PREPARATION OF DINITROCHLOROBENZENE FROM MONOCHLOROBENZENE WITH COMMERCIAL NITRIC ACID

SHAISTA BEGUM, NAEEM SHAKIR and M. ASLAM

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

(Received November 1, 1967)

2,4-Dinitrochlorobenzene is imported by the P.I.D.C. Pak Dyes Plant, Daudkhel, for the production of sulphur black dye. The possibility of making this item from locally produced monochlorobenzene and commercial nitric acid (60% has now been investigated. The literature survey showed that 2,4-dinitrochlorobenzene can be produced by using fuming nitric acid. No information in respect of the suitability of 60% nitric acid for this purpose was, however, available in the literature.

Experimental

Nitration[1].—To 280 g mixed acid (made from 140 g (98%) sulphuric acid and 140 g (60%) nitric acid was added drop-wise and with good stirring 113 g (1 mole) of monochlorobenzene, while maintaining a temperature below 5°C. Stirring was continued at 5–10°C for 1 hr after the addition was complete. The temperature was raised slowly to 50°C and kept there for another hour after which 350 g (98%) sulphuric acid was added. The mixture was then heated at 115°C (see Table 1) for another hour, cooled and pured onto ice, filtered under suction, washed with cold water and then dried. This gave about 75 g of practically pure *p*-nitrochlorobenzene. The experiment was also performed (a) at elevated temperature while using commercial nitric and sulphuric acids, and (b) by using the fuming nitric and concentrated sulphuric acids.[2] The results are given in Table 1.

Monochlorobenzene.—This compound, obtained from Kohi-Noor Insecticides Ltd., Kala Shah Kaku was distilled before use b.p. 130–31°/760 mm (lit[3] b.p. 132°/760 mm).

TABLE 1.—DATA FOR THE NITRATION OF MONOCHLOROBENZENE AT DIFFERENT TEMPERATURES.

S. No.	Sulphuric acid %	Nitric acid %	Temp °C	Yield	M.p. °C	Lit.°C M.p.°C
1.	98	60	115-20	47.5%[a]	80.5	82.5
2.	98	60	120-23	45.0%[a]	80.1	82.5
3.	98	60	125-30	31.1%[a]	76.0	82.5[1]
4.	98	Fuming	115-18	98.2%[b]	50.0	51.0[c]

(a) *p*-Nitro derivative.

(b) 2,4-Dinitro derivatives.

(c) Ref. 1, p. 90.

Discussion

Nitration of chlorobenzene at 40–50° with fuming nitric acid gives a mixture of *o*-nitrochlorobenzene and *p*-nitrochlorobenzene[1] but at higher temperatures i.e. 115–118° 2,4-dinitrochlorobenzene is obtained in 98% yield. The present investigations have shown that 60% nitric acid cannot be used for the production of dinitrochlorobenzene. At present, the manufacture of dinitrochlorobenzene in the country will have to be undertaken by importing fuming nitric acid.

References

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2. E.J. Hoffman, P.A. Dame, J. Am. Chem. Soc., **41**, 1015 (1919).

3. *Dictionary of Organic Compounds* (Eyre and Spottiswoode, London, 1965).