yields.

EXPERIMENTAL

Melting points are uncorrected and were determined in capillary tubes on an apparatus containing silicon oil. Infrared (IR) spectra were recorded using Perkin-Elmer's Spectrum RX I fourier transformed infrared (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded either on Bruker DPX-200 FT or Bruker Avance DRX-300 spectrometers, using tetramethylsilane (TMS) as an internal standard (chemical shifts in δ values, J in hertz). The electronspray mass spectroscopy (ESMS) were recorded on a Micromass LCMS system, and fast atomic bombardment mass spectroscopy (FABMS) were recorded on a Jeol/SX-102 spectrometer. Elemental analyses were performed on Carlo Erba's 108 or Elementar's Vario EL III microanalyzer. Synthesis and spectral data for **6a–d** have been published earlier.[2b]

General Procedure for the Preparation of Compounds 4a–d, and 7a–b

To a stirred solution of compounds from **2a–d** (2.0 mmol) in tetrahydrofuran (THF)–H_2O (10 mL, 50:50, v/v), 1,4-diazabicyclo[2.2.2]ocatane (DABCO) (3.0 mmol) was added at room temperature, and the reaction was allowed to continue for 20 min. Thereafter, an appropriate nucleophile (2.4 mmol) was added, and the reaction was continued at room temperature for 3 h. The THF was removed from the reaction mixture via rotary evaporation, and the residue was diluted with water (100 mL) and extracted with EtOAc (3×40 mL). The organic layers were pooled, washed with brine (50 mL), dried (anhyd. Na_2SO_4), and evaporated to yield a residue, which was purified via silica-gel chromatography employing hexane–EtOAc (90:10, v/v) to afford products **3a–d** or **7a–b** as oils or solids.

Data

Dimethyl 2-Acetyl-4-methylene-3-phenylpentanedioate **(3a)**

Yield 92% as colorless oil; ν_{max} (neat)1721 (CO and CO_2Me) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 1.98$ (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 3.49 (s, 3H, CO_2CH_3), 3.69 (s, 3H, CO_2CH_3), 3.70 (s, 3H, CO_2CH_3), 3.72 (s, 3H, CO_2CH_3), 4.39 (d, 1H, $J = 6.3$ Hz, CHAr), 4.43 (d, 1H, $J = 6.3$ Hz, CHAr), 4.47–4.76 (m, 2H, $2 \times$ CHCO), 5.72 (d, 1H, $J = 0.6$ Hz, =CH), 5.77 (s, 1H, $J = 0.7$ Hz, =CH), 6.29 (s, 1H, =CH), 6.31 (s, 1H, =CH), 7.21–7.25 (m, 10H, $2 \times$ 5ArH); MS (FAB+) m/z 291 ($M^+ + 1$). Anal. calcd. for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 66.48; H, 6.02.

Dimethyl 2-Acetyl-4-methylene-3-(4-methylphenyl)pentanedioate **(3b)**

Yield 89% as colorless oil; ν_{max} (neat) 1721 (CO), 1733 (CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 1.99$ (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.30 (s, 6H, $2 \times ArCH_3$), 3.51 (s, 3H, CO_2CH_3), 3.70 (s, 3H, CO_2CH_3), 3.71 (s, 3H, CO_2CH_3), 3.72 (s, 3H, CO_2CH_3), 4.37 (d, 1H, $J = 4.8$ Hz, CHAr), 4.41 (d, 1H, $J = 4.8$ Hz, CHAr), 4.68 (d, 1H, $J = 4.8$ Hz, CHCO), 4.72 (d, 1H, $J = 4.8$ Hz, CHCO), 5.70 (s, 1H, =CH), 5.76 (s, 1H, $J = 0.6$ Hz =CH), 6.27 (s, 1H, =CH), 6.29 (s, 1H, =CH), 7.07–7.17 (m, 8H, 2×4ArH); ^{13}C NMR (50 MHz, $CDCl_3$) $\delta = 29.4$, 31.0, 46.5, 46.6, 52.4, 52.5, 52.9, 53.1, 124.7, 125.6, 127.0, 127.7, 127.8, 128.6, 128.9, 129.1, 138.9, 139.2, 141.0, 141.7, 166.7, 166.8, 168.4, 168.4, 201.7, 201.8; MS (FAB+) m/z 305 ($M^+ + 1$). Anal. calcd. for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found. C, 67.39; H, 6.77.

2-Acetyl-3-(4-chloro-phenyl)-4-methylene-pentanedioic Acid Dimethyl Ester **(3c)**

Yield 86% as colorless oil; ν_{max} (neat)1721 (CO), 1734 (CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 2.03$ (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 3.53 (s, 3H, CO_2CH_3), 3.70 (s, 3H, CO_2CH_3), 3.71 (s, 3H, CO_2CH_3), 3.73 (s, 3H, CO_2CH_3), 4.37 (d, 1H, $J = 4.1$ Hz, CHAr), 4.41 (d, 1H, $J = 4.1$ Hz, CHAr), 4.68 (d, 1H, $J = 1.4$ Hz, CHCO), 4.72 (d, 1H, $J = 1.4$ Hz, CHCO), 5.72 (s, 1H, =CH), 5.77 (d, 1H, $J = 0.5$ Hz, =CH), 6.30 (s, 1H, =CH), 6.31 (s, 1H, =CH), 7.19–7.28 (m, 8H, 2×4ArH); MS (FAB+) m/z 325 ($M^+ + 1$). Anal. calcd. for $C_{16}H_{17}ClO_5$: C, 59.17; H, 5.28. Found. C, 59.43; H, 5.01.

Dimethyl 2-Acetyl-3-(2-chlorophenyl)-4-methylenepentanedioate **(3d)**

Yield 91% as colorless oil; ν_{max} (neat) 1723 (CO), 1730 (CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 2.09$ (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 3.53 (s, 3H, CO_2CH_3), 3.70 (s, 3H, CO_2CH_3), 3.71 (s, 3H, CO_2CH_3), 3.73 (s, 3H, CO_2CH_3), 4.64 (d, 1H, $J = 10.5$ Hz, CHAr), 4.68 (d, 1H, $J = 10.4$ Hz, CHAr), 5.15 (d, 1H, $J = 10.5$ Hz, CHCO), 5.17 (d, 1H, $J = 10.3$ Hz, CHCO), 5.85 (s, 1H, =CH), 5.91 (d, 1H, $J = 0.5$ Hz, =CH), 6.32 (s, 1H, =CH), 6.36 (s, 1H, =CH), 7.16–7.22 (m, 4H, 2×2ArH), 7.35–7.48 (m, 4H, 2×2ArH); MS (FAB+) m/z 325 ($M^+ + 1$). Anal. calcd. for $C_{16}H_{17}ClO_5$: C, 59.17; H, 5.28. Found: C, 58.97; H, 5.01.

Methyl 2-(2-Benzoyl-3-oxo-1-phenylbutyl)acrylate **(7a)**

Yield 83% as a white solid, mp 99–100°C; ν_{max} (KBr) 1715 (CO and CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 1.99$ (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 3.66 (s, 3H, CO_2CH_3), 3.73 (s, 3H, CO_2CH_3), 5.06 (d, 2H, $J = 12.0$ Hz, $2 \times$ CHAr), 5.46–5.61 (m, 2H, $2 \times$ CHCO), 5.63 (d, 1H, =CH), 5.91 (s, 1H, =CH), 6.13 (s, 1H, =CH), 6.39 (s, 1H, =CH), 7.08–7.18 (m, 6H, 2×3ArH), 7.24–7.32 (m, 6H, 2×3ArH), 7.36–7.54 (m, 6H, 2×3ArH), 7.89 (d, 2H, $J = 7.2$ Hz, ArH); MS (ES+) m/z 337.1 ($M^+ + 1$). Anal. calcd. for $C_{21}H_{20}O4_5$: C, 74.98; H, 5.99. Found. C, 75.13; H, 5.91.

Methyl 2-[2-Benzoyl-1-(4-methylphenyl)-3-oxobutyl]acrylate **(7b)**

Yield 85% as a white solid, mp 100–102°C; ν_{max} (KBr) 1719 (CO and CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 2.00$ (s, 3H, $COCH_3$), 2.20 (d, 6H, $J = 1.4$ Hz, $COCH_3$ and $ArCH_3$), 2.32 (s, 3H, $ArCH_3$), 3.66 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 5.02 (t, 2H, $J = 12.0$ Hz, $2 \times$ CH), 5.46–5.60 (m, 3H, =CH and $2 \times$ CH), 5.90 (s, 1H, =CH), 6.11 (s, 1H, =CH), 6.36 (s, 1H, =CH), 6.96 (d, 2H, $J = 8.0$ Hz, ArH), 7.11–7.15 (m, 4H, ArH), 7.26 (d, 2H, $J = 8.0$ Hz, ArH), 7.40 (t, 2H, $J = 7.9$ Hz, ArH), 7.49–7.54 (m, 3H, ArH), 7.60–7.62 (m, 1H, ArH), 7.87–7.90 (m, 2H, ArH), 8.09–8.12 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 19.6$, 19.8, 26.1, 27.0, 45.3, 45.4, 50.7, 50.8, 66.0, 66.4, 123.0, 124.6, 127.0, 127.2, 127.4, 127.6, 127.7, 127.9, 128.2, 132.3, 132.6, 134.3, 134.5, 135.3, 135.4, 135.5, 135.8, 139.6, 140.1, 165.1, 165.3, 192.6, 192.9, 201.1, 201.9; MS (ES+) m/z 351.2 ($M^+ + 1$). Anal. calcd. for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33. Found: C, 75.33; H, 6.11.

General Procedure for the Preparation of Compounds 5a–d, 10a–d, and 11a–b.

To a stirred solution of appropriate compound from **3a–d, 6a–d, and 7a–b** (1.0 mmol) in methanol (10 mL), aqueous NaOH (2 mL, 50% w/v) was added and the reaction was allowed to proceed for 4 h at room temperature. Thereafter, methanol was evaporated, and the reaction mixture was acidified with conc. HCl (up to pH 3–4). The compound was extracted with EtOAc (3×40 mL), and the solvent was evaporated to yield crude products, which were utilized further without any purification. To a stirred solution of appropriate crude product **(4a–d, 8a–d, 9a–b)** in dry toluene (10 mL), P_2O_5 (0.7 g, 5.0 mmol) was added, and the reaction mixture was allowed to proceed at room temperature for 1 h. On completion,

as evident by thin-layer chromotography (TLC) analysis and also by change in color of the reaction mixture to brown or red, the toluene was removed via rotary evaporation. The residue was diluted with EtOAc (50 mL) and filtered. The filtrate was evaporated to yield a crude product, which was purified via silica-gel chromatography employing hexane–EtOAc (90:10, v/v) to afford products **5a–d, 10a–d, and 11a–b** as oils or solids

Data

3-Acetyl-5-methylene-4-phenyldihydro-2*H*-pyran-2,6(3*H*)-dione **(5a)**

Yield 83% as a pale yellow solid, mp 71–73°C; ν_{max} (KBr) 1734 (CO) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 2.00$ (s, 3H, CH_3), 4.35 (d, 1H, $J = 4.3$ Hz, CHAr), 5.11 (d, 1H, $J = 4.3$ Hz, CHCO), 5.55 (s, 1H, =CH), 6.51 (s, 1H, =CH), 7.20–7.27 (m, 2H, ArH), 7.29–7.36 (m, 3H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) $\delta = 19.4$, 44.2, 103.8, 127.8, 128.0, 129.4, 130.9, 136.7, 142.7, 148.5, 163.3; MS (ES+) m/z 245.1 ($M^+ + 1$). Anal. calcd. for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.48; H, 5.07.

3-Acetyl-5-methylene-4-(4-methylphenyl)dihydro-2*H*-pyran-2,6(3*H*)-dione **(5b)**

Yield 79% as a pale yellow solid, mp 128–130°C; ν_{max} (KBr)1722 (CO) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 1.99$ (s, 3H, CH_3), 2.35 (s, 3H, $ArCH_3$), 4.31 (d, 1H, $J = 4.2$ Hz, CHAr), 5.09 (d, 1H, $J = 4.2$ Hz, CHCO), 5.53 (s, 1H, =CH), 6.49 (s, 1H, =CH), 7.11 (d, 2H, $J = 8.0$ Hz, ArH), 7.16 (d, 2H, $J = 8.0$ Hz, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) $\delta = 19.4$, 21.4, 43.8, 104.0, 127.8, 130.1, 130.8, 130.9, 136.9, 137.4, 139.8, 148.3, 161.7, 163.5; MS (FAB+) m/z 259 ($M^+ + 1$). Anal. calcd. for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 70.09; H, 5.23.

3-Acetyl-4-(4-chlorophenyl)-5-methylenedihydro-2*H*-pyran-2,6(3*H*)-dione **(5c)**

Yield 81% as pale yellow oil; ν_{max} (neat) 1724 (CO) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 1.99$ (s, 3H, CH_3), 4.32 (d, 1H, $J = 4.2$ Hz, CHAr), 5.07 (d, 1H, $J = 4.2$ Hz, CHCO), 5.53 (d, 1H, $J = 1.5$ Hz, =CH), 6.54 (t, 1H, $J = 0.8$ Hz, =CH), 7.15 (d, 2H, $J = 8.0$ Hz, ArH), 7.31 (d, 2H, $J = 8.0$ Hz, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) $\delta = 19.3$, 43.5, 103.3, 129.4, 129.5, 131.0, 133.5, 136.4, 141.1, 148.9, 164.5; MS

(FAB+) m/z 279 ($M^+ + 1$). Anal. calcd. for $C_{14}H_{11}ClO_4$: C, 60.34; H, 3.98. Found: C, 60.38; H, 4.19.

3-Acetyl-4-(2-chlorophenyl)-5-methylenedihydro-2*H*-pyran-2,6(3*H*)-dione **(5d)**

Yield 78% as pale yellow oil; ν_{max} (neat) 1731(CO) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 1.99$ (s, 3H, CH_3), 4.91 (q, 1H, $J = 4.2$ Hz, CHAr), 5.07 (d, 1H, $J = 4.2$ Hz, CHCO), 5.65 (q, 1H, $J = 0.6$ Hz, =CH), 6.56 (t, 1H, $J = 2.0$ Hz, =CH), 7.19–7.26 (m, 3H, ArH), 7.31–7.46 (m, 1H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) $\delta = 19.4$, 40.7, 102.5, 128.0, 129.0, 129.7, 130.4, 131.3, 133.6, 135.1, 140.3, 149.0, 163.1. MS (FAB+) m/z 279 ($M^+ + 1$). Anal. calcd. for $C_{14}H_{11}ClO_4$: C, 60.34; H, 3.98. Found: C, 60.57; H, 4.11.

6-Methyl-3-methylene-4-phenyl-3,4-dihydro-2*H*-pyran-2-one **(10a)**

Yield 93% as a pale yellow solid, mp 77–78°C; ν_{max} (KBr) 1721 (CO) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 2.00$ (s, 3H, CH_3), 4.35 (q, 1H, $J = 1.9$ Hz, CHAr), 5.11 (d, 1H, $J = 4.2$ Hz, CHCO), 5.55 (q, 1H, $J = 0.8$ Hz, =CH), 6.51 (t, 1H, $J = 0.8$ Hz, =CH), 7.20–7.23 (m, 2H, ArH), 7.26–7.38 (m, 3H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) $\delta = 19.4$, 44.2, 103.8, 127.8, 128.0, 129.4, 130.9, 136.7, 142.7, 145.5, 163.3; MS (FAB+) m/z 201 ($M^+ + 1$). Anal. calcd. for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.16; H, 6.16.

6-methyl-3-methylene-4-(4-methylphenyl)-3,4-dihydro-2*H*-pyran-2-one **(10b)**

Yield 82% as a pale yellow solid, mp 145–148°C; ν_{max} (KBr) 1725 (CO) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 1.98$ (s, 3H, CH_3), 2.35 (s, 3H, $ArCH_3$), 4.31 (q, 1H, $J = 2.0$ Hz, CHAr), 5.09 (d, 1H, $J = 4.0$ Hz, CHCO), 5.54 (s, 1H, =CH), 6.49 (s, 1H, =CH), 7.10 (d, 2H, $J = 8.1$ Hz, ArH), 7.16 (d, 2H, $J = 8.1$ Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 17.6$, 19.7, 42.1, 102.3, 126.1, 126.8, 128.4, 128.9, 135.3, 135.7, 138.1, 146.7, 161.7; MS (ES+) m/z 215.1 ($M^+ + 1$). Anal. calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.21; H, 6.73.

4-(4-Chlorophenyl)-6-methyl-3-methylene-3,4-dihydro-2*H*-pyran-2-one **(10c)**

Yield 91% as pale yellow oil; ν_{max} (neat) 1711 (CO) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) $\delta = 1.98$ (s, 3H, CH_3), 4.32 (s, 1H, CHAr), 5.06

(d, 1H, $J = 3.3$ Hz, CHCO), 5.52 (s, 1H, =CH), 6.50 (s, 1H, =CH), 7.13 (d, 2H, $J = 8.2$ Hz, ArH), 7.31 (d, 2H, $J = 8.3$ Hz, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) $\delta = 19.3$, 43.5, 103.3, 129.4, 129.5, 129.9, 131.1, 133.6, 136.4, 141.1, 148.9, 163.0; MS (ES+) m/z 235.2 ($M^+ + 1$). Anal. calcd. for $C_{13}H_{11}ClO_2$: C, 66.53; H, 4.72. Found: C, 66.61; H, 5.02.

4-(2-Chlorophenyl)-6-methyl-3-methylene-3,4-dihydro-2*H*-pyran-2-one **(10d)**

Yield 87% as pale yellow oil; ν_{max} (neat) 1716 (CO) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 1.97$ (s, 3H, CH_3), 4.90 (q, 1H, $J = 1.8$ Hz, CHAr), 5.06 (d, 1H, $J = 3.9$ Hz, CHCO), 5.63 (d, 1H, $J = 1.0$ Hz, =CH), 6.53 (s, 1H, =CH), 7.19–7.26 (m, 3H, ArH), 7.37–7.40 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 17.7$, 39.1, 100.8, 126.3, 127.3, 128.0, 128.7, 129.7, 131.9, 133.4, 138.7, 147.3; MS (ES+) m/z 235.0 ($M^+ + 1$). Anal. calcd. for $C_{13}H_{11}ClO_2$: C, 66.53; H, 4.72. Found: C, 66.39; H, 4.59.

3-Methylene-4,6-diphenyl-3,4-dihydro-2*H*-pyran-2-one **(11a)**

Yield 85%as yellow oil; ν_{max} (neat) 1716 (CO) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 4.56$ (d, 1H, $J = 1.9$ Hz, CHAr), 5.53 (q, 1H, $J = 0.8$ Hz, =CH), 5.90 (d, 1H, $J = 4.3$ Hz, CHCO), 6.56 (s, 1H, =CH), 7.22–7.38 (m, 8H, ArH), 7.68 (d, 2H, $J = 4.3$ Hz, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) $\delta = 42.9$, 102.1, 123.4, 123.5, 126.2, 126.3, 126.9, 127.7, 127.8, 1218.0, 128.5, 129.9, 131.0, 135.1, 140.5, 162.5; MS (FAB+) m/z 263 ($M^+ + 1$). Anal. calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.29; H, 5.59.

3-Methylene-4-(4-methylphenyl)-6-phenyl-3,4-dihydro-2*H*-pyran-2-one **(11b)**

Yield 79% as pale yellow oil; ν_{max} (neat) 1719 (CO) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 2.36$ (s, 3H, CH_3), 4.54 (t, 1H, $J = 2.2$ Hz, CHAr), 5.61 (d, 1H, $J = 1.3$ Hz, =CH), 5.90 (d, 1H, $J = 4.5$ Hz, CHCO), 6.56 (d, 1H, $J = 0.9$ Hz, =CH), 7.15–7.18 (m, 4H, ArH), 7.38–7.43 (m, 3H, ArH), 7.68–7.71 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 19.8$, 42.5, 102.3, 123.4, 126.2, 127.0, 127.7, 127.9, 128.0, 128.3, 128.5, 129.2, 129.9, 131.0, 135.1, 136.0, 138.1, 147.4, 161.4; MS (ES+) m/z 277.2 ($M^+ + 1$). Anal. calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.81; H, 5.99.

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