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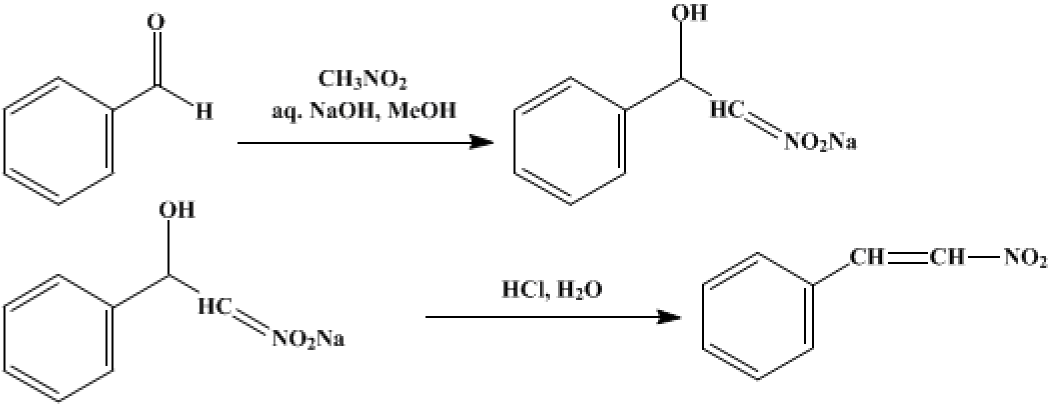
NITROSTYRENE

[Styrene, β-nitro-]



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1. Procedure

In a 6-l. wide-mouthed bottle, packed in a pail with a freezing mixture of ice and salt and fitted with a mechanical stirrer, a thermometer, and a separatory funnel, are placed 305 g. (5 moles) of nitromethane (p. 401), 530 g. (5 moles) of benzaldehyde (Note 1), and 1000 cc. of methyl alcohol. A solution of sodium hydroxide is prepared by dissolving 210 g. (5.25 moles) of sodium hydroxide in approximately an equal volume of water and cooling. It is then diluted to 500 cc. with ice and water, poured into the funnel, and added with stirring to the nitromethane mixture at such a rate that the temperature is kept at 10–15° (Note 2) and (Note 3).

A bulky white precipitate forms rapidly during the addition of the alkali. The mixture gets so thick that stirring becomes difficult and it may be advisable to add 100 cc. more of methyl alcohol. After fifteen minutes' standing, the pasty mass is converted to a clear solution by the addition of 3–3.5 l. of ice water containing crushed ice (Note 4). Hydrochloric acid (made by diluting 1000 cc. of concentrated hydrochloric acid with 1500 cc. of water) is placed in a 15-l. mixing jar and the reaction mixture run into this from the separatory funnel at such a rate that the stream just fails to break into drops (Note 5). A pale yellow crystalline mass separates almost immediately as the alkaline solution comes in contact with the acid. After the stirring is stopped, the solid settles to the bottom of the jar. The major part of the cloudy liquid layer is removed by decantation, and the residue filtered by suction and washed with water until free from chlorides. This product is freed from all but a negligible amount of water by melting in a beaker immersed in hot water. Two layers are formed, and on cooling again the lower layer of nitrostyrene freezes; the water may then be poured off. The crude nitrostyrene is purified by dissolving in 420 cc. of hot ethyl alcohol (Note 6), filtering the solution into a warm suction flask to remove solid impurities, and then cooling until crystallization is complete. The yield of crude product melting at 56–58° is 650–670 g. The yield of recrystallized nitrostyrene melting sharply at 57–58° is 600–620 g. (80–83 per cent of the theoretical amount). The whole procedure, including purification, can be done in a day.

2. Notes

1. Technical benzaldehyde which had been washed with sodium carbonate solution, dried, and distilled under reduced pressure, was used in this preparation.
2. The first few cubic centimeters of sodium hydroxide solution should be added

cautiously to the nitromethane mixture since, after a short induction period, there is a considerable evolution of heat and the temperature may rise from − 10° to 30° or even higher in spite of good stirring. If necessary, this rise in temperature is easily checked by adding a handful of crushed ice directly to the mixture. After this initial reaction the rest of the alkali may be added more rapidly.

3. The condensation induced by sodium hydroxide is almost instantaneous above 10°. The procedure may be interrupted with safety after the addition of alkali, and the product will not change on standing overnight in an ice chest.

4. After the product has been dissolved in water the resulting alkaline solution is much more sensitive and should be used up as rapidly as possible and the temperature kept below 5°.

5. The alkaline solution must be added slowly to the acid, for the reverse procedure always forms an oil containing a saturated nitro alcohol. A large excess of acid at room temperature is used, conditions which facilitate the formation of the desired unsaturated nitro compound.

6. The vapors of hot solutions of nitrostyrene are very irritating to the eyes and nose, and the skin of the face is sensitive to the solid substance.

3. Discussion

Nitrostyrene can be prepared by the condensation of benzaldehyde and nitromethane. This may be accomplished by the use of small amounts of a primary aliphatic amine,[1] a method which requires a number of days for the reaction to go to completion, or preferably by the use of alkali as first discovered by Thiele.[2] Alternatively, nitrostyrene can be prepared from benzil, nitromethane, and sodium ethoxide,[3] or from styrene and nitrosyl chloride.[4]

References and Notes

1. Knoevenagel and Walter, Ber. **37**, 4507 (1904).
2. Thiele, Ber. **32**, 1293 (1899); Thiele and Haeckel, Ann. **325**, 7 (1902).
3. Fujise, Takeuchi, Kamioka, and Tiba, Ber. **68**, 1274 (1935).
4. Perrot, Compt. rend. **202**, 494 (1936).

Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

ethyl alcohol (64-17-5)

hydrochloric acid (7647-01-0)

methyl alcohol (67-56-1)

sodium hydroxide (1310-73-2)

sodium carbonate (497-19-8)

benzaldehyde (100-52-7)

Benzil (134-81-6)

sodium ethoxide (141-52-6)

Nitromethane (75-52-5)

NITROSTYRENE,
Styrene, β-nitro- (102-96-5)

styrene (100-42-5)

nitrosyl chloride (2696-92-6)