Synthesis of α-diazo-β-keto esters, phosphonates and sulfones via acylbenzotriazole-mediated acylation of diazomethyl anion

Journal:	*Organic & Biomolecular Chemistry*
Manuscript ID	OB-ART-09-2015-001975.R1
Article Type:	Paper
Date Submitted by the Author:	30-Sep-2015

Complete List of Authors:	Rastogi, Namrata; Central Drug Research Institute, Medicinal & Process Chemistry Pramanik, Mukund; Central Drug Research Institute, Medicinal & Process Chemistry Division

Journal Name

ARTICLE

Synthesis of α-diazo-β-keto esters, phosphonates and sulfones via acylbenzotriazole-mediated acylation of diazomethyl anion†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Mukund M. D. Pramanik,[a, b] and Namrata Rastogi[a, b]*

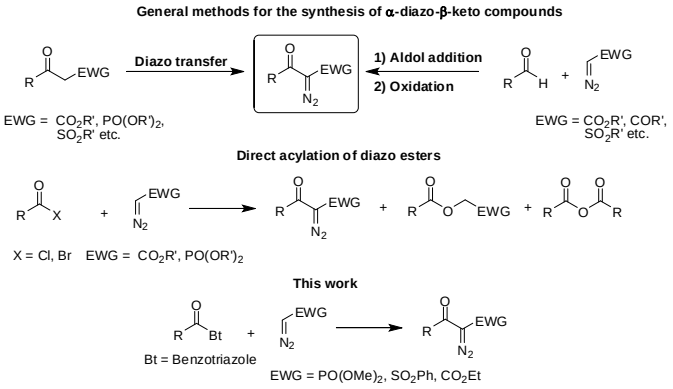
We report a method for the synthesis of α-diazo-β-keto esters, phosphonates and sulfones via acylation of corresponding diazomethyl anions with *N*-acylbenzotriazoles. The *N*-acylbenzotriazoles bearing an *o*-amino group exhibited an unprecedented trans-phosphorylation reaction leading to the isolation of hitherto unknown diazoacetyl phenylphosphoramidates.

Introduction

α-Diazo-β-ketoesters are versatile building blocks in organic chemistry.[1] Owing to their tendency to form carbenes, they participate in Wolff rearrangement, cyclopropanations, insertion reactions and several other useful transformations.[2] Despite such remarkable role of α-Diazo-β- ketoesters in organic chemistry only couple of general methods are available for their synthesis namely i) diazo transfer reaction to the active methylene group of β-ketoesters [3] and ii) oxidation of corresponding α-diazo-β-hydroxyesters.[4] Both these methods suffer from limited availability of starting substrates, multistep reaction sequences and sensitive reaction conditions (Scheme 1). Other miscellaneous methods such as electrophilic substitution of α-diazo-α-bromomagnesio compounds by different electrophiles,[5] acylation of diazoesters by acyl halides[6] or anhydrides[7] and palladium catalyzed cross-coupling reactions[8] lack generality.

Arguably, tapping into the inherent nucleophilicity of diazoesters by their direct acylation should be the most preferred method for the synthesis of α-diazo-β-ketoesters but the method so far could not be adopted as a general strategy due to lack of suitable acylating agents. Acylbenzotriazoles are activated derivatives of carboxylic acids,[9] especially useful for acylations in cases where acid halides or anhydrides are unsuitable due to the complications in their synthesis, handling and storage.[10]

However, to the best of our knowledge acylbenzotriazoles have not been utilized for acylation of diazo compounds. We hereby report our findings on employing acylbenzotriazoles for the direct acylation of α-diazo compounds for the synthesis of corresponding α-diazo-β-keto compounds (Scheme 1).

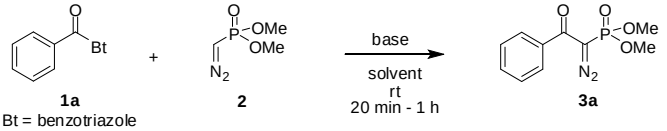


Scheme 1. Comparison of various approaches for the synthesis of α-diazo-β-keto compounds

Results and Discussion

The diazophosphonates were selected as preferred substrates for optimization reactions owing to their stability over diazoesters. The acylation of dimethyl diazomethylphosphonate (DAMP or Seyferth-Gilbert reagent)[11] **2** with *N*-acylbenzotriazole **1a** via nucleophilic addition-elimination reaction was attempted under various reaction conditions (Table 1).[12]

Table 1 Optimization of conditions for the acylation of DAMP **2** with *N*-acylbenzotriazole **1a**[a]



1a Bt = benzotriazole **2** **3a**

[a] *Medicinal and Process Chemistry Division, CSIR-Central Drug Research Institute, Lucknow 226031, India. E-mail: namrata.rastogi@cdri.res.in*
[b] *Academy of Scientific and Innovative Research, New Delhi, India*

† Electronic Supplementary Information (ESI) available: ^{1}H, ^{13}C and ^{31}P NMR spectra of all new compounds: See DOI: 10.1039/x0xx00000x

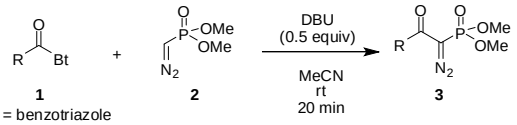
Entry	Base (equiv)	Solvent	Time	Yield of **3a** (%)[b]
1	Et_3N(1)	MeCN	1h	no reaction
2	K_2CO_3 (1)	MeCN	1h	no reaction
3	KO^tBu(1)	THF	30 min	77
4	DBU(1)	MeCN	20 min	89
5	**DBU(0.5)**	**MeCN**	20 min	**86**
6	DBU(0.2)	MeCN	20 min	52

[a]Unless otherwise noted, all reactions were performed with 1.1 mmol of **1a**, 1 mmol of **2** and base in 5 mL solvent, [b]Isolated yields.

Since *N*-acylbenzotriazole **1a** undergoes hydrolysis followed by esterification in methanol, aprotic solvents such as acetonitrile and THF were selected as reaction medium. The desired product **3a** was obtained in high yields with potassium *tert*-butoxide in THF and DBU in acetonitrile (entries 3, 4). Further optimization revealed that 0.5 equivalent of DBU in acetonitrile was the best condition for acylation of DAMP **2** with *N*-acylbenzotriazole **1a** in terms of yield and reaction economy (entry 5).

Next, for a systematic evaluation of substituent effects on the reactivity of *N*-acylbenzotriazoles as acylating agents for DAMP **2**, we subjected several *N*-acylbenzotriazoles **1a-o** to the optimized conditions (Table 2).

Table 2 Acylation of DAMP **2** with *N*-acylbenzotriazoles **1** under optimized conditions



1 Bt = benzotriazole **2** **3**

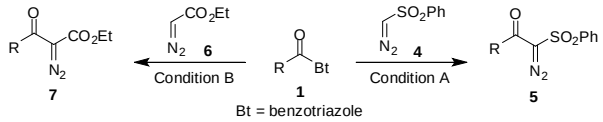
Entry	**1/3**	R	Yield of **3** (%)[a]
1	**a**	Ph	89 (82)[b]
2	**b**	4-OMe-Ph	86
3	**c**	4-NO_2-Ph	87
4	**d**	2-Br-Ph	85
5	**e**	4-Br-Ph	88
6	**f**	4-Cl-Ph	91
7	**g**	2-F-Ph	82
8	**h**	4-CF_3-Ph	76
9	**i**	2-(C≡C-Ph)Ph	82
10	**j**	2-furyl	80
11	**k**	2-indolyl	88
12	**l**	2-quinolinyl	82
13	**m**	cyclohexyl	79
14	**n**	$PhCH_2$	86
15	**o**	4-OMe-$PhCH_2$	83

[a]Isolated yields, [b]Yield of reaction at 1 gram scale

The results summarized in Table 2 affirm the general nature of the reaction in terms of acylbenzotriazoles since α-diazo-β-ketophosphonates **3a-o** were isolated in high yields with aromatic (entries 1-9), heteroaromatic (entries 10-12) as well as aliphatic (entries 13-15) *N*-acylbenzotriazoles. Also, both electron withdrawing and electron releasing substituents on the aromatic ring were well tolerated. Here it is important to note that aliphatic acylbenzotriazoles provided the α-diazo-β-ketophosphonates with DAMP anion in high yields with no trace of pyrazoles as reported previously.[13]

To further enhance the scope of the methodology, we subjected α-diazomethyl phenylsulfone **4** and ethyl diazoacetate (EDA) **6** to acylation with acylbenzotriazoles **1**. While α-diazo-β-keto-phenylsulfones **5** were isolated in excellent yields under the same conditions optimized for DAMP acylation, LDA was required for the generation of ethyl diazoacetate anion and subsequent acylation with acylbenzotriazole (Table 3).

Table 3 Scope of diazo compounds



7 **6** **1** **4** **5**

Condition A: DBU (0.5 equiv), MeCN, rt, 10 min

Condition B: LDA (1.5 equiv), THF, -78 °C - rt, 2h

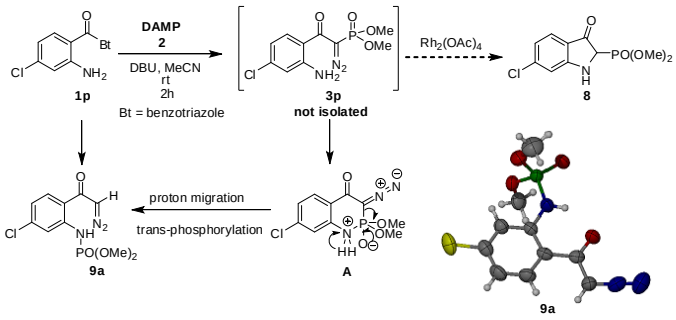
Entry	**1**	R	Product **(5/7)**	Yield of **5/7** (%)[a]
1	**a**	Ph	**5a**	90 (85)[b]
2	**b**	4-OMe-Ph	**5b**	91
3	**c**	4-NO_2-Ph	**5c**	85
4	**e**	4-Br-Ph	**5e**	93
5	**f**	4-Cl-Ph	**5f**	94
6	**g**	2-F-Ph	**5g**	83
7	**h**	4-CF_3-Ph	**5h**	79
8	**j**	2-furyl	**5j**	79
9	**k**	2-indolyl	**5k**	87
10	**l**	2-quinolinyl	**5l**	87
11	**m**	cyclohexyl	**5m**	88
12	**a**	Ph	**7a**	62 (58)[b]
13	**b**	4-OMe-Ph	**7b**	76
14	**e**	4-Br-Ph	**7e**	66
15	**f**	4-Cl-Ph	**7f**	69
16	**j**	2-furyl	**7j**	60

[a]Isolated yields, [b]Yield of reaction at 1 gram scale.

The results in Table 3 evidently show that the reaction is general for a variety of diazo compounds since diazosulfones as well as diazocarboxylates can be acylated with acylbenzotriazoles bearing diverse substituents. Here it is noteworthy that acylation of all the diazo compounds could be carried out both in small scale and gram scale with comparable yields (Table 2, entry 1; Table 3, entries 1 & 12). Also, the benzotriazole byproduct could be isolated easily and reused for the synthesis of starting acylbenzotriazoles, making it a very economic reaction.

In order to demonstrate the practical application of this methodology, we employed 2-amino-4-chloro-benzoylbenzotriazole **1p** for the direct acylation of DAMP **2** with the intent of subjecting the expected α-diazo-β-ketophosphonate **3p** to the rhodium carbenoid mediated insertion reaction with *o*-amino group for the synthesis of phosphonylated oxindole **8**.[14] However, the product isolated was characterized as dimethyl 5-chloro-2-(2-diazoacetyl)phenylphosphoramidate **9a** by spectroscopic and X-ray analysis (Scheme 2).[15] Mechanistically, formation of diazoacetyl phenylphosphoramidate can be explained via the

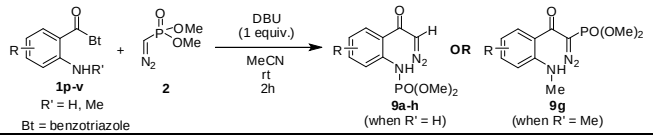
formation of α-diazo-β-ketophosphonate **3p** which cyclises to the intermediate **A** due to close proximity of the phosphonate group to the nucleophilic amino group. This six-membered intermediate undergoes trans-phosphorylation through intramolecular proton transfer yielding the diazoacetyl phenylphosphoramidate **9** (Scheme 2).[16]



Scheme 2 Plausible mechanism for trans-phosphorylation reaction

Such trans-phosphorylation reaction was exhibited by other N-*o*-amino benzoylbenzotriazoles **1q-u** as well (Table 4) and corresponding diazoacetyl phenylphosphoramidates **9b-f** were isolated in moderate to good yields. Notably, in case of *N*-*o*-methylamino benzoylbenzotriazole **1v** the normal substitution product **9g** was isolated (entry 7). However, attempts to cyclise **9a** as well as **9g** via rhodium carbenoid mediated insertion for the synthesis of oxindole scaffold led to an unidentified product mixture.

Table 4 Reaction of *N*-*o*-amino benzoylbenzotriazoles **1p-v** with DAMP **2**[a]



Entry	1	R/R'	9	Yield of 9 (%)[b]
1	**p**	4-Cl/H	**a**	58
2	**q**	H/H	**b**	46
3	**r**	3-Me/H	**c**	55
4	**s**	4,5-$(OMe)_2$/H	**d**	68
5	**t**	3,5-$(Br)_2$/H	**e**	65
6	**u**	6-F/H	**f**	47
7	**v**	H/Me	**g**	80

[a]Unless otherwise noted, all reactions were performed with 1 mmol of **1**, 1.1 mmol of **2** and 1.1 mmol of DBU in 5 mL MeCN, [b]Isolated yields.

Conclusions

In summary, we devised an efficient strategy for the synthesis of α-diazo-β-ketophosphonates, α-diazo-β-keto-phenylsulfones and α-diazo-β-keto-carboxylate esters from readily available and shelf stable *N*-acylbenzotriazoles in high yields. The reactions were scalable with camparable yields at large scale and also the by-product benzotriazole could be reused without any significant loss of activity. The reaction of *N*-*o*-amino benzoylbenzotriazoles with DAMP followed an unprecedented migration of phosphonate group from carbon to nitrogen to afford novel diazoacetyl phenylphosphoramidates. Currently, these diazoacetyl phenylphosphoramidates **9a-g** are being investigated for their behaviour towards metal carbenoid mediated N-H insertion reactions.

Experimental Section

General experimental information

All reactions were monitored by TLC, visualization was effected with UV and/or by developing in iodine. Chromatography refers to open column chromatography on silica gel (Merck, 100-200 mesh). Melting points were recorded on a Precision melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer's RX I FTIR spectrophotometer. NMR spectra were recorded on a Brucker Avance spectrometer at 400 or 500 MHz (^{1}H), 100 or 125 MHz (^{13}C), and 162 MHz (^{31}P). Chemical shifts are reported in δ (ppm) relative to TMS as the internal standard for ^{1}H and ^{13}C and phosphoric acid as the external standard for ^{31}P. The ^{13}C and ^{31}P spectra were proton decoupled and in case of ^{1}H NMR, the standard abbreviations such as s, d, t, q, m, dd referring to singlet, doublet, triplet, quartet, multiplet and doublet of doublet respectively, are used to describe spin multiplicity. The coupling constants (*J*) are given in Hz. The ESI-HRMS spectra were recorded on Agilent 6520- Q-TofLC/MS system.

Since diazo compounds are potentially hazardous (toxic and explosive), all the reactions were performed in fume hood with proper safety measures. All reactions were conducted in oven-dried glass wares under Nitrogen. THF was dried over sodium benzophenone ketyl. All other solvents and reagents were used as obtained from commercial sources. EDA, DAMP and diazomethylphenylsulfone were prepared according to the standard protocols.[17] Acyl benzotriazoles were prepared from corresponding carboxylic acids following the literature procedure.[18]

General procedure for the DBU catalyzed acylation of diazo compounds with acyl benzotriazoles 1

To a stirred solution of acyl benzotriazole **1** (1.1 mmol) in dry MeCN (5 mL) was added the diazo substrate (1.0 mmol) followed by DBU (0.5 – 1.0 mmol, see tables 2, 3, 4) and the reaction mixture was stirred at room temperature for 10 min. to 2 hours (see Tables 2, 3, 4). Acetonitrile was distilled off under reduced pressure and crude residue was directly subjected to column chromatograpy on silica gel using hexane/ethyl acetate as eluent to afford the pure product **3**/**5**/**9**.

Dimethyl 1-diazo-2-oxo-2-phenylethylphosphonate (3a).[19] Yellow viscous liquid (219 mg, 86%). R_f 0.50 (70% EtOAc/hexane); **IR** (Film, cm^{-1}): 1039, 1216, 1279, 1390, 1636, 2117, 3016; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.58 (m, 2H), 7.43 – 7.48 (m, 1H), 7.35 – 7.39 (m, 2H), 3.73 (d, $^3J_{H\text{-}P}$ = 11.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 187.4 (d, $^2J_{C\text{-}P}$ = 9.2 Hz, C_{Ar}), 136.7 (d, $^3J_{C\text{-}P}$ = 2.9 Hz, C_{Ar}), 132.5 (C_{Ar}H), 128.7 (C_{Ar}H x 2), 127.3 (C_{Ar}H x 2), 62.9 (d, $^1J_{C\text{-}P}$ = 217.4 Hz, CN_2), 54.0 (d, $^2J_{C\text{-}P}$ = 5.9 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz,

$CDCl_3$) δ 13.82; **HRMS** for $C_{10}H_{11}N_2O_4P$: calcd. (MH^+): 255.0529, found: 255.0522.

2-Diazo-1-phenyl-2-(phenylsulfonyl)ethanone (5a).[3c] Yellow solid (258 mg, 90%), Mp 128-130 °C. R_f 0.50 (25% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1025, 1069, 1156, 1215, 1385, 1645, 2109, 2400; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 – 8.00 (m, 2H), 7.57 – 7.61 (m, 1H), 7.47 – 7.51 (m, 5H), 7.35 – 7.38 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.6 (CO), 141.5 (C_{Ar}), 135.8 (C_{Ar}), 134.2 ($C_{Ar}H$), 133.1 ($C_{Ar}H$), 129.1 ($C_{Ar}H$ x 2), 128.9 ($C_{Ar}H$ x 2), 128.1 ($C_{Ar}H$ x 2), 127.5 ($C_{Ar}H$ x 2), 83.4 (CN_2); **HRMS** for $C_{14}H_{10}N_2O_3S$: calcd. (MH^+): 287.0485, found: 284.0476.

Dimethyl 5-chloro-2-(2-diazoacetyl)phenylphosphoramidate (9a). Colorless solid (176 mg, 58%), Mp 100-102 °C. R_f 0.50 (70% EtOAc/hexane); **IR** (KBr, cm^{-1}): 1024, 1225, 1294, 1499, 1581, 2112, 3067; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.00 (d, $^2J_{H\text{-}P}$ = 10.2 Hz, 1H), 7.42 (d, *J* = 1.9 Hz, 1H), 7.23 (dd, *J* = 1.6 Hz, *J* = 8.6 Hz, 1H), 6.84 (dd, *J* = 2.0 Hz, *J* = 8.6 Hz, 1H), 5.81 (s, 1H), 3.74 (d, $^3J_{H\text{-}P}$ = 11.5 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.2 (CO), 143.6 (C_{Ar}), 140.4 (C_{Ar}), 129.3 ($C_{Ar}H$), 120.8 ($C_{Ar}H$), 118.7 (d, $^2J_{C\text{-}P}$ = 7.2 Hz, C_{Ar}), 118.6 ($C_{Ar}H$), 55.9 (CN_2), 53.7 (d, $^2J_{C\text{-}P}$ = 4.4 Hz, {PO}OCH_3 x 2); **^{31}P NMR** (161.9 MHz, $CDCl_3$) δ 3.04; **HRMS** for $C_{10}H_{11}ClNO_4P$ (cyclised product after N_2 elimination): calcd. (MH^+): 276.0187, found: 276.0199.

Selected X-Ray Crystallographic data for **9a**, $C_{10}H_{11}ClN_3O_4P$: *M* = 303.64, Triclinic, *P*1, *a* = 5.927(5) Å, *b* = 8.999(5)Å, *c* = 13.598(5)Å, *V* = 685.6(7)Å^3, α = 106.549(5)°, β = 97.092(5)°, γ = 94.090(5)°, *Z* = 2, D_c = 1.471 g cm^{-3}, μ(Mo-Kα) = 0.408 mm^{-1}, *F*(000) = 312, Reflections Collected/unique = 8330/2555 observed = 1509 [*R*(int) = 0.050]. Final R indices [$I>2\sigma(I)$], *R*1 =0.0565, wR_2 = 0.1463 S = 1.04.

General procedure for the LDA catalyzed acylation of EDA 6 with acyl benzotriazoles 1

To diisopropylamine (1.5 mmol, 0.2 mL) in anhydrous THF (5 mL) was added n-BuLi (1.4 mmol, 0.9 mL, 1.6 M in hexane) dropwise at -78 °C to generate LDA. The mixture was stirred for 30 minutes followed by dropwise addition of EDA **6** (1 mmol, 114 mg) dissolved in 1 mL of THF. After stirring for another 30 minutes the acyl benzotriazole **1**(1.1 mmol) dissolved in 1 mL THF was added into the reaction mixture in one portion. The reaction mixture was stirred at -78 °C for 1h before gradually warming it to the room temperature. The reaction was quenched by saturated solution of NH_4Cl (aq.) upon completion (TLC monitoring). The reaction mixture was extracted with ethyl acetate (15 mL x 3) and the combined organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The crude mixture was subjected to column chromatograpy on silica gel using hexane/ethyl acetate as eluent to afford the pure product **7**.

Ethyl 2-diazo-3-oxo-3-phenylpropanoate (7a).[2b] Yellow oil (135 mg, 62%), R_f 0.50 (30% EtOAc/hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.57 (m, 2H), 7.43 – 7.48 (m, 1H), 7.33 – 7.37 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H); **HRMS** for $C_{11}H_{10}N_2O_3$: calcd. (MH^+): 219.0764, found: 219.0752.

Acknowledgements

M. M. D. P. thanks CSIR, New Delhi for the Ph. D. fellowship. We thank SAIF division of CSIR-CDRI for the analytical support. We gratefully acknowledge the financial support by CSIR-Network project 'BSC0102' (CSIR-CDRI-THUNDER). CDRI Communication No: (will be inserted if accepted for publication).

Notes and references

1 For For recent reviews, see: (a) Y. Zhang and J. Wang, *Chem. Commun.,* 2009, 5350; (b) T. Hashimoto and K. Maruoka, *Bull. Chem. Soc. Jpn.,* 2013, **86**, 1217; (c) A. Ford, H. Miel, A. Ring, C. N.Slattery, A. R. Maguire and M. A. Mckervey, *Chem. Rev.,* 2015, DOI: 10.1021/acs.chemrev.5b00121.

2 (a) M. P. Doyle, R. Duffy, M. Ratnikov and L. Zhou, *Chem. Rev.,* 2010, **110**, 704; (b) R. Pasceri, H. E. Bartrum, C. J. Hayes and C. J. Moody, *Chem. Commun.,* 2012, **48**, 12077; (c) X. Cui, X. Xu, L. Wojtas, M. M. Kim and P. X. Zhang, *J. Am. Chem. Soc.,* 2012, **134**, 19981; (d) Z. Shi, C. D.Koester, M. Boultadakis-Arapinis and F. Glorius, *J. Am. Chem. Soc.,* 2013, **135**, 12204; (e) T. Achard, C. Tortoreto, I. A. Poblador-Bahamonde, L. Guenee, T. Buergi and J. Lacour, *Angew. Chem., Int. Ed.,* 2014, **53**, 6140; (f) M. L. Hossain, F. Ye, Y. Zhang and J. Wang, *Tetrahedron,* 2014, **70**, 6957; (g) J. Jeong, P. Patel, H. Hwang and S. Chang, *Org. Lett.,* 2014, **16**, 4598; (h) X. Li, G. M. Sun, K. Liu, Q. Jin and P. N. Liu, *Chem. Commun.,* 2015, **51**, 2380.

3 (a) B. Shi, A. J. Blake, W. Lewis, I. B. Campbell, B. D. Judkins and C. J. Moody, *J. Org. Chem.*, 2010, **75**, 152; (b) M. Presset, D. Mailhol, Y. Coquerel and J. Rodriguez, *Synthesis*, 2011, 2549; (c) J. L. Kiara and J. R. Suarez, *Adv. Syn. Catal.*, 2011, **353**, 575; (d) M. K. Muthyala, S. Choudhary and A. Kumar, *J. Org. Chem.*, 2012, **77**, 8787; (e) S. G. Collins, O. C. M. O'Sullivan, P. G. Kelleher and A. R. Maguire, *Org. Biomol. Chem.*, 2013, **11**, 1706; (f) T. H. Jepsen and J. L. Kristensen, *J. Org. Chem.*, 2014, **79**, 9423; (g) L. J. Dutra, C. Saibert, D. S. Vicentini and M. M. Sá, *J. Mol. Catal. A: Chem.*, 2014, **386**, 35.

4 (a) G. Deng, B. Xu and J. Wang, *Tetrahedron*, 2005, **61**, 10811; (e) J. R. Davies, P. D. Kane and C. J. Moody, *J. Org. Chem.*, 2005, **70**, 7305; (f) P. H. Li, M. M. Majireck, I. Korboukh and S. M. Weinreb, *Tetrahedron Lett.*, 2008, **49**, 3162; (g) M. O. Erhunmwunse and P. G. Steel, *J. Org. Chem.*, 2008, **73**, 8675.

5 E. Cuevas-Yañez, J. M. Muchowski and R. Cruz-Almanza, *Tetrahedron Lett.*, 2004, **45**, 2417.

6 (a) H. Staudinger, J. Becker and H. Hirzel, *Chem. Ber.*, 1916, **49**, 1978; (b) J. H. Looker and D. N. Thatcher, *J. Org. Chem.*, 1958, **23**, 403; (c) H. J. Bestmann and H. Kolm, *Chem. Ber.*, 1963, **96**, 1948; (d) Y.-C. Kuo, T. Aoyama and T. Shioiri, *Chem. Pharm. Bull.,* 1982, **30**, 526; (e) J. P. Marino, M. H. Osterhout, A. T. Price, S. M. Sheehan and A. Padwa, *Tetrahedron Lett.*, 1994, **35**, 849.

7 F. Weygand, W. Schwenke and H. J. Bestmann, *Angew., Chem.* 1958, **70**, 506.

8 C. Peng, J. Cheng and J. Wang, *J. Am. Chem. Soc.*, 2007, **129**, 8708.

9 For important reviews on acylbenzotriazoles, see: (a) A. R. Katritzki, K. Suzuki and Z. Wang, *Synlett,* 2005, 1656; (b) A. R. Katritzki and S. Rachwal, *Chem. Rev.*, 2010, **110**, 1564; (c) A. R. Katritzki and S. Rachwal, *Chem. Rev.*, 2011, **111**, 7063.

10 (a) A. R. Katritzki and K. Kirichenko, *ARKIVOC*, 2006, **4**, 119; (b) A. R. Katritzki, K. Widyan and K. Kirichenko, *J. Org. Chem.*, 2007, **72**, 5802; (c) A. R. Katritzki, P. P. Mohapatra and L. Huang, *ARKIVOC*, 2008, **9**, 62; (d) I. Celik and A. A. A. Abdel-Fattah, *Tetrahedron*, 2009, **65**, 4923; (e) S. M. Lin, J. L. Zhang, J. X. Chen, W. X. Gao, J. C. Ding, W. K. Su and H. Y. Wu, *J. Braz. Chem. Soc.*, 2010, **21**, 1616; (f) C. Larrivée-Aboussafy, B. P. Jones, K. E. Price, M. A. Hardink, R. W. Mclaughlin, B. M. Lillie, J. M. Hawkins and R. Vaidyanathan, *Org. Lett.*, 2010, **12**, 324; (g) S. S. Panda, C. El-Nachef, K. Bajaj and A. R. Katritzki, *Eur. J. Org. Chem.*, 2013, 4156.; (h) S. Sahu, I. O. Lebedyeva, S. S. Panda and A. R. Katritzki, *Synthesis*, 2013, **45**, 1256; (i) V. Dhayalan, R. Murakami and M. Hayashi, *Tetrahedron: Asymmetry*, 2013, **24**, 543.

11 (a) R. S. Marmor and D. Seyferth, *Tetrahedron Lett.*, 1970, **11**, 2493; (b) D. Seyferth, R. S. Marmor and P. Gilbert, *J. Org. Chem.*, 1971, **36**, 1379; (c) J. C. Gilbert and U. Weerasooriya, *J. Org. Chem.*, 1982, **47**, 1837.

12 For nucleophilic substitution reaction of DAMP anion, see: M. M. D. Pramanik, A. K. Chaturvedi and N. Rastogi, *Chem. Commun.*, 2014, **50**, 12896.

13 A. Gioiello, A. Khamidullina, M. C. Fulco, F. Venturoni, S. Zlotsky and R. Pellicciari, *Tetrahedron Lett.,* 2009, **50**, 5978.

14 For selected recent reviews about insertion reactions of diazo compounds, see: (a) C. J. Moody, *Angew. Chem., Int. Ed.,* 2007, **46**, 9148; (b) S.-F. Zhu and Q.-L. Zhou, *Acc. Chem. Res.,* 2012, **45**, 1365; (c) D. Gillingham and N. Fei, *Chem. Soc. Rev.*, 2013, **42**, 4918; (d) F. Hu, Y. Xia, C. Ma, Y. Zhang and J. Wang, *Chem. Commun.,* 2015, **51**, 7986.

15 Crystal structure of compound **9a** has been deposited at the Cambridge Crystallographic Data Center and allocated the reference no. CCDC 1417598.

16 For examples of phosphonate group migration, see: (a) R. H. Churi, and C. E. Griffin, *J. Am. Chem. Soc.,* 1966, **88**, 1824; (b) W.-C. Chang, M. Dey, P. Liu, S. O. Mansoorabadi, S.-J. Moon, Z. K. Zhao, C. L. Drennan and H. W. Liu, *Nature,* 2013, **496**, 114.

17 For diazosulfone preparation, see: (a) S. Zhu, J. V. Ruppel, H. Lu, L. Wojtas and X. P. Zhang, *J. Am. Chem. Soc.,* 2008, **130**, 5042; For DAMP preparation, see: (b) T. Du, F. Du, Y. Ning and Y. Peng, *Org. Lett.*, 2015, **17**, 1308; For EDA preparation, see: (c) J. Jeong, D. Lee and S. Chang, *Chem. Commun.,* 2015, **51**, 7035.

18 (a) A. R. Katritzki, C. Cai and S. K. Singh, *J. Org. Chem.,* 2006, **71**, 3375; (b) N. Kanişkan, Ş. Kökten and İ. Çelic, *ARKIVOC,* 2012, **8**, 198; (c) Ş. Kökten and Çelic, İ. *Synthesis,* 2013, **45**, 2551.

19 D. F. Taber, S. Bai and P.-F. Guo, *Tetrahedron Lett.,* 2008, **49**, 6904.