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研究论文

2-取代-5,5-二硝基嘧啶-4,6-二酮的合成和反应

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摘要 研究了2-取代嘧啶-4,6-二酮的硝化反应, 产物为2-取代-5,5-二硝基嘧啶-4,6-二酮(**3**), 收率＞80%, **3**与亲核试剂反应形成开环产物. 2-位取代基为烷基时, 嘧啶环5-位和侧链的*α*-位都发生反应, 当取代基为甲基时, 硝化产物为2-(二硝基亚甲基)-5,5-二硝基嘧啶-4,6-二酮(**1**), **1**的水解产物为1,1-二氨基-2,2-硝基乙烯 (FOX-7)和二硝基甲烷(**2**). 2-位取代基为羟基时, 硝化产物为5,5-二硝基巴比妥酸(**7b**), **7b**水解可制得偕二硝基乙酰基脲(**9b**), **9b**与KOH作用生成偕二硝基乙酰基脲钾盐(**10b**)和二硝基甲烷钾盐(**11**). 2-位取代基为氨基时, 硝化开环生成偕二硝基乙酰基胍(**9a**), **9a**与KOH作用生成偕二硝基乙酰基胍钾盐(**10a**)和**11**. 当2-位无取代基时, 硝化产物无法分离, 结构推测为**7c**. 考察了亲核试剂对FOX-7收率的影响并对FOX-7的三种合成方法进行了评价, 对反应机理进行了探讨.

关键词 2-取代-5,5-二硝基嘧啶-4,6-二酮 硝化 开环 1,1-二氨基-2,2-二硝基乙烯(FOX-7) 二硝基甲烷钾盐 反应机理

分类号

Synthesis and Reactions of 2-Substituted-1,4,5,6-tetrahydro-5,5- gem-dinitropyrimidine-4,6-diones

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Abstract Nitration of some 2-substituted-1,4,5,6-tetrahydro-pyrimidine-4,6-diones gave several new 2-substituted-1,4,5,6-tetrahydro-5,5-gem-dinitropyrimidine-4,6-diones (**3**) in high yields (＞80%). The gem- dinitro products formed were easily attacked by nucleophiles with the formation of gem-dinitroacetyl derivatives, which in turn could be further hydrolyzed to the salts of dinitromethane. When the substituent at position 2 was an alkyl group, the nitration occurred both at position 5 and *α*-carbon atom of the side chain. If the alkyl group was methyl, the product would be 2-(dinitromethylene)-5,5-dinitropyrimidine-4,6-dione (**1**), which was hydrolyzed to form 1,1-diamino-2,2-dinitroethylene (FOX-7) and dinitromethane (**2**). When the substituent was hy-droxyl, the nitrated product was 5,5-dinitrobarbituric acid (**7b**), which was hydrolyzed to form gem-dinitroacetylurea (**9b**). **9b** reacted with KOH to form potassium gem-dinitroacetylurea (**10b**) and potassium dinitromethane (**11**). When the substituent was amino, gem-dinitroacetylguanidine (**9a**) could be synthesized by hydrolytic cleavage of nitrated product. **9a** reacted with KOH to form potassium gem-dinitroacetylguanidine (**10a**) and **11**. When there was no substituent at position 2, **7c** with its structure being postulated was obtained. The effect of different nucleophiles on yield of FOX-7 was compared. Three different synthetic routes to FOX-7 were appraised. The reaction mechanism was discussed.

Key words 2-substituted-1 4 5 6-tetrahydro-5 5-gem-dinitropyrimidine-4 6-dione nitration ring cleavage 1 1-diamino-2 2-dinitroethylene (FOX-7) potassium dinitromethane reaction mechanism

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