CHEMISTRY LETTERS, pp. 1303-1306, 1982.

SYNTHESIS OF METHYL 1,5- AND 1,7-AZULENEQUINONE-3-CARBOXYLATES

Tadayoshi MORITA, Fumiaki ISE, and Kahei TAKASE Department of Chemistry, Faculty of Science, Tohoku University Aoba, Aramaki, Sendai 980

Methyl 1,5- and 1,7-azulenequinone-3-carboxylates were synthesized by oxidation of methyl 3-acetoxy-7-methoxy- and 3-acetoxy-5-methoxyazulene-1-carboxylates with ceric ammonium nitrate, respectively.

Although the chemistry of quinone<sup>1)</sup> and azulenes<sup>2)</sup> has a long and colorful history and several reports of highly annelated azulenequinones have appeared,<sup>3)</sup> no simple azulenequinone, one of the non-benzenoid quinones, had been known until we reported the synthesis of 1,2-azulenequinones (1).<sup>4)</sup> Non-annelated 2,6-azulene-quinone derivatives<sup>5)</sup> have been synthesized but isolated only in a form of dimer. Recently, a theoretical prognosis of azulenequinones has been reported.<sup>6)</sup> We now report the synthesis of 1,5- (<u>2b</u>) and 1,7-azulenequinone derivatives (<u>3b</u>) as the first example of simple extended azulenequinones.



A 5-chloroazulene derivative  $(\underline{4})$  was synthesized by application of the azulene synthesis reaction<sup>7)</sup> of troponoid with an active methylene compound in the presence of base. The reaction of 5-chloro-2-tosyloxytropone<sup>8)</sup> with methyl cyanoacetate in the presence of MeONa in anhydrous MeOH led to  $\underline{4}$  [orange, mp 176-177.5 °C] in 80% yield. Smooth deamination of  $\underline{4}$  to dimethyl 5-chloroazulene-1,3-dicarboxylate ( $\underline{5}$ ) [red, mp 185.5-186 °C] was achieved in 90% yield by diazotization with isopentyl nitrite and sulfuric acid in the presence of hydroquinone.<sup>7a,9</sup>) Methoxylation of 5 succeeded by a modification of the reaction of 6-haloazulenes<sup>10</sup>) with nucleophilic reagents. Heating of 5 with NaOMe-MeOH in anhydrous benzene gave a 5-methoxyazulene derivative (6) [red, mp 195-197 °C] in 90% yield. Half demethoxycarbonylation<sup>11a)</sup> of the diester 6 with 100% phosphoric acid<sup>7,11)</sup> (90 °C, 10 m) nicely gave a mixture (1:1) of the monoesters, methyl 5- (7) [green, mp 66.5-67 °C] and 7-methoxyazulene-1-carboxylates (8) [green, mp 65.5-66 °C] in 70% yield which could be separated by a column chromatography (silica gel, benzene). To date only benzoyloxylation<sup>3,9b,12)</sup> of azulenes with benzoyl peroxide has been known as a method for direct acyloxylation of azulenes, but, sometimes, the yield was low. Therefore, lead tetraacetate (LTA) was employed herein as an acetoxylation reagent. Treatment of 8 with 3 eq. of LTA in PhH-pyridine-DMSO afforded methyl 3-acetoxy-7-methoxyazulene-1-carboxylate (9) [green, mp 129-130 °C] in 75% yield. In a like fashion, acetoxylation of 7 led to methyl 3-acetoxy-5-methoxyazulene-1-carboxylate (10) [green, mp 133-134 °C] in 60% yield.



Structural assignment of all the intermediates and detail of the reaction sequence will be discussed elsewhere. Finally, direct oxidation of dihydroxyazulene derivatives 9 and 10 with ceric ammonium nitrate<sup>13)</sup> gave methyl 1,5- (2b) [yellow needles, mp 141-142 °C (dec)] and 1,7-azulenequinone-3-carboxylates (3b) [yellow needles, mp 137-138 °C (dec)], in 71 and 73% yields, respectively. The individual structural assignment rests on the spectral data (IR, UV, MS, and NMR) and the following chemical evidence. Reductive acetylation of 2b and 3b with Zn-AcOH-Ac<sub>2</sub>O afforded methyl 3,7- (<u>11</u>) [green, mp 126-128 °C] and 3,5-diacetoxyazulene-1-carboxylates (<u>12</u>) [green, mp 136-137 °C] in 25 and 40% yields, respectively. The mass spectra of <u>2b</u> and <u>3b</u> show the corresponding molecular ion peak at m/e 216.<sup>14)</sup> The IR spectra of these quinones show three main bands in the carbonyl region [<u>2b</u> (KBr): 1725sh, 1711, 1648, and 1590 cm<sup>-1</sup>; <u>3b</u> (KBr): 1724sh, 1711, 1641, and 1590 cm<sup>-1</sup>] due to the characteristic absorption of tropone<sup>15)</sup> and the unsaturated 5-membered cyclic ketone with methoxycarbonyl group. The electronic spectra (Fig. 1) of quinones (<u>2b</u> and <u>3b</u>) have three absorption bands in the region of 220

compound	Н-2	H-4	rin H-5	g proto H-6	ns <sup>a)</sup> H-7	H-8	H-8 CO <sub>2</sub> CH <sub>3</sub> O		COCH <sub>3</sub>	
<u>2b</u>	7.09	7.81		7.03	7.19	7.43	3.9	8		
<u>3b</u>	7.02	7.83	7.20	6.95		7.35	3.9	9		
<u>11</u>	8.24	9.41		7.53	7.27	8.29	3.9	2 2.	38 and	2.43
12	8.32	9.58	7.51	7.46		8.10	3.9	3 2.	38 and	2.42
a) The numbering of <u>11</u> and <u>12</u> corresponds to those of <u>2b</u> and <u>3b</u> , respectively. Table 2. ${}^{13}$ C-NMR Data <sup>16)</sup> of <u>2b</u> and <u>3b</u> (at 50.3 MHz, in CDCl <sub>3</sub> , chemical shift in $\delta$ ppm from TMS)										
compound	c <sub>1</sub>	°2	с <sub>3</sub>	C4	с <sub>5</sub>	C <sub>6</sub>	с <sub>7</sub>	c <sub>8</sub>	C <sub>3a</sub>	C <sub>8a</sub>
<u>2b</u>	192.2	138.2	152.2	134.7	187.2	144.6	134.1	130.1	142.2	136.1
<u>3b</u>	193.6	135.5	152.7	128.6	135.9	140.8	187.6	135.0	140.5	136.6
Table 3. Ha 	lf-wave , <u>3b</u> , an <sup>E</sup> 1	Potenti id <u>lb</u> (V	als of vs SCP	5)	4.0 log <b>ε</b>	Y.				- <u>2b</u> - <u>3b</u>

Table 1	•	<sup>1</sup> H-NMR	Data	of	<u>2b</u> ,	<u>3b</u> ,	<u>11</u> ,	and	<u>12</u>	(at	200	MHz,
		in CDCl <sub>2</sub> ,		chemical		shift in		n opp	om :	from	TMS)	

a) Ref. 4).

2b

 $\frac{3b}{1b^a}$ 

-0.54

-0.50

-0.40

-1.00



300

Fig. 1.

400

UV spectra of 2b and 3b.

500

 $\lambda/nm$ 

In the <sup>1</sup>H-NMR spectra (Table 1) of <u>2b</u> and <u>3b</u>, the ring protons appear upper field than those of the corresponding dihydroxyazulene derivatives (<u>11</u> and <u>12</u>) and the chemical shifts of H-6 and H-7 of <u>2b</u> (H-6 and H-5 for <u>3b</u>) are similar to those of H-2 ( $\delta$  6.93) and H-3 ( $\delta$  7.31) of tropone.<sup>17</sup>) In the <sup>13</sup>C-NMR data (Table 2), the order of the average shifts<sup>18</sup>) (149.1 for <u>2b</u>; 148.6 for <u>3b</u>) of the ring carbons agree with those of the polarographic half-wave potentials<sup>19</sup>) (Table 3) which were determined in an anhydrous MeCN (at 25 °C, dropping-mercury electrode to SCE, supporting electrolyte 0.1 M NEt<sub>4</sub>ClO<sub>4</sub>). These potentials (E<sub>1</sub>) parallel with the decreasing order of the LUMO energies<sup>6</sup> of the corresponding parent azulenequinones (-0.63, -0.66, and -0.70 eV for <u>2a</u>, <u>3a</u>, and <u>1a</u>, respectively). REFERENCES

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- 19) We thank Dr. Y. Kato of Tohoku Univ. for the measurement of polarographic data.