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N,*N*′-双(间氯苯基)-3,4-二氨基呋咱的合成

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摘要：介绍了新型炸药 *N*,*N*′-双(2,4-二硝基苯并氧化呋咱基)-3,4-二氨基呋咱的重要中间体 *N*,*N*′-双(间氯苯基)-3,4-二氨基呋咱的合成。即在碱性介质中，二氯乙二肟与间氯苯胺反应，生成化合物(Ⅲ)。化合物(Ⅲ)在乙二醇的氢氧化钠溶液中高温脱水，制得化合物(Ⅳ)。根据红外光谱、核磁共振、元素分析、质谱等分析数据确定了它们的结构。

关键词：有机化学；呋咱；*N*,*N*′-二间氯苯二氨基乙二肟；*N*,*N*′-双(间氯苯基)-3,4-二氨基呋咱
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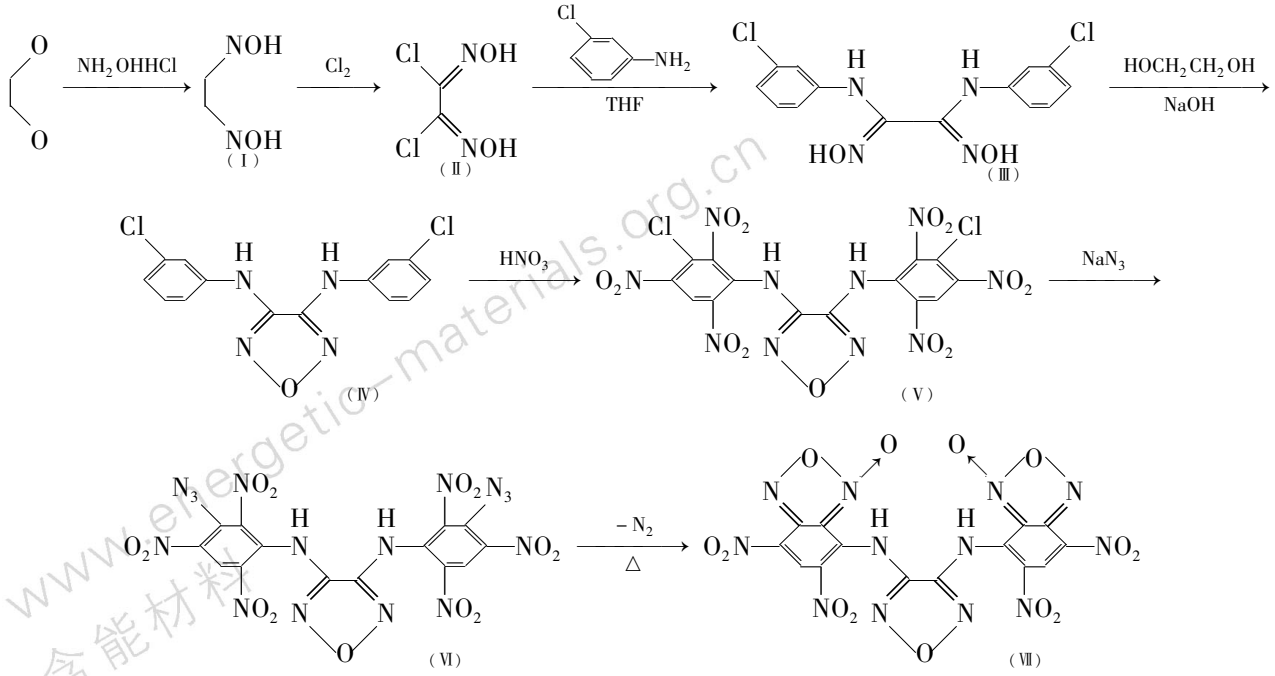
1 引 言

钝感高能炸药的合成研究一直是近年来的热门课题。关于这方面的研究，国内外有大量的文献报道[1~6]。本文试图探索一种呋咱与硝基苯并氧化呋咱相结合的高能低感炸药。众所周知，在单质炸药分子中引入特征密度高的基团——呋咱或氧化呋咱可提高单质炸药密度，而杂环或稠环的引入常可提高炸药的热稳定性，降低其机械感度[7]。因此，我们设计了一种呋咱与硝基苯并氧化呋咱相结合的新型炸药——*N*,*N*′-双(2,4-二硝基苯并氧化呋咱基)-3,4-二氨基呋咱。其合成的关键是呋咱基与硝基苯并氧化呋咱基的连接，本文选择从乙二醛出发，经氨化，氯化，缩合，脱水等工艺达到连接。再进一步硝化，叠氮化，环化，得到目标化合物。

具体合成路线如下：



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2 实 验

2.1 仪器及试剂

所用试剂均为化学纯。XT-4A数字熔点测定仪

(温度计未经校正),Magna IR560 红外光谱仪,arx400 核磁共振仪,ZAB-HS 质谱仪,Elementar Vario EL 元素分析仪。

2.2 乙二肟(Ⅰ)

将 55 g NaOH 溶于 150 ml 水中,在冰水浴冷却下,加入盐酸羟胺 139 g,搅拌溶解后,滴加 40% 乙二醛溶液 114 ml。反应 15 min 后,于室温反应过夜。过滤,水洗,干燥,得乙二肟 70 g(80%),其熔点为 170 ~ 173 ℃(文献值[8]176 ~ 178 ℃)。

2.3 二氯乙二肟(Ⅱ)

将 50 g 乙二肟加入 1 000 ml 水中,边搅拌边加入 250 ml 浓盐酸。强烈搅拌下,将乙二肟溶解,然后用冰浴冷却,缓慢通氯气 15 min。随后于 0 ℃迅速通入氯气,反应 2 h,过滤,干燥,得化合物(Ⅱ) 47 g(53%),其熔点为 198 ~200 ℃(分解,文献值[9]198 ~199 ℃)。

2.4 *N*,*N*′-二间氯苯基-二氨基乙二肟(Ⅲ)

将 15.7 g 化合物(Ⅱ)和间氯苯胺 42 ml 溶于 200 ml 四氢呋喃中,再加入碳酸氢钠 16.8 g,回流反应 3 h,降温,过滤,并用少量四氢呋喃洗涤。母液经减压蒸馏驱除溶剂,并用氯仿充分洗涤后得到白色粉末 25.9 g (81%),其熔点为 206 ~208 ℃。IR(KBr) cm^{-1}: 3 437, 3 343, 2 801, 1 645, 1 593, 1 493, 1 098, 688。^{1}HNMR (丙酮-d_6) δ ppm: 9.88(s,2H, N—OH), 7.78(s, 2H, —NH—), 6.80 ~7.14(m, 8H, —C_6H_4—)。MS (EI) m/z 338, 320, 305, 153, 127, 111, 92, 75。元素分析(%) $C_{14}H_{12}C_{l2}N_4O_2$; 计算值 C 49.58,H 3.57, N 16.52; 实测值 C 49.44,H 3.38,N 16.50。

2.5 *N*,*N*′-双(间氯苯基)-3,4-二氨基呋咱(Ⅳ)

将 10 g 化合物(Ⅲ)加入 100 ml NaOH(1.2 g)的乙二醇溶液中,升温溶解,并于 140 ℃下反应 3 h,冷却,过滤,洗涤,干燥得化合物(Ⅳ)6.2 g(63%),其熔点为 191 ~192 ℃。IR(KBr) cm^{-1}: 3 380, 1 624, 1 593, 1 550, 1 493, 1 440, 830, 778, 683。^{1}HNMR(丙酮-d_6) δ ppm: 8.25(s, 2H, —NH—), 7.03 ~7.69(m, 8H, —C_6H_4—)。MS(EI), m/z 320, 290, 153, 138, 127, 111, 75。元素分析(%) $C_{14}H_{10}C_{l2}N_4O$; 计算值 C 52.36, H 3.14,N 17.44; 实测值 C 52.26,H 3.18,N 17.32。

3 结 论

以乙二醛为原料,经四步反应合成目标化合物,反应条件缓和,操作简便。缩合,脱水两步总得率达 50% 以上,宜于大批量生产。其后的硝化,叠氮化及脱氮环化已有相关的文献[10]可供参考,可进一步合成最终的目标化合物。

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(下转 218 页)

Analyzing the Gases Released from Aged JOB Explosives by Using Solid Phase Microextraction Coupled with GC/MS

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Abstract: Three kinds of adsorbant solid phase microextractions (SPME) were used to study the gases released from aged JOB explosives. These gases were obtained by storing the explosives in a closed vessel and heating them for a certain period of time. The extraction and adsorption properties of these SPMEs and the qualitative identification of the gas components have been examined by using SPME coupled with GC/MS analytical techniques. The results show that SPMEs can adsorb selectively and preconcetrate the trace organic volatiles (such as solvents, impurities) and some inorganic gases from explosives and its pertinent materials aged at different conditions. Furthermore, the ageing mechanism of JOB explosives was also explored.

Key words: analytical chemistry; solid phase microextraction; GC/MS; JOB explosives; age

(上接214页)

Synthesis of *N*,*N*′-Bis(3-chlorophenyl)-3,4-diaminofurazan

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Abstract: Synthesis of *N*,*N*′-bis(3-chlorophenyl)-3,4-diaminofurazan(BCPDAF) is a proposed intermediate for synthesizing a novel explosive – *N*, *N*′-bis (2′,4′-dinitrobenzofuroxan)-3,4-diaminofurazan (BNFDAF) which is predicted to have low mechanical sensitivity and high thermal stability. In this paper, the synthesis of BCPDAF is described in detail. The condensation of dichloroglyoxime with 3-chloroaniline in basic media gives *N*,*N*′-bis (3-chlorophenyl) diaminoglyxime which can then be converted to BCPDAF *via* dehydration in a NaOH-$HOCH_2CH_2OH$ solution at high temperature. It is presumed that BNFDAF could be formed from BCPDAF *via* nitration, azidation and denitrification. The structures of BCPDAF and its intermediate have been determined by IR, ^{1}HNMR, MS and elemental analysis.

Key words: organic chemistry; furazan; *N*, *N*′-bis(3-chlorophenyl)-diaminoglyoxime; *N*, *N*′-bis(3-chlorophenyl)-3,4-diaminofurazan