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Thermal Reactions of Tributyltin Hydride with α-Azido Esters: Unexpected Intervention of Tin Triazene Adducts under Both Nonradical and Radical Conditions

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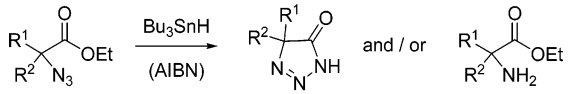


R^1 = H, Me, Et, Ph; R^2 = Ph, COOEt, MeC=NOBn

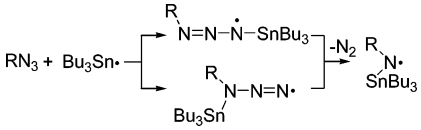
Thermal reaction of various α-azido esters with Bu_3SnH in refluxing benzene results in smooth production of 3-(tributylstannyl)-1-triazene adducts affording cyclized 1,2,3-triazol-4-ones in preference to reduced amines and thence provides a new useful method for the preparation of these triazole derivatives. In the presence of AIBN the occurrence of triazene products still remains important or even exclusive and, consequently, generation of the expected stannylaminyl radicals is seriously limited. With 2-azidomalonates and α-azido-*β*-keto esters stannyltriazenes can similarly occur in the absence of the radical initiator, but in the latter cases the ensuing triazenes undergo preferential cyclization onto the ketone moiety to give reactive hydroxytriazolines. Contrary to α-azido esters, in the presence of AIBN α-azido-*β*-keto esters as well as azidomalonates give rise only to the usual stannylaminyl radicals. A possible explanation for the different behavior of the mono- and dicarbonyl azides in the presence of AIBN is put forward.

Introduction

Organic azides are important intermediates that have found extensive use in the synthesis of acyclic and cyclic nitrogen-containing compounds. The utility of these versatile intermediates stands from their fair ability to react with electrophilic, nucleophilic, and radical species, additionally acting as 1,3-dipoles in cycloaddition reactions as well as affording reactive nitrenes under thermal and photochemical conditions.[1] The thermal reactions with tributyltin hydride (Bu_3SnH), in the absence and in the presence of a radical initiator (AIBN), are included among the popular azide reactions.

In the absence of AIBN, Bu_3SnH normally converts the azides to amines through thermally unstable stannyltriazene adducts.[2] In the presence of AIBN (usually 0.1 equiv), derived stannyl radicals would react with azides to give stannylaminyl radicals through loss of nitrogen by intermediate 1,3- and/or 3,3-triazenyl radicals (Scheme 1).[3,4]

SCHEME 1



The actual intervention of stannylaminyl radicals in numerous azide processes mediated by Bu_3SnH/AIBN is well documented. The stannylaminyl radicals are undoubtedly the key intermediates in worthwhile processes including, inter alia, conversions of cyclic azidoalkyl ketones to medium-sized lactams,[3a−c] rearrangements of alkyl azides to alkylideneanilines,[5] 1,5-H radical transfers

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(2) (a) Bartra, M.; Urpf, F.; Vilarrasa, J. *Tetrahedron Lett.* **1987**, *28*, 5941−5944. (b) Wasserman, H. H.; Brunner, R. K.; Buynak, J. D.; Carter, C. G.; Oku, T.; Robinson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 519−521. (c) Otvos, L.; Beres, J.; Sagi, G.; Tomoskozi, I.; Gruber, L. *Tetrahedron Lett.* **1987**, *28*, 6381−6384. (d) Redlich, H.; Roy, W. *Liebigs Ann. Chem.* **1981**, 1215−1222. (e) Mukai, C.; Kobayashi, M.; Kubota, S.; Takahashi, Y.; Kitagaki, S. *J. Org. Chem.* **2004**, *69*, 2128−2136.

(3) (a) Kim, S.; Joe, G. H.; Do, J. Y. *J. Am. Chem. Soc.* **1993**, *115*, 3328−3329. (b) Kim, S.; Kim, S. S.; Seo, H. S.; Yoon, K. S. *Tetrahedron* **1995**, *51*, 8437−8446. (c) Kim, S.; Joe, G. H.; Do, J. Y. *J. Am. Chem. Soc.* **1994**, *116*, 5521−5522. (d) Dang, H.-S.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1493−1497.

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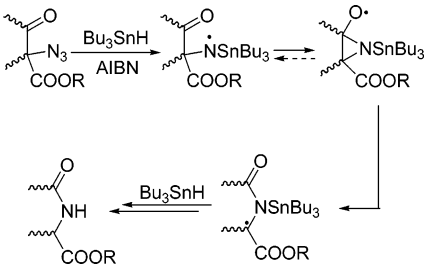
SCHEME 2



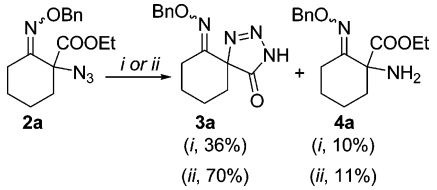
from carbon to *N*-tributyltin substituted nitrogen,[6] ring expansions of azidoazabiciclo[2.2.1]heptanes to diazabiciclo[3.2.1]octanes[7] and, additionally, tandem cyclizations of azidoalkylmalononitriles leading to pyrrolopyrroles and pyrrolopyiridines.[8] However, it is worth noting that the general view that generation of those nitrogen intermediates would entail primary stannyl radical addition to azide has never been proved.

In a recent work we have found that cyclic and acyclic α-azido-*β*-keto esters react with Bu_3SnH under radical conditions to give lactams/amides arising from regiospecific NH insertion.[9] In light of Kim's previous observations that stannylaminyl radicals undergo highly efficient intramolecular addition to carbonyl groups,[3a−c] we proposed the mechanism outlined in Scheme 2, entailing initial 3-exo cyclization of derived stannylaminyl radical onto the adjacent ketone group.[9]

Results and Discussion

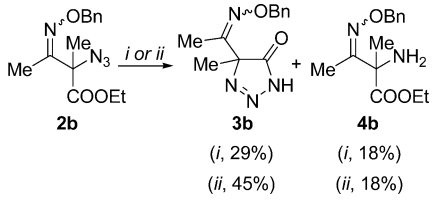
Following our research interest in the synthetic utility of stannylaminyl radicals,[8] we became interested in the radical reactivity of azido oximes derived from azido keto esters. We reasoned that replacement of the ketone moiety with the derived oxime might encourage 3-exo cyclization of stannylaminyl radical, thus possibly further encouraging the outcome of our NH insertion process. Although the addition of aminyl radicals to imino acceptors was virtually unknown,[3c] numerous reported data clearly indicated that the carbon-centered counterparts can add to oxime ethers and hydrazones much more readily than to carbonyl acceptors.[10]

SCHEME 3[a]



[a] Reagents: *i*, Bu_3SnH, AIBN; *ii*, Bu_3SnH.

SCHEME 4[a]



[a] Reagents: *i*, Bu_3SnH, AIBN; *ii*, Bu_3SnH.

We then decided to investigate the radical reactivity of the azido oximes **2a**,**b**, shown in Schemes 3 and 4, with Bu_3SnH. These new azides were easily prepared by treating the respective α-azido-*β*-keto esters **1a**,**b**, already available in our laboratory,[9] with benzyloxyamine according to known methodology.

The azido compounds **2a** and **2b** were reacted with Bu_3SnH (1.1 equiv) and AIBN (0.1 equiv) in refluxing benzene for ca. 5 h, using conditions strictly comparable with those previously employed to achieve entire conversion of their ketone precursors **1a**,**b** into the NH inserted amide products.[9] Surprisingly, both reactions led to isolation of the cyclized triazolones **3a** and **3b**, in 36% and 29% yield, respectively, along with minor amounts of the reduced amines **4a** and **4b** (10−18%), while providing no evidence at all for any cyclization of either stannylaminyl radical onto the imino carbon (Schemes 3 and 4 and Table 1, entries 1 and 4). In the absence of AIBN the azides **2a**,**b** similarly gave the respective triazolones **3a**,**b** and amines **4a**,**b**, though under both circumstances the reactions were curiously somewhat faster and, additionally, the isolated yields of the compounds **3a** and **3b** were significantly enhanced (70% and 45%, respectively, Schemes 3 and 4 and Table 1, entries 3 and 5).

These data suggested that, largely irrespective of the radical initiator, the hydride should perform addition to the azides **2a**,**b** to give 3-(tributylstannyl)-1-triazene adducts.[11] Such intermediates might conceivably afford the observed triazoles **3a**,**b**, upon intramolecular acyl substitution of the ester moiety, and the corresponding amines **4a**,**b** by usual thermal fragmentation (Scheme 5).

Diminished yields of triazolones **3a**,**b** in the presence of AIBN were likely caused by parallel intervention of stannylaminyl radicals, which would mainly afford unidentified material along with small amounts of the reduced amines **4a**,**b**. This possibility was roughly supported by repeated reaction of azide **2a** in the presence of a tripled amount of AIBN (0.3 equiv), in which case there was further suppression of triazolone **3a** (28%) but no concomitant enhancement of amine **4a** (Table 1, entry 2).

(4) (a) Frankel, M.; Wagner, D.; Gertner, D.; Zikha, A. *J. Organomet. Chem*. **1967**, *7*, 518−520. (b) Samano, M. C.; Robins, M. J. *Tetrahedron Lett.* **1991**, *32*, 6293−6294. (c) Poopeiko, N. E.; Pricota, T. I.; Mikhailopulo, I. A. *Synlett* **1991**, 342. (d) Hornemann, A. M.; Lundt, I. *J. Org. Chem.* **1998**, *63*, 1919−1928. (e) Montevecchi, P. C.; Navacchia, M. L.; Spagnolo, P. *Eur. J. Org. Chem.* **1998**, 1219−1226. (f) Hays, D. S.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 2796−2797. (g) Benati, L.; Leardini, R.; Minozzi, M.; Nanni, D.; Spagnolo, P.; Strazzari, S.; Zanardi, G. *Tetrahedron* **2002**, *58*, 3485−3492. (h) Zaitseva, V. E.; Dyatkina, N. B.; Kraevskii, A. A.; Skaptsova, N. V.; Turina, O. V.; Gottikh, B. P.; Azhaev, A. V. *Bioorgan. Khim.* (*Moscow*) **1984**, *10*, 670−680; *Chem. Abstr.* **1984**, *101*, 192378c.

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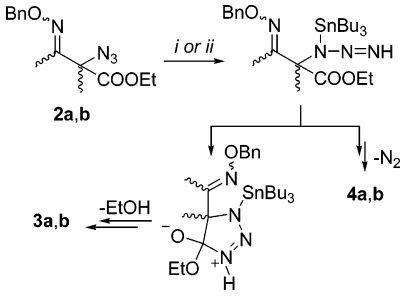
(10) (a) Fallis, A. G.; Brinza, I. M. *Tetrahedron* **1997**, *52*, 17543−17594. (b) Friestad, G. K. *Tetrahedron* **2001**, *57*, 5461−5496.

TABLE 1. Yields of Products from Thermal Reactions of Azides 1a,b, 2a−e, and 17a,b with Bu_3SnH and Bu_6Sn_2[a]

			yield (%)[b]		
entry	azide	reagent[c]	triazolone	amine	other
1	**2a**	A	**3a** (36)	**4a** (10)	**2a** (20)
2	**2a**	A[d]	**3a** (28)	**4a** (10)	**2a** (20)
3	**2a**	B	**3a** (70)	**4a** (11)	
4	**2b**	A	**3b** (29)	**4b** (18)	**2b** (15)
5	**2b**	B	**3b** (45)	**4b** (18)	
6	**2c**	A	**3c** (50)	**4c** (29)	
7	**2c**	B	**3c** (48)	**4c** (28)	
8	**2d**	A	**3d** (25)	**4d** (49)	**5** (10), **6** (7)
9	**2d**	B	**3d** (23)	**4d** (27)	**5** (20), **6** (10)
10	**2d**	C		**4d** (22)	**2d** (55)
11	**2e**	A	**3e** (12)	**4e** (13)	**2e** (25), **9**(20)
12	**2e**	B	**3e** (23)	**4e** (12)	**2e** (55), **9** (5)
13	**2e**	C			**2e** (24), **9** (4), **10** (46)
14	**1a**[e]	A			**13a** (81)
15	**1a**	B			**13a** (30), **15a** (40)
16	**1b**[e]	A			**13b** (80)
17	**1b**	B			**13b** (27), **15b** (66)
18	**17a**	A		**19a** (58)	
19	**17a**	B	**18a** (65)	**19a** (12)	
20	**17b**	A		**19b** (58)	
21	**17b**	B	**18b** (50)	**19b** (14)	

[a] Reactions were normally carried out in refluxing benzene for 2−5 h. [b] Isolated by column chromatography. [c] Reagent A: Bu_3SnH (1.1 equiv), AIBN (0.1 equiv). Reagent B: Bu_3SnH (1.1 equiv). Reagent C: Bu_6Sn_2 (1.1 equiv), DTBHN (0.3 equiv). [d] AIBN (0.3 equiv). [e] See ref 9.

SCHEME 5[a]

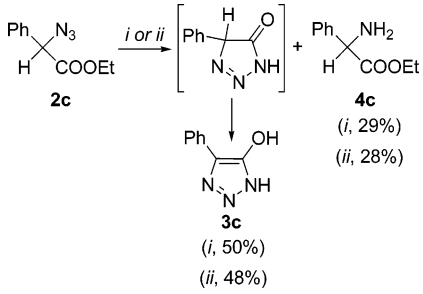


[a] Reagents: *i*, Bu_3SnH, AIBN; *ii*, Bu_3SnH.

Although the above reactions frustrated our initial objective, they were, however, rewarding since they seemed to reveal unexpected aspects of the reactivity of Bu_3SnH with azides. In fact, though a few 3*H*-1,2,3-triazol-4-ones are known to arise from catalytic hydrogenation of certain α-azido esters,[12] the observed production of the compounds **3a**,**b**, especially under "radical" conditions, was quite unpredictable. Apart from the general absence of triazole products in our previous reactions of azido keto esters with Bu_3SnH/AIBN, there was no precedented evidence for any possible intervention of stannyltriazene adduct in the reported reactions of alkyl azides with Bu_3SnH/AIBN.

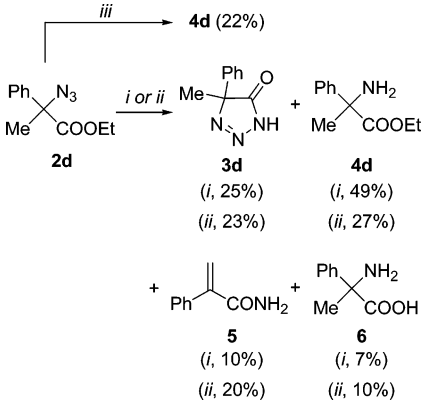
To ascertain whether other simple α-azido esters might display a similar behavior, we chose to examine the three azido acetates **2c**−**d** shown in Schemes 6, 7, and 9. These

SCHEME 6[a]



[a] Reagents: *i*, Bu_3SnH, AIBN; *ii*, Bu_3SnH.

SCHEME 7[a]



[a] Reagents: *i*, Bu_3SnH, AIBN; *ii*, Bu_3SnH; *iii*, Bu_6Sn_2, DTBHN.

compounds were readily prepared through bromination of the parent compounds and subsequent treatment of the crude bromide with sodium azide.

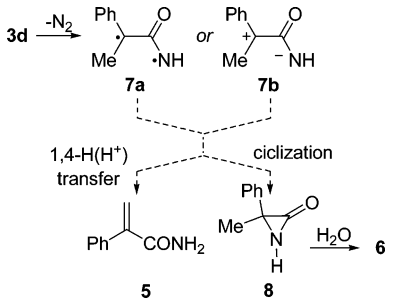
The azide **2c** underwent total reaction with Bu_3SnH within ca. 2 h in both the absence and the presence of 0.1 equiv of AIBN, giving virtually identical results. In both cases chromatographic separation furnished the hydroxytriazole **3c** (48−50%), which clearly was the aromatic enol tautomer of the original triazolone, along with minor amounts of the reduced amine **4c** (28−29%) (Scheme 6 and Table 1, entries 6 and 7). Evidently, in line with that encountered with the above congeners **2a**,**b**, the hydride could exhibit a marked tendency to form stannyltriazene adduct with this azide in a manner totally irrespective of the radical initiator.

The azido ester **2d** was similarly consumed within ca. 3 h upon analogous treatment with Bu_3SnH in the absence and the presence of the radical initiator. The reaction of **2d** with tin hydride alone isolated the corresponding triazolone **3d**, but in moderate yield (23%), together with the amine **4d** to a similar extent. These products were, however, accompanied by comparable amounts of the propenamide **5** (20%) and minor amounts of the amino acid **6** (10%) (Scheme 7 and Table 1, entry 9). The latter compounds were likely due to partial decomposition of the rather unstable triazolone **3d** under the experimental conditions. According to previous studies of the thermolysis of related triazoles,[13] the triazolone **3d** underwent presumed extrusion of nitrogen to give a singlet diradical species **7a** or a zwitterion **7b**. Either species could then afford the amide **5** via 1,4-transfer of a hydrogen or proton from methyl to nitrogen and the

(11) Theoretical data, which will be reported elsewhere, predict that of the three possible methyl(trimethylstannyl)triazene structural isomers the 3,3-disubstituted-1-triazene isomer should form by far most easily.

(12) (a) Hohenlohe-Oehringen, K. *Monatsch. Chem.* **1958**, *89*, 562−569. (b) Hohenlohe-Oehringen, K. *Monatsch. Chem.* **1958**, *89*, 597−601.

SCHEME 8

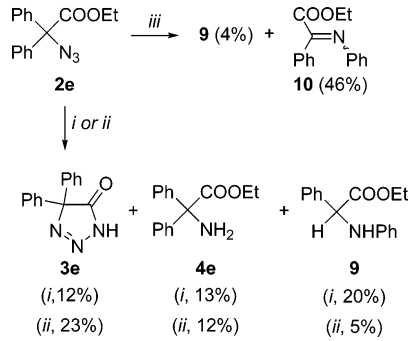


aziridinone **8** upon parallel cyclization. Eventual hydrolysis of **8** would yield the observed amino acid **6** (Scheme 8). In the presence of the radical initiator the azide **2d** furnished the same products, but in this case the reduced amine **4d** occurred in a noticeably higher yield (49%) at the expense of the overall triazolone products **3d** (25%), **5** (10%), and **6** (7%) (Scheme 7 and Table 1, entry 8). The chemical behavior of the azide **2d** was therefore consistent with that of the congeners **2a**−**c**, but this azide could clearly point to significant intervention of stannylaminyl radical under the radical conditions.

With the azide **2d** we investigated also the reactivity with stannyl radicals generated by thermal reaction of hexabutylditin (Bu_6Sn_2) with *tert*-butoxyl radicals arising from di-*tert*-butyl hyponitrite (DTBHN).[14] With this reaction we aimed at excluding any possible intervention of transient 3,3/1,3-stannyltriazenyl radical(s), which would be the presumable stannylaminyl radical precursors (Scheme 1), in the observed production of cyclized triazolone **3d**. The azide **2d**, after being preliminarily shown to be quite inert toward Bu_6Sn_2 or DBTHN, was then reacted under our standard conditions with 1.1 equiv of the distannane and 0.3 equiv of DTBHN. Chromatography of the crude gave much unchanged azide (55%) and, as the only identifiable product, the amine **4d** in 22% yield (Table 1, entry 10). Since the amine **4d** conceivably was the expected H-abstraction product of stannylaminyl radical, it was concluded that the triazenyl precursor(s) should not be able at all to afford triazolone **3d**.[15,16]

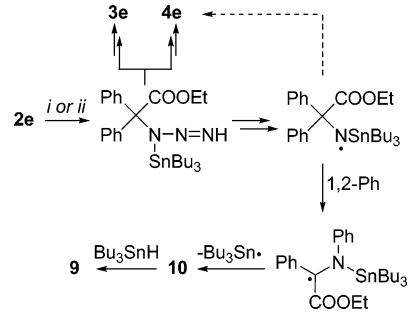
The corresponding reactions of the azidodiphenylacetate **2e** were significantly slower than those of the azides **2c** and **2d**. Within 3 h the usual reaction with the hydride furnished unchanged azide **2e** to a major extent (55%), in addition to minor amounts of triazolone **3e** (23%),

SCHEME 9[a]



[a] Reagents: *i*, Bu_3SnH, AIBN; *ii*, Bu_3SnH; *iii*, Bu_6Sn_2, DTBHN.

SCHEME 10[a]



[a] Reagents: *i*, Bu_3SnH, AIBN; *ii*, Bu_3SnH.

amine **4e** (12%), and rearranged aniline **9** (5%) (Scheme 9 and Table 1, entry 12). The latter compound likely arose from a primary stannylaminyl radical. Indeed, according to previous data with various diaryl- and triaryl-substituted methyl azides,[5] the stannylaminyl radical would undergo 1,2-Ph migration from carbon to nitrogen followed by β-elimination of stannyl radical from the resultant carbon radical to give the unobserved imine **10.** Subsequent reduction of **10** by the tin hydride would eventually afford the observed aniline **9** (Scheme 10). It is therefore plausible that the derived stannyltriazene intermediate, besides affording triazolone **3e** and amine **4e**, interestingly suffered some homolyitic fragmentation yielding a stannylaminyl radical that then rearranged to the eventual aniline **9** (Scheme 10).

In the presence of AIBN the reaction still gave a noticeable amount of unreacted azide **2e** (25%); in this case the rearranged aniline **9** was isolated as the major product (20%), whereas triazolone **3e** (12%) and amine **4e** (13%) were obtained to a minor extent (Scheme 9 and Table 1, entry 11).

To lend strict support to the likely involvement of stannylaminyl radicals in the formation of the aniline **9**, the azide **2e** was additionally reacted with Bu_6Sn_2/DTBHN. This reaction also resulted in the recovery of a marked amount of azide **2e**, but however gave a fair yield of the expected imine **10** along with small amounts of the reduced aniline **9** (Scheme 9 and Table 1, entry 13).

On the whole, the observed data suggested that also in the case of the poorly reactive azide **2e** the presence of the initiator, though probably bringing about effective generation of stannylaminyl radical, could not cause essential suppression of stannyltriazene adduct.

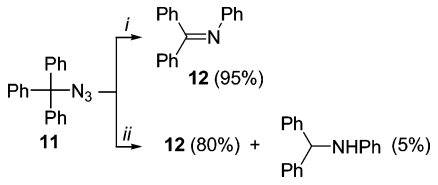
(13) (a) Kadaba, P. K.; Stanovnik, S.; Tisler, M. 1,2,3-Triazolines. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Boulton, A. J., Eds.; Academic: New York, 1985; Vol. 37, pp 217−349. (b) Bourgois, J.; Bourgois, M.; Texier, F. *Bull. Soc. Chim. Fr.* **1978**, 485−527. (c) Trost, B. M.; Runge, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 2483−2485. (d) Quast, H.; Meischner, G.; Seiferling, B. *Chem. Ber.* **1987**, *120*, 217−223.

(14) (a) Renaud, P.; Ollivier, C. *J. Am. Chem. Soc.* **2001**, *123*, 4717−4727. (b) Renaud, P.; Ollivier, C.; Panchaud, P. *Angew. Chem., Int. Ed.* **2002**, *41*, 3460−3462. (c) Renaud, P.; Ollivier, C.; Panchaud, P.; Zigmantas, S. *J. Org. Chem.* **2004**, *69*, 2755−2759.

(15) The hexabutylditin/DTBHN method was not applicable to the azidophenylacetate **2c** owing to the tendency of *tert*-butoxyl radical to perform abstraction of the azide benzylic hydrogen.

(16) The present use of the hexabutylditin/DTBHN method is virtually unprecedented in the radical chemistry of azides, largely dominated by the use of Bu_3SnH/AIBN. In principle, replacement of Bu_3SnH with hexabutylditin might be an appealing alternative since the distannane, contrary to the tin hydride, is thermally inert toward azides; unfortunately stannylaminyl radicals, like the alkyl counterparts, are in turn inert toward the distannane and therefore unable to propagate a chain reaction.

SCHEME 11[a]



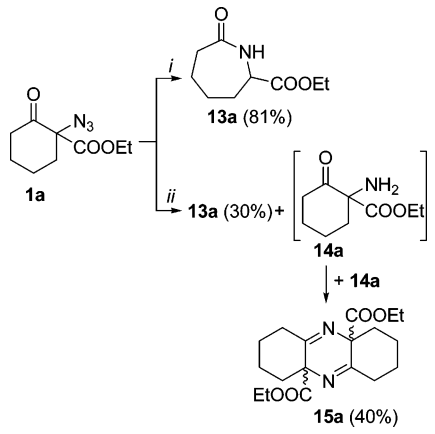
[a] Reagents: *i*, Bu_3SnH, AIBN; *ii*, Bu_3SnH.

The above observation that the presumed triazene derived from azide **2e** might furnish stannylaminyl radical upon homolitic fragmentation led us to incidental examination of the behavior of triphenylmethyl azide **11**. This azide was reported by Kim[5] to undergo highly efficient rearrangement to diphenylmethyleneaniline **12** upon radical reaction with Bu_3SnH and AIBN under high dilution (Scheme 11). We here found almost identical results by reacting the azide **11** with the sole hydride under our conditions (Scheme 11). We therefore discovered that the presumable triazene arising from **11** should be able to furnish stannylaminyl radical in an effective fashion.

The general tendency of our azido esters **2a**−**e** to yield triazene intermediates with Bu_3SnH both in the presence and in the absence of AIBN was in apparent contrast with our previous proposal that stannylaminyl radicals should be primarily responsible for the NH insertion process of azido keto esters (Scheme 2). To clarify this point, we turned our study back to the reactivity of the two azido keto esters **1a**,**b** with Bu_3SnH alone. As mentioned above, in the presence of the initiator these azides were cleanly converted to the corresponding NH inserted amides **13a**,**b** in high yield (Schemes 12 and 13 and Table 1, entries 14 and 16).

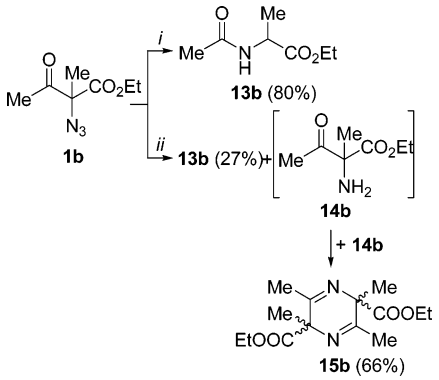
In the absence of the initiator they were presently found to lead to the same compounds **13a**,**b**, but these occurred to a modest extent and were accompanied by major amounts of the respective dihydropyrazines **15a**,**b**, clearly ascribable to self-condensation of the initial amines **14a**,**b** (Schemes 12 and 13 and Table 1, entries 15 and 17).[17] These observations strongly suggested that stannyltriazene adducts were initially formed to give rise to transient hydroxytriazolines **16a**,**b**, through cyclization onto the more reactive ketone moiety, in preference to usual triazolones. According to previous data of thermal decomposition of hydroxytriazoline analogues,[18] the intermediates **16a**,**b** were the likely precursors of both the observed amides **13a**,**b** and (most of) the reduced amines **14a**,**b** as shown in Scheme 14. Despite the fact that we had discovered a triazene route to the compounds **13a**,**b**, stannylaminyl radicals were still believed to be the primary intermediates in the previously observed formation of **13a**,**b**. It seemed indeed unreasonable that in the presence of the radical initiator the possible stannyltriazenes should undergo exclusive cyclization to triazolines **16a**,**b** and/or that these triazolines should undergo exclusive decomposition to those compounds **13a**,**b**.

SCHEME 12[a]



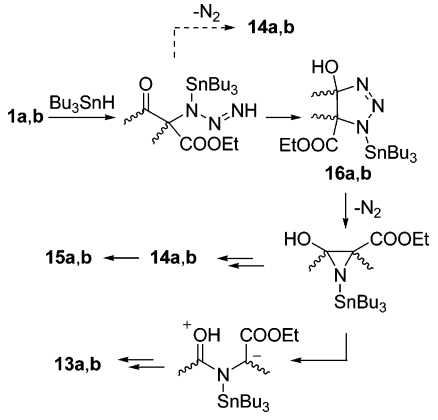
[a] Reagents: *i*, Bu_3SnH, AIBN; *ii*, Bu_3SnH.

SCHEME 13[a]



[a] Reagents: *i*, Bu_3SnH, AIBN; *ii*, Bu_3SnH.

SCHEME 14

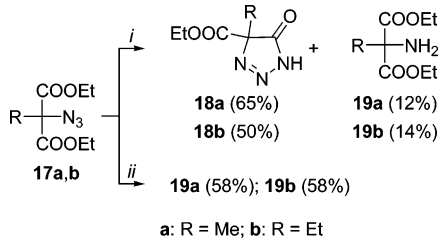


We considered that a possible reason for the different behavior of α-azido-*β*-keto esters under radical conditions might be due to the concomitant presence of two carbonyl substituents on the same carbon bearing the azido group. Indeed we were pleased to next ascertain that our consideration was strictly substantiated by the findings with the azidomalonates **17a**,**b**. In the absence of AIBN these substrates led to the expected triazolones **18a**,**b** (50−65%), which were accompanied by minor amounts of the respective amines **19a**,**b** (12−14%) (Scheme 15 and Table 1, entries 19 and 21). However, in the presence of the initiator they failed to furnish any triazole **18a**,**b**, but

(17) Benati, L.; Calestani, G.; Leardini, R.; Minozzi, M.; Nanni, D.; Spagnolo, P.; Strazzari, S.; Zanardi, G. *Tetrahedron* **2002**, *58*, 3485−3492.

(18) Benati, L.; Montevecchi, P. C.; Spagnolo, P.; Foresti, E. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2845−2850.

SCHEME 15[a]



[a] Reagents: *i*, Bu_3SnH; *ii*, Bu_3SnH, AIBN.

preferred instead to give only the amines **19a**,**b**, which under these circumstances presumably arose from exclusive reduction of derived stannylaminyl radicals (Scheme 15 and Table 1, entries 18 and 20).

Thus, the bulk of the general evidence provided by all the above azido compounds **1a**,**b**, **2a**−**e**, and **17a**,**b** let us conclude that with α-azido esters Bu_3SnH can exhibit a fair tendency to form 3-(tributylstannyl)-1-triazene adducts[11] even in the presence of AIBN, provided that an additional carbonyl group not be present on the same carbon bearing the azido moiety, in which case the usual occurrence of the radical tin hydride reaction can take place. The evidence provided by our α-azido esters might also lead us to suspect that Bu_3SnH should be able to form analogous 3-alkyl-3-(tributylstannyl)-1-triazenes[11] in its common radical reactions with alkyl azides eventually affording stannylaminyl radicals. In principle, derived 3-alkyl-3-(tributylstannyl)-1-triazenes might undergo easy radical H-abstraction yielding 3,3-triazenyl radicals and thence the stannylaminyl ones by loss of nitrogen.[19] However, a possibile triazene route to stannylaminyl radical is clearly rejected by our theoretical data predicting that H-abstraction from that type of triazene should be energetically much less feasible than that from Bu_3SnH[19] and, additionally, by the known fact that thermal tin hydride additions to alkyl azides are not usually fast.[2]

The actual reasons for the curious behavior displayed by Bu_3SnH with α-azido esters in the presence of AIBN remain unclear at this stage. A tentative explanation might be that with those carbonyl azides the hydride might give rise to some coordination of tin with the carbonyl oxygen and the adjacent inner, electron-rich azido nitrogen. Such coordination would discourage radical chain reaction with azide while encouraging alternative addition to the azido moiety. On the other hand, in the case of azido keto esters and azidomalonates, Bu_3SnH would prefer coordination of tin with the two adjacent carbonyl oxygens, which then might allow the normal occurrence of the expected radical chain process. However, we wish to note that our efforts to gain IR and/or NMR spectral evidence for possible coordination of Bu_3SnH with azido ester **2c** or azidomalonate **17a** were inconclusive.

Regardless of interesting mechanistic implications, the present reactions of Bu_3SnH with α-azido esters discovered a new useful synthetic entry to 3,5-dihydro-4*H*-1,2,3-triazol-4-ones, which represent a still scarcely known class of triazole derivatives.[20] Although 3-alkyl derivatives are available through reaction of ester enolates with alkyl azides,[13c,d,21] there are very few examples of the 3*H*(1*H*)-triazolones, including compound **3e**, and these arise from catalytic hydrogenation of corresponding α-azido esters.[12,22] This method, however, appears to be of very limited scope since in other cases those azides are totally converted into amino esters.[23] To achieve further information about this point, we were eventually led to examine briefly the behavior of the compounds **1b**, **2c**, **17a**, as well as that of **3e**, upon catalytic hydrogenation at room temperature. Under these conditions the azidophenylacetate **2c** furnished only small amounts of the hydroxytriazole **3c** (6%)[22] and gave instead the amine **4c** in a useful yield (50%). The azido keto ester **1b** and the azidomalonate **17a** gave exclusively the pyrazine **15b** (70%) and the amine **19a** (80%), respectively. Moreover, the azidodiphenylacetate **2e** actually furnished the triazolone **3e**,[24] but in a yield significantly lower (26%) than that previously reported (40%).[12a] In our hands the amine **4e** was in fact preferentially formed in 66% yield. It therefore appears that catalytic hydrogenation should be used to accomplish reduction of α-azido esters to amines, whereas the thermal reaction with Bu_3SnH should be preferred to achieve alternative conversion into triazol-4-ones.

In conclusion, the thermal reaction of Bu_3SnH with α-azido esters results in smooth production of 3-tributylstannyl-1-triazene adducts affording cyclized 1,2,3-triazol-4-ones in preference to reduced amines and thence provides a useful protocol for the preparation of these triazole derivatives. In the presence of AIBN the occurrence of triazene products is not (substantially) suppressed and, consequently, the expected generation of stannylaminyl radicals can be (largely) prevented. With 2-azidomalonates and α-azido-*β*-keto esters stannyltriazenes similarly occur in the absence of the radical initiator, but in the latter cases the ensuing triazenes undergo preferential cyclization onto the ketone moiety to give reactive hydroxytriazolines. Contrary to α-azido esters, in the presence of AIBN, α-azido-*β*-keto esters as well as azidomalonates only afford stannylaminyl radicals. This fact possibly results from a different coordination mode of the tin hydride with the mono- and dicarbonyl azides.

(19) Theoretical data, which will be reported elsewhere, predict that H-abstraction from 3-methyl-3-(trimethystannyl)-1-triazene by the 2-cyano-2-propyl radical (from AIBN) is an exothermic process; analogous H-abstraction from Bu_3SnH is also predicted to be exothermic, but with a significantly lower E_a value.

(20) (a) Quast, H.; Hergenrother, T.; Banert, K.; Peters, E.-M.; Peters, K.; Schnering, H. G. *Chem. Ber.* **1993**, *126*, 103−108 and references therein. (b) Banert, K.; Lehmann, J.; Quast, H.; Meichsner, G.; Regnat, D.; Seiferling, B. *J. Chem. Soc., Perkin Trans. 2* **2002**, 126−134.

(21) (a) Quast, H.; Seiferling, B. *Tetrahedron Lett.* **1982**, *23*, 4681−4684. (b) Quast, H.; Meichsner, G.; Seiferling, B. *Ann. Chem.* **1986**, 1891−1899.

(22) The already known hydroxytriazole **3c** has been prepared using two peculiar low-yielding procedures; see: Begtrup, M.; Pedersen, C. *Acta Chem. Scand.* **1964**, *18*, 1333−1336 and ref 12b.

(23) (a) Hanessian, S.; Vanasse, B.; Yang, H.; Alpegiani, M. *Can. J. Chem.* **1993**, *71*, 1407−1411. (b) Estevez, J. C.; Smith, M. D.; Lane, A. L.; Crook, S.; Watkin, D. J.; Besra, G. S.; Brennan, P. J.; Nash, R. J.; Fleet, G. W. J. *Tetrahedron*: *Asymmetry* **1996**, *7*, 387−390. (c) Brandstetter, T. W.; de la Fuente, C.; Kim, Y.-Ha; Cooper, R. I.; Watkin, D. J.; Oikonomakos, N. G.; Johnson, L. N.; Fleet, G. W. J. *Tetrahedron* **1996**, *52*, 10711−10720. (d) Smith, M. D.; Long, D. D.; Martin, A.; Campbell, N.; Bleriot, Y.; Fleet, G. W. J. *Synlett* **1999**, 1151−1153.

(24) The triazolone **3e** has been shown to undergo interesting cationic and thermal polymerizations yielding poly(α,α-diphenylglycine); see: Ikeda, K.; Smets, G.; L'Abbè, G. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 1167−1176 and 1177−1183.

Experimental Section

Physical and spectral data of the already known azides **2c**[25] and **2e**[12a] were consistent with those reported. The azidomalonates **17a**[26] and **17b**[26] were known compounds, but no spectral features were available: diethyl 2-azido-2-methylmalonate (**17a**) was an oil [IR (liquid film) ν_{max} (cm^{-1}) 2120 (N_3), 1745 (CO); ^1H NMR (300 MHz) δ 1.32 (6 H, t, J = 7.1 Hz), 1.60 (3 H, s), 4.30 (4 H, ABX_3, J_{AB} = 10.8 Hz, J_{AX} = 7.2 Hz, J_{BA} = 10.8 Hz, J_{BX} = 7.2 Hz); ^{13}C NMR (75.45 MHz) δ 14.5, 21.0, 63.3 (CH_2), 68.8 (C), 168.3 (C)]; diethyl 2-azido-2-ethylmalonate (**17b**) was a yellowish oil [IR (liquid film) ν_{max} (cm^{-1}) 2124 (N_3), 1746 (CO); ^1H NMR (300 MHz) δ 0.92 (3 H, t, J = 7.4 Hz), 1.32 (6 H, t, J = 7.1 Hz), 1.98 (2 H, q, J = 7.4 Hz), 4.31 (4 H, q, J = 7.1 Hz); ^{13}C NMR (75.45 MHz) δ 8.7, 14.7, 28.0 (CH_2), 63.3 (CH_2), 73.1 (C), 168.0 (C)]. Hitherto unknown ethyl 2-azido-2-phenylpropanoate (**2d**) was an oil [IR (liquid film) ν_{max} (cm^{-1}) 2104 (N_3), 1738 (CO); ^1H NMR (300 MHz) δ 1.27 (3 H, t, J = 7.1 Hz), 1.81 (3 H, s), 4.26 (2 H, q, J = 7.1 Hz), 7.29−7.45 (5 H, m); ^{13}C NMR (75.45 MHz) δ 14.7, 25.1, 63.0 (CH_2), 69.8 (C), 126.2, 129.1, 129.4, 139.7 (C), 172.1 (C)].

Synthesis of the Oxime Ester Azides 2a,b. A methanol (120 mL) solution containing the corresponding keto ester azide **1a**,**b** (20 mmol), *O*-benzylhydroxylamine hydrochloride (22 mmol), pyridine (22 mmol), and anhydrous magnesium sulfate (2 g) was refluxed for 2−3 h, until TLC monitored the virtual disappearance of the starting material. Evaporation of the solvent under reduced pressure gave an oily residue mainly consisting of the aimed oxime **2a**,**b**. Chromatography of the crude **2a** gave pure ethyl 1-azido-2-[(benzyloxy)imino]-cyclohexanecarboxylate (**2a**) (60%) as an oil [IR ($CHCl_3$) ν_{max} (cm^{-1}) 2112 (N_3), 1742 (CO); ^1H NMR (300 MHz) δ 1.24 (3 H, t, J = 7.1 Hz), 1.38−1.55 (1 H, m), 1.59−1.86 (4 H, m), 2.06−2.21 (2 H, m), 3.03−3.14 (1 H, m), 4.21 (2 H, ABX_3, J_{AB} = 10.8 Hz, J_{AX} = 7.2 Hz, J_{BA} = 10.8 Hz, J_{BX} = 7.2 Hz), 5.07 (2 H, s), 7.23−7.37 (5 H, m); ^{13}C NMR (75.45 MHz) δ 14.6, 21.2 (CH_2), 23.0 (CH_2), 24.6 (CH_2), 34.8 (CH_2), 62.6 (CH_2), 70.3 (C), 76.9 (CH_2), 128.4, 128.8, 128.9, 138.1 (C), 156.1 (C), 170.5 (C)]. Chromatographic purification of **2b** gave pure ethyl 2-azido-3-[(benzyloxy)imino]-2-methylbutanoate (**2b**) (90%) as an oil [IR (liquid film) ν_{max} (cm^{-1}) 2113 (N_3), 1732 (CO); ^1H NMR (300 MHz) δ 1.25 (3 H, t, J = 7.1 Hz), 1.58 (3 H, s), 1.90 (3 H, s), 4.22 (2 H, ABX_3, J_{AB} = 10.8 Hz, J_{AX} = 7.1 Hz, J_{BA} = 10.8 Hz, J_{BX} = 7.1 Hz), 5.12 (2 H, s), 7.28−7.46 (5 H, m); ^{13}C NMR (75.45 MHz) δ 11.9, 14.7, 21.1, 62.9 (CH_2), 70.1 (C), 77.1 (CH_2), 128.5, 128.8, 129.0, 128.2 (C), 154.7 (C), 170.8 (C)].

Physical and analytical data for all new products **3a**,**b**,**d**, **4a**,**b**, **15a**,**b**, and **18a**,**b** were as follows:

1,2,3-Triazaspiro[4,5]dec-1-ene-4,6-dione-6-(*O*-benzyloxime) (**3a**) was a solid [mp 91−93 °C; IR ($CHCl_3$) ν_{max} (cm^{-1}) 3431 (NH), 1753 (CO); ^1H NMR (300 MHz) δ 1.57−1.75 (1 H, m), 1.80−2.08 (5 H, m), 2.36−2.51 (1 H, m), 3.14−3.25 (1 H, m), 5.00 (1 H, A part of AB, J = 11.7 Hz), 5,05 (1 H, B part of AB, J = 11.7 Hz), 7.23−7.40 (5 H, m), 11.19 (1 H, br s, NH); ^{13}C NMR (75.45 MHz) δ 21.7 (CH_2), 24.1 (CH_2), 24.3 (CH_2), 33.8 (CH_2), 77.2 (CH_2), 81.2 (C), 128.6, 129.0, 129.0, 137.6 (C), 154.4 (C), 178.1 (C); MS (ESI^-) 271 $(M - 1)^-$]. Anal. Calcd for $C_{14}H_{16}N_4O_2$: C, 61.75; H, 5.92; N 20.58. Found: C, 61.87; H, 5.94; N, 20.52.

5-[(Benzyloxy)ethanimidoyl]-5-methyl-3,5-dihydro-4*H*-1,2,3-triazol-4-one (**3b**) was an oil [IR (liquid film) ν_{max} (cm^{-1}) 3302 (NH), 1740 (CO); ^1H NMR (300 MHz) δ 1.47−1.68 (3 H, m), 1.70−2.05 (4 H, m), 5.02−5.20 (2 H, m), 7.21−7.38 (5 H, m); ^{13}C NMR (75.45 MHz) δ 11.5, 17.4, 76.5 (CH_2), 80.8 (C), 127.9, 128.1, 128.3, 137.1 (C), 150.7 (C), 178.1 (C); MS (ESI^-) 245 $(M - 1)^-$]. Anal. Calcd for $C_{12}H_{14}N_4O_2$: C, 58.53; H, 5.73; N, 22.75. Found: C, 58.67; H, 5.74; N, 22.71.

5-Methyl-5-phenyl-3,5-dihydro-4*H*-1,2,3-triazol-4-one (**3d**) was a solid compound showing some propensity to suffer unknown decomposition [IR ($CHCl_3$) ν_{max} (cm^{-1}) 3408 (NH), 1744 (CO); ^1H NMR (300 MHz) δ 1.74 (3 H, s), 7.06−7.64 (5 H, m), 11.6 (1 H, br s); ^{13}C NMR (75.45 MHz) δ 23.8, 79.5 (C), 126.3, 128.2, 128.6, 135.7 (C), 180.5 (C); MS (ESI^-) 174 $(M - 1)^-$]. Anal. Calcd for $C_9H_9N_3O$: C, 61.70; H, 5.18; N, 23.99. Found: C, 61.80; H, 5.22; N, 23.91.

Ethyl 1-amino-2-[(benzyloxy)imino]cyclohexanecarboxylate (**4a**) was a yellow oil [IR (liquid film) ν_{max} (cm^{-1}) 3313 and 3378 (NH_2), 1732 (CO); ^1H NMR (300 MHz) δ 1.23 (3 H, t, J = 7.1 Hz), 1.46−1.82 (5 H, m), 2.09−2.47 (4 H, m), 2.80−2.95 (1 H, m), 4.16 (2 H, ABX_3, J_{AB} = 10.8 Hz, J_{AX} = 7.1 Hz, J_{BA} = 10.8 Hz, J_{BX} = 7.1 Hz), 5.08 (2 H, s), 7.21−7.40 (5 H, m); ^{13}C NMR (75.45 MHz) δ 14.7, 22.2 (CH_2), 23.4 (CH_2), 25.5 (CH_2), 38.2 (CH_2), 61.9 (CH_2), 62.5 (C), 76.4 (CH_2), 128.2, 128.6, 128.8, 138.6 (C), 159.9 (C), 176.8 (C); MS (ESI^+) 291 $(M + 1)^+$ and 313 $(M + 23)^+$]. Anal. Calcd for $C_{16}H_{22}N_2O_3$: C, 66.18; H, 7.64; N, 9.65. Found: C, 66.38; H, 7.67; N, 9.68.

Ethyl 2-amino-3-[(benzyloxy)imino]-2-methylbutanoate (**4b**) was a yellow oil [IR (liquid film) ν_{max} (cm^{-1}) 3321 and 3384 (NH_2), 1732 (CO); ^1H NMR (300 MHz) δ 1.23 (3 H, t, J = 7.1 Hz), 1.49 (3 H, s), 1.88 (5 H, br s), 4.16 (2 H, q, J = 7.1 Hz), 5.10 (2 H, s), 7.21−7.40 (5 H, m); ^{13}C NMR (75.45 MHz) δ 11.1, 14.0, 23.8, 61.4 (CH_2), 61.9 (C), 75.9 (CH_2), 127.6, 128.0, 128.2, 134.7 (C), 137.9 (C), 157.9 (C); MS (ESI^+) 265 $(M + 1)^+$]. Anal. Calcd for $C_{14}H_{20}N_2O_3$: C, 63.62; H, 7.63; N, 10.60. Found: C, 63.82; H, 7.66; N, 10.56.

Diethyl 1,2,3,4,6,7,8,9-octahydro-4a,9a-phenazinedicarboxylate (**15a**) was an unresolved solid mixture of the *cis*/*trans* isomers in unknown ratio. Anal. Calcd for $C_{18}H_{26}N_2O_4$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.79; H, 7.86; N, 8.40. Repeated chromatography separated small amounts of the pure geometrical isomers. The cis (or trans) isomer was a solid [mp 148−150 °C; IR ($CHCl_3$) ν_{max} (cm^{-1}) 1742 (CO); ^1H NMR (400 MHz) δ 1.27 (6 H, t, J = 7.1 Hz), 1.34−1.53 (4 H, m), 1.76−1.87 (4 H, m), 1.92−2.01 (2 H, m), 2.23 (2 H, td, J_t = 13.5 Hz, J_d = 5.0 Hz), 2.44 (2 H, dt, J_d = 13.2 Hz, J_t = 3.0 Hz), 2.75 (2 H, dq, J_d = 13.5 Hz, J_q = 3.0 Hz), 4.22 (4 H, m); ^{13}C NMR (100 MHz) δ 14.7, 24.1 (CH_2), 28.2 (CH_2), 38.5 (CH_2), 38.6 (CH_2), 62.4 (CH_2), 66.6 (C), 169.6 (C), 169.8 (C); MS (ESI^-) 333 $(M - 1)^-$]. The trans (or cis) isomer was a solid [mp 163−165 °C; IR ($CHCl_3$) ν_{max} (cm^{-1}) 1740 (CO); ^1H NMR (400 MHz) δ 1.26 (6 H, t, J_t = 7.2 Hz), 1.36 (2 H, td, J_t = 13.6 Hz, J_d = 4.0 Hz), 1.46 (2 H, qt, J_q = 13.1 Hz, J_t = 4.0), 1.66 (2 H, qt, J_q = 13.5 Hz, J_t = 3.4 Hz), 1.79−1.87 (2 H, m), 1.90−1.98 (2 H, m), 2.44−2.59 (4 H, m), 2.84 (2 H, ddd, J_1 = 13.5 Hz, J_2 = 5.5 Hz, J_3 = 3.0 Hz), 4.19 (4 H, q, J_q = 7.2 Hz); ^{13}C NMR (100 MHz) δ 14.7, 23.7 (CH_2), 27.2 (CH_2), 38.2 (CH_2), 40.0 (CH_2), 62.3 (CH_2), 66.3 (C), 169.3 (C), 169.9 (C); MS (ESI^-) 333 $(M - 1)^-$].

Diethyl 2,3,5,6-tetramethyl-2,5-dihydro-2,5-pyridazinedicarboxylate (**15b**) was an unresolved oily mixture of the *cis*/*trans* isomers in unknown ratio. Anal. Calcd for $C_{14}H_{22}N_2O_4$: C, 59.56; H, 7.85; N, 9.92. Found: C, 59.77; H, 7.87; N, 9.89. Repeated chromatography separated small amounts of the pure geometrical isomers. The cis (or trans) isomer was a solid [mp 47−48 °C; IR ($CHCl_3$) ν_{max} (cm^{-1}) 1742 (CO); ^1H NMR (300 MHz) δ 1.32 (6 H, t, J = 7.1 Hz), 1.59 (6 H, s), 2.26 (6 H, s), 4.31 (4 H, ABX_3, J_{AB} = 10.8 Hz, J_{AX} = 7.1 Hz, J_{BA} = 10.8 Hz, J_{BX} = 7.1 Hz); ^{13}C NMR (75.45 MHz) δ 13.8, 22.9, 23.4, 62.0 (CH_2), 64.7 (C), 165.3 (C), 169.5 (C); MS (ESI^+) 283 $(M + 1)^+$ and 305 $(M + 23)^+$]. The trans (or cis) isomer was a solid [mp 59−61 °C; IR ($CHCl_3$) ν_{max} (cm^{-1}) 1737 (CO); ^1H NMR (300 MHz) δ 1.27 (6 H, t, J = 7.1 Hz), 1.59 (6 H, s), 2.10 (6 H, s), 4.20 (4 H, ABX_3, J_{AB} = 10.8 Hz, J_{AX} = 7.1 Hz, J_{BA} = 10.8 Hz, J_{BX} = 7.1 Hz); ^{13}C NMR (75.45 MHz) δ 13.9, 22.9, 23.9, 61.8 (CH_2), 64.5 (C), 165.9 (C), 169.4 (C); MS (ESI^+) 283 $(M + 1)^+$ and 305 $(M + 23)^+$].

Ethyl 4-methyl-5-oxo-4,5-dihydro-1*H*-1,2,3-triazole-4-carboxylate (**18a**) was an oil [IR (liquid film) ν_{max} (cm^{-1}) 3426 (NH), 1765 (CO), 1742 (CO); ^1H NMR (300 MHz) δ 1.28 (3 H,

(25) Heras, M.; Ventura, M.; Linden, A.; Villalgordo, J. M. *Tetrahedron* **2001**, *57*, 4371−4388.
(26) Forster, M. O.; Muller, R. *J. Chem. Soc.* **1910**, 134.

t, J = 7.1 Hz), 1.73 (3 H, s), 4.26 (2 H, q, J = 7.1 Hz), 11.06 (1 H, br s); ^{13}C NMR (75.45 MHz) δ 14.4, 18.1, 64.1 (CH_2), 81.6 (C), 163.6 (C), 176.6 (C); MS (ESI$^-$) 170 $(M - 1)^-$/(ESI$^+$) 194 $(M + 23)^+$]. Anal. Calcd for $C_6H_9N_3O_3$: C, 42.10; H, 5.30; N, 24.55. Found: C, 42.19; H, 5.32; N, 24.51.

Ethyl 4-ethyl-5-oxo-4,5-dihydro-1*H*-1,2,3-triazol-4-carboxylate (**18b**) was a yellowish oil [IR (liquid film) ν_{max} (cm^{-1}) 3438 (NH), 1761 (CO), 1740 (CO); ^{1}H NMR (300 MHz) δ 0.88 (3 H, t, J = 7.5 Hz), 1.28 (3 H, t, J = 7.1 Hz), 2.35 (2 H, ABX_3, J_{AB} = 14.9 Hz, J_{AX} = 7.5 Hz, J_{BA} = 14,9 Hz, J_{BX} = 7.5 Hz), 4.26 (2 H, q, J = 7.1 Hz), 10.64 (1 H, br s); ^{13}C NMR (75.45 MHz) δ 7.3, 13.8, 26.3 (CH_2), 63.2 (CH_2), 85.0 (C), 162.6 (C), 174.8 (C); MS (ESI$^-$) 184 $(M - 1)^-$/(ESI$^+$) 208 $(M + 23)^+$]. Anal. Calcd for $C_7H_{11}N_3O_3$: C, 45.40; H, 5.99; N, 22.69. Found: C, 45.55; H, 6.01; N, 22.61.

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Supporting Information Available: General remarks; general synthesis of azides **2c**−**e** and **17a**,**b**; experimental procedures for reactions of azides **1a**,**b**, **2a**−**e**, **11**, and **17a**,**b** with tributyltin hydride, for reactions of azides **2d**,**e** with hexabutylditin/di-*tert*-butyl hyponitrite as well as for hydrogenation of azides **1b**, **2c**, **2e**, **17a**; ^{1}H and ^{13}C NMR spectra of compounds **2a**, **2b**, and **2d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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