

# Synthesis of 2,3-Di-(2-adamantylidene)succinic Anhydride: a Highly Non-photochromic Overcrowded Fulgide†

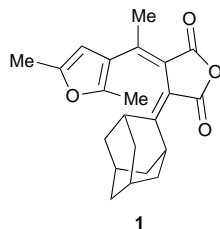
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Abdullah M. Asiri

Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah, P.O. Box 9027, Saudi Arabia

A two-step Stobbe condensation of adamantan-2-one with dimethyl succinate and then dimethyl (2-adamantylidene)succinate affords a half-ester **5**, which on hydrolysis and dehydration gives the title fulgide **7**.

Stobbe<sup>1</sup> first introduced the term 'fulgide' to describe derivatives of 2,3-di(methylidene)succinic anhydride. Since the beginning of this century many fulgides have been prepared and their photochromic properties investigated.<sup>2–4</sup> Heller and co-workers<sup>5</sup> synthesised (*E*)-2-(2-adamantylidene)-3-[1-(2,5-dimethyl-3-furyl)ethylidene]succinic anhydride **1** as the first example of a photochromic fulgide containing the rigid and bulky adamantylidene group. In view of our long standing interest in the development of novel fulgides for application in the field of optical data storage, the synthesis of non-photochromic highly overcrowded 2,3-di(2-adamantylidene)succinic anhydride and its mono derivative were undertaken.



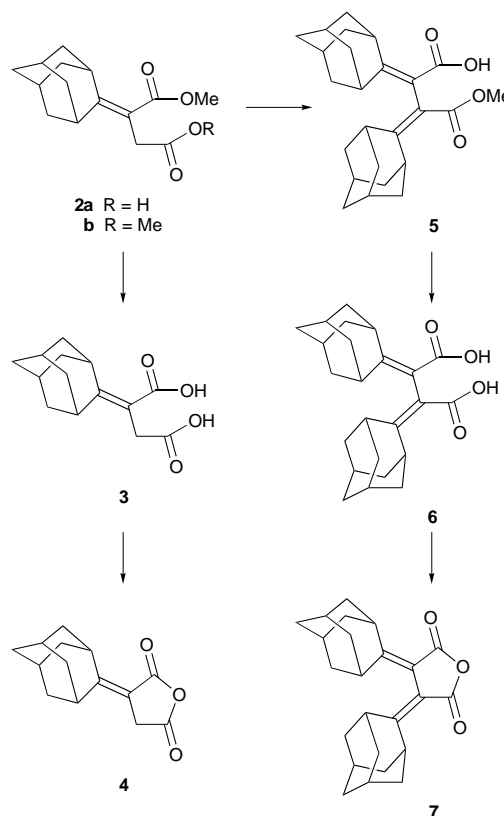
Stobbe condensation of adamantan-2-one and dimethyl succinate in toluene using potassium *tert*-butoxide as a base afforded 1-methyl hydrogen 2-(2-adamantylidene)succinate **2a** (Scheme 1). The composition of the acid ester **2a** was confirmed by hydrolysis to the diacid **3**, which was converted into (2-adamantylidene)succinic anhydride **4** by boiling with acetyl chloride. The mass spectrum of the cyclic anhydride **4** showed a molecular ion at  $m/z$  232 and a base peak at  $m/z$  160, which corresponds to the loss of one molecule of both carbon monoxide and carbon dioxide. The acid ester **2a** was re-esterified to give dimethyl (2-adamantylidene)succinate **2b** using acetyl chloride and methanol.

A second Stobbe condensation of the diester **2b** and adamantan-2-one afforded methyl hydrogen 2,3-di(2-adamantylidene)succinate **5**. The latter was hydrolysed by boiling in 10% alcoholic KOH to give the diacid **6** as a colourless powder, which was cyclised to the title fulgide **7** in boiling acetyl chloride. The mass spectrum of **7** showed the base peak at  $m/z$  364, in agreement with its chemical composition  $C_{24}H_{28}O_3$ . To the best of our knowledge, **7** is believed to be the most overcrowded fulgide prepared so far.

## Experimental

Melting points were determined on a Reichardt hot-stage microscope and were uncorrected. <sup>1</sup>H NMR spectra were obtained for solutions in CDCl<sub>3</sub> with Me<sub>4</sub>Si as internal standard using a Bruker WM360 spectrometer. Mass spectra were recorded on a Varian MAT CH5 spectrometer. Microanalyses were carried out using a Perkin Elmer 240B analyser. IR spectra were recorded for solutions on a Perkin Elmer 1600 FTIR spectrometer.

**1-Methyl Hydrogen 2-(2-Adamantylidene)succinate 2a.**—A mixture of dimethyl succinate (75 g, 0.51 mol) and adamantan-2-one



Scheme 1

(75 g, 0.50 mol) in warm dry toluene (250 ml) was added dropwise to a suspension of potassium *tert*-butoxide (56 g, 0.50 mol) in dry toluene (150 ml) with stirring at room temperature. When the addition was complete, the reaction mixture was stirred for a further 12 h and then poured onto crushed ice (250 g) and stirred for 10 min. The toluene layer was separated and washed with water (2 × 50 ml). The combined aqueous solutions were acidified with concentrated hydrochloric acid to liberate the acid ester **2a** as a colourless powder which was recrystallised from acetone as colourless cubes (62 g, 64%), mp 136–139 °C (lit.,<sup>5</sup> 138–139 °C).

**Dimethyl (2-Adamantylidene)succinate 2b.**—Methyl hydrogen (2-adamantylidene)succinate (60 g, 0.23 mol) was dissolved in absolute methanol (250 ml). Acetyl chloride (25 ml) was added dropwise with stirring at room temperature over a period of 30 min. When the addition was complete the mixture was refluxed for 6 h. The solvent was removed under reduced pressure and the residue was distilled under vacuum to afford the diester **2b** as pale yellow oil (56 g, 89%), bp 145–160 °C at 1 mmHg;  $\delta_H$  1.78–2.0, 2.88 (14 H, m, adamantylidene), 3.38 (2 H, s, CH<sub>2</sub>), 3.66 (3 H, s, CH<sub>3</sub>O), 3.70 (3 H, s, CH<sub>3</sub>O).

**2-Adamantylidenesuccinic Anhydride 4.**—A warm solution of 10% ethanolic potassium hydroxide (100 ml) was added to the acid ester **2a** (2 g, 7.57 mmol) and then the solution was boiled for 6 h. The solvent was removed and the residual dipotassium salt was dissolved in water (100 ml) and acidified with concentrated hydrochloric acid. The liberated diacid **3** was extracted with diethyl ether (2 × 50 ml), dried (MgSO<sub>4</sub>) and filtered and the diethyl ether was removed from the filtrate under reduced pressure to give the diacid **3**. The latter was dehydrated by boiling with acetyl chloride (50 ml)

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1997, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

for 3 h. The excess of acetyl chloride was removed under reduced pressure and the residue crystallised from ethanol to give the *anhydride* **4** as pale yellow cubes (0.9 g, 51%), mp 174–175 °C;  $\delta_{\text{H}}$  1.50–2.20, 3.43 (14 H, m, adamantylidene), 3.30 (2 H, s, CH<sub>2</sub>);  $\nu_{\text{max}}/\text{cm}^{-1}$  1806 (C=O), 1753 (C=O);  $m/z$  258 (14%, M<sup>+</sup>), 232 (73), 188 (68), 160 (100), 117 (48) (Found: C, 72.65; H, 6.97. C<sub>14</sub>H<sub>16</sub>O<sub>3</sub> requires C, 72.41; H, 6.90%).

*2,3-Di(2-adamantylidene)succinic Acid* **6**.—A mixture of adamantan-2-one (15 g, 0.1 mol) and dimethyl (2-adamantylidene) succinate (28 g, 0.1 mol) in toluene (100 ml) was added dropwise with stirring to a suspension of potassium *tert*-butoxide (100 ml) in toluene (50 ml) at room temperature. Stirring was continued for 12 h. Work-up as described for compound **1a** gave the acid ester **5** as a brown gum, which was hydrolysed as described for compound **3** to afford the *diacid* **6** which was recrystallised from ethanol–chloroform (1:1 v/v) as a colourless powder (7.5 g, 49%), mp 288 °C (Found: C, 75.26; H, 7.93. C<sub>24</sub>H<sub>30</sub>H<sub>4</sub> requires C, 75.39; H, 7.85%).

*2,3-Di(2-adamantylidene)succinate Anhydride* **7**.—A mixture of the *diacid* **6** (5 g, 13.1 mol) was boiled with acetyl chloride (20 ml) for 10 h. Work-up as described for compound **4** gave the crude

fulgide as white powder (3.8 g, 80%). Recrystallisation from toluene gave the *fulgide* **4** as white needles, mp 258–260 °C;  $\delta_{\text{H}}$  1.1–2.50, 4.20 (14 H, m, adamantylidene);  $\nu_{\text{max}}/\text{cm}^{-1}$  1809 (C=O), 1756 (C=O);  $m/z$  364 (100%, M<sup>+</sup>), 366 (14), 292 (21) (Found: C, 79.26; H, 7.83%. C<sub>24</sub>H<sub>28</sub>O<sub>3</sub> requires C, 79.12; H, 7.69%).

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