Benzyl chloroformate structure

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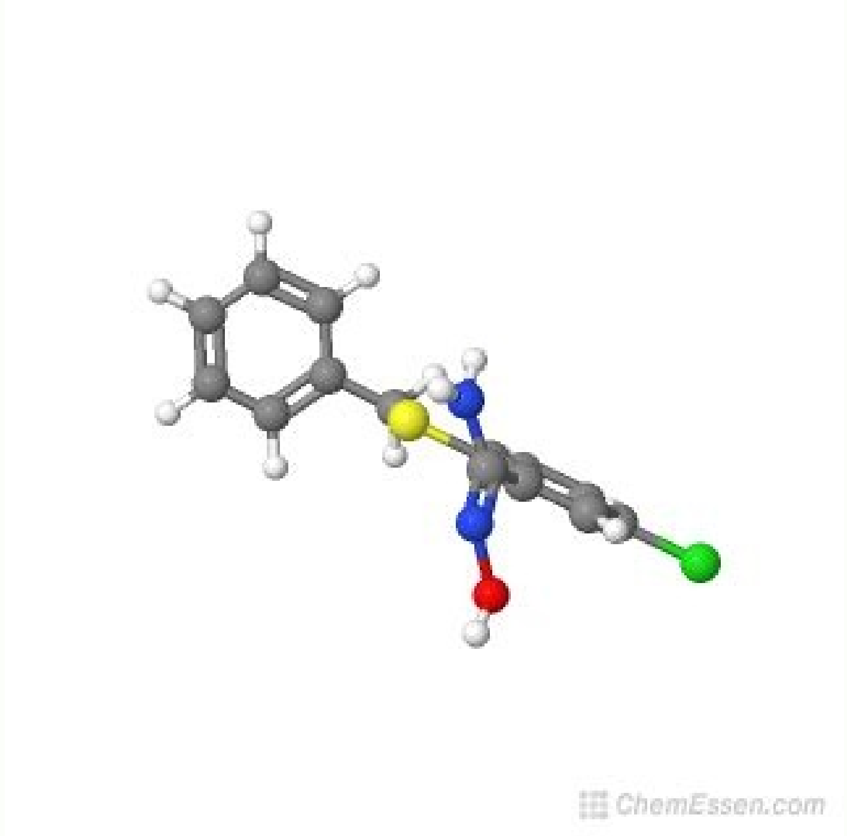

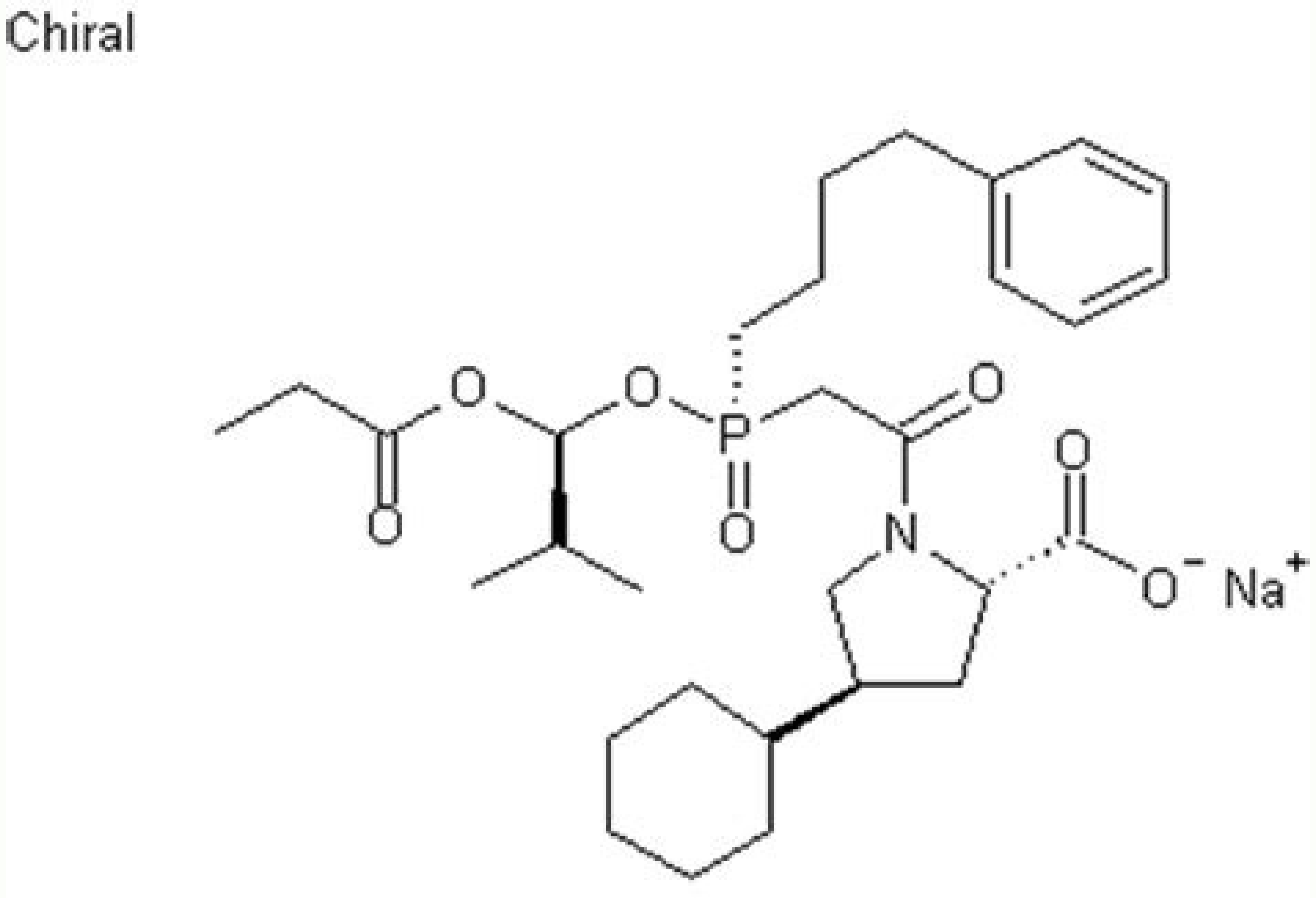

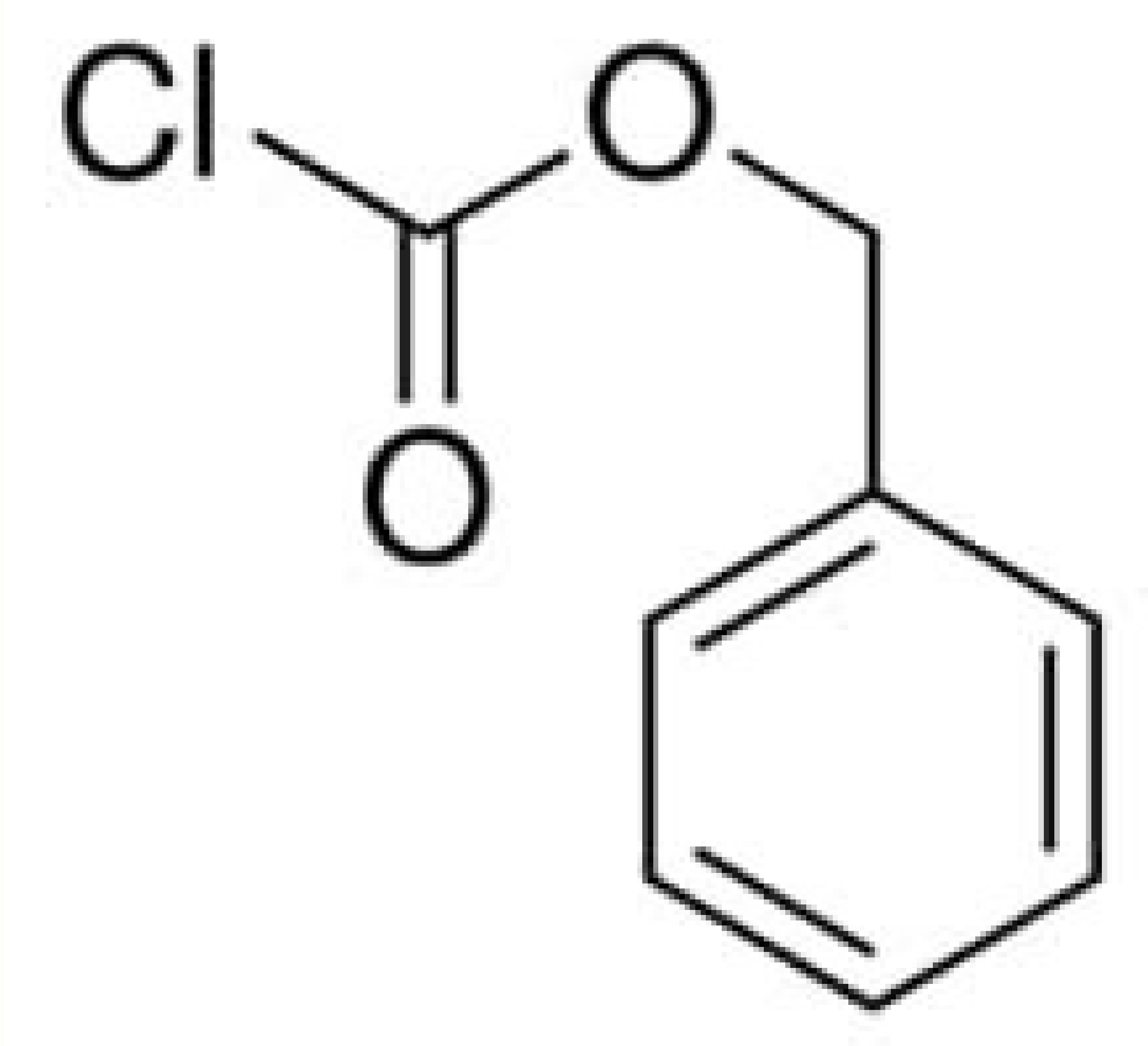

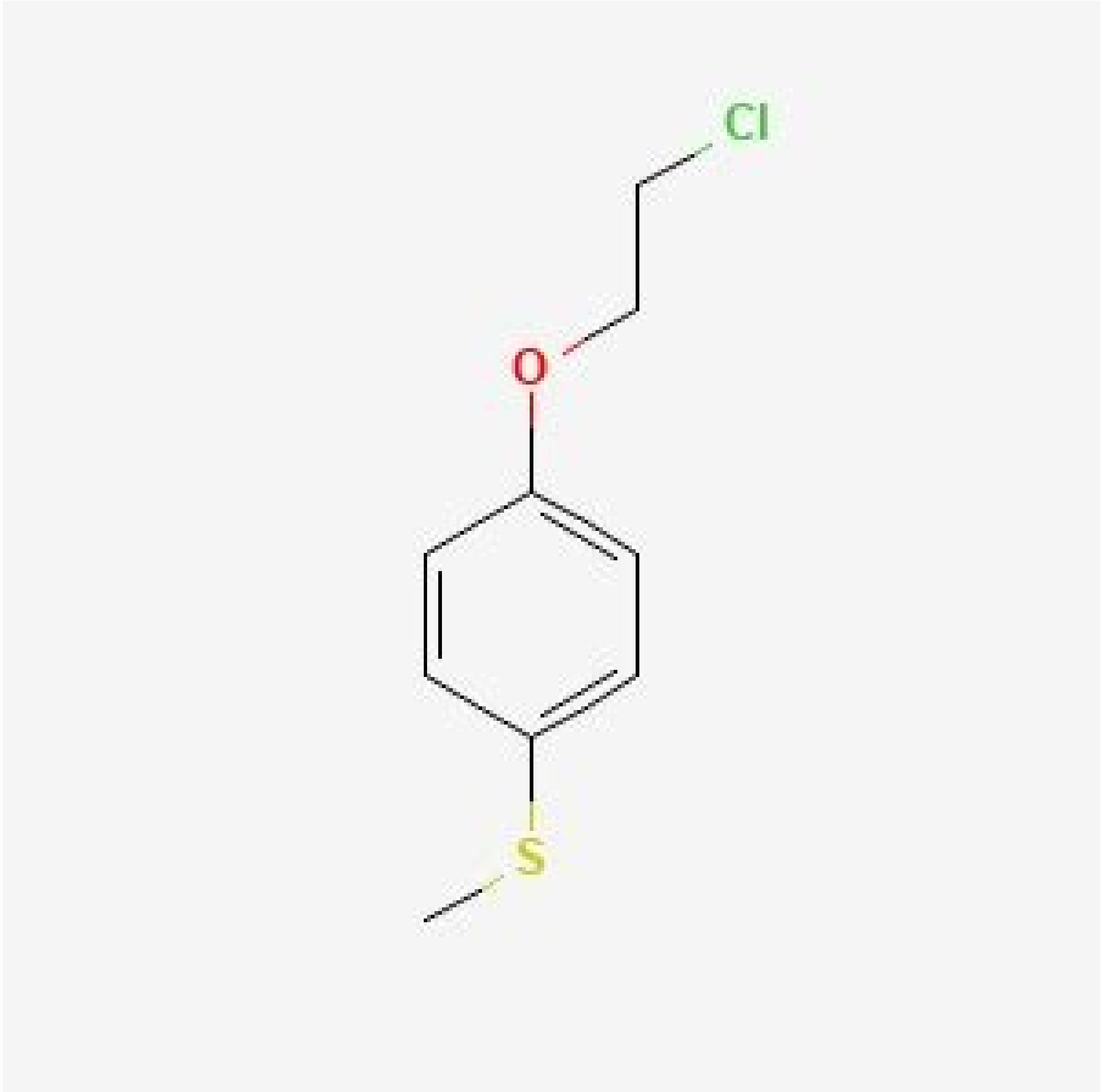

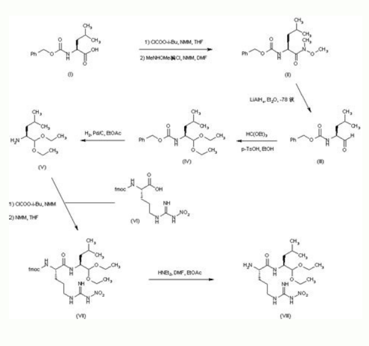

This content is from the eCFR and is authoritative but unofficial. Print/PDF Display Options Published Edition "COCl2" redirects here. For the compound CoCl2, see Cobalt(II) chloride. Not to be confused with phosphine, phosphene, oxalyl chloride, or phosgene oxime. Chemical compound Phosgene[1] Names Preferred IUPAC name Carbonyl dichloride[2] Other names Carbonyl chlorideCGCarbon dichloride oxideCarbon oxychlorideChloroformyl chlorideDichloroformaldehydeDichloromethanoneDichloromethanalCollongite Identifiers CAS Number 75-44-5 Y 3D model (JSmol) Interactive image ChEBI CHEBI:29365 Y ChemSpider 6131 Y ECHA InfoCard 100.000.792 EC Number 200-870-3 PubChem CID 6371 RTECS number SY5600000 UNII 117K140075 Y UN number 1076 CompTox Dashboard (EPA) DTXSID0024260 InChI InChI=1S/CCl2O/c2-1(3)4 YKey: YGYAWVDWMABLBF-UHFFFAOYSA-N YInChI=1/CCl2O/c2-1(3)4Key: YGYAWVDWMABLBF-UHFFFAOYAH SMILES ClC(Cl)=O Properties Chemical formula COCl2, also CCl2O Molar mass 98.92 g/mol Appearance Colorless gas Odor Suffocating, like musty hay[3] Density 4.248 g/L (15 °C, gas)1.432 g/cm3 (0 °C, liquid) Melting point −118 °C (−180 °F; 155 K) Boiling point 8.3 °C (46.9 °F; 281.4 K) Solubility in water Insoluble, reacts[4] Solubility Soluble in benzene, toluene, acetic acidDecomposes in alcohol and acid Vapor pressure 1.6 atm (20°C)[3] Magnetic susceptibility (χ) −48·10−6 cm3/mol Structure Molecular shape Planar, trigonal Dipole moment 1.17 D Hazards GHS labelling: Pictograms [5] Signal word Danger Hazard statements H280, H314, H330[5] Precautionary statements P260, P280, P303+P361+P353+P315, P304+P340+P315, P305+P351+P338+P315, P403, P405[5] NFPA 704 (fire diamond) 4 0 1 Flash point Non-flammable Threshold limit value (TLV) 0.1 ppm Lethal dose or concentration (LD, LC): LC50 (median concentration) 500 ppm (human, 1 min)340 ppm (rat, 30 min)438 ppm (mouse, 30 min)243 ppm (rabbit, 30 min)316 ppm (guinea pig, 30 min)1022 ppm (dog, 20 min)145 ppm (monkey, 1 min)[6] LCLo (lowest published) 3 ppm (human, 2.83 h)30 ppm (human, 17 min)50 ppm (mammal, 5 min)88 ppm (human, 30 min)46 ppm (cat, 15 min)50 ppm (human, 5 min)2.7 ppm (mammal, 30 min)[6] NIOSH (US health exposure limits): PEL (Permissible) TWA 0.1 ppm (0.4 mg/m3)[3] REL (Recommended) TWA 0.1 ppm (0.4 mg/m3) C 0.2 ppm (0.8 mg/m3) [15-minute][3] IDLH (Immediate danger) 2 ppm[3] Safety data sheet (SDS) [1] Related compounds Related compounds ThiophosgeneFormaldehydeCarbonic acidUreaCarbon monoxideChloroformic acid Except where otherwise noted, data are given for materials in their standard state (at 25 °C [77 °F], 100 kPa). Y verify (what is YN ?) Infobox references Chemical compound Phosgene is the organic chemical compound with the formula COCl2. It is a toxic, colorless gas; in low concentrations, its musty odor resembles that of freshly cut hay or grass.[7] Phosgene is a valued and important industrial building block, especially for the production of precursors of polyurethanes and polycarbonate plastics. Phosgene is extremely poisonous and was used as a chemical weapon during World War I, where it was responsible for 85,000 deaths. It was a highly potent pulmonary irritant and quickly filled enemy trenches due to it being a heavy gas. It is classified as a Schedule 3 substance under the Chemical Weapons Convention. In addition to its industrial production, small amounts occur from the breakdown and the combustion of organochlorine compounds, such as chloroform.[8] Structure and basic properties Phosgene is a planar molecule as predicted by VSEPR theory. The C=O distance is 1.18 Å, the C−Cl distance is 1.74 Å and the Cl−C−Cl angle is 111.8°.[9] It is one of the simplest acyl chlorides, being formally derived from carbonic acid. Production Industrially, phosgene is produced by passing purified carbon monoxide and chlorine gas through a bed of porous activated carbon, which serves as a catalyst:[8] CO + Cl2 → COCl2 (ΔHrxn = −107.6 kJ/mol) This reaction is exothermic and is typically performed between 50 and 150 °C. Above 200 °C, phosgene reverts to carbon monoxide and chlorine, Keq(300 K) = 0.05. World production of this compound was estimated to be 2.74 million tonnes in 1989.[8] Phosgene is fairly simple to produce, but is listed as a Schedule 3 substances under the Chemical Weapons Convention. As such, it is usually considered too dangerous to transport in bulk quantities. Instead, phosgene is usually produced and consumed within the same plant, as part of an "on demand" process. This involves maintaining equivalent rates of production and consumption, which keeps the amount of phosgene in the system at any one time fairly low, reducing the risks in the event of an accident. Some batch production does still take place, but efforts are made to reduce the amount of phosgene stored.[10] Inadvertent generation Upon ultraviolet (UV) irradiation in the presence of oxygen, simple organochlorides such as chloroform (CHCl3) slowly convert into phosgene.[11] Phosgene is also formed as a metabolite of chloroform, likely via the action of cytochrome P-450.[12] Carbon tetrachloride (CCl4) can turn into phosgene when exposed to heat in air. This was a problem as carbon tetrachloride is an effective fire suppressant and was formerly in widespread use in fire extinguishers.[13] There are reports of fatalities caused by its use to fight fires in confined spaces.[14] Carbon tetrachloride's generation of phosgene and its own toxicity mean it is no longer used for this purpose.[13] History Phosgene was synthesized by the Cornish chemist John Davy (1790–1868) in 1812 by exposing a mixture of carbon monoxide and chlorine to sunlight. He named it "phosgene" from Greek φῶς (phos, light) and γεννάω (gennaō, to give birth) in reference of the use of light to promote the reaction.[15] It gradually became important in the chemical industry as the 19th century progressed, particularly in dye manufacturing. Reactions and uses The reaction of an organic substrate with phosgene is called phosgenation.[8] Synthesis of carbonates Diols react with phosgene to give either linear or cyclic carbonates (R = H, alkyl, aryl): HOCR2−X−CR2OH + COCl2 → 1⁄n [OCR2−X−CR2OC(O)−]n + 2 HCl An example is the reaction of phosgene with bisphenol A to form polycarbonates.[8] Synthesis of isocyanates The synthesis of isocyanates from amines illustrates the electrophilic character of this reagent and its use in introducing the equivalent synthon "CO2+":[16] RNH2 + COCl2 → RN=C=O + 2 HCl (R = alkyl, aryl) Such reactions are conducted on laboratory scale in the presence of a base such as pyridine that neutralizes the hydrogen chloride side-product. On an industrial scale, phosgene is used in excess to increase yield and avoid side reactions. The phosgene excess is separated during the work-up of resulting end products and recycled into the process, with any remaining phosgene decomposed in water using activated carbon as the catalyst. Industrial uses Phosgene is used in industry for the production of aromatic di-isocyanates like toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI), which are precursors for production of polyurethanes. It is also used to form polycarbonates, via a reaction with bisphenol A. More than 90% of the worldwide produced phosgene is used in these processes, with the biggest production units located in the United States (Texas and Louisiana), Germany, Shanghai, Japan, and South Korea. The most important producers are Dow Chemical, Covestro, and BASF. Phosgene is used in the production of aliphatic diisocyanates such as hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI), which are precursors for the production of advanced coatings. Phosgene is also used to produce monoisocanates, used as pesticide precursors (e.g. methyl isocyanate (MIC). Laboratory uses In the research laboratory, due to safety concerns phosgene nowadays finds limited use in organic synthesis. A variety of substitutes have been developed, notably trichloromethyl chloroformate ("diphosgene"), a liquid at room temperature, and bis(trichloromethyl) carbonate ("triphosgene"), a crystalline substance.[17] Aside from the widely used reactions described above, phosgene is also used to produce acyl chlorides from carboxylic acids: RCO2H + COCl2 → RC(O)Cl + HCl + CO2 For this application, thionyl chloride is commonly used instead of phosgene in academic settings. Phosgene is used to produce chloroformates such as benzyl chloroformate: ROH + COCl2 → ROC(O)Cl + HCl In these syntheses, phosgene is used in excess to prevent formation of the corresponding carbonate ester. With amino acids, phosgene (or its trimer) reacts to give amino acid N-carboxyanhydrides. More generally, phosgene acts to link two nucleophiles by a carbonyl group. For this purpose, alternatives to phosgene such as carbonyldiimidazole (CDI) are safer.[18] CDI itself is prepared by reacting phosgene with imidazole. Phosgene is stored in metal cylinders. In the US, the cylinder valve outlet is a tapered thread known as "CGA 160" that is used only for phosgene. Other reactions Phosgene reacts with water to release hydrogen chloride and carbon dioxide: COCl2 + H2O → CO2 + 2 HCl Analogously, upon contact with ammonia, it converts to urea: COCl2 + 4 NH3 → CO(NH2)2 + 2 NH4Cl Halide exchange with nitrogen trifluoride and aluminium tribromide gives COF2 and COBr2, respectively.[8] Chemical warfare US Army phosgene identification poster from World War II Further information: Chemical weapons in World War I and Second Italo-Ethiopian War It is listed on Schedule 3 of the Chemical Weapons Convention: All production sites manufacturing more than 30 tonnes per year must be declared to the OPCW.[19] Although less toxic than many other chemical weapons such as sarin, phosgene is still regarded as a viable chemical warfare agent because of its simpler manufacturing requirements when compared to that of more technically advanced chemical weapons such as tabun, a first-generation nerve agent.[20] Phosgene was first deployed as a chemical weapon by the French in 1915 in World War I.[21] It was also used in a mixture with an equal volume of chlorine, with the chlorine helping to spread the denser phosgene.[22][23] Phosgene was more potent than chlorine, though some symptoms took 24 hours or more to manifest. Following the extensive use of phosgene during World War I, it was stockpiled by various countries.[24][25][26] Phosgene was then only infrequently used by the Imperial Japanese Army against the Chinese during the Second Sino-Japanese War.[27] Gas weapons, such as phosgene, were produced by Unit 731. Toxicology and safety American Red Cross and Medical Research Committee, "An Atlas of Gas Poisoning" plate II, phosgene patient Phosgene is an insidious poison as the odor may not be noticed and symptoms may be slow to appear.[28] The odor detection threshold for phosgene is 0.4 ppm, four times the threshold limit value. Its high toxicity arises from the action of the phosgene on the –OH, –NH2 and –SH groups of the proteins in pulmonary alveoli (the site of gas exchange), respectively forming ester, amide and thioester functional groups in accord with the reactions discussed above. This results in disruption of the blood–air barrier, eventually causing pulmonary edema. The extent of damage in the alveoli does not primarily depend on phosgene concentration in the inhaled air, with the dose (amount of inhaled phosgene) being the critical factor.[29] Dose can be approximately calculated as "concentration" × "duration of exposure".[29][30] Therefore, persons in workplaces where there exists risk of accidental phosgene release usually wear indicator badges close to the nose and mouth.[31] Such badges indicate the approximate inhaled dose, which allows for immediate treatment if the monitored dose rises above safe limits. [31] In case of low or moderate quantities of inhaled phosgene, the exposed person is to be monitored and subjected to precautionary therapy, then released after several hours. For higher doses of inhaled phosgene (above 150 ppm × min) a pulmonary edema often develops which can be detected by X-ray imaging and regressive blood oxygen concentration. Inhalation of such high doses can eventually result in fatality within hours up to 2–3 days of the exposure. The risk connected to a phosgene inhalation is based not so much on its toxicity (which is much lower in comparison to modern chemical weapons like sarin or tabun) but rather on its typical effects: the affected person may not develop any symptoms for hours until an edema appears, at which point it could be too late for medical treatment to assist.[32] Nearly all fatalities as a result of accidental releases from the industrial handling of phosgene occurred in this fashion. On the other hand, pulmonary edemas treated in a timely manner usually heal in the mid- and longterm, without major consequences once some days or weeks after exposure have passed.[33][34] Nonetheless, the detrimental health effects on pulmonary function from untreated, chronic low-level exposure to phosgene should not be ignored; although not exposed to concentrations high enough to immediately cause an edema, many synthetic chemists (e.g. Leonidas Zervas) working with the compound were reported to experience chronic respiratory health issues and eventual respiratory failure from continuous low-level exposure. If accidental release of phosgene occurs in an industrial or laboratory setting, it can be mitigated with ammonia gas; in the case of liquid spills (e.g. of diphosgene or phosgene solutions) an absorbent and sodium carbonate can be applied.[35] Accidents The first major phosgene-related incident happened in May 1928 when eleven tons of phosgene escaped from a war surplus store in central Hamburg.[36] Three hundred people were poisoned, of whom ten died.[36] In the second half of 20th century several fatal incidents implicating phosgene occurred in Europe, Asia and the US. Most of them have been investigated by authorities and the outcome made accessible to the public. For example, phosgene was initially blamed for the Bhopal disaster, but investigations proved methyl isocyanate to be responsible for the numerous poisonings and fatalities. Recent major incidents happened in January 2010 and May 2016. An accidental release of phosgene gas at a DuPont facility in West Virginia killed one employee in 2010.[37] The US Chemical Safety Board released a video detailing the accident.[38] Six years later, a phosgene leak occurred in a BASF plant in South Korea, where a contractor inhaled a lethal dose of phosgene.[39] See also Bhopal disaster Carbonyl bromide Carbonyl fluoride Diphosgene Formaldehyde Oxalyl chloride Thiophosgene Triphosgene Perfluoroisobutene Bis(trifluoromethyl) disulfide References ^ Merck Index, 11th Edition, 7310. ^ Nomenclature of Organic Chemistry: IUPAC Recommendations and Preferred Names 2013 (Blue Book). Cambridge: The Royal Society of Chemistry. 2014. p. 798. doi:10.1039/9781849733069-FP001. ISBN 978-0-85404-182-4. ^ a b c d e NIOSH Pocket Guide to Chemical Hazards. "#0504". National Institute for Occupational Safety and Health (NIOSH). ^ "PHOSGENE (cylinder)". Inchem (Chemical Safety Information from Intergovernmental Organizations). 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ISBN 0444824456. ^ "DuPont Corporation Toxic Chemical Releases | CSB". ^ Fatal Exposure: Tragedy at DuPont, retrieved 2021-07-02 ^ Archived at Ghostarchive and the Wayback Machine: "Fatal Exposure: Tragedy at DuPont". YouTube. External links Davy's account of his discovery of phosgene International Chemical Safety Card 0007 CDC - Phosgene - NIOSH Workplace Safety and Health Topic NIOSH Pocket Guide to Chemical Hazards U.S. CDC Emergency Preparedness & Response U.S. EPA Acute Exposure Guideline Levels Regime For Schedule 3 Chemicals And Facilities Related To Such Chemicals, OPCW website CBWInfo website Use of Phosgene in WWII and in modern-day warfare Retrieved from " the email address you signed up with and we'll email you a reset link. Text for H.R.4521 - 117th Congress (2021-2022): United States Innovation and Competition Act of 2021 11 Which statement about the pyranose form of mannose is not correct? A) it exists as two anomeric stereoisomers. B) it reacts with Tollens' reagent to give a silver mirror. (i.e. it is a reducing sugars) C) reaction with excess CH 3 I and AgOH gives a non-reducing penta-O-methyl derivative. D) it resists reduction with aqueous sodium borohydride. Phosgene is the organic chemical compound with the formula COCl 2.It is a toxic, colorless gas; in low concentrations, its musty odor resembles that of freshly cut hay or grass. Phosgene is a valued and important industrial building block, especially for the production of precursors of polyurethanes and polycarbonate plastics.. Phosgene is extremely poisonous and was used as ... The Code of Federal Regulations (CFR) is the official legal print publication containing the codification of the general and permanent rules published in the Federal Register by the departments and agencies of the Federal Government. The Electronic Code of Federal Regulations (eCFR) is a continuously updated online version of the CFR. It is not an official ... 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(i.e. it is a reducing sugars) C) reaction with excess CH 3 I and AgOH gives a non-reducing penta-O-methyl derivative. D) it resists reduction with aqueous sodium borohydride. A separate drafting site is available with paragraph structure matching the official CFR formatting. ... reacting the chloroformate derivatives of one or more of the polyols or polyesters named in this paragraph with one or more of the polyamines named in this ... (3,5-di-tert-butyl-4-hydroxy-benzyl)-triazine-2,4,6 (1H,3H,5H)-trione ... Phosgene is the organic chemical compound with the formula COCl 2.It is a toxic, colorless gas; in low concentrations, its musty odor resembles that of freshly cut hay or grass. Phosgene is a valued and important industrial building block, especially for the production of precursors of polyurethanes and polycarbonate plastics.. Phosgene is extremely poisonous and was used as ... 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