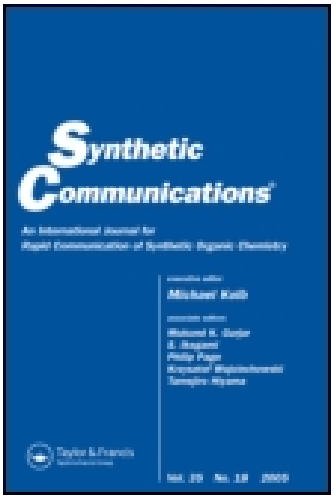

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Nitration of Ethyl Carbamates of Phenylenediamines and Aniline

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Nitration of Ethyl Carbamates of Phenylenediamines and Aniline

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Abstract:: The methyl and ethyl carbamates of aniline and the diethyl dicarbamates of 1,2-, 1,3-, and 1,4-phenylenediamine were prepared. Nitration of the carbamates gave ring mono-, di-, or trinitro-derivatives in good yield.

Keywords: aniline, carbamates, nitration, phenylenediamines, urethanes

It was recently shown that a trialkyl 1,3,5-triaminobenzene tricarbamate readily underwent nitration to give the corresponding 2,4,6-trinitro analog in excellent yield.[1] Therefore, an investigation into the nitration of carbamates of aniline and the phenylenediamines seemed worthwhile.

The alkyl carbamates of aniline were prepared by two routes. The methyl carbamate **1** was prepared by reacting aniline with methyl chloroformate (Scheme 1).[2] The ethyl carbamate **2** was prepared by Curtius rearrangement of benzoyl azide in good yield (Scheme 2).[3,4]

The literature contained some discrepancies regarding the nitration of alkyl *N*-phenylcarbamates. Curry and Mason alleged that the nitration of **2** had not been studied previously.[5] They added, without detail, that nitration of **2** (acetic anhydride/fuming nitric acid) gave only ethyl 2,4-dinitrophenylcarbamate. A thorough literature search found that the nitration of alkyl *N*-phenylcarbamates had been investigated as far back as 1877 by Losanitch,[6] 1886 by Hentschel,[7] and 1891 by van Romburgh.[8] By

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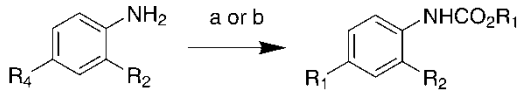


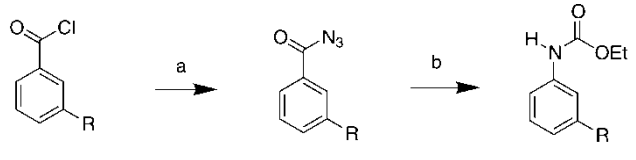
aniline **1** R_1 = Me, R_2,R_4=H
1,2-phenylenediamine **4** R_1=Et,R_2=$NHCO_2Et$,R_4=H
1,4-phenylenediamine **5** R_1=Et,R_2=H,R_4=$NHCO_2Et$

Scheme 1. a) $ClCO_2Me$, pyridine, $CHCl_3$; b) $ClCO_2Et$, pyridine, $CHCl_3$.

treating **1** with nitric/sulfuric acids, Hentschel isolated a solid melting at 189°C that he believed was tetranitrodiphenylurea[9,10] based upon combustion analysis. Hentschel's procedure was repeated by van Romburgh, who isolated a product melting at 192°C and identified it as methyl 2,4,6-trinitrophenylcarbamate (**6**). Later, Crocker and Lowe obtained a similar substance melting at 192°C by reacting potassium cyanate with 1-chloro-2,4,6-trinitrobenzene (picryl chloride) in methanol.[11]

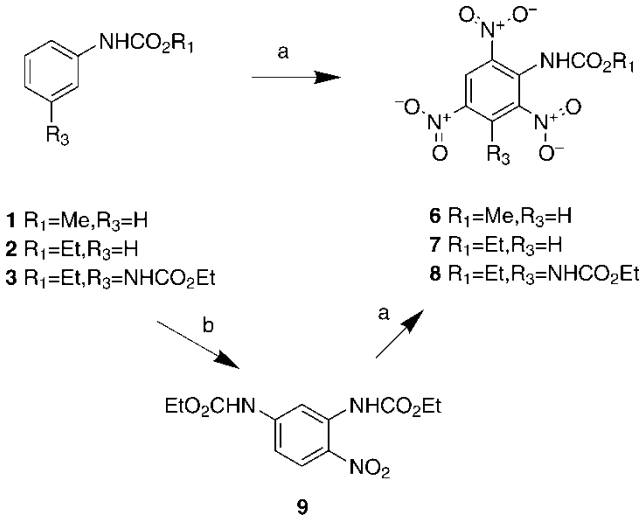
Therefore, the research of Hentschel and van Romburgh on the nitration of alkyl *N*-phenylcarbamates was repeated using a mixture of concentrated sulfuric acid and a slight excess of 100% nitric acid. When **1** was treated under these conditions, a solid melting at 195°C was obtained in high yield. Nuclear magnetic resonance (NMR) spectroscopy (^1H, ^{13}C) support the trinitro derivative with the structural assignment of **6** (Scheme 3). Similar nitration of the ethyl analog **2** gave **7** in high yield as well.

The bis-Curtius rearrangement of isophthaloyl diazide was carried out to obtain the diethyl dicarbamate of 1,3-phenylenediamine (**3**) uneventfully (Scheme 2).[12] Nitration of **3** in concentrated sulfuric acid/100% nitric acid gave what was thought to be the unreported diethyl 1,3-diamino-2,4,6-trinitrophenyldicarbamate (**8**) (Scheme 3). At the time of this writing, the recent patent of O'Keefe was discovered that described this reaction using a slightly different acid mixture.[13] It was found that nitration of **3** in concentrated nitric acid gave the mono-nitrated product **9** with the nitro group at the 4-position. Several attempts were made to prepare a dinitro derivative of **3**, but mixtures were obtained by thin-layer chromatography (TLC).



benzoyl chloride R = H **benzoyl azide R = H** **2** R = H
isophthaloyl dichloride R = COCl **isophthaloyl diazide R = CON_3** **3** R = $NHCO_2Et$

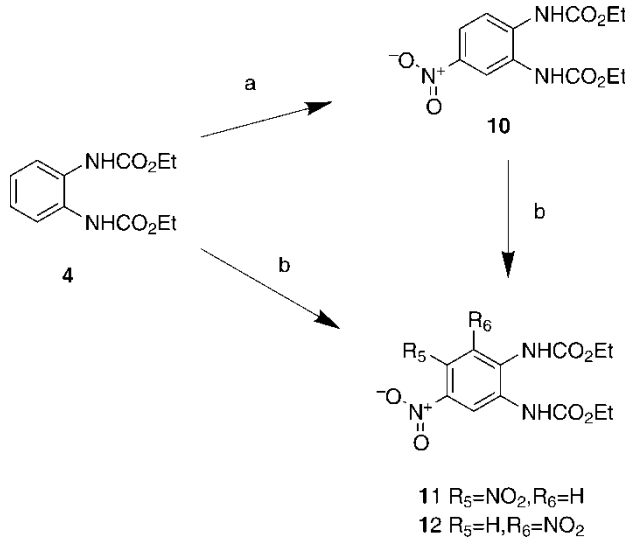
Scheme 2. a) NaN_3, H_2O, THF; b) EtOH, reflux.



Scheme 3. a) Conc. H_2SO_4, 3 equiv 100% HNO_3, 0°C to rt; b) Conc. HNO_3, 0°C to rt.

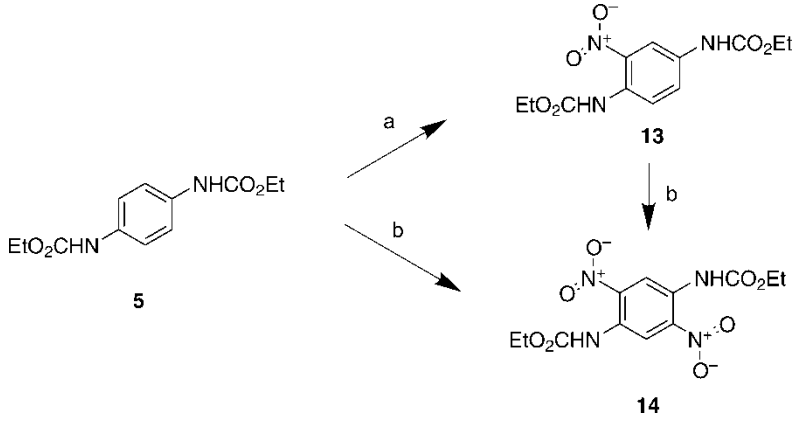
The dicarbamates of 1,2- and 1,4-phenylenediamines (**4** and **5**) were also prepared by reaction with ethyl chloroformate in the presence of pyridine (Scheme 1).[14,15] It appeared from the literature that nitration of **4** and **5** had not been studied. Nitration of **4** in concentrated nitric acid at room temperature gave clean mononitration at the 4-position to give **10** (Scheme 4). This is in keeping with previous reports regarding nitration of bis-*N*,*N*′-acetamides of phenylenediamines.[16,17] Dinitration of **4** occurred when treated with concentrated sulfuric acid/100% nitric acid or 100% nitric acid/acetic acid. The product was a 1:1 mixture of the unreported 4,5- and 4,6-dinitro isomers, **11** and **12**, based on ^{1}H NMR Spectroscopy. Further nitration of **10** also gave the same 1:1 mixture of **11** and **12**. In both cases, the yield of the dinitration products **11** and **12** was good, and no attempt was made to separate the mixture. Curiously, the nitration of disulfonamides of 1,2-phenylenediamine give the 4,5-dinitro isomer in good yield.[18,19]

Nitrating **5** with concentrated sulfuric acid/100% nitric acid caused considerable hydrolysis of the carbamate groups (Scheme 5). TLC analysis of the reaction showed a large amount of an orange-colored polar spot at the origin. The product from nitration at the 2-position (**13**) could be isolated under these conditions by brief treatment at 0°C. A better method to prepare **13** was to treat a solution of **5** in acetic acid with 1 equivalent of concentrated nitric acid at room temperature. This result parallels the studies on bis-*N*,*N*′-acetamides of phenylenediamines.[16,17] Dinitration of **5** to give the unreported **14** could be achieved simply by stirring in concentrated nitric acid at room temperature. NMR spectroscopy (^{13}C) proved that the nitro groups of **14** are in the 2,5-positions. Reaction of **13** with concentrated nitric acid also gave **14**.



Scheme 4. a) Conc. HNO_3; b) Conc. H_2SO_4, 100% HNO_3.

In conclusion, the diethyl carbamates of the phenylenediamines and aniline were prepared. The carbamates generally gave clean reactions under nitration conditions. The carbamates of aniline and 1,3-phenylenediamine readily underwent nitration to give trinitro products. Nitration of 1,4-phenylenediamine dicarbamate gave the 2,5-dinitro isomer selectively. Initial nitration of 1,2-phenylenediamine dicarbamate gave the 4-nitro isomer, and subsequent nitration produced a mixture of 4,5- and 4,6-dinitro isomers.



Scheme 5. a) HOAc, 1 equiv conc. HNO_3; b) Conc. HNO_3.

EXPERIMENTAL

Melting points were collected on an electrothermal capillary melting-point apparatus and are not corrected. All NMR spectra were obtained on a Bruker AC-200 spectrometer (^{1}H at 200 MHz, ^{13}C at 50 MHz) and are referenced to solvent or tetramethylsilane. Benzoyl chloride, isophthaloyl dichloride, and 1,2-, 1,3-, and 1,4-phenylenediamines, and all other reagents, were purchased from Aldrich Chemical Co. (Milwaukee) and used as received. Elemental analysis was performed by Atlantic Microlab, Inc. (Norcross, GA).

Methyl *N*-Phenylcarbamate (1)

A 1-L Erlenmeyer flask equipped with magnetic stirbar was charged with 200 mL of $CHCl_3$, 9.3 g of aniline (0.1 mol), and 10.27 g of pyridine (0.13 mol, 1.3 equiv). The mixture was stirred in an ice bath while 11.28 g of methyl chloroformate (9.2 mL, 0.12 mol, 1.2 equiv) was added dropwise over 1 h. The internal temperature remained at $\sim$12°C. After checking the reaction by TLC (SiO_2; hexanes/Et_2O) for completion, the mixture was poured onto 300 g of crushed ice and H_2O. The organic phase was washed three times with 200-mL portions of H_2O. The organic layer was washed with brine and then dried with anhydrous $MgSO_4$. The filtrate was rotary evaporated, leaving 13.96 g of an oil that slowly crystallized under vacuum. The crude was recrystallized from hexanes to give 12.7 g of the title compound as colorless plates (84%). Mp 43–45°C (lit.[2] 47°C). δ_H ($CDCl_3$): 7.39 (d, $J = 8.0$ Hz, 2H), 7.26 (t, $J = 7.6$ Hz, 2H), 7.08 (bs, 1H), 7.03 (t, $J = 7.0$ Hz, 2H), 3.73 (s, 3H); δ_C ($CDCl_3$): 154.42, 138.07, 129.04, 123.46, 118.96, 52.33.

Ethyl *N*-Phenylcarbamate (2)

A 250-mL round-bottomed flask equipped with magnetic stirbar was charged with 19 g of NaN_3 (0.29 mol, 5 equiv) and 50 mL of H_2O. The mixture was allowed to stir until all the solids dissolved. The mixture was cooled in an ice bath, and a solution of 8 g of benzoyl chloride (0.057 mol) in 20 mL of THF was added over 15 min. After stirring in the ice bath for 1 h, the mixture was extracted twice with 100-mL portions of Et_2O. The organic phases were collected and washed with 50 mL of H_2O, washed with 50 mL of saturated aqueous Na_2CO_3, and finally 50 mL of brine. After drying over $MgSO_4$, the filtrate was transferred to a 500-mL of round-bottomed flask, and the solvent was rotary evaporated (10 Torr, rt), leaving a light yellow semicrystalline mass of benzoyl azide [δ_H ($CDCl_3$): 8.07–7.97 (m, 2H), 7.61 (tt, $J = 7.5$ and 1.4 Hz, 1H), 7.44 (tt, $J = 7.2$ and 1.7 Hz, 2H); δ_C ($CDCl_3$): 172.48, 134.37, 130.74, 129.52, 128.71]. Ethanol (200 mL) and a

stirbar were added to the flask, and the solution was refluxed for 12 h. Evaporation of the solvent left a pale green oil that slowly crystallized. The product was sufficiently pure (8.1 g, 86%). Mp 45–47°C (lit.[3] 52°C). δ_H ($CDCl_3$): 7.45–7.24 (m, 4H), 7.05 (t, $J = 7.5$ Hz, 1H), 6.76 (bs, 1H), 4.23 (q, $J = 7.1$ Hz, 2H), 1.31 (t, $J = 7.5$ Hz, 3H); δ_C ($CDCl_3$): 153.88, 138.19, 129.19, 129.15, 123.51, 118.91, 61.35, 14.70.

Diethyl 1,3-Phenylenediamine Dicarbamate (3)

A 500-mL round-bottomed flask equipped with magnetic stirbar was charged with 70 mL of H_2O, followed by 25.7 g of NaN_3 (0.396 mol, 10 equiv). The mixture was stirred in an ice bath until complete dissolution. An addition funnel was attached and charged with a solution of 8 g of isophthaloyl dichloride (0.039 mol) in 30 mL of THF. The addition was made over 15 min. Copious white solids began to form, and the mixture was stirred for 1 h in the ice bath. Ether (200 mL) was added, and the solids slowly dissolved. The aqueous phase was extracted twice more with 100-mL portions of Et_2O. The organic phases were collected and washed twice with 200-mL portions of H_2O. The organic phase was washed with 100 mL of saturated aqueous Na_2CO_3 and then 200 mL of brine and dried over anhydrous $MgSO_4$. The Et_2O was rotary evaporated (10 Torr, rt) leaving 8.45 g of isophthaloyl diazide (98% of theory) [δ_H ($CDCl_3$): 8.65 (t, $J = 1.7$ Hz, 1H), 8.27 (dd, $J = 7.8$ and 1.7 Hz, 2H), 7.59 (td, $J = 7.9$ and 0.7 Hz, 1H); δ_C ($CDCl_3$): 171.64, 134.87, 131.58, 130.55, 129.47] as a white solid. Absolute EtOH (500 mL) and a stirbar were added to the flask, and the mixture was refluxed for 18 h. The mixture was rotary evaporated, leaving 8.6 g of an off-white solid. Recrystallization from MeCN gave the title compound as a white powder (6.7 g, 67%). Mp 140–142°C (lit.[12] 143–145°C). δ_H ($CDCl_3$): 7.59 (t, $J = 1.8$ Hz, 1H), 7.33–7.09 (m, 3H), 6.93 (bs, 2H), 4.26 (q, $J = 7.1$ Hz, 4H), 1.33 (t, $J = 7.4$ Hz, 6H); δ_H (DMSO): 9.54 (s, 2H), 7.69 (s, 1H), 7.20–7.01 (m, 3H), 4.11 (q, $J = 6.5$ Hz, 4H), 1.23 (t, $J = 7.2$ Hz, 6H); δ_C ($CDCl_3$): 153.86, 138.98, 129.72, 113.62, 109.10, 61.42, 14.69; δ_C (DMSO): 153.51, 139.62, 128.73, 112.65, 108.71, 60.03, 14.52.

Diethyl *N*,*N*′-1,2-Phenylenediamine Dicarbamate (4)

A 500-mL Erlenmeyer flask equipped with magnetic stirbar was charged with 20 g of 1,4-phenylenediamine (0.185 mol), 44 g of pyridine (44.98 mL, 0.55 mol, 3 equiv), and 200 mL of $CHCl_3$. The mixture was stirred in an ice bath while 39 mL of ethyl chloroformate (43.9 g, 0.41 mol, 2.2 equiv) was added over 30 min. The mixture was stirred at rt for 1 h. The mixture was washed twice with 200-mL portions of H_2O and 200 mL of brine and then dried over anhydrous $MgSO_4$. The solvent was rotary evaporated, leaving a

crude solid (44.3 g, 95%). Recrystallization from EtOH gave the title compound as white needles. Mp 79–81°C (lit.[14] 88°C). δ_H ($CDCl_3$): 7.52–7.41 (m, 2H), 7.21 (bs, 2H), 7.16–7.04 (m, 2H), 4.21 (q, $J = 7.2$ Hz, 4H), 1.29 (t, $J = 7.0$ Hz, 6H); δ_C ($CDCl_3$): 155.03, 130.13, 125.65, 124.42, 61.75, 14.62.

Diethyl *N*,*N*′-1,4-Phenylenediamine Dicarbamate (5)

A procedure similar to **4** was used. 1,4-Phenylenediamine (20 g, 0.185 mol), 44 g of pyridine (44.98 mL, 0.55 mol, 3 equiv), 39 mL of ethyl chloroformate (43.9 g, 0.41 mol, 2.2 equiv), and 200 mL of $CHCl_3$ gave 42 g of crude solid (90%). Recrystallization from EtOH gave the title compound as chunky, clear crystals. Mp 196–199°C (lit.[15] 196°C). δ_H (DMSO): 9.45 (s, 2H), 7.36 (s, 4H), 4.12 (q, $J = 6.9$ Hz, 4H), 1.25 (t, $J = 7.3$ Hz, 6H); δ_C (DMSO): 153.63, 133.97, 59.98, 14.54.

Methyl *N*-2,4,6-Trinitrophenylcarbamate (6)

A 500-mL round-bottomed flask equipped with magnetic stirbar was charged with 50 mL of conc. H_2SO_4. The flask was cooled in an ice bath before adding 12.7 g of **1** (0.084 mol) in one portion. The cooling bath was removed to allow the solids to dissolve. The cooling bath was replaced, and 11.3 mL of 100% HNO_3 (17 g, 0.27 mol, 3.2 equiv) was added dropwise by addition funnel over 30 min. The color of the mixture became dark brown. Shortly after all the HNO_3 was added, a solid precipitated and the mixture solidified. The cooling bath was removed, and the mixture was stirred at rt for 8 h. The mixture was poured onto 1 L of vigorously stirred crushed ice and H_2O. The tan solid was collected on a coarse-porosity glass frit and washed with copious H_2O. The crude solid (24 g, quant.) was air dried on the frit and then recrystallized from 1,4-dioxane/EtOH to give the title compound as tan-colored needles. Mp 195–197°C (lit.[8] 192°C). δ_H (DMSO): 10.68 (s, 1H), 8.96 (s, 1H), 3.71 (s, 3H); δ_H ($CDCl_3$): 9.55 (bs, 1H), 9.15 (s, 2H), 3.88 (s, 3H); δ_C (DMSO): 153.78, 144.25, 143.08, 130.82, 124.95, 53.65. Elemental analysis calculated for $C_8H_6N_4O_8$: C, 33.58; H, 2.11; N, 19.58. Found: C, 33.88; H, 2.11; N, 19.52.

Ethyl *N*-2,4,6-Trinitrophenylcarbamate (7)

A 500-mL round-bottomed flask equipped with magnetic stirbar was charged with 30 mL of conc. H_2SO_4, and the flask was cooled in an ice bath. In one portion, 6.08 g of **2** (0.037 mol) were added, and the mixture was stirred until all solids dissolved. Over 30 min, 5 mL of 100% HNO_3 (0.12 mol, 3.2 equiv) were added dropwise, keeping the internal temperature at or

colder than 10°C. The mixture became dark brown, and the cooling bath was removed. After stirring at rt for 8 h, the mixture was poured onto 500 g of crushed ice. After the ice had melted, the light yellow precipitate was filtered on a medium-porosity glass frit, washed several times with H_2O, and air-dried on the frit (11 g, quant.). The crude product was recrystallized from EtOH to give the title compound as pale yellow, glistening plates (9.2 g, 83%). Mp 141–143°C (lit.[8] 144°C). δ_H ($CDCl_3$): 9.49 (bs, 1H), 9.11 (s, 2H), 4.29 (q, $J = 7.2$ Hz, 2H), 1.36 (t, $J = 3$H); δ_C ($CDCl_3$): 152.11, 142.35, 141.32, 133.24, 125.54, 64.50, 14.37. Elemental analysis calculated for $C_9H_8N_40_8$: C, 36.01; H, 2.69; N, 18.66. Found: C, 36.13; H, 2.71; N, 18.58.

Diethyl *N*,*N*′-1,3-Diamino-2,4,6-trinitrophenyl Dicarbamate (8)

A 50-mL round-bottomed flask equipped with magnetic stirbar was charged with 5 mL of conc. H_2SO_4. The flask was placed in an ice bath to stir until cold. In a single portion, 3 g of **3** (3.9 mmol) were added, and the solids were allowed to dissolve. Nitric acid (100%, 1.5 mL, 3.2 equiv) was added dropwise over 5 min. The color immediately became dark red. The cooling bath was removed, and the mixture was stirred at rt for 30 min. After becoming warm, the color changed to light brown. The mixture was poured onto 100 g of crushed ice and H_2O. The pale yellow precipitate was collected on a coarse-porosity glass frit, washed well with H_2O, and air-dried (4.6 g, quant.). Recrystallization of the crude solid from EtOH gave 2.6 g of the title compound as an off-white powder (56%). Mp 227–230°C (dec., lit. 225–228°C[13], 226°C[20]). δ_H (DMSO): 10.62 (s, 2H), 8.86 (s, 1H), 4.13 (q, $J = 7.1$ Hz, 4H), 1.21 (t, $J = 7.0$ Hz, 6H); δ_C (DMSO): 153.46, 143.53, 141.35, 129.54, 125.09, 62.23, 14.18. Elemental analysis calculated for $C_{12}H_{15}N_5O_{10}$: C, 37.22; H, 3.38; N, 18.08. Found: C, 36.93; H, 3.41; N, 1786.

Diethyl *N*,*N*′-1,3-Diamino-4-nitrophenyl Dicarbamate (9)

A 1 g sample of **3** was added to 10 mL of conc. nitric acid. After stirring 1 h, the solution was poured onto crushed ice and water. The pale yellow solid was collected on a medium porosity glass frit. This was recrystallized from EtOH, yielding pale yellow crystals. Mp 120–122°C. δ_H ($CDCl_3$): 10.11 (s, 1H), 8.51 (s, 1H), 8.22 (d, $J = 9.3$ Hz, 1H), 7.53 (s, 1H), 7.47 (dd, $J = 9.3$ and 2.2 Hz, 1H), 4.29 (q, $J = 6.7$ Hz, 2H), 4.26 (q, $J = 7.1$ Hz, 2H), 1.35 (t, $J = 7.5$ Hz, 3H), 1.33 (t, $J = 7.1$ Hz, 3H); δ_C ($CDCl_3$): 153.57, 153.14, 145.83, 137.21, 130.88, 128.17, 111.77, 107.90, 62.29, 62.20, 14.58, 14.55.

Diethyl *N*,*N*′-4-Nitro-1,2-diaminobenzene Dicarbamate (10)

A 100-mL Erlenmeyer flask equipped with a magnetic stirbar was charged with 10 mL of conc. HNO_3. The mixture was stirred in an ice bath, and 1 g of **4** (3.9 mmol) was added in one portion. The cooling bath was removed, and the mixture was stirred at rt for 4 h. After this time, a tan solid had precipitated. The mixture was poured onto 100 g of crushed ice and H_2O, and a tan solid precipitated (850 mg, 74%). The solid was recrystallized from EtOH to give the title compound as soft white needles. Mp 173–175°C. δ_H ($CDCl_3$): 8.32 (d, $J = 2.7$ Hz, 1H), 8.10 (dd, $J = 9.2$ and 2.4 Hz, 1H), 7.99 (d, $J = 9.0$ Hz, 1H), 7.39 (bs, 1H), 6.78 (bs, 1H), 4.3 (q, $J = 7.0$ Hz, 2H), 4.29 (q, $J = 7.2$ Hz, 2H), 1.36 (t, $J = 7.2$ Hz, 3H); δ_H (DMSO): 9.29 (s, 1H), 9.18 (s, 1H), 8.44 (d, $J = 2.2$ Hz, 1H), 7.99–7.84 (m, 2H), 4.15 (q, $J = 7.1$ Hz, 2H), 4.14 (q, $J = 7.1$ Hz, 2H), 1.24 (t, $J = 7.0$ Hz, 6H); δ_C (DMSO): 154.09, 153.61, 142.52, 136.36, 129.21, 121.92, 119.49, 118.40, 61.19, 61.03, 14.39, 14.36.

Diethyl 4,5-Dinitro-1,2-diaminobenzenedicarbamate (11) and Diethyl 4,6-Dinitro-1,2-diaminobenzenedicarbamate (12)

A 50-mL Erlenmeyer flask equipped with magentic stirbar was charged with 10 mL of conc. H_2SO_4 and cooled in an ice bath. In one portion, 1 g of **4** (3.9 mmol) was to the flask, and the cooling bath was removed. After most of the solids had dissolved, the cooling bath was replaced. Nitric acid (100%, 0.4 mL, 9.8 mmol, 2.5 equiv) was added dropwise over 2 min. The cooling bath was removed, and the mixture was stirred at rt for 1 h. The mixture was poured onto 100 g of cracked ice, and the tan solid was collected on a coarse frit and air-dried (1.3 g, 96%). ^{1}H NMR showed the product was a 1:1 mixture of the title compounds: diethyl 4,5-dinitro-1,2-diaminobenzenedicarbamate **(11)** δ_H (DMSO): 9.73 (s, 2H), 8.52 (s, 2H), 4.21 (q, $J = 7.4$ Hz, 4H), 1.29 (t, $J = 7.0$ Hz, 6H); and diethyl 4,6-dinitro-1,2-diaminobenzenedicarbamate **(12)** δ_H (DMSO): 9.78 (bs, 1H), 9.6 (bs, 1H), 8.85 (d, $J = 2.6$ Hz, 1H), 8.39 (d, $J = 2.6$ Hz, 1H), 4.11 (q, $J = 7.4$ Hz, 4H), 1.23 (t, $J = 7.4$ Hz, 6H).

Diethyl *N*,*N*′-2-Nitro-1,4-diaminobenzene Dicarbamate (13)

A 100-mL Erlenmeyer flask equipped with magnetic stirbar was charged with 20 mL of glacial HOAc, 1 g of **5** (3.9 mmol), and 387 μL of conc. HNO_3 (270 mg, 4.3 mmol, 1.1 equiv). The mixture was stirred at rt for 3 h. A bright yellow solid had precipitated during the reaction. The mixture was poured onto 100 g of crushed ice and H_2O. The bright yellow solid was collected on a coarse-porosity glass frit, washed with H_2O, and air dried (1.15 g, 97%). The

crude product was recrystallized from EtOH to give the title compound as fine yellow needles. Mp 143–145°C. δ_H ($CDCl_3$): 9.65 (s, 1H), 8.51 (d, $J = 9.3$ Hz, 1H), 8.35 (d, $J = 2.9$ Hz, 1H), 7.64 (dd, $J = 9.6$ and 2.6 Hz, 1H), 6.78 (s, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 4.27 (q, $J = 7.4$ Hz, 2H), 1.36 (t, $J = 7.1$ Hz, 3H), 1.34 (t, $J = 7.1$ Hz, 3H); δ_C ($CDCl_3$): 153.68, 153.52, 136.39, 133.10, 131.06, 126.58, 121.81, 115.27, 62.15, 61.95, 14.68, 14.61.

Diethyl *N*,*N*′-2,5-Dinitro-1,4-diaminobenzene Dicarbamate (14)

A 250-mL Erlenmeyer flask equipped with magnetic stirbar was charged with 50 mL of conc. HNO_3 and stirred in an ice bath. After cooling down, 5 g of **5** (0.0198 mol) were added in one portion. The color immediately became yellow, and the cooling bath was removed. The solids dissolved within 15 min, making an orange solution. Then, suddenly, a bright yellow solid precipitated. The mixture was warmed and stirred in a 55°C bath for 30 min before pouring onto 500 g of crushed ice and H_2O. The light yellow precipitate was harvested on a coarse-porosity glass frit and washed with copious H_2O. The solid was air dried on the frit (6.5 g, 96%) and recrystallized from EtOH to give the title compound as fine yellow needles. Mp 204–206°C. δ_H ($CDCl_3$): 8.45 (s, 2H), 8.12 (s, 2H), 4.27 (q, $J = 7.2$ Hz, 4H), 1.35 (t, $J = 7.0$ Hz, 6H); δ_H (DMSO): 9.99 (s, 2H), 7.78 (s, 2H), 4.12 (q, $J = 7.1$ Hz, 4H), 1.22 (t, $J = 6.9$ Hz, 6H); δ_C (DMSO): 153.89, 137.43, 129.89, 128.35, 61.47, 14.26.

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REFERENCES

1. Davis, M. C. Tricarbamate of 1,3,5-triaminobenzene via Curtius rearrangement of trimesic acid and subsequent nitration. *Synth. Commun.* **2007**, *37*, 1457–1462.
2. Hentschel, W. Ueberführung von carbanilsäureäther in amidobenzoësäuer. *Chem. Ber.* **1885**, *18*, 977–981.
3. Curtius, Th. Hydrazide und azide organischer säuren, VII: Abhandlung, XXXI: Ueber benzazid und einige säureazide der fettreihe. *J. Prakt. Chem.* **1895**, *52*, 210–226.
4. Curtius, Th. Umlagerung von säureaziden, $R.CON_3$, in derivate alkylirter amine (ersatz von carboxyl durch amide). *Chem. Ber.* **1894**, *27*, 778–781.
5. Curry, H. M.; Mason, J. P. Carbamates and N-nitrocarbamates. *J. Amer. Chem. Soc.* **1951**, *73*, 5043–5046.

6. Losanitch, S. M. Ueber die einwirkung von saltpetersäure auf zusammengesetzte harnstoffe, guanidine und urethane. *Chem. Ber.* **1877**, *10*, 690–691.
7. Hentschel, W. Ueber einige abkömmlinge des carbanilsauren methyls. *J. Prakt. Chem.* **1886**, *34*, 423–427.
8. Romburgh, M. P. van. Sur l'acide azotique sur les éthers de l'acide phénylamidoformique. *Recl. Trav. Chim. Pays-Bas* **1891**, *10*, 135–143.
9. The melting point of 2,2′,4,4′-tetranitrodiphenylurea is 218°C: Reudler, J. F. L. L' action de l'acide azotique sur les phénylurées. *Recl. Trav. Chim. Pays-Bas* **1914**, *33*, 35–84.
10. Kogan, I. M.; Kutepov, D. F. The nitration of diphenylurea (carbanilide). *J. Gen. Chem. USSR (Engl. Transl.)* **1951**, *21*, 1419–1424.
11. Crocker, J. C.; Lowe, F. H. Picryl derivatives of urethanes and thiourethanes. *J. Chem. Soc.* **1904**, *35*, 646–654.
12. Curtius, Th.; Davidis, E. Hydrazide und azide organischer säuren, part XIII: Die hydrazide und azide der phtalsäuren. *J. Prakt. Chem.* **1896**, *54*, 66–87.
13. O'Keefe, D. M. DATB and its bis-urethane. U.S. Patent 4,833,265, May 23, 1989.
14. Snape, H. L. Certain aromatic cyanates and carbamates. *J. Chem. Soc.* **1886**, *49*, 254–260.
15. Schiff, H.; Ostrogovich, A. Uramide, urethane und oxamäthane der p- und m-phenylendiamine. *Liebigs Ann. Chem.* **1896**, *293*, 371–388.
16. Ladenburg, A. Ueber das verhalten der diamine gegen salpetrige säure. *Chem. Ber.* **1884**, *17*, 147–150.
17. Phillips, M. A. The formation of 2-methylbenzimidazoles. *J. Chem. Soc.* **1928**, 172–177.
18. Cheeseman, G. W. H. Quinoxalines and related compounds, part VI. Substitution of 2,3-dihydroquinoxaline and its 1,4-dimethyl derivative. *J. Chem. Soc.* **1962**, 1170–1176.
19. Siri, O.; Braunstein, P. Tuning the synthesis of a dinitroaromatic towards a new trinitroaromatic stabilized energetic material. *New J. Chem.* **2005**, *29*, 75–79.
20. Lorang, H. F. J. Nitration of α-4-methoxy- and α-4-ethoxy-phenyl-β-ethylurea. *Recl. Trav. Chim. Pays-Bas* **1927**, *46*, 635–652.