SHORT COMMUNICATIONS

UTILIZATION OF D.D.T. WASTE FOR THE SYNTHESIS OF 5-CHLORO-7-IODO-8-HYDROXYQUINOLINE AMOEBICIDE FROM p-DICHLOROBENZENE

Mohammad Zafar Shah, Iftikhar Ahmad, M.K. Bhatty and Karimullah

West Regional Laboratories, Pakistan Council of Scientific and Industrial Research, Lahore

Introduction

During the preparation of monochlorobenzene from benzene for the manufacture of D.D.T., considerable amount of p-dichlorobenzene is formed as a bye-product which at present is going waste in the country. This waste has been successfully utilized in the synthesis of 5-chloro-7-iodo-8-hydroxyquinoline which is a powerful amoebicide[1] and is largely used in the treatment of amoebic dysentery.

Turski and Lepach[2] appear to be the only workers who have carried out a synthesis of the amoebicide from p-dichlorobenzene. An outline of their procedure indicates that they convert p-dichlorobenzene into p-dichloronitrobenzene of which one chloro-group is then replaced by a hydroxy-group. The resulting chloronitrophenol is reduced to aminochlorophenol which is consequently changed into chloro-oxine through Skraup's synthesis. Chloro-oxine is finally iodinated with potassium iodide.

Unfortunately, however, the exact details of the above procedure are not mentioned. Therefore, the studies described in this communication had to be carried out and the above procedure reinvestigated and modified in order to establish optimum conditions for the synthesis of this amoebicide from p-dichlorobenzene.

Experimental

Materials

p-Dichlorobenzene: The waste from the D.D.T. manufacture was subjected to distillation for the removal of a tarry matter. The distillate was chilled in an ice-bath and the resultant crystalline p-dichlorobenzene was filtered off from the residual o-dichlorobenzene.

Nitrating mixture: A mixture of nitric acid (1.41d.) and sulphuric acid (1.83d.) in the ratio of 42:58 respectively was employed for the nitration of p-dichlorobenzene.

All the chemicals used in these investigations were of commercial grade.

Equipment

An autoclave fitted with heating arrangement and a stirrer was employed besides the usual laboratory-ware.

Procedure

Nitration of p-Dichlorobenzene to 2:5-Dichloronitrobenzene.—Nitrating mixture (577 ml.) was placed in a round bottom 2-litre flask and while shaking the flask and keeping its temperature below 70°, p-dichlorobenzene (500 g.) was added in small portions. The flask was fitted with a water condenser and heated at 95-100° for 6 hours. The reaction mixture was shaken occasionally during heating. After the heating was over, the reaction mixture was poured in ice-cold water when 2:5-dichloronitrobenzene separated out as a solid mass. The solid was washed with water several times and dried (yield 95%).

Conversion of 2:5-Dichloronitrobenzene into 4-Chloro-2-Nitrophenol.—2:5-Dichloronitrobenzene (200 g.) was heated in the autoclave with 90 g. of sodium hydroxide in 300 ml. of water at a temperature of 160-162°, and pressure 40-45 lb./sq. in., for one hour. The resulting product was steam-distilled to remove the unchanged 2:5-dichloronitrobenzene. The residual mass was neutralized with hydrochloric acid and again steam-distilled to recover 4-chloro-2-nitrophenol (yield 63%).

5-Chloro-Oxine from 4-Chloro-2-Nitrophenol.—4-Chloro-2-nitrophenol (100 g.) was refluxed with 200 m. each of glycerine, glacial acetic acid and sulphuric acid (1.83d.) in a 2-litre round bottom flask for 6 hours. The resulting solid mass was thoroughly extracted with 2 percent sulphuric acid. The extract was filtered and neutralized with

sodium carbonate solution when 5-chloro-oxine precipitated out. This precipitate was filtered, washed with water several times and dried (yield 80% and m.p. 123°).

Iodination of 5-Chloro-Oxine.—5-Chloro-oxine (12 g.) was dissolved by heating in a solution of 4.0 g. of potassium hydroxide in 266 ml. of water. The solution was cooled and treated with a solution of 5.6 g. of potassium iodide in 34 ml. of water. The mixture was warmed and then cooled to room temperature. It was treated with 100 ml. of 5 percent bleaching powder slurry. A yellow brown precipitate was obtained which was allowed to stand overnight. The precipitate was filtered and freed from free-iodine with sodium thiosulphate and water. The unchanged 5-chloro-oxine was removed by washing the precipitate with 1 percent hydrochloric acid. The crude product was recrystallised from glacial acetic acid. Its m.p. was 179-180° and the yield was 74 percent.

Discussion and Conclusion

The D.D.T. waste as obtained from the factory contains considerable proportion of a tarry matter. p-Dichlorobenzene can, however, be directly recovered from it by chilling and filtering but the material obtained is highly contaminated, with the result that subsequent products are not obtained in the desired state of purity and form. The waste has, therefore, got to be distilled to first obtain a purified mixture of ortho-and para-chlorinated benzenes. The ratio of o-to p-dichlorobenzene in the distillate is roughly 3:1, respectively.

In these studies, leading to the synthesis of 5-chloro-7-iodo-8-hydroxyquinoline from p-Dichlorobenzene, conditions under which maximum yield of the products was obtained had to be closely established.

In the nitration step, the maximum yield of p-dichloronitrobenzene could only go upto 95 percent. Ganopolskii[3] claims 99% yield of the product under nitration conditions which are quite different from those followed here. But unfortunately his procedure in our hand could give yield only upto 30%. Similarly, the yield of the nitrated product obtained by the method described by Kiprianov and Mikhailenko,[4] is much less than that claimed by these workers.

In the preparation of 4-chloro-2-nitrophenol from 2:5-dichloronitrobenzene, the replacement of a chloro- by a hydroxy-group could not be effected under ordinary conditions. This was, therefore, brought about under pressure in an autoclave. This replacement has been studied by Kiprianov and Mikhailenko,[4] David and Blangey,[5] Fevre, Saunders and Turner,[6] and Venkataraman[7] under different conditions in an autoclave. However, in our investigations, under the reaction conditions suggested by Kiprianov *et al.* only a yield of 40-50 percent was obtained. For the rest of the cases, the yield of the phenol was rather low and the end product was either in the charred or resinified state. The reaction conditions of Kiprianov *et al.* were, therefore, modified so that the yield of the phenol was raised to 63 percent.

Skraup's synthesis was carried out according to Bose.[8] Starting with chloronitrophenol, chloro-oxine was obtained in a yield of 80 percent instead of 60 percent as claimed by this worker.

Iodination of 5-chloro-oxine was first reported in a patent from Basler Chemische Fabrik.[9] The iodo-derivative was prepared by heating 5-chloro-oxine in potassium hydroxide solution with a solution of iodine in potassium iodide. Coll and Coll[10] suspended 5-chloro-oxine in a solution of sodium hydroxide and then treated it with a solution of potassium iodide and sodium hypochlorite. They obtained the product in 81-85 percent yield. Bose effected the iodination of 5-chloro-oxine with iodine dissolved in sodium hydroxide solution and claimed a yield of 99.9 percent based on the 5-chloro-oxine used. Gupta[11] suggested the iodination of 5-chloro-oxine with potassium iodide in the presence of bleaching powder. No yield is quoted by this worker.

On repeating the work of all these investigators, only Gupta's method was found to give a yield of 74 percent. In all other cases, the yield was nowhere nearer to those claimed in literature.

In these studies, therefore, it has been established that p-dichlorobenzene, at present going waste in the country, can be utilised in the production of 5-chloro-7-iodo-8-hydroxyquinoline. Starting from p-dichlorobenzene, the overall yield of the end product is upto 37 percent. A comparative study of the yields of the products at each step of this synthesis reveals that our yields have uniformly been higher than those described earlier.

It is worthwhile to mention that the production of the amoebicide can be taken up in the country rather effectively as almost all the chemicals required are easily available.

References

1. M.M. Green, J. Am. Pharm. Assoc. (Prac. Pharm. Edn.), **7,** 150 (1946).
2. J.S. Turski and H. Lepach, Przemysl. Chem., **22,** 518 (1938).
3. M. Ganopolskii, Org. Chem. Ind. (U.S.S.R.), **1,** 342-4 (1936).
4. A.I. Kiprianov and P.I. Mikhailenko, Ukr. Khem. Zh. 5, Tech. pt., 225-39 (1930).
5. H.E. Fierz-David and L. Blangey, *Fundamental Processes of Dye Chemistry*, Translation from Fifth Australian Edition (Interscience Publishers Ltd., London, 1949), p. 109.
6. L. Fevre, L.M. Saunders and E.E. Turner, J. Chem. Soc., 1173 (1927).
7. K. Venkataraman, *The Chemistry of Synthetic Dyes* (Academic Press Inc., Publishers, New York, 1952), Vol. I, p. 119.
8. M.K. Bose, J. Indian Chem. Soc., **22,** 169 (1945).
9. Basler Chemische Fabrik, German Patent No. 117, 767.
10. A.L. Coll and G.P. Coll, Afinidad, **28,** 101, 163 (1951).
11. R.S. Gupta, J. Indian Chem., Soc., **22,** 171 (1945).

EFFECT OF HEAT ON PETKOLINS—CHLORINATED PESTICIDES, UNDER ATMOSPHERIC CONDITIONS

SHABBIR AHMAD QURESHI AND JAVED MAHMOOD

Engineering Division, Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

Introduction

Petkolins—a series of pesticides recently developed by the Council of Scientific and Industrial Research, are obtained by the chlorination of petroleum-hydrocarbons, indigenous as well as imported, in presence of an additive and sunlight.[1] Petkolins are relatively less volatile as compared with the original hydrocarbons when stored under atmospheric conditions. In order to assess the losses on storage, it was considered necessary to know the extent of the loss in weight when heated over temperatures range of 20 to 60°C., over and above the usual atmospheric temperatures.

Apparatus and Experimental Procedure

The apparatus used is a conventional type thermostat which needs no explanation or further discussion. A 25 ml. beaker previously weighed was used to hold 10 g. of the sample. When the temperature is set, the beaker is placed at the platform immersed in water and allowed to stand for 8 hours. The beaker was then taken out, cooled to room temperature and weighed. The difference in weight is recorded as loss in weight of the sample heated.

Results and Discussion

Three different types of the Petkolins namely A, S and M were heated at 20, 25, 30, 40, 45, 50, 55 and 60°C. for period of eight hours under atmospheric conditions and the loss calculated. The percent loss as function of temperature is given in Table 1, which shows that Petkolins

TABLE 1.—LOSS IN WEIGHT OF PETKOLINS AT DIFFERENT TEMPERATURES.

No.	Temperature °C.	Petkolin loss percent		
		"A"	"S"	"M"
1.	20	0.250	0.107	0.164
2.	25	0.300	0.164	0.257
3.	30	0.464	0.228	0.571
4.	35	0.892	0.664	1.085
5.	40	1.714	1.407	1.707
6.	45	1.118	1.692	2.621
7.	50	3.100	2.428	3.235
8.	55	4.511	3.707	4.564
9.	60	5.742	4.514	5.785

when allowed to stand at 25°C. lose 0.164 to 0.300 percent of their contents as compared to 4.514 to 5.785 percent when left at 60°C. in open containers.

At a lower temperature for example at 20°C., the volatility of the Petkolins is in the order of A > M > S. At higher temperatures i.e. from 30 to 50°C. the order of volatility may be represented as M > A > S. Thus an overall view of these results would show that Petkolin-S is the least volatile while Petkolins-A and M are relatively more volatile under atmospheric temperature and pressure.

A log (L) Vs log (t) plot in Fig. 1 indicates that there exists a relationship of the type L=K (t)$^{3.313}$' between the loss percent and the corresponding temperature. Petkolins-A and M fall
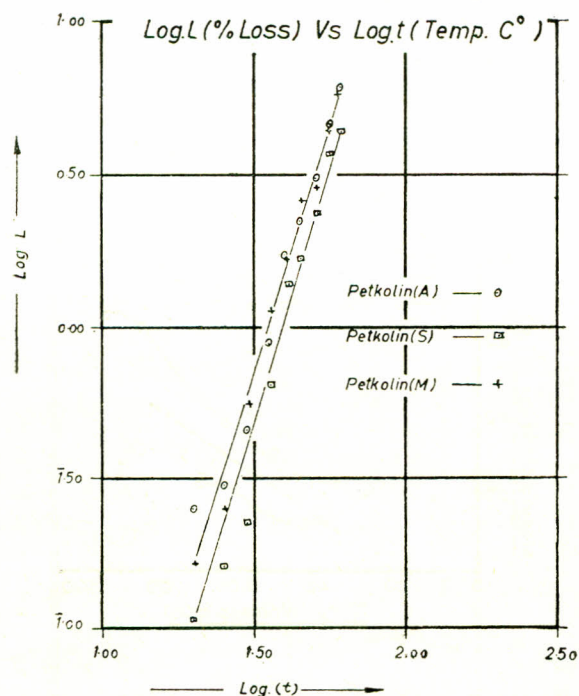

Fig. 1.

on the same line while Petkolin-S is represented by another almost parallel line. The value n is 3.313 and that of K varies i.e. for Petkolin A and M its value is (-4.728) and for Petkolin-S, the K is (-4.93).

Conclusion

Petkolins are volatile chloro-hydrocarbons; their volatilities being a function of the temperature and the pressure. Analysis of the Petkolins at different temperatures, shows that there is practically little or no change in its chlorine contents. This means that there is no change in the insecticidal properties of the Petkolin, nor does it appear to affect the stability of the product.

Reference

1. S.A. Qureshi, Pakistan J. Sci. Ind. Res., **8,** 248 (1965).

THE DISTRIBUTION AND DIAMENSION OF MEDULLATION AND THEIR INTER-RELATIONSHIP WITH THE TENSILE PROPERTIES OF HARNAI WOOL FIBRES

TAJ ALI WAZIR AND FAIZULLAH KHAN

Wool Research Division, North Regional Laboratories, Pakistan Council of Scientific and Industrial Research, Peshawar

Introduction

It has been found that medullated fibres do not dye as well as do non-medullated wool fibres owing to light reflection[1] from the enclosed air in the medulla and the corresponding thickness of the cortex. In order to estimate the value and suitability of Harnai wool for manufacturing and dyeing purposes, it is necessary to find out its medullation or hairiness and its relation to the tensile characteristics of the same wool fibres. For this purpose, 45 samples of Harnai wool collected from the Quetta and Kalat divisions were tested for medulla distribution, i.e. continuous, interrupted and fragmental medulla, and tensile properties. The number and length of the medullary fragments were also determined. The relation between fibre thickness and medulla thickness and that between breaking strength and medulla thickness were studied. The diameter of fibre and medulla were determined by means of a projection microscope (Lanameter), while for breaking strength and elongation a single-fibre testing machine was used. Subsequently tenacity, and tensile strength of the fibre and percentage-length and percentage-volume of the medulla were calculated.

Experimental

1. *Medullation.*—The samples were cut down[2] to lengths of 1″, 2″ and 3″ and sub-samples of 30,60 and 90 mg., respectively, were weighed out. Each sub-sample was sorted for true, heterotypical, and medullated wool, by means of the benzene method.

2. *Measurement of Medulla.*—40-80 fibres in groups of 6-8 fibres were aligned length-wise on a slide covered by a coverslip. The diameter of continuous medulla in the medullated wool fibres and the corresponding diameter of the same wool fibres at eight different points were determined by means of a projection microscope (Lanameter), and the mean of these readings gave the

average diameter. With fibres of interrupted medulla, the diameter of the medulla was measured at the points of interruption. In addition to the points of interruption, the diameter of the same medulla at eight more points was also determined. Finally, the diameter of the fragmental medulla, the number of fragments, and the mean length of the fragments were determined.

3. *Dynamometric Measurements.*—The breaking strength[3] and elongation at break of the same single wool fibres as used in medulla measurements were determined by means of a single-fibre testing machine.

Calculation

The percentage volume of the medulla, breaking strength, elongation at break and tensile strength were calculated as below:—

Percentage volume of the medulla[4] $= Im \times \pi_r^2 / \pi_R^2$

Where $\pi_r^2 =$ mean cross-sectional area of the medulla.

$\pi_R^2 =$ mean cross-sectional area of the fibre.

% length $= IM = Nm/Nw \times 100$

Where $Nm =$ No. of medullated fibre.

$Nw =$ Total No. of fibres tested in the same sub-sample.

Tensile strength $=$ Breaking force in g./area of cross section in cm.[2]

Results and Discussion

From Fig. 1, it appears that medulla thickness is related to fibre thickness in that as the fibre diameter increases, the medulla diameter also increases. This relation is well defined with fibres of continuous or fragmental medulla but less marked with fibre of interrupted medulla. The maximum medulla diameter observed was 64.9μ against 95.5μ for the corresponding fibre diameter.

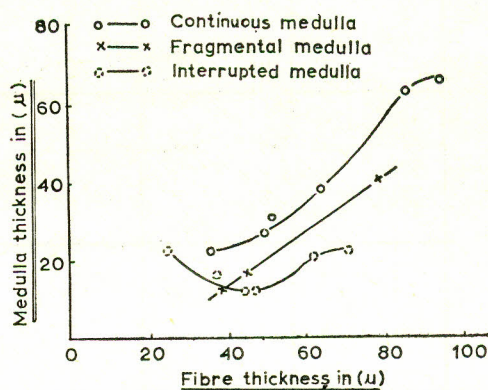From Tables 1, 2 and 3, it is clear, that all the medullated wool fibres are continuously medullated

Fig. 1.

TABLE 1.—DISTRIBUTION OF PERCENTAGE LENGTH AND PERCENTAGE VOLUME IN CONTINUOUS MEDULLA OF HARNAI WOOL FIBRES.

Type of fibres	No. of fibres tested	No. of fibres with continuous medulla	Mean fibre diameter (μ)	Mean medulla diameter (μ)	% Length	% Volume
Heterotypical	40	12	46.7	25.2	30	9.4
,,	50	40	37.6	24.2	80	35.5
,,	40	40	45.2	27.1	100	8.9
Medullated	60	60	65.6	43.7	100	44.4
,,	60	60	47.4	27.0	100	33.0
,,	60	60	69.3	37.8	100	29.5
,,	60	60	92.5	64.9	100	48.3
Heterotypical	70	70	67.0	37.1	100	32.3
Medullated	70	70	62.9	38.9	100	37.6
,,	80	80	51.3	31.2	100	28.4
,,	80	80	84.5	63.6	100	58.0
,,	50	50	89.7	50.8	100	26.5
,,	50	50	62.6	59.8	100	91.2
,,	50	50	48.9	26.1	100	29.1
Heterotypical	40	4	49.8	26.4	10	2.7

TABLE 2.—DISTRIBUTION OF PERCENTAGE LENGTH AND PERCENTAGE VOLUME IN INTERRUPTED MEDULLA OF HARNAI WOOL FIBRES.

Type of fibres	No. of fibres tested	No. of fibres with interrupted medulla	Mean fibre diameter (μ)	Mean medulla diameter (μ)	% Length	% Volume
Heterotypical	40	4	70.0	22.6	10	1.0
,,	40	8	44.2	13.8	20	2.0
,,	40	4	24.4	22.6	10	7.8
,,	40	24	37.4	17.0	60	12.0
,,	40	24	61.3	21.6	60	7.3
,,	40	4	44.2	14.2	20	2.0

TABLE 3.—DISTRIBUTION OF PERCENTAGE LENGTH AND PERCENTAGE VOLUME IN FRAGMENTAL MEDULLA OF HARNAI WOOL FIBRES.

Type of fibres	No. of fibres tested	No. of fibres with fragmental medulla (Mean)	Mean fibre diameter (μ)	Mean medulla diameter (μ)	% Length	% Volume
Heterotypical	40	24	46.4	13.7	60	5.1
,,	40	32	44.2	13.5	80	4.7
,,	40	4	36.0	23.4	10	4.4
,,	40	16	38.3	13.5	40	5.4
,,	40	12	78.2	41.1	30	8.7
,,	40	12	44.1	17.6	30	5.0

TABLE 4.—THE TENSILE PROPERTIES OF THE SAME HARNAI WOOL FIBRES HAVING CONTINUOUS MEDULLA (TABLE 1).

Types of fibres	No. of fibres tested	No. of fibres with continuous medulla	Mean elongation at break (%)	Mean tensile strength mg./cm.²
Heterotypical	40	12	31.7	438539.7
,,	50	40	18.1	2673914.3
,,	40	40	33.2	2473662.9
Medullated	60	60	20.0	1897533.2
,,	60	60	18.4	1079969.9
,,	60	60	12.7	1894219.3
,,	60	60	16.8	808473.3
Heterotypical	70	70	24.5	483719.4
Medullated	70	70	31.3	1035018.2
,,	80	80	13.1	1439511.5
,,	80	80	33.0	2166753.4
,,	50	50	13.3	596230.7
,,	50	50	40.0	955350.4
,,	50	50	17.0	1523298.3
Heterotypical	40	4	14.6	1290322.7

Density	(Medullated wool)	=	1.160
,,	(Heterotypical wool)	=	1.172
,,	(True wool)	=	1.304

TABLE 5.—THE TENSILE PROPERTIES OF THE SAME HARNAI WOOL FIBRES HAVING INTERRUPTED MEDULLA (OF TABLE 2)

Type of fibres	No. of fibres tested	No. of fibres with continuous medulla	Mean elongation at break %	Mean tensile strength mg./cm.^{2}
Heterotypical	40	4	42.4	868993.4
,,	40	8	44.4	2332711.4
,,	40	4	18.4	3360215.3
,,	40	24	15.6	1138513.2
,,	40	24	21.2	751613.6
,,	40	4	47.2	1999947.8

TABLE 6.—THE TENSILE PROPERTIES OF THE SAME HARNAI WOOL FIBRES HAVING FRAGMENTAL MEDULLA (OF TABLE 3)

Type of fibres	No. of fibres tested	No. of fibres with continuous medulla	Mean elongation at break %	Mean tensile strenght mg./cm.^{2}
Heterotypical	40	24	28.9	653610.9
,,	40	32	15.3	1201834.3
,,	40	4	18.6	916422.4
,,	40	16	15.2	1913614.3
,,	40	12	16.0	381752.5
,,	40	12	38.0	2185164.3

and in heterotypical wool fibre, 41.6% are of continuous, 23.7% are of interrupted and 34.7% are of fragmental medulla. The true wool fibres were found to be totally free from medulla.

With the fragmental medulla of fibres of mean length 2.5 in., the number of fragments per fibre varied from 8 to 63 (mean 18), whilst the length of the fragments varied from 16 to 64µ (mean 32.1µ).

In the previous study,[9] it has been shown that Harnai wool consists of 55% of true wool, which is totally free from medulla, whilst the remaining 45% of the fibres consist of medullated and heterotypical wool with continuous, interrupted and fragmental medulla. With these fibres, it was also noted that the diameter of the medulla is related to the corresponding diameter of the fibre.

References

1. Wool Science Review, **13**, 36 (1954).
2. W.V. Bergen and H.R. Mauersbergen. *American Wool Hand Book* (Textile Book Publishers, Inc. N.Y., 1948), p. 142.
3. A.A. Wakil and Amir Mohammad Pakistan J. Sci. Ind. Res., **6,** 1 (1963).
4. Wool Science Review, **13,** 43 (1954).
5. J. Meybeck and G. Gianda, International Conference, Australia. Vol. D,P. 135, (1955).
6. Ernest R. Kaswell, *Textile Fibre Yarn and Fabric* (Reinhold Publishing Corp. N.Y. 1950). p. 10.
7. Bruce E. Nortsuch. *Introduction to Textile Chemistry* (John Willey & Sons, Inc. N.Y. 1950), p. 108.
8. A.A. Wakil and Amir Mohammad, Pakistan J. Sci. Ind. Res., **6,** 15 (1963).
9. A.A. Wakil and Amir Mohammad, Science and Industry.
10. A.A. Wakil and Amir Mohammad, Pakistan J. Sci. Ind. Res. (In Press).
11. Mumtaz Ahmad, Science and Industry, **1,** 99 (1963).