

**IMIDOYLBENZOTRIAZOLES : STABLE ALTERNATIVES
TO IMIDOYL CHLORIDES**

Alan R. Katritzky*, Christian V. Stevens, Gui-Fen Zhang, and Jinlong Jiang

University of Florida, Department of Chemistry,
Center for Heterocyclic Compounds
P.O. Box 117200, Gainesville, FL 32611-7200, U.S.A.

Norbert De Kimpe[†]

Laboratory for Organic Chemistry, Faculty of Agricultural and
Applied Biological Sciences, University of Gent,
Coupure Links 653, 9000 Gent, Belgium

Dedicated with admiration and affection on his 75th anniversary to Rolf Huisgen whose achievements have been an inspiration to us all.

Abstract – Imidoylbenzotriazoles were prepared from the corresponding amides and 1,1'-sulfinyldibenzotriazole, generated *in situ* from 1-trimethylsilylbenzotriazole and thionyl chloride. The imidoylbenzotriazoles are stable precursors for the synthesis of imidates and thioimidates.

Imidoyl chlorides are useful and versatile intermediates in organic synthesis.¹ They are precursors for the synthesis of a multitude of functional groups such as imidates,² thioimidates,³ amidines,⁴ imidoyl cyanides,⁵ alkylated imines⁶ *etc.* Imidoyl chlorides are generally prepared *in situ* by treatment of the corresponding amides with phosgene, diphosgene, oxalyl dichloride, phosphorus pentachloride, phosphorus trichloride or arylphosphorane chlorides.^{1a} Although the preparation of imidoyl chlorides normally provides good yields, side-reactions such as self-condensation have been reported at elevated temperatures if α -CH groups are

present in the imidoyl chloride.⁷ A major disadvantage in the use of imidoyl chlorides is their extreme lability towards hydrolysis. Therefore, imidoyl chlorides are seldom isolated or purified.

We previously⁸ described the preparation of a series of 1-imidoylbenzotriazoles (**4**) and called attention to their potential use as stable substitutes for imidoyl chlorides. The imidoylbenzotriazoles (**4**) were previously obtained by treatment of secondary amides with phosphorus oxychloride in the presence of triethylamine and trapping of the intermediate imidoyl chlorides by benzotriazole.⁸ This method gave good results for imidoylbenzotriazoles with aromatic substituents on nitrogen. We now describe a method which is more general and allows the synthesis of *N*-alkyl substituted imidoylbenzotriazoles. We have now studied the reactions of **4** with sodium alkoxides and sodium thiolates (Scheme 2).

RESULTS AND DISCUSSION

Preparation of 1,1'-sulfinyldibenzotriazole (2) *in situ* for the preparation of imidoylbenzotriazoles (4). 1,1'-Sulfinyldiimidazole as an imidazole transfer reagent has recently been reviewed.⁹ 1,1'-Sulfonyldibenzotriazole has also shown to be a versatile reagent for the dehydration of aldoximes and amides to nitriles.¹⁰ However, the analogue 1,1'-sulfinyldibenzotriazole (**2**) has not been previously reported. We now describe the preparation *in situ* of reagent (**2**) and its use as a benzotriazole transfer reagent for the conversion of amides to imidoylbenzotriazoles (**4**).

1,1'-Sulfinyldibenzotriazole (**2**) was prepared from 1-trimethylsilylbenzotriazole and thionyl chloride at 0-20 °C in tetrahydrofuran; its structure was supported by nmr data. It is stable in THF solution under an anhydrous atmosphere but is decomposed instantaneously to benzotriazole by water. In all cases, we used the solution of 1,1'-sulfinyldibenzotriazole (**2**) directly for the next step.

Imidoylbenzotriazoles (**4**) were prepared from amides and 1,1'-sulfinyldibenzotriazole (**2**) at 20 °C (Scheme 1). The mechanism for the formation of **4** probably involves intermediates such as **3** which are similar to those found in the reaction of amides with phosphorus halides. Dissociation of 1,1'-sulfinyldibenzotriazole leads to the formation of the benzotriazolylsulfonium cation which adds to the amido oxygen. Consequently, benzotriazolate attacks the imonium function of **3** with subsequent elimination of the benzotriazolylsulfinate ion (Scheme 1).

Scheme 1

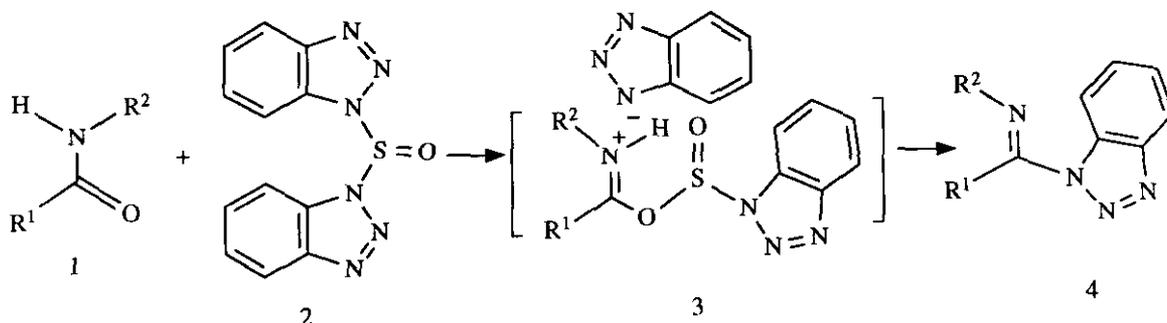


Table 1 : Preparative Data of Imidoylbenzotriazoles (4).

No. R ¹	R ²	Yield (%)	<i>E/Z</i>	Molecular Formula	mp (°C)	Lit. mp or CHN Analysis Found (Required)			
						C%	H%	N%	
4a	Ph	41	87/13	C ₁₉ H ₁₄ N ₄	130-132	76.32 (76.39)	4.67 (4.73)	18.75 (18.78)	
4b	Ph	15 ^a	89/11	C ₂₀ H ₁₆ N ₄	108-109	77.19 (76.90)	5.17 (5.16)	18.01 (17.94)	
4c	Ph	61	79/21	C ₁₇ H ₁₈ N ₄	oil	73.56 (73.36)	6.52 (6.52)	20.13 (20.13)	
4d	Ph	75	80/20	C ₁₇ H ₁₈ N ₄	69-69	73.32 (73.35)	6.49 (6.52)	20.21 (20.13)	
4e	Ph	15 ^b	76/24	C ₁₄ H ₁₂ N ₄	86-87	71.12 (71.16)	5.30 (5.12)	23.32 (23.72)	
4f	Me	49	95/5	C ₁₄ H ₁₂ N ₄	107-108			108 °C ⁸	
4g	Me	<i>p</i> -BrC ₆ H ₄	37	95/5	C ₁₄ H ₁₁ N ₄ Br	160-162		164 °C ⁸	
4h	Me	<i>p</i> -EtOC ₆ H ₄	25	100/0	C ₁₆ N ₁₆ N ₄ O	99-100	68.55 (68.55)	5.84 (5.75)	19.77 (19.99)
4i	<i>p</i> -MeC ₆ H ₄	Ph	62	90/10	C ₂₀ H ₁₆ N ₄	100-101	76.84 (76.90)	5.13 (5.16)	18.09 (17.94)
4j	<i>p</i> -BrC ₆ H ₄	<i>i</i> -Bu	58	79/21	C ₁₇ H ₁₇ N ₄ Br	73-74	57.41 (57.15)	4.95 (4.80)	15.52 (15.68)

^a 67% yield and ^b >80% yield calculated based on the ¹H nmr spectrum.

Products (4) were purified by column chromatography; preparative and spectroscopic data are summarized in Tables 1, 3 and 4. The characteristic carbon signals of C=N in the ¹³C nmr spectra appeared at a higher field (ca. 154 ppm) than the corresponding C=O signals of the amides (ca. 165 ppm), which is especially important for monitoring those reactions in which the products readily decompose on tlc. Most imidoylbenzotriazoles (4) thus prepared were obtained as a mixture of *E* and *Z* isomers according to the nmr spectra presumably with the *E*-isomer, derived from the more stable (*E*)-benzotriazolylsulfinium cation (3) (Scheme 1) via an addition/elimination mechanism, predominating. 4h was obtained as a single isomer, presumably this is also

Scheme 2

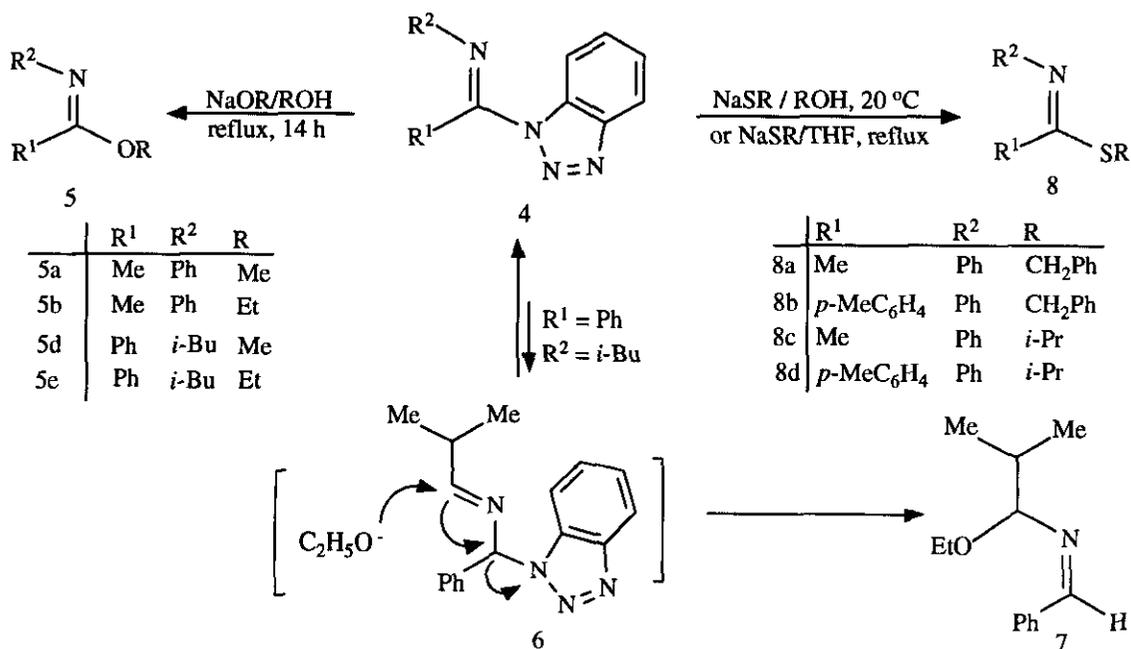


Table 2: Preparative Data of Imidates (5), Compound (7) and Thioimidates (8)

Cpd.	Reaction Solvent	yield (%)	bp (°C/mmHg)	Molecular Formula	CHN Analysis, Found (Required)		
					C%	H%	N%
5a	Methanol	85	77-79/10 ^a	C ₉ H ₁₁ NO	—————		
5b	Ethanol	70	51-54/2 ^b	C ₁₀ H ₁₃ NO	—————		
5d	Methanol	72	oil	C ₁₂ H ₁₇ NO	75.71 (75.39),	8.95 (8.90),	7.10 (7.33)
5e	Ethanol	43	oil	C ₁₃ H ₁₉ NO	75.71 (76.00),	9.12 (9.33),	6.87 (6.87)
7 ^c	Ethanol	8	oil	C ₁₃ H ₁₉ NO	75.66 (76.00),	9.10 (9.33),	7.15 (6.87)
8a	Ethanol	94	oil	C ₁₅ H ₁₅ NS	79.96 (80.30),	6.90 (7.16),	5.91 (5.85)
8b	Ethanol	91	oil	C ₂₁ H ₁₉ NS	79.17 (79.46),	6.03 (6.03),	4.41 (4.41)
8c	THF	77	oil	C ₁₁ H ₁₅ NS	68.61 (68.36),	7.97 (7.83),	7.22 (7.25)
8d	THF	90	oil	C ₁₇ H ₁₉ NS	76.12 (75.79),	7.33 (7.11),	5.11 (5.20)

^a Lit. bp¹¹ 91-92 °C/17mmHg; ^b lit. bp¹² 212-213 °C; ^c Nmr data of compound (7): ¹H Nmr δ 0.94, (d, J = 6.8 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H), 1.24 (t, J = 7.0 Hz, 3H), 1.98 (septet, J = 6.8 Hz, 1H), 3.35 (m, 1H), 3.59 (m, 1H), 4.35 (d, J = 6.8 Hz, 1H), 7.45 (m, 3H), 7.80 (m, 2H), 8.32 (s, 1H); ¹³C Nmr δ 15.11, 17.61, 17.88, 33.84, 64.09, 102.11, 128.19, 128.56, 130.86, 135.77, 158.99.

Table 3: ^1H Nmr Data ^a (δ , multiplicity, J (Hz), integration) of Imidoylbenzotriazoles (4).

No	Benzotriazol-1-yl group				R ¹	R ²
	H-4	H-5	H-6	H-7		
4a	8.14 (d, 8.3)	7.50 (t, 8.2)	7.62 (t, 8.2)	8.48 (d, 8.3)		6.84 (d, 7.8, 2H), 7.02 (t, 7.8, 1H), 7.34-7.43 (m, 5H), 7.22 (t, 7.8, 2H) ^b
4b	8.08 (d, 8.3)	7.50 (m)	7.62 (m)	8.51 (d, 8.3)	7.20 - 7.60 (m, 10H), ^a	4.75 (maj., s, 2H), 4.63 (min., s, 2H) ^c
4c	8.10 (d, 8.3)	7.48 (m)	7.60 (m)	8.47 (d, 8.3)	7.25 - 7.55 (m, 5H)	0.94 (maj., t, 7.3, 3H), 0.86 (min., t, 7.3, 3H), 1.46 (maj., m, 2H), 1.30 (min., m, 4H), 1.73 (maj., m, 2H), 3.55 (maj., t, 6.8, 2H), 3.35 (min, t, 6.5, 2H)
4d	8.10 (d, 8.3)	7.50 (m)	7.60 (m)	8.52 (d, 8.3)	7.37 - 7.62 (m, 5H)	1.02 (maj., d, 6.7, 3H), 0.93 (min., d, 6.7, 3H), 2.04-2.12 (m, 1H), 3.35 (maj., d, 6.5, 2H), 3.18 (min., d, 6.5, 2H),
4e	7.95 (d, 8.3)	7.33 (m)	7.45 (m)	8.27 (d, 8.3)	7.02 - 7.48(m, 5H)	3.25 (maj., s, 3H), 3.14 (min., s, 3H)
4f	8.12 (d, 8.3)	7.47 (t, 8.2)	7.60 (t, 8.2)	8.53 (d, 8.3)	2.75 (maj., s, 3H), 3.00 (min., s, 3H)	6.95 (d, 7.6, 2H), 7.18 (t, 7.6, 1H), 7.42 (t, 7.6, 2H)
4g	8.16 (d, 8.3)	7.15 (t, 8.3)	7.67 (t, 8.3)	8.46 (d, 8.3)	2.70 (s, 3H)	7.00 (d, 8.6, 2H), 7.58 (d, 8.6, 2H)
4h	8.10 (d, 8.2)	7.46 (d, 8.1)	7.58 (t, 8.1)	8.45 (d, 8.2)	2.76 (s, 3H)	1.44 (t, 7.0, 3H), 4.06 (q, 7.0, 2H), 6.87 (d, 8.8, 2H), 6.96 (d, 8.8, 2H)
4i	8.11 (d, 8.3)	7.46 (t, 8.3)	7.56 (t, 8.3)	8.43 (d, 8.3)	2.31 (s, 3H), 6.85 (d, 7.5, 2H), 7.02 (t, 7.5, 1H), 7.12 (d, 7.8, 2H), 7.20 (d, 7.5, 2H), 7.24 (d, 7.8, 2H) ^b	
4j	8.08 (d, 8.3)	7.42 (t, 8.2)	7.66 (t, 8.2)	8.51 (d, 8.3)	7.27 (d, 8.5, 2H), 7.66 (d, 8.5, 2H)	1.02 (maj., d, 6.6, 6H), 0.96 (min., d, 6.6, 6H), 2.07 (m, 1H), 3.34 (maj., d, 6.4, 2H), 3.16 (min., d, 6.6, 2H)

^aSignals for the benzotriazole and aromatic rings of the minor isomers could not be assigned:

^bsignals for R¹ and R² could not be assigned; ^c maj. = major isomer, min. = minor isomer.

the more thermally stable *E*-isomer. Acetamide derivatives (4f-h) apparently give higher *E*-stereoselectivity (Table 1).

Imidoylbenzotriazoles (4) are stable at room temperature for months in a pure state (without any special precautions) which makes them the convenient alternatives to the sensitive imidoyl chlorides. The *N*-aryl substituted imidoylbenzotriazoles (4) are more stable towards hydrolysis than the imidoylbenzotriazole with an *N*-alkyl substituent. Thus, *N*-aryl substituted imidoylbenzotriazoles can be isolated on a silica gel column, while purification of *N*-alkyl substituted imidoylbenzotriazoles requires a basic alumina column to avoid decomposition.

Table 4: ^{13}C Nmr Data ^a (ppm) of Imidoylbenzotriazoles (4).

No	Benzotriazol-1-yl group ^a						C=N	R ¹	R ²
	C-4	C-5	C-6	C-7	C-7a	C-3a			
4a	119.9	125.5	129.2	115.3	131.9	146.4	153.7	120.5, 121.4, 124.1, 128.2 128.8, 130.1, 130.3, 146.9 ^b	
4b	119.2	126.4	129.7	114.9	131.3	145.8	155.2	124.7, 126.4, 126.9, 128.0, 128.2, 128.5, 129.9, 139.0, 54.74 (55.09) ^c	
4c	119.7	125.1	130.0	115.2	131.8	146.3	154.4	128.1, 128.6, 128.8, 130.8	13.8 (13.7), 20.5 (20.45) 33.4 (32.7), 51.2 (51.8)
4d	119.6	125.0	128.7	115.2	131.8	146.3	154.5	128.8, 129.9, 130.9, 131.5	20.7 (20.6) 30.0 (29.7), 59.1 (59.2)
4e	119.7	125.0	130.0	114.9	131.7	146.1	155.8	110.2, 120.1, 124.4, 127.9 128.4, 128.5, 128.6, 131.5	38.8 (38.7)
4f	119.7	124.3	125.4	115.7	131.3	146.6	154.0	16.2	120.2, 147.3 129.2 (two signals overlap)
4g	119.4	125.4	129.3	115.2	130.6	145.9	154.4	16.3	116.6, 122.4 131.7, 146.1
4h	119.6	125.3	129.1	115.7	131.3	146.6	156.0	16.2	14.9, 63.7, 115.0 121.6, 140.2, 154.0
4i	119.7	125.3	128.9	115.1	131.9	147.0	153.7	110.4, 120.3, 121.3, 123.9, 127.2 128.7, 130.0, 140.5, 146.3, 21.4 ^a	
4j	119.6	125.1	130.1	115.1	131.6	146.2	153.3	124.3, 128.8 131.8 (two signals overlap)	20.6 (20.4), 29.9 (29.5) 59.1 (59.5)

^a Signals for benzotriazole and aromatic rings of the minor isomers could not be assigned; ^b signals for R¹ and R² could not be assigned; ^c values in brackets correspond to the minor isomer.

Preparation of alkyl imidates (5) using imidoylbenzotriazoles (4). Reaction of imidoylbenzotriazoles (4) with two equivalents of alkoxide in alcohol led to imidates (5) in good to excellent yields (Scheme 2). The *N*-aryl substituted imidoylbenzotriazoles, after basic aqueous work up, gave the imidates (5a-c) with >95% purity according to the ¹H and ¹³C nmr spectra. Imidoylbenzotriazoles (4) with R¹= aryl (4d) and R¹= CH₃ (4f, with acidic protons) both gave imidates (5) in the same range of yields. The formation of imidates (5) probably involves an addition of the sodium alkoxide to the C=N bond followed by the elimination of the benzotriazole group. Reaction of *N*-isobutylimidoylbenzotriazole (4d) with sodium ethoxide gave a mixture of the expected imidate (5e) and the rearranged product (7) which were isolated in 43% and 8% yields, respectively. With methoxide, imidate (5d) was isolated in 72% yield and the rearranged product similar to 7 was detected in 5% yield by the ¹H nmr spectrum but was not isolated. The mechanism for the formation of the rearranged product (7) probably involves an R_{ONa}-catalyzed-rearrangement of the C=N double bond followed by an S_N' reaction with sodium alkoxide (Scheme 2).

Table 5 : ^1H Nmr Spectroscopic Data (δ , multiplicity, J(Hz), integration) of 5 and 8.

No	R ¹	R ²	R
5a	1.80 (s, 3H)	6.74 (dd, 7.4, 0.9, 2H), 7.01 (tt, 7.3, 0.9, 1H), 7.26 (td, 7.51, 1.39, 2H)	3.77 (s, 3H)
5b	1.81 (s, 3H)	6.74 (d, 7.2, 2H), 7.01 (t, 7.5, 1H), 7.26(t, 8.1, 2H)	1.33 (t, 7.1, 3H), 4.21 (q, 7.1, 2H)
5d	7.28-7.42 (m, 5H)	0.88 (d, 6.5, 6H), 1.79 (d, 6.5, 1H), 3.07 (d, 6.6, 2H)	3.80 (s, 3H)
5e	7.38 (m, 5H)	0.87 (d, 6.6, 6H), 1.78 (septet, 6.5, 1H), 3.07 (d, 6.6, 2H)	1.33 (t, 7.3, 3H), 4.24 (q, 7.3, 2H)
8a	1.98 (s, 3H)	6.73 (d, 7.3, 2H), 7.07 (t, 7.3, 1H), 7.2-7.3 (m, 2H), 7.38 (d, 7.1, 2H)	4.28 (s, 2H), 7.2-7.4 (m, 5H)
8b ^a	2.29 (s, 3H), 6.9-7.3 (m, 4H)	6.71 (d, 6.9, 2H), 6.95-6.98 (m, 1H), 7.06 (d, 6.9, 2H)	4.20 (br, 2H), 6.9-7.3 (m, 5H)
8c	1.95 (s, 3H)	6.74 (d, 7.5, 2H), 7.03 (t, 7.5, 1H), 7.28 (t, 7.5, 2H),	1.40 (d, 6.8, 6H), 3.86 (septet, 6.8, 1H)
8d ^a	2.14 (s, 3H)	6.38 (m, 2H), 6.60 (m, 7H)	0.65 (d, 6.8, 6H), 3.95 (m, 1H)

^a Spectrum was recorded at 65 °C.

In the absence of sodium alkoxide, refluxing imidoylbenzotriazole (**4f**) in ethanol led to the complete recovery of the starting material, which proves the necessity of a base during the reaction and also demonstrates the thermal stability of imidoylbenzotriazoles (**4**). The imidoylbenzotriazoles (**4**) can thus be seen as stable precursors for imidates (**5**) and alternatives to the labile imidoyl chlorides.

Preparation of alkyl thioimidates (8) from imidoylbenzotriazoles (4). In an analogous and convenient way, imidoylbenzotriazoles (**4**) were reacted with sodium thiolates, generated *in situ* from thiols and a base, to give the corresponding thioimidates (**8**) in good yield. Thioimidates (**8a-b**) were prepared in ethanol at room temperature whilst the preparation of imidates (**5**) required reflux for 10 h, apparently because thiolates are more nucleophilic than alkoxides. Under reflux, the same reaction gave a mixture of imidate (**5**) and thioimidate (**8**). With the more sterically hindered isopropylthiolate (for **8c-d**), a small amount of imidates (**5**) was still produced even at room temperature. The formation of the side products (**5**) can be avoided when THF is used as a solvent. Reaction in THF is slower and reflux is necessary to complete the reactions. Basic conditions are required to prepare thioimidates (**8**) as evidenced by refluxing phenylmethanethiol and imidoylbenzotriazole (**4f**) in THF resulting in recovery of the starting materials. All products were purified by distillation or column chromatography without decomposition. The spectroscopic data are summarized in Tables 5 and 6. Structures were confirmed by elemental analyses.

Table 6: ^{13}C Nmr Spectroscopic Data of Compounds (5) and (8).

No	R ¹	R ²	R	C=N
5a	15.9	121.2, 122.9, 129.0, 149.2	53.1	161.7
5b	16.1	121.0, 122.7, 128.8, 149.2	14.1, 61.3	161.1
5c	127.9, 128.1, 128.2, 132.6	20.4, 30.5, 52.7	57.6	160.3
5d	127.9, 128.0, 128.1, 128.2, 128.5, 129.0, 130.2, 132.9	20.4, 30.5, 57.7	14.4, 60.8	159.9
8a	21.2	120.0, 123.2, 129.0, 150.5	34.0, 126.9, 128.4, 128.9, 137.9	165.0
8b ^a	21.2, 128.3, 128.7, 128.8, 139.9	120.9, 123.3, 129.1, 150.5	36.2, 127.0, 128.4, 128.9, 137.8	165.8
8c	21.6	119.9, 123.0, 128.9, 150.9	22.6, 24.5, 34.5	165.8
8d ^b	21.29, 120.43, 120.46, 129.54, 120.57, 120.64, 120.68, 120.73, 120.76, 120.82, 120.89, 120.94, 123.18, 128.19, 128.35, 128.61, 128.68		23.26, 36.20	150.76

^a The spectrum was recorded at 65 °C; ^b Good spectrum could not be obtained and signals for R¹ and R² could not be assigned.

The reaction of imidoylbenzotriazoles (4) with very strong nucleophiles such as Grignard or lithium reagents did not give satisfactory results. Grignard reactions of *N*-aryl substituted imidoylbenzotriazoles (4) were studied previously. They usually gave a complicated mixture of a variety of compounds, some of which resulted from nucleophilic attack on the benzotriazole nitrogen.⁸ Grignard reactions of *N*-alkyl substituted imidoylbenzotriazole (4), attempted in the present work, gave only amides, formed from hydrolysis of the starting material. The reaction of 4 with butylamine resulted in recovery of the imidoylbenzotriazole, while lithium butylamide gave a complex mixture.

In summary, the benzotriazole transfer reagent, 1,1'-sulfinylbenzotriazole, has allowed the development of a general route to imidoylbenzotriazoles, which provides stable alternatives to labile imidoyl chlorides, as illustrated by convenient preparations of imidates and thioimidates.

EXPERIMENTAL SECTION

Tetrahydrofuran and ether were distilled from sodium/benzophenone ketyl under nitrogen before use. Melting points were determined using a Bristoline melting point apparatus and are uncorrected. ^1H and ^{13}C nmr were recorded in CDCl_3 on a Varian VXR-300 (300 MHz) or a GE QE300 (300 MHz) spectrometer using TMS as an internal standard for ^1H nmr and CDCl_3 for ^{13}C nmr. Elemental analyses were performed in this Department under the supervision of Dr. D. Powell.

General Procedure for the synthesis of imidoylbenzotriazoles (4).

To a solution of 1-trimethylsilylbenzotriazole (5.73 g, 30 mmol) in 20 ml of tetrahydrofuran at 0 °C, thionyl chloride (1.8 g, 15 mmol) was added dropwise, the reaction mixture was stirred for 1 h at 0 °C and subsequently at room temperature for 6 h. The amide (10 mmol) was then added and the mixture was stirred at room temperature or at reflux. The solvent was evaporated and the crude mixture was purified by column chromatography to yield the imidoylbenzotriazole (4).

General procedure for the synthesis of imidates (5).

To a solution of imidoylbenzotriazole (**4f** or **4d**) (6 mmol) in 10 ml of the dry alcohol, 2 equiv. of the corresponding alkoxide (prepared from the alcohol and 1 equ. of sodium) was added and the reaction mixture refluxed for 16 h. The mixture was then poured into an aqueous solution of sodium hydroxide (1 N) and extracted with dichloromethane (3 x 30 ml). The organic layer was dried (MgSO_4), filtered and the solvent evaporated under reduced pressure. The resulting imidates (**5**) were obtained as pure oils. Compound (**7**) was isolated by column chromatography from the reaction of **4d** with sodium ethoxide. Nmr data are given as a footnote in Table 3.

General procedure for the synthesis of thioimidates (8).

To a solution of 5 mmol sodium ethoxide in 30 ml of dry ethanol, 5 mmol of thiol was added dropwise and stirred for 15 min. The imidoylbenzotriazole (**4**) (2.5 mmol) dissolved in 10 ml of dry ethanol was then added and the mixture stirred for 16 h at room temperature. The mixture was then poured into an aqueous sodium hydroxide solution (1 N, 30 ml), extracted with dichloromethane (3 x 30 ml), dried (MgSO_4) and the solvent removed under reduced pressure. The crude product was purified by column chromatography (Merck silica gel 230-400 mesh) using hexanes as eluent.

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