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Derivatives and Synthesis of Heterocyclic Compound: Thiophene

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Perspective

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DESCRIPTION

Thiophene, having the formula (C_4H_4S,) is a heterocyclic chemical. It is aromatic, as evidenced by its extensive substitution reactions, and consists of a planar five-membered ring. It has a benzene-like odour and is colourless. It is similar to benzene in most of its reactions. Furan (C_4H_4O), Selenophene (C_4H_4Se), and Pyrrole (C_4H_4NH) are thiophene analogues that differ by the heteroatom in the ring. Thiophene was detected in benzene as a contaminant. When isatin (an indole) is combined with sulfuric acid and crude benzene, it produces a blue dye. The production of blue indophenin had long been thought to be a benzene reaction. Viktor Meyer was able to identify thiophene as the real chemical causing this reaction. Thiophene and its derivatives are found in petroleum, occasionally in amounts of up to 3%. The Hydrodesulphurization (HDS) method removes thiophenic content from oil and coal. Under H_2 pressure, the liquid or gaseous feed is passed over a molybdenum disulfide catalyst in HDS. Thiophenes are hydrogenolyzed to produce hydrocarbons and hydrogen sulphide. Thiophene is therefore transformed to butane and H_2S. Benzothiophene and dibenzothiophene are more common and more dangerous in petroleum.

Occurence

Between 2012 and 2017, the rover Curiosity at Gale crater (Mars) found thiophene derivatives at nanomole quantities in 3.5 billion year old Martian soil deposits. It is a significant milestone for the Mars Science Laboratory (MSL) mission in its long and arduous search for organic materials on Mars. The Sample Analysis at Mars (SAM) instrument heated lacustrine mudstone samples to high temperatures (500°C to 820°C), allowing gas chromatography-mass spectrometry (GC-MS) investigations of the generated gases and the discovery of aromatic and aliphatic chemicals, including numerous thiophene compounds. Carbon-sulfur linkages in macromolecules may have contributed to the

long-term preservation of organic materials. Organic sulphur is expected to be present in 5% of organic compounds analysed by the SAM instrument. The origin and mechanism of production of these molecules, whether biotic or abiotic, are still unknown, but their discovery raised the intriguing subject of thiophenic chemicals as a putative ancient bio signature on Mars.

Synthesis

Thiophenes, due to their high stabilities, are formed in a variety of reactions involving sulphur sources and hydrocarbons, particularly unsaturated ones. Meyer's first synthesis of thiophene, described the same year he discovered it, uses acetylene and elemental sulphur. Thiophenes are traditionally synthesised by reacting 1, 4-diketones, diesters, or dicarboxylates with sulfidizing reagents such as P_4S_{10}, as in the Paal-Knorr thiophene synthesis. Specialized thiophenes can be made in the same way, either using Lawesson's reagent as the sulfidizing agent or with the Gewald reaction, which involves the condensation of two esters in the presence of elemental sulphur. The Volhard-Erdmann cyclization is another approach.

Thiophene is produced on a small scale, with roughly 2,000 metric tons produced globally each year. The vapour phase reaction between a sulphur source, often carbon disulfide, and a C-4 source, typically butanol, is used in the production. At 500°C -550°C, these reagents come into contact with an oxide catalyst.

Derivatives of thiophene

Thienyl: Thiophene deprotonates to form the thienyl group, C_4H_3S. Although the anion does not exist in its pure form, organolithium derivatives do. Thus, thiophene reacts with butyl lithium to form 2-lithiothiophene, commonly known as 2-thienyllithium. When this reagent combines with electrophiles, it produces thienyl derivatives such as thiol. Thienyl lithium is oxidised to yield 2, 2'-dithienyl $(C_4H_3S)_2$. Thienyl lithium is used in the synthesis of higher order mixed cuprates. Dithienyl, an analogue of biphenyl, is produced by coupling thienyl anion equivalents.

Ring fused thiophene: Benzothiophene is produced by fusing thiophene with a benzene ring. Dibenzothiophene or naphthothiophene is produced by fusing two benzene rings. Isomers of thienothiophene are formed by the fusion of two thiophene rings.

Uses of thiophene

Thiophenes are essential heterocyclic compounds that are frequently employed as building blocks in various agrochemicals and medicines. A physiologically active compound's benzene ring can frequently be substituted by a thiophene without losing activity. Examples include the NSAID lornoxicam, a thiophene analogue of piroxicam, and sufentanil, a thiophene analogue of fentanyl.