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# SYNTHESIS OF BENZOTRIFUROXANE (BTF) 36

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DEVELOPMENT DIVISION

JULY - SEPTEMBER 1971

SANL 900-007

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Section G

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## ABSTRACT

This work is to find an improved method for the synthesis of benzotrifuroxane which could be conveniently scaled up. Three batches were made; the first following the LLL procedure, the second with modifications in the initial addition step, and the third with changes in fluid system and handling procedures going from the intermediate to the final product.

## DISCUSSION

The starting material for the reaction, trinitrotrichlorobenzene (TNTClB), was obtained from LLL in a reasonably pure form. The additional required reagents were purchased commercially.

The reaction scheme (Fig. 1) involved the conversion

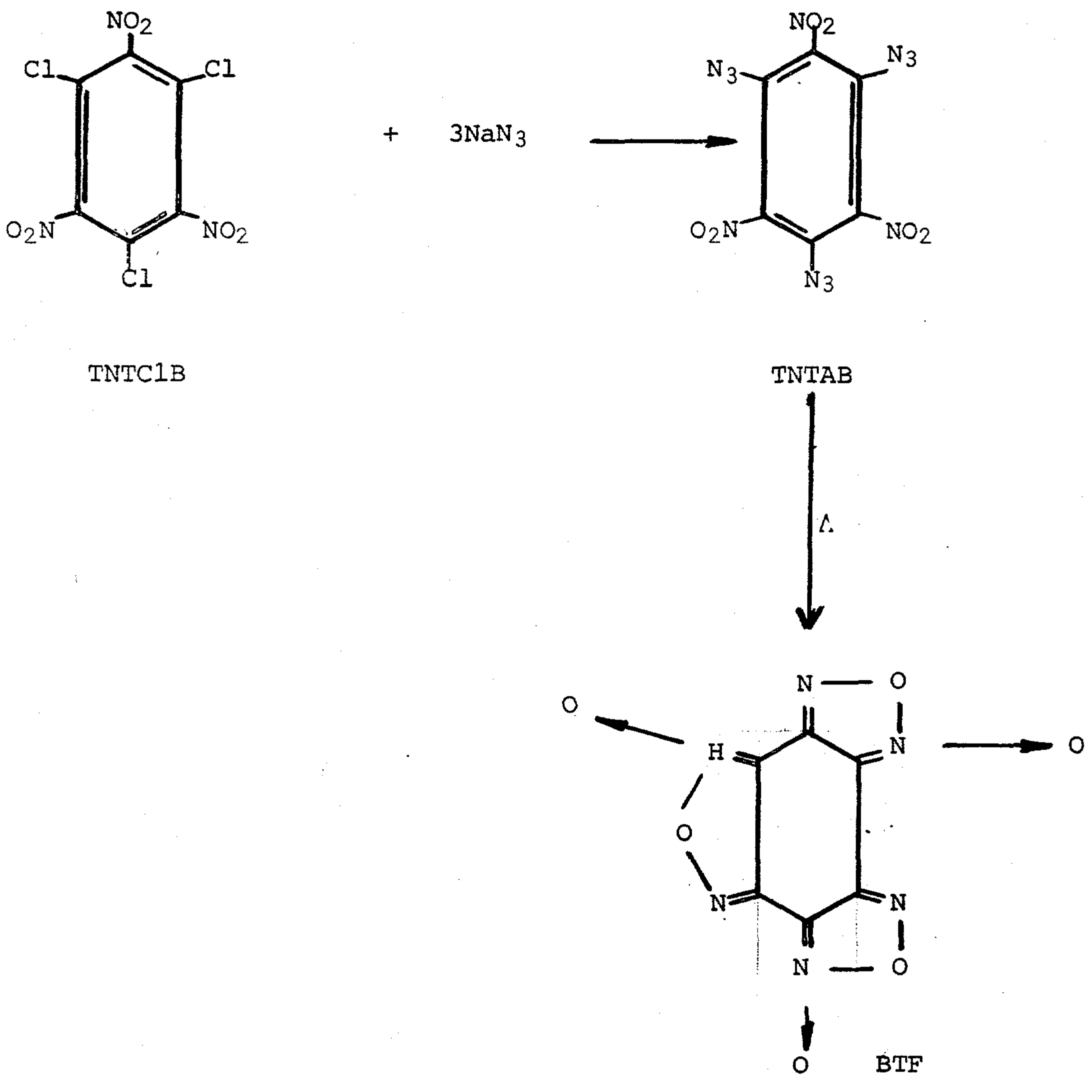

Fig. 1.

of TNTClB to trinitrotriazidobenzene (TNTAB) and subsequently to benzotrifuroxane (BTF). The initial reaction used sodium azide ($NaN_3$) in ethyl alcohol for the replacement of the chloride with the azide group. The conversion to BTF involved heating the TNTAB in an unreactive fluid medium.

The first batch was run following the LLL method but on a reduced scale.

> *The setup consisted of a 250 ml flask fitted with a thermometer, mechanical stirring and an open solids addition port. The flask was surrounded by 21 C water in a circulating water bath. To the flask was added 50 ml of 95% ethanol and 3.18g of finely divided sodium azide. This mixture was allowed to stir for 15 minutes at which time the ethanol appeared to be saturated with a quantity of undissolved sodium azide remaining in the flask. The TNTClB was added in approx. 0.5g portions over a one hour time period. Samples were taken of the reaction product prior to each addition. After the addition was completed the reaction mixture was allowed to stir for 45 minutes. The reaction mixture was allowed to settle and the liquid layer was decanted. Two 20 ml ethanol washes were used to remove undesired impurities. The product was dried by filtration. The product was then added to 25 ml of propanoic acid.*

This product was subsequently lost due to an incident unrelated to the BTF project.

The samples that were taken during the addition of the TNTClB were examined with aid of a microscope. The initial samples examined up to 50% completion of addition were made up of predominantly single crystals, rod-like in shape. As addition continued the crystal clusters began forming and many very fine particles were observed.

A second batch was made with variations in the initial addition step. The scale was the same as the first batch.

> *The reaction was run in a 500 ml 3 - necked flask fitted with mechanical stirring, thermometer and a graduated addition funnel. The reaction temperature was held constant by placing the reaction flask in a circulating water bath. TNTClB, 5.3g, was added to 150 ml of ethanol in the flask. A second solution was made using 20 ml of $H_2O$ and 60 ml of ethanol to dissolve 3.2g of sodium azide. This solution was placed in the graduated addition funnel. The stirring was started and the addition (Table I) completed in 33 minutes. The reaction mixture was allowed to stir for 6 hours.*

*Table I. Addition of Sodium Azide & Reaction Temperature*

| | $NaN_3$ Solution | |
|---|---|---|
| min | ml | C |
| 0 | 0 | 20.5 |
| 10 | 20 | 21.0 |
| 20 | 44 | 21.5 |
| 30 | 74 | 21.0 |
| 33 | 80 | 21.0 |
| 40 | 80 | 21.0 |
| 90 | 80 | 21.0 |
| 120 | 80 | 21.0 |

*After 3 hours from start of addition a small amount of unreacted TNTClB was still observable in the flask. At the end of 6 hours none of the unreacted TNTClB was observed.*

*The suspended product was allowed to settle and the majority of the fluid was removed with a filter stick. Approximately 150 ml of 95% ethanol was added with stirring. The fluid was again removed with the aid of a filter stick. The washing process was repeated several more times. It was observed that the color of the fluid layer was similar after each washing and it was therefore felt the desired product was being lost in the washing. A 50% ethanol wash was then used in a further effort to remove unreacted sodium azide. A product was precipitated in a finely divided form which made the filter stick operation difficult. As much fluid as possible was removed this way. A 100 ml water wash was then used with similar difficulties as were found in the 50% ethanol wash. It was assumed that after this extensive washing procedure all sodium azide & TNTClB impurities and much of the product had been removed.*

*The damp product was added to 45 ml of propanoic acid in a 100 ml distilling flask. The flask, fitted with a reflux condenser, was placed in an ethylene glycol heating bath. The heat was turned on and at 80 C it was observed that all the solids had gone into solution. The propanoic acid was refluxed for 1/2 hour at a temperature between 135 and 140 C. The cooled solution was poured into 400 ml of distilled water through a coarse fritted filtering funnel. The precipitation was then filtered out. The yield from this reaction was less than 10% of theorotical.*

*DTA: MP 195 C, exothermic decomp. 265 C*

*CHN: Calc. for CNO: C, 28.6; N, 33.4; 0, 38.0*

*Found: C, 28.0; N, 32.8; 0, 39.2.*

The purity of this product seemed adequate. The low yield was undoubtedly caused in part by the excessive washing procedure used. The undesirable parts of this procedure occurred in the washing and handling of the TNTAB intermediate.

A third batch was started in an attempt to overcome some of these problems. The scale of this reaction was identical to the previous one. A change in the first reaction from that previously described was use of 70 ml of ethanol solution containi containing 20 ml of water used to dissolve the sodium azide. The addition time and the reaction temperatures were essentially the same. When the reaction was complete, 150 ml of water was added, the mixture was stirred and fluids removed with a filter stick. The evaporated residue from water/alcohol mixture showed very little TNTAB as indicated by DTA. To the solid residue was added 400 ml of xylene and 100 ml of water. Samples from both of these layers were taken. The DTAs indicated that the product was in the xylene layer.

A portion of the xylene layer was heated in an oil bath at the reflux temperature (∿ 140 C). Much evolution of gas was observed.

## FUTURE WORK; COMMENTS; CONCLUSIONS

Future work will include the isolation of the product from xylene solution, further work on improving yield and scale up. The work to this point indicates that a method of synthesis may be possible which does not involve the handling of a dry filler.