Synthesis of Substituted 9,10-Dihydroanthracenes by the Reduction of Anthraquinones in Hydriodic Acid[1]

ROGER N. RENAUD AND J. CAMPBELL STEPHENS
Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R6

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Substituted 9,10-dihydroanthracenes were synthesized by reducing the corresponding anthraquinone with a mixture of hydriodic acid, phosphorus, and iodine.

La synthèse de quelques dihydro-9,10 anthracènes par réduction de l'anthraquinone correspondante avec le système acide iodhydrique – phosphore – iode est exposée.

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In connection with a spectroscopic investigation, we became interested in the synthesis of 1- and 2-substituted 9,10-dihydroanthracenes. Since many substituted anthraquinones are easily available, we decided to utilize these compounds as precursors for the 9,10-dihydro derivatives. Reducing agents such as lithium aluminum hydride (1, 2), sodium borohydride (3), aluminum alkoxides (4), diborane (5), zinc dust in basic medium (6), cyclohexyl-*p*-toluene sulfonate (7), diphenylsilane (8), sodium hydrosulfite (9), and nickel–aluminum alloy (10) give mainly 9,10-dihydroxy-9,10-dihydroanthracene, 9,10-dihydroxyanthracene, anthrone, anthrol, and/or anthracene. Organotin hydrides (11) do not reduce anthraquinone.

Sanchorawala and co-workers (12) have conducted an elaborate study of the reduction of 2-substituted anthraquinones by sodium borohydride in the absence and in the presence of aluminum chloride or boron fluoride. They obtained a very low yield of 9,10-dihydroanthracene when the substituent was hydrogen, and no dihydro compounds when the substituent was either chlorine, methyl, methoxy, or *t*-butyl.

The reduction of quinones in general under Wolff–Kishner conditions gives phenolic products resulting from the decomposition of the monosemicarbazone intermediate in presence of potassium hydroxide (13). Backer and coworkers (14) prepared polyaryl- and polymethyl-9,10-dihydroanthracenes by the Clemmensen reaction. Even though high yields of product can be obtained by this method, it requires long heating periods during which continuous addition of concentrated hydrochloric acid is required.

It is well known that a mixture of hydriodic acid and phosphorus reduces a variety of organic substrates including aryl olefins, arylcarbinols, aryl ketones, benzils, glycols, α-haloketones, and α,β-epoxyketones. In addition, a few quinones have also been reduced by this reagent to the corresponding hydrocarbons (15, 16). However, the reduction of substituted anthraquinones is reported to give anthrone (14) and/or anthracene (6), depending on the experimental conditions.

Our preliminary study with hydriodic acid and phosphorus at different temperatures and concentrations has revealed that anthraquinone can be reduced to 9,10-dihydroanthracene in good yields. The best result is obtained when a small amount of elemental iodine is present in the original mixture. However, the action of elemental iodine is not well understood. Under the best experimental conditions for anthraquinone (Table 1, run 1) many substituted anthraquinones were reduced to the 9,10-dihydro derivatives. The crude products obtained are usually better than 95% pure. Analytically pure compounds can be obtained by recrystallization or by direct sublimation. Only the product of reduction of 1-chloroanthraquinone, which was an oil containing some nonchlorinated compounds, was purified with difficulty. The purification was done by a fractional distillation under reduced pressure in a Späth bulb.

The only quinone of the series which could not be reduced to the dihydro derivative was 1-hydroxyanthraquinone. An unidentified product containing an equivalent of six methylene groups in addition to two keto groups was ob-

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TABLE 1. Reduction of substituted anthraquinones to substituted 9,10-dihydroanthracenes

				Elemental analysis (%)					
				C		H		Cl	
Run	Substituent	Yield*	Melting point† (°C)	Found	Calcd.	Found	Calcd.	Found	Calcd.
1	H	77	108–109 [108] (6)	92.98	93.33	6.65	6.67		
2	1-Cl	50	Oil	77.93	77.32	5.04	5.12	16.39	16.56
3	2-Cl	90	65–66	77.92	78.32	4.91	5.12	16.21	16.56
4	2-CH_3	92	53–54 [51] (17)	92.45	92.78	7.31	7.22		
5	2-COOH	15	182–183	80.11	80.35	5.26	5.35		
6	2-$C(CH_3)_3$	88	43–44	91.30	91.52	8.36	8.48		

*The yields are based on purified products.
†The numbers in square brackets correspond to the values reported in the literature.

tained. Pleus (18) claimed that he had prepared 9,10-dihydro-1-hydroxyanthracene from quinizarin in the presence of hydriodic acid and phosphorus at 0°. However, the reduction of 1-hydroxyanthraquinone, done under the same experimental conditions as Pleus, gave only the starting material.

Unfortunately, this method is not applicable to the reduction of deuterated anthraquinones, since rapid exchange occurs between the aromatic deuterium and the hydriodic acid proton. For instance, 1,4,5,8-tetradeuterioanthraquinone (96.8% d_4) (17) gave a product whose analysis was 3% d_2, 17% d_1, and 80% d_0. However, 1,4,5,8-tetradeuterio-9,10-dihydroanthracene can be prepared in 65% yield under the Clemmensen reduction conditions (14) from the corresponding quinone, without any deuterium scrambling.

Experimental

A stirred mixture of red phosphorus (4.2 g), iodine (1 g), 47% solution of hydriodic acid (30 ml), and quinone (15 mmol) was heated in an oil bath at 140 °C for 24 h. The mixture was allowed to cool down to room temperature and diluted with 200 ml of water. The resulting suspension was collected in a Buchner funnel and extracted with ether. The ethereal solution was washed with a solution of sodium thiosulfate, a solution of sodium bicarbonate and finally with water. (In the case of 9,10-dihydroanthracene-2-carboxylic acid, the washings with sodium thiosulfate and with sodium bicarbonate were omitted.) The solution was dried over sodium sulfate and evaporated to dryness. The product obtained was in general over 95% pure. Further purification was accomplished either by sublimation or by recrystallization from ethanol.

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