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Tropone

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TROPONE

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Abstract: Tropone is produced in 80-94% yield by heating tropylium fluoborate with sodium carbonate in acetonitrile.

Ten years ago we published a new preparation of tropone. Unfortunately, the preparation itself was well hidden in the article,[3] which dealt mainly with mechanistic speculations and the correction of some earlier data; thus many researchers are unaware of it. In the meantime, we have refined this preparation into an exceedingly easy and reproducible procedure which several groups[4,5,6] have found to be preferable to the selenium dioxide procedure of Radlick, even as improved by Agosta[7] and Rigby.[8] Our preparation uses no toxic materials and produces no dangerous (and expensive to dispose of) wastes. We therefore wish to take this opportunity to report our current procedure and our current understanding of how it works.

Tropylium fluoborate is converted rapidly and nearly quantitatively into a 1:1 mixture of tropone and cycloheptatriene when warmed in acetonitrile in the presence

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of sodium carbonate. Neither inert atmosphere nor refluxing is necessary. After brief warming, both the acetonitrile and the cycloheptatriene can be removed on a rotary evaporator, leaving a mixture of tropone, sodium fluoborate, and excess sodium carbonate. Indeed, a convenient method is to conduct the reaction on the rotary evaporator with the warming bath at 50°, accomplishing both of these steps at once.[9] The resulting slurry is taken up in dichloromethane, filtered, and concentrated again, leaving brown tropone[10] which can be used as is, or conveniently distilled (without need of fractionation) at reduced pressure with only minor losses. Yields of 80-94% are routine, meaning that 40-47% of the tropylium salt is converted into tropone.

The role of the sodium carbonate in this reaction remained mysterious for some time, as did the mechanism of the reaction which occurred without sodium carbonate in dimethyl sulfoxide (DMSO).[3,12] We now believe that both reactions proceed by the same mechanism (eq 1): adventitious moisture, unavoidably present in both acetonitrile and DMSO, combines with tropylium salt to make tropyl alcohol, which transfers hydride to another molecule of tropylium salt, giving tropone and cycloheptatriene. The sodium carbonate accelerates the reaction by scavenging protons and especially by replenishing the water as it is used up, maintaining a constant but low concentration of water. It is critical that the water concentration be kept low—too much changes the course of the reaction between tropyl alcohol and tropylium salt, leading to ditropyl ether.[10] Strong evidence for our proposed mechanism would be to show that the reaction does not occur when water is absent. Unfortunately, we were not able to produce acetonitrile completely devoid of water, but in painstakingly dried solvent, the reaction was considerably slower.

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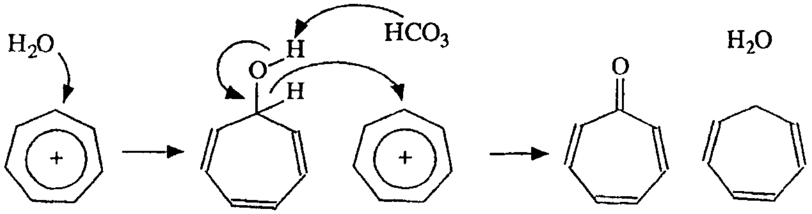

(1)

Experimental: In a dry, 1-L three-necked round-bottomed flask was placed 25.0 g (0.236 mol) of anhydrous sodium carbonate and 400 mL of acetonitrile. The flask was placed in an oil bath maintained at 50 °C while stirring. A total of 67.3 g (0.378 mol) of tropylium fluoborate[13] was added in 1–2 g portions over the course of about 30 min. The mixture was allowed to stir a further 30 min, cooled, filtered, and concentrated on a rotary evaporator. The residue was taken up in 150 mL of dichloromethane, filtered and concentrated again. The residue was distilled to give 17.3 g (86%) of tropone, bp 66°/0.6mm.

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9. We thank Carl Johnson and Mark Scialdone for this suggestion. In our hands this approach led to a somewhat lower yield, though it is not obvious why it should.

10. Occasionally tropone produced in this manner is contaminated by significant amounts of ditropyl ether. The extent of the contamination can easily be determined by NMR or tlc, and seems to depend on the moisture content of the salt and/or the solvent. Ditropyl ether slowly disproportionates to tropone and cycloheptatriene on standing, but as noted by ter Borg,[11] the process is acid catalyzed. We have found that addition of a few drops of methanesulfonic acid to a dichloromethane solution rapidly converts ditropyl ether to tropone and cycloheptatriene.

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