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SYNTHESIS OF 1,2- AND 1,4-bis[α-(2,4,6-TRINITROANILINO)-ACETAMIDO]BENZENE AS NEW INSENSITIVE EXPLOSIVES

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SYNTHESIS OF 1,2- AND 1,4-*bis*[α-(2,4,6-TRINITROANILINO)-ACETAMIDO]BENZENE AS NEW INSENSITIVE EXPLOSIVES[†]

Submitted by
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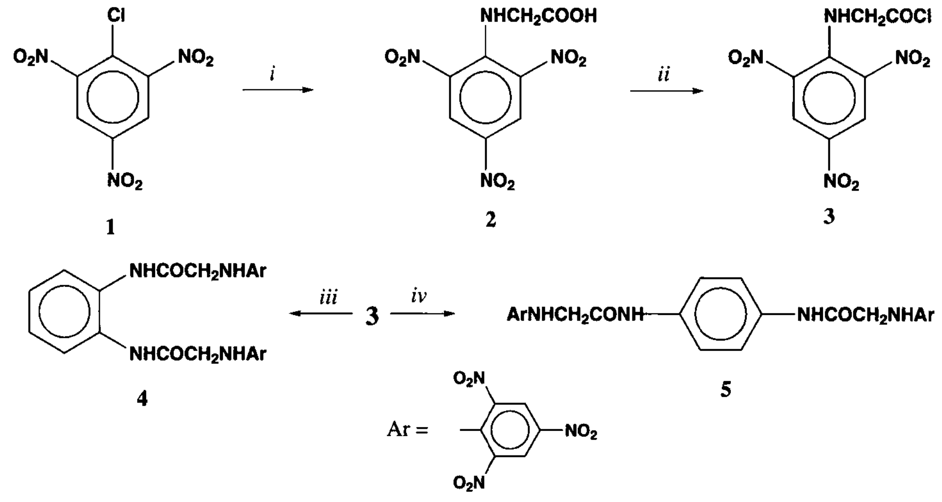
There is a critical need in industry for explosive compositions which would be safe, reliable and stable at above 350° temperatures. For example, it is sometimes necessary to shoot explosive devices into hot wells at temperatures which may reach as high as 200-300°. In the steel industry, open hearth furnaces are tapped with explosive shaped charges in tap holes at temperatures above 500°. The explosives available at present, which have the best possible thermal properties, must have the shaped charges jacketed with heavy insulation. Even so, the charge must be initiated within 3-4 min. from the time it is set in place or it may fail due to thermal instability.[1] There is also a growing demand in connection with space programs for explosive compounds which are stable at elevated temperatures and low pressure. The temperature of conventional explosives subjected to aerodynamic heating on high speed aircrafts may rise above 80°, hence making them unsuitable for space aircraft applications.[2]

Explosives with improved high temperature properties, usually called "Heat Resistant Explosives" have emerged to meet such requirements. Nitro compounds such as TNT (2,4,6-trinitrotoluene) and picric acid have been found to be very useful heat resistant explosives.[2-4] They are of special interest because of their ability to withstand the high temperature and low pressure encountered in space aircraft applications.[1-4] No doubt, the manufacture of these explosives is so crucial that sometimes, even complex synthetic routes are adopted for the synthesis of heat resistant explosives. The importance of nitro compounds as heat resistant explosives led us to investigate the synthesis of new highly insensitive explosives such as 1,2-*bis*[α-(2,4,6-trinitroanilino)acetamido]benzene and 1,4-bis[α-2,4,6-trinitroanilino- acetamido]benzene (*Scheme*).

These two new explosives are condensation products of 1,2- and 1,4-phenylenediamines with 2,4,6 trinitroanilinoacetic acid chloride [TNAAC, 3]. 2,4,6-Trinitroanilinoacetic acid [TNAA, 2] and its lead salts have been reported as energetic materials and additives in propellant formulations.[5] The theoretically calculated velocities of detonation [VOD] and impact sensitivities for **4** and **5** indicate these to be highly explosives but stable[3,5] up to 400°.



i) HCl•NH$_2$CH$_2$COOH, Na$_2$CO$_3$ *ii*) PCl$_3$ *iii*) *o*-phenylenediamine *iv*) *p*-phenylenediamine

Scheme

EXPERIMENTAL SECTION

All chemicals were of analytical grade. Solvents were distilled before use. ^{1}H NMR spectra were recorded on a 90 MHz varian FT90A nmr instrument and IR spectra were recorded on a FT-IR Paragon-500 Perkin Elmer instrument.

Synthesis of 2,4,6-Trinitroanilinoacetic Acid (TNAA, 2).- A mixture of glycine (412 mg, 5 mmol), Na$_2$CO$_3$ (530 mg, 5 mmol) in water (20 mL) and picryl chloride (1238 mg, 5 mmol) in acetone (20 mL) was stirred at 25° for 1h. The reaction mixture was cooled to 10° and acetone was removed under reduced pressure. The solid obtained was dissolved in a minimum amount of distilled water and neutralized with dil. HCl. The product was collected, dried under vacuum at 40° and recrystallized from hot water to give 801 mg (58%) of yellow solid, mp. 158-160° (dec.); IR: 3568, 3498, 3322, 3088, 2924, 2564, 1870, 1724, 1684, 1626, 1590, 1534 cm^{-1} ; ^{1}H NMR (D$_2$O): δ 3.9 (s, 2H, CH$_2$), 8.8 (s, 2H, Ar-H).

Anal. Calcd. for C$_{12}$H$_6$O$_8$N$_4$: C, 33.57; H, 2.09; N, 19.38. Found: C, 33.64; H, 2.02; N, 19.44

2,4,6-Trinitroanilinoacetyl Chloride (TNAAC, 3).- A mixture of TNAA (1430 mg, 5 mmol) and PCl$_5$ (1043 mg, 5 mmol) in chloroform (25 mL) was refluxed for 3 h. Then the reaction mixture was cooled to 0°. The product was collected, washed with cold hexane, dried and recrystallized from hot water to yield 809 mg (53%) of yellow solid, mp. 101-104°; IR: 1780 cm^{-1} (C=O), 3300 cm^{-1} (NH); 1560 cm^{-1} (NO$_2$); ^{1}H NMR: δ 4.0 (d, 2H, CH$_2$), 9.0 (s, 2H, Ar-H), 9.5 (m, 1H, NH).

Anal. Calcd. for C$_{12}$H$_5$ClO$_7$N$_4$: C, 31.52; H, 1.64; N, 18.39. Found: C, 31.43; H, 1.58; N, 18.48

Synthesis of 1,2- and 1,4-*bis*-[α-(2,4,6-Trinitroanilino)acetamido]benzene (4 and 5).- A mixture of o-phenylenediamine or *p*-phenylenediamine (270 mg, 2.5 mmol) and TNAAC (1525 mg, 5 mmol) in DMF (50 mL) was stirred at 25° for 3 h. The orange colored product formed was collected, washed and dried. Yield of **4** = 805 mg (25%), mp. 410° (dec.); IR: 1652,1620 cm^{-1} (C=O), 3448, 3316 cm^{-1}(NH), 1574 cm^{-1} (NO_2); ^{1}H NMR: δ 4.3 (d, 4H, 2xCH_2), 8.2 (s, 4H, Ar-H),9.2 (s, 4H, Ar-H), 9.5 (m, 2H, NH), 9.7 (m, 2H, NH).

Anal. Calcd. for $C_{22}H_{16}N_{10}O_8$: C, 48.18; H, 2.92; N, 25.55. Found: C, 48.10; H 2.81; N, 25.66

Yield of **5**: (1095 mg, 34%), mp. 430° (dec.); IR: 1650, 1630 cm^{-1} (C=O), 3400, 3310 cm^{-1} (NH), 1570 cm^{-1} (NO_2); ^{1}H NMR: δ 4.4 (d, 4H, 2xCH_2), 8.5 (s, 4H, Ar-H), 9.3 (s, 4H, Ar-H), 9.4 (m, 2H, NH), 9.6 (m, 2H, NH).

Anal. Calcd for $C_{22}H_{16}N_{10}O_8$: C, 48.18; H, 2.92; N, 25.55. Found: C, 48.22, H, 2.87, N, 25.47

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