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(Tosylimino)phenyl-λ^3-iodane as a Reagent for the Synthesis of Methyl Carbamates via Hofmann Rearrangement of Aromatic and Aliphatic Carboxamides

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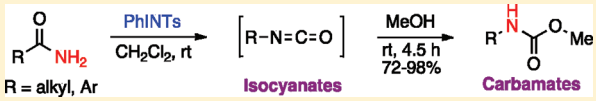
Supporting Information

ABSTRACT: A new, mild procedure for the Hofmann rearrangement of aromatic and aliphatic carboxamides using (tosylimino)-phenyl-λ^3-iodane, PhINTs, as a reagent is reported. Because of the mild reaction conditions, this method is particularly useful for the Hofmann rearrangement of substituted benzamides, which usually afford complex reaction mixtures with other hypervalent iodine oxidants. The mild reaction conditions and high selectivity in the reaction of carboxamides with PhINTs allow the isolation of the initially formed labile isocyanates or their subsequent conversion to stable carbamates by treatment with alcohols.



In recent years, hypervalent iodine compounds have emerged as environmentally friendly and efficient oxidizing reagents for various synthetically useful oxidative transformations.[1] Organohypervalent iodine(III) compounds are particularly useful as the oxidants in Hofmann-type rearrangements, which have been utilized in numerous synthetic works.[2−5] The most common reagents for Hofmann-type rearrangements include (diacetoxyiodo)benzene,[2] [bis(trifluoroacetoxy)iodo]-benzene,[3] [hydroxy(tosyloxy)]iodobenzene,[4] and their recyclable analogues.[5] All these reagents, however, are powerful oxidants, incompatible with many functional groups and substituted phenyl rings, such as phenol ethers. We decided to investigate a milder oxidant, tosylimino-λ^3-iodane, PhINTs, as a potential reagent for Hofmann-type rearrangement of alkyl- and arylcarboxamides. In recent years, PhINTs and other *N*-tosyliminoiodanes, ArINTs, have found broad synthetic application as useful reagents for the aziridination of alkenes and the amidation reactions of various organic substrates.[6] Herein, we wish to report the use of PhINTs as a mild reagent for Hofmann rearrangement of aromatic and aliphatic carboxamides to the respective isocyanates, which can be subsequently trapped with methanol to afford respective carbamates as the final isolable products. Because of the mild reaction conditions, this method is particularly useful for the Hofmann rearrangement of substituted benzamides, which usually afford complex reaction mixtures in reactions with other hypervalent iodine oxidants.[2d,3b,4d,7]

First, we have investigated the Hofmann rearrangement of *p*-toluamide **2a** using PhINTs **1** (1.2 equiv) at room temperature in different solvents. The initially formed *p*-isocyanatotoluene **3a** was subsequently converted to the respective carbamate **4a** by treatment with methanol for 4.5 h at room temperature; the yields of product **4a** under different reaction conditions are shown in Table 1. Out of several solvents tested (Table 1), the reaction in dichloromethane was found to give the best results, affording 98% of carbamate **4a** after 30 min of the initial reaction (entry 7). For comparison, under similar conditions the reaction of *p*-toluamide **2a** with (diacetoxyiodo)benzene, $PhI(OAc)_2$, gave a complex mixture of products, which, according to NMR, contained only 71% of carbamate **4a**. Because of the mild reaction conditions and high selectivity in the reaction of *p*-toluamide **2a** with PhINTs, we were also able to isolate the initially formed, labile, *p*-isocyanatotoluene **3a** in 80% preparative yield.

Using the optimized reaction conditions, we have investigated the conversion of various substituted benzamides and alkylcarboxamides **2** to the respective carbamates **4** (Table 2). In general, all aromatic substrates with either electron-donating or electron-withdrawing substituents afforded products **4** in good yields (entries 1−12). However, the reactions of benzamides with a bulky *ortho*-substituent or with an electron-withdrawing group in the phenyl ring required longer time. In particular, the reaction of 2,4-dichlorobenzamide **4i** required 4 h and the use of 1.5 equiv of reagent **1** for completion (entry 8). The most sterically hindered benzamide, 2,4,6-trimethylbenzamide, did not react with reagent **1** even after 24 h of stirring at room temperature (entry 13). As expected, various aliphatic amides, including benzylcarboxamides, primary, second, tertiary and cyclic alkylcarboxamides, have also smoothly reacted with tosyliminoiodane **1** giving respective carbamates **4** in excellent yields (entries 14−23). Compared to the known methods of Hofmann rearrangement of alkylcarboxamides using other hypervalent iodanes, our method affords products **4** in similar yields, and the reaction is compatible with different substituents.[2c,d,7c]

The mild reactions conditions and high selectivity in the reaction of carboxamides **2** with PhINTs allow the isolation of the initially formed isocyanates **3** or subsequent conversion of these highly reactive intermediates to other final stable products. For example, the trapping of isocyanate **3a** with 2-propanol or 2-methyl-2-propanol instead of methanol afforded

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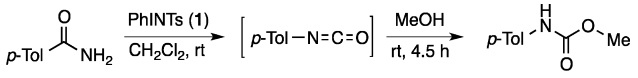
Table 1. Optimization of Hofmann Rearrangement with Iminoiodane 1.[a]

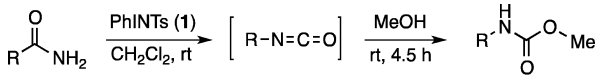


2a 3a 4a

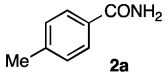
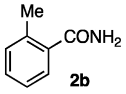
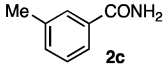
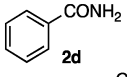
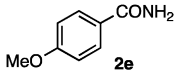
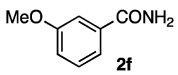
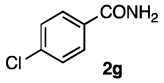
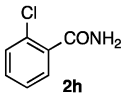
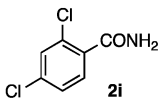
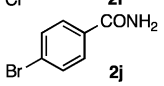
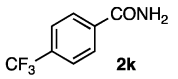
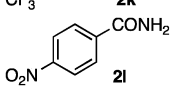
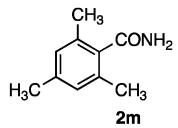
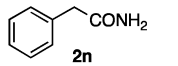
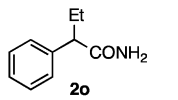
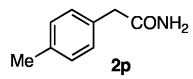
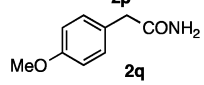
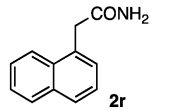
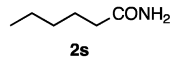
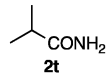
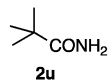
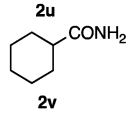
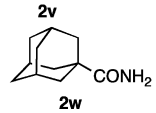
entry	time (h)	solvent	yield of 4a[b] (%)
1	1.5	MeCN	(2)
2	1.5	MeOH	(39)
3	1.5	$CHCl_3$	(53)
4	1.5	AcOEt	*c*
5	1.5	THF	*c*
6	1.5	CH_2Cl_2	97[d] (100)
7	0.5	CH_2Cl_2	98[d] (100)
8[e]	0.5	CH_2Cl_2	(71)

[a]All reactions were performed using 1 equiv of *p*-toluamide **2a** and 1.2 equiv of reagent **1** at room temperature. [b]Numbers in parentheses show yields determined from ^{1}H NMR spectra of reaction mixture. [c]No reaction. [d]Yields of products isolated by preparative TLC. [e](Diacetoxyiodo)benzene was used instead of reagent **1**.

Table 2. Synthesis of Carbamates by Hofmann Rearrangement with Iminoiodane 1[a]



2 3 4

Entry	Time (h)	Carboxamide **2**	Carbamate **4**	Yield (%)[b]
1	0.5	 **2a**	**4a**	98
2	1	 **2b**	**4b**	97
3	0.5	 **2c**	**4c**	98
4	0.5	 **2d**	**4d**	93 (97)
5	0.5	 **2e**	**4e**	90
6	0.5	 **2f**	**4f**	96
7	1	 **2g**	**4g**	94
8	1.5	 **2h**	**4h**	94
9[c]	4	 **2i**	**4i**	80
10	1.5	 **2j**	**4j**	98
11	1.5	 **2k**	**4k**	85
12	1.5	 **2l**	**4l**	75
13[c]	24	 **2m**	-[d]	-[d]
14	1.5	 **2n**	**4n**	97
15	1.5	 **2o**	**4o**	97
16	1.5	 **2p**	**4p**	91
17	1.5	 **2q**	**4q**	86
18	1	 **2r**	**4r**	95
19	1	 **2s**	**4s**	92
20	1.5	 **2t**	**4t**	74
21	1	 **2u**	**4u**	72
22	0.5	 **2v**	**4v**	85
23	0.5	 **2w**	**4w**	83 (78)

[a]All reactions were performed using 1 equiv of amide and 1.2 equiv of reagent **1** at room temperature unless noted otherwise. [b]Isolated yields; the yields shown in parentheses correspond to the literature[2d] data for the synthesis of carbamates **4** from carboxamides **2** using $PhI(OAc)_2$ in KOH/MeOH. [c]1.5 equiv of reagent **1** was used. [d]No reaction.

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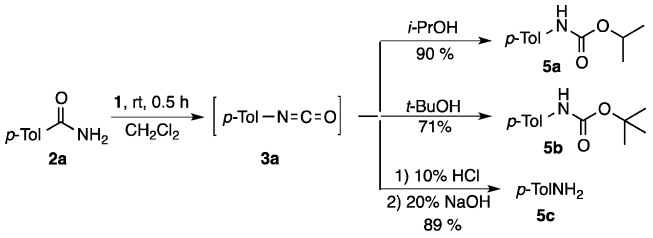
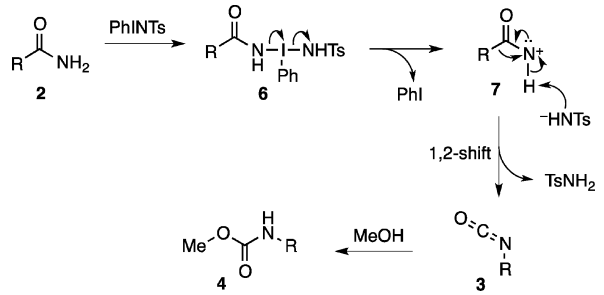
the respective carbamates **5a** and **5b** in good yields, and the treatment of isocyanate **3a** with 10% aqueous HCl followed by basic workup gave *p*-toluidine **5c** in 89% yield (Scheme 1).

Scheme 1. Conversion of *p*-Toluamide 2a to Carbamates 5a,b and *p*-Toluidine 5c



Based on the previously reported mechanistic studies of Hofmann rearrangement using other hypervalent iodine reagents,[3a,b,4f] we propose that the reaction starts from the formation of amidoiodane **6** (Scheme 2). Subsequently, the

Scheme 2. Proposed Reaction Mechanism



reductive elimination of iodobenzene and the 1,2-alkyl or -aryl shift to the electron-deficient nitrenium nitrogen atom in the intermediate **7** afford isocyanate **3**. Subsequent addition of an alcohol to isocyanate **3** gives the final carbamate **4**.

In summary, we have reported a new, mild procedure for the Hofmann rearrangement of aromatic and aliphatic carboxamides using iminoiodane PhINTs as a reagent. Because of the mild reaction conditions, this method is particularly useful for the Hofmann rearrangement of substituted benzamides, which usually afford complex reaction mixtures in the reactions with other hypervalent iodine oxidants. The mild reaction conditions and the high selectivity in the reaction of carboxamides with PhINTs allow the isolation of the initially formed labile isocyanates or their subsequent conversion to stable carbamates by treatment with alcohols.

EXPERIMENTAL SECTION

All reactions were performed under dry nitrogen atmosphere with flame-dried glassware. All commercial reagents were ACS reagent grade and used without further purification. Carboxamides **2** were from commercial sources. Dichloromethane was distilled from CaH_2 immediately prior to use. Diethyl ether was distilled from Na/benzophenone. NMR spectra were recorded at 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). Chemical shifts (δ) are reported in parts per million and referenced relative to tetramethylsilane.

***N*-(4-Methylphenylsulfonyl)imino-phenyl-λ^3-iodane (1).**[8] 1-Diacetoxy-phenyl-λ^3-iodane (670 mg, 2.1 mmol) was added to a stirred mixture of potassium hydroxide (292 mg, 2.1 mmol) and *p*-toluenesulfonamide (356 mg, 5.2 mmol) in methanol (7.8 mL). The resulting clear yellow solution was stirred for 2.5 h at 0 °C and 0.5 h at room temperature and then poured into distilled water (49 mL). Over a period of 12 h a yellow precipitate formed, which was then filtered, washed with hexane and dichloromethane several times, and dried in vacuo to give 528 mg (68%) of product **1**, isolated as light yellow solid: mp 103−103.7 °C dec (lit.[8] mp 104−105 °C); IR (KBr) cm^{-1} 3422, 3056, 2925, 1594, 1444, 1266, 1131, 1124, 1081, 866, 820, 742; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.69 (d, J = 7.8, 2H), 7.59−7.41 (m, 3H), 7.33−7.26 (m, 2H), 7.06 (d, J = 7.8, 2H), 2.27 (s, 3H).

General Procedure for Hofmann Rearrangement of Carboxamides 2 with Imino-λ^3-iodane 1. *N*-(4-Methylphenylsulfonyl)-iminophenyl-λ^3-iodane **1** (34 mg, 0.090 mmol) was added to a solution of carboxamide **2** (0.075 mmol) in dichloromethane (1.5 mL) under stirring at room temperature. A change of the initially heterogeneous mixture to a homogeneous solution was observed after several minutes. The reaction mixture was stirred for 0.5−4 h (see Table 2), methanol (1.52 mL) was added, and stirring was continued for additional 4.5 h at room temperature. Then the reaction mixture was concentrated and separated by preparative TLC (hexane−ethyl acetate, 2: 1 or 3: 1) to afford analytically pure carbamates **4**.

Methyl *N*-(4-Methylphenyl)carbamate (4a).[9] Reaction of *p*-toluamide **2a** (10 mg, 0.075 mmol) according to the general procedure afforded 12 mg (98%) of product **4a**, isolated as colorless needles (recrystallized from dichloromethane−hexane): mp 98.3−99 °C (lit.[9] mp 97−99 °C); IR (KBr) cm^{-1} 3328, 1704, 1599, 1538, 1231; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, J = 8.5 Hz, 2H), 7.11 (d, J = 8.5 Hz, 2H), 6.52 (br s, 1H), 3.77 (s, 3H), 2.30 (s, 3H).

Methyl *N*-(2-Methylphenyl)carbamate (4b).[9] Reaction of *o*-toluamide **2b** (10 mg, 0.075 mmol) according to the general procedure afforded 12 mg (97%) of product **4b**, isolated as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (brs, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.16 (d, J = 7.5 Hz, 1H), 7.03 (t, J = 7.5 Hz, 2H), 6.38 (brs, 1H), 3.78 (s, 3H), 2.25 (s, 3H).

Methyl *N*-(3-Methylphenyl)carbamate (4c).[10] Reaction of *m*-toluamide **2c** (10 mg, 0.075 mmol) according to the general procedure afforded 12 mg (98%) of product **4c**, isolated as colorless needles (recrystallized from dichloromethane−hexane): mp 69−69.3 °C (lit.[11] mp 70−72 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24−7.12 (m, 3H), 6.88 (d, J = 7 Hz, 1H), 6.57 (br s, 1H), 3.77 (s, 3H), 2.33 (s, 3H).

Methyl *N*-Phenylcarbamate (4d).[12] Reaction of benzamide **2d** (9 mg, 0.075 mmol) according to the general procedure afforded 11 mg (96%) of product **4d**, isolated as a white amorphous solid: IR (KBr) 3314, 1702, 1604, 1546, 1237 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 8 Hz, 2H), 7.31 (t, J = 8 Hz, 2H), 7.07 (t, J = 8 Hz, 1H), 6.61 (br s, 1H), 3.78 (s, 3H).

Methyl *N*-(4-Methoxyphenyl)carbamate (4e).[12] Reaction of *p*-methoxybenzamide **2e** (11 mg, 0.075 mmol) according to the general procedure afforded 12 mg (90%) of product **4e**, isolated as colorless needles (recrystallized from dichloromethane−hexane): mp 87.8−89.3 °C (lit.[13] mp 88 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, J = 9 Hz, 2H), 6.85 (d, J = 9 Hz, 2H), 6.45 (brs, 1H), 3.79 (s, 3H), 3.76 (s, 3H).

Methyl *N*-(3-Methoxyphenyl)carbamate (4f).[14] Reaction of *m*-methoxybenzamide **2f** (11 mg, 0.075 mmol) according to the general procedure afforded 13 mg (96%) of product **4f**, isolated as a white amorphous solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (t, J = 7.8 Hz, 1H), 7.12 (br s, 1H), 6.86 (d, J = 7.8 Hz, 1H), 6.62 (dd, J = 7.8, 2.5 Hz, 1H), 6.60 (b rs, 1H), 3.80 (s, 3H), 3.78 (s, 3H).

Methyl *N*-(4-Chlorophenyl)carbamate (4g).[9] Reaction of *p*-chlorobenzamide **2g** (12 mg, 0.075 mmol) according to the general procedure afforded 13 mg (94%) of product **4g**, isolated as a colorless needles (recrystallized from dichloromethane−hexane): mp 115.6−116.1 °C (lit.[9] mp 114−115 °C); IR (KBr) cm^{-1} 3345, 1701, 1606, 1546, 1238, 1092; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 8.8 Hz, 2H), 6.59 (br s, 1H), 3.78 (s, 3H).

Methyl *N*-(2-Chlorophenyl)carbamate (4h).[9] Reaction of *o*-chlorobenzamide **2h** (12 mg, 0.075 mmol) according to the general procedure afforded 13 mg (94%) of product **4h**, isolated as a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 8 Hz, 1H), 7.34 (d, J = 8 Hz, 1H), 7.27 (t, J = 8 Hz, 1H), 7.15 (br s, 1H), 6.99 (t, J = 8 Hz, 1H), 3.81 (s, 3H).

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Methyl *N*-(2,4-Dichlorophenyl)carbamate (4i).[15] Reaction of 2,4-dichlorobenzamide **2i** (14 mg, 0.075 mmol) according to the general procedure afforded 13 mg (80%) of product **4i**, isolated as colorless needles (recrystallized from dichloromethane−hexane): mp 67.6−68.3 °C (lit.[15] mp 58−62 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, J = 9 Hz, 1H), 7.36 (d, J = 3 Hz, 1H), 7.25 (dd, J = 9, 3 Hz, 1H), 7.09 (br s, 1H), 3.81 (s, 3H).

Methyl *N*-(4-Bromophenyl)carbamate (4j).[16] Reaction of *p*-bromobenzamide **2j** (15 mg, 0.075 mmol) according to the general procedure afforded 17 mg (98%) of product **4j**, isolated as a white solid (recrystallized from dichloromethane−hexane: mp 125.1−125.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.8 Hz, 2H), 6.58 (brs, 1H), 3.78 (s, 3H).

Methyl *N*-(4-Trifluoromethylphenyl)carbamate (4k).[17] Reaction of *p*-trifluoromethylbenzamide **2k** (14 mg, 0.075 mmol) according to the general procedure afforded 14 mg (85%) of product **4k**, isolated as colorless needles (recrystallized from dichloromethane−hexane): mp 128.3−129 °C (lit.[17] mp 129−130 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 6.74 (br s, 1H), 3.80 (s, 3H).

Methyl *N*-(4-Nitrophenyl)carbamate (4l).[17] Reaction of *p*-nitrobenzamide **2l** (12 mg, 0.075 mmol) according to the general procedure afforded 11 mg (75%) of product **4l**, isolated as yellow needles (recrystallized from dichloromethane−hexane): mp 177.2−178 °C (lit.[18] mp 176−177 °C); IR (KBr) cm^{-1} 3391, 1740, 1595, 1508, 1326, 1219; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 7.8 Hz, 2H), 7.56 (d, J = 7.8 Hz, 2H), 6.93 (br s, 1H), 3.83 (s, 3H).

Methyl *N*-Benzylcarbamate (4n).[7c] Reaction of 2-phenylacetamide **2n** (10 mg, 0.075 mmol) according to the general procedure afforded 12 mg (97%) of product **4n**, isolated as colorless needles (recrystallized from dichloromethane−hexane): mp 62.2−62.9 °C (lit.[7c] mp 63−65 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (t, J = 7.8 Hz, 2H), 7.31−7.25 (m, 3H), 4.98 (br s, 1H), 4.37 (d, J = 5.5 Hz, 2H), 3.70 (s, 3H).

Methyl *N*-(1-Phenylpropyl)carbamate (4o).[19] Reaction of 2-phenylbutanamide **2o** (12 mg, 0.075 mmol) according to the general procedure afforded 14 mg (97%) of product **4o**, isolated as a light brown oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, J = 7.5 Hz, 2H), 7.32−7.28 (m, 3H), 5.11 (br s, 1H), 4.68−4.54 (m, 1H), 3.66 (s, 3H), 1.92−1.72 (m, 2H), 0.92 (t, J = 7.5 Hz, 3H).

Methyl *N*-(4-Methylbenzyl)carbamate (4p).[7c] Reaction of 2-(*p*-tolyl)acetamide **2p** (11 mg, 0.075 mmol) according to the general procedure afforded 12 mg (91%) of product **4p**, isolated as colorless needles (recrystallized from dichloromethane−hexane): mp 71.5−72.2 °C (lit,[7c] mp 68−70 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, J = 7.5 Hz, 2H), 7.14 (d, J = 7.5 Hz, 2H), 4.92 (brs, 1H), 4.33 (d, J = 5.5 Hz, 2H), 3.70 (s, 3H), 2.34 (s, 3H).

Methyl *N*-(4-Methoxybenzyl)carbamate (4q).[7c] Reaction of 2-(*p*-methoxyphenyl)acetamide **2q** (12 mg, 0.075 mmol) according to the general procedure afforded 13 mg (86%) of product **4q**, isolated as colorless needles (recrystallized from dichloromethane−hexane): mp 73−73.8 °C (lit.[7c] mp 73−74 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 4.91 (br s, 1H), 4.30 (d, J = 6 Hz, 2H), 3.80 (s, 3H), 3.69 (s, 3H).

Methyl *N*-[(1-Naphthyl)methyl]carbamate (4r).[7c] Reaction of 1-naphthaleneacetamide **2r** (14 mg, 0.075 mmol) according to the general procedure afforded 16 mg (95%) of product **4r**, isolated as colorless needles (recrystallized from dichloromethane−hexane): mp 86.2−86.6 °C (lit.[7c] mp 84−86 °C); IR (KBr) cm^{-1} 3304, 1696, 1547, 1262; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, J = 8 Hz, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.81 (d, J = 9 Hz, 1H), 7.58−7.48 (m, 2H), 7.47−7.40 (m, 2H), 4.97 (br s, 1H), 4.83 (d, J = 6 Hz, 2H), 3.71 (s, 3H).

Methyl *N*-Pentylcarbamate (4s).[20] Reaction of hexanamide **2s** (9 mg, 0.075 mmol) according to the general procedure afforded 10 mg (92%) of product **4s**, isolated as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.62 (br s, 1H), 3.66 (s, 3H), 3.22−3.06 (m, 2H), 1.49 (quint, J = 7 Hz, 2H), 1.38−1.24 (m, 4H), 0.90 (t, J = 7 Hz, 3H).

Methyl *N*-Isopropylcarbamate (4t).[7c] Reaction of isobutyramide **2t** (13 mg, 0.15 mmol) according to the general procedure afforded 13 mg (74%) of product **4t**, isolated as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.46 (br s, 1H), 3.80 (m, 1H), 3.65 (s, 3H), 1.15 (d, J = 6.5 Hz, 6H).

Methyl *N*-*tert*-Butylcarbamate (4u).[21] Reaction of trimethylacetamide **2u** (15 mg, 0.15 mmol) according to the general procedure afforded 14 mg (72%) of product **4u**, isolated as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.60 (br s, 1H), 3.62 (s, 3H), 1.32 (s, 9H).

Methyl *N*-Cyclohexylcarbamate (4v).[7c] Reaction of cyclohexanecarboxamide **2v** (10 mg, 0.075 mmol) according to the general procedure afforded 10 mg (85%) of product **4v**, isolated as colorless needles (recrystallized from dichloromethane−hexane): mp 74.6−75.2 °C (lit.[7c] mp 73.5−74.5 °C); IR (KBr) cm^{-1} 3346, 2934, 1695, 1538, 1229; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.53 (br s, 1H), 3.65 (s, 3H), 3.48 (br s, 1H), 1.98−1.86 (m, 2H), 1.75−1.65 (m, 2H), 1.64−1.56 (m, 1H), 1.40−1.28 (m, 2H), 1.22−1.06 (m, 3H).

Methyl *N*-(1-Adamantanyl)carbamate (4w).[7c] Reaction of 1-adamantanecarboxamide **2w** (13 mg, 0.075 mmol) according to the general procedure afforded 13 mg (83%) of product **4w**, isolated as colorless needles (recrystallized from dichloromethane−hexane): mp 118.4−118.9 °C (lit.[7c] mp 118−120 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.51 (br s, 1H), 3.61 (s, 3H), 2.08 (s, 3H), 1.93 (s, 6H), 1.67 (s, 6H).

***p*-Isocyanatotoluene (3a).** *N*-(4-Methylphenylsulfonyl)-iminophenyl-λ^3-iodane **1** (34 mg, 0.09 mmol) was added to a solution of *p*-toluamide **2a** (10 mg, 0.075 mmol) in dichloromethane (1.5 mL) and stirred at room temperature for 0.5 h. After completion of the reaction, the mixture was concentrated and separated by preparative TLC (hexane−ethyl acetate = 2: 1) to afford 8 mg (80%) of *p*-isocyanatotoluene **3a**, isolated as a brown oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.5 Hz, 2H), 2.33 (s, 3H). The obtained product is identical to a commercially available sample.

Isopropyl *N*-(4-Methylphenyl)carbamate (5a).[22] Reaction of *p*-toluamide **2a** (10 mg, 0.075 mmol) according to the general procedure with isopropanol instead of methanol afforded 13 mg (90%) of product **5a**, isolated as colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H), 6.46 (br s, 1H), 5.00 (sept, J = 6.2 Hz, 1H), 1.29 (d, J = 6.2 Hz, 6H).

***tert*-Butyl *N*-(4-Methylphenyl)carbamate (5b).**[23] Reaction of *p*-toluamide **2a** (10 mg, 0.075 mmol) according to the general procedure with 2-methyl-2-propanol instead of methanol afforded 11 mg (71%) of product **5b**, isolated as colorless needles (recrystallized from dichloromethane−hexane): mp 85.4−86 °C (lit.[23] mp 86 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, J = 8 Hz, 2H), 7.09 (d, J = 8 Hz, 2H), 6.37 (br s, 1H), 2.29 (s, 3H), 1.51 (s, 9H).

***p*-Toluidine (5c).**[24] *N*-(4-Methylphenylsulfonyl)iminophenyl-λ^3-iodane **1** (67 mg, 0.18 mmol) was added to a solution of *p*-toluamide **2a** (20 mg, 0.15 mmol) in dichloromethane (3 mL) and stirred at room temperature for 0.5 h. Then 10% HCl (3 mL) was added and the resulting reaction mixture stirred at 50 °C for 1 h. After completion of the reaction, the mixture was extracted with dichloromethane. The aqueous layer was treated with 20% NaOH, and then the mixture was extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate, concentrated, and then separated by preparative TLC (hexane−ethyl acetate, 3:1) to afford 14 mg (89%) of analytically pure *p*-toluidine **5c**, isolated as a brown solid (recrystallized from dichloromethane−hexane): mp 45.8−46.5 °C (lit.[24] mp 41−44 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (d, J = 8 Hz, 2H), 6.61 (d, J = 8 Hz, 2H), 3.56 (br s, 2H), 2.28 (s, 3H).

■ ASSOCIATED CONTENT

Supporting Information

Copies of NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For books and selected reviews on hypervalent iodine chemistry, see: (a) Varvoglis, A. *Hypervalent Iodine in Organic Synthesis*; Academic Press: London, 1997. (b) *Hypervalent Iodine Chemistry*; Wirth, T., Ed.; Springer-Verlag: Berlin, 2003. (c) Ochiai, M.; Miyamoto, K. *Eur. J. Org. Chem.* **2008**, 4229−4239. (d) Uyanik, M.; Ishihara, K. *Aldrichim. Acta* **2010**, *43*, 83−91. (e) Silva, J. L. F.; Olofsson, B. *Nat. Prod. Rep.* **2011**, *28*, 1722−1754. (f) Brand, J. P.; Gonzalez, D. F.; Nicolai, S.; Waser, J. *Chem. Commun.* **2011**, *47*, 102−115. (g) Yusubov, M. S.; Maskaev, A. V.; Zhdankin, V. V. *ARKIVOC* **2011**, *(i)*, 370−409. (h) Zhdankin, V. V. *J. Org. Chem.* **2011**, *76*, 5841−5851.

(2) (a) Zhang, L.-h.; Chung, J. C.; Costello, T. D.; Valvis, I.; Ma, P.; Kauffman, S.; Ward, R. *J. Org. Chem.* **1997**, *62*, 2466−2470. (b) Okamoto, N.; Miwa, Y.; Minami, H.; Takeda, K.; Yanada, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9693−9696. (c) Landsberg, D.; Kalesse, M. *Synlett* **2010**, 1104−1106. (d) Moriarty, R. M.; Chany, C. J. II; Vaid, R. K.; Prakash, O.; Tuladhar, S. M. *J. Org. Chem.* **1993**, *58*, 2478−2482.

(3) (a) Loudon, G. M.; Radhakrishna, A. S.; Almond, M. R.; Blodgett, J. K.; Boutin, R. H. *J. Org. Chem.* **1984**, *49*, 4272−4276. (b) Boutin, R. H.; Loudon, G. M. *J. Org. Chem.* **1984**, *49*, 4277−4284. (c) Hernandez, E.; Velez, J. M.; Vlaar, C. P. *Tetrahedron Lett.* **2007**, *48*, 8972−8975. (d) Davies, S. G.; Dixon, D. J. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1869−1876.

(4) (a) Moriarty, R. M.; Enache, L. A.; Zhao, L.; Gilardi, R.; Mattson, M. V.; Prakash, O. *J. Med. Chem.* **1998**, *41*, 468−477. (b) Liu, S. J.; Zhang, J. Z.; Tian, G. R.; Liu, P. *Synth. Commun.* **2005**, *36*, 823−827. (c) Della, E. W.; Head, N. J. *J. Org. Chem.* **1995**, *60*, 5303−5313. (d) Lazbin, I. M.; Koser, G. F. *J. Org. Chem.* **1986**, *51*, 2669−2671. (e) Vasudevan, A.; Koser, G. F. *J. Org. Chem.* **1988**, *53*, 5158−5160. (f) Lazbin, I. M.; Koser, G. F. *J. Org. Chem.* **1987**, *52*, 476−477.

(5) (a) Yusubov, M. S.; Funk, T. V.; Chi, K.-W.; Cha, E.-H.; Kim, G. H.; Kirschning, A.; Zhdankin, V. V. *J. Org. Chem.* **2008**, *73*, 295−297. (b) Tohma, H.; Maruyama, A.; Maeda, A.; Maegawa, T.; Dohi, T.; Shiro, M.; Morita, T.; Kita, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 3595−3598. (c) Liu, S. J.; Zhang, J. Z.; Tian, G. R.; Liu, P. *Synth. Commun.* **2005**, *36*, 823−827.

(6) (a) Dauban, P.; Dodd, R. H. *Synlett* **2003**, 1571−1586. (b) Chang, J. W. W.; Chan, P. W. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 1138−1140. (c) Li, C.; Zhang, L. *Org. Lett.* **2011**, *13*, 1738−1741. (d) Llaveria, J.; Beltran, A.; Diaz-Requejo, M. M.; Matheu, M. I.; Castillon, S.; Perez, P. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 7092−7095. (e) Yoshimura, A.; Nemykin, V. N.; Zhdankin, V. V. *Chem.—Eur. J.* **2011**, *17*, 10538−10541.

(7) (a) Barlin, G. B.; Pausacker, K. H.; Riggs, N. V. *J. Chem. Soc.* **1954**, 3122−3125. (b) Radhakrishna, A. S.; Parham, M. E.; Riggs, R. M.; Loudon, G. M. *J. Org. Chem.* **1979**, *44*, 1746−1747. (c) Zagulyaeva, A. A.; Banek, C. T.; Yusubov, M. S.; Zhdankin, V. V. *Org. Lett.* **2010**, *12*, 4644−4647.

(8) Takada, H.; Nishibayashi, Y.; Ohe, K.; Uemura, S.; Baird, C. P.; Sparey, T. J.; Taylor, P. C. *J. Org. Chem.* **1997**, *62*, 6512−6518.

(9) Crane, Z. D.; Nichols, P. J.; Sammakia, T.; Stengel, P. J. *J. Org. Chem.* **2011**, *76*, 277−280.

(10) Pandey, R. K.; Dagade, S. P.; Dongare, M. K.; Kumar, P. *Synth. Commun.* **2003**, *33*, 4019−4027.

(11) Fujisaki, S.; Tomiyasu, K.; Nishida, A.; Kajigaeshi, S. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1401−1403.

(12) Ito, Y.; Ushitora, H. *Tetrahedron* **2006**, *62*, 226−235.

(13) Gogoi, P.; Konwar, D. *Tetrahedron Lett.* **2007**, *48*, 531−533.

(14) Yang, Q.; Robertson, A.; Alper, H. *Org. Lett.* **2008**, *10*, 5079−5082.

(15) Davis, M. C. *Synth. Commun.* **2009**, *39*, 1100−1108.

(16) Singh, S. K.; Verma, M.; Singh, K. N. *Indian J. Chem., Sect. B Org. Chem. Incl. Med. Chem.* **2008**, *47B*, 1545−1548.

(17) Huang, X.; Keillor, J. W. *Tetrahedron Lett.* **1997**, *38*, 313−316.

(18) Wilshire, J. F. K. *Aust. J. Chem.* **1990**, *43*, 1817−1826.

(19) Miyabe, H.; Yamaoka, Y.; Takemoto, Y. *J. Org. Chem.* **2006**, *71*, 2099−2106.

(20) Hiegel, G. A.; Hogenauer, T. J. *Synth. Commun.* **2005**, *35*, 2091−2098.

(21) Hutchby, M.; Houlden, C. E.; Ford, J. G.; Tyler, S. N. G.; Gagne, M. R.; Lloyd-Jones, G. C.; Booker-Milburn, K. I. *Angew. Chem., Int. Ed.* **2009**, *48*, 8721−8724.

(22) Ghosh, R.; Nethaji, M.; Samuelson, A. G. *J. Organomet. Chem.* **2005**, *690*, 1282−1293.

(23) Xiong, T.; Li, Y.; Lv, Y.; Zhang, Q. *Chem. Commun.* **2010**, *46*, 6831−6833.

(24) Li, Y.; Zhu, X.; Meng, F.; Wan, Y. *Tetrahedron* **2011**, *67*, 5450−5454.