A Novel Synthetic Approach to Ethers

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1-Methoxymethylbenzotriazole undergoes lithiation at the methylene group and the carbanion affords substitution products with various electrophiles. Grignard reagents replace the benzotriazole residues of some of the compounds thus obtained to give the corresponding methyl ethers.

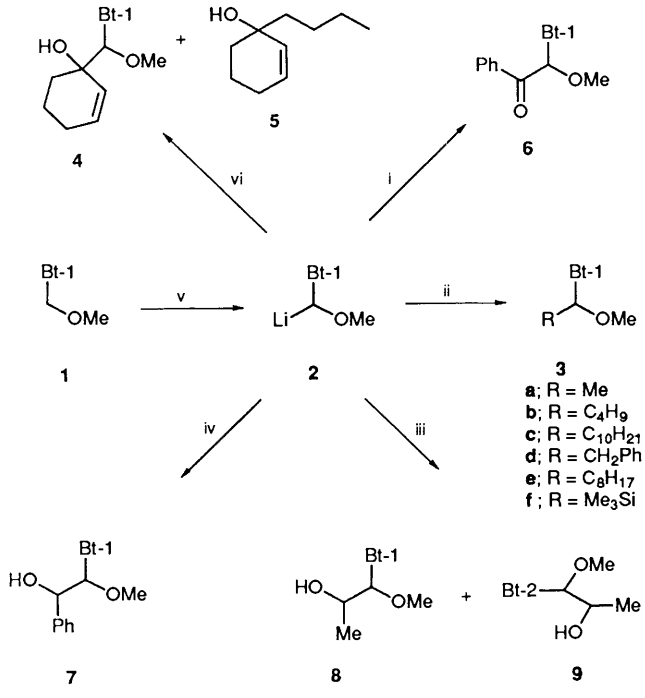
Most general methods for the synthesis of ethers[1,2] are based on the formation of one of the C–O bonds. The most common method for the preparation of dialkyl or aryl/alkyl ethers, the Williamson synthesis, has recently been further developed.[3–6] Transformations of substituents on C-1 or C-2 of molecules where the C–O–C bond already exists have also been used for ether syntheses. Thus, one of the alkoxy groups of an acetal may be replaced by hydrogen with triethylsilane,[7] or by an alkyl group using an organometallic compound.[8–10] The halogen atoms in α-chloroalkyl[11] and β-chloroalkyl[12] ethers may be replaced by alkyl or aryl groups with organometallic compounds, and those in α-chloro ethers with hydrogen by reaction with silanes.[13]

A general and versatile method for the preparation of dialkyl and aryl alkyl ethers involving the displacements of the benzotriazolyl groups† from 1-(α-alkoxyalkyl)benzotriazoles with Grignard reagent has recently been disclosed from our laboratory.[14] The starting benzotriazolylmethyl alkyl/aryl ethers were obtained by several routes including: (i) from benzotriazole, an aldehyde and an alcohol; (ii) from 1-(α-chloroalkyl)benzotriazole and an alkoxide; and (iii) from an acetal or ketal and benzotriazole. This led to considerable versatility. However, neither in this nor in any other previously published ether synthesis has it been possible to effect electrophilic substitution alpha to an ether group, although the formation of organometallic compounds of type ROCH(Li)R′ by tin–lithium exchange has recently been reported in enantioselective syntheses of 2-hydroxyalkanoic acids and of secondary alkanols[15] and in the investigation of the configurational stability of α-bromoalkyllithium compounds.[16] We now describe such a route and its application in a new approach to α,α-disubstituted methyl ethers.

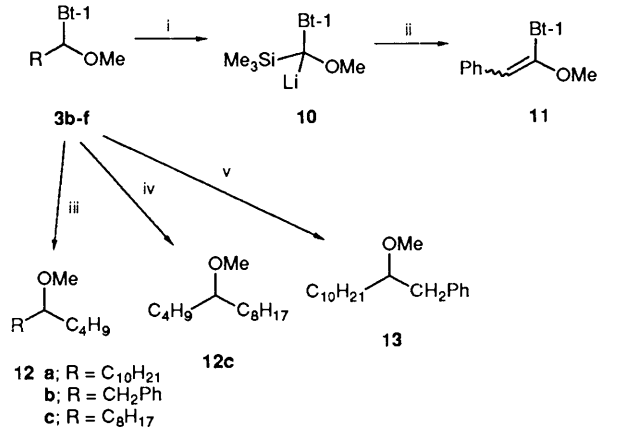
The easily available benzotriazolylmethyl methyl ether **1**[17] undergoes lithiation to afford the derivative **2**. The lithio derivative **2** is shown to react with various electrophiles to yield substituted benzotriazolylmethyl ethers. Further interactions of these compounds with Grignard reagents afford α,α-disubstituted ethers. This appears to be a general synthetic route which should allow the synthesis of a wide range of ethers.

Results and Discussion

Preparation of α-Benzotriazolylalkyl Methyl Ethers.—Benzotriazolylmethyl methyl ether **1** was prepared by the reported method[17] and lithiated with butyllithium in THF at −78 °C to give **2** (Scheme 1). The use of lithium diisopropylamide[18] did not lead to successful reaction. Alkyl halides reacted readily with the lithio derivative **2** to give the corresponding alkylated compounds **3a–e** in yields of 70 to 85%. Structure confirmation of **3a–e** utilized the standard spectroscopic methods (Tables 1,3,4). The trimethylsilyl derivative **3f** was obtained from **2** and trimethylsilyl chloride. Further lithiation of **3f** afforded the lithium derivative **10** which on treatment with benzaldehyde



Scheme 1 *Reagents:* i, $PhCO_2Et$; ii, RX; iii, MeCHO; iv, PhCHO; v, BuLi; vi, cyclohex-2-enone



Scheme 2 *Reagents:* i, BuLi (R = Me_3Si); ii, PhCHO; iii, BuMgI; iv, $C_8H_{17}MgI$ (R = C_4H_9); v, $PhCH_2MgBr$ (R = $C_{10}H_{21}$)

† Bt-1 = 1*H*-benzotriazol-1-yl and Bt-2 = 2*H*-benzotriazol-2-yl.

Table 1 Lithiations of 1-methoxymethylbenzotriazole and reactions with electrophiles

Compd.	R	Electrophile used	Yield (%)	Physical form	M.p.[a] (°C)	Molecular formula	Found (calcd.) (%) C	H	N	*m/z* Found (calcd.)	ν_{max}/cm^{-1} [b]
3a	Me	MeI	85	Oil		$C_9H_{11}N_3O$				177.0905 (177.0908)	2995, 2940, 2832, 1613, 1588, 1383, 1210, 1150
3b	Bu	BuBr	80	Oil		$C_{12}H_{17}N_3O$				219.1370 (219.1372)	2933, 2872, 1613, 1588, 1337, 1276, 1148
3c	Undecyl	$C_{10}H_{21}Br$	71	Oil		$C_{18}H_{29}N_3O$				304.2385 ($M^+ + 1$) (304.2389)	2925, 2854, 1613, 1588, 1338, 1277, 1093
3d	$PhCH_2$	$PhCH_2Br$	81	Oil		$C_{15}H_{15}N_3O$				254.1298 ($M^+ + 1$) (254.1293)	3029, 2934, 1613, 1587, 1495, 1452, 1227, 1086
3e	Octyl	$C_8H_{17}Br$	67	Oil		$C_{16}H_{25}N_3O$				275.1993 (M^+) (275.1997)	2919, 2858, 1227, 1613, 1588, 1454, 1227, 1098
3f	Me_3Si	Me_3SiCl	75	Prisms	77–78	$C_{11}H_{17}N_3OSi$	55.76 (56.16)	7.43 (7.23)	18.06 (17.87)		1612, 1587, 1341, 1248, 1155, 1113, 1051, 949
4		Cyclohex-2-enone	45	Oil		$C_{14}H_{17}N_3O_2$				259.1580 (259.1572)	3342, 2936, 1708, 1649, 1613, 1588, 1092
5		Cyclohex-2-enone	12	Oil		$C_{10}H_{18}O$				154.1020 (154.1016)	3350, 2995, 1630, 1612, 1210, 1150
6		$PhCO_2Et$	51	Micro	73–74	$C_{15}H_{13}N_3O_2$	67.57 (67.42)	4.90 (4.87)	15.82 (15.73)		1705, 1613, 1597, 1579, 1338, 1280, 1227, 1159, 1093
7		PhCHO	53	Needles	152	$C_{15}H_{15}N_3O_2$	67.23 (66.91)	5.66 (5.58)	15.44 (15.61)		3190, 1613, 1590, 1357, 1276, 1138, 1086
8, 9		MeCHO	80	Oil		$C_{10}H_{13}N_3O_2$				207.0809 (207.0816)	3093, 1621, 1451, 1593, 1275, 1210, 1093
11		PhCHO	10	Oil		$C_{15}H_{13}N_3O$				251.1059 (M^+) (251.1058)	2995, 1630, 1610, 1385, 1223, 1086

[a] From ethanol. [b] Neat except **3f**, **6** and **7** which were in Nujol.

Table 2 Replacement of benzotriazole groups in **3b–f**

Starting material No.	R	Grignard reagent	Product No.	R	Yield (%)	Molecular formula	*m/z* Found (calcd.)	ν_{max}/cm [b]
3c	Undecyl	BuMgI	**12a**	Undecyl	64	$C_{16}H_{34}O$	242.2675 ($M^+ + 1$) (242.2688)	2928, 1465, 1099
3d	$PhCH_2$	BuMgI	**12b**	$PhCH_2$	68	$C_{13}H_{20}O$	193.1593 ($M^+ + 1$) (193.1592)	2928, 1605, 1493, 1099
3e	Octyl	BuMgI	**12c**	Octyl	57	$C_{14}H_{30}O$	157.1586 [($M^+ + 1$) − C_4H_9][c] (157.1592)	2926, 1465, 1099
3b	Bu	$C_8H_{17}MgI$	**12c**	Bu^n	60	*d*		
3c	Undecyl	$PhCH_2MgBr$	**13**	—	50	$C_{19}H_{32}O$	277.2532 ($M^+ + 1$) (277.2531)	2994, 1603, 1495, 1101

[a] From ethanol. [b] Neat. [c] Peak of fragmentation. [d] Same product as previous entry.

gave the styryl compound **11** as a mixture of *cis*- and *trans*-isomers (Scheme 2). A similar conversion of trimethylsilyl derivatives was described recently as an intermediate stage in the synthesis of the β,γ-unsaturated *O*,*S*-acetals.[19]

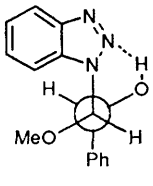
Table 3 ^{1}H NMR Spectral data of methyl ethers

			Benzotriazole ring[14]				
No.	MeO	C*H*OMe	**4**	**5**	**6**	**7**	Other groups
3a	3.22	6.17 (q, *J* 6.0)	8.09 (d)	7.40 (t)	7.50 (t)	7.78 (d)	1.18 (Me, 3 H, d, *J* 6.0)
3b	3.24	5.95 (t, *J* 7.0)	8.10 (d)	7.40 (t)	7.50 (t)	7.80 (d)	0.85 (3 H, t, *J* 7.0), 1.1–2.4 (6 H, m)
3c	3.20	5.90 (t, *J* 7.0)	8.10 (d)	7.30 (t)	7.48 (t)	7.80 (d)	0.88 (3 H, t, *J* 7.0), 1.12–1.87 (m, 19 H)
3d	3.23	6.13 (t, *J* 7.0)	8.09 (d)	7.39 (t)	7.48 (t)	7.72 (d)	3.40 (1 H, dd, *J* 7) and 3.43 (1 H, dd, *J* 7) (2 H, CH_2Ph), 7.01 (2 H, m, Ph), 7.21 (3 H, m, Ph)
3e	3.23	5.95 (t, *J* 7.0)	8.10 (d)	7.40 (t)	7.50 (t)	7.80 (d)	0.87 (3 H, t, *J* 7.0), 1.15–2.30 (m, 14 H)
3f	3.18	5.50 (s)	7.92 (d)	7.25 (t)	7.32 (t)	7.54 (d)	0.01 (s, 9 H, Me_3Si)
4	3.32	6.10 (s)	8.08 (d)	7.30 (t)	7.48 (t)	7.92 (d)	1.5–2.1 (m, 6 H), 2.86 (br s, OH), 5.28 (br d, 1 H), 5.82 (d, 1 H)
6	3.50	7.20 (s)	7.30–8.10 (m, 9 H, Bt and Ph)				
7	3.39	5.92 (d, *J* 7.2)	8.02 (d)	7.37 (t)	7.48 (t)	7.62 (d)	3.19 (d, OH), 5.35 (dd, CH, *J* 7.2), 7.02 (m, 2 H, Ph), 7.15 (m, 3 H, Ph)
8,9[a]	3.21 **8** 3.28 **9**	5.78 (d, *J* 6.0) **8** 5.90 (d, *J* 6.0) **9**	8.15 (d, 1 H, Bt-1, **8**), 7.6 (t, 1 H, Bt-1), 7.5 (m) and 8.0 (m) (Bt-1 **8** and Bt-2 **9**)				0.97 (d, 3 H, CH_3, *J* 6.0) **9**, 1.35 (d, 3 H, CH_3, *J* 6.0) **8**, 3.28 (OH) (**8** and **9**), 4.55 (m, 1 H) (**8** and **9**)
11	3.62, 3.96		8.12 (d), 8.02 (d)	7.58 (t) *b*	*b*	7.78 (d), 7.71 (d)	6.10 (s, 1 H), 6.28 (s, 1 H), 6.65 (m, 2 H, Ph) and 7.0 (m, 3 H, Ph), 7.23–7.48 [m, Ph, 5-H (Bt) and 6-H (Bt)]
12a	3.33	3.12–3.13 (m)					0.86–0.94 (m, 6 H, 2 × CH_3), 1.27 (br s) and 1.42–1.49 (m) (24 H, 12 × CH_2)
12b	3.31	3.26–3.34 (m)					0.87 (3 H, t, CH_3), 1.26–1.43 (6 H, m, 3 × CH_2), 2.72 (1 H, dd, *J* 7) and 2.80 (1 H, dd, *J* 7) (CH_2Ph), 7.17–7.28 (m, 5 H, Ph)
12c	3.32	3.12 (m)					0.86–0.93 (m, 6 H, 2 × CH_3), 1.28 (br s) and 1.41–1.46 (m) (20 H, 10 × CH_2)
13	3.35	3.35–3.40 (m)					0.8–1.5 (m, 21 H, $C_{10}H_{21}$), 2.70 (1 H, dd) and 2.81 (1 H, dd) (CH_2Ph), 7.1–7.3 (m, 5 H, *Ph*CH_2)

[a] The mixture of **8** and **9** in a ratio of 1:2 (in [$^2H_6$]DMSO). A trace of the second diastereoisomer **8*** is detected in the mixture: δ 1.65 (d, 3 H, CH_3), 3.30 (s, 3 H, OCH_3), 8.14 (d, 1 H, Bt-1); the other signals are obscured by those of **8** and **9**. [b] The signal is obscured by phenyl protons.

Table 4 ^{13}C NMR spectral data of methyl ethers

			Benzotriazole ring[14]						
No.	MeO	*C*HOMe	**4**	**5**	**6**	**7**	**3a**	**7a**	Substituents
3a	56.12	88.35	119.97	124.14	127.42	111.01	146.70	131.07	20.75
3b	56.38	92.30	119.99	124.02	127.33	111.06	146.71	131.13	13.68, 21.96, 26,79, 34.11
3c	56.46	92.41	120.08	124.14	127.38	111.14	146.80	131.18	14.04, 22.61, 24.75, 28.90, 29.22, 29.25, 29.37, 29.46, 29.56, 31.81, 34.46
3d	56.66	92.63	120.11	124.16	127.09	110.97	146.63	131.26	41.14, 127.51, 128.49, 129.23, 135.01
3e	56.45	92.42	120.09	124.13	127.37	111.13	146.81	131.21	14.00, 22.55, 24.75, 28.91, 29.03, 29.39, 31.71, 34.48
3f	59.21	88.29	119.96	123.89	127.19	110.68	146.19	133.25	−3.22
4	57.63	93.65	120.02	124.32	127.79	110.70	146.13	132.40	18.93, 23.16, 25.11, 44.94, 129.42, 132.81
6	57.10	89.04	120.01	124.59	127.29	111.68	146.74	131.85	128.29, 129.13, 133.38, 134.44, 188.55
7	57.23	94.35	120.00	124.21	127.72	110.70	146.13	132.08	74.78, 126.38, 128.34, 128.57, 137.11
8	56.26	95.20	119.32	124.50	127.81	111.64	146.03	132.36	17.45, 67.35
9	56.57	95.37	114.80	124.52	124.52	114.80	145.97	145.97	19.07, 67.96
11	56.87 (57.92)		119.81 (119.84)	124.26 (124.59)	127.84 (127.89)	110.30 (110.38)	145.00 (145.69)	132.28 (132.64)	101.15, 107.99, 120.07 (120.11), 126.63 (126.69), 127.54 (127.58), 128.56 (128.63)
12a	56.29	81.07							14.07, 22.68, 22.92, 25.28, 27.49, 29.34, 29.52, 29.55, 29.63, 29.88, 31.91, 33.14, 33.45
12b	56.95	82.36							14.06, 22.79, 27.52, 33.22, 40.17
12c	56.32	81.02							14.07, 22.61, 22.92, 25.28, 27.49, 29.29, 29.61, 29.89, 31.89, 33.15, 33.47
13	56.96	82.36							14.11 (CH_2Ph), 22.70, 25.34, 29.32, 29.63, 29.76, 31.93, 33.57, 40.21 ($C_{10}H_{21}$), 125.96, 128.19, 129.40, 139.24 (Ph)



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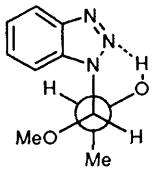

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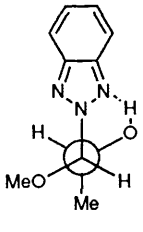

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Scheme 3

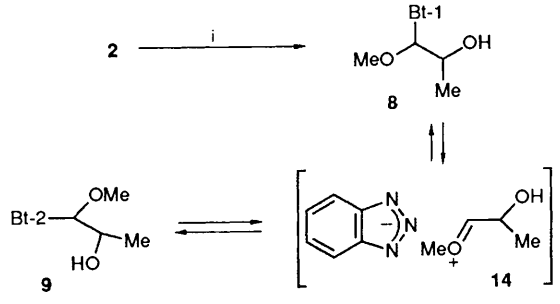
The structures of the products from the interactions of the lithio derivative **2** with carbonyl-containing electrophiles depended on the electrophile used. The reactions of **2** with ethyl benzoate and benzaldehyde smoothly yielded the expected ketone **6** and alcohol **7** respectively (Scheme 1). Interestingly, only a single diastereoisomer was detected for compound **7** in the NMR spectrum of the crude product. Perhaps the configuration is determined by the arrangement of the bulky benzotriazol-1-yl and phenyl substituents and is stabilized by the intramolecular hydrogen bond as shown in Scheme 3.

Cyclohex-2-enone yielded a mixture which was separated by

column chromatography to give compounds **4** and **5** in yields of 45 and 12% respectively (Scheme 1). The formation of 3-butyl-3-hydroxycyclohexene **5** clearly results from reaction of the ketone with excess of butyllithium. However, the formation of the tertiary alcohol **4** was surprising, in view of our experience of Michael addition to this enone by the lithio derivative of *p*-bis-(benzotriazol-1-yl)methyltoluene.[18] Presumably the lower steric hindrance in **2** allowed attack at the carbonyl group. The structure **4** was unambiguously established by the ^1H and ^{13}C NMR data (Tables 3 and 4), in particular, by the signals for =CH at δ 5.28 and 5.82.

The chemical shifts of the benzotriazolyl proton and carbon signals in **3a–f**, **4**, **6**, **7** and **11** (Tables 3 and 4) clearly established the structures as the benzotriazol-1-yl isomers by comparison with reported examples.[14]

The use of acetaldehyde in reaction with **2** gave a mixture of three isomers as demonstrated by the ^1H and ^{13}C NMR data. Each isomer had molecular mass 207. All the isomeric products were thus the result of interaction of **2** and acetaldehyde in 1:1 ratios. The analysis of the NMR data leads to the conclusion that the mixture consisted of two structural isomers **8** and **9** (Scheme 1) in a ratio of 1:2, with the diastereoisomer of **8**–**8*** as a minor by-product. It has been well established that the ^1H NMR signals for benzotriazol-1-yl and benzotriazol-2-yl derivatives are distinct and easily recognized.[14,20] The aromatic signals for isomer **8** were clearly less intense than those of **9**, which allowed the aliphatic signals to be unequivocally assigned. The isomeric ratio was determined by a comparison of the integrals of the methyl and methoxy signals. Traces of diastereoisomer **8*** were revealed by weak signals for the methyl and methoxy groups as well as by a doublet for the 4-H benzotriazol-1-yl proton at δ 8.14 which slightly overlapped the signal of **8**. The hydroxy protons of all isomers overlapped the strong signals of the methoxy groups and were determined by difference after deuteriation. We failed to separate these isomers by chromatography—only single spots were found on TLC plates developed with various solvent mixtures.



Scheme 4 *Reagents:* i, MeCHO

In benzotriazole (BtH) chemistry, the formation of two structural isomers (Bt-1 and Br-2) has often been encountered.[14,20,21] Isomerization of Bt-1 to Bt-2 was also observed,[14] as was equilibration in solution between forms Bt-1 and Bt-2.[21] In nearly all cases the Bt-1 form dominates. The dominant formation of the Bt-2 isomer **9** thus needs explanation. Obviously, the primary product of the interaction between **2** and acetaldehyde is the Bt-1 isomer **8** (Scheme 4). However, its isomerization is facilitated in three ways: (i) the bulk of the methoxy group destabilizes **8** relative to **9**; (ii) the stability of the intermediate cation **14** lowers the interconversion barrier; and (iii) the higher basicity of the Bt-2 isomer[25] makes a hydrogen bond in structure **9** more stabilizing than in **8** (Scheme 3).

These effects have previously been discussed in relation to similar benzotriazole rearrangements.[19,22–25] However, these factors are the same for the possible formation of the Bt-2 isomer of **7**. The isolation of the latter compound only as the Bt-1 isomer (Tables 3, 4) may reflect electron repulsions in **7** which lower the stability of the intermediate cation of type **14**. The most favourable conformations of **8** and **9** are depicted in Scheme 3 and **8** is similar to the phenyl substituted ether **7**.

Grignard Reactions of α-Benzotriazolyl Methyl Ethers.—In our previous work,[14] we have shown the use of toluene as solvent allows the replacement of the benzotriazolyl group in reactions of α-(*N*-benzotriazolyl)alkyl ethers by the allyl group from a Grignard reagent. Accordingly, the present compounds should act as ether precursors. Indeed, the α-(*N*-benzotriazolyl)-undecyl **3c**, -benzyl **3d** and -octyl **3e** methyl ethers each reacted smoothly with butylmagnesium iodide to yield the expected products **12a–c**, respectively, in 57–68% yield (Scheme 2). Two further Grignard reactions also succeeded, that of **3b** with octylmagnesium iodide which gave **12b** (identical with the specimen prepared using **3e** above) and that of **3c** with benzylmagnesium bromide to give **13**, Table 2.

In these transformations we have in two steps assembled compounds of general formula RR′CHOMe using $BtCH_2OMe$ in effect as a $MeOCH^{+\ -}$-synthon. This synthetic method should be applicable to the synthesis of a wide variety of ethers.

Experimental

M.p.s were determined on a Thomas-Hoover capillary m.p. apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR 300 spectrometer (300 and 75 MHz, respectively), using $CDCl_3$ as solvent (unless otherwise stated) and tetramethylsilane as an internal reference. ^1H and ^{13}C NMR chemical shifts are reported in ppm (δ). *J*-Values are given in Hz. High resolution mass spectra were recorded on a Krafts AEI MS 30 spectrometer. IR spectra were recorded as neat samples (unless otherwise stated) on a Perkin-Elmer 1600 series FTIR. Elemental analyses were performed on a Carbo Erba 1106 elemental analyser. Commercially available reagent grade solvents were dried over Na–benzophenone. Flash column chromatography was run over silica gel (EM Merck 60, 230–400 mesh).

General Procedure for Reactions of 1-Methoxymethylbenzotriazole with Electrophiles.—A solution of 1-methoxymethylbenzotriazole **1** (1.50 g, 9 mmol) or the α-trimethylsilyl derivative **3f** (2.11 g, 9 mmol) in THF (40 cm^3) was cooled to −78 °C and treated with BuLi (2.5 mol dm^{-3} in hexane; 4.4. cm^3, 11 mmol). The mixture was stirred for 2 h, a solution of the electrophile (11 mmol) in THF (10 cm^3) added and the reaction was slowly warmed to room temperature and stirred overnight. The resulting solution was poured into saturated aqueous NH_4Cl (100 cm^3) and extracted with CH_2Cl_2 (2 × 50 cm^3). The combined extracts were dried over $MgSO_4$ and evaporated to give the crude product.

On isolation of compounds **3f**, **6** and **7**, the residue was triturated with diethyl ether (20 cm^3) and refrigerated overnight to give crystalline products which were collected.

The other products were purified by flash chromatography with the following eluents: **3a**, hexane–ether, 2:1; **3b–e**, chloroform–light petroleum, 3:1; **4**, **5**, hexane–ether, 1:2; the mixture of **8** and **9**, ether; and **11**, ether–light petroleum ether, 1:2. The analysis and spectroscopic data are in Tables 1,3,4.

3-Butyl-3-hydroxycyclohexene **5** was obtained as a by-product from the reaction of **1** with cyclohex-2-enone (Table 1) and was separated as the first fraction by flash chromatography; δ_H 0.89 (t, 3 H, CH_3), 1.23–2.0 (m, 13 H), 5.60 (d, 1 H) and 5.75 (m, 1 H). δ_C 14.02, 19.01, 23.24, 25.19, 25.67, 35.34, 42.03, 69.58, 129.43 and 132.93.

General Procedure for the Synthesis of the Ethers **12a–c**, **13**.—A solution of the appropriate α-benzotriazolyl ether (3.3 mmol)

in toluene (40 cm^3) was heated to boiling and the Grignard reagent (6.6 mmol of 1.2–1.5 mol dm^{-3} solution in ether) was added slowly. The mixture was refluxed for 48 h, poured into ice-water and extracted with ether (2 × 30 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated to give the crude product which was purified by flash column chromatography (chloroform–hexane, 1:3), see Tables 2–4.

References

1 H. Meerwein, in *Methoden der Organische Chemie* (Houben-Weyl), 1965, vol. VI/3.
2 J. F. Stoddart, in *Comprehensive Organic Chemistry*, Pergamon, New York, 1979, vol. 1, p. 819.
3 A. McKillop and M. E. Ford, *Tetrahedron*, 1974, **30**, 2467.
4 J. M. Reuter and R. G. Salomon, *J. Org. Chem.*, 1977, **42**, 3360.
5 F. Camps, J. Coll and J. M. Moreto, *Synthesis*, 1982, 186.
6 V. K. Bhalerao, B. S. Nanjundiah, H. R. Sonawane and P. M. Nair, *Tetrahedron*, 1986, **42**, 1487.
7 J. Kato, N. Iwasawa and T. Mukaiyama, *Chem. Lett.*, 1985, 743.
8 Y. Gendreau and J. F. Normant, *Bull. Soc. Chim. Fr.*, 1979, 305.
9 E. Wenkert and T. W. Ferreira, *Organometallics*, 1982, **1**, 1670.
10 A. D. Abell and R. A. Massay-Westropp, *Aust. J. Chem.*, 1985, **38**, 1031.
11 R. G. Mukhina and E. V. Shklyaeva, *Sint. Metody Osn. Elementoorg. Soedin.*, 1982, 38 (*Chem. Abstr.*, 1983, **99**, 194058n).
12 C. G. Screttas and M. Micha-Screttas, *J. Org. Chem.*, 1982, **47**, 3008.
13 H. Uno, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 2471.
14 A. R. Katritzky, S. Rachwal and B. Rachwal, *J. Org. Chem.*, 1989, **54**, 6022.
15 D. Hoppe, F. Hintze and P. Tebben, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1422.
16 R. W. Hoffmann, T. Ruhland and M. Bewersdorf, *J. Chem. Soc., Chem. Commun.*, 1991, 195.
17 A. R. Katritzky, S. Rachwal and B. Rachwal, *J. Chem. Soc., Perkin Trans. 1*, 1987, 791.
18 A. R. Katritzky and W. Kuzmierkiewicz, *J. Chem. Soc., Perkin Trans. 1*, 1987, 819.
19 S. Hackett and T. Livinghouse, *J. Org. Chem.*, 1986, **51**, 879.
20 A. R. Katritzky, S. Rachwal and B. Rachwal, *J. Chem. Soc., Perkin Trans. 1*, 1990, 1717.
21 A. R. Katritzky, R. Rachwal and B. Rachwal, *J. Chem. Soc., Perkin Trans. 1*, 1987, 799.
22 J. R. L. Smith and J. S. Sadd, *J. Chem. Soc., Perkin Trans. 1*, 1975, 1181.
23 A. R. Katritzky and K. Yannakopoulu, *Heterocycles*, 1989, **28**, 1121.
24 A. R. Katritzky, N. Najzarek and Z. Dega-Szafran, *Synthesis*, 1989, 66.
25 J. Catalan, R. M. Claramunt, J. Elguero, J. Laynez, M. Menendez, F. Anvia, J. H. Quian, M. Taagepera and R. W. Taft, *J. Am. Chem. Soc.*, 1988, **110**, 4105.

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