Synthesis and characterization of 1,3-bis-(2,4,6-trichlorophenyl)-1H-triazene (BTCPT)

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1,3-Bis(2,4,6-trichlorophenyl)-1H-triazene (BTCPT) has been obtained as a by-product during the synthesis of 1,3,5-trichlorobenzene (Sym.TCB) by diazotization of 2,4,6-trichloroaniline in the presence of \( \text{NaNO}_2/\text{HCl} \) and ethyl alcohol at 0-5°C and characterized by elemental analysis, IR, NMR and mass spectra.

1,3,5-Triamino-2,4,6-trinitrobenzene (TATB), a well known thermally stable explosive, has been synthesized on a laboratory scale from 3,5-dinitrobenzoic acid, 3,5-dichloroanisole, selective reduction of 2,4,6-trinitrotoluene (TNT) and recently from 2,4,6-trinitroaniline and 1,1,1-trimethylhydraziniumiodide through "vicarious nucleophilic substitution (VNS)" routes. For synthesis of TATB, 1,3,5-trichlorobenzene (Sym.TCB) is also a starting material. The synthesis of TATB from Sym.TCB has been scaled-up to a pilot plant level due to ease in scaling up and cost of the resulting TATB. Therefore, synthesis of Sym. TCB, which is not available in India, has been studied by us in detail.

A literature survey indicates that most of the information available on the synthesis of TCB is patented. Further, a schematic route for synthesis of TATB from aniline has also been given via formation of TCB. We also studied this route which results in TCB along with a by-product, a maroon coloured compound, identified as 1,3-bis(2,4,6-trichlorophenyl)-1H-triazene (BTCPT) and not reported through this route by the original researchers. However, Hantzsch has reported BTCPT from 2,4,6-trichloroaniline on treatment with amyl nitrite/\( \text{H}_2\text{SO}_4 \) in the presence of alcohol and analysed it with the help of elemental analysis and melting point.

In the present investigation, we report synthesis of BTCPT from 2,4,6-trichloroaniline through diazotisation and its detailed characterization.

Results and Discussion

The title compound 1,3-bis(2,4,6-trichlorophenyl)-1H-triazene (BTCPT) was prepared as shown in Scheme I.

2,4,6-Trichloroaniline (TCA) was prepared by chlorination of aniline and used as a starting material.
for diazotization. It is interesting to observe that diazonium chloride is stable at 0 - 5°C after addition of ethyl alcohol. However, when the temperature rises to 15°C and above, formation of gas starts alongwith simultaneous precipitation of a maroon coloured compound. The formation of triazene in the presence of ethanol takes place due to presence of unreacted 2,4,6-trichloroaniline which subsequently reacts with 2,4,6-trichlorodiazonium chloride to form BTCPT. However, use of a strong acid like conc. H2SO4 in place of conc. HCl during diazotisation prevents formation of BTCPT.

BTCPT is a maroon coloured solid compound which melts (with decomposition) at 139-40°C. The poor yield of BTCPT is because of the fact that it is a by-product while major product is TCB. The compound has been characterised by elemental analysis and spectral data (IR, NMR and mass).

The IR spectrum of BTCPT shows strong absorption band at 3436 cm⁻¹ for -N-H stretching while aromatic C-H stretching appears at 3090 cm⁻¹. The -C=C- and -N=N- stretching frequencies appear at 1562 and 1494 cm⁻¹ respectively. The -C-Cl bending (out of plane) appears at 1376 cm⁻¹. In ¹H NMR spectrum, -NH proton resonate at δ 10.2 ppm while chemical shifts of CH protons of aromatic rings is displayed at δ 7.4 ppm. The electron impact mass spectrum (EI MS) shows a molecular ion peak at m/z 404 while other molecular ion species such as m/z 224, 208, 195, 180, 145 and 110 are due to 2,4,6-trichlorophenyl triazene ion, 2,4,6-trichlorodiazonium ion, 2,4,6-trichloroiminium ion, 2,4,6-trichlorobenzene ion and di and mono chlorobenzene ions respectively. The observed elemental analysis data of BTCPT is also in close agreement with the calculated values. The elemental analysis and spectral data fully support the structure of 1,3-bis(2,4,6-trichlorophenyl)-1H-triazene as proposed.

In conclusion, 1,3-bis(2,4,6-trichlorophenyl)-1H-triazene (BTCPT), a dark maroon coloured compound, which is likely to find applications in the dye industry where maroon colour is of prime importance, has been synthesized with excellent purity and fully characterized.

Experimental Section

The melting point was determined on open capillary tubes and is uncorrected. The IR spectrum was recorded on Perkin-Elmer Infrared Spectrophotometer using KBr matrix. ¹H NMR spectrum was recorded on Bruker 90 MHz using chloroform-d₄ as a solvent and TMS as an internal standard. Electron Impact mass spectrometry (EI MS) was recorded on double focusing JEOL-DS mass spectrometer at 70 eV using direct insertion technique. Elemental analysis was performed on Carlo-erba elemental analyzer, EA 1108. 2,4,6-Trichloroaniline, prepared in the laboratory by chlorination of aniline and melting point 77.3 - 77.8°C, was used as a starting material. Sodium nitrite, hydrochloric acid and ethyl alcohol were SQ grade and obtained from Glaxo (India).

Synthesis of 1,3-bis(2,4,6-trichlorophenyl)-1H-triazene (BTCPT). To a one-litre three-necked round-bottomed flask, hydrochloric acid (50 mL) was transferred. After this, 2,4,6-trichloroaniline (10 g, 0.05 mole) was added to it. The reaction mixture was cooled 0°C and at this stage, sodium nitrite (7 g, 0.1 mole) dissolved in distilled water (10 mL) was added dropwise through dropping funnel maintaining temperature at 0-5°C with continuous stirring. To this, cooled ethyl alcohol (75 mL) was also added dropwise and reaction mixture was allowed to attain ambient temperature slowly and kept overnight. The product was filtered, washed with ethanol to remove TCB, dried and recrystallized from chloroform, m p 139-40°C (lit 141°C), yield 21% (2.1 g). IR (KBr) : 3436 (-NH Str.), 3090 (Ar.H Str.), 1376 (-N-H bending) and 1562 (C=C Str.) cm⁻¹; ¹H NMR (CDCl₃, TMS) : δ 10.2 (s, 1H), 7.4 (s,4H); EI MS (70 eV) m/z: 404 (mol ion peak), 224,208,195,180 (base peak), 145 and 110. Anal Caled for C₂₂H₁₉N₅Cl₆: C, 35.64; H, 1.23; N, 10.26. Found: C, 35.49; H, 1.10; N, 10.26 %.

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