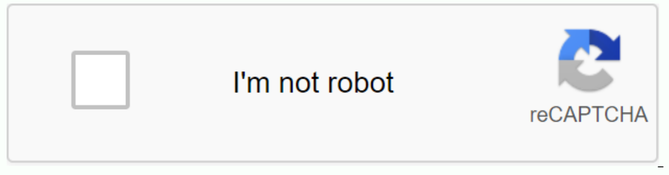

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Diazotization reaction mechanism pdf

Sandmeyer response Named after Traugott Sandmeyer Response Type Replacement Type Replacement Identifiers Organic Chemistry Portal Sandmeyer Reaction RSC ontology ID RXNO: 000021 The Sandmeyer reaction is a chemical Reaction used to synthesize the diazonium salts with copper salts as [1] [2] [3] This is an example of a radical-nucleophilic aromatic replacement. The Sandmeyer response provides a method through which one can perform unique transformations on bench, such as halogenation, cyanide, trifluoromethylation, and hydroxylation. The reaction was discovered by Swiss chemistry Traugott Sandmeyer in 1884 when he attempted to synthesise phenycosetics of benzenediazonium chlorite and cuprous athics. Instead, the main product he isolated was phenols chlorid. [4] In modern times, the Sandmeyer response refers to any method for replacing an aromatic amino group via the preparation of its diasonium salt, followed by its displacement with a nuclear war in the presence of catalytic copper(I) salts. (Due to the low cost of copper salts, a stoichiometric amount is often employed for better reactivity even when catalysis is possible.) The most common in service Sandmeyer reactions are the chlorine, bromination, cyanide, and hydroxylation reactions using CuCl, CuBr, CuCN, and Cu2O, respectively. More recently, trifluoromethylation of diazonium salts has been developed and is referred to as a 'Sandmeyer-type' response. Diazonium salts also react with boreholes, iodine, dioles, water, pituitary foric acid and others,[5] and fluorination can be performed using tetrafluoroborate anione (Balz-Schiemann response). However, since these processes do not require a metal catalyst, they are usually not referred to as Sandmeyer reactions. In numerous variants developed, other transitional metal salts, including copper (II), iron (III) and cobalt (III) were also employed. [6] Due to its wide synthetic appropriateness, the Sandmeyer reaction, together with other transformations of diasonium obligations, is complementary to electrophilic aromatic replacement. Response Conditions and Mechanism The nitrogen acid is typically prepared in situ of sodium nitride and acid. After two protonation steps, one equivalent of water is lost to form the nithrosonium ion. The nitrosonium ion then serves as an electrophyle in a response with an aromatic (or heterocyclic) amine, such as aniline, to form a diasonium salt provided by a nitrosamine intermediate. [5] Typical reaction conditions are as follows:[7][8] Chlorination: ArN2 + Cl–, CuCl, HCl (36% aq.), 50 – 100 °C; Bromination: ArN2 + HSO4–, CuBr, HBr (48% aq.), 50 – 100 °C; Systemation: ArN2 + Cl–, CuCN, KCN, H2O, Benseen, 0 °C; Hydroxypage: Cu2O, Cu (NO3)2, H2O, 25 °C. The Sandmeyer reaction is an example of a radical-nucleophylical aromatic replacement (SRC). The radical mechanism of the Sandmeyer response is supported by the detection of byproducts. [9] The from the aromatic diazo group with a halogen or pseudohalogen is initiated by a one electron transfer mechanism catalyzed by copper(I) to form a radical with the loss of nitrogen gas. [11] [11] [12] [9] The replaced areon may be formed by direct transfer of Cl, Br, CN or OH from a copper(II) species to the radical zone to produce the replaced areon and restore the buyer(I) catalyst. In an alternative proposal, a transient buyer (III) intermediate, formed from connecting the radicals with the buyer (II) species, undergoes rapid reductive elimination to afford and regenerate the product (I). [14] [14] [15] Evidence for such an organocopper intermediate, however, is weak and mostly circumstances[16][17] and the exact path may depend on substrate and reaction conditions. These possibilities are shown below. Formation of the nitrosonium ion formation of the benzenediazonium ion Single electron transfer Synthetic applications Variations on the Sandmeyer response were developed to fit various synthetic applications. These reactions usually continue by forming a diazonium salt, followed by a reaction with a buyer(I) salt to yield a replaced areon according to the scheme below. Some examples of the synthetic applications of the Sandmeyer response are provided below. One of the main uses of the Sandmeyer response is the formation of the halides. The solvent of choice for the synthesis of the jodides is diiodomethane,[18] while used for the synthesis of framides. For the synthesis of chlorids, chloropform is the solvent of choice. [20] The synthesis of (+) curcuphenol, a bioactive compound displaying antifungal and antidote activity, uses the Sandmeyer response to replace an amine group through a bromo group. [21] One bromination protocol uses a Cu(I)/Cu(II) mixture with additional quantities of bidentate ligand phenoline and phase-transfer catalyst dibenzo-18-crown-6 to convert an aryl diazonium tetrafluoroborate salt to convert an aryl bromide. [22] The Balz-Schiemann response uses tetrafluoroborate and delivers the halide-replaced product, fluorobenzene, which is not obtained by the use of copper fluorides. This reaction shows motives characteristic of the Sandmeyer response. [23] Sianation Another use of the Sandmeyer response is for sentences that allow for the formation of benzodnitriels, an important class of organic compounds. A key intermediate in the synthesis of the anti-psychotic drug, Fluanxol, is synthesized by a synthesizing by the Sandmeyer response. [24] The Sandmeyer response was also employed in the synthesis of neoamphimedine, a compound proposed to target topoisomase II as an anti-cancer drug. It has been shown that Sandmeyer-type reactions can be used to generate compounds functionalized by trifluoromethyl replacement groups. process of trifluoromethylation trifluoromethylationation unique chemical properties with a wide range of practical applications. Especially, pharmaceutical products with CF3 groups have improved metabolic stability, lipophilicity, and bioavailability. Sandmeyer-type trifluoromethylation reactions feature mild reaction conditions and a larger functional group tolerance relative to earlier methods of trifluoromethylation. [26] [27] An example of a Sandmeyer-type trifluoromethylation response is presented below. [28] Hydroxying The Sandmeyer response can also be used to convert the amines to phenols provided by the formation of an aryl diazonium salt as shown below. [8] In the presence of coperkatalisator, this response readably takes place at room temperature. The procedure reported by Cohen and collaborators appeals to cuprous oxide, along with excess cupric nitrate in neutral water. This is unlike the classic procedure (known by German name Verkochung, Verkochung), which calls for cooking the diazonium salt in aquatic acid, a process that is believed to involve the catalyst instead of radicals and is known to generate other nucleophilic additional side products in addition to the desired hydroxylation product. Triazene Treatment with a second equivalent of aniline would give a triazene. Compare for example, Diminazene (Berenil), and Isometamidium chlorine. In 1884 Die Burger and the First World War issued a statement saying that Die Burger and the 1980s appealed to Die Burger. Ueber the Ersetzung der Amidgruppe durch Chlor in den aromatischen Substanzen. Berichte der deutschen chemischen Gesellschaft. 17 (3): 1633–1635. Doi:10.1002/cber.18840170219. In 1884 Die Burger and the letters became to Die Burger. 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