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二氟二碘甲烷与乙烯基乙醚的反应及其产物的化学转化

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摘要 二氟二碘甲烷(CF2I2,1)与乙烯基乙醚和Na2S2O4在DMSO和乙醇的混合溶剂中反应得3,3-二氟-3-碘丙醛的乙缩醛[ICF2CH2CH(OEt)2](3).3在锌粉的作用下发生偶联反应生成二缩醛[(EtO)2CHCH2CF2CF2CH2CH(OEt)2](5)。缩醛3或5与烯醇硅醚在SnCl4作用下发生交叉偶联反应。3在锌粉或保险粉的引下与烯醇硅醚发生加成反应。3和5分别转化成硫缩醛ICF2CH2CH(SR)2(13),(RS)2CHCH2CF2CF2CH2CH(SR)2(14)或O,S-缩醛。13消HI得1,1-二氟乙烯衍生物。

关键词 二氟二碘甲烷 乙烯基乙醚 缩醛 二氟烯烃 硫缩醛 硫代硫酸钠 二甲基亚砜

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The reaction and its product conversion of difluorodiiodomethane with ethyl vinyl ether

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Abstract Diflorodiiodomethane (CF2I2, 1) can react with vinyl ethyl ether by Na2S2O4 in a solvent [V(EtOH): V(DMSO)=10:1] at room temperature for 8 hours to give diethyl 3,3-difluoro-3-iodopropylacetal [[ICF2CH2CH (OEt)2] (3). in 60% vyeld. The cou;oing of 3 with zinc in DMF affords [(EtO)2CHCH2CF2CF2CH2CH(OEt)2](5) in 60% yield. The SnCl4-promoted cross-coupling reaction of the acetals 3 and 5 with trimethylsilyl enol ethers produce ketones ICF2CH2CH(OEt)CH2COR (8) and RCOCH2CH (OEt)CH2CF2CF2CH2CH(OEt)CH2COR(9) respectively. 3 can add to trimethylsilyl enol ethers initiated by Zn or sodium dithionite to yield (EtO)2CHCH2CF2CH2CH (OTMS) C6H5 (10c) or (EtO)CHCH2CF2CH2COC (CH3)3(11a). The acetals 3 and 5 can be converted by BF3·Et2O into the corresponding dithioacetals ICF2CH2CH(SR)2(13), (RS) 2CHCH2CF2CF2CH2CH(SR)2(14) or O,S- acetal EtOCH(SR) CH2CF2CF2CH2CH(SR) (OEt)(15) depending upon the concentration of RSH used. The elimination of HI from 13 by ENt3 results in the formation of 1,1- difluoroethylene derivatives.

Key words ACETAL MERCAPTAL SODIUM THIOSULFATE DIMETHYLSULFOXIDE

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