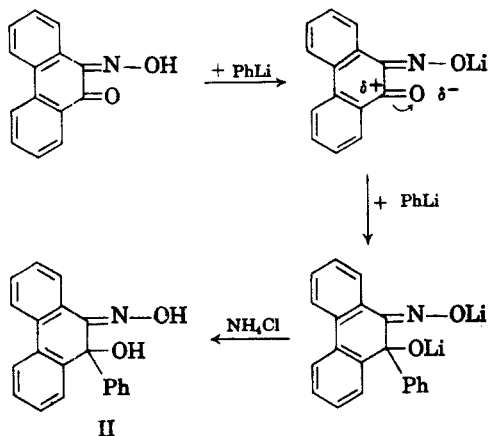


described by Mustafa *et al.*¹ the same product 9-phenyl-9,10-dihydro-10-oximino-9-hydroxyphenanthrene (II), is obtained according to the following scheme:



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, λ_{\max} (m μ) 254, ϵ_{\max} 23990, λ_{\max} (m μ) 288, ϵ_{\max} 8535, λ_{\max} (m μ) 324, ϵ_{\max} 1619.

In addition, it is noticed that the addition of organolithium compounds to the α,β -unsaturated ketones is a 1,2-addition even in cases where the organomagnesium compounds add by 1,4-addition.⁴⁻⁷

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 Ethers¹

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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 works² 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, $\text{C}_2\text{H}_5-\text{O}-\text{CF}_2\text{CH}_2\text{I}$ ³ 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 CHF_2COOH . Here again, Seffl⁴ 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^{2(d), 5}, 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, CHXYCOOR , was carried out according to the method of Young and Tarrant.⁶

(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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Preparation of $C_2H_5-O-CF_2CH_2F$. Reaction between $CF_2=CHF$ and ethanol was carried out according to the procedure given in Ref. 2(d). B.p. 33° (253 mm.); n_D^{25} 1.3145, d_4^{25} 1.118.

Anal. Calcd. for $C_4H_7F_3O$: C, 37.51; F, 44.50. Found: C, 37.72; F, 44.3.

Hydrolysis of $C_2H_5-O-CF_2CH_2F$ yielded $CFH_2COOC_2H_5$. B.p. 109° (629 mm.); n_D^{25} 1.3745, d_4^{25} 1.085. (Lit.⁷ B.p. 117° at 760 mm.)

Preparation of $C_2H_5-O-CF_2CH_2Br$. Reaction between $CF_2=CHBr$ and ethanol was carried out according to the method given in ref. 2(a). B.p. $55-56^\circ$ (104 mm.); n_D^{25} 1.3980, d_4^{25} 1.512.

Anal. Calcd. for C_4H_7BrO : C, 25.40; Br, 42.3. Found: C, 25.26; Br, 42.12.

Hydrolysis of $C_2H_5-O-CF_2CH_2Br$ yielded $CH_2BrCOOC_2H_5$. B.p. 82° (55 mm.); n_D^{25} 1.4484, d_4^{25} 1.501. Lit.⁸ d_4^{25} 1.5059; n_D^{25} 1.45420.

Preparation of CH_3-O-CF_2CHF . Reaction between $CF_2Cl-CHF$ and methanol was carried out according to the method given in ref. 2(b). B.p. 59° (107 mm.); n_D^{25} 1.4188, d_4^{25} 2.022.

Anal. Calcd. for $C_3H_4F_2O$: C, 15.02; F, 23.75. Found: C, 15.12; F, 23.46.

Hydrolysis of CH_3O-CF_2CHF yielded $CHFICOOH$ but no $CHFICOOCH_3$, m.p. 79.5° . The melting point of this acid has been variously reported as 74° ⁹ and $78.5-79^\circ$.¹⁰

Anal. Calcd. for $C_3H_4FIO_2$: C, 11.76; F, 9.31; I, 62.25. Found: C, 11.91; F, 9.51; I, 62.32.

Preparation of $C_2H_5-O-CF_2-CH_2Br$. Reaction between $CF_2=CFBr$ and ethanol was carried out according to the method given in ref. 2(a). B.p. $62-62.5^\circ$ (167 mm.); n_D^{25} 1.3710, d_4^{25} 1.571.

Anal. Calcd. for $C_4H_6BrF_2O$: C, 23.19; F, 27.53. Found: C, 23.30; F, 27.26.

Hydrolysis of $C_2H_5-O-CF_2-CH_2Br$ yielded $CHFBrCOOC_2H_5$. B.p. 98.5° (138 mm.); n_D^{25} 1.4248, d_4^{25} 1.565.

Anal. Calcd. for $C_4H_6BrFO_2$: C, 25.94; F, 10.27. Found: C, 26.24; F, 10.38.

Hydrolysis of $CHFBrCO_2C_2H_5$ with dilute HCl yielded the acid $CHFBrCOOH$, m.p. $51.5-52.5^\circ$, reported⁹ 49° .

Anal. Calcd. for $C_2H_3BrFO_2$: C, 15.31; F, 12.11. Found: C, 15.45; F, 11.80.

Reaction between CF_2Cl-CH_2I and MeOH. Twenty-five grams (0.11 mole) of CF_2Cl-CH_2I and 25 ml. of methanol were placed in a 250 cc., three-neck flask equipped with a stirrer, dropping funnel, and reflux condenser. The reaction mixture was cooled to zero degrees, by means of an external bath, and a ten percent solution of potassium hydroxide dissolved in methanol was added dropwise with stirring. After a ten percent excess of the methanolic base had been added (total, 6.72 g. of potassium hydroxide dissolved in 70 ml. of methanol), the temperature of the reaction mixture was raised to reflux for 30 min., cooled to room temperature, poured into cold water, and the heavy ether layer separated. The crude, washed product was dried over anhydrous calcium sulfate and weighed 15.3 g. (62.2%). During the drying process the crude ether eliminated hydrogen fluoride and upon distillation at reduced pressure 5.96 g. (43.2%) of the ester, $CH_2I-CO_2CH_3$, b.p. 90° (54 mm.), was isolated. n_D^{25} 1.5202, d_4^{25} 2.011. No $CH_2-OCF_2CH_2I$ was isolated.

Anal. Calcd. for $C_2H_3IO_2$: C, 18.02; H, 2.52; I, 63.50. Found: C, 18.24; H, 2.38; I, 63.71.

Attempted preparation of $CH_3-O-CF_2CH_3$. A 50 percent solution of sodium methoxide in anhydrous methanol was

introduced into the Parr hydrogenation bomb, and the bomb was sealed and tested for leaks. When leak-free, the bomb was cooled to -80° C, evacuated with a water aspirator, and 64 g. (1.0 mole) of $CF_2=CH_2$ were forced into the bomb under pressure. The bomb was removed from the cooling bath, placed in the rocker, and allowed to warm slowly to room temperature with constant agitation for about 24 hours. No fluorinated ether was isolated.

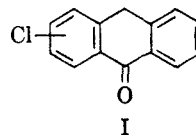
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An Unequivocal Synthesis of 3-Chloro-9-Anthrone¹

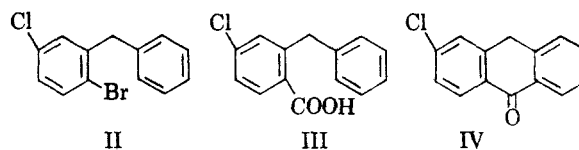
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On reduction of 2-chloroanthraquinone with tin and glacial acetic acid, Barnett and Mathews² isolated a pure compound, m.p. 156° , which they designated as 2 (or 3) - chloro-9-anthrone (I). Several years later, Barnett and Wiltshire³ un-



equivocally prepared 2-chloro-9-anthrone, m.p. 155° . Since a melting point of a mixture of these two showed a depression, it was concluded that I was 3-chloro-9-anthrone. In addition to this, a mixture of the acetate of I, m.p. 146° , and 2-chloro-9-anthryl acetate, m.p. 143° , showed a depression in the melting point.



Since some of bromide II was available,⁴ an unequivocal synthesis of IV was undertaken. The Grignard reagent of II was prepared, carbonated, and the adduct decomposed to give acid III. Cyclization of this acid with concentrated sulfuric acid gave 3-chloro-9-anthrone (IV) m.p. $155-156^\circ$.² Acetylation of IV with pyridine and acetic anhydride yielded 3-chloro-9-anthryl acetate, m.p. $146-146.5^\circ$.³

(1) This note has been abstracted from the Doctorate thesis of P. E. Newallis presented to the Virginia Polytechnic Institute in 1957.

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