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Syntheses of 9,10-Phenanthrenequinone and 9-Methoxyphenanthrene by Oxidation of Phenanthrene with Dihydroxy Phenylselenonium Benzenesulfonate

Nicolai Stuhr-Hansen^a & Lars Henriksen^a ^a Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100, Copenhagen Ø, Denmark Published online: 19 Aug 2006.

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SYNTHESES OF 9,10-PHENANTHRENEQUINONE AND 9-METHOXYPHENANTHRENE BY OXIDATION OF PHENANTHRENE WITH DIHYDROXY PHENYLSELENONIUM BENZENESULFONATE

Nicolai Stuhr-Hansen* and Lars Henriksen

Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark.

Abstract: 9,10-Phenanthrenequinone is prepared by oxidation of phenanthrene with dihydroxy phenylselenonium benzenesulfonate in boiling dioxane-water. 9-methoxyphenanthrene is obtained when the reaction is carried out in methanol.

We have previously reported¹ that a 1:1 mixture of protonated benzeneseleninic acid and diphenyl diselenide phenylselenylates phenol and anisole with high *p*-specificity. This pattern is similar to previous results with the reagent systems diphenyl diselenide - ammonium persulfate,² diphenyl diselenide *m*-nitrobenzenesulfonyl peroxide,³ (phenylseleno)dimethylsulfonium tetrafluoroborat⁴ and benzeneselenenyl chloride - silver hexafluorophosphate⁵ and suggest the phenylselenenium ion as the common intermediate.

In continuation of our observation⁶ that dihydroxy phenylselenonium ptoluenesulfonate is readily prepared and isolated as a shelf-stable reagent we initiated a survey of the application of the reagent couple diphenyl diselenide -

^{*} To whom correspondence should be addressed

dihydroxy phenylselenonium ion as a source of phenylselenenium ion for electrophilic phenylselenylation (Scheme 1).

Scheme 1

$PhSe(OH)_{2}^{+} + PhSeSePh \longrightarrow PhSe^{+} + 2 PhSeOH$

While the *p*-selective substitution pattern appeared to be general for donorsubstituted benzenes and the reaction with alkenes led to the expected addition reaction with solvent incorporation the reaction with phenanthrene (1) was anomalous and gave only selenium-free products. The reaction of dihydroxy phenylselenonium benzenesulfonate $(5)^7$ with 1 in the presence of a catalytical amount of diphenyl diselenide in refluxing methanol led to the formation of 9methoxyphenanthrene (3) as the first isolable product (Scheme 2).

Scheme 2



The optimal yield of 3 (21 %) was noted when 1 was treated with 5 in boiling methanol for 2 hours in the presence of a catalytic amount of diphenyl diselenide. 3 was not formed in absence of the diphenyl diselenide. Prolonged reaction time led to a slow disappearance of 3 and a simultaneous increase in the amount of phenanthrenequinone (6) (approximately 50 % of 6 was isolated after 2

days reflux in methanol, however contaminated with some persistent violet coloured impurity).

The only previously reported short route to **3** involves treatment of fluorenone⁸ with an excess of diazomethane (50 % yield). A rearrangement of 2,2(2',2''-Biphenylene)ethene-1-diazonium hexachloroantimonate to **3** upon methanolysis has been reported.⁹

A more clean preparation of **6** was achieved in the solvent system dioxanewater. **6** (66 %) was isolated after reflux for 4 days. We presume that the reaction in this medium proceeds *via* 9-phenanthrol (4) although the steady-state concentration of this species was too low for detection.

6 has previously been prepared by oxidation of **1** with chromic acid¹⁰ in sulfuric acid (44-48 %), iodic acid¹¹ in acetic acid (63 %) and more recently in 94 % yield with quinolinium fluorochromate (QFC).¹²

The experimental results are consistent with the following mechanistic features. The formation of **3** in methanol involves two steps as indicated in Scheme 2: 1) Phenylselenenium ion addition to the 9,10 double bond of **1** followed by addition of methanol to give **2**. 2) Attack of phenylselenenium ion on Se with elimination of diphenyl diselenide and then a proton to give **3**. A reaction related to the last step is found in the phenylselenenium ion mediated oxidation of methylketones to 1,1-dimethoxyketones¹³ although in this case the intermediary carbenium ion undergoes substitution rather than elimination. The formation of **6** in aqueous dioxane can be explained by an analogous formation of **4** the benzeneseleninate of which rearranges to **6** in a [2,3]-shift.

Since water is produced in the formation of 3 a slow hydrolysis of this enolic ether to give 4 can explain the observed slow conversion of 3 into 6.

Experimental

9-Methoxyphenanthrene (3).

A suspension of phenanthrene (1) (1.09 g, 6,1 mmol), dihydroxy

phenylselenonium benzenesulfonate (**5**) (2.08 g, 6 mmol) and diphenyl diselenide (0.1 g, 0.3 mmol) in methanol (15 ml) was refluxed for 2 hours (lower yields of **3** were obtained by refluxing the reaction mixture for a longer period). The yellow mixture was poured into a solution of sodium hydrogencarbonate (10 % aq., 50 ml) and extracted with dichloromethane-pentane (1:4, 3 x 30 ml). Removal of the solvent *in vacuo*, separation on silica gel 60 (20 g) with dichloromethane-pentane (1:4), recrystallization fra pentane (25 ml) and drying (vacuum oven) gave **3** (0.27 g, 21 %) as white crystals; m.p. 93-95 °C (lit.× 95 °C). $C_{15}H_{12}O$: found C 86.23 % H 5.77 %; calc. C 86.51 % H 5.81 %. Purity > 98 % (GC-MS); mass spectrum (EI; m/z, relative intensity): 208 (M⁺, 76), 193 (7), 176 (8), 165 (100). ¹H-NMR (CDCl₃) &: 4.04 (3 H, s), 6.91 (1 H, s), 7.38-7.71 (5 H, m), 8.24-8.45 (1 H, m), 8.50-8.63 (2 H, m). ¹³C-NMR (CDCl₃) &: 55.43, 101.95, 122.57, 124.26, 126.41, 126.93, 127.19, 127.32, 131.35, 132.98, 153.60 ppm.

9,10-Phenanthrenequinone (6).

A suspension of **1** (0.93 g, 5.2 mmol) and **5** (3.5 g, 10 mmol) in dioxane-water (10:1, 15 ml) was refluxed for 4 days. The orange mixture was poured into a solution of sodium hydrogencarbonate (10 % aq., 70 ml) and extracted with ethyl acetate (3 x 30 ml). After removal of the ethyl acetate *in vacuo* the residue was separated by flash chromatography on silica gel 60 (10 g). A non-polar fraction (1.36 g, **1** and diphenyl diselenide, 1:4; GC-MS) was washed out with dichloromethane-pentane (1:2) and the product subsequently eluted with dichloromethane. Recrystallization from toluene (40 ml) og drying (vacuum oven) gave **6** (0.69 g, 66 %) as orange flakes; m.p. 207-210 °C (lit.^x 208.5-211 °C). $C_{14}H_8O_2$: found C 80.65 % H 3.84 %; calc. C 80.76 % H 3.87 %. Mass spectrum (EI; m/z, relative intensity): 208 (M⁺, 39), 180 (100), 152 (33). ¹H-NMR (CDCl₃) &: 7.35-7.79 (4 H, m), 7.94-8.21 (4 H, m) ppm. ¹³C-NMR (CDCl₃) δ : 124.0, 129.6, 130.5, 131.1 (C=O), 136.0 ppm.

Dihydroxy phenylselenonium benzensulfonate (5).

Hot, concentrated solutions of benzeneseleninic acid (7.6 g, 40 mmol) and benzene sulfonic acid (7.1 g, 41 mmol) in acetic acid were mixed and cooled to room temperature. The product was filtered off, recrystallized from acetic acid and dried (vacuum oven). Yield 12.3 g, 89 %; m.p. 162-64 °C. $C_{12}H_{12}O_5SSe$: found C 41.76 % H 3.52 %; calc. C 41.51 % H 3.48 %. 'H-NMR (DMSO- d_6) & 7.30-7.51 (3 H, m), 7.56-7.72 (5 H, m), 7.80-7.98 (2 H, m), 10.86 ppm (2 H, s). ⁷⁷Se-NMR (DMSO- d_6) & 1161 ppm.

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