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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

E. E. Gilbert

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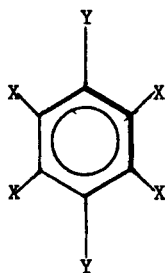
Dover, New Jersey 07801-5001

ABSTRACT

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

BACKGROUND

Recent interest in geminal diazide compounds¹ 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

^aNonexplosive decomposition, except as indicated.

^bAs given in 7.

^cRun in amyl ether.

^dIsolated only as dimer.

^eRun 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 Soyer⁸. 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) cm¹. The structure of I was established by NMR as follows: ¹H NMR (acetone d₆): δ8.03 (S, 2, ArH), δ6.87 (S, 4, ArCH); ¹³C NMR (acetone d₆): 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.

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REFERENCES

1. R.M. Moriarty, B.R. Bailey III, I. Prakash, and R.S. Miller, J. Org. Chem., 1985, 50, 3710, and papers cited therein.
2. E.E. Gilbert and W.E. Voreck, Propellants, Explos., Pyrotech., in press.
3. Y.A. Sinnema and V.F. Arens, Rec. Trav. Chim., 74, 901 (1955).

4. S. Goetzky, Ber., 64, 1555 (1931).
5. E. Ott and H. Weissenburger, Ber., 70B, 1829 (1937).
6. M.O. Forster and R. Muller, J. Chem. Soc., 97, 126 (1910).
7. L.P. Kuhn and A.C. Duckworth, "The Preparation of Some New Polyfunctional Organic Azides," Report No. 1607, Ballistic Research Laboratories, Aberdeen Proving Ground, MD, 1972 (unlimited distribution).
8. M. Kerfanto and N. Soyer, Compt. Rend. C, 264, 1072 (1967).
9. A. Hassner and M. Stern, Angew. Chem. Int. Ed. Engl. 25, 478 (1986).