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Short Communications

KINETICS OF INHIBITED DECOMPOSITION OF BENZOYL PEROXIDE WITH NOVALAC RESIN

A.H.K. Yousufzai, M.M. Zafar and S. A. Husain

PCSIR Laboratories, Karachi 39

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The decomposition of peroxides is widely used to catalyse many important reactions such as vinyl polymerisation. The decomposition of benzoyl peroxide, the most widely used initiator has been studied in detail.[1-4] Bartlett *et al.*[1] and Cass[2] measured the rates of spontaneous decomposition by iodometric titrations and showed that the disappearance of peroxide can be expressed as follows:

$$-d(p)/dt = K_d[p] + K_i[p]^x \quad (1)$$

where $-d(p)/dt$ represents the rate of decomposition of peroxide. K_d specific rate of spontaneous cleavage, K_i the specific rate of induced decomposition and x the order of induced decomposition which may vary between 0.5–2.

Stockmayar *et al.*[3] used the suppression of induced decomposition reaction by inhibitors to isolate the rate of spontaneous decomposition of benzoyl peroxides. They have shown that the rate of decomposition of peroxides in the presence of these inhibitors (dioxane, styrene, methyl methacrylate) is essentially equal to the rate of spontaneous homolytic cleavage.

Bawn and Mellish[4] have employed the highly coloured stable free radical, 2,2-diphenylpicrylhydrazyl, which is an inhibitor and combines directly with the radicals produced by the benzoyl peroxide on spontaneous decomposition. The rates were measured by colorimeter, since the highly coloured inhibitor disappears after the reaction with the radicals produced by benzoyl peroxide. Williams *et al.*[6] later found that the reproducibility achieved with this inhibitor was not good and moreover the rates of reactions were found to depend upon the history of the sample of DPPH, particularly on the solvent from which it was recrystallised and temperature of drying. The authors, however, found that the method used by Lothe and Eia[5] using the galvinoxyl radical as inhibitor was more dependable.

In the present work it has been found that the acid-catalysed phenol formaldehyde resin (novalac resin) reacts rapidly with the radicals produced by the thermal decomposition of benzoyl peroxide giving highly coloured compound, which has been measured colorimetrically. The rates of spontaneous decomposition of benzoyl peroxide were determined and were compared with already deduced values and activation energies.

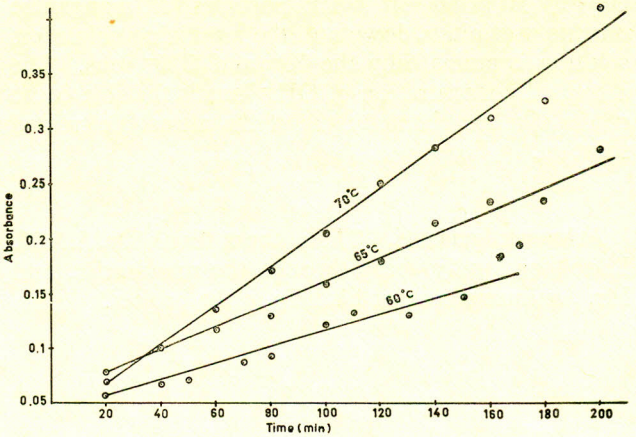

Fig. 1. The absorbance at 500 nm vs. the time of reaction plots between novalac resin and benzoyl peroxide at 60 65 and 70°C.

Table 1. Specific Rate Constants for the Spontaneous Decomposition of Benzoyl Peroxide.

Temperature (°C)	K_d(sec^{-1})	K_d (sec^{-1}) (Lit. values)
60	2.0×10^{-6}	1.95×10^{-6}
65	4.5×10^{-6}	—
70	8.9×10^{-6}	—
80	4.4×10^{-5}	4.4×10^{-5}

Experimental and Results

Materials and Methods

(1) Benzoyl peroxide of M/s Laporte Chemicals, England was used and was recrystallised in chloroform, m.p. 103°C.

(2) Novalac resin was prepared by reacting phenol with formalin (37%) in the ratio of 1:0.8 moles in the presence of an oxalic acid catalyst (3% of the weight of phenol). The resin was vacuum-dried at 80°C.

(3) Kinetic experiments were carried out in absolute ethanol (spectroscopically pure). 1.0% solution of benzoyl peroxide and 1.0% solution of novalac resin were mixed in a reaction vessel and kept in a thermostatically controlled water-bath. The samples were taken out at regular intervals of time and the colorimetric measurements were made with Specktromom 360 at 500 nm. The reactions were carried out at 60, 65, 70 and 80°C. The absorbance vs. the time of reaction plots are given in Fig. 1.

The values of activation energy obtained was 29.5 kcal/mole compared to the average lit. values of 30.0 kcal/mole.

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Pakistan J. Sci. Ind. Res., Vol. 15, No. 3, June 1972

STUDIES ON THE SYNTHESIS OF 2,4,6-TRIMERCAPTO-S-TRIAZINE AND A POLYMER OF THIOCYANIC ACID

NISAR AHMAD* and N.A. WARSI

PCSIR Laboratories, Karachi 39

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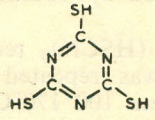
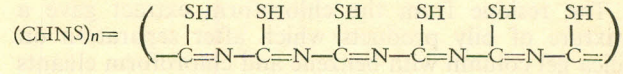
A survey of the literature on 2,4,6-trimercapto-*s*-triazine revealed that this compound can be used as a retarder for photographic emulsions[1] and as a vulcanization accelerator for chlorinated and synthetic rubbers.[2] Moreover, it also exhibits chemosterilant property and inhibits the reproduction of house-flies. The reproduction potential of 2,4,6-trimercapto-*s*-triazine (50) and that of its heavy metal salts (78) have been evaluated.[3] So it appeared interesting to investigate the synthesis of 2,4,6-trimercapto-*s*-triazine from easily available ammonium thiocyanate and sodium hydrogen sulphate. The formation of this compound from cyanuric chloride and sodium sulphide was first reported by Hofmann.[4] Later Klason[5] prepared it (yield 75%) from cyanuric chloride and potassium hydrogen sulphide. The most attractive procedure for its preparation (86% yield) has been described from cyanuric chloride and thiourea in acetone medium.[6] Its formation was also detected by Birckenbach *et al.*[7] during the synthesis of solid and liquid thiocyanic acid from potassium thiocyanate and potassium hydrogen sulphate but no information is available about the actual synthesis of 2,4,6-trimercapto-*s*-triazine and its yields. The yield of the liquid thiocyanic acid was reported to be 24.5–33.9% and the experiment was done in a specially designed evacuated equipment using liquid air for condensation of the gases.

Ammonium thiocyanate and anhydrous sodium hydrogen sulphate was used for the synthesis of 2,4,6-trimercapto-*s*-triazine. The experiments have been performed at different temperatures ranging from 100–170°C using 1–3.5 moles of sodium hydrogen sulphate for 1 mole of ammonium thiocyanate. The yields were dependent upon the temperature, molar ratios of the materials and the reaction medium. Excess of molten sodium hydrogen sulphate also serves as a reaction medium. It was observed that the optimum temperature was 130–140°C and the highest yield was obtained by reacting 3–3.5 moles of anhydrous sodium hydrogen sulphate with 1 mole of ammonium thiocyanate. 2,4,6–Trimercapto-*s*-triazine is soluble in sodium hydroxide and also in sodium bicarbonate solutions but the polymer is soluble only in sodium hydroxide solution. The selective solubility was used for the separation of the polymer from the triazine. Small amounts of sulphur impurities present in the polymer were removed by extraction with excess of carbon tetrachloride or benzene.

The experiments were carried out in boiling acetone with the same molar ratios of the starting materials as in the previous experiments. The yield of 2,4,6-trimercapto-*s*-triazine was more and the highest yield (22.8%) was obtained by reacting 3.5 moles of sodium hydrogen sulphate with 1 mole of ammonium thiocyanate. The reaction in acetone medium at room temperature yielded no 2,4,6-trimercapto-*s*-triazine and the polymer but a complex oily mixture of more than four compounds (thin layer) indicating in IR at 1715 and 2100 cm^{-1} the presence of >C=O and C—N absorption bands respectively. The authors confine to the study of synthesis of 2,4,6-trimercapto-*s*-triazine and the polymer (CHNS)*n*.



The mol wt of the polymer (≃6000) was determined by ebullioscopic method[8] in pyridine. When one compares this polymer with cyamelide,[9] a polymer of isocyanic acid obtained during the preparation of cyanuric acid, one finds a great difference between their properties and structures. Cyamelide, having free =NH groups, is insoluble in sodium hydroxide and organic solvents, while the polymer from thiocyanic acid is soluble in sodium hydroxide solution and also to some extent in some of the polar organic solvents like pyridine, dioxane and insoluble in sodium bicarbonate solution and less polar common organic solvents. The difference in solubility with that of 2,4,6-trimercapto-*s*-triazine and cyamelide and its salt formation with strong alkali suggests that it is a linear polymer having free —SH groups as indicated by the following structure:



It is less acidic than 2,4,6-trimercapto-*s*-triazine because it does not have cyclic resonance structure like that of the *s*-triazine.

Experimental

Preparation of 2,4,6-*trimercapto*-s-*triazine and the polymer* (CHNS)*n*

Method 1. Ammonium thiocyanate (7.6 g, 0.1 mole) and anhydrous sodium hydrogen sulphate (34.5g, 0.25 moles) were mixed in a round bottomed-flask fitted with a condenser having a calcium chloride-tube at the top and the mixture heated for about 30 min at 100–110°C on an oil-bath and the flask was cooled. The contents of the flask were mixed thoroughly with water and filtered. The insoluble

*Now at Org. Chemishes Institut der Universitat Bonn, Meckenheimer Allee 168, 53 Bonn, West Germany.

residue which was mainly a mixture of 2,4,6-trimercapto-*s*-triazine, sulphur and the polymer $(HSCN)_n$, was dried under vacuum.

The residue was dissolved in 10% NaOH solution (0.35 moles), filtered and the filtrate acidified with HCl to pH 1. The yellow precipitate thus obtained was washed with water, then dissolved in 5% solution of sodium bicarbonate and again filtered. The filtrate containing sodium salts of 2,4,6-trimercapto-*s*-triazine was again acidified with HCl to pH 1. The yellow pricipitate of 2,4,6-trimercapto-*s*-triazine was filtered, washed with water and dried under vacuum (yield 0.4258 g). (Found S, 55.26. $C_3H_3N_3S_3$ requires: S, 54.23%); m.p. (dec) above 360°C.)

The insoluble precipitate from sodium bicarbonate solution was that of the polymer containing some elemental sulphur. This precipitate was thoroughly washed with distilled water and dried. The polymer was further purified by extracting elemental sulphur with excess of benzene or carbon tetrachloride (200 ml for 1 g of the polymer) yield of the polymer, 3.4858 g; m.p. (dec) above 340°C.

Mol wt determined by ebullioscopic method in pyridine ≃6000.

(Found S, 55.60; $(HSCN)_n$ requires: S, 54.23%).

The experiment was repeated at three different temperatures between 100–170°C and with 0.15–0.35 moles of sodium hydrogen sulphate for 0.1 mole of ammonium thiocyanate. The results are given in Table 1. The highest yields of 2,4,6-trimercapto-*s*-triazine (7.8%) and that of the polymer (77.2%) were obtained at 130–140°C from ammonium thiocyanate and sodium hydrogen sulphate (molar ratio 1:3.5).

Method 2. (In acetone medium). Ammonium thiocyanate (0.1 mole) and anhydrous sodium hydrogen sulphate (0.35 moles) were mixed with 100 ml of acetone and stirred for 6 hr at room temperature. The solvent was evaporated under vacuum, the product taken up in chloroform and washed with water. The chloroform extract was then further washed with sodium hydroxide solution and water, dried (Na_2SO_4) filtered and evaporated to dryness. The washings with sodium hydroxide gave no precipitate after acidifying with HCl to pH 1, indicating that no 2,4,6-trimercapto-*s*-triazine or the polymer was formed.

The residue from the chloroform extract gave a mixture of oily products which after separation on silica gel column with benzene and chloroform eluants gave two main oily fractions. The compounds showed strong >C=O and C—N absorption bands in IR. These oily compounds were not studied further as the authors confined their studies to the synthesis of 2,4,6-trimercapto-*s*-triazine and the polymer alongwith its structure.

The experiment was then performed in boiling acetone with the same amount of materials as in the above experiment. The contents of the flask were refluxed for 2.5 hr, acetone was evaporated under vacuum and the residue worked up as in method No. 1. The experiment was repeated using 0.15–0.35 moles of anhydrous sodium hydrogen sulphate for 0.1 mole of ammonium thiocyanate. The results of these experiments are also summarised in Table 1. The highest yield of 22.8% for 2,4,6-trimercapto-*s*-triazine was obtained with 0.35 moles of sodium hydrogen sulphate.

TABLE 1. THE PERCENTAGE YIELD OF 2,4,6-TRIMERCAPTO-*s*-TRIAZINE AND THE POLYMER UNDER DIFFERENT CONDITIONS.

Temperature (°C)	Molar ratio (ammonium thiocyanate–sodium hydrogen sulphate)	Percentage yield of 2,4,6-trimercapto-*s*-triazine based on ammonium thiocyanate	Percentage yield of the polymer based on ammonium thiocyanate
100–110	1: 1.5	9.6	31.7
,,	1: 2	7.3	44.1
,,	1: 2.5	7.5	60.1
,,	1: 3.5	6.7	70.2
130–140	1: 1.5	8.8	46.6
,,	1: 2	8.0	70.3
,,	1: 2.5	6.5	68.1
,,	1: 3.5	7.8	77.2
160–170	1: 1.5	4.1	48.2
,,	1: 2	7.4	53.7
,,	1: 2.5	6.2	45.9
,,	1: 3.5	6.4	54.2
In boiling acetone	1: 1.5	5.6	38.1
,,	1: 2	10.5	42.4
,,	1: 2.5	11.0	59.1
,,	1: 3.5	22.8	50.1

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Pakistan J. Sci. Ind. Res., Vol. 15, No. 3, June 1972

ISOLATION OF PSORALENE AND ANGELICIN FROM PSORALEA PLICATA DEL

VIQAR UDDIN AHMAD and ANWER BASHA

Postgraduate Institute of Chemistry, University of Karachi, Karachi 32

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Psoralea plicata Del. (N.O. Papillionaceae) is a much branched under-shrub about 1–2 ft high, and is found

in the Sind and the Punjab areas of Pakistan. It can be differentiated from the more common *Psoralea corylifolia* Linn. in having trifoliate leaves instead of simple leaves in the latter species. In the present work Psoralene and Angelicin have been isolated from the shoots of *Psoralea plicata* Del.

The ether-soluble fraction of total extractive from 1435 g aerial parts of *Psoralea plicata* was dissolved in benzene and filtered through a column of deactivated neutral alumina (150 g). The column was eluted with benzene. A light yellow essential oil was eluted first followed by a fraction which on evaporation yielded an almost colourless crystallisate melting at 115°C. TLC of this crystallisate on silica gel PF 254 (Merck) plate with benzene–chloroform (1:1) showed that it is a mixture of two substances of R_f values 0.25 and 0.33. The mixture (1.5 g) was rechromatographed over neutral alumina (Brockmann activity I) and the column eluted with benzene, 30 fractions of 10 ml each were collected. The first 5 fractions which gave a single spot of R_f 0.33 on TLC plate with the above developing solvent were combined and evaporated. The crystalline residue was recrystallised from ether to yield colourless needles m.p. 137–39°C, which analysed for $C_{11}H_6O_3$ (Found: C, 71.17; H, 3.52%). $C_{11}H_6O_3$ requires: C, 70.96; H, 3.22%). It was identified as angelicin (isopsoralene) (lit. m.p. 139).[1] Its NMR is also identical with that of angelicin.[2]

The final four fractions on evaporation yielded a crystalline residue which appeared uniform on TLC plate (R_f 0.25). On recrystallisation from ether it was finally obtained as colourless prismatic needles m.p. 161–62° which analysed for $C_{11}H_6O_3$ (Found: C, 70.79; H, 3.47%), mol wt 189.1. $C_{11}H_6O_3$ requires: C. 70.96: H, 3.22%, mol wt 186). λ_{max} 247 nm 247 nm, 293 nm, shoulder at 330 nm. It was identified as psoralene, by comparison of its IR spectrum (nujol) with a standard spectrum of the compound,[3] whereby two spectra proved to be completely superimposable. It should be noted that Spath and his coworkers have reported[4] m.p. of pure psoralene as 171°C. However, Horning and Reisner[5] failed to raise its m.p. beyond 160–162°C. M.p. of chromatographically pure sample was 161–62°C. Total yields of psoralene and angelicin were 0.4 g, (0.028%) and 0.6 g (0.042%) respectively.

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Pakistan J. Sci. Ind. Res., Vol. 15, No. 3, June 1972

CHEMICAL INVESTIGATION OF PROSOPIS GLANDULOSA

M. IKRAM, M. ISRAR Khan and A. RAZZAQ

PCSIR Laboratories, Peshawar

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Prosopis glandulosa is a shrub abundantly available in West Pakistan. Manzoor-i-Khuda *et al.*[1] have investigated the leaves of the plant, but no work has been done on its fruits. They have isolated two alcohols i.e. proposal, $C_{29}H_{56}O$, m.p. 83.5°C, prosopanol $C_{30}H_{50}O_3$, m.p. 245°C, and β-sitosterol. In the present work the ripe fruits of *P. glandulosa* were investigated. Soxhlet extraction of the powdered seeds with hexane and subsequent purification of the hexane extract gave colourless crystals, m.p. 235–37°C, acetate m.p. 158–60°C. It gave grey colour with Lieberman–Burchard test and yellow to reddish colour with Salkowski test. The compound was analysed for $C_{36}H_{60}O_4$. Its acetate was analysed for $C_{40}H_{64}O_6$, showing the presence of two OH groups in the original compound. It also form 2,4-dinitrophenylhydrazone m.p. 135–36°C, indicating the presence of keto group, as well. The IR spectra of the original compound shows peaks at 3400 (OH) and 1700(C=O) cm^{-1} and its acetate shows peaks at 1735(ester), 1690 (C=O) and 1240(ester) cm^{-1}. The compound is provisionally named as prosopanol G.

A portion of the concentrated hexane extract, on column chromatography, gave a crystalline compound m.p. 139–40°C and identified to be β-sitosterol. The hexane extracted material, on further soxhlet extraction with ethanol and purification, yielded a mixture of sugars in 5% yield. The sugars were found to be sucrose, glucose and fructose by paper chromatography. The alcoholic extract of the fruits, on purification and chromatography, yielded an alkaloid m.p. 240–42°C. The alkaloid was found to be of an indole type. It could not be analysed, due to its evry small quantity.

Experimental

All m.ps. are uncorrected. The analysis was done by Dr. F.B. Strauss, Microanalytical Laboratory, Oxford. IR spectra were taken in KBr and nujol on Perkin-Elmer spectrophotometer.

Isolation of Prosopanol G. 1.5 kg of fully ripe fruits were dried, cut into small pieces and soxhleted with hexane (b.p. 62°C) for about 8 hr. The major portion of the hexane was distilled off and the concentrated extract (extract A) kept in refrigerator. A white powder settled at the bottom of the flask, which was filtered and repeatedly crystallised from methanol. The crystalline compound has m.p. 235–37°C, yield 0.054%, $[\alpha]_D^{18} = +55$ (C_2H_5OH; C=0.5). Found: C, 77.53; H. 10.82; mol wt 518. $C_{36}H_{60}O_4$ requires: C, 77.69; H, 10.79%; mol wt 556). ν_{max} (KBr)=3400 (OH) 2950, 1700=(C=O), 1460 and 1380 cm^{-1}.

It gave grey colour with Lieberman–Burchard test and yellow to reddish colour with Salkowski test.

Acetate of Prosopanol G. Its acetate was prepared by usual methods, using sodium acetate and acetic anhydride and the compound was crystallised through C_2H_5OH, m.p. 158–60°C. (Found C, 75.69; H, 9.84. $C_{40}H_{64}O_6$ requires: C, 74.96; H, 10.06%). ν_{max} (nujol)=2950, 1735 (acetate), 1690(C=O), 1240 (acetate) cm^{-1}.

Preparation of 2,4-Dinitrophenyl Hydrazone. The hydrazone of the compound was prepared by usual methods, and crystallised through ethanol, m.p. 135–360°C.

Isolation of β-Sitosterol. A small portion of extract 'A' left after the separation of steroid was chromatographed over alumina (Brockmann) using benzene for elution. Four fractions of 100 ml each were collected. First fraction on removal of solvent did not gave any crystalline product. The remaining three fractions, on removing solvent and crystallising the residue from acetone, gave a compound melting at 139–40°C. It gave positive Liebermann–Burchard test and was found to be β-sitosterol by its mixed m.p. with the authentic sample and by comparing the m.p. of its acetate.

The hexane extract also yielded a fixed oil (yield 1.33%), having the following values: sp. gr., 0.944 at 18.5°C; free fatty acid, 19 mg/100 g; saponification value, 113, acetyl value, 25; iodine value, 68 (Hanus method) and acid value, 22.8.

Isolation of Alkaloid. The seed powder after the extraction with hexane was soxhlet extracted with ethanol for about 12 hr. The extract was kept in refrigerator, when most of the sugars settled down. The yield of sugars was 5% and on paper chromatography were found to be glucose, fructose and sucrose. The mother liquor left after the separation of sugars was concentrated under reduced pressure and the residue dissolved in 5% acetic acid. The solution was extracted with chloroform till no more alkaloid was found coming in chloroform layer. The chloroform removed and the residue was obtained in very small quantity and not processed. The aqueous solution was basified with ammonium hydroxide and again extracted with chloroform till alkaloidal test in chloroform was negative. The aqueous extract was also found free from alkaloids. The chloroform extract was dried (Na_2SO_4) and solvent removed under reduced pressure. The residue dissolved in ethanol, chromatographed over alumina (Brockmann) and eluted with benzene, benzene–ethyl acetate (4:1), benzene–ethyl acetate (3:1), benzene–ethyl acetate (2:1), and lastly benzene–ethyl acetate (1:1). Fractions from benzene–ethyl acetate (1:1) gave positive alkaloid test and on TLC indicated the presence of same compound. These were combined, and solvent removed. The residue was dissolved in methanol, and a few drops of acetone added. On leaving in refrigerator, white crystals were formed, m.p. 240–42°C. They gave positive test for indole, showing the presence of indole type of alkaloids. Due to insufficient material, further studies could not be made.

Acknowledgement. The authors wish to express their thanks to Dr. S. Yusuf Ahmad, PCSIR Laboratories, Karachi for arranging the IR spectra of the compounds.

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Pakistan J. Sci. Ind. Res., Vol. 15, No. 3, June 1972

REACTION OF THIONYL BROMIDE WITH DIHYDRIC PHENOLS

S.D. SARAF,* Z.A. MALIK and Z.I. BHATTI

Institute of Chemistry, University of Islamabad, Islamabad

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Phenol on treatment with thionyl bromide at room temperature gave an immediate reaction with the evolution of hydrogen bromide, sulphur dioxide and precipitation of sulphur, and 2,4-dibromophenol was obtained in 85% yield.[1] It was shown that tropolone on treatment with thionyl bromide in dry benzene gave 3,7-dibromotropolone in 45% yield. There is no direct method for the preparation of these dibromo compounds. With phenol, bromine yields 2,4,6-tribromophenol, whereas with tropolone and bromine, a mixture of products was obtained.[2] It was, therefore, decided to investigate the reaction of thionyl bromide with some dihydric phenols, in order to find out whether this dibromination process occurs.

Frejka and Safranek[3] have reported that it is easy to prepare tribromo and tetrabromocatechol, but it is difficult to make dibromo derivatives directly. Thus, in their experiments, direct bromination of catechol in chloroform, in the cold, gave tetrabromocatechol. On the other hand, when bromine vapour was passed into a solution of catechol in chloroform at room temperature by means of a current of sulphur dioxide, 3,4-dibromocatechol was obtained.[3]

In the present work, when thionyl bromide was added to a cold solution of catechol in dry benzene, no reaction was observed. When the mixture was warmed, a vigorous reaction took place. Work-up in the usual manner gave 4,5-dibromocatechol as a light yellow solid, in 65% yield.

Kovacio [4] has reported that addition of bromine to a solution of hydroquinone in chloroform–methanol gave a tetrabromo derivative. By using 1,3-dibromo-5,5-dimethylhydantoin in carbon tetrachloride as brominating agent, hydroquinone gave a brominated product which could not be separated from the original brominating agent.[5] Similarly it has been reported, that bromination of hydroquinone with dioxan dibromide gave 2-bromo and 2,6-dibromohydroquinone

*Now at Chemistry Department, Middle East Technical University, Ankara, Turkey.

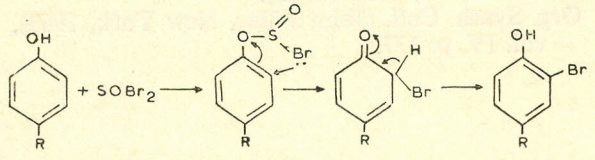
depending on the amount of the brominating agent used.[6] No direct method of preparing 2,5-dibromohydroquinone has been reported as yet. The only method reported in the literature consists of treating 1,4-dimethoxy-2,5-dibromobenzene with fuming hydrobromic acid and acetic acid, whereby, 2,5-dibromohydroquinone was isolated in 60% yield.[7]

No method, using free bromine, has been reported in the preparation of any derivative of resorcinol. A mixture of dichlorourea (ClNH.CO.NHCl) and potassium bromide has been used for the preparation of mono and dibromo derivatives of resorcinol.[8] Salvi[5] has reported that resorcinol on treatment with 1,3-dibromo-5,5-dimethylhydantoin in carbon tetrachloride gave 2,4,6-tribromoresorcinol, whereas with dioxane dibromide-4-bromoresorcinol was obtained.

Addition of thionyl bromide to resorcinol gave a brisk reaction with the evolution of sulphur dioxide and hydrogen bromide. Work-up in the usual manner left a pink residue, which was high melting and insoluble in all organic solvents. The product, which contained halogen, was soluble in hot water, from which it could not be crystallised. From its high melting point and insolubility in organic solvents, it is presumed to be a polymer. As regards the mechanism for the formation of these bromo compounds the following two possibilities may be considered.

(1) Thionyl bromide decomposes to give free bromine, sulphur dioxide and sulphur and it is this free bromine, which then reacts with the phenol to give the isolated products.

(2) Thionyl bromide reacts with phenol to give the bromosulphinate (I) as an intermediate. SN_i attack by bromine followed by the loss of sulphur dioxide and rearomatisation gives the bromo derivative as shown in scheme 1.



(I)

Where R=OH; $2\,SO=SO_2+S$.

In a similar manner, the other hydroxy group reacts to give the dibromo derivative isolated.

Mechanism 1 is unlikely, as the products isolated are not formed by reaction of these phenols with free bromine. It is the second mechanism, which in the opinion of the authors, is in operation. Every attempt to isolate the intermediate has failed, a fact which has also been reported by Darzens.[7]

Experimental

5,4-Dibromocatechol. To a cooled solution of catechol (5 g, 0.045 mole) in dry benzene (200 ml) was added thiony bromide (18.8 g, 0.090 mole). The resultant solution was heated on a water-bath for 15 min and the solvent was decanted off. The grey residue was then treated with hot benzene and the combined benzene extracts were washed with water and dried ($MgSO_4$). Removal of the solvent left a light yellow solid which was chromatographed over alumina (acidic). Elution with benzene gave a colourless solid m.p. 88–90°C. Crystallisation from benzene–light petroleum (b.p. 60–80°C) gave 4,5-dibromocatechol, m.p. 91–92°C undepressed on admixture with an authentic specimen, yield 7.8 g, 65%.

Its phenoxyacetic acid derivative, prepared by a known procedure, crystallised from hot water to give 2-hydroxy-4,5-dibromophenoxyacetic acid as colourless needles m.p. 189–91°C (lit.[9] 192°C). (Found: Br, 48.8. Calc. for $C_8H_6Br_2O_4$: Br, 49.0%).

2,5-Dibromohydroquinone. To hydroquinone (2 g, 0.018 mole) was added thionyl bromide (7.5 g, 0.036 mole) and the mixture was heated on a water-bath for 30 min. Work-up in the usual manner left a brown liquid, which on cooling solidified. Crystallisation from hot 95% ethanol gave 2,5-dibromohydroquinone as light yellow needles, m.p. 184–85°C undepressed on admixture with an authentic specimn.

Its diacetate was prepared by known procedure,[6] and crystallised from hot water to give dibromohydroquinone diacetate as colourless crystals, m.p. 160–66°C (lit,[6] 162°C). (Found: Br, 45.00. Calc. for $C_{10}H_8Br_2O_4$: Br, 45.4%)

In a similar experiment, resorcinol reacted with thionyl bromide with a vigorous reaction. A dark pink solid of high m.p. was obtained, which was insoluble in all organic solvents. The product could not be identified.

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