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Research Article

Green Synthesis of Acid Esters from Furfural via Stobbe Condensation

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Solvent-free Stobbe condensation of furfural **1** with dimethyl succinate **2** under anhydrous conditions at room temperature using dry-solid potassium tertiary butoxide gave 3-carbomethoxy, 4-furyl-3-butenoic acid **3**, which upon methylation followed by Stobbe condensation reaction with different aldehydes and/or ketones under anhydrous conditions at room temperature afforded substituted carbomethoxy acids **5a–f**. These acid ester products were saponified to the corresponding dicarboxylic acids **6a–f** which are useful in the synthesis of photochromic fulgides.

1. Introduction

Fulgides are important for their photochromic properties [1–3]. Stobbe condensation [4–10], a C–C bond forming reaction, is a pathway to fulgides. A lot of research has been done on photochromic fulgides; among them, furan ring containing fulgides [11] have maintained the interest of researchers through decades of development of organic synthesis.

During the last few years, solvent-free reactions [12, 13] for the different organic synthesis have been a field of increasing interest in synthetic organic chemistry because of their ease to occur. The present work depicts a unique one- pot synthesis method in which solvent-free conditions allow improving the yield and expediting the reaction. Here, different substituted carbonyl compounds including aldehydes, aromatic, and alicyclic, aliphatic ketones and an active methylene compound, namely, dimethyl succinate, were condensed in anhydrous condition. The reaction is feasible in a dry agate mortar at room temperature, avoiding hazards of using any solvent.

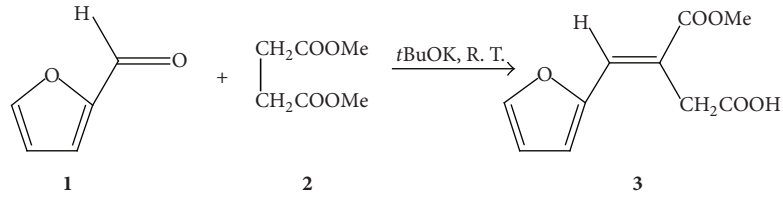
2. Experimental

All chemicals were of reagent grade quality and used without further purification. Melting points were measured on a melting point apparatus and are uncorrected. NMR spectra were recorded on a Bruker 300 MHz spectrometer. Chemical shifts are reported in ppm relative to tetramethyl silane as an internal standard. The infrared spectra were obtained on a Bruker IFS 66 V Fourier transform spectrometer using KBr pellets. The compounds were scanned for UV-visible spectra [14] using Perkin Elmer spectrophotometer.

Procedure for Preparation of 3-Carbomethoxy,4-furyl,3-butenoic Acid **(3)**. A homogenous mixture of furfural **1** (0.96 g, 0.01 mole) and dimethyl succinate **2** (1.46 g, 0.01 mole) was added to potassium tert. butoxide (1.13 g, 0.01 mole) and well ground with a pestle for 10 min. It was exposed to air for another 15 min. Upon neutralization with dil. HCl at 0°C and usual work up [15], crude product, namely, 3-carbomethoxy,4-furyl, 3-butenoic acid **3** was obtained, which was recrystallized from benzene-pet. Ether (see Scheme 1).

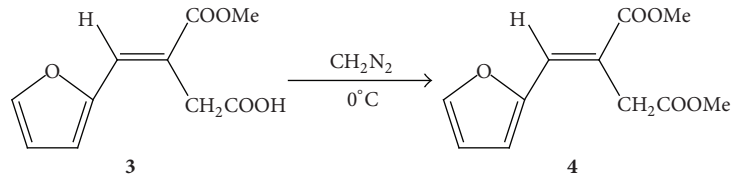
Yield 83%, ^{1}H NMR (300 MHz, $CDCl_3$) (δ/ppm): 1.25 (s, 2H), 3.04(s, 3H), 7.5 (s, 1H), 7.5701–7.580 (AMX, 3H). FTIR (KBr, cm^{-1}) 1170 (C–O), 1475.26 (aliphatic CH_2) 1654 (C=O acid), 1700 (C=O ester), 2511 (–OCH_3). UV λ_{max} (EtOH) 211.95 nm (log ε3.131). eq.wt. (found) 205.95 required for $C_{10}H_{10}O_5$ eq. wt. 210.18.

Procedure for Preparation of Methyl 3-Carbomethoxy,4-furyl,3-butenoate **(4)**. 3-Carbomethoxy,4-furyl, 3-butenoic acid **3** (1 g) in ethereal solution was esterified by



1 2 3

Scheme 1: One-pot synthesis of acid ester **3**.



3 4

Scheme 2: Methylation.

diazomethane [16] being generated from nitrosomethylurea (0.6 g) added to a reaction mixture of 50% KOH solution (4.0 mL) and ether (10.0 mL). After 15 min, the reaction mixture was washed with 10% Na_2CO_3 solution three times. The organic layer was dried over anhydrous sodium sulphate. Removal of solvent gave the crude semisolid diester, namely, methyl 3-carbomethoxy,4-furyl,*3-butenoate*, **4** (1.2 g, 90% yield) (see Scheme 2).

1,1-Cyclopentylidene-1′-carbomethoxy,3(2-furyl)-prop-2-ene-2-oic Acid **(5a).** To a neat mixture of the diester **4** (2.24 g, 0.01 mole) and cyclopentanone (0.84 g, 0.01 mole), was added dried potassium tertiary butoxide (1.13 g, 0.01 mole). The reaction mixture was well mixed and ground for 10 min. It was further exposed to air. Acidification followed by usual workup [15] gave the acid ester **5a** recrystallised from benzene-pet. ether as reddish brown crystals.

Yield 78%, ^{1}H NMR (300 MHz, DMSO) (δ/ppm): 2.58–2.59 (m, 8H, alicyclic CH_2), 3.02 (s, 3H, methoxy protons), 7.5523–7.5552 (AMX, 3H, furyl), 7.6 (s, 1H, vinyl). FTIR (KBr, cm^{-1}) 1174 (C–O), 1480 (alicyclic CH_2) 1715 (C=O acid), 1735 (C=O ester), 2511 (–OCH_3). UV λ_{max} (EtOH) 350 nm (log ε4.1). eq. wt. (found) 273.44 required for $C_{15}H_{16}O_5$ eq. wt. 276.29.

1,1-Cyclohexylidene-1′-carbomethoxy,3(2-furyl)-prop-2-ene-2-oic Acid **(5b)**. ^{1}H NMR (300 MHz, DMSO) (δ/ppm): 1.66 (s, 6H, alicyclic CH_2), 2.1 (s, 2H, alicyclic CH_2), 2.94 (s, 2H, alicyclic CH_2), 3.02 (s, 3H, methoxy protons), 6.392–6.457, 6.675–6.723, 7.662–7.674 (AMX, 3H, furyl), 7.7 (s, 1H, vinyl). FTIR (KBr, cm^{-1}) 1260 (C–O), 1480 (alicyclic CH_2) 1614 (C=C), 1684 (C=O acid), 1712 (C=O ester). UV λ_{max} (EtOH) 294 nm (log ε3.32). eq. wt. (found) 292.20 required for $C_{16}H_{18}O_5$ eq. wt. 290.30.

1,1-Isopropylidene-1′-carbomethoxy,3(2-furyl)-prop-2-ene-2-oic Acid **(5c)**. ^{1}H NMR (300 MHz, DMSO) (δ/ppm): 1.75 (s, 3H, aliphatic CH_2), 2.2 (s, 3H, aliphatic CH_2), 3.7 (s, 3H, methoxy protons), 6.429–6.442, 6.59–6.60, 7.468–7.491 (AMX, 3H, furyl), 7.6 (s, 1H, vinyl). FTIR (KBr, cm^{-1}) 1258 (C–O), 1664 (C=C), 1685 (C=O acid), 1715 (C=O ester). UV λ_{max} (EtOH) 290 nm (log ε3.2). eq. wt. (found) 252.30; required for $C_{13}H_{14}O_5$ eq. wt. 250.42.

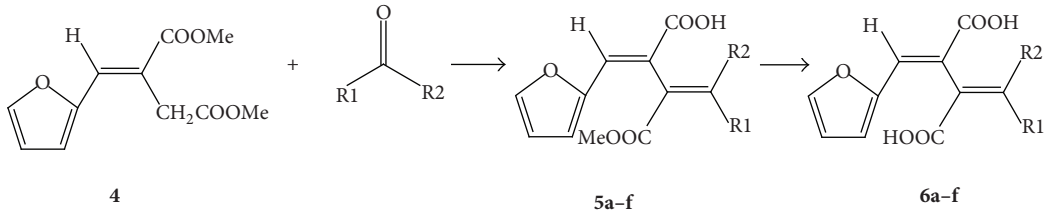
1-Furyl-3-carbomethoxy-4-phenyl Buta-1,3-diene-2-oic Acid **(5d)**. ^{1}H NMR (300 MHz, DMSO) (δ/ppm): 3.7 (s, 3H, methoxy protons), 6.376–6.389, 6.28–6.63, 7.35–7.46 (AMX, 3H, furyl), 7.5 (s, 5H, phenyl), 7.7 (s, 1H, vinyl), 7.8 (s, 1H, vinyl). FTIR (KBr, cm^{-1}) 1174 (C–O), 1480 (alicyclic CH_2) 1715 (C=O acid), 1735 (C=O ester), 2511 (-OCH_3). UV λ_{max} (EtOH) 350 nm (log ε4.1). eq. wt. (found) 295.44 required for $C_{17}H_{14}O_5$ eq. wt. 298.

1-Furyl-3-carbomethoxy-4,4-diphenyl Buta-1,3-diene-2-oic Acid **(5e)**. ^{1}H NMR (300 MHz, DMSO) (δ/ppm): 2.99 (s, 3H, methoxy protons), 6.276–6.289, 6.38–6.63, 6.55–6.76 (AMX, 3H, furyl), 7.1 (s, 5H, phenyl), 7.5 (s, 5H, phenyl), 7.52 (s, 1H, vinyl). FTIR (KBr, cm^{-1}) 634, 712 (mono-substituted Ph rings), 1172 (C–O), 1660 (C=O acid), 1710 (C=O ester), 2510 (–OCH_3). UV λ_{max} (EtOH) 254 nm (log ε4.2). eq. wt. (found) 372.00 required for $C_{23}H_{18}O_5$ eq. wt. 374.39.

1,4-Difuryl-3-carbomethoxy Buta-1,3-diene-2-oic Acid **(5f)**. ^{1}H NMR (300 MHz, DMSO) (δ/ppm): 3.72 (s, 3H, methoxy protons), 6.385–6.409, 6.632–6.663, 7.422–7.447 (AMX pattern repeated, 6H, furyl protons), 7.67 (s, 1H, vinyl), 7.77 (s, 1H, vinyl). FTIR (KBr, cm^{-1}) 634, 712 (mono-substituted Ph rings), 1200 (C–O), 1625 (C=C), 1660 (C=O acid), 1720 (C=O ester), 2500 (OCH_3). UV λ_{max} (EtOH) 333 nm (log ε4.6). eq. wt. (found) 290.00 required for $C_{15}H_{12}O_6$ eq. wt. 288.24 (see Scheme 3).

Procedure for Preparation of 1,1-Cyclopentylidene-1′,2-dicarboxy, 3 (2-furyl)-2-propene **(6a)**. Acid ester **5a** (1 g) was dissolved in 30 mL 8% alcoholic KOH and refluxed for 5 hr. It was filtered hot and cooled. Acidification with ice-cool conc. HCl gave the diacid **6a** as dark brown crystals on recrystallization from benzene pet. ether.

^{1}H NMR (300 MHz, DMSO) (δ/ppm): 1.25–2.17 [m, 8H, alicyclic CH_2] 7.20–7.26 [AMX, 3H, furyl], 7.5 [s, 1H, vinyl]. FTIR. (KBr, cm^{-1}) 1174.80 (C–O), 1488.10 (alicyclic CH_2), 1694.00 and 1710.00 (C=O unsaturated acid). UV λ_{max}



4 **5a–f** **6a–f**

Scheme 3: Synthesis of butadienes.

Table 1: Synthesis of Stobbe compounds using Diester **4**.

Entry	Ketone/aldehyde	Half-ester	Diacid
1	Cyclopentanone	**5a**	**6a**
2	Cyclohexanone	**5b**	**6b**
3	Acetone	**5c**	**6c**
4	Benzaldehyde	**5d**	**6d**
5	Benzophenone	**5e**	**6e**
6	Furfural	**5f**	**6f**

(EtOH): 357.00 nm (log ε4.6). eq. wt. (found) 130.00 required for $C_{14}H_{14}O_5$ eq. wt. 131.13.

1,1-Cyclopentylidene-1′,2-dicarboxy, 3 (2-furyl)-2-propene **(6b)**. ^{1}H NMR (300 MHz, DMSO) (δ/ppm): 1.55 (s, 6H, alicyclic CH_2), 2.1 (s, 2H, alicyclic CH_2), 2.81 (s, 2H, alicyclic CH_2), 6.383–6.396, 6.62–6.63, 7.43–7.44 (AMX, 3H, furyl), 7.69 (s, 1H, vinyl). FTIR (KBr, cm^{-1}) 1214 (C–O), 1600 (C=C), 1688 (C=O acid). UV λ_{max} (EtOH) 278 nm (log ε4.6). eq. wt.(found) 140.64 required for $C_{15}H_{16}O_5$eq. wt. 138.14.

1,1-Cyclopentylidene-1′,2-dicarboxy, 3 (2-furyl)-2-propene **(6c)**. ^{1}H NMR (300 MHz, DMSO) (δ/ppm): 1.75 (s, 3H, aliphatic CH_2), 2.32 (s, 3H, aliphatic CH_2), 6.448–6.592, 6.712-6.718, 7.468-7.48 (AMX, 3H, furyl), 7.5 (s, 1H, vinyl). FTIR (KBr, cm^{-1}) 1218 (C–O), 1600 (C=C), 1698 (C=O acid). UV λ_{max} (EtOH) 280 nm (log ε4.5). eq. wt. (found) 121.23 required for $C_{12}H_{12}O_5$ eq. wt. 118.11.

1-Furyl-2,3-dicarboxy-4 Phenyl Buta-1,3-diene **(6d)**. ^{1}H NMR (300 MHz, DMSO) (δ/ppm): 6.376–7.01, 7.331-7.429, 7.35–7.46 (AMX, 3H, furyl), 7.5 (s, 5H, phenyl), 7.72 (s, 1H, vinyl), 7.89 (s, 1H, vinyl). FTIR (KBr, cm^{-1}) 1228 (C–O), 1628 (C=C), 1690 (C=O acid). UV λ_{max} (EtOH) 370 nm (log ε4.6). eq. wt. (found) 143.28; required for $C_{16}H_{12}O_5$ eq. wt. 142.31.

1-Furyl–2,3-dicarboxy-4,4′-diphenyl Buta-1,3-diene **(6e)**. ^{1}H NMR (300 MHz, DMSO) (δ/ppm): 6.71–6.73, 6.80–6.85, 6.87–6.89 (AMX, 3H, furyl), 7.65 (s, 5H, phenyl), 7.75 (s, 5H, phenyl), 7.81 (s, 1H, vinyl). FTIR (KBr, cm^{-1}) 613, 620 (mono-substituted Ph rings), 1170 (C–O), 1648 (C=O acid), 1700 (C=O acid). UV λ_{max} (EtOH) 270 nm (log ε4.6). eq. wt. (found) 179.95 required for $C_{22}H_{16}O_5$ eq. wt. 180.19.

1,4-Difuryl–2,3-dicarboxy Buta-1,3-diene **(6f)**. ^{1}H NMR (300 MHz, DMSO) (δ/ppm): 6.2981–6.304, 6.623–6.631, 7.434–7.438 (AMX pattern repeated, 6H, furyl protons), 7.67 (s, 1H, vinyl), 7.77 (s, 1H, vinyl). FTIR (KBr, cm^{-1}) 1250 (C–O), 1635 (C=C), 1690 (C=O acid). UV λ_{max} (EtOH) 332 nm (log ε4.76). eq. wt. (found) 138.40 required for $C_{14}H_{10}O_6$ eq. wt. 137.11.

3. Results and Discussion

In the previous research [17], it was found that potassium tertiary butoxide can be smoothly used as a catalyst in Stobbe condensation under solvent-free conditions. This discovery stimulated us to explore whether it could be developed into a green [18] procedure for Stobbe condensation.

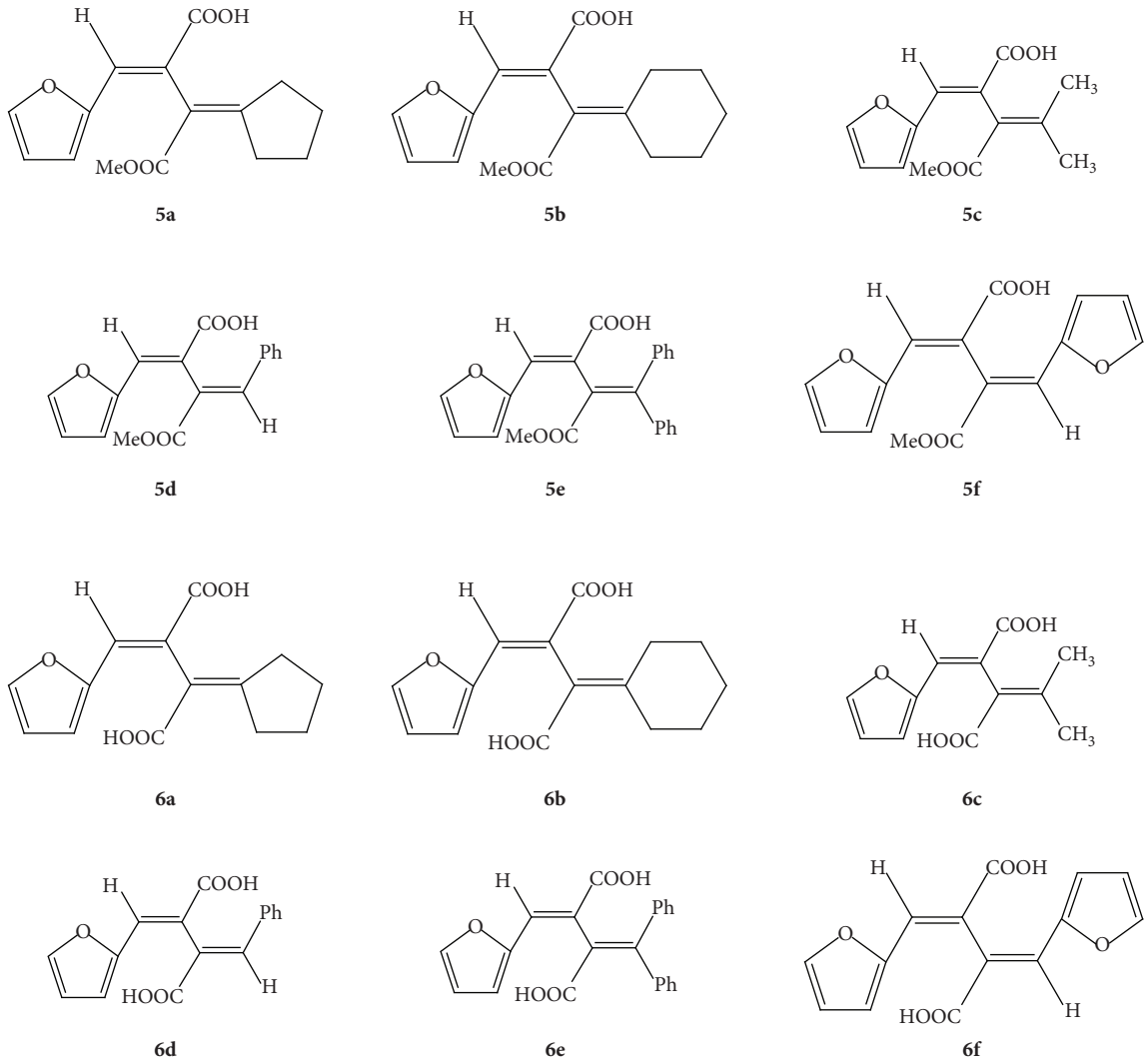
Stobbe condensation generally involves the use of metal alkoxide as a catalyst in refluxing alcohol, and particularly, butanol. On the other hand, in the present paper, the use of butanol is discarded and instead, dry solid potassium tertiary butoxide is taken for the reaction. The advantages are inexpensive and easily available materials, have short reaction time, excellent yields (the yields of the products obtained by solvent-free method were compared with the yields of the products obtained by classical method which was done simultaneously for a comparative study), and environment-friendly reaction conditions.

A well ground mixture of furfural **1** and dimethyl succinate **2** in 1 : 1 molar ratio with catalytic amount of potassium tertiary butoxide without any solvent was exposed to atmosphere at room temperature in a dry agate mortar. After neutralization with dil. HCl, crude 3-carbomethoxy,4-furyl, 3-butenoic acid, **3** which could be easily crystallized from benzene-petroleum ether. The structure of the acid ester **3,** has been analyzed by UV, IR, and NMR spectra. It is confirmed that, from both the routes, namely, classical Stobbe condensation [15] and the solvent-free reaction, the same acid ester **3** is obtained.

The acid ester product upon methylation with diazomethane [16] afforded diester, namely, methyl 3-carbomethoxy,4-furyl,3-butenoate, **4** in 95% yield.

The diester **4** is a starting material for the synthesis of various butadienes via Stobbe condensation with different aldehydes (furfural, benzaldehyde) and ketones (acetone, benzophenone, cyclopentanone, and cyclohexanone) using the base, that is, dry-solid potassium tert. butoxide in an oven-dried mortar at room temperature (see Figure 1 and Table 1).

The results indicated that, all the reactions were performed under solvent-free conditions in good yields of 70–90% (please see Table 2). The structures of these compounds were analyzed by NMR spectroscopy [19]. All the



5a **5b** **5c**

5d **5e** **5f**

6a **6b** **6c**

6d **6e** **6f**

Figure 1: Stobbe products **5a–f** and diacids **6a–f**.

Table 2: Yield and melting points of Stobbe products **3**, **5a–f**.

Compound	Yield %		mp (°C)
	Classical	Green	
3	65	83	111
5a	63	78	162
5b	75	82	120
5c	65	70	102
5d	62	74	194
5e	60	71	128
5f	69	85	160

Table 3: Yield and melting points of dicarboxylic acids **6a–f**.

Compound	Yield %	mp (°C)
6a	85	168
6b	85	177
6c	86	180
6d	90	202
6e	88	132
6f	89	230

butadienes, being derived from furfural, show a common AMX pattern in their high resolution NMR spectra, which can be seen for three furyl hydrogens nearly at 6.3, 6.6, and 7.6δ. Aromatic protons are depicted well in the aromatic zone of 7.2–7.5δ for the compound **5d** and **6d**. Similarly, the aliphatic and alicyclic protons are exhibited in their characteristic positions. Further, FTIR spectra [20] support the structures of the compounds. The typical acid carbonyl is found in the range 1670–1690 cm^{-1}, and the ester C=O appears at near 1715 cm^{-1}.

It is interesting to note that the saponification [15] reactions of the acid esters **5a–5f** afforded the diacids **6a–6f** in good yields (please see Table 3).

The presence of different substituents does not really affect the product yield. However, during cyclization of these diacids, difficulty is faced with the bulkier phenyl or naphthyl substituents, which would be discussed elsewhere.

4. Conclusion

It was concluded that, the solvent-free condensations of substituted ketones and/or aldehyde with dimethyl succinate at room temperature occurred smoothly to give substituted acid esters. As compared to the classical condensation method done by previous workers [13], wherein was required, plenty of solvents and chemicals to proceed, the green method needed much less amount of dry solid reagents; which indicates that the method is efficient from the economical point of view. No heat energy is required for the formation of acid esters, thus, proving the reaction to be feasible at ecofriendly reaction conditions. Further, this method improved the yields and shortened the reaction time.

Acknowledgments

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