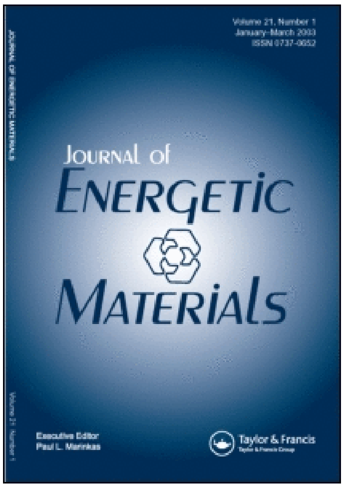


Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Synthesis of new azide: 1,3,5,-tris[(azidomethyl) dinitromethyl]benzene

Yan Hong[a]; Guan Ziaopei[b]; Chen Boren[b]
[a] Cetre of Chemistry & Bioengineering of Cancer, Beijing Polytechnic University, Beijing, (P. R. China)
[b] College of Chemical Engineering and Materials Science, Beijing Institute of Technology, Beijing, (P. R. China)

To cite this Article Hong, Yan , Ziaopei, Guan and Boren, Chen(1998) 'Synthesis of new azide: 1,3,5,-tris[(azidomethyl) dinitromethyl]benzene', Journal of Energetic Materials, 16: 1, 23 — 29

To link to this Article: DOI: 10.1080/07370659808216091

URL: http://dx.doi.org/10.1080/07370659808216091

SYNTHESIS OF NEW AZIDE:
1,3,5,-TRIS[(AZIDOMETHYL)DINITROMETHYL]BENZENE

Yan Hong *
Cetre of Chemistry & Bioengineering of Cancer, Beijing Polytechnic University, Beijing 100022 (P. R. China)
Guan Xiaopei and Chen Boren.
College of Chemical Engineering and Materials Science, Beijing Institute of Technology, Beijing 100081 (P. R. China).

ABSTRACT

1,3,5-Tris[(azidomethyl)dinitromethyl]benzene has been synthesized from tripotassium salt of 1,3,5-tris(dinitromethyl)benzene in three steps. It's structure has been established with the help of elemental analysis, IR, ^{1}H-NMR, and Mass spectroscopies. Thermal decomposition of the title compound has been studied by DTA, and some other properties are also reported.

*To whom correspondence should be sent

Journal of Energetic Materials Vol. 16, 023-029 (1998)
Published in 1998 by Dowden, Brodman & Devine, Inc.

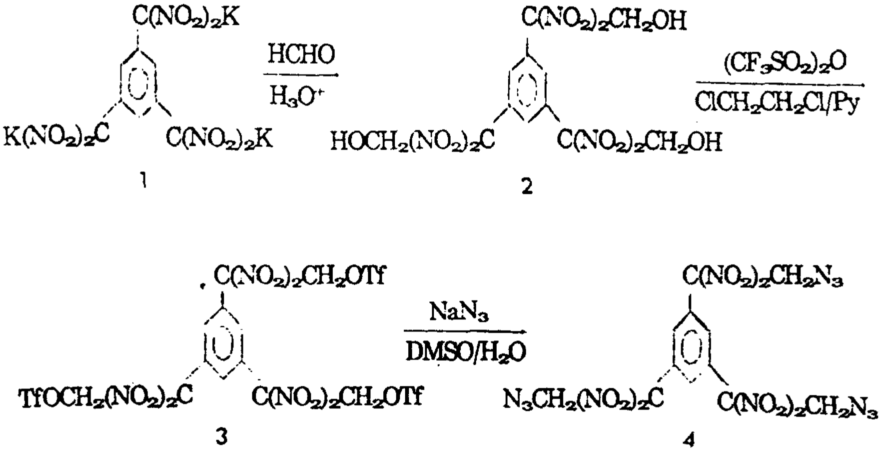
INTRODUCTION

The use of energetic additives with good properties is considered to be one of the practical ways to improve the energy content and other technical performances of solid propellants. In this aspect, the organic azides are attracting researcher's more and more attention. Some of the researchers have extended the synthetic chemistry of aliphatic azides to include other energetic groups, such as nitramine, fluoro-nitro, dinitro, and difluoroamino[1]. Although aromatic azides such as cyanuric triazide and 1,3,5-triazido benzene have in the past been considered as possibly useful energetic materials, they have not as yet found application[2]. Recently, azidomethylated benzenes have been synthesized and tested. They also havesome other desirable features, such as good thermal and hydrolytic stability, high buring rates, and reduced flash[3]. It occurred to us that it might be of interest to prepare the aromatic compounds including both azides and other energetic groups such as dinitro.

Although the compound of 1,3,5-tris(trinitromethyl)benzene has symmetrical structure and the most energetic group in the benzene, it is very easy to decompose at room temperature. Azidomethyl dinitromethyl group [$-C(NO_2)_2CH_2N_3$, $\triangle H_f^\circ$ = 245.1kJ/mol] is more energetic than the corresponding trinitromethyl group [$-C(NO_2)_3$, $\triangle H_f^\circ$ = -21.3kJ/mol] and more stable besides. In the case of $CH_2[OCH_2C(NO_2)_2CH_2N_3]_2$ and $CH_2[OCH_2C(NO_2)_3]_2$, the replacement of one NO_2 by CH_2N_3 is accompanied by a substantial increase in thermal stability and dramatic decrease in sensitivity to impact.[4] So our objective of this investigation is to synthesize the compound of 1,3,5-tris[(azidomethyl)dinitromethyl]benzene which may be more energetic and stable than 1,3,5-tris(trinitromethyl)benzene.

RESULTS

The synthesis of 1,3,5-tris[(azidomethyl)dinitromethyl]benzen(4) was performed in three steps. At first, 1,3,5-tris[(hydroxymethyl) dinitromethyl]benzene(2) was prepared by hydroxymethylation of the tripotassium salt of 1,3,5-tris(dinitromethyl)benzene(1). The aldehyde by-products in the reaction were separated by forming adducts with $NaHSO_3$[7]. Then the desired triflates 3 were prepared from 2 by conventional procedures but at a higher temperature. At last the target compound 1,3,5-tris[(azidomethyl)dinitromethyl]benzene(4) was obtained by the reaction of 3 with sodium azide.



Compound 4 is a white crystal, soluble in polar solvent, such as ether, aceton, chloroform and methylene choride, insoluble in water, tetrachloromethane and hexane. It's desity obtained by suspending method is 1.642g/cm^3. Some properties of 4 are listed in Table 1.

TABLE 1

Properties of 1,3,5-Tris[(azidomethyl)dinitromethyl]benzene(4)

Property	
Molecular formula	$C_{12}H_9N_{15}O_{12}$
Molecular weight	555.34
Desity (g/cm^3)	1.642
Melting point(℃)	128.6
Oxygen balance(CO%)	-12.97
Content of nitrogen(%)	37.74
Detonation velocity (calcd.km/s)[6]	7.08
Detonation pressure (calcd.GPa)[6]	20.5
$\triangle H_f^\circ$ (calcd.kJ/mol)[7]	882.6

Differential Thermal Analysis (DTA) was carried out from room temperature to 400℃ by using a PCR-1 DTA apparatus. The DTA curve (heating rate 10℃/min) indicates that exothermic decomposition of 4 starts at 226℃ and is completed at 234℃ with the peak maxiuma at 230℃. In order to calculate the activation energy of thermal decomposition of 4, runs were recorded at a heating rate of 2℃/min, 5℃/min, 10℃/min and 20℃/min, respectively. From the peak maxiuma tempercture obtained, the activation energy (82.7kJ/mol) of 4 was determined by applying Ozawa's method as well as Kissinger's method[8]. The value of A in the Arrhenius equation is $4.68\times10^9 s^{-1}$.

EXPERIMENTAL SECTION

Melting points (uncorrected) were measured on a WC-1 hot-stage apparatus. ^{1}H-NMR and IR spectra were recorded with a Varian T-60 spectrometer and a Shimadzu IR-408 spectrometer, respectively. A QX-80 vapor pressure osmometer was used for molecular weight determinations. Elemental analyses were performed by E.A.laboratory of Institute of Chemistry (Chinese Academy Sciences).

1,3,5-Tris[(hydroxymethyl)dinitromethyl]benzene(2)

To the slurry of tripotassium salt of 1,3,5-tris(dinitromethyl) benzen(1) (1.00g, 1.98mmol)[9] in 20mL of water was added 1mL of formaldehyde (36%) and the mixture was warmed to 40℃. After 8h, the reaction mixture was allowed to cool to room temperature, and acidified with cocentrated hydrochloride acid until the solution was PH=2. The slurry of reaction mixture was stirred for an additional 12h. The crude product was separated by filtration and reacted with aqueous solution of saturate $NaHSO_3$ in ethyl alcohol for 30 min. The precipitate that formed was filtered and washed with ethyl alcohol. The ethyl alcohol was removed in vacuo, and the residue was recrystalized from ethyl acetate/CCl_4 affording pure 1,3,5-tris[(hydroxymethy) dinitromethyl]benzene(2) (200mg, 21.1%) as a white solid, m. p. 145.2-146.2℃. ^{1}H-NMR(aceton-d_6) 8.33(3H, s), 5.12(6H, s), 3.12(3H, s)ppm, IR(KBr): 3450, 1570, 1320, 1080cm^{-1}.

Anal Calcd for $C_{12}H_{12}N_6O_{18}$: C,30.01, H, 2.52, N, 17.50. Found: C, 30.24, H, 2.49, N, 17.73.

1,3,5-Tris[(trifloxymethyl)dinitromethyl]benzene(3)

A slurry of 2 (600mg, 1.25mmol) in 10mL of 1,2-dichloroethane was warmed to 40℃. After about 10min, 2 dissolved and triflic anhydride (500μ L, 3.00mmol) was added. To this solution, pyridine (220mg, 2.90mmol) in 2mL of 1,2-dichloroethane was added dropwise at such a rate that the temperature did not exceed 40℃. After 1h, the reaction mixture was washed with coldwater and dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was recrystalized from chloroform, a white solid of 1,3,5-tris[(trifloxymethyl)dinitromethyl]benzene(3) (680mg, 62.1%) was obtained. m.p. 136.0-136.5℃. ^{1}H-NMR (aceton-d_6):

8.26(3H, s), 6.12(6H, s)ppm; IR(KBr): 1600, 1440, 1320, 1260, 1230, 1140, 1000cm^{-1}.

Anal. Calcd for $C_{15}H_9N_6O_{21}S_3F_9$: C, 20.56; H, 1.04; N, 9.59; S, 10.97; Found: C, 20.41; H, 1.15; N, 9.47; S, 10.88.

1,3,5-Tris[(azidomethyl)dinitromethyl]benzene(4)

A solution of 3 (400mg, 0.46mmol) in 10mL of 80% aquous dimethyl sulfoxide was stirred at room temperature for 12h with sodium azide (450mg, 6.85mmol). The reaction mixture was then diluted with water and extracted with chloroform. The organic layer was washed with water and dried over $MgSO_4$. Chloroform was removed in vacuo. Pure 1,3,5-tris[(azidomethyl)dinitromethyl]benzene(4) (160mg, 62.6%) was obtained as a white crystal by recrystalization from chloroform/ petroleum ether, m.p. 128.2-129.0°C. ^{1}H-NMR(aceton-d_6): 8.20(3H, s), 5.36(6H, s)ppm; IR(KBr): 2150, 1590, 1570, 1310cm^{-1}; mol wt (vapor-phase osmometer, $CHCl_3$): 559.

Anal. Calcd for $C_{12}H_9N_{15}O_{12}$: C, 25.96; H, 1.63; N, 37.84; Found C, 25.88; H, 1.72; N, 37.74.

REFERENCES

[1] E. F. Witucki and M. B. Frankel. J. Chem. Eng. Data. , *24*, 247 (1979).

[2] "Encyclopedia of Explosives and Related Items, " PATR 2700, Picatinny Arsenal, Dover, NJ, 1960 to 1983.

[3] E. E. Gilbert and W. E. Voreck, Prop. Explo. Pyrtch. *14*, 19(1989)

[4] a. Fan Nengting, Ph. D. Dissertation, Beijing Institute of Technology, China, 1984.

b. Yan Hong. Ph. D. Dissertation, Beijing Institute of Technology. China, 1994.

c. Yan Hong, Guan Xiaopei and Chen Boren, Proc. Int. Semin. 21th., Moscow. September19-20, 1995, in press.

[5] S. J. Weininger and F. R. Sterimitz, Organic Chemistry, Acadamic Press, InC. 404(1984)

[6] M. J. Kamler and S. J. Jacobs, J. Chem. Phys. *48*,23(1968).

[7] Zhou Fagi, Zha Yao He Cheng Hua Xue (Synthesis Chemistry of Explosives), Guofang Gongye Publ. House: Beijing, Peop. Rep. China, 43(1984), CA103: B 89887k(1985).

[8]a. R. B. Cassel, Perkin-Elmer Thermal Analysis Application Study, No28(1979).

b. H.·E. Kissinger, Anal. Chem. *29*, 1702(1957).

[9] Fan Nengting, Huaxue Xuebao, *43*, 484(1985), CA104: 148407z, (1985).