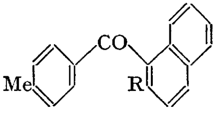
147. *Oxidations and Dehydrogenations with Selenium Dioxide.*

By G. M. Badger.

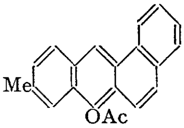
1-*p*-Toluoyl-2-methylnaphthalene (I, R = Me) has been oxidised with selenium dioxide to 1-p-*toluoylnaphthalene*-2-*carboxylic acid* (I, R = CO_2H), the constitution of which has been proved by conversion into 6-methyl-1 : 2-benzanthraquinone. Some experiments on the use of selenium dioxide as a dehydrogenating agent for hydroaromatic compounds are also reported.

Selenium dioxide was first introduced as an oxidising agent by Riley (B.P. 354,798; Riley, Morley, and Friend, *J.*, 1932, 1875). It is now finding considerable application in the preparation of compounds which are either unobtainable, or obtained only with difficulty, using other oxidising agents. (For a comprehensive review see Waitkins and Clark, *Chem. Reviews*, 1945, **36**, 235.)

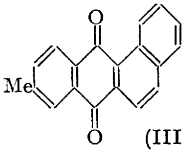
A particularly useful property of selenium dioxide is its power to oxidise activated methylene or methyl groups. Cook (*J.*, 1932, 1472; 1933, 1592) prepared 2-carboxy-1 : 1′-dinaphthyl ketone from 2-methyl-1 : 1′-dinaphthyl ketone, and oxidised 1-α-naphthoyl-2 : 6-dimethylnaphthalene to a mono-aldehyde, the constitution of which was not proved, although it was considered probable that the methyl group adjacent to the carbonyl group had been oxidised. It was therefore of interest to attempt the oxidation of 1-*p*-toluoyl-2-methylnaphthalene (I, R = Me).



(I.)



(II.)



(III.)

In aqueous suspension at 230°, selenium dioxide oxidised this ketone to 1-p-*toluoylnaphthalene*-2-*carboxylic acid* (I, R = CO_2H), which was purified *via* the *acetoxy-lactone.* Attempts to ring-close this acid to 6-methyl-1 : 2-benzanthraquinone (III) using benzoyl chloride with a trace of sulphuric acid (Badger and Cook, *J.*, 1939, 802), or with concentrated sulphuric acid at 100°, were unsuccessful. The keto-acid was, however, reduced with zinc and sodium hydroxide to 1-p-*methylbenzylnaphthalene*-2-*carboxylic acid*, which was smoothly converted into 10-*acetoxy*-6-*methyl*-1 : 2-*benzanthracene* (II) with zinc chloride in acetic anhydride–acetic acid (Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1937, **59**, 1032). The constitution was finally confirmed by oxidation of this derivative to 6-methyl-1 : 2-benzanthraquinone (III), and the synthesis therefore provides an alternative route to derivatives of the carcinogenic hydrocarbon, 6-methyl-1 : 2-benzanthracene. It is of interest that Cook (*loc. cit.*) was unable to oxidise the methyl group of 6-methyl-1 : 2-benzanthraquinone with selenium dioxide.

The efficiency of selenium dioxide as an oxidising agent appears to depend on the degree of activation of the group to be oxidised and on the temperature of reaction. This is illustrated by the fact that 9 : 10-dihydroanthracene was smoothly dehydrogenated to anthracene in boiling acetic acid, but not in alcohol, while at high temperatures anthracene was oxidised to anthraquinone. Under the same conditions phenanthrene gave no phenanthraquinone (compare Astin, Moulds, and Riley, *J.*, 1935, 901; Postowsky and Lugowkin, *Ber.*, 1935, **68**, 852). Attempts to dehydrogenate *s*-octahydroanthracene and *as*-octahydroanthracene in boiling alcohol or acetic acid were, however, unsuccessful. In aqueous suspension at 150°, with the theoretical quantity of selenium dioxide required for dehydrogenation, but not oxidation, both octahydroanthracenes gave mixtures of anthraquinone and unchanged material. In the octahydroanthracenes the hydrogen atoms are not highly activated, and the temperature required for dehydrogenation would appear to be almost identical with that required for oxidation. Hexahydropyrene (Cameron, Cook, and Graham, *J.*, 1945, 286) was dehydrogenated to pyrene in acetic acid, although a dark product was also formed.

EXPERIMENTAL.

1-p-*Toluoylnaphthalene*-2-*carboxylic Acid* (I, R = CO_2H).—A mixture of 1-*p*-toluoyl-2-methylnaphthalene (I, R = Me) (4 g.), selenium dioxide (7 g.), and water (7 c.c.) was heated in a sealed tube at 230—240° for 4 hours. The solid was extracted with hot sodium carbonate, and the crude acid precipitated with hydrochloric acid. After recrystallisation from acetic acid it formed colourless prisms, m. p. 215—218°. (Yield, 11 g. from 6 such experiments, with 5 g. ketone recovered unchanged.) The *acetoxy-lactone*, prepared by heating the acid (2 g.) with pyridine (12 c.c.) and acetic anhydride (4 c.c.) for 2 hours on the steam-bath, recrystallised from alcohol and formed colourless transparent needles, m. p. 145—147° (Found : C, 75·6; H, 5·0. $C_{21}H_{16}O_4$ requires C, 75·9; H, 4·8%). Pure 1-p-*toluoylnaphthalene*-2-*carboxylic acid*, recovered after hydrolysis of the acetoxy-lactone with potassium hydroxide, formed colourless transparent prisms from acetic acid, m. p. 220—222° (Found : C, 78·25; H, 5·0. $C_{19}H_{14}O_3$ requires C, 78·6; H, 4·8%).

Attempts to ring-close this acid with concentrated sulphuric acid at 100° for 3 hours, or with benzoyl chloride and a trace of sulphuric acid at 130°, were unsuccessful.

1-p-*Methylbenzylnaphthalene*-2-*carboxylic Acid.*—A mixture of the above acid (8·5 g.), sodium hydroxide (12 g.), zinc dust (12 g.), and water (130 c.c.) was boiled under reflux for 24 hours. After filtration, the *acid* was precipitated with hydrochloric acid, and recrystallised from 80% acetic acid. It formed colourless crystals (3·5 g.), m. p. 188—190° (Found : C, 82·3; H, 5·9. $C_{19}H_{16}O_2$ requires C, 82·6; H, 5·8%).

10-*Acetoxy*-6-*methyl*-1 : 2-*benzanthracene.*—A mixture of the above acid (1 g.), acetic acid (6 c.c.), acetic anhydride (4 c.c.), and zinc chloride (0·1 g.) was refluxed for 1 hour. Water was added and the precipitated product collected and recrystallised from acetic acid. The *benzanthracene* (0·65 g.) formed pale yellow prisms, m. p. 174·5—176° (Found: C, 84·3; H, 5·35. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·3%).

6-*Methyl*-1 : 2-*benzanthraquinone*.—10-Acetoxy-6-methyl-1 : 2-benzanthracene (0·1 g.) was boiled under reflux for ½ hour with sodium dichromate (0·5 g.) in acetic acid (5 c.c.). The product, recrystallised from glacial acetic acid, formed yellow needles, m. p. 176—177° (corr.) alone, or mixed with authentic 6-methyl-1 : 2-benzanthraquinone.

Action of Selenium Dioxide on Hydroanthracenes.—A solution of 9 : 10-dihydroanthracene (1 g.), selenium dioxide (2 g.), water (2 c.c.), and acetic acid (50 c.c.) was refluxed for 1¼ hours. The filtered solution was poured into water, and the solid collected and recrystallised from alcohol. It formed almost colourless plates (0·6 g.), m. p. 214—215°, alone or mixed with anthracene. The dehydrogenation was not effected by refluxing for a similar time in alcohol.

Similar experiments with *s*-octahydroanthracene and *as*-octahydroanthracene, gave very dark mixtures from which only the unchanged octahydroanthracenes could be isolated.

Action of Selenium Dioxide on Anthracene.—Anthracene (2 g.) was heated in a sealed tube at 220—230° for 3 hours with selenium dioxide (4 g.) and water (4 c.c.). The product, recrystallised from acetic acid, had m. p. 284—285°, alone or mixed with anthraquinone. Yield, 1·62 g.

No phenanthraquinone could be isolated from a similar experiment with phenanthrene.

Action of Selenium Dioxide on Hexahydropyrene.—A solution of hexahydropyrene (1 g.), selenium dioxide (4 g.), water (4 c.c.), and acetic acid (50 c.c.) was refluxed for 50 minutes. The product, purified from dark impurities through the sparingly soluble picrate, had m. p. 148—150°, alone or mixed with authentic pyrene. Yield, 0·3 g.

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