tracted with methylene chloride (4 × 15 mL). The combined organic extracts were washed with brine (2 × 75 mL), dried, and evaporated to dryness. Trituration of the solid residue with hexane (15 mL) followed by filtration and further washing with hexane (2 × 5 mL) provided 0.887 g (70%) of **10** as a colorless solid: mp 122–127.5 °C; λ_{max} ($CHCl_3$) 2.93, 5.83 μm; δ ($CDCl_3$) 1.42, (9 H, s, *tert*-butyl), 2.70–2.90 (2 H, m, allylic CH_2), 3.71 (3 H, s, OCH_3), 4.40–4.85 (2 H, m, R_2CHNCO_2 and NH), 5.50–5.95 (2 H, m, olefinic), 6.80 (1 H, br s, olefinic). Recrystallization of **10** from cyclohexane provided a colorless solid, mp 134–136 °C, with identical spectral properties as the material melting from 122 to 127.5 °C.[9]

5-(*tert*-Butoxycarbonylamino)-2,5-dihydrobenzoic Acid (11). A mixture of dihydrobenzoate **10** (0.177 g, 0.7 mmol) in 0.175 M NaOH solution (6.0 mL, 1.05 mmol) was stirred and heated to 55 °C for 6 h. The resultant yellow solution containing a trace of suspended solid was cooled to room temperature and filtered, and the filtrate was acidified with concentrated HCl (10 drops). The gelatinous mixture that formed was extracted with methylene chloride (4 × 5 mL), and the combined organic extract was then washed with brine (7 mL). After drying the organic layer and removal of the solvent by evaporation in vacuo, **11** was isolated as a colorless solid (0.122 g, 73%): mp 171–172 °C dec; λ_{max} ($CHCl_3$) 2.93, 3.1–3.3 (broad shoulder), 5.85 μm; δ ($CDCl_3$) 1.48 (9 H, s, *tert*-butyl), 2.80–3.00 (2 H, m, allylic CH_2), 4.55–5.15 (2 H, m, R_2CHNCO_2), 5.67–6.15 (2 H, m, olefinic), 7.10 (1 H, br s, olefinic).

Anal. Calcd for $C_{12}H_{17}NO_4$: C, 60.24; H, 7.16; N, 5.85. Found: C, 59.85; H, 6.97; N, 5.70.

Isogabaculine (3). A suspension of **11** (0.100 g, 0.4 mmol) in 0.1 N HCl (5 mL, 0.5 mmol) was stirred at 55 °C for 24 h. The mixture was cooled to room temperature and placed on a 1 × 20 cm column of Bio-Rod AG 11A8 ion retardation resin which had been previously washed with 600 mL of distilled water. The column was then eluted with distilled water, and the eluants were collected in 2-mL fractions. TLC (75% EtOH–25% H_2O–trace NH_4OH; ninhydrin spray/Δ) was used to monitor which fractions contained the amino acid (R_f 0.5). All of the product was removed from the resin in the first 20 mL of eluant. These fractions were combined and lyophilized to yield **3** as a colorless solid (0.0305 g, 55%): mp >280 °C; *m/e* 139 (P), 122, 105, 94 (base peak); δ (D_2O) −1.92 to −1.68 (2 H, m, allylic CH_2), −0.75 to −0.40 (1 H, m, R_2CHN), 0.92–1.48 (2 H, m, olefinic), 1.72–1.92 (1 H, m, olefinic).

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Registry No.—**3**, 68582-58-1; **4**, 52745-92-3; **8**, 65899-50-5; **9**, 68582-59-2; **10**, 68582-60-5; **11**, 68582-61-6; **12**, 68582-62-7.

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(8) Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded in chloroform solution using sodium chloride optics on a Perkin-Elmer 137 infrared spectrophotometer. The polystyrene absorption at 6.238 μm was used as a reference, and only selected high intensity absorptions are reported. The NMR spectra were measured in either $CDCl_3$ or $(CD_3)_2SO$ using tetramethylsilane as an internal standard. Chemical shifts are reported in parts per million (δ) relating to Me_4Si. The NMR spectrum of "isogabaculine" (**3**) was obtained from a D_2O solution of **3**, where the HDO singlet served as the internal standard (δ = 0.0). Mass spectra were determined on an LKB-9000 system by direct insertion. TLC was carried out using Merck precoated silica gel 60 F-254 plates, 0.25-mm thickness. All reactions were carried out under a nitrogen atmosphere. Organic extracts of reactions were dried over anhydrous magnesium sulfate, and solvents were removed under water aspirator pressure on a roto-vac (bath temperature <30 °C). Elemental microanalyses were performed by the Searle Laboratories Microanalytical Department.
(9) Combustion analyses of **10** repeatedly gave low (0.67–1.87%) values for C, while the found values for H and N were always within ±0.3%. In all samples, the NMR spectra were consistent with **10** and failed to exhibit the presence of impurities which would have caused the low carbon values.

Oxidation of Poly(nitro)anilines to Poly(nitro)benzenes. Synthesis of Hexanitrobenzene and Pentanitrobenzene

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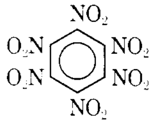
A new oxidation procedure has been developed suitable for conversion of poly(nitro)anilines to poly(nitro)benzenes (including those containing four or more nitro groups). Previously reported methods have been limited to the synthesis of trinitrobenzenes[1a,b] and a tetranitrotoluene.[1c]

Hexanitrobenzene (**1**) has been prepared by oxidation of pentanitroaniline (**2**) by peroxydisulfuric acid (hydrogen peroxide in sulfuric acid solution at 25 °C). The material is a powerful explosive.



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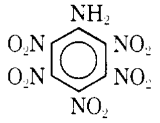

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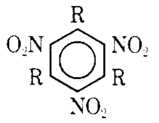
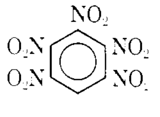


3a, R = C_6H_5O
b, R = CH_3O
c, R = NHOH
d, R = OH
e, R = NH_2

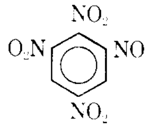
An account of the attempted preparation of **1** from trisubstituted derivatives of 1,3,5-trinitrobenzene (**3a**, R = C_6H_5O; **3b**, R = CH_3O) has been published.[2] Reaction of **3a,b** with hydroxylamine failed to yield the tris(hydroxylamino) derivative **3c**, a desired precursor to **1**. The oxidation of **3c** (said to be prepared by nitration of 1,3,5-tris(hydroxylamino)benzene) has been reported (without details) to yield **1**.[3] Our attempts to employ these synthetic routes were unsuccessful. The single crystal structure of **1** determined by X-ray crystallography was reported in 1966 without describing or referring to a method of synthesis.[4] No publication has yet appeared concerning the preparation of **1**.

Chemically, **1** resembles pentanitroaniline (**2**).[5] Reaction of **1** with aqueous sodium hydroxide solution (75 °C, 25 min), followed by acidification and conventional workup, gave 2,4,6-trinitrophloroglucinol (**3d**, 99%). Treatment of **1** in benzene solution with excess ammonia gave 1,3,5-triamino-2,4,6-trinitrobenzene (**3e**, 95%).

Our new procedure has been extended to oxidation of 2,3,4,6-tetranitroaniline[7,8] to pentanitrobenzene (**4**) and picramide to 1,2,3,5-tetranitrobenzene (**5**).[3c,9] These products, the latter soluble in the reaction mixture, were isolated in 80–90% yields by filtration and/or extraction with methylene chloride followed by recrystallization from chloroform.



4



5

Hexanitrobenzene belongs to a small group of substances, $C_x(NO_2)_y$, for which we propose the name nitrocarbons (zero-hydrogen compounds composed only of nitro groups attached to carbon). The only such materials known are tetranitromethane and hexanitroethane. A preparation of tetranitroethylene which has been reported[10] could not be repeated.

Experimental Section

WARNING! All compounds described are powerful explosives and should be handled with great care.

Hexanitrobenzene (1). Pentanitroaniline[5] (**2**, 1.0 g) was dissolved in 50 mL of fuming H_2SO_4 (20% SO_3). After cooling to 5 °C, 5 mL of 98% H_2O_2 was slowly added, keeping the temperature below 30 °C. The solution, protected by a drying tube, was stirred at 25–30 °C for 24 h and at 0 °C for 1 h. The precipitated product was removed by filtration through a sintered glass funnel and washed with concentrated H_2SO_4 (additional product is obtained by extraction of the filtrate with methylene chloride; the extracts should be worked up immediately and not stored). It was dissolved in pure, dry, warm chloroform and the solution decanted through a short column of anhydrous $MgSO_4$. The filtrate, after concentration at 25 °C to a volume of 10 mL and chilling at 0 °C for several hours, deposited small, chunky, pale yellow prisms of **1**: 0.63 g (58%); mp 240–265 °C dec; concentration of the filtrate gave 0.14 g of additional product, mp 195–245 °C. The first crop on sublimation gave very pale yellow prisms: mp 246–262 °C (lit[3b] mp 240–258 °C) (moisture must be excluded during the isolation operations); ^{13}C NMR (CD_2Cl_2) δ 138.7 relative to tetramethylsilane = 0 (lit.[6] 139.0); IR (KBr) 1560, 1320, 887 cm^{-1}; mass spectrum, strong *m/e* at 348 with very little fragmentation.

Anal. Calcd for $C_6N_6O_{12}$: C, 20.70; N, 24.14. Found: C, 20.67; H, 0.00; N, 23.74.

A 100-mg sample of **1** mixed with 3% aqueous sodium hydroxide (3 mL) was heated on the steam bath for 25 min (solution temperature 70–75 °C). After cooling to 25 °C the clear red solution was acidified with concentrated HCl and concentrated to dryness at 50 °C under reduced pressure. The residue was extracted with boiling methylene chloride. The extracts were dried with $MgSO_4$, filtered, and concentrated to dryness to yield 74 mg (99%) of trinitrophloroglucinol, mp 161–164 °C; recrystallization from water gave yellow prisms, mp 163–165 °C (lit.[5] mp 167 °C), identical with an authentic sample (strong molecular ion and parent peak at 261).

A 100-mg sample of **1** was dissolved in 20 mL of dry benzene. Dry ammonia was bubbled through the solution for 20 min to yield a yellow precipitate of 1,3,5-triamino-2,4,6-trinitrobenzene (70 mg, 95%): mp >350 °C dec (lit.[5] mp >300 °C); mass spectrum *m/e* 258 (M^+).

Pentanitrobenzene (4). 2,3,4,6-Tetranitroaniline[7] (1.0 g) was oxidized by the procedure described above for pentanitroaniline to yield 0.72 g of pentanitrobenzene, mp 130–138 °C; extraction of the filtrate with CH_2Cl_2 gave additional material (0.16 g); total yield 0.88 g (80%); recrystallization from chloroform gave yellow prisms, mp 142–143 °C: NMR ($CDCl_3$) δ 9.15 s; mass spectrum, *m/e* 303 (M^+).

Anal. Calcd for $C_6HN_5O_{10}$: C, 23.77; H, 0.33; N, 23.11. Found: C, 23.88; H, 0.32; N, 22.94.

1,2,3,5-Tetranitrobenzene (5). Picramide (1.0 g) dissolved in 100% sulfuric acid (50 mL) was treated with 98% H_2O_2 (5 mL) keeping the temperature below 30 °C. The solution was stirred for 24 h with cooling to maintain the temperature at 25–30 °C. The clear solution was extracted with four 40-mL portions of methylene chloride, and the combined extracts were stirred with $MgSO_4$ for 30 min. Filtration and concentration to dryness gave 1.05 g (93%) of **5**, mp 125–127 °C; recrystallization from chloroform gave prisms, mp 127–129 °C (lit. mp 125–126 °C[9] and 129–130 °C[1c]): NMR (CD_2Cl_2 δ 9.36 s); mass spectrum, *m/e* 258 M^+.

Anal. Calcd for $C_6H_2N_4O_8$: C, 27.92; H, 0.78; N, 21.71. Found: C, 27.86; H, 0.81; N, 21.39.

Use of 20% oleum rather than 100% sulfuric acid in the above procedure gave **5** in 62% yield.

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Registry No.—**1**, 13232-74-1; **2**, 21985-87-5; **3d**, 4328-17-0; **3e**, 3058-38-6; **4**, 68630-38-6; **5**, 3698-53-1; 2,3,4,6-tetranitroaniline, 3698-54-2; picramide, 489-98-5.

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