Synthesis of 2,6-Diamino-4-nitrotoluene

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The title compound is synthesized to prove its presence among the biodegradation products of 2,4,6-trinitrotoluene (TNT). 2,6-Dichlorotoluene is converted to 2-methyl-5-nitroisophthalic acid from which the corresponding acyl azide is formed. Rearrangement of the acyl azide in ethanol followed by hydrolysis of the dicarbamate product gives the title compound.

In a previous paper (*3*) the preparation of several reduction products of 2,4,6-trinitrotoluene (TNT) is described. These reduction products served as model compounds for a study of the products formed by biodegradation of TNT. During the course of the study, evidence was obtained (from thin-layer chromatography, gas chromatography, and mass spectrometry) to indicate that 2,6-diamino-4-nitrotoluene (I) is among the biodegradation products (*1*). The preparation of I was therefore undertaken to prove its presence among the biodegradation products.

The synthesis of I was accomplished starting with 2,6-dichlorotoluene (II) via the following sequence:

$$\text{II} \xrightarrow{\text{CuCN}} \text{2,6-dicyanotoluene (III)}$$

$$\xrightarrow[\text{H}_2\text{O}]{\text{KOH}} \text{2-methylisophthalic acid (IV)}$$

$$\xrightarrow[\text{H}_2\text{SO}_4]{\text{HNO}_3} \text{2-methyl-5-nitroisophthalic acid (V)}$$

$$\xrightarrow{\text{PCl}_5} \text{2-methyl-5-nitroisophthaloyl chloride (VI)}$$

$$\xrightarrow{\text{NaN}_3} \text{2-methyl-5-nitroisophthaloyl azide (VII)}$$

$$\xrightarrow[\text{(Curtius rearrangement)}]{\text{Ethanol}}$$

$$\text{ethyl 4-nitrotoluene-2,6-dicarbamate (VIII)}$$

$$\xrightarrow[\text{Ethanol water}]{\text{KOH}} \text{I}$$

The acyl azide (VII) when dry is very sensitive to impact; however, VII can be handled safely when damp with water and decomposes smoothly in ethanol to give the dicarbamate (VIII). The decomposition of VII in concentrated sulfuric acid at 10–15° gives I directly, but the reaction is difficult to control, and violent decomposition of the azide results if the stirring is not efficient. Attempts to prepare I by decomposition of VII in toluene followed by hydrolysis gave mainly a material that is insoluble in organic solvents. This material is presumably a polyurea formed by addition of the diamine (I) to the intermediate di-isocyanate.

Experimental

Mass spectra were determined on a Varian MAT 111, and NMR spectra on a Varian HA-100 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The melting points are uncorrected.

***2,6-Dicyanotoluene* (*III*).** A mixture of 32.2 g of 2,6-dichlorotoluene (Aldrich Chemical Co.), 64.8 g of cuprous cyanide, and 300 ml of *N*-methylpyrrolidone was refluxed under nitrogen for 24 h and then poured into 400 ml of concd. ammonium hydroxide. Workup, according to Lindsay et al. (*2*), gave 16.2 g (57.4%) of 2,6-dicyanotoluene, mp 134–135°.

***2-Methylisophthalic acid* (*IV*).** A mixture of 6.8 g of 2,6-dicyanotoluene and 45 g of 20% potassium hydroxide was refluxed for 6 h. The cooled solution was acidified to give 8.35 g (97.1%) of crude 2-methylisophthalic acid, mp 235–238 [lit. mp 228–229°, 245–248° (*2*) (*4*)].

***2-Methyl-5-nitroisophthalic acid* (*V*).** Nitric acid (90%) (100 ml) was added dropwise to 120 ml of 30% fuming sulfuric acid with cooling. The nitric–sulfuric acid mixture was stirred at 15–18° during the addition of 20.2 g of crude 2-methylisophthalic acid in small portions. After 3 h at 20–25°, the mixture was poured onto ice, and the solid was collected and washed with cold water. The yield of crude 2-methyl-5-nitroisophthalic acid (21.8 g, mp 214–16°) is 86.5%. Crystallization from water gave crystals, mp 216–218°.

***2-Methyl-5-nitroisophthaloyl chloride* (*VI*).** A mixture of 21.8 g of crude 2-methyl-5-nitroisophthalic acid and 41.6 g of phosphorous pentachloride in 100 ml of benzene was warmed to ca. 45°. When the evolution of HCl subsided, the mixture was heated to boiling and distilled until the pot temperature reached 110°. The mixture was then distilled under reduced pressure (water aspirator) until the pot temperature reached 200°. The oil in the pot solidified as it cooled to room temperature yielding 24.6 g (97.2%) of crude 2-methyl-5-nitroisophthaloyl chloride, mp 54–56°. Crystallization from benzene–hexane gave crystals, mp 55–56°.

***2,6-Diamino-4-nitrotoluene* (*I*) *via 2-methyl-5-nitroisophthaloyl azide* (*VII*) *and ethyl 4-nitrotoluene-2,6-dicarbamate* (*VIII*). Caution!** VII is very impact sensitive when dry. When damp with water, VII is not impact sensitive and can

Table I. Spectral Data for 2,6-Diamino-4-nitrotoluene and Precursors[a]

Compound	NMR spectrum[b]	Mass spectrum[c]
I	2.05 (s, CH_3)	167, 121
	4.83 (broad s, NH_2)	104, 94
	6.98 (s, Ar—H)	
IV	2.71 (s, CH_3)	
	7.38 (t, Ar—H)	
	7.96 (d, Ar—H)	
V	2.83 (s, CH_3)	225, 208, 179
	8.73 (s, Ar—H)	161, 133, 105
VI	2.11 (s, CH_3)	(265, 263, 261, parent ions, chlorine isotopes)
	8.35 (s, Ar—H)	228, 226, 190, 181
VIII	1.31 (t, ethoxy CH_3)	311, 294, 266
	2.38 (s, CH_3)	265, 248, 220
	4.22 (q, CH_2)	219, 176
	8.44 (s, Ar—H)	

[a] Elemental analyses (C, H, N) in agreement with theoretical values were obtained and submitted for review. [b] Solvent was acetone–d_6, except for compound VI for which benzene–d_6 was used. s = singlet, d = doublet, t = triplet, q = quartet. Chemical shifts are in δ units. [c] The major peaks at higher *m/e* are listed.

be handled safely. Operations involving VII should be conducted behind a safety shield.

A solution of 5.9 g of sodium azide in 45 ml of water was stirred at ca. 15° during the dropwise addition of 7.9 g of crude 2-methyl-5-nitroisophthaloyl chloride in 30 ml of acetone. Water (15 ml) was added, and the mixture containing precipitated VII was stirred at ambient temperature for 30 min. The cream-colored solid (VII) was removed by filtration and washed with cold water (**Caution!** VII is left damp with water, see note above). VII decomposed violently at 75° when an attempt to determine the melting point was made. Thin-layer chromatography (silica gel HF-254 with benzene as eluant) indicated VII was pure since only one spot was present.

The *damp* acyl azide (VII) was added in small portions to 150 ml of absolute ethanol stirred at 60°. Nitrogen gas was evolved, and the ethanol solution was then heated to boiling for 10 min. The hot solution was filtered, and the filtrate cooled in ice to give 5.6 g (60.0%) of ethyl 4—nitrotoluene-2,6-dicarbamate (VIII), mp 204–205°. NMR and mass spectral data confirmed that VIII is the dicarbamate (Table I).

A mixture of 5.5 g of VIII, 5.5 g of potassium hydroxide, 55 ml of water, and 55 ml of ethanol was heated at reflux for 3 h. The cooled reaction mixture was filtered, and the red crystals of 2,6-diamino-4-nitrotoluene (I) were washed with water. The red crystals (mp 213–215°) weighed 2.55 g (86.4%). Crystallization from acetone–water raised the melting point to 214–216°.

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NMR Spectra of Some Methyl-Substituted Diaryliodonium Compounds

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The NMR spectra of a number of methyl-substituted diaryliodonium compounds are recorded and discussed. The effects of the positively charged iodine atom on the spectra are compared to similar effects due to the presence of a carbonium ion.

In recent years there has been some interest in the synthesis and properities of diaryliodonium compounds (*1–3, 7*). In the course of some studies on these compounds, it was discovered that no NMR spectra have been reported. We now report the spectra of some symmetrical and unsymmetrical diphenyliodonium compounds bearing methyl substituents.

Experimental

The compounds were all synthesized by the methods devised by Beringer (*4, 5*). The NMR spectra were recorded on a Perkin-Elmer R-12 spectrometer, using saturated solutions of the compounds in deuteriochloroform containing 1% (v/v) of TMS. All peak positions were measured in ppm relative to TMS ($\delta_{TMS} = 0$). The NMR spectra of these compounds are relatively simple, but reveal certain interesting features.

As shown in Table I, the positively charged iodine atom produces the expected low field shift of the methyl and aromatic protons found in the work on carbonium ion species (*8, 10–13*). This can be seen by comparing the peak positions in the spectra of the 4,4′-dimethyldiphenyliodonium compounds and the spectrum of iodotoluene. This shift is 0.2–0.4 ppm to low field for the aromatic protons and 0.05–0.1 ppm to low field for the methyl protons, and is analagous to a shift of ca. 2.5 ppm to low field for the carbonium ion species relative to benzene (*9, 10*). (A better analogy might be with ammonium or sulfonium salts which, like iodonium ions, are closed shell cations.) While a direct comparison is not possible because the spectra of the carbonium ions are run in different solvents and, frequently, at different temperatures due to their general instability, the magnitude of these shifts is to be expected based on the relative size difference of the carbon and iodine species involved.

Because of the decreased solubility of the higher substituted diphenyliodonium compounds in deuteriochloroform, the bromide salt was frequently used in place of the less soluble iodide. No major differences in the NMR spectra are expected due to a difference in these anions, as shown by a comparison of the data for the bromide and iodide salts of 4,4′-dimethyldiphenyliodonium compounds and the 2,2′,4,4′,6,6′-hexamethyldiphenyliodonium (Table I).

The methyl region of the spectra for all compounds run shows absorption in only two principal regions: 2.55–2.65 ppm, due to the methyl groups ortho to the positively charged iodine atoms, and 2.25–2.35 ppm, due to the meta and para methyl groups. No distinction could be made between the absorptions due to the meta and para methyl groups.

The aromatic region of the spectra shows the characteristic patterns of substituted benzenes. The aromatic protons of the 4,4′-dimethyldiphenyliodonium compounds give rise to a