Organic Azides

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The Synthesis of α-Azidoesters and Geminal Triazides**

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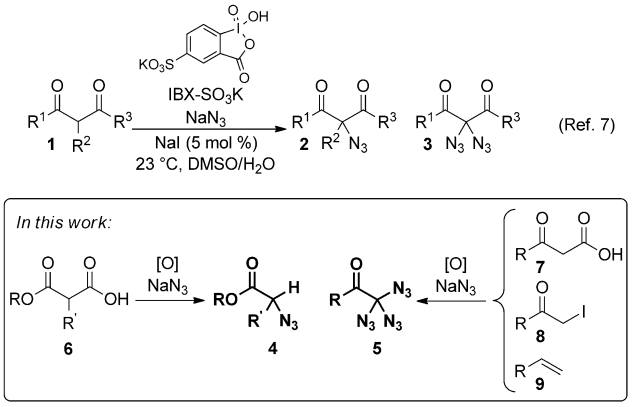
Abstract: *Three simple methods for the synthesis of geminal triazides are described: Starting from 1) 3-oxocarboxylic acids, 2) iodomethyl ketones, or 3) terminal olefins, a range of triazidomethyl ketones can be constructed under mild oxidative reaction conditions by the use of IBX-SO_3K, a sulfonylated derivative of 2-iodoxybenzoic acid (IBX), and NaN_3 as an azide source. This is the first report of representatives of this novel class of triazide compounds: Despite their high nitrogen content, the geminal triazides are easy to handle, even when preparative-scale syntheses are performed. (Caution: These procedures still require protective measures!) The triazides are now broadly available for further studies regarding their properties and reactivity. Furthermore, we show how the method can be used to provide α-azidoesters, which are potential building blocks for amino acids.*



Scheme 1. Limitations of our previous azidation protocols (see Ref. [7]) and goals of the current work.

Over the last decade, the field of organic azides has witnessed a tremendous "boom",[1] owing in part to the increased use of this class of compounds in the functionalization of biomolecules through click chemistry,[2] but also due to novel applications in materials science.[3] Therefore, the question as to how organic azides can be constructed has become a central theme of numerous studies.[1a,4–6] In this context, our laboratory is engaged in the development of methods for the direct azidation of enolizable carbonyl compounds: We have recently shown that 1,3-dicarbonyl compounds are easily functionalized with sodium azide under oxidative conditions and in a highly chemoselective manner (Scheme 1).[7] This in situ umpolung tolerates a great variety of functional groups and, depending on the substitution pattern, provides simple access to mono-azidated products **2** and di-azidated products **3**. As an oxidizing agent with a perfectly balanced oxidation power, IBX-SO_3K was used, a sulfonylated derivative of 2-iodoxybenzoic acid (IBX)[8] developed in our group to make the azidation broadly applicable.

As this method is based on the fact that the 1,3-dicarbonyl moiety is easily enolizable, we were previously unable to generate the azidated molecules **4** and **5** which do not contain an additional carbonyl group adjacent to the α-azidocarbonyl unit. Herein we report the azidation of organic carbonyl compounds under mild oxidative reaction conditions providing in a safe way α-azidoesters **4**, which may act as potential precursors of α-amino acids,[9,10] and, for the first time, preparative amounts of α-triazidocarbonyl compounds **5**. The geminal triazides **5** representing a novel class of compounds are easily accessed starting from three different types of substrates, namely 1) 3-oxocarboxylic acids **7**, 2) iodomethyl ketones **8**, and 3) terminal olefins **9**. It is now possible to use the triazides in subsequent transformations in a controllable way.

Due to their high nitrogen content, the development of a broadly applicable method for the synthesis of the geminal triazides **5** is a synthetic challenge. Besides the compounds described herein, only a limited number of polyazidated molecules have been reported with carbon atoms having a similarly high degree of azide substitution.[11] For example, Banert et al. generated the highly explosive tetraazidomethane $C(N_3)_4$ in 2007.[12] Hassner et al. described triazidomethane $HC(N_3)_3$, the handling of which is also not straightforward.[13,14] Moreover, several polyazides from higher homologues of Group 14 elements are known, some of which are highly explosive, and have a quite variable degree of azidation ranging from diazides up to hexaazides.[15] For instance, in recent work Filippou et al. isolated and chacterized Lewis base adducts of silicon tetraazide $Si(N_3)_4$ and the anionic hexaazido compounds $[Si(N_3)_6]^{2-}$ and $[Ge(N_3)_6]^{2-}$.[16]

Initially, we planned a decarboxylative strategy to construct the desired α-azidoesters **4**: Based on our previous work, we expected that the reaction of malonic acid monoesters **6** with NaN_3 in the presence of IBX-SO_3K and substoichiometric amounts of NaI in aqueous DMSO would, upon decarboxylation, directly lead to the α-azidoesters **4**.[17] Indeed, the azidation of the free carboxylic acid **6** under these conditions at 60 °C results in the exclusive formation of the decarboxylated product **4**, and the azidated

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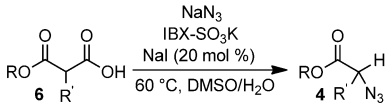
malonic acid monoester was not isolated. Table 1 summarizes the synthesis of a broad range of substituted α-azidoesters **4**: The experimental procedure is pretty simple, yields were

Table 1: Synthesis of α-azidoesters through decarboxylative oxidative azidation of malonic acid monoester.[a]

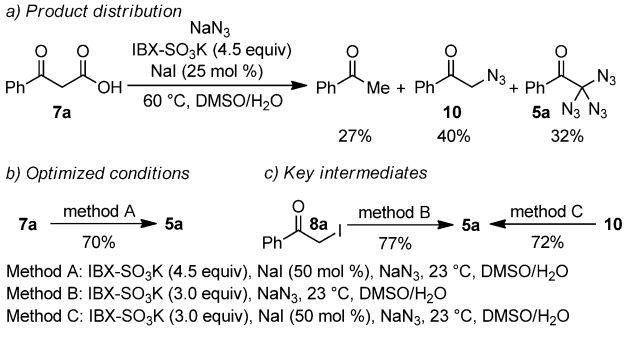


Entry	Substrate	OR	R′	Yield [%][b]
1	**6a**	OEt	CH_2Ph	93
2	**6b**	OEt	Me	98
3	**6c**	OMe	*i*Pr	83
4	**6d**	OMe	*s*Bu	83[c]
5	**6e**	OMe	*n*-octyl	68
6	**6f**	OMe	CH_2-CH = CH_2	84
7	**6g**	OMe	CH_2-CH = $C(CH_3)_2$	78
8	**6h**	OMe	CH_2-C ≡ CH	83
9	**6i**	OMe	CH_2Ph	73

[a] Conditions: substrate **6** (1 equiv), IBX-SO_3K (1.5 equiv), NaI (20 mol%), NaN_3, 60 °C, DMSO/H_2O (2:1). [b] Yield of isolated product after purification by column chromatography. [c] d.r. = 1:1.

consistently high, and numerous types of functional groups were tolerated. More detailed investigations regarding the mechanism revealed that, with the example of **6a**, oxidative iodination takes place first at the enolizable position of the malonic acid monoester. Spontaneous decarboxylization followed by nucleophilic substitution of the iodide with the azide anion then leads to the formation of the product (see the Supporting Information (SI)). In contrast to malonic acid monoesters, which are selectively converted into the monoazidated products **4**, simple carbonyl systems (e.g., esters and ketones) lacking the additional activating carbonyl group at the 3-position fail to react under the conditions.

We then investigated the decarboxylative monoazidation of 3-oxocarboxylic acids **7** with the example of **7a** (Scheme 2). We found that, aside from acetophenone and the desired monoazidation product **10**, the unexpected geminal triazide **5a** is formed in significant amounts. After optimization of the reaction conditions, we were able to increase the yield of triazide **5a** to 70%. Both the temperature and the amount of



Scheme 2. Formation of geminal triazides through decarboxylative polyazidation.

NaN_3 used in the presence of an excess of NaN_3 turned out to be important factors (method A: IBX-SO_3K (4.5 equiv), NaI (50 mol%), NaN_3, 23 °C, DMS/H_2O). Using the combination of IBX-SO_3K/NaI as a mild oxidant was particularly crucial for the formation of the triazide: All the alternative oxidation and iodination reagents that we tested were unable to effect the triple azidation. In some cases (e.g., with iodine) we only obtained the product of the monoazidation (**10**), albeit in low yields. Preliminary investigations regarding the mechanism indicate that here, too, iodination of the enolizable oxocarboxylic acid **7a** is the first step. Decarboxylation and nucleophilic substitution with NaN_3 then give monoazide **10** as the key intermediate. Under the reaction conditions, incorporation of the further azides is likely to occur two more times via iodination and substitution. As a matter of fact, we demonstrated that both iodoacetophenone **8a** and monoazide **10** react in the presence of IBX-SO_3K, NaI, and NaN_3 to give triazide **5a**.

The direct characterization of the triazidomethyl moiety of **5a** was complicated due to the fact that analytical reference data were not available for the class of geminal triazides, and the determination of the accurate mass of the molecule ion failed, too. The NMR and IR data revealed the acetophenone-related skeleton bearing azides attached to a quaternary carbon atom [selected data for **5a**: ^{13}C NMR ($CDCl_3$): δ = 93.0 ppm, $C(N_3)_3$; IR (ATR): $\tilde{\nu}$ = 2110 cm^{-1}, N_3; ^{15}N NMR ($CDCl_3$): δ = −140.0 (N_β), −147.5 (N_γ), −281.9 ppm (N_α)]. However, these data did not provide unequivocal support for the triazide $PhC(O)C(N_3)_3$, since less azidated species such as $PhC(O)C(I)(N_3)_2$ were also possible. To this end, we synthesized the compounds ^{15}N-**5a** and ^{15}N-**10** using ^{15}N-labeled $Na^{15}N_3$ (single terminal label). As shown in Figure 1, a random mixture of ^{15}N-**5a** and ^{15}N-**10** was then analyzed using both ^{1}H NMR and ^{15}N NMR (D1 = 60 s) spectroscopy: The integration of the ^{1}H NMR spectrum shows a ratio of 0.36:1 with regard to the scaffolds of ^{15}N-**5a** and ^{15}N-**10**; the integration of the nitrogen resonances shows, upon deconvolution and averaging over the two nitrogen atoms N_γ and N_α, a ratio of 1.07:1 with regard to the azides.[18] These ratios demonstrate that **5a** is the threefold azidated compound $PhC(O)C(N_3)_3$, which has a nitrogen content three times higher than that of the monoazide **10**. Nevertheless, triazide **5a** and all the other triazides **5** in the present study were converted into the corresponding tristriazoles by use of cyclooctyne. The tristriazole derivatives were unambiguously characterized by NMR and IR techniques as well as by mass spectroscopy (see SI).[19]

3-Oxocarboxylic acids **7** proved to be cumbersome to prepare and were prone to spontaneous decarboxylization to the unreactive methylketones. Instead, we drew inspiration from the conversion **8a**→**5a** as depicted in Scheme 2, and the easily accessible α-iodomethyl ketones **8** turned out to be the ideal starting materials for the synthesis of geminal triazides **5**. Table 2 lists several α-iodomethyl ketones that were successfully polyazidated in the presence of IBX-SO_3K and NaN_3 in aqueous DMSO at room temperature (method B). Addition of NaI proved unnecessary in every instance, since the substrates themselves served as the iodide source. While iodine-containing alkylketones showed low reactivity under

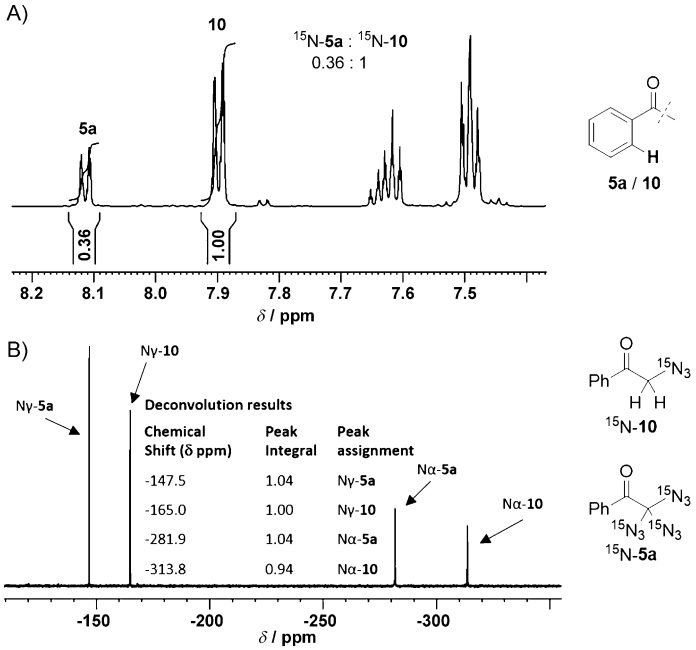
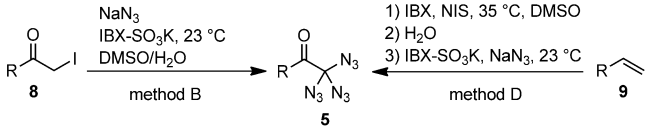


Figure 1. NMR study to determine the degree of azidation of **5a**. A) ^{1}H NMR spectrum of a mixture of ^{15}N-**5a** and ^{15}N-**10** with ^{15}N-labeled azide groups (single terminal label). B) ^{15}N NMR spectrum of the same mixture.

Table 2: Synthesis of geminal triazides.



Entry	Product	R	Yield [%][a] (B/D)[b,c]
1	**5a**	Ph	77 (B)/43 (D)
2	**5b**	2,4-$(MeO)_2C_6H_3$	30 (B)
3	**5c**	4-MeC_6H_4	61 (B)
4	**5d**	4-PhC_6H_4	59 (B)
5	**5e**	4-ClC_6H_4	58 (B)
6	**5f**	2-$MeOC_6H_4$	37 (D)
7	**5g**	3-$MeOC_6H_4$	37 (D)
8	**5h**	2-ClC_6H_4	47 (D)
9	**5i**	4-FC_6H_4	47 (D)
10	**5j**	2-naphthyl	48 (D)
11	**5k**	5-methyl-2-furyl	48 (D)
12	**5l**	2-pentyl	32 (D)

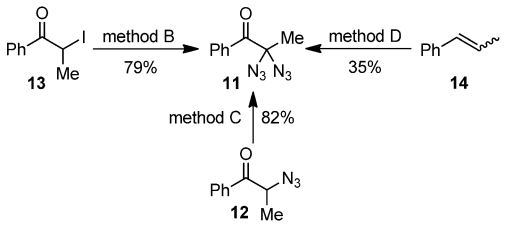
[a] Yield of isolated product after purification by column chromatography
[b] Method B: IBX-SO_3K (3 equiv), NaN_3, 23 °C, DMSO/H_2O (2:1).
[c] Method D: 1) IBX (2 equiv), NIS (1.1 equiv), 35 °C, DMSO, 2) H_2O, 3) IBX-SO_3K (3 equiv), NaN_3, 23 °C.

the reaction conditions, iodinated arylketones **5b–e** were readily converted in good yields.

Next we developed an alternative one-pot protocol that provides the triazides **5** directly from terminal olefins **9** (Table 2, method D). To this end, the olefins were first transformed into the iodomethyl ketones using IBX and *N*-iodosuccinimide (NIS) as previously described by Moorthy et al.[20] After addition of water followed by filtration, NaN_3 and IBX-SO_3K were added to the reaction mixture and finally the desired triazides **5f–l** were isolated. Of note, due to its lower oxidative power, IBX-SO_3K cannnot be used to replace IBX in the initial formation of the iodomethyl ketones. On the other hand, the use of IBX instead of IBX-SO_3K as the oxidizing agent in the polyzidation of the α-iodomethyl ketone with sodium azide results in a strongly exothermic reaction that is uncontrollable, and ends in the complete decomposition of the starting material and the evolution of gas. This observation underlines the importance of using IBX-SO_3K for the oxidative azidation step.

The class of geminal triazides **5** features an exceptionally high nitrogen content located at the α-carbonyl carbon, thus making this class of compounds attractive for potential applications as energetic materials.[21] To our surprise, triazide **5a** withstands temperatures up to 60 °C in solution; the compound remains stable without significant (or even explosive) decomposition.[22] We were able to concentrate dilute solutions with the rotary evaporator at temperatures between 30 and 35 °C without problems. The triazides **5** were obtained as pure substances, small amounts of which were stored at −20 °C. Nevertheless, extreme caution should be used in handling the geminal triazides: Due to the inherent risk of explosion, all experiments were performed with full protective measures; for each operation, temperatures were kept below 35 °C; the scale was kept small (0.2–0.6 mmol).[23]

Furthermore, diazides were smoothly accessed from the corresponding α-azidoketones through method C, from the α-iodoketones through method B, and from the olefins through method D.[24] Scheme 3 illustrates these transformations using the example of diazide **11**. These methods for the synthesis of diazides bearing only one neighboring carbonyl group are complementary to our earlier diazidation method which affords diazides with two adjacent carbonyl groups from 1,3-dicarbonyl compounds.[7]



Scheme 3. Formation of geminal diazides through oxidative azidation.

In conclusion, we have presented novel oxidative methods for the introduction of azide groups to organic molecules. In all cases, sodium azide was used as a cheap and readily available azide source, while IBX-SO_3K in combination with iodides was the perfectly balanced oxidizing agent. We were able to construct α-azidoesters starting from malonic acid monoesters. More intriguingly, we described a broadly applicable entry into geminal triazides, a neglected class of

compounds, starting from either 3-oxocarboxylic acids, α-iodomethyl ketones, or terminal olefins. Our future studies will focus on defining the reactivity and the properties of these nitrogen-rich molecules.

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[22] In preliminary studies, TGA-DSC measurements (heating rate: $5\,^{\circ}C\,min^{-1}$) for **5a** showed a thermal decomposition process, which begins at $T_{on} = 114\,^{\circ}C$ ($T_P = 140\,^{\circ}C$) and liberates a significant heat of decomposition ($\Delta H_D = -1.4\,kJ\,g^{-1}$). When droplets

of **5a** (< 0.5 mg) are applied onto a hot heating plate (> 80 °C), an immediate detonation takes place, accompanied by a flare and a bang.

[23] We synthesized triazide **5a** on a larger scale (9 mmol) only once. Due to safety concerns we concentrated the dilute solution in small portions (approximately 10 × 0.9 mmol).

[24] For alternative entries into geminal diazides, see: a) G. Schroeter, *Chem. Ber.* **1909**, *42*, 2336; b) M. O. Forster, R. Müller, *J. Chem. Soc. Trans.* **1910**, *97*, 1360; c) S. Götzky, *Chem. Ber.* **1931**, *64*, 1555; d) H. Bretschneider, N. Karpitschka, *Monatsh. Chem.* **1953**, *84*, 1091; e) L. Barash, E. Wasserman, W. A. Yager, *J. Am. Chem. Soc.* **1967**, *89*, 3931; f) R. H. McGirk, C. R. Cyr, W. D. Ellis, E. H. White, *J. Org. Chem.* **1974**, *39*, 3851; g) S. I. Al-Khalil, W. R. Bowman, M. C. R. Symons, *J. Chem. Soc. Perkin Trans. 1* **1986**, 555; h) W. Ogilvie, W. Rank, *Can. J. Chem.* **1987**, *65*, 166; i) K. Nishiyama, M. Oba, A. Watanabe, *Tetrahedron* **1987**, *43*, 693; j) J. P. Richard, T. L. Amyes, V. Jagannadham, Y.-G. Lee, D. J. Rice, *J. Am. Chem. Soc.* **1995**, *117*, 5198; k) H. Suzuki, Y. S. Hwang, C. Nakaya, Y. Matano, *Synthesis* **1993**, 1218; l) D. A. Kamble, P. U. Karabal, P. V. Chouthaiwale, A. Sudalai, *Tetrahedron Lett.* **2012**, *53*, 4195.

