An Efficient Synthesis of Ketone Enol Ethers Mediated by *N*-(1-Alkoxyalkyl)benzotriazoles

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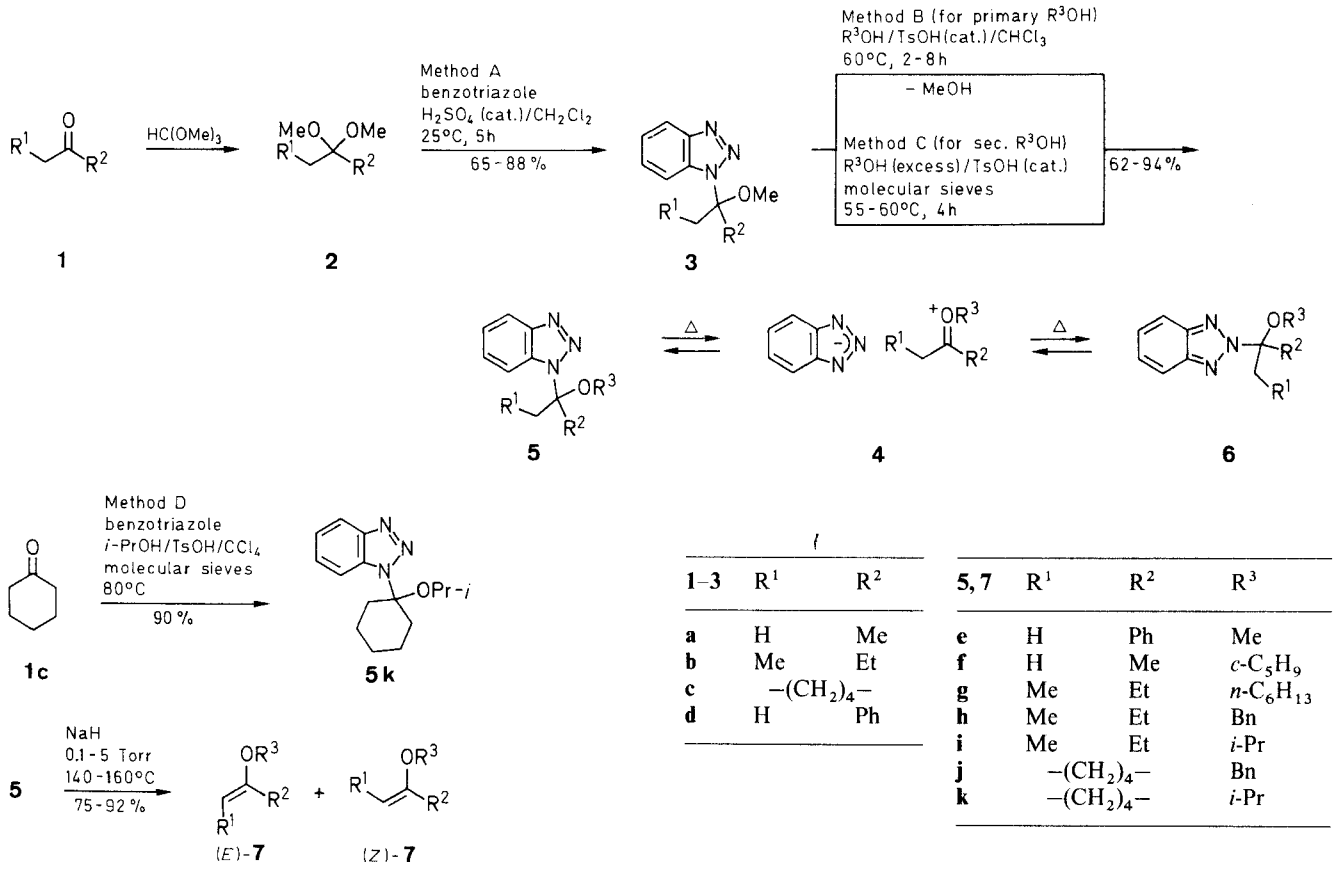
A new general method for the transformation of ketones into their enol ethers in good yield is developed via elimination of benzotriazole from *N*-(1-alkoxyalkyl)benzotriazole intermediates.

High reactivity, and especially the ability to undergo cycloadditions with electron deficient multiple bonds, makes ketone enol ethers useful reagents in the synthesis of naturally occurring heterocyclic systems such as furanones,[1] and pyranones.[2] The classical method for the synthesis of ketone enol ethers is the acid catalyzed thermolysis of ketals.[3] An improvement in this method has been recently achieved by the introduction of trimethylsilyl triflate[4] and pentacarbonyl (trimethylsilyl)-manganese $[(CO)_5MnSiMe_3]$[5,6] as neutral catalysts for the alcohol elimination. However, almost all published examples employ a primary group R in these compounds: C=C(OR). Ketone enol ethers derived from secondary alcohols can be prepared by the elimination of an alcohol from appropriate ketals bearing two secondary alkoxy groups. Such ketals are often difficult to prepare, e.g. 1,1-diisopropoxycyclohexane is formed in only 33% yield.[7] Recent reports on new synthetic routes to ketone enol ethers including reaction of 1-alkoxyalkylphosphine oxide[8] or 1-alkoxyalkylsilane[9] anions with ketones and titanium mediated methylene transfer to esters[10] gave no examples with secondary alkoxy groups.

We have reported that aldehydes and ketones can be easily transformed into the corresponding 1-(1-alkoxyalkyl)benzotriazole derivatives **5** by several routes.[11-13] Compounds **5** undergo reversible ionization at elevated temperatures to give the benzotriazolyl anion and the carboxonium cation **4**. The ion pair can recombine in a different mode giving the benzotriazol-2-yl[12,14,15] isomer **6**. Reactions of **5** with Grignard reagents provide a general method for synthesis of aliphatic ethers.[12] We now report another useful reaction of compounds **5**: strong bases can abstract the β-proton from cations **4** to give the alkyl 1-alkenyl ethers **7**.

Since acetals derived from aldehydes and higher alcohols can be relatively easily prepared and directly transformed into the corresponding enol ethers,[24] we concentrated our efforts on derivatives of ketones. Dimethyl ketals of acetone, 3-pentanone, cyclohexanone and acetophenone, **2a–d**, were converted into the corresponding 1-(1-methoxyalkyl)benzotriazoles **3a–d**, by reaction with benzotriazole and catalytic sulfuric acid (general Method A, Table 1). Replacement of the methoxy group in **3a–c** by several other primary alkoxy groups was achieved by treatment with the desired alcohol using acid catalysis and continuous removal of the methanol liberated (Method B). For secondary alcohols, a two-step procedure (Method C) gave products of higher purity.



1–3	R¹	R²
a	H	Me
b	Me	Et
c	–(CH₂)₄–	
d	H	Ph

5, 7	R¹	R²	R³
e	H	Ph	Me
f	H	Me	*c*-C₅H₉
g	Me	Et	*n*-C₆H₁₃
h	Me	Et	Bn
i	Me	Et	*i*-Pr
j	–(CH₂)₄–		Bn
k	–(CH₂)₄–		*i*-Pr

Scheme

Table 1. 1-(Benzotriazol-1-yl)alkyl Alkyl Ethers **3** and **5** Prepared

Product	Method	Yield (%)	mp (°C)	Molecular Formula[a]
3a	A	88	oil	Ref. 14
3b	A	78	52–53	$C_{12}H_{17}N_3O$ (219.3)
3c	A	70	55–56	$C_{13}H_{17}N_3O$ (231.3)
3d	A	65	68–69	$C_{15}H_{15}N_3O$ (253.3)
5f	C	70	oil	$C_{14}H_{19}N_3O$ (245.3)
5g	B	94	oil	$C_{17}H_{27}N_3O$ (289.4)
5h	B	63	84–85	$C_{18}H_{21}N_3O$ (295.4)
5i	C	62	99–100	$C_{14}H_{21}N_3O$ (247.3)
5k	D	90	88–89	$C_{15}H_{21}N_3O$ (259.4)
6j[b]	B	69	88–89	$C_{19}H_{21}N_3O$ (268.4)

[a] Satisfactory microanalyses obtained: C ±0.4, H ±0.3, N ±0.4, except for **5e** (unstable).

[b] In the case of the cyclohexanone-benzyloxy derivative, isomer **6i** was characterized instead of **5i**.

Finally, we found that cyclohexanone derivatives can also be obtained directly in a one-step procedure from cyclohexanone, benzotriazole and an alcohol (Method D). The acetophenone derivative **3d** appeared to be very sensitive to moisture, undergoing hydrolysis back to acetophenone. We therefore did not attempt its transformation to other alkoxy derivatives but used it directly for elimination to **7e**.

The 1-(benzotriazol-1-yl)alkyl alkyl ethers obtained, **3** and **5** (or **6**), were characterized by their ^{1}H- and ^{13}C-NMR and mass spectra (Table 2). ^{1}H-NMR resonances of the benzotriazolyl moiety in ethers **5** were found in the following sequence: $\delta = 7.3–7.4$ (H-6), $\delta = 7.4–7.5$ (H-5), $\delta = 7.8–8.0$ (H-7) and $\delta = 8.0–8.2$ (H-4).[12] To a first approximation, excluding long range coupling constants, the resonances can be considered as triplet, triplet,

Table 2. Spectroscopic Data of the 1-(Benzotriazol-1-yl)alkyl Alkyl Ethers **3a** and **5** (or **6**)

Product	^{1}H-NMR ($CDCl_3$/TMS)[b] δ, J(Hz)	^{13}C-NMR ($CDCl_3$/TMS)[b] δ	MS (70 eV)[c] m/z (%)
3b	0.83 (t, 6H, $J = 7.6$, $2CH_3$), 2.34 (m, 2H, CH_2), 2.48 (m, 2H, CH_2), 3.06 (s, 3H, OCH_3), 7.39 (t, 1H, $J = 7.3$, Bt), 7.46 (t, 1H, $J = 7.1$, Bt), 7.89 (d, 1H, $J = 8.5$, Bt), 8.08 (d, 1H, $J = 8.3$)	7.2 (2C, $2CH_3$), 26.4 (2C, $2CH_2$), 49.8 (OCH_3), 98.0 (NCO), 112.8 (Bt), 119.8 (Bt), 123.8 (Bt), 127.1 (Bt), 132.1 (Bt), 146.5 (Bt)	220 (41, $M^+ + 1$), 188 (2), 120 (29), 101 (100)
3c	1.43 (m, 1H), 1.76 (m, 5H), 2.31 (m, 2H), 2.50 (m, 2H), 3.02 (s, 3H, OCH_3), 7.36 (t, 1H, $J = 7.0$, Bt), 7.44 (t, 1H, $J = 7.1$, Bt), 7.89 (d, 1H, $J = 8.3$, Bt), 8.07 (d, 1H, $J = 8.2$, Bt)	22.1 (OCH_3), 25.1, 34.3 (2C), 49.5 (2C), 93.7, 112.8 (Bt), 119.8 (Bt), 123.9 (Bt), 127.0 (Bt), 131.8 (Bt), 146.7 (Bt)	232 (13, $M^+ + 1$), 130 (8), 120 (36), 113 (100)
3d	2.40 (s, 3H, CCH_3), 3.19 (s, 3H, OCH_3), 7.24 (m, 8H), 8.06 (d, 1H, $J = 8.2$, Bt)	25.7 (CH_3), 50.3 (OCH_3), 93.8 (NCO), 112.8 (Bt), 119.5 (Bt), 124.0 (Bt), 124.9 (2C, Ph), 127.2 (Bt), 128.3 (Ph), 128.4 (2C, Ph), 132.1 (Bt), 142.0 (Ph), 146.7 (Bt)	254 (3, $M^+ + 1$), 194 (5), 149 (49), 135 (100)
5f	1.33 (m, 2H), 1.51 (m, 4H), 1.59 (m, 2H), 2.03 (s, 6H, CH_3), 3.74 (quint, 1H, CHO), 7.36 (dd, 1H, $J = 7.1$, 8.2, Bt), 7.46 (dd, 1H, $J = 7.1$, 8.2, Bt), 7.92 (d, 1H, $J = 8.2$, Bt), 8.07 (d, 1H, $J = 8.3$, Bt)	23.4 ($2C_{cyclopentyl}$), 27.4 (2C, CH_3), 33.8 ($2C_{cyclopentyl}$), 75.7 (CHO), 92.2 (NCO), 113.3 (Bt), 119.7 (Bt), 124.0 (Bt), 126.8 (Bt), 131.8 (Bt), 146.8 (Bt)	246 (27, M^+), 187 (4), 160 (23), 127 (100), 120 (32), 117 (26), 91 (18)
5g	1.02–1.12 (m, 9H, $3CH_3$), 1.28–1.77 (m, 8H), 2.57–2.67 (m, 2H), 2.72–2.79 (m, 2H), 3.34 (t, 2H, $J = 6.6$, OCH_2), 7.59 (t, 1H, $J = 7.4$, Bt), 7.67 (t, 1H, $J = 6.9$, Bt), 8.16 (d, 1H, $J = 8.1$, Bt), 8.30 (d, 1H, $J = 8.3$, Bt)	7.1 (2C, $2CH_3$), 13.8 (hexyl CH_3), 22.3, 25.6, 26.5 (2C, CH_2), 29.3, 31.3, 61.9 (OC), 97.5 (NCO), 112.8 (Bt), 119.6 (Bt), 123.7 (Bt), 126.7 (Bt), 131.9 (Bt), 146.4 (Bt)	290 (56, $M^+ + 1$), 188 (22), 171 (100), 132 (12), 120 (15), 87 (76)
5h	0.87 (t, 6H, $J = 7.6$, $2CH_3$), 2.49 (m, 2H, CH_2), 2.58 (m, 2H, CH_2), 4.16 (s, 2H, $PhCH_2$), 7.21 (m, 5H, Ph), 7.28 (t, 1H, $J = 6.7$, Bt), 7.37 (t, 1H, $J = 6.1$, Bt), 7.86 (d, 1H, $J = 7.2$, Bt), 8.08 (d, 1H, $J = 6.9$, Bt)	7.26 (2C, $2CH_3$), 26.7 (2C, CH_2), 65.4 ($PhCH_2O$), 97.8 (NCO), 112.9 (Bt), 119.9 (Bt), 123.9 (Bt), 127.0 (Bt), 127.7 (Ph), 128.0 (2C, Ph), 128.3 (2C, Ph), 132.0 (Bt), 136.8 (Ph), 146.7 (Bt)	209 (38), 180 (88), 152 (11), 91 (100)
5i	0.83 (t, 6H, $J = 7.5$, $2CH_3$), 0.89 (d, 6H, $J = 6.2$, $CH(CH_3)_2$), 2.41 (m, 2H, CH_2), 2.61 (m, 2H, CH_2), 3.75 (hept, 1H, OCH), 7.35 (t, 1H, $J = 7.1$, Bt), 7.44 (t, 1H, $J = 7.1$, Bt), 7.92 (d, 1H, $J = 8.4$, Bt), 8.06 (d, 1H, $J = 8.2$, Bt)	7.5 (2C, $2CH_3$), 23.5 (2C, $CH(CH_3)_2$), 26.8 (2C, $2CH_2$), 65.9 ($CH(CH_3)_2$), 97.6 (NCO), 113.6 (Bt), 119.7 (Bt), 119.7 (Bt), 123.7 (Bt), 126.5 (Bt), 132.2 (Bt), 146.7 (Bt)	248 (18, $M^+ + 1$), 188 (5), 148 (3), 129 (100), 119 (19), 87 (72)
6j	1.50 (m, 1H), 1.68 (m, 3H), 1.82 (m, 2H), 2.63 (m, 4H), 4.26 (s, 2H, $PhCH_2$), 7.21 (m, 5H, Ph), 7.38 (m, 2H, Bt), 7.92 (m, 2H, Bt)	22.5 (2C), 24.9, 34.8 (2C), 64.5 ($PhCH_2O$), 95.8, 118.6 (2C, Bt), 126.4 (2C, Bt), 127.3 (Ph), 127.4 (2C, Ph), 128.1 (2C, Ph), 137.5 (Ph), 143.8 (2C, Bt)	210 (18), 201 (37), 189 (47), 188 (43), 180 (47), 120 (29), 119 (28), 91 (100)
5k	0.83 (d, 6H, $J = 6.2$, $CH(CH_3)_2$), 1.45 (m, 1H), 1.70 (m, 5H), 2.50 (t, 4H, $J = 5.8$), 3.77 (hept, 1H, $CH(CH_3)_2$), 7.34 (dd, 1H, $J = 8.2$, 6.9, Bt), 7.43 (dd, 1H, $J = 8.1$, 6.9, Bt), 7.90 (d, 1H, $J = 8.3$), 8.05 (d, 1H, $J = 8.2$, Bt)	22.5 (2C), 23.5 (2C, $CH(CH_3)_2$), 25.2, 35.3 (2C), 65.5 ($CH(CH_3)_2$), 93.1 (NCO), 113.6 (Bt), 119.7 (Bt), 123.6 (Bt), 126.4 (Bt), 132.0 (Bt), 146.7 (Bt)	260 (18, M^+), 200 (5), 141 (100), 119 (13), 99 (83), 91 (17), 81 (16)

[a] Product **3a** has been characterized before.[12]

[b] Obtained on a Varian VXR-300 spectrometer. Bt = benzotriazolyl.

[c] Recorded on a Finnigan Mat 4500 spectrometer.

Table 3. Alkyl Alkenyl Ethers 7 Prepared

Product	Yield (%)	*E*/*Z*	bp (°C)/mbar	Molecular Formula[a] or Lit. bp (°C)/mbar	^{1}H-NMR ($CDCl_3$/TMS)[b] δ, *J*(Hz)	^{13}C-NMR ($CDCl_3$/TMS)[b] δ	MS (7 eV)[c] *m*/*z* (%)
7e	92	[d]	100–104/60	86–89/18[22]	3.73 (s, 3H, OCH_3), 4.21 (d, 1H, J = 2.2, =CH_2), 4.66 (d, 1H, J = 2.6, =CH_2), 7.33 (m, 5H, Ph)	55.2 (OCH_3), 81.7 (CH_2), 82.1 (=CO), 125.3 (2C, Ph), 125.4 (Ph), 128.1 (2C, Ph), 128.4 (Ph)	134 (100, M^+), 103 (51), 91 (53), 78 (80), 65 (24), 51 (69)
7f	90	[d]	131–133/760	$C_8H_{14}O$ (126.2)	1.54 (m, 2$H_{cyclopentyl}$), 1.72 (m, 6$H_{cyclopentyl}$), 1.77 (s, 3H, CH_3), 3.77 (s, 1H, =CH_2), 3.84 (s, 1H, =CH_2), 4.43 (m, 1H, CHO)	21.4 (CH_3), 24.5 (2$C_{cyclopentyl}$), 32.6 (2$C_{cyclopentyl}$), 78.3 (CHO), 82.1 (=CH_2), 158.5 (=CO)	127 (19, $M^+ + 1$), 126 (14, M^+), 101 (11), 69 (23), 67 (24), 59 (100)
7g	80	62 : 38	81–82/1.3	$C_{11}H_{22}O$ (170.3)	(*E*)-**7g**: 0.89 (t, 3H, J = 6.7, hexyl), 1.03 (t, 3H, J = 7.5, CH_2CH_3), 1.20–1.50 (m, 6H_{hexyl}), 1.57 (d, 3H, J = 6.7, CH_3), 1.64 (m, 2H_{hexyl}), 2.13 (q, 2H, J = 7.5, CH_2CH_3), 3.55 (t, 2H, J = 6.4, hexyl), 4.31 (q, 1H, J = 6.8, =CH (*Z*)-**7g**: 0.90 (t, 3H, J = 6.7, hexyl), 1.02 (t, 3H, J = 7.5, CH_2CH_3), 1.20–1.50 (m, 6H_{hexyl}), 1.57 (t, 3H, J = 6.7, CH_3), 1.64 (m, 2H_{hexyl}), 2.13 (q, 2H, J = 7.5, CH_2CH_3), 3.66 (t, 2H, J = 6.4, hexyl), 4.57 (q, 1H, J = 6.7, =CH)	(*E*)-**7g**: 11.5 (CH_3CH=), 12.1 (CH_2CH_3), 14.1 (C_{hexyl}), 22.7 (C_{hexyl}), 23.4 (C_{hexyl}), 26.0 (C_{hexyl}), 29.3 (C_{hexyl}), 31.7 (CH_2CH_3), 66.4 (CH_2O), 89.6 (=CH) 158.2 (=CO) (*Z*)-**7g**: 10.2 (CH_3CH=), 12.0 (CH_2CH_3), 14.1 (C_{hexyl}), 22.7 (C_{hexyl}), 23.4 (C_{hexyl}), 25.0 (C_{hexyl}), 29.3 (C_{hexyl}), 30.1 (CH_2CH_3), 68.4 (CH_2O), 103.1 (=CH), 156.5 (=CO)	171 (33, $M^+ + 1$), 120 (10), 91 (6), 87 (100), 57 (21)
7h	80	58 : 42	78–80/3	$C_{12}H_{16}O$ (176.3)	(*E*)-**7h**: 1.02 (t, 3H, J = 7.5, CH_2CH_3), 1.51 (d, 3H, J = 6.8, CH_3), 2.12 (q, 2H, J = 7.5, CH_2CH_3), 4.37 (q, 1H, J = 6.8, =CH), 4.67 (s, 2H, $PhCH_2$), 7.08–7.29 (m, 5H, Ph) (*Z*)-**7h**: 0.98 (t, 3H, J = 7.5, CH_2CH_3), 1.50 (d, 3H, J = 6.7, CH_3), 2.08 (q, 2H, J = 7.5, CH_2CH_3), 4.50 (q, 1H, J = 6.7, =CH), 4.59 (s, 2H, $PhCH_2$), 7.08–7.29 (m, 5H, Ph)	(*E*)-**7h**: 10.6 (CH_2CH_3), 12.1 (CH_3), 23.3 (CH_2CH_3), 68.4 ($PhCH_2$), 90.7 (=CH), 127.2 (2C, Ph), 127.5 (Ph), 128.3 (2C, Ph), 138.0 (Ph), 158.4 (=CO) (*Z*)-**7h**: 10.3 (CH_2CH_3), 11.5 (CH_3), 25.0 (CH_2CH_3), 70.3 ($PhCH_2$), 103.9 (=CH), 127.4 (2C, Ph), 127.6 (Ph), 128.3 (2C, Ph), 138.0 (Ph), 158.4 (=CO)	176 (15, M^+), 106 (33), 91 (100), 77 (6)
7i	89	60 : 40	116/760	$C_8H_{16}O$ (128.2)	(*E*)-**7i**: 1.02 (t, 3H, J = 7.5, CH_2CH_3), 1.19 (d, 6H, J = 6.1, $CH(CH_3)_2$, 1.58 (d, 3H, J = 6.8, CH_3), 2.09 (q, 2H, J = 7.6, CH_2CH_3), 4.16 (hept, J = 6.1, 1H, $CH(CH_3)_2$), 4.36 (q, 1H, J = 6.7, =CH) (*Z*)-**7i**: 1.01 (t, 3H, J = 7.5, CH_2CH_3), 1.18 (d, 6H, J = 6.1, $CH(CH_3)_2$), 1.56 (dt, 3H, J = 6.6, 1.3, CH_3), 2.09 (q, 2H, J = 7.6, CH_2CH_3), 4.09 (hept, 1H, J = 6.1, $CH(CH_3)_2$), 4.66 (qt, 1H, J = 6.7, 1.0, =CH)	(*E*)-**7i**: 12.0 (CH_2CH_3), 12.1 (CH_3), 21.9 (2C, $CH(CH_3)_2$), 23.4 (CH_2CH_3), 67.0 ($CH(CH_3)_2$), 91.5 (=CH), 156.1 (=CO) (*Z*)-**7i**: 10.5 (CH_2CH_3), 11.6 (CH_3), 22.5 (2C, $CH(CH_3)_2$), 25.2 (CH_2CH_3), 68.5 ($CH(CH_3)_2$), 104.8 (=CH), 154.7 (=CO)	128 (11, M^+), 86 (66), 57 (100), 43 (21)
7j	75	100 : 0	150/0.15	74–76/0.08[23]	1.60 (m, 2H), 1.69 (m, 2H), 2.08 (m, 2H), 2.13 (m, 2H), 4.70 (s, 2H, $PhCH_2$), 4.72 (t, 1H, J = 3.9, =CH), 7.32 (m, 5H, Ph)	22.8, 23.6, 27.9, 33.1, 68.4 ($PhCH_2$), 94.5 (HC=), 118 (=CO), 127.5 (2C, Ph), 127.6, 128.4 (2C, Ph), 137.7	188 (55, M^+), 160, 171 (10), 120 (5), 91 (100)
7k	91	100 : 0	162–164/160	$C_9H_{16}O$ (140.2)	1.21 (d, 6H, J = 6.1, $CH(CH_3)_2$), 1.53 (m, 2H), 1.65 (m, 2H), 2.04 (m, 4H), 4.22, (hept, 1H, $CH(CH_3)_2$), 4.62 (t, 1H, J = 3.4, =CH)	22.0 (2C, $CH(CH_3)_2$), 22.8, 23.1, 23.7, 28.3, 67.1 ($CH(CH_3)_2$), 95.1 (=CH), 152.7 (=CO)	140 (100, M^+), 98 (64.4), 97 (37), 83 (48), 70 (63), 55 (32)

[a] Satisfactory microanalyses obtained: C ±0.26, H ±0.09.
[b] Obtained on a Varian VXR-300 spectrometer.
[c] Recorded on a Finnigan Mat 4500 spectrometer.
[d] There are no isomers for these compounds.

doublet and doublet for H-6, H-5, H-7 and H-4, respectively. Only high resolution spectra revealed ddd patterns for every one of these resonances with *meta* and *para* coupling constants in the benzotriazole ring of about $J = 1$ Hz.[16] ^{13}C-NMR Signals of the benzotriazolyl moiety in ethers **5** were assigned to the benzotriazolyl carbon atoms in the following sequence: $\delta = 112-113$ (C-7), $\delta = 119-120$ (C-4), $\delta = 123-124$ (C-5), $\delta = 127-128$ (C-6), $\delta = 132-133$ (C-7a) and $\delta = 145-146$ (C-3a) in accordance with the previous report.[12]

Compounds **5** eliminated a molecule of benzotriazole readily upon direct heating with sodium hydride at 140–160 °C; the ketone enol ether was distilled off under reduced pressure as it formed. This prevented decomposition or polymerization of the ether and resulted in high yields. Further purification was achieved by fractional distillation of the crude product (Table 3). Two of the ethers prepared, **7e** and **7j**; had been described previously. The other five ethers include representative examples of ketone enol ethers with secondary alkoxy groups, a class previously difficult to access.

Detailed examination of the ^{1}H-NMR spectra of the ethers **7g–i** revealed two quartets derived from resonances of the =CH protons at $\delta = 4.31$ and 4.57, $\delta = 4.37$ and 4.50, and $\delta = 4.36$ and 4.66, respectively, in each case in an approximate ratio of 3:2. In the ^{13}C-NMR spectra of these compounds, two peaks representing the alkenyl =CH resonance were found at $\delta = 89.6$ and 103.1 (for **7g**), $\delta = 90.7$ and 103.9 (for **7h**), and $\delta = 91.5$ and 104.8 (for **7i**), in the same ratio as the corresponding proton signals. Also some other signals in the ^{1}H- and ^{13}C-NMR spectra of these compounds were duplicated with only small differences in the chemical shifts. According to the literature,[17,18] the *Z*-isomer of a ketone derived enol ether exhibits its =CH carbon resonance at a significantly lower field than that of the *E*-isomer, the difference being 11–15 ppm. This value corresponds well with the present data and allows us to assign configuration *E* to the more abundant isomers of **7g–i**.

In conclusion, this ketone enol ether synthesis offers simplicity of workup and gives high yields of pure products. The method allows the preparation of enol ethers of ketones, not only with primary but also with secondary alkoxy groups, for which there was no general synthetic method previously described.

1-(Benzotriazol-1-yl)alkyl Methyl Ethers 3; General Procedure:
Method A: A solution of ketal **2** (200 mmol),[19–21] benzotriazole (35.74 g, 300 mmol) and H_2SO_4 (0.41 mL, 7.5 mmol) in CH_2Cl_2 (150 mL, dried over molecular sieves) is stirred at 25 °C for 5 h. The mixture is washed with 10% Na_2CO_3 (2 × 100 mL), H_2O and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure affords crude product **3** which is further purified by crystallization from hexane.

1-(Benzotriazol-1-yl)alkyl Alkyl Ethers 5; General Procedure:
Method B: A solution of ether **3** (100 mmol), an alcohol (100 mmol) and TsOH · H_2O (0.19 g, 1 mmol) in $CHCl_3$ (100 mL) is introduced into a distillation apparatus equipped with a dropping funnel. Slow distillation of the $CHCl_3$/MeOH mixture is carried out with dropwise addition of $CHCl_3$ at a rate to keep the same solution level in the flask. Progress of the reaction is monitored by NMR. When the methoxy group singlet has completely disappeared (2–8 h), work-up of the mixture is carried out as in Method A. The analytical samples are obtained by column chromatography using silica gel and hexane/EtOAc (85:15) as the eluent.

Method C: A solution of methoxy derivative **3** (100 mmol) and TsOH (0.5 g) in an alcohol (R^3OH, 1 mol) is heated at 55–60 °C over molecular sieves (4Å, 20 g) and under N_2 for 4 h. Excess R^3OH and MeOH liberated are removed by evaporation under reduced pressure to give a mixture of **3** and **5**. Treatment with R^3OH is repeated in the same manner and under the same conditions. The mixture is then diluted with dry Et_2O, filtered and the solvent evaporated. The residue is dissolved in CH_2Cl_2 (100 mL), washed with 10% Na_2CO_3 (50 mL) and dried (Na_2CO_3, 5 g). The solvent is removed under vacuum and the oil obtained is crystallized from hexane.

Method D: A solution of cyclohexanone (9.81 g, 0.1 mol), benzotriazole (11.91 g, 0.1 mol), dry *i*-PrOH (12 g, 0.2 mol) and TsOH · H_2O (2 mmol, 0.004 g) in CCl_4 (120 mL) is refluxed in a Soxhlet apparatus to allow the H_2O liberated to be removed by extraction with molecular sieves (4Å grade 514, 8–12 mesh). After 12 h, the mixture is allowed to cool to r.t. and worked up by rapid extraction (2 ×) with aq 10% Na_2CO_3, washed once with ice-cold H_2O, dried (Na_2CO_3) and the solvent removed by evaporation under reduced pressure at 50 °C.

Alkyl 1-Alkenyl Ethers 7; General Procedure:
A mixture of compound **5** (30 mmol) and NaH (60 mmol) is slowly heated (oil bath) under reduced pressure (0.1–5 Torr, depending on the molecular weight of the desired ether) in a distillation apparatus equipped with a receiver cooled in a dry ice/acetone bath. The 1-alkenyl ether distilled off in the range of 140–160 °C. The crude product (usually of purity > 90% is further purified by fractional distillation.

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