Synthesis of Hydrazines with Aromatic Substituents Using Triarylbismuth Reagents

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Received 15 March 2000; revised 22 May 2000

Dedicated to Professor Ivar Ugi on the occasion of his 70th birthday

Abstract: Smooth monoarylation of two triprotected hydrazine reagents under mild conditions has been accomplished using triarylbismuthanes in the presence of copper acetate and amine to give products **3** and **6** in excellent yield. Arylation on N^2 after selective deprotection of derivatives with alkyl or aryl substituents on N^1, resulting in compounds **8** and **9**, is also demonstrated. Furthermore, other products derived from these reagents with free *N*-alkyl and *N*-aryl functions undergo the same reaction to give substances such as **10** and **11**. As a result, the scope of the original hydrazine reagents has been further extended. A few reference compounds have also been prepared directly from phenylhydrazine.

Key words: *N*-arylations, arylbismuthanes, multisubstituted hydrazines, organometallic reagents, stepwise synthesis

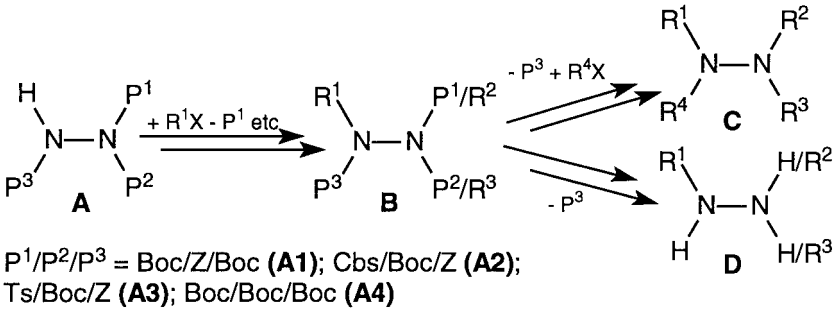
For the synthesis of substituted hydrazines[2] various triprotected reagents **A** (Scheme 1) are now available that allow convenient substitution on nitrogen in high yield.[3] The methodology developed for work with these reagents proceeds via selective deprotection of intermediates **B** and is followed by alternating substitutions and cleavages of protective groups in a stepwise fashion to furnish ultimately derivatives of type **C**. Alternatively, after complete deprotection of **B**, products such as **D** can also be obtained.

Among these reagents, **A1**–**A3** allow the full implementation of the scheme, whereas **A4** (all Boc) can only be applied for targets **C** with $R^3 = R^4$. Initially the scheme worked well for primary and benzylic R^1/R^2 and acylic R^3/R^4 substituents including a few with additional functional groups attached. More recently by cleavage of Z from **A3** it also became possible to introduce secondary R^1 moieties via reduction of ketone hydrazones.[4] Among other types of hydrazines aromatic and mixed aliphatic/aromatic species are of current interest.[5] In order to extend the scope of **A** to such compounds we have now explored aromatic substituents and this is the topic of the present communication.

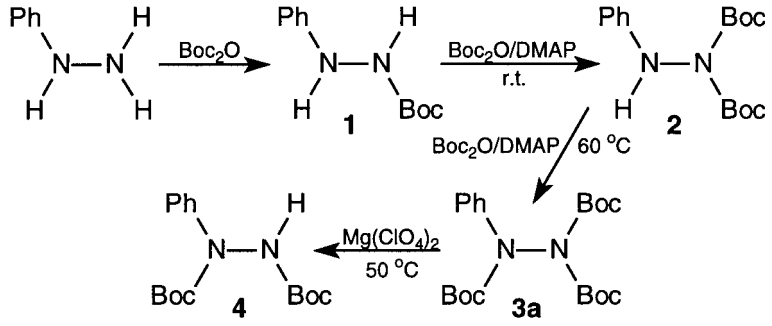
It was shown by Barton et al. that with triphenylbismuthane *N*-phenylation of a variety of amines takes place under mild conditions in the presence of copper salts.[6] More recently Chan also demonstrated that many derivatives of amines including amides, sulfonamides and carbamates with a free NH undergo this reaction, when an additional tertiary amine is added to the reaction mixture.[7] Triphenylbismuthane is now a commercially available reagent with several additional applications in synthetic chemistry and many other triarylbismuthanes have been described and are easy to make.[8] Therefore we decided to test this synthetic methodology[9] on reagents of type **A** for stepwise introduction of aromatic substituents into hydrazines.

Our initial experiments on *N*-arylation were performed with reagent **A4** using commercial triphenylbismuthane. To provide reference samples for this work, three model compounds, **2**, **3a** and **4**, were therefore first synthesized by an independent route from phenylhydrazine (Scheme 2) and carefully characterized. This scheme is based on synthetic methodology similar to that used for the preparation of **A4**.[3,10] Compound **1** was first prepared by Carpino[11] and subsequently by Pozdnev[12] and others. Pozdnev also prepared **4**.

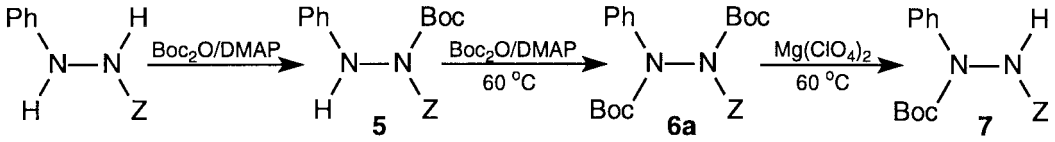
On reaction of phenylhydrazine with excess Boc_2O, as determined by TLC, the starting material quickly disappeared. Without isolation of **1**, a catalytic amount of DMAP (4-dimethylaminopyridine) was added, whereupon **2** was formed as the major product and characterized in a separate experiment. After raising the temperature to



Scheme 1



Scheme 2



Scheme 3

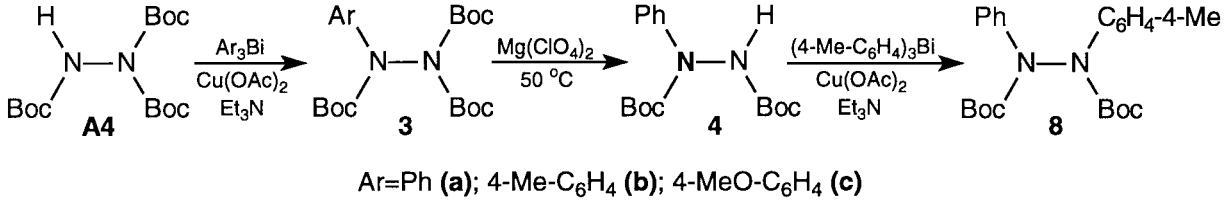
60 °C, **3a** was obtained as an oil in high yield, from which it could be obtained as a crystalline pure material, albeit with considerable loss of material. Treatment of **3a** in MeCN with $Mg(ClO_4)_2$ in catalytic amounts[13] furnished **4**, which is crystalline and more easily isolated and characterized. It is also the compound required to make **8** and similar compounds. This product could also be obtained in considerably higher yield directly from phenylhydrazine by a convenient one-pot reaction. Similarly, starting from 2-benzyloxycarbonyl-1-phenylhydrazine[14] instead of phenylhydrazine, another set of compounds **5**, **6a** and **7** was prepared by analogy to **2**, **3a** and **4** (Scheme 3). Of them **6a** was obtained as an oil, which could be converted to crystalline **7**.

It should be noted that Pozdnev prepared **4** directly from **1** with Boc_2O in boiling benzene without addition of DMAP,[12] whereas in the presence of this catalyst **2** is formed prior to **3a** and **5** prior to **6a** (see experimental part) as indicated in Schemes 2 and 3. To investigate whether **2** could also be converted to **3a** without additional DMAP, a separate, small-scale experiment with 0.2 mmol of **2** and an excess of Boc_2O (0.5 mmol) in boiling benzene was carried out (experiment not described in the experimental section), which, according to TLC, after 22 h indicated the complete conversion of **2** to **3a**. Obviously the reaction with Boc_2O at the phenyl-substituted nitrogen is rather slow both with and without addition of DMAP and requires heating, whereas in the presence of catalyst smooth dual protection occurs at the other nitrogen.[15]

The first arylation experiments involving triarylbismuthanes with addition of anhydrous $Cu(OAc)_2$ and triethylamine[7] were carried out using reagent **A4** and resulted in monoarylated products **3** (Scheme 4). No side-product was detectable chromatographically or spectroscopically in this experiment. Compounds **3a**–**c** were obtained as solids, of which **3a** was carefully compared with the reference sample previously prepared from phenylhydrazine. The two samples were identical in all respects.

These experiments were followed by similar ones with reagent **A1** (Scheme 5) to give products **6a**–**c** as oils. The spectroscopical data for **6a**, made in this way, completely matched those of the sample derived from phenylhydrazine. From these results, we conclude that once the required bismuthane is available it can be used with fair confidence to effect monoarylation of the two reagents.

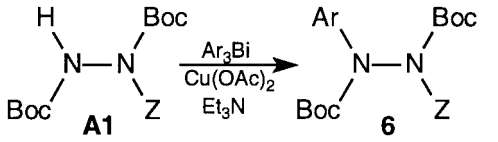
After monoarylation of **A4** and **A1** with triarylbismuthanes had been demonstrated to proceed efficiently, arylation on N^2 was examined and from compound **4** we were able to make **8** with nonidentical aryl moieties on its two nitrogens (Scheme 4). In the same manner, from two previously made monoalkylated derivatives of **A1** the corresponding N^2-arylated compounds **9** were prepared (Scheme 6, upper left part). Arylation on *N*-alkyl nitro-



Ar=Ph **(a)**; 4-Me-C_6H_4 **(b)**; 4-MeO-C_6H_4 **(c)**

Scheme 4

gens (compound **10**) and in one case also on an *N*-aryl nitrogen (compound **11**) has also been effected (Scheme 6, upper right part and lower part, respectively).



Ar=Ph **(a)**; 4-Me-C_6H_4 **(b)**; 4-MeO-C_6H_4 **(c)**

Scheme 5

The *N*-arylation experiments with bismuthanes described above were made on a rather small scale. Nevertheless, optimization experiments with respect to the amount of bismuthane required have been carried out using **A4** and Ph_3Bi in CH_2Cl_2 (Table 1). The results indicate that the amount of bismuthane can be reduced in comparison with that used in the typical experiment. Alternatively, the reaction can be performed in boiling dichloromethane.

After this work was completed, a paper appeared[16] in which a variety of *N*-arylaminophthalimides were converted to *N*-phenyl-*N*-arylaminophthalimides with triphenylbismuthane under conditions similar to those applied in the experiments referred to in Schemes 4–6. The products, which are reminiscent of **11**, were obtained in yields of 96–99% with one exception.

In conclusion, several examples have been provided on the application of triarylbismuthanes for the direct arylation of triprotected hydrazine reagents and/or subsequent stepwise introduction of such groups. The reactions take place under mild conditions and no side-products have been detected so far, as a result of which the yields were generally essentially quantitative. One drawback of the procedure is that only one aromatic residue of the bismuthane seems to be available for arylation. Furthermore, as long as the bismuthanes are made via Grignard reagents,[17] the restrictions with respect to the functional groups tolerated by the latter, at present, limit the scope of this procedure. Nevertheless, many new multisubstituted hydrazines are now in sight by simple stepwise synthesis and this methodology should also be applicable for other related reagents.[18]

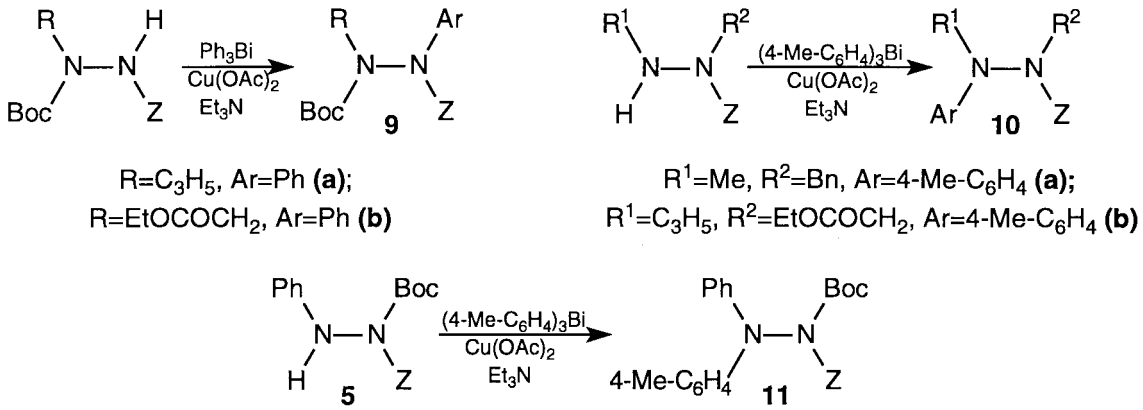
Reagents and solvents were used as supplied without prior purification. Mps were determined on a Gallenkamp apparatus and are uncorrected. TLC analyses were performed on 0.25 mm thick precoated silica plates (Merck Fertigplatten Kieselgel $60F_{254}$) with the mobile phases Et_2O/light petroleum, 1:2 (A), EtOAc/light petroleum, 1:3 (B) and toluene/Et_2O/light petroleum, 1:2:4 (C) and 1:1:2 (D). Spots were visualized by UV, acidic $KMnO_4$ or ethanolic phosphomolybdenic acid. ^1H and ^{13}C NMR spectra were recorded on a JEOL JMN EX 400 spectrometer in ~5% solution at 25 °C. Shifts are given in δ (ppm) relative to TMS ($\delta_H = 0$) and $CDCl_3$ ($\delta_C = 77.02$). IR spectra were recorded on a Mattson Polaris instrument. Solid samples were run as KBr disks and oils as films, applied as dilute solution in $CDCl_3$ to KBr disks, after evaporation of the solvent. Elemental analyses of all novel crystalline compounds were carried out by Mikro Kemi AB.

Triphenylbismuthane was of commercial origin, whereas tris(4-methylphenyl)bismuthane was made according to Combes and Finet[8] in 68% yield, yield could be increased to 90% by chromatography of the mother liquor in $CHCl_3$/light petroleum (1:10) on a short silica column. Tris(4-methoxyphenyl)bismuthane was also prepared according to the same authors (mp 197-198 °C); in this case the yield could be increased by extraction of the Celite filter cake in a Soxhlet apparatus with CH_2Cl_2.

2,2-Bis(*t*-butyloxycarbonyl)-1-phenylhydrazine (2)

To phenylhydrazine (0.541 g, 5 mmol) in MeCN (10 mL) was added Boc_2O (3.27 g, 15 mmol) in MeCN (5 mL) under mechanical stirring. After 30 min, DMAP (15.3 mg, 2.5 mol%) in MeCN (0.3 mL) was added over 3 min, and the solution left to react for 3 h at r.t. and at 4 °C overnight, whereupon TLC indicated formation of **2** and only minor amounts of **3a** and remaining **1**. (In the presence of DMAP partial conversion of **2** to **3a** was noticed on heating.) Dilution with Et_2O (40 mL), washing with 1 M $KHSO_4$/brine 1:1 (3 × 35 mL), sat. $NaHCO_3$ (5 mL), brine (3 × 5 mL), drying ($MgSO_4$) and evaporation furnished a golden oil, which after keeping at 4 °C under light petroleum afforded **2** (0.86 g, 56%) with mp 84–86 °C. The analytical sample was obtained as colourless crystals from light petroleum; mp: 88–89.5 °C; R_f 0.34 (A), 0.51 (B).

^1H NMR ($CDCl_3$): δ = 1.46 (s, 18H, Me), 6.06 (br s, 1H, NH), 6.74–7.25 (3 × m, 2+1+2H, Ar).



Scheme 6

Table 1 Optimization of Reaction between Boc_3-hydrazine **(A4)** and Ph_3Bi in the presence of $Cu(OAc)_2$ and Et_3N

Entry	Equiv Ph_3Bi[a]	Temp (°C)	Time (h)[b]	Yield[c] (%)
1	1.5/1.5/1.5	r.t.	23	98
2	1.1/1.5/1.5	r.t.	23	97
3	1.5/1.5/1.5	Reflux, CH_2Cl_2	6	98
4	1.1/1.5/1.5	Reflux, CH_2Cl_2	7	98
5	1.1/1.1/1.1	Reflux, CH_2Cl_2	>10	n.d.

[a] $Ph_3Bi/Cu(OAc)_2/Et_3N$.
[b] Reaction monitored by TLC.
[c] Isolated as an oil as described in the experimental part.

^{13}C NMR ($CDCl_3$): δ = 27.9 (Me), 83.6 (C_q), 113.3, 121.2, 129.0, 147.3 (Ar), 152.0 (Boc-CO).

FT-IR (KBr): ν = 1713 and 1747 (CO), 3309 and 3377 (NH) cm^{-1}.

Anal. Calcd for $C_{16}H_{24}N_2O_4$ (308.34): C, 62.32; H, 7.85; N, 9.08. Found: C, 62.2; H, 8.0; N, 9.1.

1,2,2-Tris(*t*-butyloxycarbonyl)-1-phenylhydrazine (3a)
Another experiment was initiated with phenylhydrazine (1.08 g, 10 mmol) and Boc_2O (9.17 g, 42 mmol in MeCN (7 mL) and left to react for 2 h at r.t., whereupon the temperature was increased to 60 °C and the reaction allowed to go to completion with monitoring by TLC (after 2 h essentially all of **2** was consumed). After a similar workup, crude **3a** was obtained as an oil (104%) contaminated with Boc_2O, which partly crystallized on standing. A solution of the oil in a small volume of light petroleum after several days deposited large, slightly yellow prisms (2.80 g, 68%) with mp 64.5−66 °C; colourless crystals with mp 65−66 °C after two recrystallizations from light petroleum; R_f 0.52 (A), 0.62 (B).

^1H NMR ($CDCl_3$): δ = 1.50 (s, 27H, Me), 7.15−7.42 (m, 5H, Ar).

^{13}C NMR ($CDCl_3$): δ = 27.9 and 28.1 (Me), 82.1 and 83.7 (C_q), 122.9, 125.7, 128.4, 140.8 (Ar), 150.3 and 152.1 (Boc-CO).

FT-IR (KBr): ν = 1729 and 1798 (CO) cm^{-1}.

Anal. Calcd for $C_{21}H_{32}N_2O_6$ (408.49): C, 61.74; H, 7.90; N, 6.86. Found: C, 61.7; H, 7.9; N, 6.9.

1,2-Bis(*t*-butyloxycarbonyl)-1-phenylhydrazine (4) from 3a
Solid $Mg(ClO_4)_2$ (0.76 g, 3.4 mmol) was added under magnetic stirring to a solution of **3a** (6.94 g, 17 mmol) in MeCN (40 mL) at 50 °C under N_2,[3,13] immediately producing an intensive evolution of gas. The reaction was monitored by TLC, which indicated that cleavage of **3a** was complete in about 10 min. The reaction mixture was quenched after 50 min by pouring into 1 M $KHSO_4$/brine (1:1, 300 mL), whereupon the aqueous phase was exhaustively extracted with Et_2O (4 × 50 mL), the combined extracts washed with brine (3 × 70 mL) and dried ($MgSO_4$). Evaporation furnished a slightly yellow solid which was recrystallized from toluene/light petroleum to give **4** (4.72 g, 90%); white needles; mp 110−111 °C (Lit.[12] mp 110−111 °C); R_f 0.42 (A), 0.54 (B).

^1H NMR ($CDCl_3$): δ = 1.49 (s, 18H, Me), 6.79/6.54 (2 × br s, together 1H, NH), 7.13−7.43 (compl. sign., 5H, Ar).

^{13}C NMR ($CDCl_3$): δ = 28.1 and 28.2 (Me), 81.5/81.8 and 82.2 (C_q), 123.6, 125.5, 128.4, 142.1 (Ar), 153.6 and 155.4 (Boc-CO).

FT-IR (KBr): ν = 1718 and 1741 (CO), 3286 (NH) cm^{-1}.

1,2-Bis(*t*-butyloxycarbonyl)-1-phenylhydrazine (4) from Phenylhydrazine (One-pot reaction)
This synthesis was initiated as described for **3a** above. After completing the reaction with Boc_2O at 60 °C, the temperature was lowered to 50 °C and solid $Mg(ClO_4)_2$ (0.2 equiv) was directly added and allowed to react as in the previous experiment. It was again confirmed that the formation of **4** was complete within 10 min. The oil was crystallized from EtOH (~3 mL) or EtOH/H_2O to give needles (2.40 g, 78% overall yield); mp 109.5−111 °C.

2-Benzyloxycarbonyl-2-(*t*-butyloxycarbonyl)-1-phenylhydrazine (5) and 2-Benzyloxycarbonyl-1,2-bis(*t*-butyloxycarbonyl)-1-phenylhydrazine (6a)
DMAP (6 mg, 0.05 mmol) was added to 2-benzyloxycarbonyl-1-phenylhydrazine[14] (0.484 g, 2 mmol) and Boc_2O (1.39 g, 6.4 mmol) in MeCN (3 mL) and allowed to react for 50 min at r.t. The reaction was monitored by TLC, which indicated that the starting material disappeared within 30 min with formation of **5** and traces of **6a**. The solution was divided into two parts, which were treated as follows:

A: One half of the solution was worked up directly, essentially as described for **2** to give a yellow oil, most of which solidified under light petroleum. This product was crystallized from toluene/light petroleum (1:2, 3 mL) to give **5** (0.197 g, 58%) as white, fine needles; mp 73−74.5 °C; R_f 0.30 (D).

^1H NMR ($CDCl_3$): δ = 1.40 (s, 9H, Me), 5.25 (s, 2H, CH_2), 6.12 (br s, 1H, NH), 6.74−7.31 (compl. sign., 10H, Ar).

^{13}C NMR ($CDCl_3$): δ = 27.8 (Me), 68.9 (CH_2), 84.2 (C_q), 113.4, 121.5, 128.2, 128.4, 128.5, 129.2, 135.1, 146.9 (Ar), 151.4 and 153.5 (CO).

FT-IR (KBr): ν = 1705 and 1778 (CO), 3351 (NH) cm^{-1}.

Anal. Calcd for $C_{19}H_{22}N_2O_4$ (342.40): C, 66.65; H, 6.48; N, 8.18. Found: C, 66.6; H, 6.5; N, 8.2.

B: The second portion of the solution was heated to 50 °C for 2 h, when TLC indicated complete reaction, and then worked up similarly to give a yellow oil. This was dissolved in light petroleum, from which the product was frozen out in an EtOH/dry ice bath and the solvent decanted. The procedure was repeated twice, whereupon the product was finally chromatographed on silica in Et_2O/light petroleum (1:3) to afford pure **6a** (0.380 g, 86%) as a pale yellow viscous oil; R_f 0.51 (D).

^1H NMR ($CDCl_3$): δ = 1.40 (s, 9H, Me), 1.49 (s, 9H, Me), 5.22 and 5.32 (ABq, *J* = 12.3 Hz, 2H, CH_2), 7.15−7.42 (m, 10H, Ar).

^{13}C NMR ($CDCl_3$): δ = 27.9 and 28.0 (Me), 69.0 (CH_2), 82.5 and 84.3 (C_q), 123.1, 124.9, 126.0, 128.5, 135.0, 140.5 (Ar), 149.9 and 152.0 (CO).

FT-IR (film): ν = 1732, 1766 and 1806 (CO), 2979 (CH) cm^{-1}.

2-Benzyloxycarbonyl-1-(*t*-butyloxycarbonyl)-1-phenylhydrazine (7) from 6a
This small scale experiment was performed with **6a** (0.145 g, 0.328 mmol) and $Mg(ClO_4)_2$ (15.2 mg, 0.068 mmol) as described for **3a** above in MeCN (4 mL) containing 1% of H_2O at 60 °C for 3.5 h with TLC monitoring. H_2O slowed the cleavage rate significantly (in the absence of H_2O, a side product was noticed). After a similar workup, the crude product was obtained as a glass which could be crystallized from toluene/light petroleum to give **7** (0.103 g, 92%); white fine crystals; mp 114−115 °C; R_f 0.32 (D).

^1H NMR ($CDCl_3$): δ = 1.43 (s, 9H, Me), 5.20 (s, 2H, CH_2), 7.06/6.87 (2 × br s, together 1H, NH), 7.15−7.42 (compl. sign., 10H, Ar).

^{13}C NMR ($CDCl_3$): δ = 28.1 (Me, Boc), 67.8 (CH_2Ph), 82.6 (C_q, Boc), 124.0, 125.9, 128.37, 128.48, 128.53 (Ar), 153.5 (CO, Boc), 156.4 (CO, Z).

Table 2 Selected Data for *N*-Aryl Substituted Hydrazines made with Ar_3Bi in the Presence of $Cu(OAc)_2$ and Et_3N

Cmpd	Structure	Yield (%); Mp (°C)	^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ, *J* (Hz)	^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ, *J* (Hz)	FT-IR (cm^{-1})
3b[a]	4-Me-C_6H_4/ Boc/Boc/ Boc	98; 99-100	1.50 and 1.51 (2 × s, 27 H, Me), 2.32 (s, 3 H, MeAr), 7.10 and 7.22, and 7.10 and 7.32 (2 × ABq, *J* = 8.1, 4 H, Ar)	20.9 (MeAr), 27.9 (Me, $NBoc_2$), 28.1 (Me, NBoc), 81.9 (C_q, NBoc), 83.6 (C_q, $NBoc_2$), 123.2, 124.7, 129.0, 135.6, 138.2 (Ar), 150.3 (CO, NBoc), 152.2 (CO, $NBoc_2$)	1725, 1746 and 1766 (CO), 2935 and 2977 (CH)
3c[b]	4-MeO-C_6H_4/ Boc/Boc/Boc	97; 69-70	1.52/1.51/1.44 (3 × s, together 27 H, 3 × Boc), 3.79/3.80 (2 × s, 3 H, OMe), 6.85/ 6.83 (2 × d, *J* = 9.2, together 2 H, Ar-$H_{2,6}$), 7.38/7.30 (2 × d, *J* = 9.2, together 2 H, Ar-$H_{3,5}$)	28.0 and 28.2 (Boc), 55.4 (OMe), 81.8/82.0 (C_q, NBoc), 83.6/83.5 (C_q, $NBoc_2$), 113.7/ 113.4, 125.9/126.9, 133.8/134.4, 157.8/158.0 (Ar), 150.4/150.6 (CO, NBoc), 152.5 (CO, $NBoc_2$	1724, 1741 and 1769 (CO), 2937 and 2984 (CH)
6a	Ph/Boc/Z/Boc	98; oil	See **6a** from **7**	See **6a** from **7**	See **6a** from **7**
6b	4-Me-C_6H_4/ Boc/Z/Boc	98; oil	1.38/1.42 (2 × s, together 9 H, BocNAr), 1.49 (s, 9 H, BocNZ), 2.31 (s, 3 H, MeAr), 5.21 and 5.32 (ABq, *J* = 12.2, together 2 H, CH_2Ph), 7.08–7.34 (m, 9 H, Ar)	20.9 (MeAr), 27.9/28.0 (2 × Boc), 68.9 (CH_2Ph), 82.2/82.5 (C_q, BocNAr), 84.2 (C_q, BocNZ), 123.5, 125.0, 128.1, 128.5, 129.0, 129.1, 135.1, 135.9, 136.3, 137.9, 138.5 (Ar), 149.9/150.1 (CO, BocNAr), 152.1/152.2 (2×CO, BocNZ+Z)	1732, 1766 and 1805 (CO), 2979 (CH)
6c	4-MeO-C_6H_4/ Boc/Z/Boc	97; oil	1.38/1.41 (2 × s, together 9 H, BocNAr), 1.51/1.50 (2 × s, 9 H, BocNZ), 3.78 (s, 3 H, OMe), 5.23 and 5.32/5.23 and 5.29 (2 × ABq, *J* = 12.1, together 2 H, CH_2Ph), 6.82/ 6.78 (d, *J* = 8.8, 2 H, Ar), 7.23-7.37 (compl. sign., 7 H, Ar)	27.9/28.0/28.1 (2×Boc), 55.4 (OMe), 69.0 (CH_2Ph), 82.2/82.3 (C_q, BocNAr), 82.4 (C_q, BocNZ), 113.5, 113.8, 126.2, 127.2, 128.1, 128.3, 128.4, 128.5, 133.5, 134.1, 135.0, 158.0, 158.2 (Ar), 150.0/150.2 (CO, Boc), 152.1/152.3 (CO, Boc), 152.4/152.6 (CO, Z)	1732, 1766 and 1805 (CO), 2839, 2935 and 2981 (CH)
8	Ph/4-Me-C_6H_4/Boc/Boc	96; oil	1.51 (s, 9 H, Boc), 1.52 (s, 9 H, Boc), 2.29 (s, 3 H, Me), 7.08–7.38 (m, 9 H, Ar)	20.9 (MeAr), 28.2 (Me, Boc), 82.1 and 82.2 (C_q, Boc), 122.7, 125.5, 128.5, 129.1, 135.4, 138.6, 141.2 (Ar), 153.1 and 153.3 (CO)	1727 (CO), 2932 and 2978 (CH)
9a	C_3H_5/Ph/Z/ Boc	96; oil	1.36/1.48 (2 sign, together 9 H, Boc), 4.04 (compl. m, 1 H) and 4.20 (dd, J_1 = 6.4, J_2 = 14.8, 1 H, C*H*$_2$CH=CH_2), 5.03-5.30 (compl. sign., 4 H, CH_2Ph, =CH_2), 5.79 (pert. m, 1 H, =CH-), 7.17–7.35 (m, 10 H, Ar)	28.1/28.2 (Me, Boc), 51.8/53.8 (*C*H_2CH=CH_2), 68.1 (CH_2Ph), 81.7/81.9 (C_q, Boc), 118.2, 118.8, 123.0, 126.0, 128.0, 128.3, 128.4, 128.5, 128.59, 128.62, 132.7, 133.1, 135.8, 135.9, 140.8, 141.1 (Ar+CH=CH_2), 154.3, 154.4 and 154.7 (CO)	1644 (allyl), 1717 and 1734 (CO), 2932, 2978, 3034 and 3067 (CH)
9b	EtOCOCH_2/ Ph/Z/Boc	97; oil	1.10/1.12 (2 × t, *J* = 7, together 3 H, C*H*$_3$CH_2), 1.35/1.45 (2 × s, together 9 H, Boc), 3.95–4.08 (m, 2 H, CH_2CO), 3.84 and 4.63/3.86 and 4.51 (2 × ABq, *J* = 17, together 2 H, C*H*$_2$CH_3), 5.14–5.32 (m, 2 H, CH_2Ph), 7.18–7.53 (m, 10 H, Ar)	13.9/14.0 (*C*H_3CH_2), 28.0/28.1 (Me, Boc), 52.6/54.0 (CH_2CO), 61.1 (*C*H_2CH_3), 68.37/ 68.40 (CH_2Ph), 82.5/82.7 (C_q, Boc), 115.3, 123.6/124.1, 126.2/126.4, 127.9, 128.2, 128.3, 128.41, 128.45, 128.53, 128.59, 135.62/135.71, 140.4/140.5 (Ar), 154.0/154.1 (CO, Boc), 154.7/154.3 (CO, Z), 168.3/168.4 (CO, CO_2Et)	1732 (CO), 2936 and 2980 (CH)
10a	Me/Bn/Z/4-Me-C_6H_4	98; oil	2.26 (s, 3 H, MeAr), 2.82 (pert. s, 3 H, MeN), 4.26 and 4.30 (Abq, *J* = 14.6, NCH_2, 1 H) and 5.11 (br sign., 3 H, OCH_2 + 2 sign. from previous ABq), 6.51 and 7.02 (ABq, *J* ≈ 8, 2+2 H, Me-Ar),-7.0–7.36 (compl. sign., ~10 H, Ar)	20.3 (MeAr), 40.1 (MeN), 52.9 (NCH_2), 67.5 (OCH_2), 112.0, 127.4, 127.7, 128.2, 128.5, 129.3, 129.7, 136.2, 137.4, 146.2 (Ar), 157.0 (CO)	1706 (CO), 2924 and 3032 (CH)

Table 2 (continued)

Cmpd	Structure	Yield (%); Mp (°C)	^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ, *J* (Hz)	^{13}C NMR (100 MHz, $CDCl_3$/TMS) δ, *J* (Hz)	FT-IR (cm^{-1})
10b	C_3H_5/ $EtOCOCH_2$/Z/ 4-Me-C_6H_4	97; oil	1.25/1.19 (2 × t, *J* = 7, together 3 H, C*H*$_3$CH$_2$), 2.27/2.24 (2 × s, together 3 H, MeAr), 4.09–4.28 (m, 4 H, C*H*$_2$CH=CH$_2$ and C*H*$_2$Me), 3.93 and 4.61/3.99 and 4.48 (2 × ABq, *J* = 17.2/18.0, together 2 H, NCH$_2$CO), 5.08–5.26 (compl. sign., 4 H, CH$_2$Ph+=CH$_2$), 5.89/5.97 (2 × m, 1 H, =CH), 6.63 and 7.02/6.69 and 7.08 (2 × ABq, *J* = 8.6, 2+2 H, Me-Ar), 7.07–7.34 (compl. sign., ~5 H, Ar)	14.1 (*C*H$_3$CH$_2$), 20.3 (MeAr), 52.5/53.6 (*C*H$_2$CH=CH$_2$), 57.1/56.7 (CH$_2$CO), 61.3 (CH$_3$*C*H$_2$), 67.9/68.0 (OCH$_2$), 112.6, 112.8, 116.2, 127.6, 127.9, 128.0, 128.3, 128.5, 128.6, 128.9, 129.7, 134.6, 135.1, 136.0, 145.2 (Ar), 156.7/155.0 (CO, Z), 169.0/169.1 (CO, CH$_2$CO)	1714-1754 (br, unresolved CO), 2938, 2982, 3032 and 3066 (CH)
11	Ph/Boc/Z/4-Me-C_6H_4	96; oil	1.34 (s, 9 H, Boc), 2.31 (s, 3 H, Me), 5.19 and 5.21 (pert. ABq, *J* ≈ 12, 2 H, CH$_2$), 6.92–7.24 (m, 14 H, Ar)	20.8 (MeAr), 28.3 (Me, Boc), 68.8 (CH$_2$Ph), 84.1 (C$_q$, Boc), 117.3, 120.0, 121.8, 127.9, 128.1, 128.3, 129.0, 129.6, 132.9, 135.1, 141.6, 144.8 (Ar), 150.9 (CO, Boc), 153.0 (CO, Z)	1760 and 1797 (CO), 2928, 2980 and 3032 (CH)

[a] Anal. Calcd for $C_{22}H_{34}N_2O_6$ (422.52): C, 62.54; H, 8.11; N, 6.63. Found: C, 62.5; H, 8.1; N, 6.6.
[b] Anal. Calcd for $C_{22}H_{34}N_2O_7$ (438.52): C, 60.26; H, 7.81; N, 6.39. Found: C, 60.5; H, 7.8; N, 6.4.

FT-IR (KBr): ν = 1690 and 1743 (CO), 3240 (NH) cm^{-1}.

Anal. Calcd for $C_{19}H_{22}N_2O_4$ (342.40): C, 66.65; H, 6.48; N, 8.18. Found: C, 67.2; H, 6.6; N, 8.0.

1,2,2-Tris(*t*-butyloxycarbonyl)-1-phenylhydrazine (3a) from A4 with Triphenylbismuthane; Typical Procedure

To a magnetically stirred mixture of **A4** (166 mg, 0.5 mmol), anhyd $Cu(OAc)_2$ (137 mg, 0.75 mmol) and Et_3N (103 μL, 0.75 mmol) in CH_2Cl_2 (1.0 mL), under N_2, was added triphenylbismuthane (330 mg, 0.75 mmol) in one portion. The mixture was stirred at r.t. until all **A4** had been consumed (TLC), which took about 23 h, whereupon the solvent was evaporated and the remainder mixed with of silica (3−4 mL). This was placed on top of a short silica column, which was eluted firstly with EtOAc/light petroleum (1:20) to remove the excess of bismuthane used. Then the EtOAc/light petroleum ratio was changed to 1:5, as a result of which pure **3a** could be eluted from the column to give, after evaporation, a colourless oil (210 mg, 100%). It could be crystallized, although with massive loss of material, from light petroleum; mp 64−65 °C.

^{1}H NMR ($CDCl_3$), ^{13}C NMR ($CDCl_3$), and FT-IR (KBr) spectra agreed with those of **3a** obtained from phenylhydrazine above.

1,2,2-Tris(*t*-butyloxycarbonyl)-1-(4-methylphenyl)hydrazine (3b), 1,2,2-Tris(*t*-butyloxycarbonyl)-1-(4-methoxyphenyl)hydrazine (3c), 2-Benzyloxycarbonyl-1,2-bis(*t*-butyloxycarbonyl)-1-phenylhydrazine (6a), 2-Benzyloxycarbonyl-1,2-bis(*t*-butyloxycarbonyl)-1-(4-methylphenyl)hydrazine (6b), 2-Benzyloxycarbonyl-1,2-bis(*t*-butyloxycarbonyl)-1-(4-methoxyphenyl)hydrazine (6c), 1,2-bis(*t*-butyloxycarbonyl)-2-(4-methylphenyl)-1-phenylhydrazine (8), 1-Allyl-2-benzyloxycarbonyl-1-(*t*-butyloxycarbonyl)-2-phenylhydrazine (9a), 2-Benzyloxycarbonyl-1-(*t*-butyloxycarbonyl)-1-(ethoxycarbonylmethyl)-2-phenylhydrazine (9b), 2-Benzyl-2-benzyloxycarbonyl-1-methyl-1-(4-methylphenyl)hydrazine (10a), 1-Allyl-2-benzyloxycarbonyl-2-(ethoxycarbonylmethyl)-1-(4-methylphenyl)hydrazine (10b) and 2-Benzyloxycarbonyl-2-(*t*-butyloxycarbonyl)-1-(4-methylphenyl)-1-phenylhydrazine (11)

These compounds were all prepared by analogy with **3a** as described in the previous paragraph. The starting materials were **A4** (for **3b** and **3c**), **A1** (for **6a**−**c**), **4** (for **8** and **12**), 1-allyl-2-benzyloxycarbonyl-1-(*t*-butyloxycarbonyl)hydrazine[3] (for **9a**), 2-benzyloxycarbonyl-1-(*t*-butyloxycarbonyl)-1-(ethoxycarbonylmethyl)hydrazine[3] (for **9b**), 2-benzyl-2-benzyloxycarbonyl-1-methylhydrazine, made from the corresponding 1-*t*-butyloxycarbonyl derivative[3] by cleavage with TFA (for **10a**), 1-allyl-2-benzyloxycarbonyl-2-(ethoxycarbonylmethyl)hydrazine, also made from the corresponding 1-*t*-butyloxycarbonyl derivative[3] by cleavage with TFA (for **10b**), and **5** (for **11**). Selected data for these compounds are listed in Table 2.

Acknowledgement

This work was supported by the Swedish Natural Science Research Council (NFR), Carl Tryggers Stiftelse and the Royal Swedish Academy of Sciences as well as by an ERASMUS scholarship (to O.L.). The authors thank a referee for bringing ref. 16 to their attention.

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Article Identifier:
1437-210X,E;2000,0,11,1591,1597,ftx,en;H01900SS.pdf