

Use of Potassium Bromate. Oxidation of Organic Sulphur Compounds

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Oxidation of various organic sulphur compounds by potassium bromate under different experimental conditions was studied.

POTASSIUM bromate in acid medium¹ could oxidise elemental sulphur and many organic sulphur compounds; the sulphur was generally converted into the hexavalent state. Sometimes the familiar bromination² of the substrate was noted which could be suppressed by using acetone as bromine scavenger³. The developing interest of the chemistry of sulphoxides and sulphones⁴ made the present investigation more attractive. Thiophenol was oxidised either to diphenyldisulphide⁵ in almost quantitative yield or to benzenesulphonic acid (identified through its sodium salt, amide and anilide derivatives) depending on the reaction conditions (*vide* experimental). When thiophenol in aqueous 2 *N* sodium hydroxide containing one molar equivalent of potassium bromate was heated (out of contact with oxygen) over a steam bath for 2 and 4 h, the yields of diphenyldisulphide were 60 and 95%, respectively. It was observed that thiophenol in alkaline medium under the aforementioned condition but in the absence of potassium bromate afforded diphenyldisulphide in only 3-5% yield in 4 h. Oxidation of benzoin in alkaline condition by sodium bromate was the only example previously known⁶.

Diphenyldisulphide was completely oxidised to benzenesulphonic acid on heating under reflux with excess of potassium bromate in acetic acid for a period of 0.5 h. But diphenylsulphide under similar condition (heating for 1 h) furnished a crude product containing diphenylsulphone and other impurities containing brominated products. Use of acetone did not improve the yield. Pure diphenylsulphone⁷, m.p. 127-128°, was isolated by chromatography over silica gel using petroleum ether (b.p. 60-80°) and benzene (90:10, v/v) as eluent. However, diphenylsulphoxide produced the sulphone, m.p. 127°, in excellent yield and in very pure state under similar condition (heating for 35 min). A mixture of 4,4'-dinitrodiphenylsulphide, (4-8) *N* H₂SO₄, acetic acid and dilute solution of potassium bromate (a little over two-thirds molar equivalent) under refluxing condition furnished the corresponding sulphone⁸⁻¹⁰ within 15 min. The purity and yield of the product were excellent. This method was

much superior to that of Fromm and Whittmann⁸, and it may be utilised in the synthesis of the well known antileprotic drug, Dapsone¹¹ (4,4'-diaminodiphenylsulphone). Absence of acetic acid as the solvent affected the yield and quality of the desired product. Potassium bromate or elemental bromine could not oxidise this sulphide in glacial acetic acid under refluxing condition for a period of 1.5 h, the unchanged sulphide was recovered in each case. Impurities in the starting material posed no problem in the isolation of pure sulphone.

An attempt to oxidise 4,4'-diacetylaminodiphenylsulphide¹² with this reagent in boiling acetic acid led to an uncharacterised mixture of compounds containing bromine. Generally this was a noticeable tendency of the ring activators to incorporate bromine atom on the ring of the aromatic sulphides. Of course, the use of acetone prevented the bromine incorporation and 4,4'-diacetylaminodiphenylsulphoxide, m.p. 278-279°¹³, M⁺ 316, was obtained in good yield within 10 min of refluxing.

However, the aliphatic sulphides exhibited the tendency of carbon-sulphur bond cleavage and a sizable amount of carboxylic acid could be obtained. Thus, dibenzylsulphide and dibenzylsulphoxide were partially oxidised to the sulphone¹⁴ by this reagent in boiling acetic acid. Much of the substrates were decomposed to generate a mixture of benzoic acid and benzaldehyde, sulphate ion (identified through BaSO₄) and a host of brominated products responding strongly to Beilstein test from which pure sulphone could be isolated in poor yield in a laborious way. In the presence of acetone, dibenzylsulphide underwent smooth oxidation to dibenzylsulphoxide by this reagent through heating under reflux in acetic acid for 0.5 h. Dibenzoyldisulphide, m.p. 132°¹⁵, readily furnished benzoic acid and sulphate ion by this process of oxidation in acetic acid under similar condition.

Dibutylsulphide and thiophene could not be oxidised to the sulphones with potassium bromate in acetic acid either at room temperature or at elevated temperature with or without acetone. In each case,

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only tarry material was obtained which strongly responded to Beilstein test. Fifty per cent of thiophene could be recovered from this tar. Dimethylsulphoxide underwent an exothermic reaction with potassium bromate in either acetic or dilute sulphuric acid and all attempts to isolate the desired sulphone through distillation failed due to small explosions.

Experimental¹⁻³

The m.ps. and b.ps. are uncorrected. Each experiment was repeated several times. Products were identified through their m.p., preparation of suitable derivatives, m.m.p. with authentic samples, elemental and spectral analyses. Ir spectra were taken in Perkin-Elmer 177, 297 and 597 spectrophotometers. Generally, the sulphones exhibited absorption¹⁸ at 1120-1170 and 1300-1380 cm^{-1} , particularly the aromatic sulphones at 1350-1380 cm^{-1} and the sulphoxides at 1050 cm^{-1} .

Diphenyldisulphide :

(i) *Under 90°, potassium bromate in excess :* Potassium bromate (0.5 g) was added in small portions to a mixture of thiophenol (1.1 g, Wilson Laboratory, Bombay) and glacial acetic acid (3 ml) with shaking. The reaction was initiated by warming and controlled at 70-75° for 0.5 h. Finally the cold reaction mixture containing some solid was poured into cold water (50 ml). The precipitated brownish solid material was filtered, washed thoroughly with water and dried to furnish diphenyldisulphide, m.p. 59-60°, in almost quantitative yield. On crystallisation from ethanol it gave colourless needles (80%), m.p. 60-61°¹⁷, m.m.p. with authentic sample remained undepressed (Found : C, 65.90; H, 4.33. $\text{C}_{12}\text{H}_{10}\text{S}_2$ requires C, 66.05; H, 4.58%); ν_{max} (nujol), 1572, 1460, 1435, 1375, 1295, 1175, 1155, 1095, 1070, 1020, 995, 900, 842, 735 and 685 cm^{-1} , identical in all respect with that of authentic sample; all protons appeared at $\delta(\text{CCl}_4)$ 7-7.6 ppm; m/e (relative intensity) 218 (35), M^+ ; 154 (16), $\text{C}_{12}\text{H}_{10}^+$; 109 (100), $\text{C}_6\text{H}_6\text{S}^+$; 77 (15), C_6H_5^+ and 69 (26), C_6HS^+ .

(ii) *By the use one-sixth molar quantity of KBrO_3 :* To a hot mixture of thiophenol (1.1 g) and glacial acetic acid (3 ml) was added potassium bromate (275 mg) in several portions. The reaction mixture started boiling briskly each time with addition of KBrO_3 , then it was heated under reflux for 0.5 h, cooled and poured on ice-cold water when solid material was obtained (1 g, 90%), m.p. 58-59°, which on crystallisation from ethanol gave colourless needles, m.p. 60-61°, m.m.p. with diphenyldisulphide remained undepressed.

In alkaline medium : Thiophenol (3.3 g) was dissolved in sodium hydroxide solution (2 N, 40 ml) and potassium bromate (5 g) was added to it. The reaction mixture was heated on a steam-bath for 4 h out of contact of oxygen, then cooled and diluted with water (60 ml). Usual work-up with a mixture of ether and benzene furnished a neutral product

(3.1 g, 94%), m.p. 58-59°, which was identified as diphenyldisulphide in the usual way. In the parallel experiments withholding the reagent it was observed that diphenyldisulphide was obtained to the extent of 3-5% yield. Use of large excess of potassium bromate or heating on the steam-bath for a longer period of time did not affect the yield of the desired product. The use of smaller quantity of the oxidant or reducing the heating period resulted in low yield of the desired product.

Benzenesulphonic acid :

(i) *From thiophenol :* To a mixture of thiophenol (11.0 g) and glacial acetic acid (33 ml) potassium bromate (17 g) was added in small portions. A violent reaction started which needed external cooling by ice. When about 3-4 g of the reagent was added the reaction subsided, brownish crystalline solid appeared which gradually dissolved on warming on a steam-bath. To the resultant brown solution potassium bromate was added portionwise (0.5 g) at regular intervals. Each addition resulted in boiling and gradually the reaction mixture turned red with the evolution of bromine vapour. It was heated under reflux for further 30 min, cooled, diluted with water (100 ml), treated with sodium bisulphite, neutralised with sodium bicarbonate and finally saturated with sodium chloride and cooled (0-5°). The crystals, thus obtained, were filtered and washed thoroughly with cold brine and dried to furnish flakes of sodium benzenesulphonate¹⁹ (9.0 g, 50%). The mother liquor on concentration yielded the second crop (4.5 g, 25%). The sodium salt was converted to the chloro-derivative by treatment with phosphorus pentachloride, and then to the amide, m.p. 150-152°¹⁹, and anilide, m.p. 109-110°¹⁹, derivatives in the usual way. The crude sodium benzenesulphonate (2 g) was cooled in ice and treated with 2 N HCl in dry ethanol (15 ml) with shaking and then filtered. The filtrate was evaporated to dryness. Dry benzene (5 × 50 ml) was added to the brown oily residue and distilled to remove water. The product, thus obtained, was dried under vacuum for several hours at about 60° and then kept in an ice chest when the product became crystalline, m.p. 45-50° (Reported m.ps. $\text{C}_6\text{H}_5\text{SO}_3\text{H}$, 1.5 H_2O , 43-44° and $\text{C}_6\text{H}_5\text{SO}_3\text{H}$, 65-66° (50-51°)¹⁹).

(ii) *From diphenyldisulphide :* To a mixture of diphenyldisulphide (1.1 g) and glacial acetic acid (3 ml) potassium bromate (1.7 g) was added and the mixture was heated on a steam-bath for 0.5 h. The reaction mixture was cooled and poured onto water (50 ml). The crystals, thus obtained, were filtered, dried and identified as the starting material (1.1 g), m.p. 58-59°, m.m.p. remained undepressed. In a separate experiment, a mixture of the reactants in the above proportions was heated under reflux for 0.5 h when bromine evolved. The reaction mixture was cooled, poured onto water (50 ml), and worked up in the aforementioned method to furnish sodium benzenesulphonate (700 mg).

Diphenylsulphone :

(i) *From diphenylsulphide :* A mixture of diphenylsulphide^{2a}, b.p. 178-184°/10-12 mm, (1 g), glacial acetic acid (5 ml) and potassium bromate (1 g) was heated under reflux for 1 h. Bromine was evolved and the cold reaction mixture was poured onto ice-water (100 ml). Usual work up with chloroform furnished a neutral brown solid (1 g) which strongly responded to Beilstein test and melted below 100°. Repeated crystallisations could not produce pure sulphone. Therefore, a column of silica gel (60-120 mesh, B.D.H., L.R.) was prepared in petroleum ether (b.p. 60-80°) and elutions were made with the same eluent followed by a mixture of petroleum ether (b.p. 60-80°) and benzene (90 : 10, v/v). The desired sulphone came in the latter part and was crystallised from ether to furnish colourless crystals of pure diphenylsulphone (100 mg), m.p. 127-128°²⁰ (Found : C, 65.94; H, 4.46. $C_{12}H_{10}O_2S$ requires C, 66.05; H, 4.58%); ν_{max} (nujol) 1580, 1460, 1450, 1380, 1315, 1298, 1185, 1160, 1110, 1075, 1030, 1007, 770, 740, 700 and 695 cm^{-1} . The materials collected in the earlier fractions during elution were impure bromo-compounds.

(ii) *From diphenylsulphoxide :* To a solution of diphenylsulphoxide¹⁴, m.p. 70° (10 g) in glacial acetic acid (30 ml) was added potassium bromate (5 g) and the reaction mixture was heated under reflux for 2 h. The reaction exhibited a strange phenomenon of developing a red colour followed by its discharge in a very periodic manner (3-7 times depending on the quantity of the substrate). After 1 h of reflux the red colour of bromine persisted and refluxing was continued for further 1 h when some bromine vapour escaped. The cooled reaction mixture was poured onto water (200 ml) when colourless crystalline material separated which was filtered, washed thoroughly with water followed by sodium bicarbonate solution and water to furnish shining crystals of diphenylsulphone (8 g, 80%), m.p. 127° which remained undepressed on admixture with the previously prepared sample.

4,4'-Dinitrodiphenylsulphone :

Potassium bromate (0.75 g, dissolved in 10 ml of warm water) was added dropwise to the boiling solution of 4,4'-dinitrodiphenylsulphide (1 g) in a mixture of glacial acetic acid (35 ml) and sulphuric acids (8 N, 10 ml) in course of 5 min. Boiling was continued for further 10 min when bromine evolved and much solid was deposited. The reaction mixture was cooled, poured onto cold water (100 ml), filtered and washed successively with water, saturated sodium bicarbonate solution, distilled water, and dried to yield 4,4'-dinitrodiphenylsulphone (1.05 g, 94%), m.p. 258-259°, which on crystallisation from acetic acid generated colourless needles, m.p. 258-260°²⁰, m.m.p. remained undepressed when mixed with a sample obtained by the method of Fromm and Whittmann⁹ and (Found : C, 46.69; H, 2.51. $C_{12}H_8N_2O_6S$ requires C, 46.75; H, 2.59%); ν_{max} (KBr) were identical in all respect exhibiting 1618,

1555, 1408, 1355, 1315, 1168, 1105, 1010, 861, 765, 738, 685, 622, 605 and 565 cm^{-1} .

4,4'-Diacetylaminodiphenylsulphoxide : A mixture of 4,4'-diacetylaminodiphenylsulphide (300 mg; m.p. 218°^{12a}) (prepared by the reduction of 4,4'-dinitrodiphenylsulphide by tin and concentrated hydrochloric acid followed by acetylation of the product with acetic anhydride), glacial acetic acid (10 ml), acetone (2 ml) and potassium bromate (135 mg) was heated under reflux for 10 min. The brown reaction mixture was cooled and poured onto ice-cold solution of salt and sodium bicarbonate. The separated pale yellow solid was filtered, thoroughly washed with cold water and dried (297 mg, 90%), m.p. 275-277°. The mass spectrum of this crude product indicated the presence of sulphone and sulphide along with the sulphoxide, *m/e* 332, $C_{16}H_{16}N_2O_4S^+$; 316, $C_{16}H_{16}N_2O_3S^+$; 300, $C_{16}H_{16}N_2O_2S^+$; 140, $C_6H_4SO_2^+$ (from sulphone); 124, $C_6H_4SO^+$ (from sulphoxide); and 108, $C_6H_4S^+$ (from sulphide). Crystallisation of the crude product from hot ethanol after charcoal treatment generated colourless crystals (200 mg, 60%), m.p. 278-279°^{12a} (Found : C, 60.60; H, 5.01. $C_{16}H_{16}N_2O_3S$ requires C, 60.76; H, 5.06%); ν_{max} (nujol) 1685, 1670, 1600, 1585, 1528, 1492, 1455, 1389, 1370, 1305, 1262, 1175, 1150, 1085, 1070, 1035, 1010, 960, 845, 835, 818, 738, 715, 700, 630, 620 and 600 cm^{-1} .

Dibenzylsulphoxide : A mixture of dibenzylsulphide¹⁴ (1 g; m.p. 49-50°), glacial acetic acid (5 ml), acetone (10 ml) and potassium bromate (0.5 g) was heated under reflux on a steam-bath for 0.5 h. The reaction mixture was then basified with sodium hydroxide (3.5 g), liquor ammonia (5 ml) and sodium sulphide (1 g), and again refluxed for 30 min and cooled. On work up with chloroform in the usual way it furnished a neutral solid, m.p. 120-125°, which was crystallised from a mixture of petroleum ether (b.p. 60-80°) and benzene (50 : 50, v/v) to afford colourless crystals (700 mg), m.p. 134°¹⁴. Recrystallisation from aqueous ethano-produced pure sample which was found to be identical in all respect with an authentic sample¹⁴ o; dibenzylsulphoxide, m.p. 134° (Found : C, 72.94; H, 6.36. $C_{14}H_{14}OS$ requires C, 73.04; H, 6.08%); ν_{max} (KBr) 1620, 1490, 1450, 1405, 1380, 1070, 1030 775, 695 and 470 cm^{-1} .

Dibenzylsulphone :

(i) *From dibenzylsulphide :* Potassium bromate (1.5 g) was added to dibenzylsulphide (2 g) dissolved in glacial acetic acid (15 ml) and the mixture was heated under reflux for 1 h. There was no evolution of bromine and the brown reaction mixture was left at room temperature when some colourless solid separated in course of 40 h. The crystals were filtered, washed with acetic acid and identified as potassium sulphate (600 mg). There was no excess of potassium bromate in the mother liquor which was diluted with water (100 ml) and on usual work up with chloroform and bicarbonate extraction followed by acidification of the alkaline layer with

concentrated hydrochloric acid no solid material could be isolated. Moreover, when the reaction was carried out in presence of large excess of potassium bromate, huge quantity of solid material, identified as benzoic acid, was obtained. The highly lachrymatory neutral organic layer furnished a brown oil which on evaporative distillation furnished (A) b.p. 145°/5-7 mm (300 mg), identified as benzaldehyde through 2,4-D.N.P., m.p. 234-236°²¹, m.m.p. with authentic sample remained undepressed, and (B) 180-195°/5-7 mm (400 mg), reddish crystals which did not contain bromine. On crystallisation from ether (B) furnished colourless dibenzylsulphone, m.p. 150-151° (Found : C, 67.88 ; H, 5.74. C₁₄H₁₄O₂S requires C, 68.29 ; H, 5.69%) ; ν_{\max} (KBr) 1605, 1500, 1460, 1415, 1385, 1330, 1305, 1285, 1250, 1190, 1145, 1130, 1120, 1075, 1050, 920, 825, 775, 760, 730, 705, 695, 628, 605, 570, 525, 500 and 450 cm⁻¹.

(ii) *From dibenzylsulphoxide* : To a solution of dibenzylsulphoxide¹⁴, m.p. 132-133° (1.5 g) in glacial acetic acid (5 ml) was added potassium bromate (0.5 g) and the mixture was heated under reflux for 0.5 h. To the resultant yellow solution the second portion of potassium bromate (0.5 g) was added, heating was continued for 0.5 h when much bromine was evolved. The cooled reaction mixture, on work up with chloroform and sodium bicarbonate, furnished the neutral part as a colourless oil (400 mg) with the characteristic smell of benzaldehyde, confirmed through m.p. and m.m.p. of the 2,4-D.N.P. derivative. This oil also contained a solid which on crystallisation from petroleum ether (b.p. 60-80°) containing a few drops of ethanol furnished the colourless crystals of dibenzylsulphone (300 mg), m.p. 150°, m.m.p. with previously prepared sample remained undepressed. The aqueous mother liquor furnished BaSO₄ (1.1 g) on treatment with BaCl₂. From the alkaline extract benzoic acid (700 mg ; m.p. 122°, m.m.p. undepressed) was obtained.

Oxidation of dibenzoyldisulphide :

Dibenzoyldisulphide was prepared in a modified way¹⁵. Dry benzene (4×100 ml) was added to hydrated sodium thiosulphate (12.5 g) and was slowly distilled to remove water. About 3 ml of water was thus removed. To this dry sodium thiosulphate were added dry benzene (25 ml) and benzoylchloride (6 ml) and the mixture was stirred at room temperature for 16 h and then heated over a steam-bath for 6 h. The benzene layer was separated and distilled to remove benzene and unreacted benzoyl chloride. The brown residue (4 g) was crystallised from hot ethanol to furnish colourless plates (3.5 g, 50%), m.p. 132-135° (Found : C, 61.40 ; H, 3.84. C₁₄H₁₀O₂S₂ requires C, 61.31 ; H, 3.65%) ; ν_{\max} (nujol) 1900 (v.w.), 1822 (v.w.), 1765, 1690, 1680, 1588, 1572, 1455, 1438, 1375, 1370, 1330, 1308, 1300, 1235, 1200, 1170, 1095, 1070, 1020, 992, 970, 925, 915, 880, 845, 770, 680, 670, 640, 625 and 608 cm⁻¹.

A mixture of dibenzoyldisulphide (162 mg), glacial acetic acid (10 ml) and potassium bromate (200 mg) was heated on the steam-bath for half an hour. The reaction mixture on usual work up with chloroform and bicarbonate afforded benzoic acid (120 mg, 85%, m.p. 121°, m.m.p. undepressed) and the aqueous mother liquor furnished BaSO₄ in almost quantitative yield.

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