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Novel synthesis of 1, 1, 3, 3, 5-tris-spiro(N, N'-dinitroethylenediamino)-cyclotriphosphazene using solid supported bismuth nitrate[§#]

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[#]This paper is dedicated to the late Prof. R. B. Mane, Department of Chemistry, Shivaji University, Kolhapur - 416 004, (INDIA)

ABSTRACT

Energetic cyclotriphosphazene possessing wide range of applications in the field of high energy materials. The simple, rapid and environmentally benign synthesis of tris-spiro (N, N'-dinitroethylenediamino)-cyclotripho sphazene using bismuth nitrate supported on silica gel under microwave irradiation has been successfully reported.

KEYWORDS

Cyclotriphosphazene;
Microwave irradiation;
Solid support;
Silica gel.

INTRODUCTION

Energetic cyclotriphosphazene is one of the most important class of high energy materials innaval research laboratory, and armament research board. A considerable interest has been concentrated on the synthesis of cyclotriphosphazenes since these are versatile materials which have wide range of applications such as propellants and explosives, since they possess better elastomeric properties which are possible and the vast range of compounds, which should be available by variation of the pedant groups on the phosphorous[1].

Polyphospahzenes are polymers containing a backbone of alternating phosphorous-nitrogen double bond and single bond and have assessed for the use in applications including specially rubbers[2], flame resistant materials[3], and membranes[4], conducting materials[5], liquid crystals[6], paints[7] and adhesives[8]. Beside these, they possess better mechanical properties and stability, therefore, widely used for developing the new energetic phosphazenes were reported and a number of potentially high energy compounds can be postulated. However, the practicality of the synthesis has been shown to be difficult in the initial investigation on the cyclic system. The reported methods, for the synthesis of tris-spiro(N, N'-dinitroethylenediamino)-cyclotripho sphazene involve the use of toxic and corrosive chemicals such as nitronium tetraflouroborate/acetonitrile, nitric acid/ acetic anhydride, these time consuming, drastic conditions, and resulting in low yield[9] .

To overcome these problems we have developed a safer methodology using environmentally friendly reagents that are easy to handle and reduces the drastic conditions of conventional methods.

The present work emphasizes on environmentally benign approach for the synthesis of energetic cyclo

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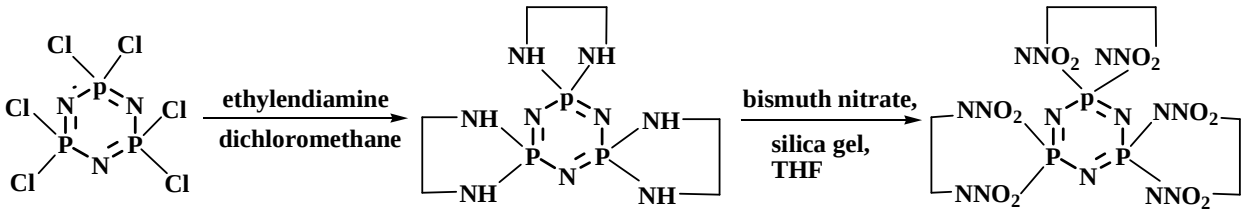

(1) (2) (3)

SCHEME 1

triphosphazene by using low cost, easily available reagents, namely bismuth nitrate[10] as nitrating reagent adsorbed on silica gel as solid support in better yield of tris-spiro(N,N'-dinitroethylenediamino)-cyclotriphos phazene**(3)**.

EXPERIMENTAL

Synthesis of tris-spiro(N, N'-ethylene amino)-cyclotriphosphazene (2)

To the refluxing solution of ethylene diamine (1.80g, 3mmol), in methylene chloride (50ml) the solution of **(1)** (12g, mmol) in dichloromethane (150ml) was added dropwise over 2hrs. An excess of dichloromethane was added and the resulting suspension was heated at reflux for 24hrs, during which white solid precipitated. The reaction mixture was filtered, washed with water(50ml), then acetone(20ml) and dried to give **(2)** 1.90 g 86% m.p. 190 ^{0}C. FTIR (KBr disc, ν, cm$^{-1)}$ 1190 (P- N- P), 32100-3400(-NH). ^{1}HNMR (δppm , $CdCl_3$) 3.80m. NH, 4.10 s, 12 H.

Synthesis of tris spiro (N,N'-dinitroethylene diamino)-cyclotriphosphazene (3)

Tris spiro(N, N'-dinitroethylenediamino) cyclo triphosphazene(1.50g, 1mmol) and silica gel (5g) was added to a suspension of bismuth nitrate (2.88g, 6 mmol) in THF(10ml). The reaction mixture was irradiated under microwave oven (at low power level), until the completion of reaction., which was monitored using TLC. The reaction mixture was poured into acetone, filtered off to afford the**(3)** 1.38g, 78 % m. p. 205 ^{0}C (lit m.p. 205^{0}C). ^{1}HNMR (δppm, $CdCl_3$), 4.3s, 12H. FTIR (KBr disc, ν, cm^{-1}) 1580, 1285(N-NO_2), 1200(P-N-P)

TABLE 1 : Physico-chemical properties of (3)

Molecular formula	$C_6H_8N_{11}P_3O_{12}$
Melting Point (^{0}C)	205
Velocity of detonation (m/sec)	7953 m/sec
Detonation pressure PCJ (Kbar)	205.58 kbar
Oxygen balance (%)	16.58 %
Density (ρ, g/cm3)	1.88 g/cm^3

RESULTS AND DISCUSSION

An environmentally benign approach for the synthesis of energetic cyclotriphosphazene by using low cost, easily available reagents, namely bismuth nitrate as nitrating reagent adsorbed on silica gel in better yield of tris spiro(N, N'-dinitroethylenediamino)-cyclo triphosphazene.

Theoretically computed explosive parameters of 1,1,3,3,5-tris-spiro(N, N'-dinitroethylenediamino) cyclotriphosphazene shows the promising application as potentially high energy compounds, propellants and explosives.

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REFERENCES

[1] D.Debenham, W.B.H.Leeming, E.J.Marshall; Proceedings of the Joint International Symposium of Energetic Materials Technology San Diego USA, **(1991)**.
[2] C.Kim, H.R.Allock; Macromolecules, **22**, 2596 **(1989)**.
[3] A.N.Mujumdar, S.G.Young, R.L., J.H.Merber, M.A.Gill; Macromolecules, **23**, 14, **(1990)**.
[4] H.R.Allock, S.Kwon; Macromolecules, **21**, 1980,

(1988).

[5] P.Golding, R.W.Milllar, N.C.Paul, D.H.Richards; Tetrahedron Lett., **30**, 6431, **(1989)**.

[6] **(a)** S.S.Krisnamurthy, K.Ramachandran, Vasudeva Murthy, A.R.Shaw, R.A.Woods; M.Inorg.Nucl. Chem.Lett., **13**, 407 **(1997)**.
(b) Ibid J.Chem.Soc.Dalton Trans., 840 **(1980)**.

[7] M.S.Chang, A.J.Matusko; J.Amer.Chem.Soc., **82**, 5756 **(1960)**.

[8] West, R.Ishikawz, M.M.Murai, F.F.Becker, B.K. Banik; Tetrahedron Lett., **41**, 8017 **(2000)**.

[9] S.Smajdar, F.F.Becker, B.K.Banik; Tetrahedron Lett., **41**, 8017 **(2000)**.

[10] D.M.Badgujar, M.B.Talawar, S.N.Asthana, P.P.Mahulikar; J.Sci.Ind.Res., **66**, 250 **(2007)**.