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Abnormal Products in the Siegrist Reaction Involving Ortho-Fluorinated Intermediates[1]

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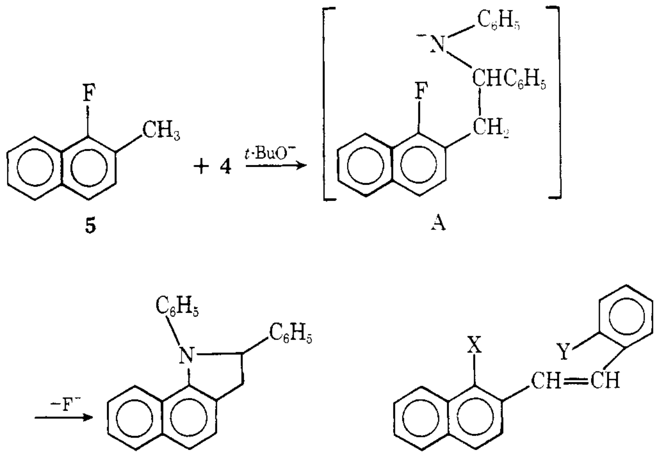
The syntheses of *trans*-1-(1 fluoro-2-naphthyl)-2-phenylethylene (1) and *trans*-1-(1-fluoro-2-naphthyl)-2-(*o*-iodophenyl)ethylene (2) via the Wittig reaction as intermediates for the attempted photochemical synthesis of 7-fluorobenz[*a*]anthracene (3) have been described.[3] Unfortunately, insufficient 3 was made (only via 2 as use of 1 failed) for adequate testing for possible carcinogenic activity. Because of our interest in preparing larger amounts of 3, we wished to develop improved methods for the synthesis of 1 and 2.

A route to substituted stilbenes which involves condensation of methylated aromatic nuclei with benzalaniline (4) in the presence of potassium *tert*-butoxide (eq 1) has been studied[4] and applied to the facile synthesis of hexahelicene and other helicenes.[5] However, no example involving an ortho halogen-substituted reactant has been reported.

$$\mathrm{ArCH_3} + \underset{\mathbf{4}}{\mathrm{C_6H_5N{=}CHC_6H_5}} \rightarrow \mathrm{ArCH{=}CHC_6H_5} + \mathrm{C_6H_5NH_2} \quad (1)$$

Consequently, we attempted to react 1-fluoro-2-methylnaphthalene (5) and 4 as above. None of the expected 1 was obtained. Instead, a complex mixture was produced from which small amounts of 2,3-dihydro-1,2-diphenylindole (6), *trans*-(1-anilino-2-naphthyl)-2-naphthyl)-2-phenylethylene (7), and *trans*-1-(1-hydroxy-2-naphthyl)-2-phenylethylene (8) were isolated. A similar reaction with 1-bromo-2-methylnaphthalene and 4 afforded *trans*-1-(1-bromo-2-naphthyl)-2-phenylethylene (9) in 58% yield with no evidence for the formation of nitrogenous products.

Scheme I



1, X = F; Y = H
2, X = F; Y = I
7, X = NHC$_6$H$_5$; Y = H
8, X = OH; Y = H
9, X = Br; Y = H

The formation of 6 probably occurs by intramolecular nucleophilic displacement of fluoride ion by anion A, produced by the addition of the 1-fluoro-2-naphthylmethyl anion to **4,** as shown in Scheme I. The formation of 7 evidently involves a base-catalyzed cleavage of a C–N bond in 6 to form **7.** We have shown that under the reaction conditions 6 is converted to **7.** The formation of **8** probably occurs by displacement of the fluorine in 5 by *tert*-butoxide followed by a normal Siegrist reaction and pyrolytic cleavage of the resulting *tert*-butyl ether.

Interestingly, the elimination of aniline to form **9** occurs more rapidly than intramolecular displacement of bromide ion in the bromo intermediate corresponding to A. Evidently, the bromine in 9 is relatively much more stable to attack by *tert*-butoxide ion or to intramolecular attack by a nitrogenous anion similar to A than is the fluorine in 1 (or A). To our knowledge the contrasting results in the reactions of 4 with 1-fluoro-2-methylnaphthalene (5) and with 1-bromo-2-methylnaphthalene provide the first evidence that the intramolecular nucelophilic displacement of fluoride occurs more easily than that of bromide. Some, but not all, evidence shows that aryl fluorides are more reactive than aryl bromides in intermolecular nucleophilic substitution.[6] The same conclusion was reached in a study[7] on the action of potassium *tert*-butoxide in Me$_2$SO on chloro-, bromo- and iodonaphthalenes which showed that the reactions proceeded via 1,2-naphthyne to give mixtures of 1- and 2-*tert*-butoxynaphthalenes, whereas both 1- and 2-fluoronaphthalene formed 1- and 2-*tert*-butoxynaphthalenes, respectively, by direct displacement of fluoride.

In order to obtain evidence as to the mechanism of formation of 6 and 7 in the Siegrist reaction, we prepared 1 as described[3] from 5,[8] prepared in improved yield (63%) by using the diazonium hexafluorophosphate[9] instead of the diazonium tetrafluoroborate.[8] On heating 1 with aniline under conditions identical to those involved in the reaction of 4 and **5,** there was obtained neither 6 nor **7,** and 85% of 1 was recovered. This fact supports the intramolecular mechanism for the formation of 6 shown in Scheme I.

When *o*-fluorotoluene was treated with 4 a 28% yield of 1-(*o*-fluorophenyl)-2-phenylethylene (10) was obtained, but no attempt to maximize the yield nor to isolate other components was made. Thus, the fluorine in **10** is less reactive than the fluorine in 1 under Siegrist conditions.

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Experimental Section[10]

1-Fluoro-2-methylnaphthalene (5). Diazotization of 1-amino-2-methylnaphthalene[11] and conversion into the diazonium hexafluorophosphate were carried out as described.[9] Pyrolysis at 170–180 °C in mineral oil for 30 min afforded crude **5**, which on redistillation afforded 63% of twice distilled **5**, bp 62 °C at 0.5 mm.[8]

Reaction of 5 with Benzalaniline (4). A mixture of 1.6 g of **5**, 1.8 g of **4**, 2.8 g of *t*-BuOK, and 15 mL of DMF was heated at 95 ± 3 °C for 90 min, cooled, and added to 150 mL of 10% HCl. The organic product, isolated as usual, was dissolved in 20 mL of ethanol. On cooling, a colorless solid separated and was recrystallized from benzene–petroleum ether (30–60 °C) to yield 420 mg (18%) of **7**, mp 167–168 °C: MS *m/e* 321;[12] NMR [$(CH_3)_4Si$, $CHCl_3$] δ 5.65 (s, 1, NH, exchanged by D_2O), 6.51–8.18 (m, 18, ArH, CH=CH). Further crystallization of the material in the mother liequor from benzene–petroleum ether (30–60 °C) afforded 100 mg (3%) of colorless **6**, mp 164–165 °C, giving blue fluorescence in benzene: MS *m/e* 321; NMR 2.98 (q, 1, J_{ac}, −4 Hz, J_{bc} = −15 Hz), 4.06 (q, 1, J_{ab} = −10 Hz, J_{bc} = −15 Hz), 5.15 (q, 1, J_{ac} = −4 Hz, J_{ab} = −10 Hz), 6.78–7.95 (m, 16, ArH). Anal. Calcd for $C_{24}H_{19}N$: C, 89.7; H, 5.9; N, 4.4. Found: C, 90.2; H, 5.9; N, 4.0.

Alkaline extraction of the material remaining in the mother liquor followed by acidification of the extract and crystallization from benzene–petroleum ether (30–60 °) afforded 200 mg (7%) of **8**: mp 150.5–151.5 °C; MS *m/e* 246;[12] NMR 5.56 (s, 1, OH exchangeable with D_2O), 6.90–8.23 (m, 13 H, ArH, CH=CH). Anal. Calcd for $C_{18}H_{14}O$: C, 87.8; H, 5.7. Found: C, 88.2; H, 5.8.

After heating a solution of 0.25 g of **1**, prepared as described[3] with 0.09 g of aniline and 1.1 g of *t*-BuOK in 10 mL of DMF for 12 h at 100–110 °C, most (85%) of the **1** was recovered, and no trace of **6** or **7** was found using TLC (neutral alumina).

***trans*-1-(1-Bromo-2-naphthyl)-2-phenylethylene (9).** A mixture of 4.4 g of 1-bromo-2-methylnaphthalne,[11] 3.6 g of **4**, 4.5 g of *t*-BuOK, and 80 mL of DMF was heated at 95 °C for 1 h, cooled, and poured into 120 mL of 10% HCl. On crystallization from ethanol of the organic products, isolated as usual, there was obtained 3.6 g (58%) of **9**: mp 115–116 °C (lit.[13] mp 121–122 °C); MS *m/e* 308, 310.[12]

1-(*o*-Fluorophenyl)-2-phenylethylene (10). In a Siegrist reaction similar to those described above (1 h at 95 °C), *o*-fluorotoluene was converted in 28% yield into **10**: mp 103.0–103.5 °C, MS *m/e* 198.[12] Anal. Calcd for $C_{14}H_{11}F$: C, 84.8; H, 5.6; F, 9.6. Found: C, 84.7, H, 5.5; F, 9.6.

The mother liquor on evaporating to dryness gave an impure oil (several spots on TLC) containing nitrogen but no fluorine on elemental analysis. No further attempt was made to purify it.

Registry No.—**4**, 538-51-2; **5**, 573-99-9; **6**, 64345-68-2; **7**, 64345-71-7; **8**, 64345-70-6; **9**, 27854-69-9; **10**, 64345-69-3; 1-bromo-2-methylnaphthalene, 2586-62-1; *o*-fluorotoluene, 95-52-3.

References and Notes

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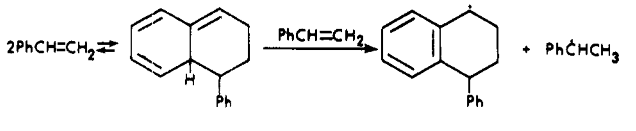
Communications

Thermal Reaction between 5-Methylene-1,3-cyclohexadiene and Styrene[1]

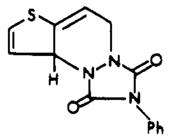
Summary: At 80 °C 5-methylene-1,3-cyclohexadiene reacts rapidly, $t_{1/2} \sim 6$ min, with styrene to produce a 3:1 mixture of 1,2- and 1,3-diphenylpropane in 90% yield. The triene does not initiate the polymerization of styrene.

Sir: The proposal[2] that the monoradical forming step in the thermal polymerization of styrene involves hydrogen atom transfer from a preformed dimer **1** to styrene (Scheme I) has received considerable support.[3] Isolation of **1** has not been accomplished yet, but an analogue **2** has been prepared and shown to initiate the polymerization of styrene.[4]

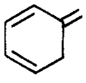
Scheme I



1



2



3

In another attempt to verify some of the chemistry attributed to **1** the corresponding parent triene, 5-methylene-1,3-cyclohexadiene (**3**), has been prepared and some of its reactions studied. The preparation of **3** by thermolysis of an ester has been reported already.[5] The search for a compound that might decompose at a much lower temperature and allow **3** to be generated slowly in styrene solution led to the alternate synthesis shown in Scheme II. Itaconic anhydride and α-pyrone were heated under N_2 in toluene at 90 °C for 65 h to

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