Preparation of Alkyl *tert*-Butyl Iminodicarbonates

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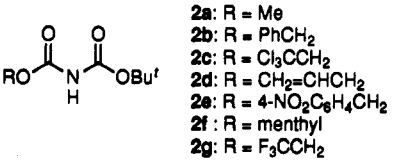
Iminodicarbonates are becoming important reagents for the introduction of protected amino functionalities into organic compounds. The most commonly employed iminodicarbonate di-*tert*-butyl iminodicarbonate (1) was originally introduced by Carpino in 1964 as an alternative Gabriel reagent.[1] The use of 1 produces a protected primary amine that can be deprotected under much milder conditions than those required for removal of a phthaloyl group. However, it was only after the introduction of convenient procedures for the preparation of 1[2,3] that it has become more widely used.[4,5]

For example, it has recently been shown that some iminodicarbonates are effective nucleophiles in Mitsunobu reactions.[6-8] The electron-withdrawing properties of the alkyl groups on the iminodicarbonate appear to be very important with compounds such as $PhCH_2OC(O)NHC(O)OCMe_2CCl_3$ giving much higher yields than the corresponding non-chlorinated analogue; compound 1 seems to be a particularly poor nucleophile in Mitsunobu reactions.[8c]

As part of our work with α-aminostannanes,[9] we desired a nitrogen nucleophile that could be used in Mitsunobu reactions and could be readily transformed into a *t*-BOC-protected amine. Reaction of α-hydroxy stannanes with 1 under Mitsunobu conditions gave only poor (<30%) yields of the alkylated iminodicarbonate. We thus decided to investigate the use of alkyl *tert*-butyl iminodicarbonates as nucleophiles under the premise that electron-withdrawing groups might increase the yields of products. Also, alkyl *tert*-butyl iminodicarbonates have the advantage that the product could be selectively deprotected to afford either alkyl or *tert*-butyl carbamates.[10,11]

Only two alkyl *tert*-butyl iminodicarbonates (other than 1) have been described in the literature: **2a** (R = Me)[2] and **2b** ($R = PhCH_2$).[8a,b] The routes to **2a** and **2b** are quite different: **2a** is prepared by oxidation of *tert*-butyl oxamate with $Pb(OAc)_4$ in the presence of MeOH[2] while **2b** may be prepared by addition of *t*-BuOH to benzoyl isocyanate[8a] or from benzyloxycarbonyl isocyanate.[8b] The use of $PhCH_2OH$ in the *tert*-butyl oxamate procedure does not produce useful yields of **2b**; other alcohols may be reacted with $PhCH_2OC(O)NCO$ to give alkyl benzyl iminodicarbonates. However, there appears to be no general route to alkyl *tert*-butyl iminodicarbonates (**2**).



1: R = t-Bu
2a: R = Me
2b: R = $PhCH_2$
2c: R = Cl_3CCH_2
2d: R = CH_2=$CHCH_2$
2e: R = 4-$NO_2C_6H_4CH_2$
2f: R = menthyl
2g: R = F_3CCH_2

We now report that compounds **2** may be conveniently prepared from alkyl chloroformates in three steps with minimal purification of intermediates and in high overall yields.

In principle, the most straightforward route to **2** is direct *tert*-butyloxycarbonylation of *O*-alkyl carbamates. Unfortunately, we found that treatment of methyl carbamate under a variety of conditions typically used for *tert*-butyloxycarbonylation of amides (*e.g.* Boc_2O, cat. DMAP, CH_3CN)[12] provided mixtures of compounds containing only small amounts of the desired iminodicarbonate **2a**. These results are in agreement with a report[8a] that attempted direct *tert*-butyloxycarbonylation of benzyl carbamate gave an intractable mixture.

We reasoned that mixtures were arising from competing further *tert*-butyloxycarbonylation of iminodicarbonate **2**. Thus a successful preparation of **2** might entail the use of a protecting group that could be easily removed after formation of an *N*-alkyliminodicarbonate. The *p*-methoxybenzyl group was chosen since (a) p-$MeOC_6H_4CH_2NH_2$ is readily available and (b) it is removed under oxidative conditions that should not affect the alkyl groups (*i.e.* R in **2**) that would be of interest.[13]

A series of iminodicarbonates were prepared as shown in the Scheme I. Reaction of 4-$MeOC_6H_4CH_2NH_2$ with alkyl chloroformates **3** under Schotten–Baumann type conditions (NaOH, THF–H_2O) gave crystalline carbamates **4**. Treatment of these carbamates with Boc_2O in the presence of DMAP then provided alkyl *tert*-butyl *N*-(*p*-methoxybenzyl)iminodicarbonates **5**.[11] Finally, oxidation of **5** with ceric ammonium nitrate (CAN)[14] furnished the desired iminodicarbonates **2** in high (75–95%) overall yields (Table I). The intermediates **4** and **5** were easily isolated by simple extractive workup and were used without further purification. The byproduct resulting from oxidation of the *p*-methoxybenzyl group, *p*-anisaldehyde, was removed by extraction with aqueous $KHSO_3$. In most cases, the crude product **2** obtained with no

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(3) Grehn, L.; Ragnarsson, U. *Synthesis* **1987**, 275.
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(5) Dibenzyl iminodicarbonate has also been used: Takeuchi, Y.; Nabetani, M.; Takagi, K.; Hagi, T.; Koizumi, T. *J. Chem. Soc. Perkin Trans. 1* **1991**, 49.
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(10) For example, treatment of an *tert*-butyl methyl *N*-alkyliminodicarbonate with NaOH provided the Boc derivative while treatment with TFA gave the methyl carbamate.[2]
(11) Very recently, *tert*-butyl [[2-(trimethylsilyl)ethyl]sulfonyl]-carbamate has been described as a useful reagent in Mitsunobu reactions: Campbell, J. A.; Hart, D. J. *J. Org. Chem.* **1993**, *58*, 2900.
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0022-3263/93/1958-7300$04.00/0

Scheme I

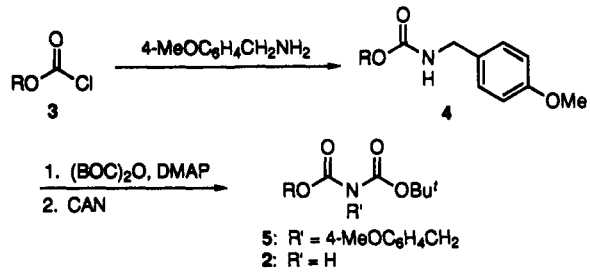


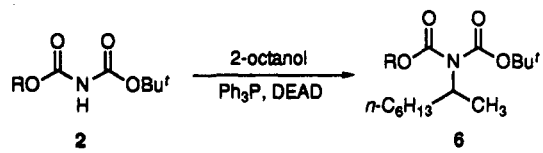
Table I. Preparation of Iminodicarbonates and Their Reaction with 2-Octanol[a]

entry	R	% yield of 2[b] (no.)	% yield of 6[c] (no.)
1	CH_3	75 (**2a**)	65 (**6a**)
2	$PhCH_2$	93 (**2b**)	62 (**6b**)
3	Cl_3CCH_2	95 (**2c**)	71 (**6c**)
4	CH_2=$CHCH_2$	85 (**2d**)	61 (**6d**)
5	4-$NO_2C_6H_4CH_2$	81 (**2e**)	76 (**6e**)
6	menthyl	80 (**2f**)	54 (**6f**)
7	F_3CCH_2	85 (**2g**)[d]	88 (**6g**)
8	$(CH_3)_3C$	*e*	40 (**6h**)

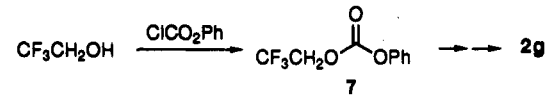
[a] The sequence shown in Scheme I was used to prepare iminodicarbonates **2**. Subsequent reaction with 2-octanol under Mitsunobu conditions (see Experimental Section) provided **6**. [b] Isolated yield of **2** based on **3**. [c] Isolated yield of **6** based on 2-octanol. [d] Isolated yield of **2** based on carbonate **7**. [e] Di-*tert*-butyl iminodicarbonate was prepared according to ref 3.

purification of intermediates was essentially pure by ^1H NMR and TLC analysis. Thus the overall conversion of **3** to **2** may be carried out with high efficiency.

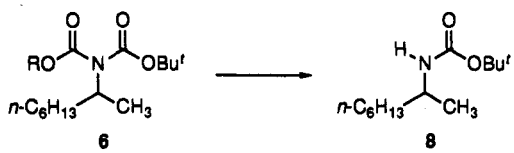
We briefly examined the reactions of these new iminodicarbonates as nucleophiles under Mitsunobu conditions. Reactions with 2-octanol proceeded in the yields shown in Table I. As anticipated, on the basis of Ragnarsson's earlier studies, those iminodicarbonates with electron-withdrawing groups (*i.e.* **2c**, R = CCl_3CH_2 and **2e**, R = 4-$NO_2C_6H_4CH_2$) gave the best yields (71–76%). Other alkyl groups gave slightly lower yields while a larger menthyl group gave only a mediocre yield. By comparison, a 40% yield of **6h** was obtained using di-*tert*-butyl iminodicarbonate (**1**) under the same conditions.



These results suggested that both electronic and steric considerations are important in Mitsunobu reactions employing alkyl *tert*-butyl iminodicarbonates as nucleophiles; one should observe better yields with alkyl groups that are relatively small and electron-withdrawing. We thus decided to prepare the CF_3CH_2 analogue **2g**. The required chloroformate is not commercially available[15] but, fortunately, a mixed carbonate served as a surrogate extremely well: Phenyl 2,2,2-trifluoroethyl carbonate (**7**) was easily prepared (CF_3CH_2OH, $ClCO_2Ph$, pyr, 100%) and reacted with 4-$MeOC_6H_4CH_2NH_2$ to provide carbamate **4g** in high yield.[16] Subsequent application of the newly developed protocol furnished the desired iminodicarbonate **2g** in 85% overall yield from **7**. Finally, and perhaps most importantly, the Mitsunobu reaction of **2g** with 2-octanol proceeded in high yield (88%), consistent with expectations.



The trifluoroethyl iminodicarbonate **6g** could be converted cleanly to *t*-BOC-protected amine **8** by base hydrolysis (1 M NaOH, THF–H_2O, rt, 96% yield). Similarly, the trichloroethyl derivative **6c** (Zn, NH_4OAc, 96% yield)[17] and the *p*-nitrobenzyl compound **6e** [H_2/$Pd(OH)_2$, 92% yield][18] were transformed into **8** under relatively mild conditions. Thus the iminodicarbonates **2c,e,g** should be especially useful as Mitsunobu nucleophiles for the synthesis of *t*-BOC-protected amines.



In summary, the three-step sequence shown in Scheme I represents a reasonably general route to alkyl *tert*-butyl iminodicarbonates. The operational simplicity of the chemistry and high overall yields observed make this route to **2** an attractive one. The ready availability of **2** should encourage their use as nucleophiles in Gabriel and Mitsunobu syntheses of protected amines.

Experimental Section

General. All reactions were carried out with dry glassware under an atmosphere of argon unless otherwise noted. All reagents were purchased (Aldrich) and used without further purification. Infrared spectra were recorded as neat liquids or Nujol mulls between NaCl plates or as KBr pellets. ^1H and ^{13}C NMR spectra were recorded with $CDCl_3$ as solvent using fields of 4.6 or 5.9 T; tetramethylsilane (^1H, δ 0.0) or $CDCl_3$ (^{13}C, δ 77.0) were used as internal references. ^1H NMR data are presented as follows: chemical shift (multiplicity, integration, *J* in hertz). Selected data for new compounds are presented in Table II. Mass spectra were recorded using EI (70 eV) ionization; compounds **4** and **5** exhibited M^+ ions while compounds **2** and **6** consistently exhibited M + 1 ions (except **2d** which showed a M + 1 – C_4H_9 ion). Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ; all new compounds gave satisfactory combustion analyses.

(1*R*,2*S*,5*R*)-Menthyl chloroformate was used and afforded derivatives with the following optical rotations: **2f:** $[\alpha]^{22}_D$ –54.4° (*c* 1.4, EtOAc); **4f:** $[\alpha]^{22}_D$ –41.6° (*c* 1.2, EtOAc); **5f:** $[\alpha]^{22}_D$ –37.5° (*c* 1.3, EtOAc).

General Procedure for the Preparation of Alkyl *N*-(*p*-Methoxybenzyl)carbamates 4. To a cooled (0 °C) solution of 4-methoxybenzylamine (1 equiv) in a 4:1 mixture of 2 M NaOH (2 equiv) and THF was added the alkyl chloroformate **3** dropwise. The ice bath was removed and the resulting mixture was stirred for 1 h. Ether was then added and the ethereal solution was washed with water, dried over $MgSO_4$, filtered, and concentrated in vacuo to give the products as white solids. Analytically pure samples were obtained by recrystallization.

(15) 2,2,2-Trifluoroethyl chloroformate has been prepared but its volatility and water sensitivity make it inconvenient to handle: Gupton, B. F.; Carroll, D. L.; Tuhy, P. M.; Kam, C. M.; Powers, J. C. *J. Biol. Chem.* **1984**, *259*, 4279. Gilligan, W. H.; Stafford, S. L. *Synthesis* **1979**, 600.

(16) Primary carbamates have been prepared by treatment of alkyl phenyl carbonates with NH_3: McLamore, W. M.; P'An, S. Y.; Bavley, A. *J. Org. Chem.* **1955**, *20*, 1379.

(17) Just, G.; Grozinger, K. *Synthesis* **1976**, 457.

(18) Shields, J. E.; Carpenter, F. H. *J. Am. Chem. Soc.* **1961**, *83*, 3066.

Table II. Selected Spectral Data for Compounds 2 and 4–6

compound	mp (°C) or R_f (solvent)[a]	IR (cm^{-1})	^1H NMR ($CDCl_3$) δ	^{13}C NMR ($CDCl_3$) δ
2a	69–70[b] (H)	3260, 1778, 1519	6.99 (br s, 1 H), 3.78 (s, 3 H), 1.49 (s, 9 H)	151.73, 149.48, 82.26, 52.70, 27.76
2c	99.5–100.5 (25:1, H/EE)	3259, 1792, 1722	7.16 (br s, 1 H), 4.79 (s, 2 H), 1.52 (s, 9 H)	149.18, 148.98, 94.45, 83.02, 74.41, 27.79
2d	0.25 (DM)	3277, 1759, 1507	6.85 (br s, 1 H), 5.92 (ddt, 1 H, J = 17.1, 10.4, 5.7 Hz), 5.35 (ddt, 1 H, J = 17.1, 1.3, 1.3), 5.26 (ddt, 1 H, J = 5.7, 1.3, 1.3 Hz), 4.65 (ddd, J = 5.7, 1.3, 1.3 Hz), 1.50 (s, 9 H)	150.83, 149.44, 131.39, 118.60, 82.20, 66.14, 27.74
2e	103–104 (5:1, H/EE)	3284, 1782, 1519	8.22 (m, 2 H), 7.55 (m, 2 H), 7.01 (br s, 1 H), 5.29 (s, 2 H), 1.50 (s, 9 H)	150.63, 149.13, 147.71, 142.50, 128.35, 123.66, 82.77, 65.77, 27.83
2f	0.25 (4:1, H/EE)	3277, 1783, 1717	6.80 (s, 1 H), 4.66 (td, 1 H, J = 4.4, 10.9 Hz), 2.1–1.8 (m, 8 H), 1.49 (s, 9 H), 0.90 (d, 3 H, J = 6.5 Hz), 0.89 (d, 3 H, J = 7.0 Hz), 0.78 (d, 3 H, J = 6.9 Hz)	150 46, 149.45, 81.40, 75.32, 46.47, 40.39, 33.63, 30.82, 27.47, 25.55, 22.86, 21.44, 20.24, 15.80
2g	91.5–92.5 (H)	3283, 1800, 1726	7.14 (br s, 1 H), 4.52 (q, 2 H, J_{HF} = 8.3 Hz), 1.50 (s, 9 H)	149.32, 149.05, 122.53 (q, J_{CF} = 277 Hz), 83.09, 60.91 (q, J_{CF} = 37 Hz), 27.66
4a	73–74 (6:1, H/EE)	3321, 1693, 1550	7.20 (m, 2 H), 6.85 (m, 2 H), 4.98 (br s, 1 H), 4.28 (d, 2 H, J = 5.8 Hz), 3.79 (s, 3 H), 3.68 (s, 3 H)	130.66, 128.65, 113.90, 55.08, 51.92, 44.46
4b	80.0–80.5 (7:1, H/EE)	3317, 1689, 1550	7.34 (s, 5 H), 7.18 (m, 2 H), 6.86 (m, 2 H), 5.13 (s, 2 H), 4.31 (d, 2 H, J = 5.8 Hz), 3.79 (s, 3 H)	158.84, 156.27, 136.43, 130.46, 128.76, 128.36, 127.96, 113.87, 66.61, 55.12, 44.45
4c	61.5–62.0 (6:1, H/EE)	3317, 1710, 1524	7.23 (m, 2 H), 6.87 (m, 2 H), 5.26 (br s, 1 H), 4.75 (s, 2 H), 4.35 (d, 2 H, J = 5.9 Hz), 3.80 (s, 3 H)	158.97, 154.52, 129.85, 128.82, 113.97, 95.54, 74.41, 55.16, 44.63
4d	46.5–47.0 (H)	3318, 1691, 1540	7.21 (m, 2 H), 6.85 (m, 2 H), 5.92 (ddt, 1 H, J = 10.4, 17.2, 5.6 Hz), 5.29 (ddt, 1 H, J = 17.2, 1.5, 1.5 Hz), 5.21 (ddt, 1 H, J = 10.4, 1.4, 1.4 Hz), 5.05 (br s, 1 H), 4.58 (d, 2 H, J = 5.6 Hz), 4.30 (d, 2 H, J = 5.6 Hz), 3.79 (s, 3 H)	158.68, 156.12, 132.74, 130.51, 128.59, 117.27, 113.72, 65.32, 54.97, 44.27
4e	103–104 (2:1, H/EE)	3298, 1692, 1522	8.20 (m, 2 H), 7.50 (m, 2 H), 7.25 (m, 2 H), 6.88 (m, 2 H), 5.21 (s, 2 H), 5.15 (br s, 1 H), 4.32 (d, 2 H, J = 5.9 Hz), 3.80 (s, 3 H)	159.03, 155.77, 147.45, 143.99, 130.13, 128.86, 127.99, 123.63, 114.01, 65.12, 63.76, 55.20, 44.63
4f	103.0–103.5 (50:1, H/EE)	3361, 1686, 1525	7.20 (m, 2 H), 6.86 (m, 2 H), 4.82 (br s, 1 H), 4.58 (td, 1 H, J = 4.3, 10.8 Hz), 4.29 (br d, J = 6.0 Hz), 3.80 (s, 3 H), 2.1–0.9 (m, 9 H), 0.90 (d, 3 H, J = 6.5 Hz), 0.88 (d, 3 H, J = 7.0 Hz), 0.79 (d, 3 H, J = 6.9 Hz)	158.62, 156.29, 130.85, 128.49, 113.68, 74.30, 54.92, 47.14, 44.18, 41.25, 34.07, 31.12, 25.98, 23.28, 21.84, 20.58, 16.23
4g	78.0–78.5 (5:1, H/EA)	3317, 1706	7.3–7.1 (m, 2 H), 6.9–6.8 (m, 2 H), 5.21 (br s, 1 H), 4.43 (q, 2 H, J = 8.5 Hz), 4.32 (d, 2 H, J = 5.9 Hz), 3.80 (s, 3 H)	158.96, 154.49, 129.80, 128.75, 123.06 (q, J_{CF} = 277 Hz), 113.90, 60.68 (q, J_{CF} = 36 Hz), 54.98, 44.55
5a	0.22 (2:1, H/EE)	1791, 1729, 1514	7.25 (m, 2 H), 6.82 (m, 2 H), 4.77 (s, 2 H), 3.82 (s, 3 H), 3.79 (s, 3 H), 1.45 (s, 9 H)	158.49, 154.40, 151.44, 129.61, 128.54, 113.23, 82.29, 54.61, 53.14, 48.57, 27.43
5b	0.30 (2:1, H/EE)	1790, 1725, 1513	7.33 (s, 5 H), 7.21 (m, 2 H), 7.01 (m, 2 H), 5.21 (s, 2 H), 4.77 (s, 2 H), 3.78 (s, 3 H), 1.43 (s, 9 H)	158.53, 153.57, 151.69, 135.14, 129.66, 128.71, 128.08, 127.86, 127.82, 113.29, 82.42, 67.97, 54.67, 48.64, 27.50
5c	69.0–69.5 (20:1, H/EE)	1782, 1703, 1514	7.29 (m, 2 H), 6.84 (m, 2 H), 4.85 (s, 2 H), 4.82 (s, 2 H), 3.79 (s, 3 H), 1.50 (s, 9 H)	158.93, 152.10, 151.61, 129.35, 129.08, 113.66, 94.50, 83.71, 75.59, 55.13, 49.22, 27.86
5d	0.30 (2:1, H/EE)	1790, 1726, 1514	7.23 (m, 2 H), 6.82 (m, 2 H), 5.93 (ddt, 1 H, J = 17.2, 10.4, 5.6 Hz), 5.34 (ddt, 1 H, J = 17.2, 1.3, 1.3 Hz), 5.24 (ddt, 1 H, J = 10.4, 1.3, 1.3 Hz), 4.78 (s, 2 H), 4.69 (ddd, 2 H, J = 5.6, 1.3, 1.3 Hz), 3.79 (s, 3 H), 1.46 (s, 9 H)	158.58, 153.61, 151.64, 131.46, 129.73, 128.74, 118.17, 113.33, 82.47, 77.00, 66.94, 54.77, 48.66, 27.58
5e	0.20 (2:1, H/EE)	1789, 1726, 1521	8.18 (m, 2 H), 7.47 (m, 2 H), 7.22 (m, 2 H), 6.83 (m, 2 H), 5.32 (s, 2 H), 4.80 (s, 2 H), 3.79 (s, 3 H), 1.46 (s, 9 H)	158.84, 153.75, 151.56, 147.49, 142.77, 129.63, 128.76, 128.02, 123.55, 113.61, 83.22, 66.66, 55.07, 49.12, 27.78
5f	0.30 (8:1, H/EE)	1789, 1722, 1514	7.23 (m, 2 H), 6.83 (m, 2 H), 4.76 (AB quartet, 2 H, $\Delta\delta$ = 0.04, J = 15 Hz), 4.68 (td, 1 H, J = 4.3, 9.8 Hz), 3.78 (s, 3 H), 2.04 (m, 1 H), 1.8–0.9 (m, 8 H), 0.89 (d, 3 H, J = 6.5 Hz), 0.83 (d, 3 H, J = 7.0 Hz), 0.72 (d, 3 H, J = 6.9 Hz)	158.70, 153.48, 152.40, 130.39, 128.78, 113.56, 82.56, 55.13, 48.80, 47.03, 40.75, 34.09, 31.51, 31.31, 27.95, 25.77, 23.09, 22.58, 21.91, 20.76, 16.00, 14.04
5g	0.40 (2:1, H/EE)	1755, 1706, 1515	7.3–7.2 (m, 2 H), 6.9–6.2 (m, 2 H), 4.79 (s, 2 H), 4.53 (q, 2 H, J_{HF} = 8.4 Hz), 3.78 (s, 3 H), 1.48 (s, 9 H)	159.00, 152.44, 151.55, 129.24, 122.79 (q, J_{CF} = 277 Hz), 113.67, 83.76, 62.06 (q, J_{CF} = 37 Hz), 55.06, 49.23, 27.72
6a	0.25 (2:1, DM/EE)	1747, 1707	4.29 (ddq, 1 H, J = 8.6, 6.8 Hz), 3.79 (s, 3 H), 1.67 (m, 1 H), 1.52 (m, 1 H), 1.50 (s, 9 H), 1.28 (d, 3 H, J = 6.8 Hz), 1.26 (m, 8 H), 0.86 (unresolved t, 3 H)	154.99, 152.50, 81.89, 53.29, 52.85, 34.32, 31.46, 28.77, 27.66, 26.38, 22.27, 18.78, 13.72

Table II (Continued)

compound	mp (°C) or R_f (solvent)[a]	IR (cm^{-1})	^1H NMR ($CDCl_3$) δ	^{13}C NMR ($CDCl_3$) δ
6b	0.30 (2:1, DM/EE)	1743, 1704	7.35 (m, 5 H), 5.20 (s, 2 H), 4.29 (ddq, 1 H, J = 8.7, 6.8 Hz), 1.80 (m, 1 H), 1.50 (m, 1 H), 1.43 (s, 9 H), 1.28 (d, 3 H), 1.24 (m, 8 H), 0.87 (unresolved t, 3 H)	154.36, 152.72, 135.59, 128.32, 128.07, 82.20, 67.93, 53.58, 34.45, 31.59, 28.89, 27.73, 26.52, 22.41, 18.95, 13.91
6c	0.30 (2:1, DM/EE)	1752, 1714	4.82 (s, 2 H), 4.33 (ddq, 1 H, J = 8.7, 6.8, 6.8 Hz), 1.72 (m, 1 H), 1.55 (m, 1 H), 1.53 (s, 9 H), 1.34 (d, 3 H, J = 6.8 Hz), 1.25 (m, 8 H), 0.85 (unresolved t, 3 H)	152.50, 152.18, 94.69, 83.08, 75.38, 54.24, 34.37, 31.62, 28.89, 27.75, 26.52, 22.42, 18.92, 13.91
6d	0.30 (2:1, DM/EE)	1745, 1706	6.00 (ddt, 1 H, J = 17.2, 10.3, 5.6 Hz), 5.36 (dq, 1 H, J = 17.2, 1.5 Hz), 4.66 (dt, 2 H, J = 10.3, 1.3 Hz), 4.66 (dt, 2 H, J = 5.6, 1.4 Hz), 4.29 (ddq, 1 H, J = 8.7, 6.8, 6.8 Hz), 1.78 (m, 1 H), 1.52 (m, 1 H), 1.50 (s, 9 H), 1.29 (d, 3 H), 1.26 (m, 8 H), 0.87 (unresolved t, 3 H)	154.23, 152.66, 131.83, 118.13, 82.10, 66.77, 53.45, 34.40, 31.56, 28.86, 27.76, 26.48, 22.38, 18.88, 13.85
6e	0.20 (2:1, DM/EE)	1743, 1705	8.24 (m, 2 H), 7.57 (m, 2 H), 5.30 (s, 2 H), 4.31 (ddq, 1 H, J = 8.7, 6.8, 6.8 Hz), 1.79 (m, 1 H), 1.55 (m, 1 H), 1.49 (s, 9 H), 1.30 (d, 3 H), 1.25 (m, 8 H), 0.87 (unresolved t, 3 H)	154.12, 153.38, 147.59, 143.13, 128.06, 123.62, 82.73, 66.38, 53.93, 34.47, 31.61, 28.90, 27.81, 26.55, 22.42, 18.99, 13.90
6f	0.35 (2:1, DM/EE)	1740, 1702	4.67 (td, 1 H, J = 10.8, 4.3 Hz), (ddq, 1 H, J = 8.8, 6.8, 6.8 Hz), 1.5–0.8 (m, 11 H), 2.03 (m, 2 H), 1.70 (m, 2 H), 1.49 (s, 9 H), 1.29 (d, 3 H, J = 6.8 Hz), 1.26 (m, 8 H), 0.91 (d, 3 H, J = 6.5 Hz), 0.90 (d, 3 H, J = 7.1 Hz), 0.79 (d, 3 H, J = 6.9 Hz)	154.12, 153.16, 81.98, 76.52, 53.41, 47.18, 40.81, 34.30, 34.18, 31.75, 29.03, 27.95, 26.69, 25.96, 23.21, 22.51, 21.94, 20.73, 19.28, 16.10, 13.99
6g	0.25 (2:1, DM/EE)	1753, 1716	4.52 (q, 2 H, J_{HF} = 8.3 Hz), 4.4–4.2 (m, 1 H), 1.9–1.7 (m, 1 H), 1.6–1.4 (m, 1 H), 1.50 (s, 9 H), 1.31 (d, 3 H, J = 6.9 Hz), 1.3–1.1 (m, 8 H), 0.88 (t, 3 H, J = 7 Hz)	152.65, 152.18, 122.84 (q, J_{CF} = 277 Hz), 83.12, 61.70 (q, J_{CF} = 37 Hz), 54.30, 34.24, 31.62, 28.88, 27.52, 26.48, 22.42, 18.67, 13.83
6h	0.35 (2:1, DM/EE)	1741, 1704	4.21 (ddq, 1 H, J = 8.8, 6.8, 6.8 Hz), 1.70 (m, 1 H), 1.50 (m, 1 H), 1.50 (s, 9 H), 1.27 (d, 3 H, J = 6.8 Hz), 1.27 (m, 8 H), 0.89 (unresolved t, 3 H)	153.18, 81.38, 52.84, 34.54, 31.64, 28.89, 27.82, 26.50, 22.38, 18.84, 13.85

[a] DM = CH_2Cl_2, EA = EtOAc, EE = Et_2O, H = hexanes. [b] Literature[2] mp 75–77 °C.

General Procedure for the Preparation of Alkyl *tert*-Butyl *N*-(*p*-Methoxybenzyl)iminodicarbonates (5). To a 0.25 M solution of *N*-(4-methoxybenzyl)carbamate **4** in CH_3CN was added DMAP (0.15 equiv) followed by di-*tert*-butyl dicarbonate (1.2 equiv).[12] The resulting mixture was stirred overnight and then diluted with ether. The ethereal solution was washed with 20% saturated $KHSO_4$, saturated $NaHCO_3$, and water, dried over $MgSO_4$, and concentrated in vacuo to provide crude *N*-(4-methoxybenzyl)iminodicarbonate **5**. Analytically pure samples were obtained by recrystallization or flash chromatography.

General Procedure for the Preparation of Alkyl *tert*-Butyl Iminodicarbonates 2. To a 0.25 M solution of **5** (1 equiv) in 3:1 CH_3CN/H_2O was added CAN (4 equiv) and the resulting mixture was stirred for 1 h.[14] Ether was then added and the mixture was washed with several portions of 10% $NaHCO_3$ and water, dried over $MgSO_4$, filtered, and concentrated in vacuo. To the mixture of iminodicarbonate and *p*-anisaldehyde was added 3 M $KHSO_3$ (20 equiv) and the two-phase system was stirred for 15 min. Then ether was added, the layers were separated, and the ether layer was concentrated in vacuo. The residue was similarly treated with $KHSO_3$ twice more to provide crude iminodicarbonates (>95% pure) which could be used without further purification. Overall yields of **2** from chloroformates **3** or carbonate **7** are listed in Table I. Analytically pure samples were then prepared by recrystallization or flash chromatography.

General Procedure for the Preparation of *N*-(2-Octyl)-iminodicarbonates 6. To a ~0.3 M solution of (±)-2-octanol (1 equiv) in THF was added iminodicarbonate **2** (1.1 equiv) and PPh_3 (1.1 equiv). A solution of DEAD (1.1 equiv) in THF (0.5 mL) was then added and the resulting mixture was stirred overnight and then concentrated in vacuo. Flash chromatography (30 g silica/g substrate, 2:1 CH_2Cl_2/Et_2O) of the resulting oil provided the products as colorless oils in the yields shown in Table I.

Phenyl 2,2,2-Trifluoroethyl Carbonate (7) was prepared by reaction of CF_3CH_2OH with $ClCO_2Ph$ (100% yield) in pyridine.[16] bp (air bath) 70 °C/0.4 torr; IR (neat) 1775, 1311, 1240, 1173 cm^{-1}; ^1H NMR δ 7.4–7.1 (m, 5 H), 4.58 (q, 2 H, J_{HF} = 8.1 Hz); ^{13}C NMR δ 152.47, 150.77, 129.34, 126.22, 122.55 (q, J_{CF} = 277 Hz), 120.48, 63.35 (q, J_{CF} = 37 Hz); MS *m/e* (rel int) 220 (M^+, 74), 176 (30), 141 (17), 107 (44), 77 (100). Anal. Calcd for $C_9H_7F_3O_3$: C, 49.10; H, 3.21. Found: C, 49.30; H, 3.31.

***tert*-Butyl *N*-(2-Octyl)carbamate (8). From 6c:** A solution of **6c** (100 mg, 0.248 mmol) in THF (1 mL) was treated with Zn dust (200 mg) followed by 1 M NH_4OAc (aqueous). The slurry was stirred at rt for 16 h, diluted with Et_2O, and filtered through Celite. Flash chromatography (2 g silica, 2:1 CH_2Cl_2/Et_2O) of the concentrated filtrate furnished **8** (55 mg, 96% yield) as a colorless oil. **From 6e:** A mixture of **6e** (100 mg, 0.245 mmol) and $Pd(OH)_2$ (6 mg) in THF (1 mL) was stirred under a balloon of H_2 for 16 h at rt. The mixture was diluted with Et_2O (20 mL) and filtered through a pad of Celite. Concentration of the filtrate followed by flash chromatographic purification gave **8** (52 mg, 92% yield). **From 6g:** A solution of **6g** (100 mg, 0.28 mmol) in THF (2 mL) was stirred with 1 M NaOH (2 equiv) for 4 h at rt. Extractive workup provided **8** (62 mg, 96% yield) as the only product: IR (neat) 3338, 1699, 1517, 1371, 1172 cm^{-1}; ^1H NMR δ 4.76 (br s, 1 H), 3.61 (br m, 1 H), 1.44 (s, 9 H), 1.31 (m, 8 H), 1.10 (d, 3 H, J = 6.5 Hz), 0.88 (unresolved t, 3 H); ^{13}C NMR δ 155.39, 78.82, 46.51, 37.33, 31.77, 29.15, 28.40, 25.93, 22.54, 21.24, 14.01; MS *m/e* (rel int) 230 (M + 1, 21), 174 (75), 144 (65), 130 (47), 88 (72). Anal. Calcd for $C_{13}H_{27}NO_2$: C, 68.08; H, 11.86; N, 6.11. Found: C, 67.86; H, 11.85; N, 6.08.

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Supplementary Material Available: Mass spectral data and combustion analyses for compounds **2c–g**, **4a–g**, **5a–g**, and **6a–h** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.