A Novel Addition–Rearrangement of *O*-(1-Benzotriazolylalkyl)oximes with Organolithium Reagents. Convenient Non-oxidative Conversions of Aldehydes into Amides

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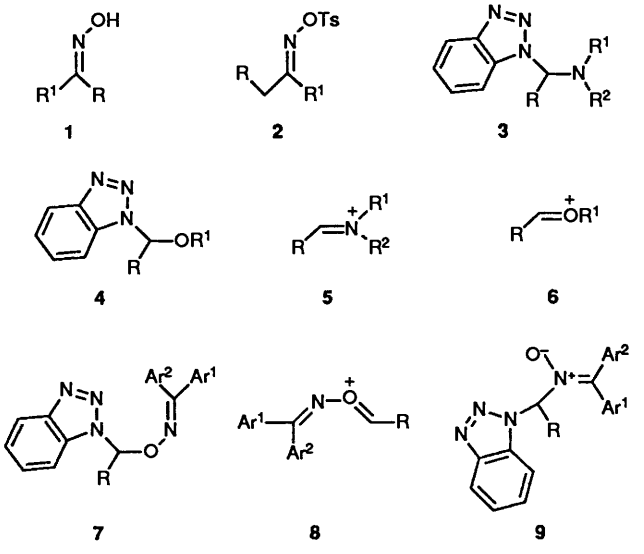
Condensation of an aldehyde, an oxime and benzotriazole gives an *O*-(1-benzotriazolylalkyl)oxime which undergoes an addition–rearrangement on treatment with an organolithium reagent. This reaction provides a novel non-oxidative method for the transformation of aldehydes into amides which has afforded several new *N*-monosubstituted amides with crowded structures. Grignard reactions of the *O*-(1-benzotriazolylalkyl)oximes give alcohols as the major products.

There are several well-known rearrangements of oxime derivatives, some of which constitute satisfactory syntheses. The Beckmann reaction[1] in which an oxime **1**, on successive treatment with an acid and water, gives a secondary amide is well known. In the Neber rearrangement an oxime arylsulfonate **2** is treated with base followed by acid hydrolysis to give an α-amino ketone.[2] The mechanisms of both rearrangements have been thoroughly studied and the leaving group OH_2 or OTs is considered to play a critical role. The substitution of the OH_2 by the migrating group to form an intermediate nitrilium salt in the Beckmann rearrangement and the loss of the OTs group to form a saturated nitrene in the Neber rearrangement are key steps. Few examples of oxime derivatives where a leaving group is at another position in the molecule have been reported.



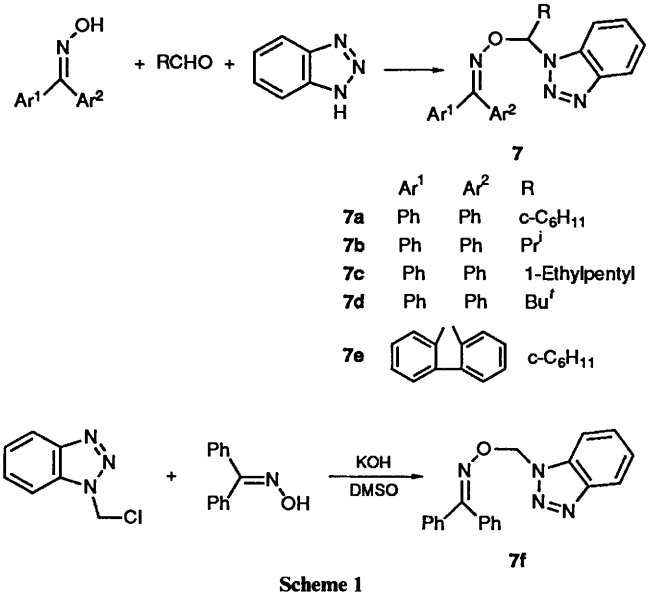
In this laboratory, benzotriazole has been widely exploited as a synthetic auxiliary.[3] The syntheses of Mannich-type derivatives **3** and **4** were achieved in excellent yields. The benzotriazole groups in **3** and **4** can be displaced easily either by reduction with hydride, or by reaction with organolithiums, Grignard reagents or zinc reagents (RLi, RMgBr or R_2Zn), leading to secondary or tertiary amines or to ethers, in high yields. The lone pair on the exocyclic nitrogen atom in **3** or on the oxygen atom in **4** assists in the departure of the benzotriazole anion giving a reactive cationic intermediate **5** or **6**, which is susceptible to nucleophilic addition to give a variety of useful organic compounds.

We now report new *O*-(1-benzotriazolylalkyl)oximes **7** and investigations of their reactions with organometallic reagents. Organolithiums in refluxing THF (tetrahydrofuran) gave unexpected addition–rearrangements which led to *N*-substituted amides **10**. Alkyl and vinyl Grignard reagents gave alcohols **12b–d** as the major products with small yields of products in which the benzotriazole group of **7** had been displaced by the alkyl group, *e.g.* **11a**.

Results and Discussion

Preparation of O-(1-*Benzotriazolylalkyl*)*oximes.* *O*-(1-Benzotriazolylalkyl)oximes **7a–e** were prepared in moderate to good yields by Mannich type condensations of an oxime, an aldehyde and benzotriazole in refluxing toluene containing a catalytic amount of toluenesulfonic acid. The solid *O*-(1-benzotriazolylalkyl)oximes were easily purified by recrystallization. Condensations of benzophenone oxime, benzotriazole and butanal or heptanal under the same conditions failed to yield the desired compounds and gave messy NMR spectra probably due to aldol condensations. Benzaldehyde was not sufficiently reactive to give the required oxime ether. Oxime derivative **7f** was prepared in a high yield from benzotriazol-1-ylmethyl chloride and benzophenone oxime anion in DMSO (dimethyl sulfoxide) (Scheme 1).

The crystalline *O*-(1-benzotriazolylalkyl)oximes were



	Ar^1	Ar^2	R
7a	Ph	Ph	c-C_6H_{11}
7b	Ph	Ph	Pr^i
7c	Ph	Ph	1-Ethylpentyl
7d	Ph	Ph	Bu^t
7e			c-C_6H_{11}

Scheme 1

Table 1 Preparation of *O*-(1-benzotriazolylalkyl)oximes

Compound	Yield (%)	Molecular formula	M.p. (°C) (solvent)	Found (%) (Requires) C	H	N
7a	65	$C_{26}H_{26}N_4O$	164.5–165.5 (ethyl acetate)	76.1 (76.07)	6.35 (6.38)	13.7 (13.65)
7b	52	$C_{23}H_{22}N_4O$	139.5–140.5 (ethyl acetate)	74.2 (74.57)	5.95 (5.99)	14.75 (15.12)
7c	60	$C_{28}H_{30}N_4O$	81–81.5 (hexane)	75.8 (76.03)	7.15 (7.09)	12.95 (13.13)
7d	45	$C_{24}H_{24}N_4O$	160.0–161.0 (ethyl acetate)	74.65 (74.97)	6.25 (6.29)	14.7 (14.69)
7e	55	$C_{26}H_{24}N_4O$	188–187 (ethanol)	76.4 (76.45)	5.9 (5.92)	13.75 (13.72)
7f	83	$C_{20}H_{16}N_4O$	145.0–146.0 (ethyl acetate)	73.0 (73.15)	4.9 (4.91)	17.2 (17.06)

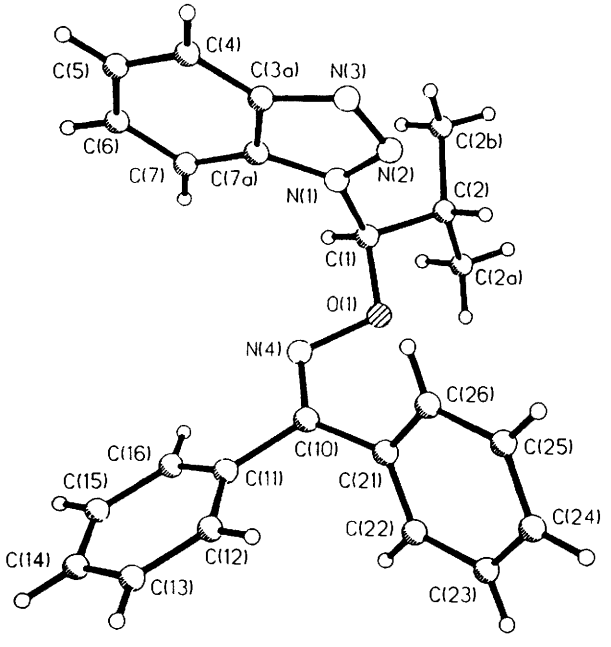
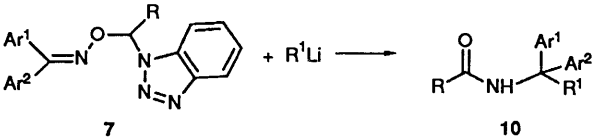


Fig. 1 Solid state molecular conformation of **7b**, with atom labelling

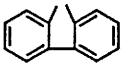
characterized by their NMR spectra and elemental analyses. The X-ray crystal structure of **7b** is shown in Fig. 1. This was determined to confirm the structure of compounds **7**, and particularly to exclude the possible isomeric structures **9**.

In the NMR spectra, the CH groups adjacent to the oxygen atoms displayed strongly deshielded signals (6.50–6.60 ppm for the protons and 94.8–99.8 ppm for the carbon atoms). The two CH_3 doublets in **7b** appeared at 0.74 and 1.17 ppm. This unusually large separation could be rationalized from Fig. 1. One methyl group is deshielded by the benzotriazole ring; the steric hindrance from the two phenyl rings and the benzotriazole group prevent rotation of the isopropyl group. The characteristic C=N signals in the ^{13}C NMR spectra were at 154–160 ppm. The ^{13}C NMR signals of the two phenyl groups in each of the *O*-(1-benzotriazolylalkyl)oximes **7** are different. Again, one ring is clearly more deshielded by the benzotriazole group than the other. Some of the signals of the aliphatic carbons, for example in **7c**, are also doubled.

Reactions of O-(1-*Benzotriazolylalkyl*)*oximes with Organolithium Reagents*.—The reactions of *O*-(1-benzotriazolylalkyl)-oximes with organolithium reagents were carried out in THF. Two equivalents of an alkyl- or aryl-lithium were found essential for the complete transformation of *O*-(1-benzotriazolylalkyl)oximes into amides. The use of one equivalent of an organolithium reagent led to a 50% recovery of the starting material. The products formed depended on the R group in *O*-(1-benzotriazolylalkyl)oximes **7**. When R was secondary, **7a–c** and **7e**, they underwent very clean addition–rearrangements to give exclusively *N*-monosubstituted amides **10a–g**, Scheme 2.



7 **10**

	Ar^1	Ar^2	R^1	R
10a	Ph	Ph	Bu	c-C_6H_{11}
10b	Ph	Ph	Me	c-C_6H_{11}
10c	Ph	Ph	Bu	Pr^i
10d	Ph	Ph	Me	Pr^i
10e	Ph	Ph	Ph	Pr^i
10f	Ph	Ph	Bu^s	Pr^i
10g	Ph	Ph	Me	3-Heptyl
10h	Ph	Ph	H	H
10i			Bu	c-C_6H_{11}

Scheme 2

When R=H **7f**, the reaction gave the amide **10h** as the major product with a significant amount of a by-product of structure $Ph_2C{=}NH$ **13** (benzophenone imine). It showed a strong carbon signal at 178 ppm for the imine carbon atom and a broad proton signal at 9.37 ppm for the =NH in the crude product. Benzophenone imine was prepared by a literature method [4] and its NMR spectra showed these two characteristic signals confirming the presence of this imine as a by-product in the reaction. With a tertiary R, **7d**, no amide was found in the reaction mixture and the NMR spectra showed only aromatic signals and the carbon signal at 178 ppm in the ^{13}C NMR spectrum.

The structures of the new amides were assigned from the following evidence. The high resolution mass spectrum of compound **10a** gave a strong molecular peak for $C_{24}H_{31}NO$ of 349.2411 (required 349.2409). The base peak 222.1410 ($C_{17}H_{18}$) was formed by McLafferty rearrangement. The other two strong peaks 292.1701 ($C_{20}H_{22}N$) and 182.0962 ($C_{13}H_{12}N$) were formed by loss of the C_4H_9 fragment from the molecular ion and by further loss of a cyclohexylcarboxyl fragment. The infrared spectrum showed a band at 3440 cm^{-1} for NH and a strong band at 1680 cm^{-1} for amide C=O. Some aspects of the NMR spectra of the amides are worthy of note. The quaternary carbons adjacent to the nitrogen atom are usually at 60–70 ppm,

Table 2 Preparation of *N*-monosubstituted amides

Compound	Yield (%)	Molecular formula	M.p. (°C)	Solvent for recrystallization	Found (%) (Required) C	H	N
10a	93	$C_{24}H_{31}NO$	188.0–190.0	hexane–ethyl acetate	81.9 (82.49)	8.85 (8.94)	3.85 (4.01)
10b	95	$C_{21}H_{25}NO$	144.0–145.5	hexane–ethyl acetate	81.7 (82.04)	8.3 (8.20)	4.5 (4.56)
10c	90	$C_{21}H_{27}NO$	134.0–135.0	hexane–ethyl acetate	81.4 (81.51)	8.9 (8.79)	4.45 (4.53)
10d	87	$C_{18}H_{21}NO$	148.5–149.5	hexane–ethyl acetate	80.75 (80.86)	8.1 (7.92)	5.2 (5.24)
10e	82	$C_{23}H_{23}NO$	194.0–194.5[a]	hexane–ethyl acetate	84.25 (83.85)	7.1 (7.04)	4.1 (4.25)
10f	78	$C_{21}H_{27}NO$	150.0–151.0	hexane–ethyl acetate	81.3 (81.51)	8.8 (8.79)	4.35 (4.53)
10g	75	$C_{25}H_{35}NO$	71.0–74.5	hexane	81.55 (81.69)	8.7 (9.04)	4.4 (4.33)
10h	55	$C_{14}H_{13}NO$	1345.5–135.5[b]	hexane–ethyl acetate	79.65 (79.59)	6.2 (6.20)	6.45 (6.63)
10i	58	$C_{24}H_{29}NO$	235–236	ethyl acetate	82.5 (82.90)	8.3 (8.41)	3.90 (4.03)

[a] Lit.,[5] m.p. 192 °C. [b] Lit.,[6] m.p. 134 °C.

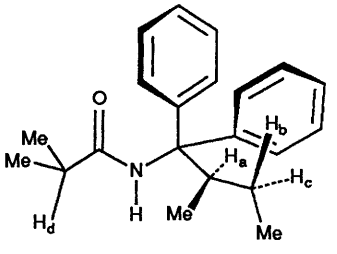


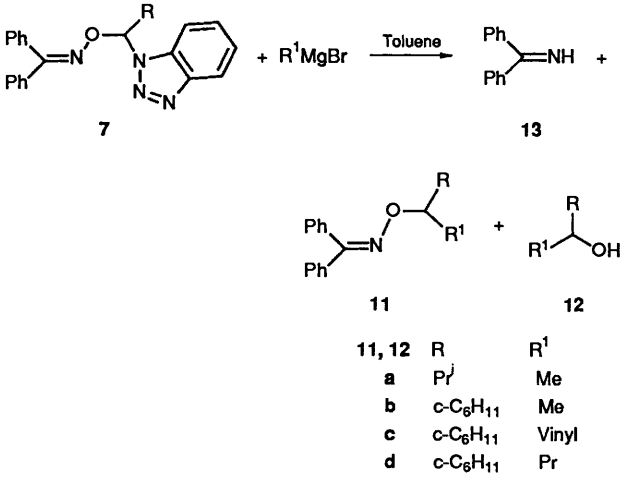
Fig. 2

however, the quaternary carbon signal of the fluorene group in **10i** appeared at much lower field (106.5 ppm). The NH proton is at 6.10–6.60 ppm and the carbonyl carbon at 174–176 ppm. Because of the crowded structures, the CH_2 protons (C-1 of the butyl group) in **10a**, **10c** and **10i** close to a phenyl ring are deshielded and show complex multiplets. The ^1H NMR spectrum of the new amide **10f** was carefully assigned by the spin–spin decoupling method. The two protons of the CH_2 group resonated separately at 0.45 ppm (H_b) and 1.65 ppm (H_c) respectively and irradiation of either of them caused the two doublets of the terminal methyl group to collapse to one doublet. H_a appeared as a one proton multiplet at 3.30 ppm and when it was irradiated the doublet of the methyl group at 0.87 ppm collapsed to a singlet. Even the methyls of the isopropyl group were magnetically non-equivalent and resonated as two doublets at 1.06 ppm. Irradiation of the heptet at 2.20 ppm caused this to collapse to two singlets at 1.02 and 1.08 ppm.

The locations of H_a at an unusually low field (3.30 ppm) and of H_b at an abnormally high field (0.45 ppm) let us deduce the conformation of **10f** (see Fig. 2).

This orientation of the CH and CH_2 groups exists because the two bigger CH_3 groups rotate away from the phenyl rings. The compound also shows two distinct sets of four aromatic carbon signals.

Grignard Reactions of O-(1-*Benzotriazolylalkyl*)*oximes*.—The Grignard reactions of *O*-(1-benzotriazolylalkyl)oximes were more complicated than expected. After attempted reactions of **7b** with methylmagnesium iodide or phenylmagnesium bromide in THF at room temperature or at reflux for 24 h the starting material was recovered unchanged. Reactions of methylmagnesium iodide with **7b** in refluxing toluene gave only 12% of *O*-alkyloxime **11a**, the rest of the material was probably 1,2-dimethylpropanol **12a** which evaporated with the toluene during work-up. After reaction of oxime **7a** with methylmagnesium iodide, or vinyl- or propyl-magnesium bromide small amounts of the *O*-alkyloximes **11b–d** could be detected in the crude NMR spectra, but the isolated products (*ca.* 70% in each case) proved to be the alcohols **12b–d**. They were identical with authentic samples prepared from cyclohexanecarbaldehyde and the respective Grignard reagents. The proton signals and the carbon signals of the CH groups adjacent to the oxygen atoms in **11** and **12** were different. The smaller signals of **11** in the crude products were at 79–84 ppm in the ^{13}C NMR spectra and at about 4.10–4.30 ppm in ^1H NMR spectra. In contrast, the carbon signals of the alcohols **12** were found below 78 ppm and the proton signals were at about 3.5 ppm. The ratios of **11** to **12** could be calculated based on the integration of these two proton signals and were about 1 to 5 in each case. The crude products also showed strong signals at *ca.* 178 ppm in the ^{13}C NMR spectra which were probably due to $Ph_2C{=}NH$ **13** as mentioned above. Compound **7f**, derived from formaldehyde, failed to react with either methylmagnesium iodide or phenylmagnesium bromide in refluxing toluene over two days.



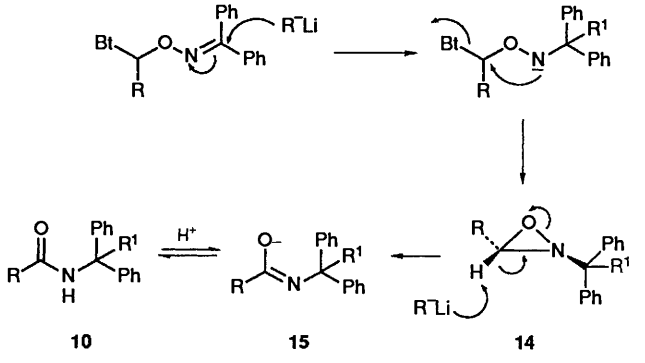
11, 12	R	R^1
a	Pr^i	Me
b	c-C_6H_{11}	Me
c	c-C_6H_{11}	Vinyl
d	c-C_6H_{11}	Pr

Scheme 3

O-(1,2-Dimethylpropyl)benzophenone oxime **11a** obtained from the reaction of **7b** with methylmagnesium iodide was

isolated (12%) and its structure established by the NMR spectroscopic data and the mass spectrum. The high resolution mass spectrum gave a strong molecular ion ($C_{18}H_{21}NO$) at 267.1623 (required 267.1622) and a signal at 155 ppm in the ^{13}C NMR spectrum is reasonable for the C=N carbon signal. The alcohols **12b–d** were isolated by distillation from reactions of **7a** with methylmagnesium iodide, vinyl-and propyl-magnesium bromide, respectively. Their spectra were identical with those of the corresponding alcohols obtained from reactions of cyclohexanecarbaldehyde with methylmagnesium iodide and vinyl- and propyl-magnesium bromide.[7]

The proposed mechanism for the addition–rearrangement reaction is shown in Scheme 4. Nucleophilic addition of an



Scheme 4

organolithium reagent to the C=N bond gives a nitrogen anion which causes an intramolecular nucleophilic substitution to displace the benzotriazole to give an oxaziridine **14**. The second molecule of the organolithium reagent acts as a base to deprotonate the oxazoline ring which opens *via* the imide **15** to the amide. Grignard reagents are apparently not powerful enough to attack the hindered C=N bond. Several recent papers describe the addition of organolithium reagents to oxime C=N bonds.[8] The formation of amides in the present work is facilitated by the easy displacement of the benzotriazole group. The mechanism of formation of *O*-alkyloximes **11** in Grignard reactions is probably *via* the intermediate **8** based on the fact that the reaction needs assistance from the isopropyl group at the carbon atom adjacent to the oxygen in **7b**. Easy rupture of the N–O bond (bond strength[9] 48 kcal mol^{-1})* is the possible reason for the formation of alcohols **12**.

In conclusion, although Grignard reactions of *O*-(1-benzotriazolylalkyl)oximes afforded alcohols which are better available directly from the corresponding aldehydes and Grignard reagents, a new addition–rearrangement reaction with organolithium reagents has been discovered which produces amides. This provides a mild, non-oxidative route from aldehydes to amides in which the carbon attached to the amide nitrogen is tertiary.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Varian VXR 300 MHz spectrometer in $CDCl_3$ using $(CH_3)_4Si$ as an internal reference for ^1H spectra and $CDCl_3$ for ^{13}C NMR spectra, *J* values are given in Hz. Elemental analyses were performed at the University of Florida. THF and toluene were freshly distilled from sodium–benzophenone ketyl immediately before use.

Representative Procedure for the Preparation of O-(1-*Benzotriazolylalkyl*)*oximes.*—O-(1-*Benzotriazol*-1-*yl*-1-*cyclohexyl*-*methyl*)*benzophenone oxime* **7a**. A mixture of cyclohexanecarbaldehyde (8.7 g, 77.7 mmol), benzotriazole (9.1 g, 76.5 mmol) and toluenesulfonic acid (0.5 g) was stirred overnight in toluene (150 cm^3). Benzophenone oxime (15 g, 76.5 mmol) in toluene (75 cm^3) was added and the mixture refluxed under a Dean–Stark trap for 24 h. The solvent was removed under vacuum and ether (100 cm^3) was added. The mixture was refrigerated for 10 h and the substituted oxime collected in a 65% yield; δ_H 1.02–1.29 (m, 6 H), 1.60–1.77 (m, 3 H), 2.03–2.38 (m, 2 H), 6.53 (d, *J* 9.5, 1 H), 7.15–7.52 (m, 13 H) and 8.06 (d, *J* 7.0, 1 H); δ_C 25.22, 25.91, 28.02, 29.03, 40.12, 96.10, 11.20, 119.77, 123.84, 127.00, 127.89, 127.95, 128.06, 128.92, 128.96, 129.76, 132.12, 132.58, 135.18, 146.31 and 159.60. Other data are shown in Table 1.

Similarly prepared were the following.

O-(1-*Benzotriazol*-1-*yl*-2-*methylpropyl*)*benzophenone oxime* **7b**. δ_H 0.74 (d, *J* 6.5, 3 H), 1.17 (d, *J* 6.5, 3 H), 2.70 (m, 1 H), 6.45 (d, *J* 9.0, 1 H), 7.16–7.50 (m, 13 H) and 8.05 (d, *J* 7.0, 1 H); δ_C 18.04, 18.82, 31.50, 97.04, 111.20, 119.79, 123.85, 127.03, 127.89, 127.95, 128.08, 128.89, 128.97, 129.80, 132.02, 132.56, 135.11, 146.32 and 159.65.

O-(1-*Benzotriazol*-1-*yl*-2-*ethylhexyl*)*benzophenone oxime* **7c**. δ_H 0.72 (m, 3 H), 0.85–1.35 (m, 9 H), 1.62 (m, 2 H), 2.42 (m, 1 H), 6.65 (dd, 1 H), 7.20–7.50 (m, 13 H) and 8.08 (m, 1 H); δ_C 9.93, 9.97, 13.69, 13.91, 21.46, 21.51, 22.50, 22.89, 27.60, 27.89, 28.15, 41.36, 41.43, 94.73, 94.83, 111.20, 111.26, 119.74, 123.96, 125.55, 127.10, 128.08, 128.00, 128.78, 128.00, 128.94, 129.80, 132.16, 132.22, 132.65, 135.02, 135.05, 146.20 and 159.74.

O-(1-*Benzotriazol*-1-*yl*-2,2-*dimethylpropyl*)*benzophenone oxime* **7d**, δ_H 1.03 (s, 9 H), 6.60 (s, 1 H), 7.15–7.40 (m, 10 H), 7.50 (m, 3 H) and 8.03 (m, 1 H); δ_C 26.04, 37.33, 99.80, 112.32, 119.48, 123.55, 126.85, 127.89, 127.97, 128.09, 129.04, 129.18, 129.87, 132.56, 132.69, 134.87, 145.84 and 159.97.

O-(*Benzotriazol*-1-*ylcyclohexylmethyl*)*fluorenone oxime* **7e**. δ_H 1.20 (m, 4 H), 1.40 (m, 2 H), 1.70 (m, 2 H), 1.85 (m, 1 H), 2.35 (m, 1 H), 2.85 (m, 1 H), 6.60 (d, *J* 9.5, 1 H), 7.05–7.55 (m, 11 H), 7.85 (d, *J* 7.5, 1 H), 8.05 (d, *J* 7.0) and 8.35 (d, *J* 7.0); δ_C 25.17, 25.27, 25.88, 28.10, 29.33, 40.05, 95.35, 110.76, 119.68, 119.84, 119.90, 121.84, 123.92, 127.39, 127.77, 128.22, 129.16, 129.99, 130.28, 131.43, 132.56, 134.64, 140.18, 141.65, 146.19 and 154.00.

O-(*Benzotriazol*-1-*ylmethyl*)*benzophenone oxime* **7f**. A mixture of benzophenone oxime (10.0 g, 51 mmol) in DMSO (100 cm^3) and NaOH (4.0 g, 100 mmol) in water (50 cm^3) was heated in an oil bath maintained at 60 °C for 30 min. Benzotriazolylmethyl chloride (8.5 g, 51 mmol) in DMSO (20 cm^3) was added and stirring continued at 60 °C for 5 h. The mixture was poured onto ice and the product collected and recrystallized (ethanol–ethyl acetate) to give a white solid (85%); δ_H 6.5 (s, 2 H), 7.05–7.55 (m, 12 H), 7.80 (d, *J* 9.0) and 8.06 (d, *J* 7.0, 1 H); δ_C 78.86, 127.95, 128.11, 128.22, 129.05, 129.86, 132.18, 133.10, 135.14, 110.53, 119.70, 124.07, 127.61, 132.18, 146.11 and 159.88.

Representative Procedure for the Preparation of N-*Monosubstituted Amides.*—N-(1,1-*Diphenylpentyl*)*cyclohexanecarboxamide* **10a**. Butyllithium (2.5 mol dm^{-3}; 4.5 cm^3, 11.2 mmol) was added to a solution of *O*-(1-benzotriazol-1-yl-1-cyclohexylmethyl)benzophenone oxime **7a** (2.0 g, 4.90 mmol) in THF (80 cm^3) over 2 min under argon at −78 °C. The solution was stirred, allowed to warm to room temperature over *ca.* 2 h and refluxed for 2 h. The product was quenched with water (30 cm^3) and diluted with diethyl ether (80 cm^3). The organic layer was washed with 3 mol dm^{-3} NaOH (30 cm^3 × 2), dried ($MgSO_4$) and the solvent removed to give the amide; δ_H 0.83 (t, *J* 7.0, 3 H), 1.10–1.90 (m, 14 H), 2.15 (m, 1 H), 2.63 (m, 2 H), 6.20 (s, 1 H) and 7.15–7.35 (m, 10 H); δ_C 14.08, 22.82, 25.70, 26.48, 29.76, 37.07, 46.25, 64.30, 126.34, 126.53, 128.10, 145.63 and 174.62. Other data are shown in the Table 2.

* 1 cal = 4.184 J.

Table 3 Atomic coordinates ($\times 10^4$)

Atom	*x*	*y*	*z*
N(1)	1076(4)	778(1)	5000[a]
N(2)	1027(4)	859(1)	7103(19)
N(3)	629(4)	743(2)	8269(22)
C(3A)	422(4)	580(2)	6904(23)
C(4)	−4(4)	415(2)	7311(23)
C(5)	−126(4)	279(2)	5620(26)
C(6)	175(5)	297(2)	3527(26)
C(7)	608(5)	456(2)	3088(23)
C(7A)	723(4)	598(2)	4827(24)
C(1)	1521(4)	875(2)	3338(21)
C(2)	1466(4)	1110(1)	3273(22)
C(2A)	1889(4)	1196(2)	1308(22)
C(2B)	754(4)	1180(2)	2911(24)
O(1)	2175(3)	827(1)	4006(18)
N(4)	2296(3)	612(1)	3441(21)
C(10)	2826(5)	553(2)	4381(23)
C(11)	3048(4)	334(2)	3728(22)
C(12)	3430(4)	220(2)	5251(24)
C(13)	3626(5)	15(2)	4688(24)
C(14)	3450(4)	−70(2)	2596(25)
C(15)	3080(4)	43(2)	1113(24)
C(16)	2891(4)	247(2)	1670(23)
C(21)	3230(4)	677(1)	5991(22)
C(22)	3872(4)	713(1)	5444(22)
C(23)	4270(5)	816(2)	6989(21)
C(24)	4029(4)	878(2)	9035(23)
C(25)	3381(5)	844(2)	9589(24)
C(26)	2971(4)	743(2)	8015(22)

[a] Origin defining coordinate.

N-(1,1-*Diphenylethyl*)*cyclohexanecarboxamide* **10b**. δ_H 1.15–2.15 (m, 11 H), 2.20 (s, 3 H), 6.13 (s, 1 H) and 7.15–7.35 (m, 10 H); δ_C 25.58, 29.58, 27.36, 45.94, 61.73, 126.26, 126.77, 128.17, 146.17 and 174.74.

N-(1,1-*Diphenylpentyl*)*isobutanamide* **10c**. δ_H 0.83 (t, *J* 7.0, 3 H), 1.08–1.22 (m, 8 H), 1.32 (m, 2 H), 2.41 (m, 1 H), 2.65 (m, 2 H), 6.12 (s, 1 H) and 7.15–7.35 (m, 10 H); δ_C 14.08, 19.63, 22.83, 26.49, 36.37, 37.15, 64.35, 126.36 126.57, 128.11, 145.59 and 175.45.

N-(1,1-*Diphenylethyl*)*isobutanamide* **10d**. δ_H 1.15 (d, *J* 7.0, 6 H), 2.21 (s, 3 H), 2.37 (m, 1 H), 6.12 (s, 1 H) and 7.20–7.35 (m, 10 H); δ_C 19.65, 27.44, 36.30, 61.96, 126.39, 128.98, 128.36, 146.30 and 175.35.

N-(*Triphenylmethyl*)*isobutanamide* **10e**. δ_H 1.13 (m, 6 H), 2.42 (m, 1 H), 6.57 (s, 1 H) and 7.13–7.45 (m, 15 H); δ_C 19.52, 36.45, 69.96, 69.99, 126.88, 127.85, 128.56, 144.82 and 175.38.

N-(1,1-*Diphenyl*-2-*methylbutyl*)*isobutanamide* **10f**. δ_H 0.45 (m, 1 H), 0.87 (d, *J* 7.0, 3 H), 0.95 (dd, *J* 7.0, 3 H), 1.06 (dd, *J* 7.0, 6 H), 1.65 (m, 1 H), 2.20 (m, 1 H), 3.30 (m, 1 H), 6.08 (s, 1 H) and 7.20–7.40 (m, 10 H); δ_C 12.40, 14.48, 19.40, 19.42, 25.68, 36.40, 38.61, 68.54, 126.68, 126.78, 127.30, 127.36, 128.45, 128.50, 142.65, 143.40 and 175.14.

N-(1,1-*Diphenylethyl*)-2-*ethylhexanamide* **10g**. δ_H 0.78–1.60 (m, 20 H), 1.98 (m, 1 H), 2.65 (m, 2 H), 6.10 (s, 1 H) and 7.15–7.35 (m, 10 H); δ_C 12.15, 13.94, 14.00, 22.75, 22.94, 26.16, 26.51, 29.81, 32.62, 37.31, 50.40, 64.75, 126.59, 126.69, 127.96, 145.57, 145.61 and 174.62.

N-(*Diphenylmethyl*)*formamide* **10h**. δ_H 6.23 (d, *J* 8.5, 1 H), 6.85 (b, 1 H), 7.15–7.40 (m, 10 H) and 8.10 (s, 1 H); δ_C 55.57, 127.28, 127.46, 128.57, 140.83 and 160.37.

N-(9-*Butylfluoren*-9-*yl*)*cyclohexanecarboxamide* **10i**. δ_H 0.70–1.85 (m, 18 H), 2.0 (m, 1 H), 2.35 (m, 2 H), 5.85 (s, 1 H), 7.25–7.40 (m, 4 H) and 7.50–7.75 (m, 4 H); δ_C 13.8, 22.68, 25.65, 29.64, 37.81, 45.80, 66.82, 106.50, 119.82, 123.35, 127.71, 128.22, 140.02, 148.10 and 175.45.

Representative Procedure for the Grignard Reactions of **7**.—O-(1,2-*Dimethylpropylbenzophenone oxime* **11a**. MeMgI (16.5 mmol) in ether (40 cm^3) was dropped into a solution of *O*-(1-benzotriazol-1-yl-2-methylpropyl)benzophenone oxime **7b** (1.5 g, 4 mmol) in toluene (60 cm^3) at room temperature. After most of the ether had been removed by distillation on an oil bath (80 °C), the solution was refluxed overnight. The product was quenched with water (10 cm^3) and extracted with diethyl ether (40 cm^3 × 2). The organic layer was washed with 3 mol dm^{-3} NaOH (2 × 20 cm^3), dried ($MgSO_4$), the solvent removed and the residue purified *via* a silica gel column eluted with chloroform to give *O*-(1,2-dimethylpropyl)benzophenone oxime as an oil (0.13 g, 12%) (Found: M^+, 267.1622. $C_{18}H_{21}NO$ requires *M*, 267.1623); δ_H 0.87 (dd, 6 H), 1.21 (d, *J* 6.5, 3 H), 1.90 (m, 1 H), 4.13 (m, 1 H) and 7.18–1.18 (m, 10 H); δ_C 16.81, 16.61, 18.59, 32.20, 84.52, 127.76, 128.07, 128.21, 128.38, 128.81, 129.40, 133.68, 137.07 and 155.42.

1-*Cyclohexylethanol* **12b**. Obtained from the reaction of **7a** with methylmagnesium iodide in 75% yield. Purified by distillation (b.p. 71–74 °C/5 mmHg); δ_H 0.90–1.35, 1.62–1.92 (m, 14 H), 2.30 (br s, 1 H) and 3.55 (m, 1 H); δ_C 20.28, 26.53, 26.24, 26.16, 28.66, 28.45, 45.11 and 72.05.

1-*Cyclohexylallyl alcohol* **12c**. Obtained from the reaction of **7a** with vinylmagnesium bromide in 70% yield. Purified by distillation (b.p. 73–76 °C/3 mmHg); δ_H 0.85–1.95 (m, 6 H), 2.05–1.90 (m, 5 H), 2.05 (br s, 1 H), 3.82 (dd, 1 H), 5.15 (m, 2 H) and 5.85 (m, 1 H); δ_C 26.00, 26.05, 26.43, 28.30, 28.63, 43.35, 77.60, 115.27 and 139.75.

1-*Cyclohexylbutan*-1-*ol* **12d**. Obtained from the reaction of **7a** with propylmagnesium bromide in 70% yield. Purified by distillation (b.p. 79–82 °C/3 mmHg); δ_H 0.88 (t, *J* 7.0, 3 H), 0.90–1.85 (m, 15 H), 3.0 (br s, 1 H) and 3.35 (m, 1 H); δ_C 13.98, 18.98, 26.11, 26.26, 26.44, 27.65, 29.11, 36.13, 43.48 and 75.68.

Benzophenone imine **13**. Obtained in the reaction of **7a** with propylmagnesium bromide in 60% yield. Purified by distillation (b.p. 130–132 °C/1 mmHg) (lit.,[4] b.p. 137 °C/0.5 mmHg). Repeating the literature preparation[4] gave a product (65% yield) with identical spectra; δ_H 7.25–7.80 (m, 5 H) and 9.37 (br, 1 H); δ_C 127.71, 127.80, 129.28, 138.70 and 177.70.

X-Ray Crystal Structure Determination.—Crystal data. $C_{23}H_{22}N_4O$, FW = 370.4. Orthorhombic, a = 20.718(14), b = 63.84(4), c = 5.935(5) Å, V = 7898(9) $Å^3$ (by least-squares refinement on 25 accurately centred reflections with $2\theta > 13°$, λ = 0.7107 Å) at −80 °C. Space group *F*dd2, Z = 16, D_x = 1.246 g cm^{-3}. Crystal dimensions 0.60 × 0.16 × 0.04 mm, μ (Mo-Kα) = 0.74 cm^{-1}, $F(000)$ = 3136.

Data collection and processing.[10] Nicolet R3m four-circle diffractometer, $\omega/2\theta$ scan mode ($1.5 \leqslant \theta \leqslant 28°$, $+h$, k, l), graphite-monochromated Mo-Kα radiation; 2006 unique reflections measured at −80 °C, giving 806 with $I > 2.5\sigma(I)$. No absorption correction or crystal decay.

Structure solution and refinement. Direct methods gave all non-hydrogen atoms. Full-matrix least-squared refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions with isotropic temperature factors. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$, with $w = [\sigma^2(F_o) + 0.0005F_o^2]^{-1}$. Final R and R_w values are 0.051 and 0.048 with S = 1.06. Final difference map features < 0.26 e $Å^{-3}$. For programs and computers see reference.[10] Final non-hydrogen atom coordinates are given in Table 3. Hydrogen atom coordinates, bond lengths and angles and thermal parameters have been deposited at the CCDC.* There are no unusual features in the bonding geometry or molecular packing.

* For details of the Cambridge Crystallographic Data Centre deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1992, Issue 1.

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