Reference : Vogel's Textbook of Practical Organic Chemistry 5ed edition p1035

Experiment 6.136 ω-NITROSTYRENE

$$Ph{\cdot}CHO + Me{\cdot}NO_2 \xrightarrow{-H_2O} Ph{\cdot}CH{=}CH{\cdot}NO_2$$

Equip a 1500-ml three-necked flask with a thermometer, mechanical stirrer and a dropping funnel. Place 61 g (54 ml, 1 mol) of nitromethane (1), 106 g (101 ml, 1 mol) of purified benzaldehyde (Expt 6.133) and 200 ml of methanol in the flask and cool it with a mixture of ice and salt to about −10 °C. Dissolve 42 g of sodium hydroxide in 40–50 ml of water, cool and dilute to 100 ml with ice and water; place this cold solution in the dropping funnel. Add the sodium hydroxide solution, with vigorous stirring, to the nitromethane mixture at such a rate that the temperature is held at 10–15 °C. Introduce the first few ml cautiously since, after a short induction period, the temperature may rise to 30 °C or higher; check the rise in temperature, if necessary, by adding a little crushed ice to the reaction mixture. A bulky white precipitate forms; if the mixture becomes so thick that stirring is difficult, add about 10 ml of methanol. After standing for about 15 minutes, add 700 ml of ice-water containing crushed ice; the temperature should be below 5 °C. Run the resulting cold solution immediately from a dropping funnel and with stirring into 500 ml of 4 M hydrochloric acid contained in a 3-litre flask; adjust the rate of addition so that the stream just fails to break into drops. A pale yellow crystalline precipitate separates almost as soon as the alkaline solution mixes with the acid. The solid settles to the bottom of the vessel when the stirrer is stopped. Decant most of the cloudy liquid layer, filter the residue by suction and wash it with water until free from chlorides. Transfer the solid to a beaker immersed in hot water; two layers form and on cooling again, the lower layer of nitrostyrene solidifies; pour off the upper water layer. Dissolve the crude nitrostyrene in 85 ml of hot ethanol. (CAUTION: *nitrostyrene vapours are irritating to the nose and eyes, and the skin of the face is sensitive to the solid.*) Filter through a hotwater funnel and cool until crystallisation is complete. The yield of pure ω-nitrostyrene, m.p. 57–58 °C, is 125 g (85%).

Note. (1) The commercial material may be redistilled and the fraction having b.p. 100–102 °C collected.