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TRICHLORONITROSOBENZENE - A RAW MATERIAL FOR TATB SYNTHESIS

Z. L. Estes

DEVELOPMENT DIVISION

JULY 1977

Process Development
Endeavor No. 106

Mason & Hanger-Silas Mason Co., Inc.
Pantex Plant
P. O. BOX 30020
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806-335-1581

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INTRODUCTION

In the usual synthesis of s-triaminotrinitrobenzene (TATB), s-trichlorobenzene (TCB), is first nitrated to s-trichlorotrinitrobenzene (TCTNB) and then aminated with ammonia. The s-TCB is obtained as a byproduct from another synthesis operation or from 2,4,6-trichloroaniline. Isomerization of 1,2,4-trichlorobenzene is another possible source.

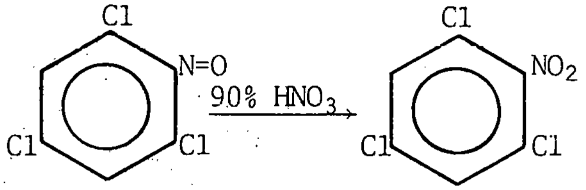
Eastman Chemical Company (Kingsport, Tennessee) is a large producer of 2,4,6-trichloroaniline (TCA) which is used in the synthesis of photographic chemicals; however, they are unwilling to convert this to either the s-TCB or trichloronitrobenzene due to environmental concerns. They have proposed instead to convert TCA to 1,3,5-trichloro-2-nitrosobenzene in large quantity.

DISCUSSION

Two samples of trichloronitrosobenzene were submitted by Eastman for experimental use. Both samples were apparently of high purity by gas chromatography, although both were tan colored powders suggesting the possible presence of oxidation products.

Trial attempts to oxidize the trichloronitrosobenzene with 70% nitric acid were unsuccessful. After four hours at room temperature only one percent was converted to trichloronitrobenzene. Warming the reaction mixture slowly to 50 C produced dark colored reaction products and the reaction became exothermal. Similar results were obtained when trichloronitrosobenzene was added to the usual reaction mixtures of sodium nitrate-oleum or nitric acid-oleum.

The addition of trichloronitrosobenzene to 90% (fuming) nitric acid at room temperature produced entirely different results. The oxidation reaction proceeded rapidly and smoothly to the desired trichloronitrobenzene:

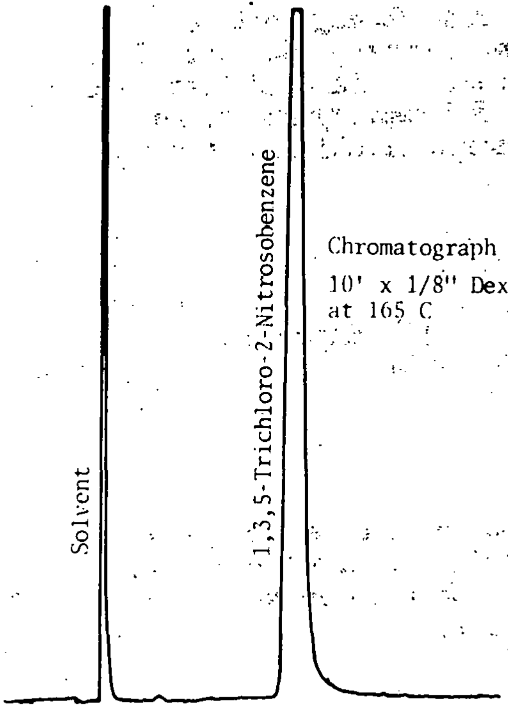


Drowning the reaction mixture in water resulted in a 98.6% recovery of trichloronitrobenzene (a tan colored powder).

Fig. 1 is a gas chromatogram of the original sample showing the presence of a trace (~ 0.05%) of an unknown compound (probably the dichloro compound). Fig. 2 illustrates the separation obtainable between the nitroso and nitro compounds by gas chromatography on a prepared mixture.

Figs. 3 through 6 show the rapid conversion of the nitroso compound to the trichloronitrobenzene in 90% nitric acid with the appearance and disappearance of small amounts of unknown oxidation products. The samples being taken at 30 second, 1, 3 and 6 minute intervals.

In another experiment, oleum was added to the 90% nitric acid reaction mixture ten minutes after the addition of the nitroso compound and the temperature was then increased to 150 C for four hours. The resulting product was pure white TCTNB (90.2%) containing the usual 2.0% dinitrotrichlorobenzene and 7.8% tetrachlorodinitrobenzene as obtained from the nitration of s-TCB.



Chromatograph Column:
10' x 1/8" Dexsil 300
at 165 C

Fig. 1. 1,3,5-Trichloro-2-Nitrosobenzene (Eastman Chemical Company)

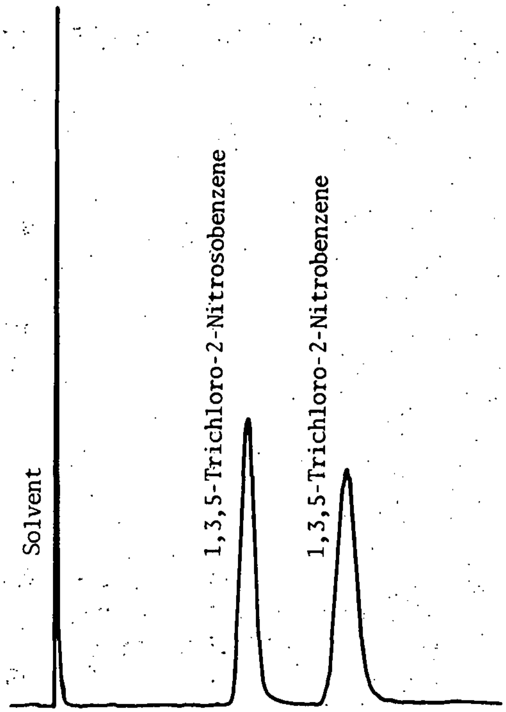
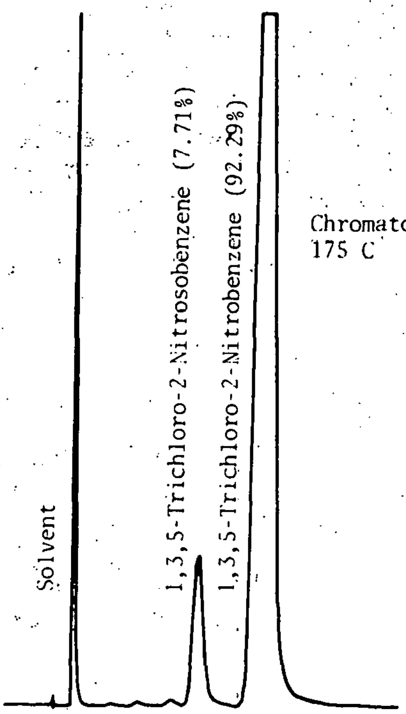
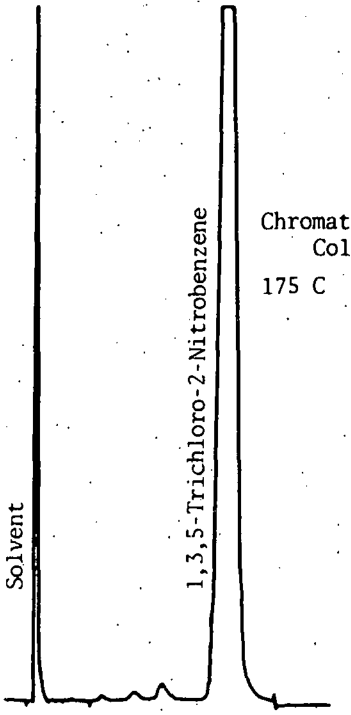


Fig. 2. Separation of Trichloronitrosobenzene and trichloronitrobenzene at 165 C.



Chromatograph Column:
175 C

Fig. 3. Conversion of Trichloronitrosobenzene to Trichloronitrobenzene in 90% Nitric Acid (23 C) after 30 Seconds



Chromatograph Column: 175 C

Fig. 4. Conversion of Trichloronitrosobenzene to Trichloronitrobenzene in 90% Nitric Acid (23 C) after 1 Minute

Chromatograph Column: 175 C

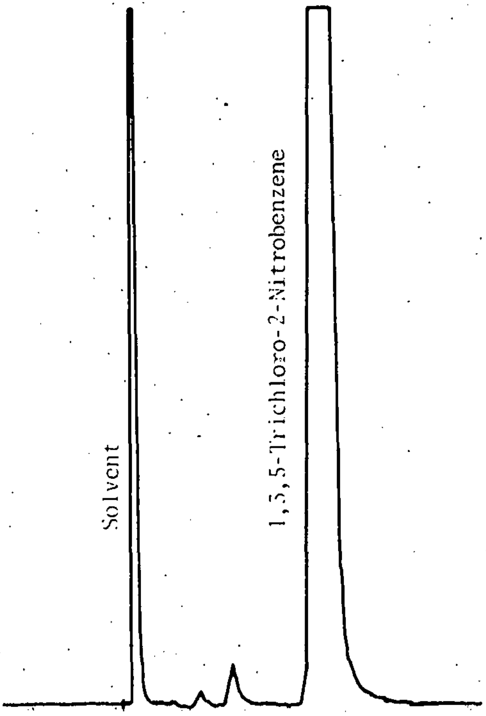


Fig. 5. Conversion of Trichloronitrosobenzene to Trichloronitrobenzene in 90% Nitric Acid (23 C) after 3 Minutes

Chromatograph Column: 175 C

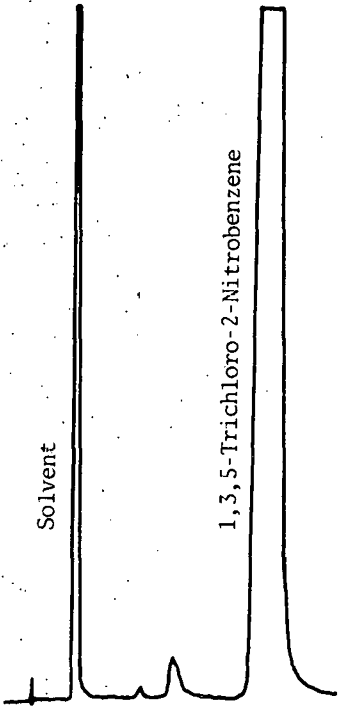


Fig. 6. Conversion of Trichloronitrosobenzene to Trichloronitrobenzene in 90% Nitric Acid (23 C) after 6 Minutes

CONCLUSION

With only slight modification of the present procedure, 1,3,5-trichloro-2-nitrosobenzene can probably be utilized in the production of the TATB intermediate TCTNB as easily as TCB. This conclusion of course neglects toxicity considerations, the effects of trace impurities, consistancy of supply, and cost. Further study is indicated.