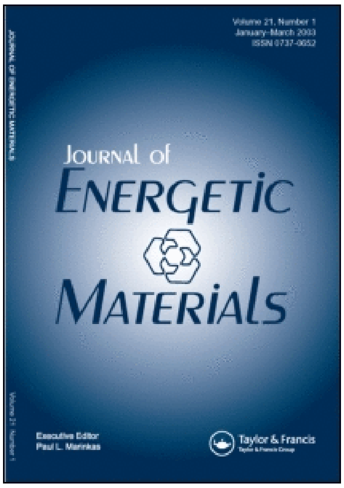

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A novel energetic polyazide: 1,2,4,5-tetrakis (diazidomethyl) benzene

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RESEARCH NOTE

A NOVEL ENERGETIC POLYAZIDE: 1,2,4,5-TETRAKIS (DIAZIDOMETHYL) BENZENE

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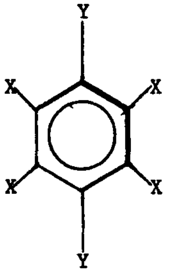
ABSTRACT

The subject compound (I), containing eight geminal azide groups, was prepared and briefly evaluated.

BACKGROUND

Recent interest in geminal diazide compounds[1] has prompted us to report the preparation of the subject compound (I) of this type. It was made for comparison with the primary azide hexakis-(azidomethyl)benzene (II), the properties of which we have recently studied in some detail.[2]



I. X = $-CH(N_3)_2$; Y = H

II. X = Y = $-CH_2N_3$

III. X = $-CHBr_2$; Y = H

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TABLE 1. GEMINAL DIAZIDES

COMPOUND	DECOMPOSITION TEMP (°C)[a]
1,1-Diazidodiethyl ether[3]	81[b]
Diazidodiphenylmethane[4]	120[c]
Diazidomalononitrile[5]	– [d]
Diazidomalonamide[1]	140[e]
N,N'-Dimethyldiazidomalonamide[1]	140[e]
Dimethyl diazidomalonate[1]	130 (expl.); 140[e]
Diethyl diazidomalonate[6]	180 (expl.)
3,3-Diazido-2,4-pentanedione[7]	140
3,3-Diazido-2,4-pentanediol[7]	135
3,3-Diazido-2,4-dinitratopentane[7]	145 ± 10; 165 (expl.)
Diazidomethane[9]	f

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[a] Nonexplosive decomposition, except as indicated.

[b] As given in 7.

[c] Run in amyl ether.

[d] Isolated only as dimer.

[e] Run in dodecane.

[f] "Explosive" (no data given).

Few geminal diazides have been made, those known to us are listed in Table 1. All are thermally unstable; Compound I is also unstable since it decomposes at the melting point (106-8°).

PREPARATION

The starting compound for making I was 1,2,4,5-tetrakis (dibromomethyl) benzene (III) which was prepared by photochemical bromination of the corresponding commercially available (Aldrich Chemical Company) tetrakis (bromomethyl) benzene, by the procedure of Kerfanto and Soyer[8]. III (0.5 g - 0.65 mmole), ground sodium azide (0.5g - 7.7 mmole), and N,N-dimethylformamide (10 mL) were mixed and stirred magnetically in a test tube for 3 hours in a 70-80° water bath. The mixture was poured into water, 6 drops of 15% hydrochloric acid were added, and the mixture was allowed to stand for 3 hours for complete separation of the suspended solid. It was filtered and washed with water. The filter paper with product was removed from the filter and dried to constant weight; the dry product was then easily removed. The crude yield varied from 83 to 95% in check runs; m.p. (ex methanol) 106-8° (dec., gas evolution); IR (KBr): 2100 (asym. azide) (S), 1370 (m), 1330 (m), 1240 (sym. azide) (S), 1180 (S), 945 (S), 830 (S), 740 (S), 550 (W), 400 (W) cm^1. The structure of I was established by NMR as follows: ^{1}H NMR (acetone d_6): δ8.03 (S,2, ArH), δ6.87 (S, 4, ArCH); ^{13}C NMR (acetone d_6: δ135.4 (ArC), 127.25 (ArCH), 75.3 (-CH).

PERFORMANCE TESTS

(I) was easily detonated by a hammer blow on a hard surface, or by scraping with a spatula - in this case with flame formation. It exploded upon addition to 80% sulfuric acid at 90°. Slow heating in a melting point apparatus showed melting at 106-8° with gas evolution; continued heating to 180° gave further gas evolution and color formation, but without detonation. Detonation did occur upon rapid heating on a spatula over a low flame. No visual change was noted upon heating for 5 hours at 95°.

Comparison with II, which contains only primary azide groups, expectedly showed that I is less stable and more sensitive. II was less easily detonated by impact with a hammer, and not easily by scraping with a spatula. It could be decomposed by 80% sulfuric acid at 90° without explosion. II has a higher melting point (162-5°), and like I decomposes with gas evolution at the melting point. II, like I, explodes upon rapid heating.

ACKNOWLEDGMENT

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