

## SIMPLE PREPARATION OF A HELICAL QUINONE

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**SUMMARY:** *p*-Divinylbenzene and *p*-benzoquinone combine to give a [5]-helicene-bis-quinone. This procedure uses no light and gives a helicene with an interesting functional group. It is notably simple. An enzymatic hydrolysis is used to obtain the quinone optically active.

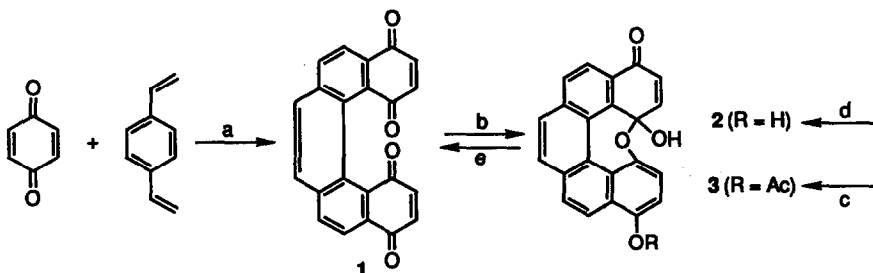
Helicenes are scarce in amount, although not in variety,<sup>1</sup> probably because the key reaction used to prepare them, the photocyclization of stilbenes,<sup>1,2</sup> is constrained (to prevent photodimerizations<sup>3</sup>) to solutions that are very dilute. Because of their scarcity, and because only few have been made with functional groups,<sup>4</sup> helicenes have rarely been used as precursors for other materials<sup>1,9b,10</sup> or as reagents.<sup>6c,9c,11</sup> This is unfortunate, for the helical conjugated structure endows the molecules with exceptional electronic properties, shown by enormous optical activity,<sup>1,10</sup> and with the ability to induce high asymmetry in chemical transformations.<sup>6c,9c,11</sup> Thus procedures that make helicenes without using light,<sup>12</sup> and that make helicenes with useful functionality could be of great benefit.

Quinones are studied here because, by reacting with either electron donors,<sup>13,14</sup> or dienes,<sup>15</sup> many give materials with mobile electrons that are unusually delocalized.

Reported in this paper is a simple way to make an interestingly functionalized helicene, the bis-quinone **1**, in one step from inexpensive precursors, and to obtain it optically active. When 6.8 g of 1,4-divinylbenzene<sup>16</sup> in 250 mL of toluene is refluxed with 12 eq. of benzoquinone and a crystal each of trichloroacetic acid<sup>17</sup> and 4-*t*-butylcatechol, it gives (see the Scheme), after separation from black insoluble material and chromatography through neutral alumina (pet. ether-CH<sub>2</sub>Cl<sub>2</sub>), 2.93 g (a 17% yield) of the helical quinone **1**, an orange solid, mp 200 °C.<sup>18</sup> The yield is not high, but few syntheses use procedures this simple or reagents so available.

Sodium dithionite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) in H<sub>2</sub>O-CH<sub>2</sub>Cl<sub>2</sub> (1:1) containing 1 mole K<sub>2</sub>CO<sub>3</sub> gives hemiketal **2**,<sup>18</sup> a yellow-orange solid that does not melt below 260 °C, whose structure is shown by its complex <sup>13</sup>CNMR spectrum. In acetone there are 22 lines, including one at δ92.17 ppm, characteristic of quinone monoketals.<sup>19</sup> The monoacetate of this hemiketal,<sup>18</sup> a yellow solid formed using acetic

## Scheme



Reagents and yields: a) PhMe, cat.  $\text{CCl}_3\text{CO}_2\text{H}$ , reflux, 33 hr, 17% yield; b) aq.  $\text{Na}_2\text{S}_2\text{O}_4$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{N}_2$ , 30 min., 94% yield; c) pyridine,  $\text{Ac}_2\text{O}$ , 18hr, 98% yield; d) bovine pancreas, sodium taurocholate, 1:1 ether- $\text{H}_2\text{O}$ , pH 7.0, 85% yield; e)  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ , 3:1  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ , 6.5hr, 100% yield.

anhydride in pyridine at room temperature, when hydrolyzed with the aid of "bovine pancreas acetone powder" (from Sigma Chemical Co.)<sup>20,21</sup> generates the hemiketal optically active (a 33% yield was isolated at 40% conversion), and it gives the optically active acetate as well (in 52% yield). Ceric ammonium nitrate in 3:1 acetonitrile-water oxidizes this optically active hemiketal to the stereoisomer of 1 that is dextrorotatory at the D-line of sodium and 3 to 1's mirror image. The enantiomeric excesses were measured as 62% and 76% respectively.<sup>22</sup>

The kinetics of the rate at which optically active quinone 1 in *o*-dichlorobenzene racemizes is first order, with  $\Delta H^\ddagger = 116.2 \pm 0.4 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -16.4 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$ . The half-life at 133 °C is 8.9 minutes and at 25 °C should be 6 years. In contrast, for the parent [5]helicene the corresponding half-life, at 25 °C, is 15h ( $\Delta H^\ddagger = 95.8 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -17.2 \text{ J mol}^{-1} \text{ K}^{-1}$ ).<sup>23</sup>

The Diels-Alder reaction has previously been effected between styrenes (among them 1,5-divinylnaphthalenes<sup>24</sup>) and various dienophiles,<sup>25</sup> including quinones,<sup>17,24,26</sup> and between *p*-divinylbenzene and derivatives of maleic anhydride.<sup>27</sup> However, it has not been carried out with quinones and divinylbenzenes, nor has it been used to make helicenes. The combination of divinylaromatics and quinones should give a number of interesting ring systems.

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