

**Chemistry of Succinylsuccinic Acid Derivatives; VI'.  
A Specific Synthesis of *p*-Phenylenediamine**

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Starting from aliphatic materials such as diketene or succinic esters, a route via dialkyl succinylsuccinate, to *p*-phe-

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Table. Compounds 1-9 prepared

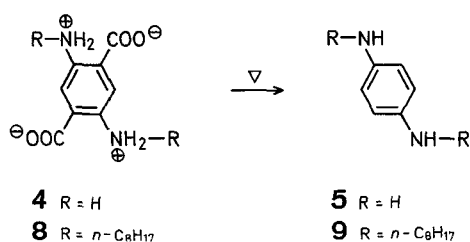
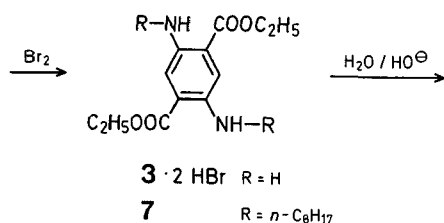
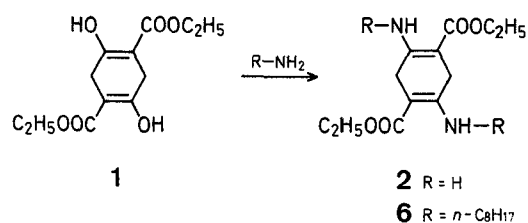
Prod- uct	Yield [%]	m.p. [°C]	Molecular formula <sup>a</sup> or Lit. m.p. [°C]	<sup>1</sup> H-N.M.R. (CDCl <sub>3</sub> /TMS) δ [ppm]								
				ethyl ester		<i>n</i> -octyl chain			ring		enol	NH or NH <sub>2</sub> <sup>δ</sup>
				CH <sub>3</sub>	CH <sub>2</sub>	CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>6</sub>	CH <sub>2</sub> -N	CH <sub>2</sub>	CH		
1		131-132° (C <sub>2</sub> H <sub>5</sub> OH)	128° <sup>12</sup>	1.30 (t)	4.25 (q)	—	—	—	3.15 (s)	—	12.10	—
2	96	184° (C <sub>2</sub> H <sub>5</sub> OH)	178° <sup>2</sup>	1.30 (t) <sup>b</sup>	4.17 (q)	—	—	—	3.12 (s)	—	—	6.15 (br s)
3	92	205-207° (dec) (ether washed)	C <sub>12</sub> H <sub>18</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>4</sub> (414.3)	1.30 (t)	4.30 (q)	—	—	—	—	7.70 (s)	—	8.43 (br s)
4 <sup>13,14</sup>	96	>300° (H <sub>2</sub> O washed)	C <sub>8</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub> (196.2)	—	—	—	—	—	—	7.30 (s)	—	8.22 (br s)
5	85	140°	140° <sup>15</sup>	—	—	—	—	—	—	6.53 (s)	—	3.24 (s)
6	88	72-73° (C <sub>2</sub> H <sub>5</sub> OH)	C <sub>28</sub> H <sub>50</sub> N <sub>2</sub> O <sub>4</sub> (478.7)	1.30 (t)	4.17 (q)	0.90 (t)	1.30 (m)	3.12 (t)	3.20 (s)	—	—	—
7	97	79-80° (C <sub>2</sub> H <sub>5</sub> OH)	C <sub>28</sub> H <sub>48</sub> N <sub>2</sub> O <sub>4</sub> (476.7)	1.40 (t)	4.37 (q)	0.90 (t)	1.30 (m)	3.18 (t)	—	7.30 (s)	—	6.50 (br s)
8	94	230° (dec) (H <sub>2</sub> O washed)	C <sub>24</sub> H <sub>40</sub> N <sub>2</sub> O <sub>4</sub> (420.6)	—	—	0.83 (t) <sup>b</sup>	1.29 (m)	3.10 (t)	—	7.23 (s)	—	9.50 (br s)
9	88	79°	76° <sup>10</sup>	—	—	0.87 (t)	1.30 (m)	3.03 (t)	—	6.51 (s)	—	3.10 (s)

<sup>a</sup> All products gave satisfactory microanalysis results (C ± 0.30, H ± 0.29, N ± 0.30, Br - 0.45).

<sup>b</sup> Spectrum measured in DMSO-*d*<sub>6</sub> solution.

nylenediamine is presented. Because of its specificity, this procedure requires no isomer separation.

Thus, by treating succinylsuccinic esters (**1**) with ammonia or primary amines, the corresponding 2,5-diamino-1,4-cyclohexadiene-1,4-dicarboxylates (**2** or **6**) are obtained<sup>2,3</sup>. Aromatisation of these enamines<sup>4,5</sup>, followed by hydrolysis and decarboxylation<sup>6</sup>, leads to the respective *p*-phenylenediamine (**5** or **9**) according to the following scheme.



In contrast to the 2,5-dialkylaminoterephthalates, internal cyclisation<sup>4,7</sup> during attempted decarboxylation appears feasible for the corresponding arylamino compounds<sup>8</sup>.

While appearing advantageous, despite its degradative character, for the preparation of *N,N'*-dialkyl-*p*-phenylenediamines<sup>9,10</sup>, this procedure requires improved access to the succinylsuccinates to become of industrial importance for the production of *p*-phenylenediamine<sup>11</sup>.

#### Diethyl 2,5-Diamino-1,4-cyclohexadiene-1,4-dicarboxylate (2):

Diethyl succinylsuccinate (**1**; 256 g, 1 mol) in ethanol (2.5 l) is charged into a glass-lined autoclave. The solution is pressurised with ammonia (37.4 g, 2.2 mol) and heated at 80 °C for 12 h to give **2**; yield: 244 g (96% based on **1**).

#### Diethyl 2,5-Diaminobenzene-1,4-dicarboxylate Dihydrobromide (3):

Into a solution of **2** (127 g, 0.5 mol) in chloroform (2.5 l), a solution of bromine (40 g, 0.5 mol) in chloroform (1 l) is added during 1 h. The solid product is filtered, washed with ether (3 × 100 ml), and dried to give **3**; yield: 190 g (92%).

#### 2,5-Diaminoterephthalic Acid (4):

Compound **3** (103.5 g, 0.25 mol) is boiled in 10% aqueous sodium hydroxide solution (400 ml) until complete dissolution. Neutralisation with aqueous hydrogen chloride precipitates a solid which is filtered, washed with methanol (3 × 50 ml) and dried under reduced pressure to give **4**; yield: 47.5 g (96%).

#### *p*-Phenylenediamine (5):

Following the procedure of Griess<sup>6</sup>, compound **4** (39.2 g, 0.2 mol) is sublimed under a slow stream of nitrogen at 270-330 °C to give **5**; yield: 18 g (85%).

#### Diethyl 2,5-Bis[octylamino]-1,4-cyclohexadiene-1,4-dicarboxylate (6):

To *n*-octylamine (284.4 g, 2.2 mol) at 80 °C, in an inert atmosphere, **1** (256 g, 1 mol) is introduced portionwise and allowed to react for 2 h. The reaction mixture is then taken up in petroleum ether (2000 ml) and dried with sodium sulphate. Upon cooling to -15 °C, a precipitate forms, which is collected and vacuum dried at 50 °C, to give **6**; yield: 420 g (88% based on **1**).

**Diethyl 2,5-Bis[octylamino]benzene-1,4-dicarboxylate (7):**

To a solution of **6** (358.5 g, 0.75 mol) in chloroform (1.5 l), bromine (120 g, 0.75 mol) is added during 15 min and the mixture is allowed to react for 40 min. After cooling, the residual hydrogen bromide is removed by successive washings with 10% aqueous sodium hydroxide (600 ml) and water (600 ml). The neutral solution is dried with sodium sulphate and evaporated under reduced pressure to give **7**; yield: 345 g (97%).

**2,5-Bis[octylamino]terephthalic Acid (8):**

In a solution of ethanol (250 ml) and aqueous sodium hydroxide (10%, 500 ml), **7** (238 g, 0.5 mol) is heated under reflux for 2 h. The solution is cooled to room temperature, neutralised with hydrochloric acid, the resulting precipitate is washed with water, and dried in vacuo at 100 °C to give **8**; yield: 196.7 g (94%).

Alternatively, *n*-octylamine (54.3 g, 0.42 mol) is heated to 80 °C in an inert atmosphere, **1** (51.2 g, 0.2 mol) is added, the slightly exothermic reaction is continued for 1.5 h at 90 °C, and then the temperature is raised for 0.5 h to 140 °C. The reaction mixture is cooled to 40–45 °C and chloroform (100 ml) is introduced, followed by bromine (32 g, 0.2 mol). After heating under reflux for 1 h, volatile materials are stripped off using a water pump at 60–70 °C. Ethanol (320 ml) and aqueous sodium hydroxide (10%, 400 ml) are added and heating under reflux is continued until complete dissolution. A water-ethanol azeotrope is distilled off to remove the ethanol and the volume is kept constant by addition of water. The solution is neutralised with hydrochloric acid, the resulting precipitate is collected, washed with water, and dried in vacuo at 100–110 °C to give **8**; yield: 80 g (95% based on **1**).

***N,N'*-Dioctyl-*p*-phenylenediamine (9):**

Compound **8** (105 g, 0.25 mol) is distilled under reduced pressure at a bath temperature of 230–240 °C. A main fraction of **9** is collected at 221–223 °C/0.225 torr; yield: 73.25 g (88%).

Alternatively, compound **8** (21 g, 0.05 mol) is heated under a slow argon stream for 0.5 h at 240 °C, to give crude **9**; yield: 16.58 g (100% based on **8**). Recrystallisation from ethanol (180 ml) gives pure **9**; yield: 11.15 g (67%).

*Dedicated to Professor H. Batzer in honour of his 60th birthday.*

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