

# Use of Potassium Bromate : Oxidation of Various Organic Compounds

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**Various organic compounds have been oxidised using potassium bromate in acidic medium.**

POTASSIUM bromate is relatively unknown in the multitude of oxidising agents used in organic chemistry although it has a great potentiality<sup>1</sup>. Its brominating action towards the aromatic nucleus<sup>2</sup> is in competition with the oxidising action and depends largely on the reaction conditions, particularly the strength and nature of the acid and the substrate used.

Anthracene and phenanthrene have been oxidised very smoothly by potassium bromate in boiling acetic acid to the corresponding quinones in very good yields and in pure state through simple work up followed by a single crystallisation. This method seems to be much superior to the conventional methods<sup>3a, 4, 5a</sup> of preparation and purification of these quinones. Evolution of bromine vapour was noted in every experiment. On the other hand naphthalene and acenaphthene did not furnish any pure quinone on several attempts of oxidation by this reagent under various conditions. Diphenylmethane has also been oxidised to benzophenone<sup>6</sup> in almost quantitative yield under similar conditions. Pure  $\alpha$ -tetralone could not be prepared from tetralin by oxidation with potassium bromate in boiling acetic acid for 15 min, possibly due to formation of bromo compounds. When the same reaction was carried out in presence of acetone as bromine scavenger,  $\alpha$ -tetralone (2,4-DNP, m.p. 257°<sup>8b</sup>) was obtained in very poor yield together with other oxidation products. Acetone, however, remained practically unaffected when heated under reflux with potassium bromate in acetic acid. Insufficient quantity of potassium bromate oxidised benzyl alcohol to benzaldehyde<sup>7</sup> (as major product) together with benzoic acid but when the reagent was used in excess, benzoic acid was obtained in quantitative yield. Benzoin was similarly oxidised to benzil<sup>8</sup> in excellent yield which slowly furnished benzoic acid on prolonged heating with excess of the

reagent. Cyclohexanone could not be derived from cyclohexanol<sup>9</sup> under similar conditions, but a sweet smelling compound behaving like an ester was obtained. With this reagent in dilute mineral acid cyclohexanol underwent extensive dehydration and in dilute acetic acid it remained unaffected. The method of  $\text{HO}^{10}$  was also ineffective in this case. Benzophenone was obtained quantitatively when a mixture of benzoic acid, acetic acid and potassium bromate was left at room temperature for two weeks, but when kept for one week the yield was reduced to 50%. However, benzoic acid and 9-hydroxyfluorene-9-carboxylic acid underwent very smooth oxidative decarboxylation by this reagent in boiling acetic acid to produce within 15 min benzophenone<sup>11</sup> and fluorenone<sup>12a</sup>, respectively. In the latter case a small quantity of a bromo-derivative was also obtained, m.p. 148-149°<sup>12b</sup> showing distinctive absorption bands in the ir spectrum at 1415, 1360, 1260, 1055, 840 and 455  $\text{cm}^{-1}$  which were absent in that of fluorenone, the use of acetone during oxidation prevented the simultaneous bromination. When 9-methoxy-10-anthraldehyde<sup>13</sup> was heated under reflux with potassium bromate and a mixture of acetic acid and acetone for 15 min, it was noted very surprisingly that no corresponding carboxylic acid was derived but instead, 9,10-anthraquinone was obtained in excellent yield.

## Experimental<sup>1</sup>

A. *9,10-Anthraquinone*: A mixture of anthracene (8.5 g), acetic acid (100 ml) and potassium bromate (8.2 g) was heated under reflux for 6 min followed by further addition of potassium bromate (8.2 g) and continuing the refluxing for 9 min more. The reaction mixture deposited a yellow solid on cooling which was poured onto water (200 ml), filtered and washed thoroughly with water followed

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by ethanol (2 × 15 ml) to produce air dried material (10.5 g; 100%), m.p. 255-264°. It was crystallised from benzene to furnish pale yellow needles, m.p. 285°<sup>12c</sup>; m.m.p. with authentic 9,10-anthraquinone<sup>12a</sup> remained undepressed and their comparative ir spectra were identical in all respect,  $\nu_{\max}^{(KBr)}$ : 1680, 1593, 1384, 1334, 1305, 1287, 1171, 937, 810, 695 and 622 cm<sup>-1</sup>.

**B. 9,10-Phenanthrenequinone**: To a boiling mixture of phenanthrene (8.5 g) and acetic acid (100 ml) was added potassium bromate (16.5 g in two portions) and the reaction mixture was heated under reflux for 90 min when bromine was evolved. The orange yellow reaction mixture was cooled, poured onto water (200 ml), the separated material (8 g; 76%), m.p. 170-175°, was collected by aforementioned method and crystallised from hot benzene to give orange red crystals, m.p. 202°<sup>12a</sup>, identified as 9,10-phenanthrenequinone through m.m.p. with authentic sample and identical ir spectra,  $\nu_{\max}^{(KBr)}$ : 1676, 1593, 1452, 1386, 1296, 1285, 1231, 770, 764, 719 and 529 cm<sup>-1</sup>.

**C. Benzophenone from diphenylmethane and benzoic acid**: Similarly, a mixture of diphenylmethane (10 g), acetic acid (40 ml) and potassium bromate (15 g) was heated under reflux for 1 hr. The reaction mixture was cooled and poured onto water. The separated material was worked up in the usual way with chloroform followed by bicarbonate wash to furnish a neutral fraction (11 g) which was distilled to produce a colourless oil (8.5 g; 80%), b.p. 155-160°/6 mm, which solidified on standing, m.p. 48° and was characterised as benzophenone<sup>12e</sup> through m.m.p. with authentic sample, 2,4-DNP, m.p. 238°<sup>12e</sup> and identical ir spectra,  $\nu_{\max}^{(KBr)}$ : 1655, 1595, 1575, 1450, 1385, 1320, 1280, 1180, 1150, 1080, 1030, 1000, 950, 920, 820, 770, 710, 700, 640 and 607 cm<sup>-1</sup>.

In a similar way a mixture of benzoic acid (2.1 g), acetic acid (25 ml) and potassium bromate (1.5 g) was heated under reflux for 15 min. The cooled reaction mixture was worked up with chloroform to yield benzophenone (1.7 g; 100%), m.p. 48°<sup>12e</sup>, identified in the usual way.

**D. Oxidation of tetralin**: A mixture of tetralin (13.2 g), acetone (7 ml), glacial acetic acid (50 ml) and potassium bromate (13.5 g) was heated under reflux for 3 hr. The mixture gradually turned dark red. The cooled reaction mixture was poured onto water and worked up with chloroform in the usual way. The red liquid, obtained after removal of the solvent, was distilled twice under reduced pressure to furnish two fractions; (i) b.p. 70-78°/14 mm, (2.7 g), (ii) b.p. 82-84°/14 mm (7.5 g), none responded to Beilstein test for halogen. The latter fraction exhibited the carbonyl band in the ir spectrum at  $\nu_{\max}^{(film)}$  1720 (s) and 1685 (s) cm<sup>-1</sup> and gave in poor yield a red 2,4-DNP which after purification by elution with benzene through a column of neutral alumina melted at 257°<sup>12b</sup>.

#### E. Oxidation of benzyl alcohol:

(i) (*With insufficient potassium bromate*): A mixture of freshly distilled benzyl alcohol (10.8 g), acetic acid (25 ml) and potassium bromate (6.7 g) was heated under reflux for 25 min. Bromine was evolved as usual. The colourless reaction mixture containing deposited solid was cooled, poured onto water and worked up in the usual way with chloroform to produce a neutral part (5.5 g; 51%), b.p. 175-180°. It gave an orange-red 2,4-DNP in good yield, m.p. 236°<sup>12f</sup>, m.m.p. with authentic 2,4-DNP of benzaldehyde remained undepressed. The acidic product derived through sodium bicarbonate extraction followed by acidification and usual work up furnished benzoic acid, crystallised from hot water, (3 g; 49%), m.p. 118-119°<sup>12g</sup>, m.m.p. undepressed. This experiment was repeated in dilute acetic acid (1:1; v/v) with no significant change in product composition.

(ii) (*With excess of potassium bromate*): A mixture of benzyl alcohol (6 g), potassium bromate (12 g) and acetic acid (50 ml) was heated under reflux for 0.5 hr, then poured onto water and worked up with chloroform and sodium bicarbonate in the usual way. The acidic product on crystallisation from hot water gave pure benzoic acid (6.0 g; 96%), m.p. 120-122°<sup>12g</sup>.

**F. Benzil**: A mixture of benzoin (2 g), glacial acetic acid (20 ml) and potassium bromate (2 g) was heated under reflux for 0.5 hr. The cold reaction mixture was poured onto water when a yellow solid separated which was filtered and washed thoroughly with sodium bicarbonate solution followed by water. The air dried material (2 g 100%), m.p. 93-94°, was crystallised from ethanol to produce yellow needles, m.p. 95°<sup>12h</sup>, m.m.p. with authentic benzil remained undepressed and the ir spectra were identical,  $\nu_{\max}^{(nujol)}$ : 1650, 1530, 1450, 1330, 1220, 1185, 1010, 890, 805, 730, 710, 690 and 650 cm<sup>-1</sup>. Benzil, on similar treatment with excess of potassium bromate in boiling acetic acid for 1 hr, underwent oxidation to produce benzoic acid in only 10% yield. The remaining portion was found to be unchanged benzil.

**G. Fluorenone from 9-hydroxyfluorene-9-carboxylic acid**:

(i) A mixture of 9-hydroxyfluorene-9-carboxylic acid (2.5 g; m.p. 167°<sup>12a</sup>), acetic acid (25 ml) and potassium bromate (1 g) was heated under reflux for 15 min. The cooled reaction mixture was poured onto water and worked up in the usual way with chloroform to furnish a yellow neutral liquid (2.5 g) which solidified on standing and responded to Beilstein test for halogen. The product on chromatography over neutral alumina did not afford pure fluorenone. Hence the crude material was treated with a little benzene and filtered to remove the insoluble residue (marked A) which responded to Beilstein test. The mother liquor on subsequent evaporative distillation at

125°/4 mm gave yellow crystals (1 g), m.p. 82-83°<sup>12a</sup>, which was free from Beilstein test. The ir spectrum,  $\nu_{\text{max}}^{\text{(KBr)}}$ : 1835, 1720, 1615, 1605, 1455, 1385, 1300, 1190, 1150, 1100, 920, 815, 765, 745, 735, 670, 652, 500 and 432  $\text{cm}^{-1}$ . It furnished a 2,4-DNP, m.p. 293° (Lit. m.p. 283°<sup>5b</sup>). (Found: C, 63.03; H, 3.22,  $\text{C}_{19}\text{H}_{12}\text{N}_4\text{O}_4$  requires C, 63.33; H, 3.33%).

The residue (marked A) on several crystallisations from a (1 : 1; v/v) mixture of petroleum ether (60-80°) and benzene furnished a yellow crystalline material (0.1 g), m.p. 148-149° which contained bromine and was suggestive of 2-bromofluorenone (Lit. m.p. 149°<sup>12b</sup>). It exhibited several additional absorption bands in the ir spectrum at 1415, 1360, 1260, 1055, 840 and 455  $\text{cm}^{-1}$  which were absent in that of fluorenone.

(ii) A mixture of 9-hydroxyfluorene-9-carboxylic acid (0.5 g), acetic acid (25 ml), acetone (5 ml) and potassium bromate (400 mg) was heated under reflux for 15 min. The greenish reaction mixture was cooled and worked up in the aforementioned method to furnish a yellow solid (300 mg; 75%), m.p. 77-78°, which on crystallisation from a mixture of petroleum ether (60-80°) and benzene (1 : 1; v/v) yielded beautiful crystals, m.p. 82-83°<sup>12a</sup>, identified as fluorenone in the usual way.

H. *Oxidation of 9-methoxy-10-anthraldehyde* : A mixture of 9-methoxy-10-anthraldehyde<sup>13</sup> (100 mg; m.p. 167°), acetic acid (5 ml), acetone (5 ml) and potassium bromate (250 mg) was heated under reflux for 30 min. The solution was found to deposit a yellow solid on the wall of the flask. The cold reaction mixture was poured onto water and extracted in the usual way with chloroform. The organic layer was extracted with sodium bicarbonate solution which on acidification did not furnish any solid material. The neutral part on removal of the solvent furnished a yellow solid (99.8 mg), m.p. 275-280°. It was crystallised from ethanol to produce yellow needles (80 mg), m.p. 284-285°, which remained undepressed on admixture with an authentic sample of 9,10-anthraquinone<sup>12c</sup>. The ir spectrum of this product was found to be identical in all respect with

that of an authentic sample of 9,10-anthraquinone. It was further observed that the starting material gave a red 2,4-DNP derivative, m.p. 215-218°<sup>12</sup> whereas the product did not.

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