

On repeating the experiment described for the Fries rearrangement of catechol dipropionate, we were able to isolate a lower boiling fraction (at approximately the same temperature described in reference 4) and which possessed the same melting point (104–105°) as described by these authors. This product proved to be catechol by melting point and mixture melting point determinations. It is to be noticed that no analytical figures are given for this compound.<sup>4</sup>

#### EXPERIMENTAL<sup>5</sup>

*Preparation of 2,3-dihydroxypropiofenone* (IV, R = C<sub>2</sub>H<sub>5</sub>). (a) *Action of ethylmagnesium iodide on 2,3-dimethoxybenzaldehyde*. A solution of the aldehyde (I) (5 g.) in anhydrous ether was added dropwise to the ethylmagnesium iodide (from 6.5 g. ethyl iodide and 0.9 g. magnesium) while cooling in ice. When the addition was complete the reaction mixture was refluxed for 1 hr. and left to stand, at room temperature, overnight. After decomposition with dilute acetic acid and ice, the ethereal layer was shaken with sodium bisulfite solution and then with water. It was then dried (Na<sub>2</sub>SO<sub>4</sub>), the ether driven off, and the remaining oil distilled to give II (R = C<sub>2</sub>H<sub>5</sub>) as a colorless liquid, b.p. 108–110°/2 mm., yield 3.9 g.

(b) *Preparation of 2,3-dimethoxypropiofenone*. The previously described carbinol (3.5 g.) was added to a mixture of potassium dichromate (7 g.), water (35 ml.), and concentrated sulfuric acid (3.2 g.). The reaction mixture was immediately steam-distilled, and the distillate was extracted with ether, dried (Na<sub>2</sub>SO<sub>4</sub>), and then the ether was driven off. III (R = C<sub>2</sub>H<sub>5</sub>) was obtained as a colorless oil b.p. 114°/2 mm. yield 2.48 g.

The 2,4-dinitrophenylhydrazone derivative was crystallized from ethyl acetate in reddish brown crystals m.p. 219°.

*Anal.* Calcd. for C<sub>17</sub>H<sub>15</sub>O<sub>6</sub>N<sub>4</sub>: N, 14.97. Found: N, 15.20.

The semicarbazone was crystallized from methyl alcohol in colorless crystals m.p. 188°.

*Anal.* Calcd. for C<sub>12</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub>: C, 57.35; H, 6.8; N, 16.7. Found: C, 57.39; H, 6.8; N, 16.56.

(c) *Demethylation of 2,3-dimethoxypropiofenone* (III, R = C<sub>2</sub>H<sub>5</sub>). The previously described ketone (III, R = C<sub>2</sub>H<sub>5</sub>) (2.8 g.) was refluxed with hydriodic acid (sp. gr. 1.96) (11 g.) and an equal volume of glacial acetic acid for 6 hr. The reaction mixture was then poured onto ice and left overnight. The precipitated product was filtered off, dissolved in benzene, and the dark solution treated with charcoal. To the filtrate after concentration, a few drops of petroleum ether (40–60°) were added, whereby 2,3-dihydroxypropiofenone separated out. It was recrystallized from petroleum ether (40–60°) in pale yellow crystals, m.p. 53°, yield 41%. It gave a green color with alcoholic ferric chloride solution which changed to red on the addition of sodium carbonate solution.

*Anal.* Calcd. for C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>: C, 65.1; H, 6.1. Found: C, 65.7; H, 6.2.

The 2,4-dinitrophenylhydrazone derivative was crystallized from ethyl acetate m.p. 229°.

*Anal.* Calcd. for C<sub>15</sub>H<sub>14</sub>O<sub>6</sub>N<sub>4</sub>: N, 16.2. Found: N, 15.7.

*Preparation of 2,3-dihydroxybutyrophenone* (IV, R = n-C<sub>2</sub>H<sub>5</sub>). (i) *Action of propylmagnesium iodide on 2,3-dimethoxybenzaldehyde*. A solution of the aldehyde (I) (5 g.) in anhydrous ether was added dropwise to propylmagnesium iodide (from 6.2 g. propyl iodide and 0.9 g. magnesium) while cooling in ice. The reaction mixture was treated as in (a) and the carbinol (II, R = n-C<sub>2</sub>H<sub>5</sub>) was obtained as a colorless liquid, yield 3.5 g.

(5) Microanalyses were carried out by Alfred Bernhardt, Germany. Melting points are not corrected.

Its phenylurethane derivative was crystallized from petroleum ether (60–80°) m.p. 130°.

*Anal.* Calcd. for C<sub>15</sub>H<sub>22</sub>O<sub>4</sub>N: C, 69.3; H, 7.0; N, 4.25. Found: C, 69.4; H, 7.2; N, 4.4.

(ii) *Preparation of 2,3-dimethoxybutyrophenone* (III, R = n-C<sub>2</sub>H<sub>5</sub>). The above carbinol (II, R = n-C<sub>2</sub>H<sub>5</sub>) (3.5 g.) was oxidized as previously described in (b). It was obtained as a colorless liquid, b.p. 112–113°/0.6 mm., yield 2.5 g.

The semicarbazone was crystallized from ethyl alcohol in colorless crystals m.p. 153.5°.

*Anal.* Calcd. for C<sub>13</sub>H<sub>19</sub>N<sub>3</sub>O<sub>3</sub>: N, 15.84; Found: N, 15.99.

(iii) *Demethylation of 2,3-dimethoxybutyrophenone*. This ketone (2.1 g.) was similarly treated as in (c) to give 2,3-dihydroxybutyrophenone (IV, R = n-C<sub>2</sub>H<sub>5</sub>) in pale yellow crystals, "from petroleum ether (60–80°)" m.p. 61°, yield, 0.7 g. It gave a bluish green color with alcoholic ferric chloride solution which turned reddish brown on adding sodium carbonate solution.

*Anal.* Calcd. for C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>: C, 66.65; H, 6.7. Found: C, 66.5; H, 6.8.

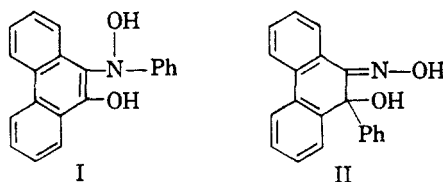
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### A Note on the Mode of Addition of Phenyllithium to Phenanthrenequinone Monoxime

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Mustafa *et al.*<sup>1</sup> claimed that phenanthrenequinone monoxime reacts with phenyllithium by 1,4-addition to give 10-phenylhydroxylamino-9-hydroxyphenanthrene (I).



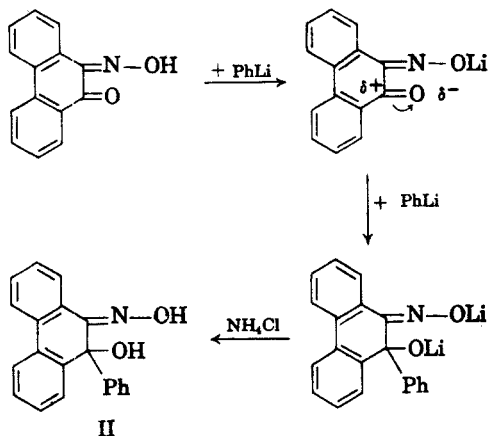
The main line of evidence upon which these authors assigned the above structure is that they obtained the same compound (I) by the action of phenylmagnesium bromide on the same oxime,<sup>2</sup> and they verified the identity of the two products by a mixture melting point experiment.

We have proved<sup>3</sup> that the mode of addition of phenylmagnesium bromide to phenanthrenequinone monoxime is 1,2-addition, thus producing 9-phenyl-9,10-dihydro-10-oximino-9-hydroxyphenanthrene (II). We have now found that when phenyllithium is allowed to react with phenanthrenequinone monoxime, under the same conditions

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(3) W. I. Awad and A. R. A. Raouf, *J. Org. Chem.*, **23**, 282 (1958).

described by Mustafa *et al.*<sup>1</sup> the same product 9-phenyl-9,10-dihydro-10-oximino-9-hydroxyphenanthrene (II), is obtained according to the following scheme:



The identity of the phenyllithium product and the phenylmagnesium bromide product is again verified by melting point and mixture melting point experiment, as well as by ultraviolet spectrum,  $\lambda_{\max}$  (m $\mu$ ) 254,  $\epsilon_{\max}$  23990,  $\lambda_{\max}$  (m $\mu$ ) 288,  $\epsilon_{\max}$  8535,  $\lambda_{\max}$  (m $\mu$ ) 324,  $\epsilon_{\max}$  1619.

In addition, it is noticed that the addition of organolithium compounds to the  $\alpha,\beta$ -unsaturated ketones is a 1,2-addition even in cases where the organomagnesium compounds add by 1,4-addition.<sup>4-7</sup>

#### EXPERIMENTAL

**Reaction of phenanthrenequinone monoxime with phenyllithium.** A solution of phenanthrenequinone monoxime (1 g.) in dry benzene (40 ml.) was treated with phenyllithium (from 16 g. bromobenzene and 1.5 g. lithium). The reaction mixture was kept overnight at room temperature in a nitrogen atmosphere and under reduced pressure. The substance dissolved completely and the color of the solution changed from orange to reddish brown. The reaction mixture was poured slowly into 100 ml. of saturated aqueous ammonium chloride solution, and shaken thoroughly. The ether-benzene layer was separated, dried over anhydrous sodium sulfate, filtered, and evaporated. The solid residue upon crystallization from benzene gave 9-phenyl-9,10-dihydro-10-oximino-9-hydroxyphenanthrene, II, as colorless needles, m.p. 162° undepressed on admixture with a sample of the product from the interaction between phenanthrenequinone monoxime and phenylmagnesium bromide, yield 50%. It gave a blue color with concentrated sulfuric acid and the color then turned to purple.

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## Preparation and Properties of Some Fluorohaloethyl Alkyl Ethers<sup>1</sup>

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In this study the following olefins were studied under base-catalyzed conditions:  $\text{CF}_2=\text{CHBr}$ ,  $\text{CF}_2=\text{CFI}$ ,  $\text{CF}_2=\text{CFBr}$ ,  $\text{CF}_2=\text{CH}_2$  and  $\text{CF}_2=\text{CHI}$ . This and other previously reported works<sup>2</sup> bring to completion the work on the ethers of the type  $\text{R}-\text{O}-\text{CF}_2-\text{CXYH}$  where X and/or Y is H, F, Cl, Br or I. It was found that  $\text{CF}_2=\text{CH}_2$  did not react with methanol even under autogenous pressure, while  $\text{CF}_2=\text{CHI}$  (in the form of  $\text{CF}_2\text{Cl}-\text{CH}_2\text{I}$ ) reacted quite readily with methanol but the ether,  $\text{CH}_3-\text{O}-\text{CF}_2\text{CH}_2\text{I}$  could not be isolated. Instead, only  $\text{CF}_2\text{ICOOCH}_3$  was found. In contrast to this,  $\text{C}_2\text{H}_5-\text{O}-\text{CF}_2\text{CH}_2\text{I}$ <sup>3</sup> was isolated when  $\text{CF}_2=\text{CHI}$  was treated with ethanol. In the hydrolysis of  $\text{CH}_3-\text{O}-\text{CF}_2-\text{CHF}_2\text{I}$  we failed to obtain  $\text{CH}_3\text{OCO}-\text{CHF}_2\text{I}$ . Each time the hydrolysis was attempted, the only product isolated was the free acid  $\text{CHF}_2\text{COOH}$ . Here again, Seffl<sup>4</sup> reported no difficulty in hydrolyzing  $\text{C}_2\text{H}_5-\text{O}-\text{CF}_2\text{CHF}_2\text{I}$  to  $\text{C}_2\text{H}_5\text{OCO}-\text{CHF}_2\text{I}$  and isolating the ester.

In the present work, no difficulty was experienced in preparing  $\text{C}_2\text{H}_5-\text{O}-\text{CF}_2\text{CH}_2\text{Br}$  even after this ether had been in contact with water for moderate periods of time during its isolation and purification. In contrast to this stability,  $\text{C}_2\text{H}_5\text{O}-\text{CF}_2\text{CH}_2\text{Cl}$  as shown by others<sup>2(d), 5</sup>, undergoes hydrolysis to  $\text{C}_2\text{H}_5\text{OCOCH}_2\text{Cl}$  quite readily when allowed to remain in contact with water even for short periods of time. We are unable to reconcile the differences in hydrolytic stability of the two ethers,  $\text{C}_2\text{H}_5\text{OCF}_2\text{CH}_2\text{Cl}$  and  $\text{C}_2\text{H}_5\text{OCF}_2\text{CH}_2\text{Br}$ .

#### EXPERIMENTAL

The hydrolysis of the ethers,  $\text{RO}-\text{CF}_2\text{CXYH}$ , to the corresponding ester,  $\text{CHXYCOOR}$ , was carried out according to the method of Young and Tarrant.<sup>6</sup>

(1) This paper represents part of a thesis submitted by H. L. Cummings to the Graduate School, University of Colorado, in partial fulfillment of the requirements for the Ph.D. degree.

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