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# Reaction Between 1,3-Dicarbonyl-Containing CH Acids and Dialkyl Acetylenedicarboxylates in the Presence of Silica Gel in Solvent-Free Conditions: An Efficient Method for the Synthesis of Electron-Poor Alkenes and Pyranes

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**Abstract:** A two-component condensation reaction between a 1,3-dicarbonylcontaining CH acid and an electron-poor acetylenic ester efficiently provides fully substituted electron-poor alkenes and pyranes in a one-pot reaction in the presence of silica gel in solvent-free conditions.

**Keywords:** Acetylenic ester, CH acid, 1,3-diketone, electron-poor alkene, pyrane, silica gel, solvent-free conditions

## INTRODUCTION

Environmentally friendly synthesis of organic compounds without using of organic solvents has come several steps closer in recent years.<sup>[1]</sup> Organic reactions using conventional organic solvents, especially chlorinated hydrocarbons, have posed a serious threat to the environment because of their toxicity and volatile nature.<sup>[1]</sup> In this regard, solvent-free catalytic organic reactions have received tremendous attention in recent times.<sup>[2]</sup>

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#### **Electron-Poor Alkenes and Pyranes**

Solvent-free conditions are especially suitable for organic synthesis. Environmentally benign synthesis can be easily designed using this methodology:

- The use of large volumes of solvent is avoided, reducing solvent emissions and redistillation.
- Workup is considerably simplified because in many cases the pure product can be obtained directly from the crude reaction mixture by simple extraction, distillation or sublimation.
- Recyclable solid supports can be used, replacing highly polluting mineral acids and oxidants.
- Scale-up is facilitated by the absence of solvent.
- Safety is increased by reducing the risk of overpressure and explosions.<sup>[3]</sup>

For several years, acetylenic esters have been attracting the attention of organic chemists.<sup>[4–8]</sup> Acetylenic esters are reactive systems and take part in many chemical syntheses.<sup>[4–8]</sup> The compounds almost act as Michael acceptors in the organic reactions.<sup>[9]</sup> In the recent years, there has been increasing interest in the applications of acetylenic esters in multicomponent<sup>[10–14]</sup> synthesis. Because of the atom economy, convergent character, and simplicity of one-pot procedures, multicomponent condensation reactions (MCRs) have an advantageous position among other reactions. The discovery and development of novel MCRs is receiving growing interest from industrial chemistry research groups and represents a new challenge for organic chemists and to the basic understanding of organic chemistry itself.<sup>[15]</sup>

Silica gel as an additive promotes many condensation reactions in solvent-free conditions.<sup>[16–21]</sup> Continuing our interest in solvent-free synthesis (Ramazani reaction),<sup>[6]</sup> herein we report on a hitherto unknown two-component reaction, which, starting from simple and readily available precursors, affords fully functionalized electron-poor alkenes and pyranes in a one-pot reaction in the presence of silica-gel powder in solvent-free conditions.

## **RESULTS AND DISCUSSION**

The 1,3-dicarbonyl-containing CH acids 1, 4, 6, and 8 and dialkyl acetylenedicarboxylates 2 in the presence of silica-gel powder underwent a smooth 1:1 addition reaction in solvent-free conditions at 90 °C in 30 min to produce compounds 3, 5, 7, 9, 10, and 11(Scheme 1–4). The reaction proceeded smoothly and cleanly under mild conditions, and no side reactions were

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#### Scheme 1.

observed. In the absence of the silica-gel powder, the starting materials were not reacted under reaction conditions (90 °C, 30 min) in the solvent-free system. The reaction also did not occur in dichloromethane solutions after several days. Thin-layer chromatography (TLC) indicated the formation of products 3, 5, 7, 9, and 11 on the silica-gel surface. Compounds 10 are not stable and rearranged to products 11 due to staying at room temperature in solvent (CHCl<sub>3</sub>), neat or on the silica-gel surface. The conversion of compounds 10 to products 11 is fairly fast in CHCl<sub>3</sub> (or CDCl<sub>3</sub>) solution, and it was completed less than 20 min. In the other cases (silica-gel surface, neat, and in solvents of CH<sub>2</sub>Cl<sub>2</sub>, ethyl acetate, and petroleum ether), the conversion is very slow and was not complete after several days. These results show that products 11 are more stable than compounds 10. We have not investigated the role of CHCl<sub>3</sub> (or CDCl<sub>3</sub>) solution in the fast conversion of the compounds 10 to compounds 11. It seems that the presence of trace amounts of HCl (or DCl) in the CHCl<sub>3</sub> (or CDCl<sub>3</sub>) solution may be the factor as acid catalyst in the increasing of the conversion rate. In the case of the mixture of compounds 10 and 11, we prepared the <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum. The chemical shifts ( $\delta_H$ ) for 10 [3.54 and 3.66 (6 H, 2 s, 2 OCH<sub>3</sub>); 5.28 (1 H,1 s, = CH); 7.43-8.14 (10 H, m, arom); 17.20 (1 H, 1 s, OH)] and 11 [3.35 (2 H, 1 s, CH<sub>2</sub>); 3.52 and 3.64 (6 H, 2 s, 2 OCH<sub>3</sub>); 7.43-8.14 (10 H, m, arom)] were assigned from the spectra. The relative population of



Scheme 2.



Scheme 3.

**10:11** (40:60) was estimated on the basis of <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum of the mixture. About after 10 min, the intermediate **10** was completely converted to the product **11** in CDCl<sub>3</sub> solution at room temperature and in the <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum, signals of only **11** were observed. The <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectra of compounds **5** show the presence of two estereoisomers (**E** and **Z**) for each alkenes. The relative population of **E** and **Z** isomers were determined via their <sup>1</sup>H NMR spectra (see Experimental section).

The mechanism of the reaction between the 1,3-dicarbonylcontaining CH acids 1, 4, 6, and 8 and dialkyl acetylenedicarboxylate 2 in the presence of silica-gel powder in solvent-free conditions has not been established experimentally. Michael addition of the enol form of 1,3-dicarbonyl-containing CH acid to the acetylenic ester in the presence of silica gel as general acid–base catalyst may be considered as a plausible mechanism.<sup>[6]</sup> The structures of the products were deduced from their IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra (see Experimental section).



Scheme 4.

## CONCLUSIONS

In summary, we have found a new and efficient method for the synthesis of fully substituted electron-poor alkenes and pyranes from 1,3-dicarbonyl-containing CH acids and electron-poor acetylenic esters, in a one-pot reaction in the presence of silica gel in solvent-free conditions. We believe the reported method offers a mild, simple, and efficient route for the preparation of substituted electron-poor alkenes and pyranes. Its ease of workup, high yields, and fairly short reaction times make it a useful addition to modern synthetic methodologies. Other aspects of this process are under investigation.

## EXPERIMENTAL

Starting materials and solvents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. Flash chromatography columns were prepared from Merck silica-gel powder. Elemental analyses for C and H were performed using a Heraeus CHN-O-Rapid analyzer. IR spectra were measured on a Shimadzu IR-460 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured (CDCl<sub>3</sub> solution) with a Bruker DRX-250 Avance spectrometer at 250.0 and 62.5 MHz, respectively.

## **General Procedure**

A homogenous mixture of 1,3-dicarbonyl-containing CH-acid derivative (1 mmol), dialkyl acetylenedicarboxylate (1 mmol), and powdered silica gel (0.7 g) were heated in a oven at 90 °C for 30 min and then placed over a column of silica gel (12 g). The column chromatography was performed using ethyl acetate-light petroleum ether (1:10) as eluent. The solvent was removed under reduced pressure, and the products were obtained as oils. Relative populations of *E* and *Z* stereoisomers for the compounds **5a–5b** were determined via their <sup>1</sup>H NMR spectra. The characterization data of the new compounds are given next.

## Data

Dimethyl (E)-2-[(Z)-1-Acetyl-2-hydroxy-1-propenyl]-2-butendioate (3a)

Yellow oil, yield 80%, IR (neat) ( $\nu_{max}$ , cm<sup>-1</sup>): 2954 (CH, alipha); 1727 (C=O, ester); 1612 (C=C, alkene). Anal. calcd for C<sub>11</sub>H<sub>14</sub>O<sub>6</sub> (242): C,

54.54; H, 5.83. Found: C, 54.51; H, 5.80%.<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_H$ : 1.95 (6H, 1s, 2CH<sub>3</sub>); 3.75 and 3.84 (6H, 2s, 2OCH<sub>3</sub>); 7.08 (1H, 1s, =CH); 16.57 (1H, 1s, OH). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta_C$ : 23.50 (2CH<sub>3</sub>); 52.24 and 53.16 (2OCH<sub>3</sub>); 106.98, 139.87 (2C); 132.03 (CH = ); 165.08 and 166.7 (C = O of ester); 189.93 (C = O of keton).

Diethyl (E)-2-[(Z)-1-Acetyl-2- hydroxyl-1-propenyl]- 2- butenedioate (3b)

Yellow oil, yield 75%, IR (neat) ( $\mu_{max}$ , cm<sup>-1</sup>) : 2954 (CH, alipha); 1727 (C=O, ester); 1612 (C=C, alkene). Anal. Calcd. for C<sub>13</sub>H<sub>18</sub>O<sub>6</sub> (270): C, 57.77; H, 6.71. Found: C, 57.74; H, 6.67%. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{H^{\pm}}$  1.24 and 1.30 ( 6H, 2 t,  ${}^{3}J_{HH}$  = 7.25 Hz, 2CH<sub>3</sub> of 2Et); 1.94 (6H, 1s, 2CH<sub>3</sub>); 4.18 and 4.28 (4H, 2q,  ${}^{3}J_{HH}$  = 7.25 Hz, 2OCH<sub>2</sub> of 2Et); 7.06 (1H, 1s, =CH); 16.51 (1H, 1s, OH). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta_{C^{\pm}}$  14.00 and 14.10 (2CH<sub>3</sub> of 2Et); 23.44 (2CH<sub>3</sub>); 61.19 and 62.14 (2OCH<sub>2</sub>); 107.13 and 139.49 (2C); 132.29 (CH = ); 164.76 and 166.15 (2C = O of ester); 189.84 (C = O of keton).

Dimethyl-(*E*)-2-[1-(2,2-dimethylpropanoyl)-3,3-dimethyl-2-oxobutyl]-2-butenedioate (5a)

Colorless oil, yield 50%, IR (neat) ( $\mu_{max}$ , cm<sup>-1</sup>): 2954 (CH, alipha); 1727 (C=O, ester); 1612 (C=C, alkene). Anal. calcd for C<sub>17</sub>H<sub>26</sub>O<sub>6</sub> (326): C, 62.56; H, 8.03. Found: C, 62.52; H, 8.00%.<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{H}$ : 1.15 (18H, 1s, 6CH<sub>3</sub> of 2 t-Bu); 3.8 and 3.82 (6H, 2s, 2OCH<sub>3</sub>); 6.67 (1H, 1s, =CH); 6.80 (1H, 1s, CH).<sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta_C$ : 26.75 (6CH<sub>3</sub> of 2 t-Bu); 45.86 (2C of 2 t-Bu); 52.15 and 52.9 (2 OCH<sub>3</sub>); 55.35 and 124.70 (2CH); 130.86 (1C), 165.79 and 166.84 (2 C=O of ester); 210.58 (C=O of ketone).

Dimethyl-(*Z*)-2-[1-(2,2-dimethylpropanoyl)-3,3-dimethyl-2-oxobutyl]-2-butenedioate (5a)

Colorless oil, yield 45%, IR (neat) ( $\mu_{max}$ , cm<sup>-1</sup>): 2954 (CH, alipha); 1727 (C=O, ester); 1612 (C=C, alkene); 1240 (C-O, ether). Anal. Calcd. for C<sub>17</sub>H<sub>26</sub>O<sub>6</sub> (326): C, 62.56; H, 8.03. Found: C, 62.52; H, 8.00%. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_H$ : 1.17 (18H, 1s, 6CH<sub>3</sub> of 2 t-Bu); 3.74 and 3.79 (6H, 2s, 2CH<sub>3</sub> of 2 OMe); 5.55 (1H, 1s, =CH); 6.10 (1H, 1s, CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta_C$ : 27.06 (6 CH<sub>3</sub> of 2 t-Bu); 45.35 (2C of 2 t-Bu); 52.11 and 52.77 (2OCH<sub>3</sub>); 55.95 and 129.54 (2CH); 134.51 (C); 165.44 and 166.69 (2 C=O of ester); 205.17 (C=O of ketone).

Diethyl (*E*)-2-[1-(2,2-Dimethylpropanoyl)-3,3-dimethyl-2-oxobutyl]-2-butenedioate (**5b**)

Colorless oil, yield 55%. IR (neat) ( $\nu_{max}$ , cm<sup>-1</sup>): 2950 (CH, alipha); 1727 (C=O, ester); 1612 (C=C, alkene); 1240 (C-O, ether). Anal. calcd. for C<sub>19</sub>H<sub>30</sub>O<sub>6</sub> (354): C, 64.38; H, 8.53. Found: C, 64.35; H, 8.49%. <sup>1</sup>H NMR (CDCl<sub>3</sub>) $\delta_H$ : 1.12 (18H, 1s, 6CH<sub>3</sub> of 2 t-Bu); 1.27 (6H, t, <sup>3</sup>J<sub>HH</sub>=7.25 Hz, 2CH<sub>3</sub> of 2OEt); 4.22 and 4.25 (4H, 2q, <sup>3</sup>J<sub>HH</sub>=7.25 Hz, 2OCH<sub>2</sub> of 2OEt); 6.63 (1H, 1s, =CH); 6.79 (1H, 1s, CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta_C$ : 13.89 and 14.05 (2CH<sub>3</sub> of 2OEt); 26.73 (6CH<sub>3</sub> of 2 t-Bu); 45.77 (2C of 2 t-Bu); 61.16 and 62.06 (2 OCH<sub>2</sub> of 2OEt); 55.24 and 124.93 (2CH); 130.84 (1C), 165.38 and 166.34 (2 C=O of ester); 210.41 (2C=O of ketone).

Diethyl (*Z*)-2-[1-(2,2-Dimethylpropanoyl)-3,3-dimethyl-2-oxobutyl]-2-butenedioate (**5b**)

Colorless oil, yield 40%. IR (neat) ( $\nu_{max}$ , cm<sup>-1</sup>): 2961 (CH, alipha.); 1727 (C = O, carbonyl); 1240 (C-O, ether). Anal. calcd. for C<sub>19</sub>H<sub>30</sub>O<sub>6</sub> (354): C, 64.38; H, 8.53. Found: C, 64.35; H, 8.49%. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_H$ : 1.17 (18H, 1s, 6CH<sub>3</sub> of 2 t-Bu); 1.27 (6H, t,  ${}^3J_{HH}$  = 7.25 Hz, 2CH<sub>3</sub> of 2OEt); 4.19 and 4.24 (4H, 2q,  ${}^3J_{HH}$  = 7.25 Hz, 2OCH<sub>2</sub> of 2OEt); 5.57 (1H, 1s, =CH); 6.09 (1H, 1s, CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta_C$ : 13.83 and 14.01 (2CH<sub>3</sub> of 2OEt); 27.08 (6CH<sub>3</sub> of 2 t-Bu); 45.32 (2C of 2 t-Bu); 61.11 and 61.94 (2 OCH<sub>2</sub> of 2OEt); 55.35 and 130.01 (2CH); 133.89 (1C), 165.06 and 166.18 (2 C = O of ester); 205.29 (2C = O of ketone).

5-Ethyl-4-methyl-6-methyl-2-oxo-2H-pyran-4,5-dicarboxylate (7a)

Yellow oil, yield 80%. IR (neat) ( $\nu_{max}$ , cm<sup>-1</sup>): 2961 (CH, alipha); 1727 (C = O, carbonyl); 1688 (C = C, alkene); 1263 (C-O of ether). Anal. calcd. for C<sub>11</sub>H<sub>12</sub>O<sub>6</sub> (240): C, 55.00; H, 5.04. Found: C, 54.97; H, 4.95%. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{H}$ : 1.32 (3H, t, <sup>3</sup>*J*<sub>HH</sub> = 7.25 Hz, CH<sub>3</sub> of OEt); 2.49 (3H, 1s, CH<sub>3</sub>); 3.88 (3H, 1s, CH<sub>3</sub> of OCH<sub>3</sub>), 4.3 (2H, 1q, <sup>3</sup>*J*<sub>HH</sub> = 7.25 Hz, CH<sub>2</sub> of OEt); 6.46 (1H, 1s, = CH).<sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta_{C}$ : 13.94 (CH<sub>3</sub> of OEt); 19.36 (CH<sub>3</sub>); 53.16 (OCH<sub>3</sub>); 62.07 (OCH<sub>2</sub> of OEt), 113.65 (CH); 109.32, 145.94 and 159.74 (3C); 164.18, 164.67 and 166.94 (3 C = O of ester or lactone).

Methyl-5-benzoyl-6-methyl-2-oxo-2H-pyran-4-carboxylate (7b)

Yellow oil, yield 80%. IR (neat)  $(v_{max}, cm^{-1})$ : 2961 (CH, alipha); 1757 (C=O, carbonyl); 1688 (C=C, alkene); 1263 (C-O of ether). Anal.

#### **Electron-Poor Alkenes and Pyranes**

Calcd. for  $C_{15}H_{12}O_5$  (272): C, 66.17; H, 4.44. Found: C, 66.14; H, 4.40%. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_H$ : 2.19 (3H,1s, CH<sub>3</sub>); 3.62 (3H, 1s, OCH<sub>3</sub>); 6.78(1H, 1s, HC =); 7.47–7.84 (4H, m, arom).<sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta_C$ : 18.62 (CH<sub>3</sub>); 53.18 (OCH<sub>3</sub>); 144.77 (HC =); 115.30, 115.57, and 160.50 (3C); 128.89, 129.08, 133.98 and 136.69 (4CH, arom); 162.80 and 163.58 (2C = O of ester); 192.31 (C = O of keton).

Ethyl-5-benzoyl-6-ethyl-2-oxo-2*H*-pyran-4-carboxylate (7c)

Yellow oil, yield 80%. IR (neat) ( $v_{max}$ , cm<sup>-1</sup>): 2961 (CH, alipha); 1757 (C=O, carbonyl); 1688 (C=C, alkene); 1263 (C-O of ether). Anal. Calcd. for C<sub>16</sub>H<sub>14</sub>O<sub>5</sub> (286): C, 67.13; H, 4.93. Found: C, 67.10; H, 4.90%. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_H$ : 1.06 (3H, 1 t, <sup>3</sup>J<sub>HH</sub>=7.25 Hz, CH<sub>3</sub> of OEt); 2.19 (3H, 1s, CH<sub>3</sub>); 4.06 (2H, 1q, <sup>3</sup>J<sub>HH</sub>=7.25 Hz, CH<sub>2</sub> of OEt); 6.79 (1H, 1s, = CH); 6.92–7.88 (5H, m arom). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta_C$ : 13.46 (CH<sub>3</sub> of Et); 18.84 (CH<sub>3</sub>); 62.79 (CH<sub>2</sub> of Et); 115.81 (CH); 115.42, 145.15, 160.65 (3C); 128.99, 129.04, 133.98, 137.01 (4CH, arom); 162.64, 163.06 (2C = O of ester); 192.29 (C = O of ketone).

Ethyl-5-benzoyl-2-oxo-6-phenyl-2*H*-pyran-4-carboxylate (9b)

Brown oil; yield 34%. Anal. Calcd. for  $C_{21}H_{16}O_5$  (348): C, 72.41; H, 4.63. Found: C, 71.38; H, 4.60%. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{H}$ : 1.12 (3H, t, <sup>3</sup>*J*<sub>HH</sub> = 7.25 Hz, CH<sub>3</sub> of OEt); 4.18 (2H, q, <sup>3</sup>*J*<sub>HH</sub> = 7.25 Hz, OCH<sub>2</sub> of OEt); 7.27 (1H, 1s, = CH); 7.28–8.16 (10H, m, arom). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta_{C}$ : 13.55 (CH<sub>3</sub> of OEt); 62.84 (OCH<sub>2</sub> of OEt); 116.00, 128.52, 128.65, 128.69, 129.11, 131.25, 133.68, and 134.67 (11CH); 131.01, 136.80, 145.20, and 160.20 (4C); 161.20 and 163.50 (2C = O of ester); 193.00 (C = O of keton).

Dimethyl (Z)-2-[(E)-1-Benzoyl-2-hydroxy-2-phenyl-1-ethyenyl]-2-butenedioate (10a)

Brown oil; yield 80%, IR (neat) ( $\nu_{max}$ , cm<sup>-1</sup>): 3350 (OH, alcohol); 3035 (CH, arom); 2954 (CH, alipha); 1727 (C = O, ester); 1612 (C = C, alkene), <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{H}$ : 3.54 and 3.66 (6H, 2s, 2OCH<sub>3</sub>); 5.28 (1H, 1s, = CH); 7.43–8.14 (10H, m, arom); 17.20 (1H, 1s, OH).

Dimethyl 2-(1-Benzoyl-2-oxo-2-phenylethylidene)succinate (11a)

Green oil; yield 80%; IR (neat) ( $\nu_{max}$ , cm<sup>-1</sup>): 3035 (CH, arom); 2954 (CH, alipha); 1727 (C=O, ester); 1710 (C=O, keton); 1612 (C=C, alkene).

Anal. calcd. for C<sub>21</sub>H<sub>18</sub>O<sub>6</sub> (366): C, 68.85; H, 4.95. Found: C, 68.80; H, 4.92%. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{H}$ : 3.35 (2H, 1s, CH<sub>2</sub>); 3.52 and 3.64 (6H, 2s, 2OCH<sub>3</sub>); 7.43–8.14 (10H, m, arom). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta_{C}$ : 34.79 (CH<sub>2</sub>); 52.01 and 52.24 (2OCH<sub>3</sub>); 128.54, 128.75, 129.54, 130.54, 133.57, and 134.62 (10CH); 134.95, 135.79, 145.20, and 152.44 (4C); 165.24 and 169.46 (2C = O of ester); 191.38 and 192.03 (2C = O of keton).

Diethyl (*Z*)-2-[(*E*)-1-Benzoyl-2-hydroxy-2-phenyl-1-ethyenyl]-2butenedioate (11a)

Brown oil; yield 66%. IR (neat) ( $\nu_{max}$ , cm<sup>-1</sup>): 3350 (OH, alcohol); 3035 (CH, arom); 2954 (CH, alipha); 1727 (C = O, ester); 1612 (C = C, alkene).<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{H}$ : 0.97 and 1.24 (6H, 2t,  ${}^{3}J_{HH}$  = 7.25 Hz, 2CH<sub>3</sub> of 2OEt); 4.03 and 4.14 (4H, 2q,  ${}^{3}J_{HH}$  = 7.25 Hz, 2OCH<sub>2</sub> of 2OEt); 6.87 (1H, 1s, = CH); 7.28–8.16 (10H, m, arom); 17.05 (1H, 1s, OH).

Diethy2-(1-benzoyl-2-oxo-2-phenylethylidene)succinate (11b)

Green oil; yield 66%. IR (neat) ( $\nu_{max}$ , cm<sup>-1</sup>): 3035 (CH, arom); 2954 (CH, alipha); 1727 (C = O, ester); 1710 (C = O, keton); 1612 (C = C, alkene). Anal. Calcd. for C<sub>23</sub>H<sub>22</sub>O<sub>6</sub> (394): C, 70.04; H, 5.62. Found: C, 70.01; H, 5.59%. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta_{H}$ : 0.97 and 1.24 (6H, 2 t,  ${}^{3}J_{HH}$  = 7.25 Hz, Hz, 2CH<sub>3</sub> of 2OEt); 3.32 (2H, 1s, CH<sub>2</sub>); 4.03 and 4.14 (4H, 2q,  ${}^{3}J_{HH}$  = 7.25 Hz, 2OCH<sub>2</sub> of 2OEt); 7.26–8.16(10H, m, arom). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta_{C}$ : 13.35 and 14.07 (2CH<sub>3</sub> of 2OEt); 34.14(CH<sub>2</sub>); 61.88 and 62.05 (2OCH<sub>2</sub> of 2OEt); 128.66, 128.87, 129.78, 130.71, 133.81, and 134.87 (10CH); 135.55, 136.80, 145.20, and 152.09 (4C); 164.79 and 169.24 (2C = O of ester); 191.30 and 192.03 (2C = O of keton).

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