The homologation of carbonyl compounds by single carbon insertion reactions

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Dedicated to Professor Alexander T. Balaban on the occasion of his 75th birthday

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Abstract
This short review describes the methods of single carbon insertion reactions into carbonyl compounds.

Keywords: Insertion, rearrangement, carbonyl compounds, migration

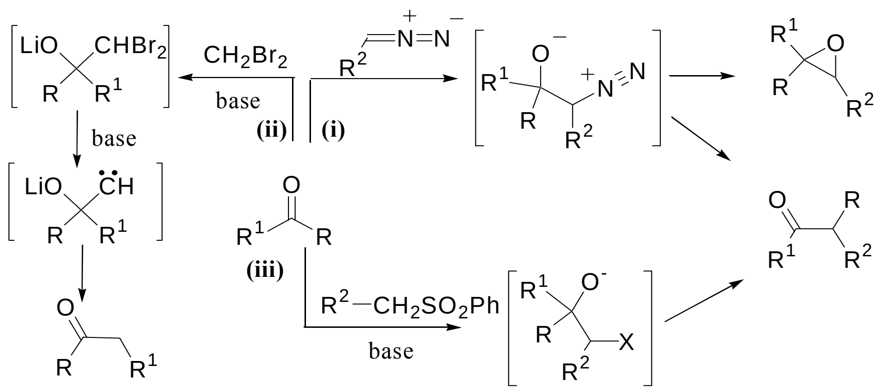
Contents

1. Introduction
2. Single carbon insertion *via* β-oxido carbenoid intermediates
3. Single carbon insertion *via* α-lithioalkyl sulfone intermediates
4. General overview of benzotriazole-mediated single carbon insertion
5. Bt-mediated insertion with C-linked substituents on the carbon atom α to Bt
6. Bt-mediated insertion with Het-linked substituents on the carbon atom α to Bt
7. Insertion with C- and Het-linked substituents on the carbon atom α to Bt
8. Examples of *bis*-Bt Insertion
9. Intramolecular insertion
10. Selectivity in the rearrangement steps
11. Conclusion

1. Introduction

Carbon chain extension or ring expansion of carbonyl compounds by one-carbon unit is a frequently encountered synthetic objective. Carbon insertion reactions are the most straightforward and most commonly used strategy for this purpose. Classical insertion reactions utilizing diazo compounds are known for diazoalkanes as well as functionalized diazo compounds such as ethyl diazoacetate etc. (Scheme 1(**i**)).[1a–j] However, the use of diazo compounds is not usually possible on the large scale and many attempts have been made to find other insertion methods avoiding diazo compounds.

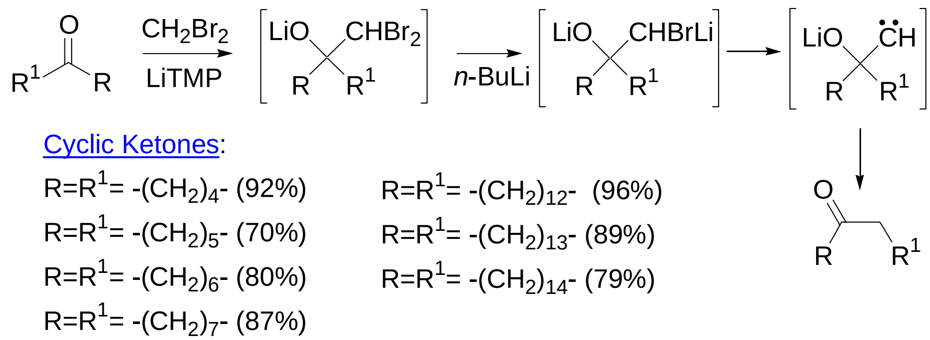
β-Oxido carbenoid chemistry was initiated by Yamamoto using dihalomethyllithiums[2a,b] (Scheme 1(**ii**)) and then expanded significantly by Satoh and Yamakawa who utilized 1-chloroalkyl aryl sulfoxides as one carbon homologating agents.[3a–c] Trost introduced sulfone-assisted insertions: published examples have all involved the insertion of either CHSPh or CHOMe groups, utilizing α-thio and α-alkoxy sulfones[4a] (Scheme 1(**iii**)).



Scheme 1. **(i)** insertion by diazo compounds. (**ii**) insertion via *β*-oxido carbenoid intermediates. (**iii**) insertion via *α*-lithioalkyl sulfone intermediates.

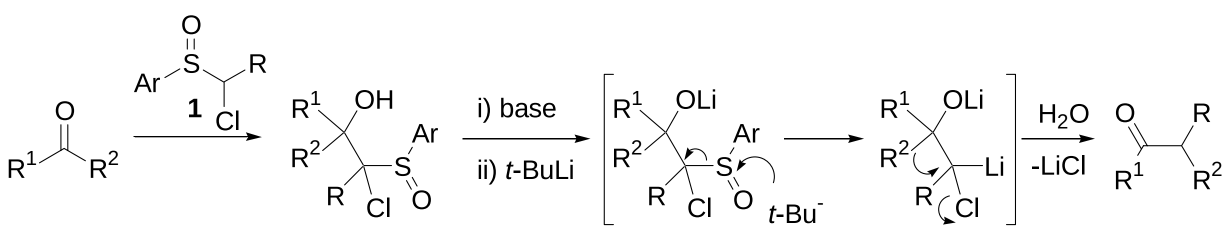
2. Single carbon insertion *via β*-oxido carbenoid intermediates

The Yamamoto method is presented in more detail in Scheme 2. This approach depends crucially on the generation in situ of dibromomethyllithium from methylene bromide and its addition to carbonyl compounds in the presence of lithium dialkylamide. Depending on the structure of the ketone the dibromomethyllithium carbonyl adduct may rapidly form the corresponding epoxide; to avoid this the reaction should be performed between –70 °C and –100°C. Although the dibromomethyllithium carbonyl adducts are extremely thermally unstable, several one-carbon homologated cyclic ketones were synthesized in high yields by this method (Scheme 2).[2a,b]



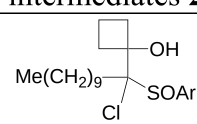
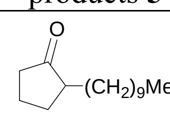
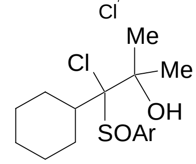
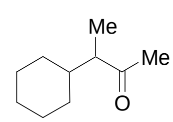
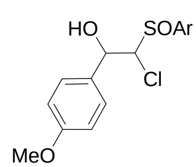
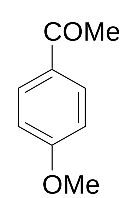
Scheme 2

The modification by Satoh and Yamakawa[3a–c] of this method for the one-carbon homologation of carbonyl compounds is based on the rearrangement of *β*-oxido carbenoids **4** generated via ligand exchange of the sulfinyl group of α-chloro *β*-hydroxy sulfoxide **3** with *t*-BuLi to give homologated ketones **5** (Scheme 3): Table 1 shows examples where selective migration occurs to form a single regioisomer. Most insertions into cyclic ketones and aromatic or aliphatic aldehydes are regioselective with formation of single regioisomers; however, insertions into aryl-alkyl ketones lead to both aryl- and alkyl-migration.

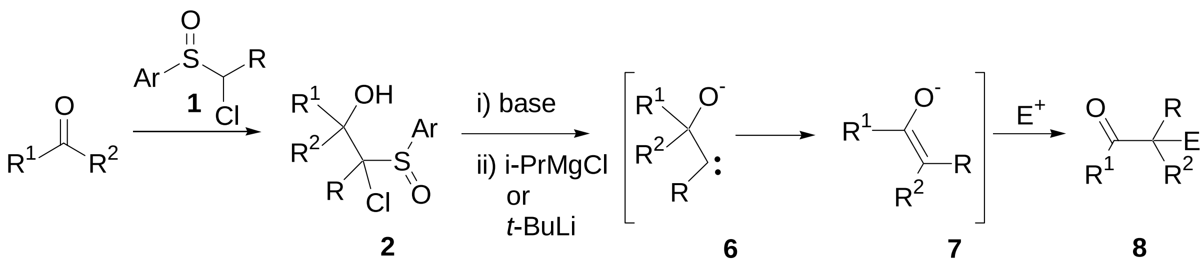


Scheme 3

Table 1. Examples of carbon insertion via *β*-oxido carbenoid intermediates

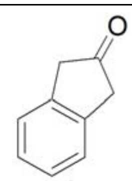
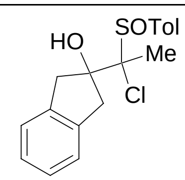
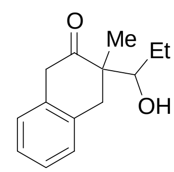
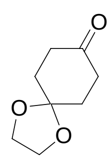
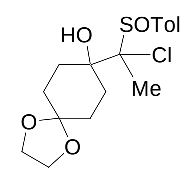
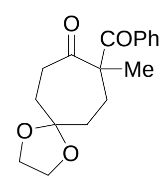
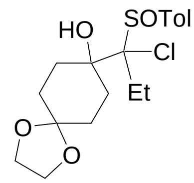
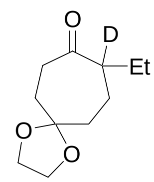
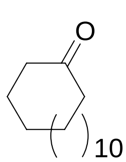
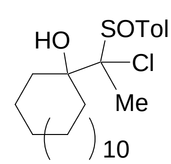
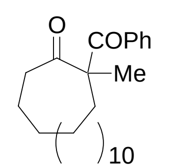
Reagent	Carbonyl substrate	Number of examples	Average yield, %	Examples of intermediates **2**	Examples of products **5**	Ref.
ClRCHSOAr R = Alk	Cyclic ketones	9	68			3b,c
	Aliphatic and mixed ketones	2	58			3b
$ClCH_2SOAr$	Aromatic, aldehydes, cyclic and mixed ketones	7	52			3b

Recently, Satoh and Miyashita reported one-carbon homologations of cyclic ketones by treatment of adducts **2** derived from the 1-chloroalkyl sulfoxides **1** with *t*-BuMgCl or LDA followed by reaction with *i*-PrMgCl. Then the enolate intermediates **7** generated in situ from the rearrangement of **6** were trapped with an electrophile to give the α,α-disubstituted homologated ketones **8** (Scheme 4) (Table 2).[3a]



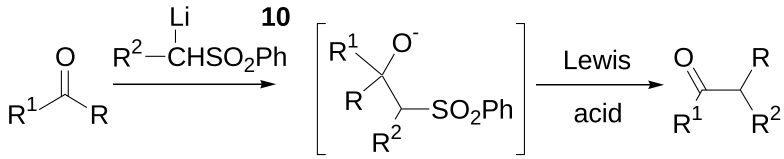
Scheme 4

Table 2. Examples of carbon insertion via *β*-oxido carbenoid intermediates

Cyclic ketone	Electrophile	Number of examples	Average yield, %	Examples of intermediates **2**	Examples of products **8**	Ref
	EtCHO	1	38			3a
	ClCOOEt PhCHO PhCOCl	R = Me 3	58			3a
	CD_3OD ClCOOEt EtCHO	R = Et or $(CH_2)_4Ph$ 6	49			
	ClCOOEt EtCHO PhCOCl	3	59			3a

3. Single carbon insertion *via* α-lithioalkyl sulfone intermediates

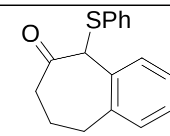
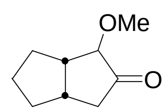
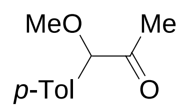
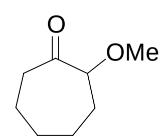
Trost introduced a useful insertion methodology by reaction of α-lithioalkyl sulfones **10** with ketones **9** to form intermediates **11** followed by aluminium-based Lewis acid-induced ring expansion to α-phenylthio and α-methoxy ketones **12** as shown in Scheme 5 and Table 3 (entries 1 and 2). Published examples of this approach have all concerned cyclic or bicyclic ketones and α-thio or α-alkoxy sulfones.



9 **11** **12**

Scheme 5

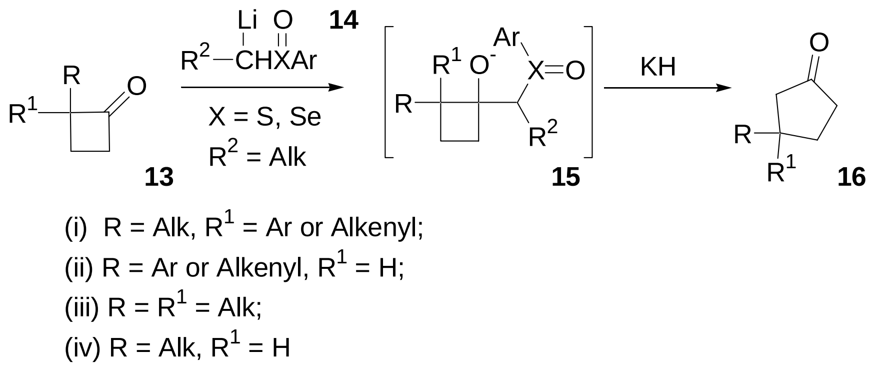
Table 3. Examples carbon insertion *via* α-lithioalkyl sulfone intermediates

	Reagent **10**	Ketone	Number of examples	Average yield, %	Examples of products **12**	Ref
1	$PhSCH_2SO_2Ph$	Cyclic and bicyclic 4-, 5- and 6-ring	6	73		4a
2	$MeOCH_2SO_2Ph$	" "	5	68		4a
3	$MeOCH_2SO_2Ph$	Aryl-alkyl ketones and dialkyl ketones	3	74		4b,c
4	$MeOCH_2SO_2Ph$	Cyclic	4	61		4b,c

Later, Trost's sulfone homologation procedure for the transformation of ketones **9** into their higher homologues **12** was extended by Taylor to aryl-alkyl ketones, dialkyl ketones and novel cycloalkanones utilizing $ZrCl_4$ promoted conditions in the rearrangement step (Scheme 5 and Table 3; entries 3 and 4).

α-Lithioalkyl aryl sulfoxides and selenoxides are effective reagents for the ring expansion of a variety of cyclobutanones to cyclopentanones.[4d] Intermediates **15** produced from **14** and cyclobutanones **13** undergo rapid ring expansion upon treatment with potassium hydride to give

16 in good yields (Scheme 6 and Table 4). Using **14** the carbon atom inserted into the cyclobutanone can be unsubstituted, monosubstituted, or disubstituted.[4d]



Scheme 6

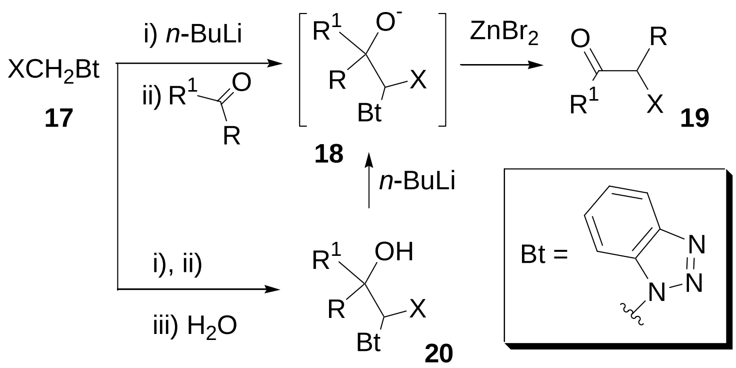
Table 4. Ring expansion of cyclobutanones to cyclopentanones *via* α-lithioalkyl aryl sulfoxide and selenoxide intermediates

Cyclobutanone **13**	Reagent **14**	Number of examples **16**	Average yield, %	Ref
(i) and (ii)	2-ClPhS(O)R^2	16	57	4d
(i) and (ii)	ArS(O)R^2 Ar = Ph, 2-ClPh	5	57	4d
(i), (iii) and (iv)	PhSe(O)R^2	8	43	4d

4. General overview of benzotriazole-mediated single carbon insertion

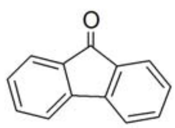
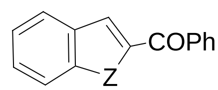
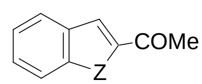
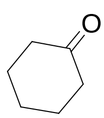
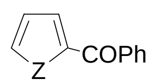
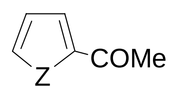
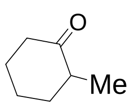
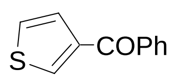
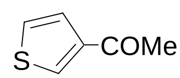
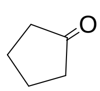
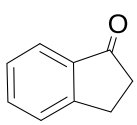
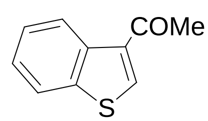
Benzotriazole derivatives **17** may also be used in one-carbon homologation as shown in Scheme 7.[5a–d] Carbonyl compounds that can be utilized as starting materials include aliphatic, aromatic aldehydes and many types of ketones (Table 5). Monosubstituted benzotriazolylmethanes **17**, which can be successfully inserted include 1-(arylmethyl)-, 1-(heteroarylmethyl)-, 1-(alkenylmethyl)-, 1-(alkoxymethyl)-, and 1-[(phenylthio)methyl]-benzotriazoles, which allow the preparation of wide variety of α-functionalized ketones. The generality of our methodology is also exemplified by successful insertions of disubstituted methylene groups into carbonyl compounds when disubstituted reagents of type Bt-CHXY are utilized.

Insertion into ketones can be performed by use of our procedure in a simple one-step operation. The lithium alcoholate **18** generated from **17** and a ketone undergoes a subsequent rearrangement catalyzed by zinc bromide to give the homologated ketones **19**. An alternative two-step procedure includes the formation of benzotriazolyl alcohols **20**, which undergo rearrangement *via* their lithium alcoholates **18** to give **19** (Scheme 7).



Scheme 7

Table 5. Examples of carbonyl compounds utilized in Bt-mediated insertion

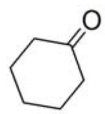
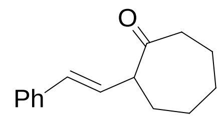
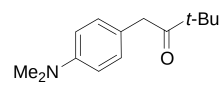
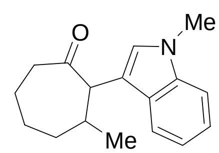
Carbonyl substrate					Ref
Ketones				Aldehydes	
Cyclic	Di-alkyl	Di-aryl	Alkyl-Aryl		
	*t*-BuCOMe	 Z = O, S	 Z = O, S	Ph(CH$_2$)$_2$CHO	5a–d
	Bn$_2$CO	 Z = O, S	 Z = O, S	*t*-BuCHO	5a–d
	*i*-PrCOMe			4-ClC$_6$H$_4$CHO	5a–d
	_____	4-PyCOPh	PhCOMe	*p*-TolCHO	5a–c
	_____	_____		PhCHO	5b–d

5. Bt-mediated insertion with C-linked substituents on the carbon atom α to Bt

A large variety of C-linked substituents can be carried by the carbon atom that is inserted next to carbonyl group. As shown in Scheme 7 and Table 6 these include vinyl groups, aryl groups and heteroaryl groups.

Insertion of aryl-linked[6a,b] and vinyl-linked[6c] carbons into carbonyl compounds has previously been achieved by direct insertion of the corresponding diazo compounds, but, this procedure is limited by low regioselectivity and handling difficulties. An advantage of the benzotriazole-mediated methodology is the possibility of introducing a heteroaryl group attached to the inserted carbon; the 1-methyl-1*H*-indol-3-yl and 5-methylthiophene-2-yl groups, for example, were introduced in this way.[5a–c]

Table 6. C-linked substituents on the carbon atom α to Bt

17 X	C-linked group inserted	Carbonyl substrate	Number of examples	Average Yield, %	Examples of products **19**	Ref.
Vinyl	CH-vinyl		1	60		5a
Ar	CH-Ar	Aromatic and aliphatic aldehydes; aliphatic, cyclic and mixed ketones	11	57		5a, c
Het	CH-Het	Aromatic and aliphatic aldehydes; aliphatic, cyclic and mixed ketones	10	76		5a–c

6. Bt-mediated insertion with Het-linked substituents on the carbon atom α to Bt

Similarly, a whole variety of heteroatom-linked substituents can be carried by the inserted carbon atom. As shown in Scheme 7 and Table 7 this can include various O-linked, S-linked and N-linked groups.

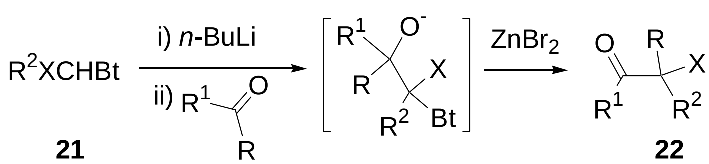
1-Methoxymethyl-1*H*-benzotriazole, 1-phenoxymethyl-1*H*-benzotriazole, 1-methylsulfanylmethyl-1*H*-benzotriazole, 1-phenylsulfanylmethyl-1*H*-benzotriazole and 9-benzotriazol-1-ylmethyl-9*H*-carbazole (for **17** see Scheme 7 and Table 7) are readily available and versatile reagents. They enable the transformation of a wide range of aldehydes and ketones into corresponding functionalized one-carbon homologues **19**.[5a,b] Published examples of the insertions of α-methoxymethylene and phenylthiomethylene groups to form α-methoxy and α-phenylthio alkyl ketones by the Trost[4a] method all involve cyclic ketones.

Table 7. Het-linked substituents on the carbon atom α to Bt

17 X	Het-linked group inserted	Carbonyl substrate	Number of examples	Average Yield, %	Examples of products **19**	Ref.
OMe	CHOMe	Aromatic and aliphatic aldehydes; aromatic, cyclic and mixed ketones	7	58	PhCH(OMe)COMe	5a,b
OPh	CHOPh	Aromatic and aliphatic ketones	2	50	PhCOCH(OPh)Ph	5a,b
SMe	CHSMe	Aromatic aldehyde and mixed ketone	2	67	$PhCOCH_2SMe$	5a,b
SPh	CHSPh	Aromatic and aliphatic aldehydes; aromatic, and mixed ketones	5	73	PhCH(SPh)COPh	5b
NRR′	CHNRR′	Aromatic aldehydes and mixed ketone	3	76	PhCH(Cb)COMe	5b

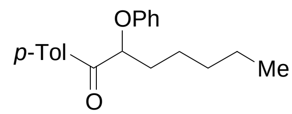
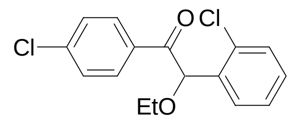
7. Insertion with C- and Het-linked substituents on the carbon α to Bt

It is possible to insert a carbon atom carrying two substituents with a reagent of type **21** (Scheme 8). In these examples one substituent is an alkyl or aryl group and the other is an *O*-linked, *S*-linked or *N*-linked group. Examples of such insertion reactions to aromatic aldehydes and cyclic ketones to give higher homologues **22** are shown in Scheme 8 and Table 8.



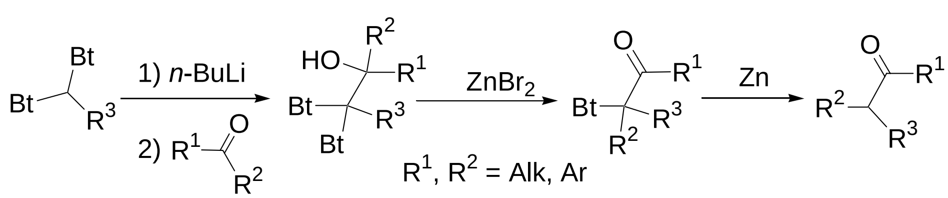
Scheme 8

Table 8. C- and Het-linked substituents on the carbon atom α to Bt

21 X	Simultaneous insertion of two group	Carbonyl substrate	Number of examples	Average Yield, %	Examples of products **22**	Ref
OPh	Alkyl-C-OPh	*p*-TolCHO	1	81		5b
OEt	Ar-C-OEt	Aromatic aldehyde and cyclic ketone	2	71		5a,b
SPh	R^2-C-SPh R^2 = Alk, Ar	Aromatic aldehyde and cyclic ketone	2	70	PhCH(SPh)COPh	5b
NRR'	Alk-C-NRR’	PhCHO	1	56	PhCOCH(Cb)Me	5b

8. Examples of *bis*-Bt insertion

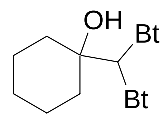
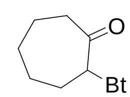
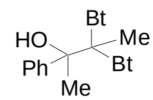
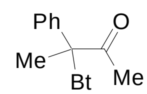
One example missing from the above is the insertion of carbon carrying a single alkyl group. This is not easy using an alkylbenzotriazole because the acidity of the α-hydrogen is low and yields are poor. However, this limitation has been overcome by using (alkylidene)bisbenzotriazoles **23** (Scheme 9, Table 9).[5d] Insertion here gives the expected intermediate **24** containing two benzotriazole groups one of which is eliminated during the rearrangement to give ketone **25** and the other one can easily be eliminated by treatment with Zn metal to give functionalized ketone **26**.[7a] Intermediates **25** with an α-benzotriazolyl group are of significant synthetic utility for transformations to diketones,[7b,c] or olefins,[7d–g] for directed regioselective α-alkylation,[7h] and for heterocyclic ring synthesis.[7i]



23 **24** **25** **26**

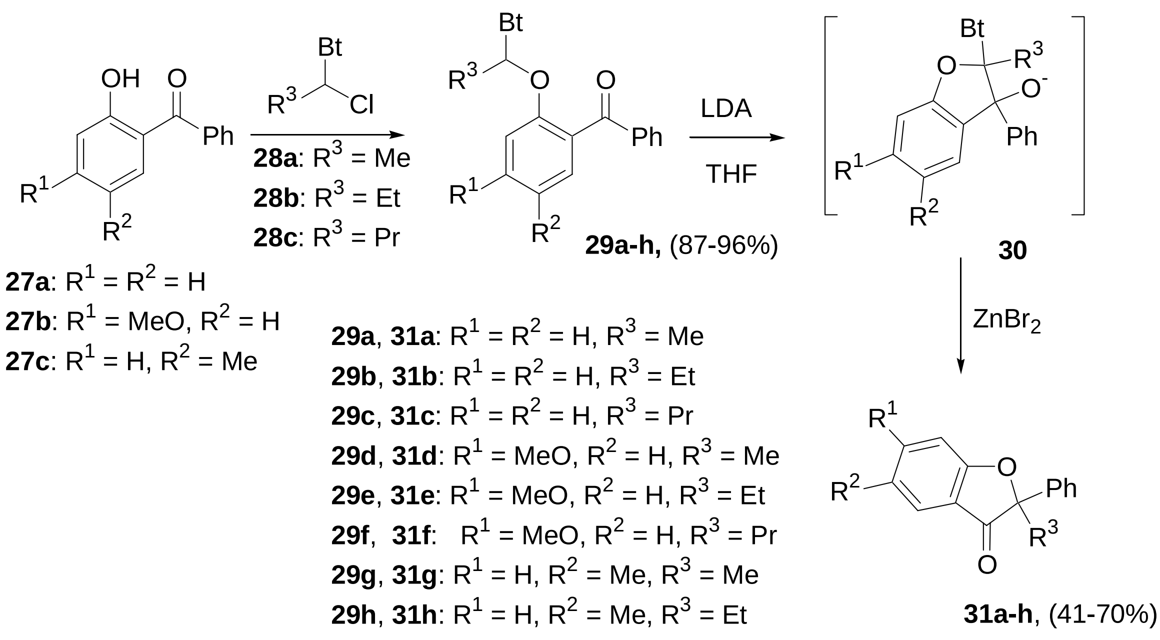
Scheme 9

Table 9. *Bis*-Bt examples

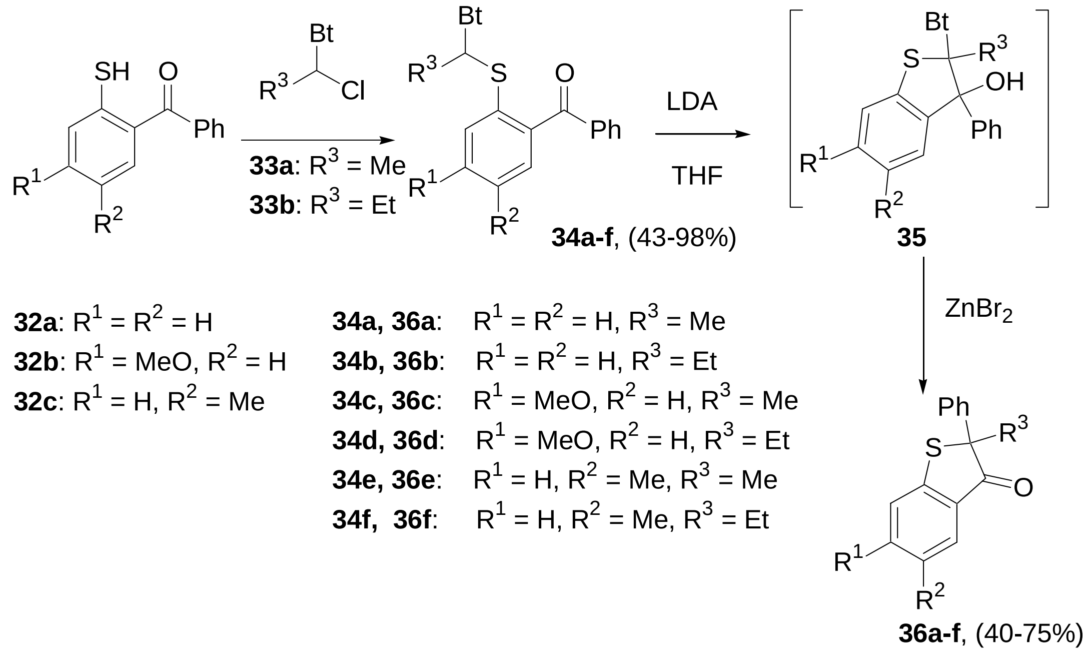
R^3	Bt-CX is inserted	Carbonyl substrate	Number of examples	Average Yield, %	Examples of intermediates	Examples of products **25**	Ref
H	Bt-CH	Aromatic, aliphatic, mixed and cyclic ketones	5	60			5d
Me	Bt-CMe	Aromatic, aliphatic, mixed and cyclic ketones	4	38			5d

9. Intramolecular insertion

Intramolecular reaction of the carbonyl group of adducts **29** or **34** with a benzotriazole-activated nucleophilic α-carbon to give intermediates **30** or **35** is also possible (Schemes 10 and 11).[8a] Intermediates **30** and **35** can be isolated as corresponding alcohols or directly treated with Lewis acid to give inserted ketones **31** and **36** respectively. This method is valuable for the synthesis of 3-alkyl-3-aryl-2,3-dihydrobenzofuran-2-ones, which are important intermediates for the synthesis of the anti-cancer compound, diazonamide A,[8b,c] analgesics[8d] and antidepressants.[8d]



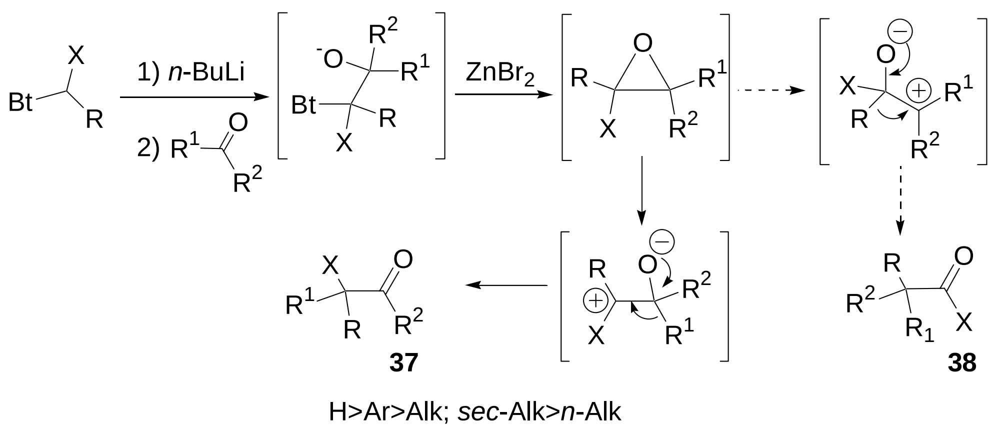
Scheme 10



Scheme 11

10. Selectivity in the rearrangement steps

If an unsymmetrical ketone is used as the starting material, then obviously two products **37** and **38** could occur from the rearrangement (Scheme 12). The mechanism of rearrangement was discussed in previous publications,[5a–c] and involves zinc bromide-promoted oxirane ring-closure-ring-opening followed by migration of the group that can best stabilize an electron deficiency (Scheme 12).



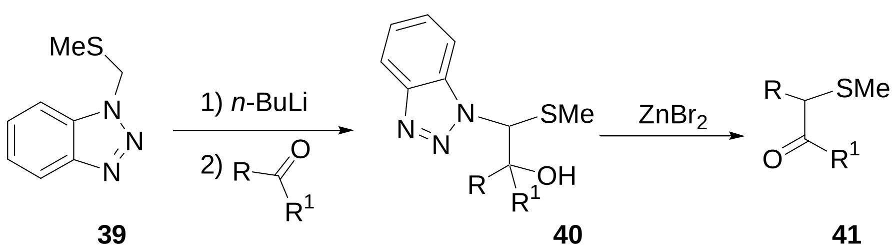
Scheme 12

The selectivity of benzotriazole-mediated insertions is notable.[5a–c] In most cases, single regioisomers **37** were produced by migration of the R^1 shown in Scheme 12 and Table 10. Similar migration aptitudes were found in other pinacol-type rearrangements H>Ar>Alk; *sec*-Alk>*n*-Alk.[9a,b]

Table 10. Selectivity of migration

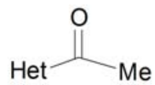
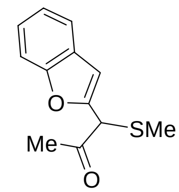
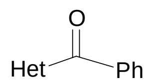
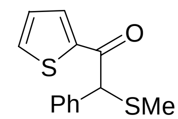
R^1 Migrating group	R^2 Non- migrating group	R	X
H	$Ph(CH_2)_2$-	H	H, OMe, SPh, Ar
i-Pr	Me	H	OPh, Ar
H	4-ClC_6H_4	H	OEt, SPh, Ar
Ph	Me	H	SPh, OMe, Ar
Ph	Me	Ph, Me	SPh
H	Ph	H	SPh, SMe, OMe, Ar
Ph	4-pyridyl	H	OMe
H	4-MeC_6H_4	H	C_5H_{11}

To extend the synthetic utility of benzotriazolyl-mediated one carbon insertion, the migratory aptitude of π-electron-rich heterocycles of 2-benzotriazolyl alcohols **40** in the presence of alkyl and aryl groups has been investigated recently.[5e] It was demonstrated that electron rich heteroaryl groups migrate more easily than the methyl group but less easily than a phenyl group (Scheme 13 and Table 11).



Scheme 13

Table 11. Examples of migration

Migrating group (R)	Non-migrating group (R^1)	Carbonyl substrate	Number of examples	Average Yield, %	Examples of products **41**
2-thienyl 3-thienyl 2-furyl 2-benzofuryl 2-benzothienyl 3-benzothienyl	Me		6	53	
Ph	2-thienyl 3-thienyl 2-furyl 2-benzofuryl 2-benzothienyl		5	41	

11. Conclusions

Results compiled and discussed in this short review demonstrate the value of single carbon-insertion methods for the homologation of carbonyl compounds in organic synthesis. The benzotriazole-mediated carbon-insertion method described in this review seems to be general, highly regioselective and applicable to most aldehydes and ketones allowing the introduction of a variety of substituents attached to the inserted carbon atom.

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