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SYNTHESIS OF PHENYL-2-NITROPROPENE

HTML by Rhodium

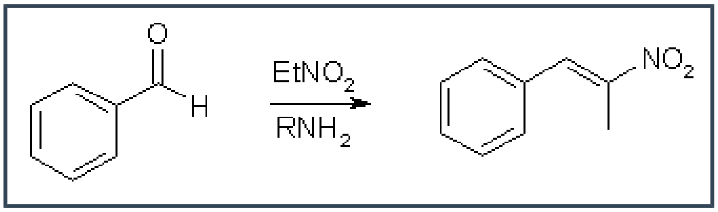
PHENYL-2-NITROPROPENE (METHYLAMINE CATALYSIS)

Written by GC_MS

Phenyl-2-Nitropropene à la Barium: 1 mol benzaldehyde, 1.2 mol nitroethane and 15 mL diluted aqueous methylamine in 150 mL alcohol. Stirred and slightly heated for ca 4 hours. The reaction mixture is brought over into a beaker and cooled in the fridge (4°C). If precipitation doesn't commence at this point, water is poured in and the mixture put back in the fridge. The P2NP oil layer will slowly (or sometimes quickly) start forming a crystalline layer. If it doesn't, scratching the wall with e.g. a glass rod will help. If even this won't help, it means you probably fucked something up. The yields I have had using this "adaptation": 81% (*i*-PrOH), 79% (*i*-PrOH), 75% (EtOH) and 71% (EtOH) (yields calculated after crystallizing once; I store my crystals in the freezer and also recrystallize them prior to use).

PHENYL-2-NITROPROPENE (CYCLOHEXYLAMINE CATALYSIS)

Written by Dreamer



To 55 g (0.5mol) Benzaldehyde in a 500mL Flask were added 40 g (0.5mol) Nitroethane and 10mL Cyclohexylamine. All was refluxed for 6h on a water bath. The result were 2 layers. One orange layer at the bottom with phenyl-2-nitropropene and a clear layer at the top with cyclohexylamine and maybe a little bit (~1mL) of H_2O. 50mL of H_2O were added and then sucked off with a pipette until the phenyl-2-nitropropene crystallized (it crystallized when it came in contact with air in presence of 15mL H_2O). I added 200mL 95% denaturated ethanol to the orange crystals. The color of the now needle-like crystals changed from orange to white-yellow. The crystals were filtered. Yield 65 g, 78% of theory.

PHENYL-2-NITROPROPENE (*N*-BUTYLAMINE CATALYSIS)

Written by Zorohustra

CHEMICALS

- 80 mL Toluene (ACS)
- 40 mL Benzaldehyde (~99%)
- 30 mL Nitroethane (>99%)
- 10 mL *n*-Butylamine (p.a.)

PROCEDURE

The reactants and amine catalysts were dissolved in the toluene in a 250mL RB flask, boiling stones were added and a Dean-Stark setup was rigged (10mL trap). The goal was to boil the solution quite heavily to achieve fast dripping from the double surface condenser, a heating mantle was used.

When the solution had boiled for an hour 2.7mL water was in the trap. At six hours something like 7.0mL (100% of theory) had settled in the trap, perhaps this happened some thirty minutes earlier, because the chemist took a short nap. The solution was dumped into a 250mL beaker, and allowed to cool to room temperature, it was seeded with some phenylnitropropene crystals, and slowly cooled to around -10°C (freezer). The crystals looked *really* nice and no further purification was needed (Yield 35g). The filtrate was concentrated under vacuum and cooled like above. Dirty crystals fell and they were recrystallized from 50mL MeOH (Yield 6g). The total yield from both crops amounted to 41g (64%)

Hmm, hmm the chemist thought, perhaps Benzene will increase the yield, its lower boiling point would probably decrease destruction of formed phenylnitropropene. Said and done, the same procedure, setup and chemicals as above was used in a second experiment, but with 80mL of nice 99.9% benzene as solvent instead of the toluene.

After boiling the solution for 6h, 3.3mL of water was collected, after 14h 6.7mL, and after 19h 6.9mL was collected, and the chemist turned the heating off, thinking: "I will never get 7.0mL due to the higher solubility of water in Benzene then in Toluene, I'm just killing yield now"

The solution was concentrated under vacuum, care taken never even to smell any Benzene. Dumped the solution in a 250mL beaker, it solidified completely and just 150mL of MeOH was added. This was enough to dissolve the crystals when boiling. Yield: 42g (65.6%).

All right, the yield is just above 60% with both Toluene and Benzene, lower temperature results in a slower reaction. But there are cases when *n*-Butylamine is a much faster catalyst and the temperature is even lower, such as when using MeOH as solvent. The chemist decided to try the reaction and setup once more but with 60mL cyclohexane as solvent, but after 20h of boiling only 4.2mL water had collected in the trap, and when cooling down the clear yellow reaction mixture crystals refused to form, so the solution is concentrated under vacuum to give crystals, but the yield sucked as less than 10g of product could be isolated (<15% yield).

LITERATURE METHODS

PHENYL-2-NITROPROPENE

n-Butylamine Catalysis[1]

One mole of benzaldehyde, one mole of nitroethane, 5 mL of n-butylamine and 100 mL of anhydrous ethanol were refluxed for 8 hours in a 1000 mL round-bottomed flask. When the contents were cooled and stirred a heavy, yellow, crystalline mass formed immediately. After recrystallization from anhydrous ethanol, the 1-phenyl-2-nitropropene weighed 105 g (64%), mp 65°C.

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Cyclohexylamine Catalysis[2]

Nitroethane (1.0 mL, 13.9 mmol) and cyclohexylamine (1.3 mL) were added to benzaldehyde (1.0 mL, 9.8 mmol) in glacial acetic acid (5.3 mL). The mixture was held at 100°C for 6 h, cooled and diluted with water (1 mL). The reaction mixture was cooled overnight in a water bath. The crystals formed were filtered and air dried. The crude solid was recrystallised from ethanol to give (E)-2-nitro-1-phenylprop-1-ene (0.99 g, 62%), mp 64–65°C.

PHENYL-2-NITROPROPENE

Ammonium Acetate Catalysis[3]

A solution of benzaldehyde (6.4 g) and ammonium acetate (1.0 g) in nitroethane (20 mL) was heated to reflux for 5 h. On cooling, after removal of the solvent, the residue was purified by column chromatography on silica gel 60 N (neutral; hexane-chloroform, 2:1, v/v), then recrystallized from hexane and gave 1-phenyl-2-nitropropene as a light yellow crystals weighing 6.2g (63%), mp 71-73°C.

REFERENCES

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2. J. Chem. Soc. Perkin Trans. 1, No. 3, pp. 501-504 (1998)
3. J. Chin. Chem. Soc., Vol. 49, pp. 505-508 (2002)