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## A New Synthesis of 9-Vinyl- and 9-Isopropenylanthracene Derivatives

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Recently the polymerization of 9-vinyl- and 9-isopropenylanthracenes has attracted attention<sup>1</sup> 8. However, the synthesis of the starting monomers presents some difficulties. New syntheses of the 9-alkenylanthracenes 1a-e are now described.

Compound 1a was previously prepared by (a) Wittig reaction of 9-formylanthracene<sup>6,14</sup>, a rapid method which gives good yields or (b) by reaction of 9-formylanthracene with methylmagnesium iodide and hydrolysis to give 9-(1-hydroxyethyl)-anthracene and subsequent dehydration of the latter with potassium hydrogen sulfate<sup>9</sup> to give 1a in poor yield. Compound 1b cannot be prepared from 9-acetylanthracene by these methods<sup>6,9</sup>. We have previously described the synthesis of 1b from 9-bromoanthracene by a tedious process<sup>10</sup>.

The present method involves the reaction of a vinyl Grignard reagent 3 with anthrone, 9-methylanthrone, or 1,4-dimethylanthrone (2;  $R^2 = H$  or  $CH_3$ ,  $R^3 = H$  or  $CH_3$ ) in analogy to the preparation of 9-alkyl- (but not -vinyl- or -isopropenyl)-anthracenes from anthrone<sup>11,12,13</sup>.

Two experimental procedures are employed:

Method A: Vinylmagnesium bromide (3;  $R^1 = H$ ) is reacted with anthrone (2;  $R^2$ ,  $R^3 = H$ ) and the resultant alcohol 4a (80% yield) is dehydrated to give 1a in quantitative yield. Alcohol 4e is ob-

320 Communications SYNTHESIS

Table. Anthracene Derivatives 1a-e and Alcohols 4a and 4e prepared

Prod- uct	Method	Yield [%]	m.p. [°C]		Molecular formula <sup>a</sup>	'H-N.M.R. (CDCl <sub>3</sub> /TMS) <sup>b</sup> δ [ppm]
			found	reported	Minuta	<i>ս</i> լիկույ
4a	A	80	78°	_	C <sub>16</sub> H <sub>14</sub> O (222.3)	2.65 (s, 1 H, OH); 3.80 (s, 2 H, H-10); 4.6 [m, 1 H, H(a)]; 4.8 [m, 1 H, H(b)]; 5.9 [m, 1 H, H(x)]; 7.5 (m, 8 H <sub>arom</sub> ); $J_{H(a), H(b)} = 2$ Hz; $J_{H(a), H(x)} = 17$ Hz; $J_{H(b), H(x)} = 10$ Hz
1a	A B	100 75	64°	64-65°1; 65°6		5.52 [q, 1 H, H(a)]; 5.85 [q, 1 H, H(b)]; 7.1-8.4 [m, 9 H <sub>arom</sub> + H(x)]; $J_{H(a),H(b)} = 2$ Hz; $J_{H(a),H(b)} = 17$ Hz, $J_{H(b),H(b)} = 12$ Hz
1b	В	70	79°	79°8	$C_{17}H_{14}$ (218.3)	2.20 (m, 3 H, CH <sub>3</sub> ); 5.1 [m, 1 H, H(a)]; 5.7 [m, 1 H, H(b)]; 7.2–8.3 (m, 9 H <sub>arom</sub> )
1c	В	75	75°	***************************************	C <sub>18</sub> H <sub>16</sub> (232.3)	2.70 (s, 3 H, H <sub>3</sub> C—C-4); 2.80 (s, 3 H, H <sub>3</sub> C—C-1); 5.20 [q, 1 H, H(a)]; 5.80 [q, 1 H, H(b)]; 7.4–8.3 [m, $7 H_{arom} + H(x)$ ]; $J_{H(a), H(b)} = 2 Hz$ ; $J_{H(a), H(x)} = 17 Hz$ ; $J_{H(b), H(x)} = 12 Hz$
1d	В	15	96°	· Parision	C <sub>19</sub> H <sub>18</sub> (246.4)	2.60 (d, 3 H, H <sub>3</sub> C—C-15); 2.75 (s, 3 H, H <sub>3</sub> C—C-4); 2.90 (s, 3 H, H <sub>3</sub> C—C-1); 5.15 [m, 1 H, H(a)]; 5.7 [m, 1 H, H(b)]; 7.15 (s, 2 H, H-2, H-3); 7.45 (q, 2 H, H-6, H-7); 8.0 (m, 1 H, H-5); 8.25 (m, 1 H, H-8); 8.60 (s, 1 H, H-10)
4e <sup>c</sup>	Α	45 <sup>d</sup>		Marror	-	1.35, 1.70 (2 d, 3 H, CH <sub>3</sub> ); 2.20, 2.40 (s, 1 H, OH); 4.00, 4.05 (2 q, 1 H, H-10); 5.0 [m, 2 H, H(a), H(b)]; 6.0 [m, 1 H, H(x)]; 7.2-8.0 (m, 8 H <sub>arom</sub> ); $J_{H(a),H(b)} = 2$ Hz; $J_{H(a),H(b)} = 17$ Hz; $J_{H(b),H(b)} = 10$ Hz
1e	A	100	113°	112°6	C <sub>17</sub> H <sub>14</sub> (218.3)	2.80 (s, 3 H, CH <sub>3</sub> ); 5.35 [q, 1 H, H(a)]; 5.75 [q, 1 H, H(b)]; 7.0-8.2 [m, 8 H <sub>arom</sub> + H(x)]; $J_{\text{H(a),H(b)}} = 2 \text{ Hz}$ ; $J_{\text{H(a),H(x)}} = 18 \text{ Hz}$ ; $J_{\text{H(b),H(x)}} = 11 \text{ Hz}$

Satisfactory microanalyses obtained: C  $\pm 0.27$ , H  $\pm 0.09$ .

Two isomers detected by 'H-N.M.R. spectrometry but they have not been separated. Yield estimated by 'H-N.M.R. spectrometry.

tained similarly in 45% yield. The yield seems to decrease with increasing steric hindrance, thus 1b, c, and d could not be prepared by this method.

Method B: in order to obtain 1b, c, and d in spite of the steric hindrance, the reaction is carried out at a higher temperature. Thus, after addition of ketone 1 to a solution of the Grignard reagent 2, toluene is added and the solvent removed by distillation until the boiling temperature rises to 85-90 °C. The alcohol 4 is not obtained in this method, probably because it undergoes immediate aromatization with resultant reduction in the steric hindrance under these conditions.

It should be noted that during preparation of 1a by method A using stoichiometric amounts of 2 and 3 (R<sup>1</sup> = H), 9-anthrylanthrone (7) is obtained as a by-product by the mechanism shown helow.

9-Vinylanthracene (1a); Typical Procedure for Method A:

Anthrone (2; 9.7 g, 0.05 mol) is slowly added to a solution of vinylmagnesium bromide [3; R1; prepared from magnesium (2.4 g, 0.1 mol) and bromoethene (10.7 g, 0.1 mol) in tetrahydrofuran (200 ml)]. The mixture is heated under reflux for 2 h and then hydrolyzed by addition of saturated ammonium chloride solution (250 ml). Ether (250 ml) is then added, the ether layer is separated, dried with anhydrous magnesium sulfate, and the solvent distilled. The alcohol 4a is crystallized from methanol; yield: 8.1 g (80%); m.p. 78°C.

The alcohol 4a is heated under reflux in absolute ethanol (100 ml) for 2 h, the solvent is distilled, and the residue (4.5 g) is purified by column chromatography on neutral aluminum, eluting with benzene; to give pure 9-vinylanthracene (1a); yield: 4.1 g (100%); m.p. 64 °C (Lit. 1, m.p. 64-65 °C, Lit.6 m.p. 65 °C).

$$\begin{array}{cccc} C_{16}H_{12} & calc. & C \ 94.08 & H \ 5.92 \\ (204.3) & found & 94.10 & 5.91 \end{array}$$

When anthrone is added in equimolar amount (0.1 mol), 9-anthrylanthrone (7) is also obtained; yield: 3.5 g; m.p.  $> 250 \,^{\circ}\text{C}$ .

<sup>1</sup>H-N.M.R. (CDCl<sub>3</sub>):  $\delta = 4.60$  (s, 1 H); 7.4 ppm (m, 17 H).

## 9-Isopropenylanthracene (1b); Typical Procedure for Method B:

Anthrone (9.7 g, 0.05 mol) is added to a solution of 2-propenylmagnesium bromide prepared from magnesium (2.4 g, 0.1 mol) and 2-propenyl bromide (12.1 g, 0.1 mol) in tetrahydrofuran (200 ml). Toluene (150 ml) is then added and tetrahydrofuran is distilled until the boiling temperature reaches 85-90 °C. The mixture is heated under reflux for 2 h and then hydrolyzed by addition of saturated ammonium chloride solution (250 ml). Ether (250 ml) is added, the ether layer is separated, dried with anhydrous magnesium sulfate, and the solvent evaporated. The residue is crystallized from ethanol (it can also be purified by column chromatography or neutral alumina, eluting with benzene); yield: 7.5 g (70%); m.p. 79 °C (Lit.8, m.p. 79 °C).

$C_{17}H_{14}$	calc.	C 93.54	H 6.46
(218.3)	found	93.81	6.39

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Numbering of protons:

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