SYNTHESIS AND USE OF BENZYL TERT-BUTYL IMINODICARBONATE, A VERSATILE REAGENT FOR THE PREPARATION OF AMINES

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Dedicated to the memory of Dr Karel Bláha, our colleague and friend.*

An efficient synthesis of benzyl tert-butyl iminodicarbonate (*IV*), starting from benzoyl isocyanate, is reported. Reaction of the isocyanate with benzyl alcohol gave benzyl N-benzoylcarbamate (*II*) which on exhaustive tert-butoxycarbonylation via the non-isolated triacyl amine *III*, after aminolysis, provided the title compound. The sodium salt *V* was alkylated with various halides under Gabriel conditions to give in high yields the corresponding benzyloxycarbonyl tert-butoxycarbonyl diprotected amines. Similarly, compound *IV* was alkylated with alcohols under Mitsunobu conditions to give some additional amines of this type, from which the protecting groups can be removed selectively under mild conditions.

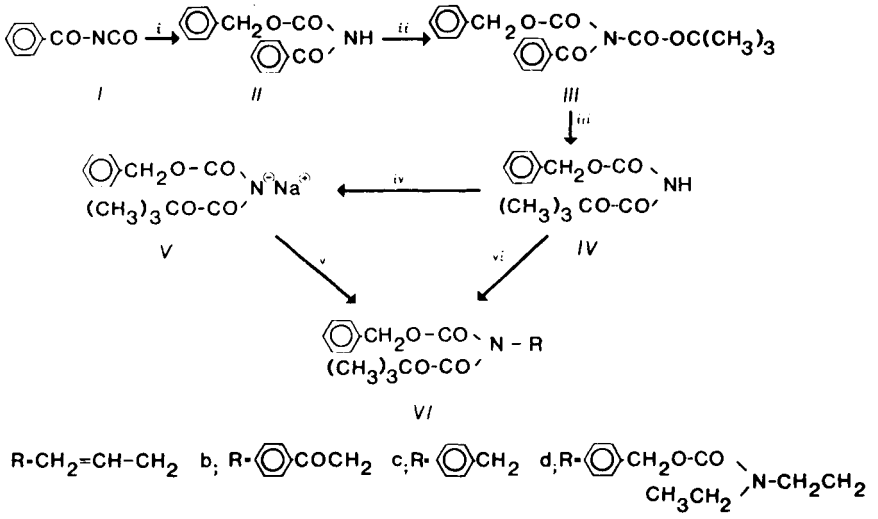
In connection with explorations of new strategies to selectively protected polyamines[1,2], we became interested in general mild methods for the conversion of various functional groups to the corresponding amines. In this context, an improved synthesis of di-tert-butyl iminodicarbonate was elaborated and the utility of this amine precursor in the Gabriel reaction[3] was further demonstrated[4]. Later, preliminary experiments have also indicated its value in the Mitsunobu[5] procedure.

In order to achieve more flexibility in the aforementioned methods, access to amine precursors with two different protective groups is highly desirable. Preferably, these groups should be orthogonal and smoothly removable by mild procedures in optional order. Although some promising candidates in this respect such as benzyl N-benzoylcarbamate[6], tert-butyl methyl iminodicarbonate[7] and diethyl N-(tert-butoxycarbonyl)phosphoramidate[8] have appeared earlier, we considered benzyl tert-butyl iminodicarbonate (*IV*) more attractive for this purpose. This hitherto unknown compound, obtained before only as a component of a complex reaction mixture[7], was prepared by a novel efficient synthesis from readily available

* Two related N-diacylated compounds from our laboratory were being studied by K. B. at the time of his decease.

starting materials. Moreover, its applicability in the Gabriel and Mitsunobu reactions is demonstrated.

The synthetic route leading to *IV* is summarized in Scheme 1. Benzoyl isocyanate (*I*) readily reacts with benzyl alcohol in dichloromethane under anhydrous conditions providing *II* in essentially quantitative yield. This compound has been prepared and used previously but no experimental details were given[6]. Treatment of *II* with



SCHEME 1

Reagents: *i*, $PhCH_2OH$, CH_2Cl_2; *ii*, Boc_2O, DMAP, CH_3CN; *iii*, DEAEA, CH_3CN; *iv*, $NaOCH_3$, CH_3OH, $-30°C$; *v*, RBr, DMF, $-30°C$; *vi*, ROH, Ph_3P, diethyl azodicarboxylate, CH_3CN, 20°C

a slight excess of di-tert-butyl dicarbonate (Boc_2O) in dry acetonitrile in the presence of the powerful acylation catalyst 4-dimethylaminopyridine[9] (DMAP) afforded the unstable triacylamine *III*. Attempts to isolate *III* only gave a mixture containing *III* and *IV* as well as other compounds. When such a contaminated sample of *III* was subjected to 2-(diethylamino)ethylamine (DEAEA) in dry acetonitrile, *IV* was formed in fair yield together with the major side product tert-butyl N-benzoylcarbamate. Preliminary attempts to accomplish this cleavage with a weak base (morpholine) instead of DEAEA furnished a complex mixture from which a moderate yield of *IV* could be isolated after a laborious workup. Due to the inherent lability of *III* it was discovered that a higher yield of less contaminated *IV* could be obtained by a convenient one pot procedure from *II* using stepwise additions of Boc_2O/DMAP and DEAEA in dry acetonitrile without isolation of the sensitive intermediate *III*. The overall yield of pure *IV* from *II* was 80% after chromatography. This compound, a colourless viscous oil, was sufficiently stable to be handled without

special precautions. Although it was suspected that *IV* could be partially decomposed under strongly alkaline conditions[10], it was in fact cleanly and quantitatively converted to the corresponding sodium salt *V* by a slight deficit of sodium methoxide in dry methanol at low temperature.

Alternative routes to *IV* were also investigated but the outcome of these studies has sofar been rather disappointing. Initially, a direct approach from benzyl carbamate, was examined. However, treatment of this compound with one equivalent of Boc_2O in the presence of DMAP according to an established procedure[11] only provided an intractable mixture. Inspection of the ^1H NMR spectrum of this crude product revealed the presence of considerable amounts of starting material together with several other products which were not further studied. Integration indicated that the contents of *IV* in this crude mixture did not exceed 10%.

In principle, *IV* should be accessible by reductive cleavage of the nitrogen–nitrogen bond[12] in 1,2-dibenzyl 1,2-di-tert-butyl hydrazotetracarboxylate (*VIII*), although in practice, due to the presence of the benzyl function, the choice of methods that can be applied in this specific case is rather restricted. The mentioned compound is readily available in excellent yield by exhaustive tert-butoxycarbonylation of dibenzyl hydrazodicarboxylate. Somewhat surprisingly, however, the hydrazotetracarboxylate resisted several reduction methods, such as $Al(Hg)–CO_2$ in moist ether[12], $Na_2S_2O_4$–$NaHCO_3$ in aqueous dimethylformamide[13], $(CH_3)_2S.BH_3$ in tetrahydrofuran[14] and $NaBH_4$–trifluoroacetic acid in tetrahydrofuran[15] and ^1H NMR as well as TLC of the resulting reaction mixtures indicated that the starting material remained largely unchanged. Furthermore, using tetra-tert-butyl hydrazotetracarboxylate (*VII*) as a model substrate, no detectable cleavage of its nitrogen–nitrogen bond was observed with 1,4-cyclohexadiene–Pd in tetrahydrofuran[16], H_2–Pd in 80% aqueous acetic acid and $NaBH_4$–$NiCl_2$ in methanol[17]. (The reduction experiments are not described in the Experimental). Even if such a reduction method for the tetra-tert-butyl compound could be found, it would hardly give a more convenient synthesis of di-tert-butyl iminodicarbonate than the one already available[4]. For compound *IV*, however, it might be more attractive.

As is evident from Scheme 1, alkylation of *IV* can be effected by two different methods. First, the corresponding sodium salt *V* smoothly reacts with alkyl bromides such as allyl bromide and benzyl bromide in dry dimethylformamide at low temperature to give the expected *VIa* and *VIc*, respectively, of high purity in excellent yields. Similar Gabriel syntheses have been carried out earlier using the potassium salts of tert-butyl methyl iminodicarbonate[7] and di-tert-butyl iminodicarbonate[4] and the alkylated products have generally been obtained in satisfactory yields. Even the very reactive phenacyl bromide underwent this nucleophilic displacement reaction, thus affording the fully protected aminoketone *VIb* in good yield. An earlier attempt to use a phenacyl bromide derivative in an analogous conversion at higher temperature was claimed to furnish a complex mixture[7]. A closer examination of Gabriel re-

actions involving this reagent revealed that minor amounts of *trans*-1,2,3-tribenzoylcyclopropane[18] were often present in the crude mixtures. A preliminary study indicates that the formation of this side product could be suppressed by employing lower reaction temperatures and by avoiding excess phenacyl bromide.

The condensation of hydroxy compounds with miscellaneous reagents using triphenylphosphine–diethyl azodicarboxylate in an aprotic solvent is often referred to as the Mitsunobu reaction[5]. More recently, the mechanistic aspects of this useful reaction have attracted further attention[19,20]. This exceptionally mild procedure is widely employed with success in work with sensitive compounds[21,22]. Among novel approaches to the Mitsunobu reaction particularly the one applying diethyl N-(tert-butoxycarbonyl)phosphoramidate should be recorded here[23].

A preliminary experiment showed that di-tert-butyl iminodicarbonate could be converted to the corresponding N-ethyl analogue in 86% yield with ethanol in dry acetonitrile by a slight excess of triphenylphosphine–diethyl azodicarboxylate[5]. Therefore it was not unexpected that *IV* was readily benzylated with benzyl alcohol under the same conditions to give *VIc* in high yield after a simple workup. When certain other diacylamines such as *II* were subjected to Mitsunobu conditions, significant O-alkylation sometimes occurred[5]. However, in the case of *IV*, no sign of this side reaction could be observed as judged from the ^{1}H NMR spectrum of the crude reaction product.

One important aim of this work is to extend the Mitsunobu approach to design new pathways to polyamines related to naturally occurring substances. The alkylation of *IV* with a protected aminoalcohol well illustrates the potential value of this method in this respect and the resulting substance *VId* has already been used as a model compound in a recent study of protected polyamine derivatives[1,2]. Particularly, the selective removal of one of the blocking groups in such doubly protected amines and the subsequent alkylation of the remaining urethane function offer challenging perspectives in the field of polyamine synthesis, although limitations similar to those previously encountered in the alkylation of amides[24] can be anticipated.

EXPERIMENTAL

Melting points were recorded on a Gallenkamp apparatus and are uncorrected. All solvents used were of analytical grade and dried over molecular sieve (4A, activated at 320°C for 2 days). TLC analyses were performed on 0·25 mm thick precoated silica plates (Merck DC-Fertigplatten Kieselgel 60 F-254) eluting with (A) heptane–diethyl ether (2 : 1), (B) toluene–acetonitrile (2 : 1) and (C) dichloromethane–diethyl ether (12 : 1). Spots were visualized by UV light at 254 nm, by exposure to iodine vapors or, after brief heating, by exposure to chlorine followed by dicarboxidine spray[25] (violet-blue spots). NMR spectra were recorded in $CDCl_3$ unless otherwise stated, on a Jeol FX90Q instrument at 90 MHz (^{1}H) or 22·5 MHz (^{13}C) with tetramethylsilane as internal standard.

Benzyl N-Benzoylcarbamate (*II*)

To a solution of benzoyl isocyanate[26] (*I*) (12·5 g, 85 mmol) in dichloromethane (85 ml) was added dropwise under vigorous stirring benzyl alcohol (9·64 g, 89·5 mmol, dried over 4 A molecular sieve) dissolved in dichloromethane (85 ml) during 30 min. The clear colourless reaction mixture became lukewarm and after a further 2 h stirring at ambient temperature, the solvent was stripped off at room temperature. The oily residue solidified after trituration with cold heptane (150 ml), and after a few hours in the cold, the precipitate was collected and thoroughly rinsed with cold heptane (3 × 30 ml) and dried in air. The crude material (21·8 g, quant. yield) was recrystallized from heptane–ethyl acetate (4 : 1, 40 ml/g), affording 20·1 g (93%) of pure *II* as white needles, m.p. 117·0—117·5°C. TLC (A, B, C) gave one spot. ^{1}H NMR: 8·28 bs, 1 H (NH); 7·32—7·87 m, 10 H (arom. H); 5·23 s, 2 H (CH_2).

Benzyl Tert-butyl Iminodicarbonate (*IV*)

A solution of recrystallized dried *II* (5·10 g, 20 mmol) and DMAP (244 mg, 2·0 mmol) in acetonitrile (40 ml) was slowly treated under rapid stirring with Boc_2O (4·45 g, 20·4 mmol) dissolved in acetonitrile (20 ml) for 20 min with exclusion of atmospheric moisture. The colourless, almost clear reaction mixture was stirred at room temperature and after 3 h TLC (A) indicated that most of the starting material had been consumed. A solution of DEAEA (2·44 g, 21 mmol) in acetonitrile (20 ml) was slowly added under vigorous stirring over a period of 20 min and the stirring was continued for 2 h at ambient temperature. The pale yellow solution was partitioned between ether (600 ml) and 0·2M citric acid (300 ml) and the ethereal extract was washed in turn with 0·2M citric acid (5 × 150 ml), 1M-$NaHCO_3$ and saturated aqueous NaCl (3 × 150 ml each) and dried over $MgSO_4$. Evaporation to dryness at room temperature afforded a pale yellow oil (4·97 g), containing *IV* together with some impurities. This crude product was dissolved in petroleum ether–ether (3 : 1) and the slightly turbid solution was applied to a silica column (25 × 6 cm). Slow elution with the same solvent mixture first gave minor amounts of Boc_2O followed by *IV* (4·02 g, 80%), obtained as a colourless oil. TLC (A, B, C) gave one spot. For $C_{13}H_{17}NO_4$ (251·3) calculated: 62·14% C, 6·82% H, 5·57% N; found: 62·6% C, 7·1% H, 5·7% N. ^{1}H NMR: 7·35 s, 5 H (arom. H); 7·04 bs, 1 H (NH); 5·17 s, 2 H (CH_2); 1·48 s, 9 H (CH_3). ^{13}C NMR: 150·9 (CH_2O—CO); 149·3 (Me_3CO—CO); 135·2, 128·6, 128·4 (arom. C); 82·6 (Me_3C); 67·5 (CH_2); 28·0 (CH_3). Attempted recrystallization from heptane (10 ml/g, −70°C) gave a solid which melted well below room temperature. Continued elution of the column furnished impure tert-butyl N-benzoylcarbamate as a white solid. ^{1}H NMR: 7·4—7·9 m (arom. H); 1·54 s (CH_3).

Attempted Preparation of Benzyl Tert-butyl N-Benzoyliminodicarbonate (*III*)

A solution of *II* (2·55 g, 10 mmol) in acetonitrile (20 ml) containing DMAP (61 mg, 0·5 mmol) was slowly treated with Boc_2O (2·40 g, 11 mmol) in acetonitrile (5 ml) as described above. When TLC (A) indicated essentially complete reaction (6 h) the resulting mixture was partitioned between ether (200 ml) and 0·2M citric acid (100 ml) and the ether extract was washed and dried as above. Removal of the solvent furnished an almost colurless oil (3·47 g). ^{1}H NMR (CD_3CN) indicated the product contained ≈90% of *III*: 7·2—7·9 m (arom. H); 5·20 s (CH_2); 1·30 s (CH_3). The remainder was impure *IV*. Attempted preparative chromatography on silica partially decomposed the product and small amounts of impure *III* was obtained.

Sodium Benzyl Tert-butyl Iminodicarbonate (*V*)

To a solution of *IV* (1·10 g, 4·38 mmol) in methanol (4·3 ml) was cautiously added 5·4M-$NaOCH_3$

in methanol (0·77 ml, 4·2 mmol) under rapid stirring at −30°C over a period of 10 min. After another 10 min, cold dry ether (100 ml) was slowly introduced at this temperature to give a thick voluminous precipitate which, after standing overnight at −25°C, was collected as a fine-grained solid, rinsed with cold ether (3 × 5 ml) and dried in high vacuo overnight. The yield of *V* was 1·12 g (98% as calculated from $NaOCH_3$); m.p. ≈230°C (dec.). ^{1}H NMR (hexadeuteriodimethyl sulfoxide): 7·30 s, 5 H (arom. H); 4·89 s, 2 H (CH_2); 1·34 s, 9 H (CH_3). This salt was completely stable in hexadeuteriodimethyl sulfoxide for 3 days at room temperature.

Benzyl Tert-butyl N-Allyliminodicarbonate (*VIa*)

Dried fine-grained *V* (546 mg, 2·0 mmol) was suspended in DMF (6 ml) and sonicated to disperse any lumps. The resulting thick slurry was chilled to −30°C and treated dropwise with a chilled solution of allyl bromide (267 mg, 2·2 mmol) in DMF (4 ml) for 15 min. under vigorous stirring. The white suspension was agitated for 30 min. at −20°C and for 5 h at ambient temperature whereupon the reaction mixture became clear. Ether (120 ml) and 1M-$KHSO_4$ (120 ml) were added with shaking and the organic phase was washed in turn with 1M-$KHSO_4$, 1M-$NaHCO_3$ and saturated aqueous NaCl (3 × 30 ml each) and dried over $MgSO_4$. Removal of the solvent left an almost colourless oil which was chromatographed on silica with petroleum ether–ether (3 : 1) as eluant to give 539 mg (93%) of *VIa* as a colourless liquid, pure by TLC (A). For $C_{16}H_{21}NO_4$ (291·4) calculated: 65·96% C, 7·27% H, 4·81% N; found: 66·1% C, 7·5% H, 4·9% N. ^{1}H NMR: 7·36 s, 5 H (arom. H); 5·65–6·07 m, 1 H (CH_2=C**H**); 5·22 s, 2 H (Ph**C**H_2); 5·03–5·25 m, 2 H (CH_2=CH); 4·20–4·29 m, 2 H (CH_2=CH–CH_2); 1·47 s, 9 H (CH_3). ^{13}C NMR: 153·6 (CH_2O–CO); 151·7 (Me_3C–CO); 135·5, 128·5, 128·2, 128·1 (arom. C): 133·4 (CH_2=CH); 116·6 (CH_2=CH); 82·9 (CMe_3); 68·3 (PhCH_2); 48·6 (CH_2=CH–CH_2); 27·9 (CH_3). Attemped crystallization from heptane gave a crystalline solid which melted below room temperature.

Benzyl Tert-butyl N-Phenacyliminodicarbonate (*VIb*)

A suspension of *V* (546 mg, 2·0 mmol) in DMF (6 ml) was treated with phenacyl bromide (398 mg, 2·0 mmol) in DMF (4 ml) as described for *VIa*. A similar workup afforded a semisolid residue (750 mg) which was taken up in petroleum ether–ether (3 : 1, 30 ml). The insoluble white powder (≈40 mg) was filtered off and the clear solution was chromatographed on silica in the above solvent mixture. The oily, TLC (A) pure product weighing 637 mg (86%) was triturated with cold heptane (5 ml, −20°C) and the resulting solid recrystallized from heptane–ether (7 : 1) (20 ml/g) to give tiny needles with m.p. 57–57·5°C. For $C_{21}H_{23}NO_5$ (369·4) calculated: 68·28% C, 6·28% H, 3·79% N; found: 68·2% C, 6·2% H, 3·6% N. ^{1}H NMR: 7·88–7·98 m, 2 H (arom. H, phenacyl); 7·30–7·60 m, 3 H (arom. H, phenacyl); 7·33 s, 5 H (arom. H, benzyl); 5·23 s, 2 H (PhCH_2); 5·10 s, 2 H (phenacyl CH_2); 1·44 s, 9 H (CH_3). ^{13}C NMR: 193·1 (phenacyl CO); 153·7 (CH_2O–CO); 151·6 (Me_3CO–CO); 135·3, 134·9, 133·6, 128·7, 128·5, 128·3, 128·2, 127·9 (arom. C); 83·5 (CMe_3); 68·7 (PhCH_2); 52·3 (phenacyl CH_2); 27·9 (CH_3). The insoluble white powder collected by filtration above consisted of *trans*-1,2,3-tribenzoylcyclopropane. Recrystallization from ethyl acetate (80 ml/g) afforded white crystals, m.p. 220–221°C (ref.[18] m.p. 219°C). ^{1}H NMR: 7·96–8·25 m, 6 H (arom. H); 7·31–7·66 m, 9 H (arom. H); 4·24 t, 1 H (CH); 3·77 d, 2 H (2 × CH). ^{13}C NMR: 196·0 (PhCO); 193·0 (PhCO); 136·4, 133·9, 133·6, 128·8, 128·7, 128·5 (arom. C); 36·4 (CH); 30·4 (CH).

Benzyl Tert-butyl N-Benzyliminodicarbonate (*VIc*)

A) Gabriel synthesis. This compound was prepared from benzyl bromide and *V* following the detailed procedure for *VIa*. The yield of chromatographed *VIc*, obtained as a colourless oil,

pure by TLC (A), was 637 mg (93%). Crystallization from heptane (8 ml/g, −70°C) afforded fluffy needles, m.p. 32–32·5°C. For $C_{20}H_{23}NO_4$ (341·4) calculated: 70·36% C, 6·79% H, 4·10% N; found: 70·4% C, 6·7% H, 4·0% N. ^{1}H NMR: 7·32 s, 5 H (arom. H, $PhCH_2O$); 7·27 s, 5 H (arom. H, $PhCH_2N$); 5·22 s, 2 H (CH_2O); 4·84 s, 2 H (CH_2N); 1·41 s, 9 H (CH_3). ^{13}C NMR: 153·9 (CH_2O—CO); 151·9 (Me_3CO—CO); 137·9, 135·4, 128·5, 128·3, 128·2, 127·4, 127·2 (arom. C); 83·1 (CMe_3); 68·4 ($PhCH_2O$); 49·6 ($PhCH_2N$); 27·9 (CH_3).

B) Mitsunobu synthesis. A solution of *IV* (754 mg, 3·00 mmol), dried benzyl alcohol (357 mg, 3·30 mmol) and triphenylphosphine (905 mg, 3·45 mmol) in acetonitrile (9 ml) was treated dropwise under rapid stirring with diethyl azodicarboxylate (627 mg, 3·60 mmol) dissolved in acetonitrile (6 ml) at ambient temperature over a period of 20 min with exclusion of atmospheric moisture. The reaction was slightly exothermic and the clear solution became bright yellow. After stirring overnight (20 h), the mixture was partitioned between ether (200 ml) and 0·2M citric acid (100 ml). The pale yellow ether extract was washed in turn with 0·2M citric acid, 1M-$NaHCO_3$ and saturated aqueous NaCl (3 × 50 ml each) and dried over $MgSO_4$. Removal of the solvent gave a semisolid yellowish residue which was suspended in petroleum ether–ether (3 : 1, 20 ml). The insoluble material was filtered off and washed with the same solvent mixture and the combined filtrate was chromatographed as above. The yield of *VIc*, pure by TLC, was 784 mg (77%). This product was identical in every respect with that obtained by the Gabriel synthesis.

N-Benzyloxycarbonyl-N-ethyl-2-aminoethanol (*VId* precursor)

A solution of N-ethyl-2-aminoethanol (8·91 g, 100 mmol) in 1M-Na_2CO_3 (20 ml) and 2M-NaOH (50 ml) was treated dropwise under vigorous stirring with benzyloxycarbonyl chloride (15·9 g, 86% w/w, 80 mmol) at room temperature. The resulting mixture was stirred for 16 h and extracted with ether (2 × 150 ml). The ethereal extract was exhaustively washed with dilute HCl, 1M-$NaHCO_3$ and brine and dried over $MgSO_4$. Evaporation furnished a pale yellow oil which was meticulously dried in high vacuo at 60°C to remove contaminating benzyl alcohol. The yield of crude product, obtained as an oil, suitable for further work, was 6·14 g (34% calculated on benzyloxycarbonyl chloride). TLC (C) gave one spot. ^{1}H NMR: 7·34 s, 5 H (arom. H); 5·13 s, 2 H ($PhCH_2$); 3·74 t, 2 H (CH_2—OH); 3·42 t, 2 H (N—CH_2—CH_2—OH); 3·36 q, 2 H (CH_3—CH_2—N); ≈2·64 s, 1 H (OH); 1·13 t, 3 H (CH_3—CH_2—N).

N^1,N^2-Dibenzyloxycarbonyl-N^2-tert-butoxycarbonyl-N^1-ethyl-1,2-ethylenediamine (*VId*)

Synthesized from the above protected amino alcohol and *IV* by the Mitsunobu reaction as described for *VIc*. After a similar workup, the crude product was purified by chromatography on silica in CH_2Cl_2–ether (20 : 1), affording *VId*, pure by TLC (C), as a light brown oil in 79% yield. For $C_{25}H_{32}N_2O_6$ (456·5) calculated: 65·77% C, 7·06% H, 6·14% N; found: 65·2% C, 7·1% H, 6·1% N. ^{1}H and ^{13}C NMR data were in complete agreement with those of an authentic sample[2].

Tetra-tert-butyl Hydrazotetracarboxylate (*VII*)

A solution of Boc-$NHNH_2$ (1·32 g, 10 mmol) in acetonitrile (10 ml) was left with Boc_2O (2·40 g, 11 mmol) after thorough mixing at room temperature for 1 h. The solvent was removed under reduced pressure and the solid residue was redissolved in acetonitrile (10 ml). Additional Boc_2O (4·80 g, 22 mmol) was added, followed by DMAP (244 mg, 2·0 mmol) under rapid stirring. The reaction mixture became yellow and evolution of a gas occurred. After 1 h at ambient

temperature, TLC (B) gave essentially one spot. The mixture was left overnight and then taken to dryness at room temperature. The brownish solid residue was partitioned between ether (200 ml) and 1M-$KHSO_4$ (100 ml). The organic extract was washed in turn with 1M-$KHSO_4$, 1M-$NaHCO_3$ and saturated aqueous NaCl (3 × 50 ml each), dried over $MgSO_4$ and treated with decolourizing carbon. Evaporation to dryness afforded a solid which was washed with cold petroleum ether (3 × 10 ml) and dried at reduced pressure to yield 3·86 g (89%) of TLC pure (B) product. Recrystallization from petroleum ether (30 ml/g, decolourizing carbon) gave after drying in vacuo 3·4 g of white crystals, m.p. 123–123·5°C. For $C_{20}H_{36}N_2O_8$ (432·5) calculated: 55·54% C, 8·39% H, 6·48% N; found: 55·8% C, 8·8% H, 6·5% N. ^{1}H NMR: 1·50 s, 36 H (CH_3). ^{13}C NMR: 149·1 (CO); 83·6 (CMe_3); 27·9 (CH_3).

1,2-Dibenzyl 1,2-Di-tert-butyl Hydrazotetracarboxylate (*VIII*)

Recrystallized dibenzyl hydrazodicarboxylate[27] (4·50 g, 15 mmol) was dissolved in acetonitrile (30 ml) together with DMAP (0·37 g, 3·0 mmol) and treated with Boc_2O (7·20 g, 33 mmol) in small portions under vigorous stirring at ambient temperature. A brisk evolution of a gas was immediately observed and the yellow reaction mixture was left at room temperature. After 1 h TLC (B) indicated complete reaction and the solvent was stripped off at reduced pressure. The residual yellow oil was partitioned between ether (200 ml) and 1M-$KHSO_4$ (100 ml) and worked up by analogy with the previous procedure. Evaporation to dryness left 7·22 g (96%) as a pale yellow oil, pure by TLC (A, B). Chromatography on silica using CH_2Cl_2–acetone (9 : 1) as eluant afforded a colourless oil which could not be brought to crystallize. For $C_{26}H_{32}N_2O_8$ (500·5) calculated: 62·39% C, 6·44% H, 5·60% N; found: 62·3% C, 6·5% H, 5·7% N. ^{1}H NMR: 7·35 s, 10 H (arom. H); 5·29 and 5·13 q, 4 H (J = 12, CH_2); 1·39 s, 18 H (CH_3). ^{13}C NMR: 150·7 (CH_2O—CO); 148·6 (Me_3CO—CO); 134·9, 128·5, 128·2 (arom. C); 84·6 (CMe_3); 68·9 (CH_2); 27·7 (CH_3).

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