A General and Efficient Synthesis of α-Azido Ketones

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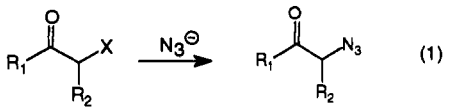
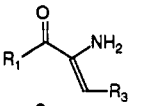
Introduction

Although α-azido ketones 1 have been known for a long time,[2] few reports of their synthetic utility have appeared because few systematic studies have been performed. Scattered papers describing their chemistry reveal that they behave quite differently than the related α-azido esters and that they could have significant synthetic utility. Their pyrolysis leads to α-imino ketones[3-5] (presumably *via* nitrenes) or 2-acylimidazoles if β-carbon atoms are not present.[3] The lability of α-azido ketones under basic conditions has been known for a long time.[6] Treatment of 1 with bases gives α-imino ketones[5,6] or tautomeric α-amino enones.[7-12] The transformation α-azido ketones 1 into symmetrical 1,4-pyrazines during catalytic reduction[13] or upon treatment with sodium hydrogentelluride[14] or by the action of triphenylphosphine[15] have also been reported. These reactions were suggested to take place by the dimerization of the first-formed α-amino ketones and α-(triphenylphosphoranediyl)imino ketones, respectively. Azides 1 were shown to be useful starting materials in the synthesis of oxazoles, as well, either by a *Staudinger*-type reaction performed in the presence of acid chlorides[16,17] or *via* a β-(acyloxy)vinyl azide intermediate.[18] An interesting oxidative ring cleavage of steroidal α-azido ketones to give cyano carboxylic acids has also been published.[19]

With three exceptions,[7,20,21] α-azido ketones 1 have been prepared by nucleophilic substitutions of α-halo ketones 2 (X = Cl, Br) (eq 1). This reaction provides good yields for phenacyl halides but is much less effective for compounds with β-hydrogens or conjugating groups at the β carbon. In these cases only a steady-state concentration of the keto azide 1 can be detected during the course of the reaction. The product actually isolated is the α-amino enone 3.[5,6,12] The preparation of α-azido ketones from unsymmetric ketones also requires that the starting α-halo ketone 2 be prepared regiospecifically. This can be a limiting factor as well. These arguments may explain the fact that most papers describing the transformations of 1 use only phenacyl azides 1 (R_1 = Ph, R_2 = H) or 2-alkylated phenacyl azides 1 (R_1 = Ph, R_2 = alkyl).



2 (X = Cl, Br) 1 (1)



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The enhanced reactivity[22] of α-((4-nitrobenzene)sulfonyl)oxy ketones (α-nosyloxy ketones) 4 toward nucleophiles and the highly efficient synthesis of 4 by oxidative sulfonyloxylation[22-27] suggested that these compounds could provide a versatile route to α-azido ketones. Such has proven to be the case and we wish to report a new and very general preparation of α-azido ketones 1.

Results and Discussion

Starting α-nosyloxy ketones **4a-f,h-m** were prepared by the reaction of enol acetates **5a-f**,[23] enamine **6h**,[24] or β-keto esters **7i-l**[25,27] with *bis*(*p*-nitrobenzenenesulfonyl) peroxide (pNBSP) according to literature procedures. Nosyloxy ketone **4m** (R_1 = Ph, R_2 = Ph) was prepared from deoxybenzoin and pNBSP.[24] Nosyloxylation was found to work well in the case of benzocyclanone enol acetates **5d-f** but failed to give the desired product **4g** upon treatment of thio analogue **5g** with pNBSP. In the latter case only thiochromone (**8g**) was obtained, which probably originates from initial electrophilic attack of the pNBSP on the sulfur atom followed by a loss of *p*-nitrobenzenesulfonic acid and the acetate group.

To find the optimal conditions for the azide displacement needed to produce α-azido ketones 1 from α-nosyloxy ketones 4, the reaction of nosylate **4h** with sodium azide was studied in various solvents. As shown in Table 1, high yields of **1h** were achieved in all of the solvents screened, although the reaction times were different since

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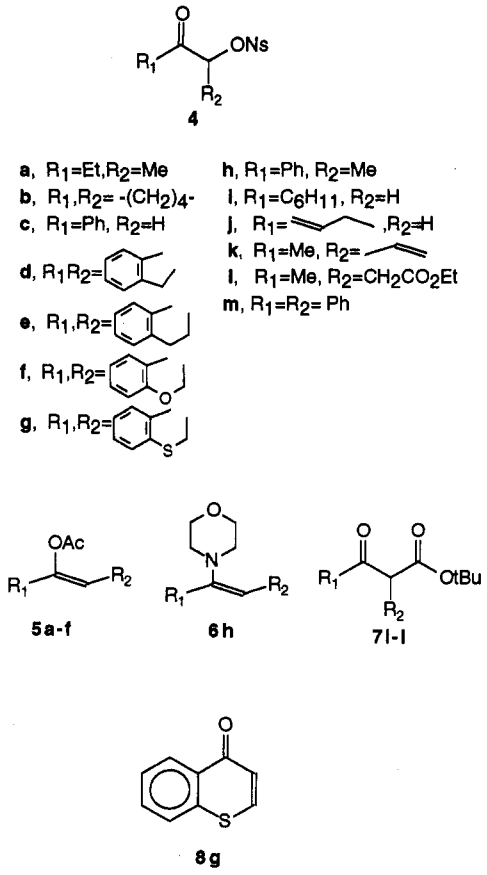

the solubility of sodium azide in these solvents varied widely. Careful examination of the reaction mixture in both acetone and ethanol solvents showed that no α-hydroxy ketone was formed. This product might be expected from azide attack on the carbonyl group in the first step of the reaction, similar to the process found earlier in the reaction of α-nosyloxy ketones with methoxide and amine nucleophiles.[26] The absence of any α-hydroxy ketone in the product mixture suggests that the azide nucleophile does not add to the carbonyl group but instead attacks the α-carbon and displaces the nosylate group directly (S_N2). This assumption requires additional validation, however.

Using sodium azide in acetone at room temperature, α-nosyloxy ketones **4a–f,h–m** were converted into the corresponding α-azido ketones **1a–f,h–m**. As shown by the data in Table 2, the reaction provides high yields for precursors having diverse structures. The only factors which appear to reduce the yields to any extent are the volatility of the azide (e.g. **1a,k**) or the instability of the product (e.g. **1e**). The nosyloxy approach to **1** gave good results in the case of sensitive azides such as **1f,l,m**. Starting from the corresponding α-bromo ketones **2f,l** (X = Br) only enamines **3** were formed instead of azides **1f**[8] and **1l**,[12] although some azide **1l** could be isolated by chromatography with a shorter reaction time.[12] Even the highly unstable 2-azido-1-tetralone (**1e**) was available from nosylate **4e**, illustrating the mildness of this method. It is interesting that all cyclic α-azido ketones seem to be less stable than the acyclic representatives, although the moderate lability is characteristic for the whole series.

In summary, the nucleophilic substitution of α-(4-nitrobenzenesulfonyl)oxy ketones **4** with azide ion provides an improved, general, and efficient method for the synthesis of α-azido ketones **1**. The advantages of this approach using α-nosyloxy ketones rather than halo analogues are the mild reaction conditions which allow the high-yield preparation of base-sensitive products as exemplified by **1f,l,m** and possibility of regioselective synthesis of the azides from the corresponding nosylates, which themselves can be prepared regiospecifically.[27] Studies on the synthetic applications of the azides prepared are in progress.

Table 1. Reaction of 2-Nosyloxy-1-phenyl-1-propanone (4h) with Sodium Azide[a]

entry	solvent	time	1h yield (%)
1	Me_2CO	100 min	93
2	EtCOMe	85 min	95
3	EtOH	105 min	82 + 2.3% unreacted **4h**
4	CH_2Cl_2	10 days	80 + 9.3% unreacted **4h**
5	CH_2Cl_2[b]	45 h	82

[a] All reactions were performed at room temperature; yields refer to isolated products. [b] In the presence of 10 mol % of dibenzo-18-crown-6 catalyst.

Table 2. Synthesis of α-Azido Ketones 1 from α-Nosyloxy Ketones 4

substrate	time	yield (%)	lit. yield (%)
4a	75 min	68	–
4b	7 h	84	"good"[5]
4c	60 min	95	86,[18] 93[3]
4d	105 min	80	–
4e	9 h	55[c]	–
4f	4.5 h	76	*d*
4h	100 min	93	77,[4] 80[18]
4i	90 min	96	–
4j	65 min	81	–
4k	135 min	70	–
4l	105 min	94	*b*
4m	105 min	80	39[4]

[a] All reactions were performed in acetone at room temperature; yields refer to pure products. [b] Secondary product ethyl 3-amino-4-oxo-2-pentenoate was isolated in 73% yield from the reaction of bromo analogue.[12] [c] 90% purity, see Experimental Section. [d] Only secondary product 3-aminochromone was isolated in 76% yield from the reaction of the bromo analogue. Formation of chromone (product of β-elimination) was also reported.[8]

Experimental Section

General. All chemicals were of reagent grade and used as received from the vendors. Melting points are uncorrected. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra were recorded in $CDCl_3$ solution, using TMS as internal standard. IR spectra were measured neat unless otherwise stated. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Column chromatography separation were performed using silica gel 60 (70–230 mesh) (Aldrich); thin-layer chromatography (TLC) was carried out on silica gel 60A (Whatman, MK6F).

Starting nosylates **4a,b,c,e** were synthesized by from the corresponding enol acetates **5a,b,c,e**,[23] **4h** from enamine **6h**,[24] **4m** from deoxybenzoin,[24] and **4i,j,k,l** from the corresponding β-keto esters **7i,j,k,l**,[27], respectively.

Caution: While the azides prepared in this study have never exhibited any tendency toward violent decomposition, they should be handled with precautions appropriate for materials capable of such behavior. Furthermore the use of sodium azide in dichloromethane as described in Table 1 should be avoided as this combination has recently been reported to form explosive mixtures!

4-Acetoxy-2*H*-1-thiochromene (5g) was synthesized from 4*H*-1-thiochroman-4-one (25.03 mmol) by using the procedure of Saito *et al.*[28] to give 4.53 g (88%) of pure product as yellowish crystals: mp 72.5–75 °C (hexane–EtOAc); IR (KBr) 1757, 1666, 1169 (br); ^{1}H NMR δ 7.25 (dd, 1H), 7.08–7.15 (m, 3H), 5.70 (t,

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J = 5.6 Hz, 1H), 3.58 (d, J = 5.6 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR 168.9, 146.7, 133.6, 129.0, 128.7, 127.2, 125.5, 122.9, 110.59, 24.4, 20.8. Anal. Calcd for $C_{11}H_{10}O_2S$ (206.27): C, 64.05; H, 4.89. Found: C, 64.08; H, 4.74.

This compound was mentioned in ref 29 without any physical or spectroscopic data.

2-[(4-Nitrobenzenesulfonyl)oxy]-1-indanone (4d). 3-Acetoxyindene **5d**[30] (1.74 g, 10.00 mmol) was treated with *bis*(p-nitrobenzenenesulfonyl) peroxide (4.10 g, 10.51 mmol) according to the literature procedure[23] to give 2.61 g (78%) of crystalline **4d**: mp 145–146.5 °C (hexane–EtOAc); IR (KBr) 1734 , 1543, 1379, 1353, 1186 cm^{-1}; ^{1}H NMR δ 8.44, 8.26 (AB q, 4H), 7.67–7.73 (m, 2H), 7.41–7.48 (m, 2H), 5.31 (dd, J = 8.0, 4.8 Hz, 1H), 3.74 (dd, 1H, J = 17.2, 8.0 Hz), 3.34 (dd, J = 17.2, 4.8 Hz, 1H); ^{13}C NMR 197.2, 150.8, 149.8, 142.2, 136.7, 133.3, 129.6, 128.7, 126.7, 124.8, 124.38, 79.5, 33.7. Anal. Calcd for $C_{15}H_{11}NO_6S$ (333.32): C, 54.05; H, 3.33; N, 4.20; S, 9.62. Found: C, 54.11; H, 3.48; N, 4.20; S, 9.61.

3-[(4-Nitrobenzenesulfonyl)oxy]-4-chromanone (4f). 4-Acetoxy-2*H*-1-chromene (**5f**)[28] (1.15 g, 6.05 mmol) was reacted with *bis*(*p*-nitrobenzenenesulfonyl) peroxide (2.6 g, 6.43 mmol) at −75 °C for 70 min.[23] Workup followed by column chromatography (2.5 × 40 cm, eluant: hexane–EtOAc = 4:1) afforded 753 mg (36%) of **4f**: mp 133.5–135 °C (hexane–EtOAc); IR (KBr) 1710, 1534, 1363, 1350, 1211, 1189, 1041, 1020 cm^{-1}; ^{1}H NMR δ 8.42, 8.21 (AB q, 4H), 7.55 (dd, 1H), 7.53 (ddd, 1H), 7.05 (ddd, 1H), 7.01 (dd, 1H), 5.33 (dd, J = 10.4, 5.2 Hz, 1H), 4.71 (dd, J = 11.2, 5.2 Hz, 1H), 4.54 (dd, J = 11.2, 10.4 Hz, 1H); ^{13}C NMR 185.1, 161.2, 150.9, 141.6, 137.2, 129.6, 127.7, 124.4, 122.6, 119.2, 118.0, 75.4, 68.8. Anal. Calcd for $C_{15}H_{11}NO_7S$ (349.32): C, 51.58; H, 3.17; N, 4.01; S, 9.18. Found: C, 51.67; H, 3.03; N, 3.92; S, 9.20.

Chromone (**8f**) (287 mg, 32.5%) was isolated from the fraction eluting subsequently.

4*H*-1-Thiochromone (8g). 4-Acetoxy-4*H*-1-thiochromene (**5g**) (620 mg, 3.01 mmol) was treated with *bis*(p-nitrobenzenesulfonyl)peroxide (1.35 g, 3.34 mmol).[23] The reaction mixture was worked up after 55 min and a short-column chromatography (3.5 × 12 cm; eluant: hexane–EtOAc = 9:1) of the crude product afforded pure **8g** (287 mg, 59%): mp 74–76 °C, lit.[31] mp 78–80 °C; IR (KBr) 1628, 1368 cm^{-1}; ^{1}H NMR δ 8.55 (dd, 1H), 7.83 (d, J = 10.6 Hz, 1H), 7.62–7.52 (m, 3H), 7.02 (d, J = 10.6 Hz).

General Procedure for the Synthesis of α-Azido Ketones 1: 2-Azido-1-phenyl-1-propanone (1h). A mixture of 2-[(4-nitrobenzenesulfonyl)oxy]-1-phenyl-1-propanone (**4h**) (1.68 g, 5.01 mmol), sodium azide (0.65 g, 10.00 mmol), and acetone (75 mL) was stirred at room temperature for 100 min (TLC monitoring), and then poured into water and extracted with CH_2Cl_2 (3 × 75 mL). The organic extracts were washed with saturated $NaHCO_3$ solution (75 mL) and water (150 mL), dried ($MgSO_4$), and evaporated *in vacuo*. The residue was purified by column chromatography (2.5 × 40 cm; eluant: hexane–EtOAc = 4:1) to give **1h** as a pale yellow oil (816 mg, 93%): lit.[4] bp 75 °C/0.5 torr; IR 2985, 2124, 2097, 1694 cm^{-1}; ^{1}H NMR δ 7.95 (dd, 1H), 7.62 (dd, 1H), 7.50 (dd, 2H), 4.71 (q, J = 7.2 Hz, 1H), 1.57 (d, J = 7.2 Hz, 3H); ^{13}C NMR 196.7, 134.3, 133.9, 128.9, 128.6, 58.4, 16.4. Anal. Calcd for $C_9H_9N_3O$: C, 61.70; H, 5.18; N, 23.99. Found: C, 61.81; H, 5.23; N, 23.88.

2-Azido-3-pentanone (1a) was prepared from 2-[(4-nitrobenzenesulfonyl)oxy]-3-pentanone (**4a**) (431 mg, 1.50 mmol) in a reaction time of 75 min at rt. The crude product (purity was checked by TLC and ^{1}H-NMR) is a pale yellow oil (129 mg, 68%): IR 2093, 1723, 1454, 1255 cm^{-1}; ^{1}H NMR δ 3.93 (q, J = 7.2 Hz, 1H), 2.67 (q, J = 7.6 Hz, 2H), 1.44 (d, J = 7.2 Hz, 3H), 1.09 (t, J = 7.6 Hz, 3H); ^{13}C NMR 208.2, 63.0, 32.4, 15.9, 7.4. Anal. Calcd for $C_5H_9N_3O$ (127.15): C, 47.23; H, 7.13; N, 33.05. Found: C, 47.33; H, 7.03; N, 32.83.

2-Azidocyclohexanone (1b) was prepared from 2-[(4-nitrobenzenesulfonyl)oxy]cyclohexanone (**4b**) (449 mg, 1.50 mmol) after 7 h at rt. Short-column chromatography (3.5 × 10 cm, eluant: hexane–EtOAc = 9:1) afforded **1b** (176 mg, 84%) as a pale yellow oil of high purity (lit.[5] "yellow oil"): IR 2945, 2867, 2100, 1718, 1451, 1265 cm^{-1}; ^{1}H NMR δ 3.93 (dd, J = 11.4, 6.6 Hz, 1H), 1.66–2.56 (m, 8H); ^{13}C NMR 205.6, 66.5, 40.8, 33.6, 27.1, 23.8. Elemental analysis could not be obtained for **1b** due to slow decomposition of the sample on storage.

2-Azido-1-phenylethanone (1c) was prepared from 2-[(4-nitrobenzenesulfonyl)oxy]-1-phenylethanone (**4c**) (482 mg, 1.50 mmol) after 60 min at rt. The crude product (purity was checked by TLC and ^{1}H-NMR) is a nearly colorless oil of high purity (321 mg, 95%) which solidifies in the refrigerator: lit.[4] mp 17 °C; IR 2195, 2105, 1698, 1286 cm^{-1}; ^{1}H NMR 7.99 (dd, 1H), 7.63 (m, 1H), 7.50 (dd, 2H), 4.57 (s, 2H); ^{13}C NMR 193.3, 134.3, 134.1, 129.0, 127.9, 54.9. Elemental analysis could not be obtained for **1c** due to slow decomposition of the sample on storage.

2-Azido-1-indanone (1d) was prepared from 2-[(4-nitrobenzenesulfonyl)oxy]-1-indanone (**4d**) (500 mg, 1.50 mmol) after 105 min at rt. Purification by short-column chromatography (3.5 × 10 cm; eluant: hexane–EtOAc = 3:1) gave **1d** (209 mg, 80%): mp 45–47 °C; IR (KBr) 2084, 1718, 1437, 1270 cm^{-1}; ^{1}H NMR δ 7.80 (dd, 1H), 7.65 (ddd, 1H), 7.41–7.46 (m, 2H), 4.32 (dd, J = 8.1, 4.7 Hz), 3.51 (dd, J = 17.0, 8.1 Hz, 1H), 2.94 (dd, J = 17.0, 4.7 Hz, 1H); ^{13}C NMR 210.7, 151.2, 136.1, 134.2, 128.2, 126.6, 124.6, 62.0, 33.0. Anal. Calcd for $C_9H_7N_3O$ (173.18): C, 62.42; H, 4.07; N, 24.26. Found: C, 62.67; H, 4.09; N, 24.13.

Azide **1d** slowly decomposes at room temperature.

2-Azido-1-tetralone (1e) was prepared from 2-[(4-nitrobenzenesulfonyl)oxy]-1-tetralone (**4e**) (347 mg, 0.999 mmol) after 9 h at rt. Purification by filtration through a short pad of neutral alumina (Fluka) (4 × 2 cm, washed with CH_2Cl_2) gave **1e** (102 mg, 55%) as an unstable deep purple oil (ca. 90% purity according to ^{1}H-NMR): IR 2937, 2103, 1694, 1456, 1266 cm^{-1}. ^{1}H NMR δ 8.07 (dd, 1H), 7.52 (ddd, 1H), 7.35 (ddd, 1H), 7.26 (dd, 1H), 4.24 (dd, J = 12.0, 4.8 Hz, 1H), 3.08 (dd, J = 7.6, 4.4 Hz, 2H), 2.37, 2.14 (2 × m, 2 × 1H).

Azide **1e** is highly unstable, a fast decomposition proceeds in pure form.

3-Azido-4-chromanone (1f) was prepared from 3-[(4-nitrobenzenesulfonyl)oxy]-4-chromanone (**4f**) (524 mg, 1.50 mmol) after 4.5 h at rt. The crude product contained a small amount of unreacted **4f** and chromone (**8f**) beside the azide **1f**. Column chromatography (2.5 × 35 cm; eluant: hexane–EtOAc = 4:1) yielded **1f** as a pale yellow oil (216 mg, 76%): IR 2116, 1701, 1283, 1234, 1215, 1019 cm^{-1}; ^{1}H NMR δ 7.92 (dd, 1H), 7.53 (ddd, 1H), 7.08 (ddd, 1H), 6.99 (dd, 1H), 4.51 (dd, J = 11.4, 10.4 Hz, 1H), 4.39 (dd, J = 10.4, 5.1 Hz, 1H), 4.25 (dd, J = 11.4, 5.1 Hz, 1H); ^{13}C NMR 188.6, 161.4, 136.8, 127.7, 122.2, 119.4, 117.9, 68.9, 60.0. Anal. Calcd for $C_9H_7N_3O_2$ (189.18): C, 57.14; H, 3.73; N, 22.21. Found: C, 57.18; H, 3.81; N, 22.30.

2-Azido-1-cyclohexylethanone (1i) was prepared from 1-cyclohexyl-2-[(4-nitrobenzenesulfonyl)oxy]ethanone (**4i**) (327 mg, 0.999 mmol) after 90 min at rt. The crude product (purity was checked by TLC and ^{1}H-NMR) is a pale yellow oil which solidifies in the freezer (160 mg, 96%): IR 2931, 2856, 2104, 1720, 1451, 1284 cm^{-1}; ^{1}H NMR δ 4.00 (s, 2H), 2.41 (m, 1H), 1.20–1.85 (m, 10H); ^{13}C NMR 207.2, 55.8, 48.4, 28.2, 25.6, 25.4. Anal. Calcd for $C_8H_{13}N_3O$ (167.21): C, 57.47; H, 7.84; N, 25.13. Found: C, 57.49; H, 7.68; N, 24.92.

1-Azido-5-hexen-2-one (1j) was prepared from 1-[(4-nitrobenzenesulfonyl)oxy]-5-hexen-2-one (**4j**) (1.103 g, 3.69 mmol) after 65 min at rt. The crude product was purified by passing through a short pad of silica (4 × 2 cm, washed with hexane–EtOAc = 4:1) to afford a light yellow oil (413 mg, 81%): IR 2105, 1728, 1642, 1280 cm^{-1}; ^{1}H NMR δ 5.80 (m, 1H), 5.06 (dd, J = 17.2, 1.0 Hz, 1H), 5.02 (dd, J = 17.2, 11.0 Hz, 1H), 3.95 (s, 2H), 2.56 (t, J = 7.6 Hz, 2H), 2.38 (m, 2H); ^{13}C NMR 203.7, 136.3, 115.9, 57.5, 39.1, 27.3. Elemental analysis could not be obtained for **1j** due to slow decomposition of the sample on storage.

3-Azido-5-hexen-2-one (1k) was prepared from 3-[(4-nitrobenzenesulfonyl)oxy]-5-hexen-2-one (**4k**) after 135 min at rt. The crude product (purity was checked by TLC and ^{1}H-NMR) is a yellow oil of high purity (97 mg, 70%): IR 2104, 1724, 1643, 1266 cm^{-1}; ^{1}H NMR δ 5.79 (m, 1H), 5.22 (dd, J = 17.2, 1.2 Hz, 1H), 5.19 (dd, J = 10.0, 1.2 Hz, 1H), 3.91 (dd, J = 7.6, 5.6 Hz, 2H), 2.60, 2.48 (2 × m, 2 × 1H); 2.28 (s, 1H). ^{13}C NMR 204.6,

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132.1, 119.3, 67.9, 35.1, 27.2. Elemental analysis could not be obtained for **1k** due to slow decomposition of the sample on storage.

Ethyl 3-azido-4-oxopentanoate (**1l**) was prepared from ethyl 3-[(4-nitrobenzenesulfonyl)oxy]-4-oxopentanoate (**4l**) (260 mg, 0.753 mmol) after 105 min at rt. The crude product (purity was checked by TLC and ^{1}H-NMR) is a yellow oil of high purity (130 mg, 94%): IR 2104, 1729 br, 1259, 1192, 1028 cm^{-1}; ^{1}H NMR δ 4.25 (dd, J = 7.2, 5.6 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 2.92 (dd, J = 16.8, 5.6 Hz, 1H), 2.71 (dd, J = 16.8, 7.2 Hz, 1H), 2.33 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H);^{13}C NMR 203.7, 169.9, 64.4, 61.4, 35.5, 27.4, 14.1. Anal. Calcd for $C_7H_{11}N_3O_3$ (185.18): C, 45.40; H, 5.99; N, 22.69. Found: C, 45.54; H, 5.89; N, 22.65. This compound was mentioned in ref 12 without any yield, physical, or spectroscopic data.

2-Azido-1,2-diphenylethanone (**1m**) was prepared from 2-[(4-nitrobenzenesulfonyl)oxy]-1,2-diphenylethanone (**4m**) (1.191 g, 3.00 mmol) after 105 min at rt and was purified by recrystallizing from hexane to give **1m** (568 mg, 80%), mp 82–84 °C (lit.[4] mp 85 °C); IR (KBr) 2140, 2095, 1684 cm^{-1}; ^{1}H NMR 7.88 (dd, 2H), 7.52 (m, 1H), 7.36–7.41 (m, 7H), 5.72 (s, 1H); ^{13}C NMR 194.3, 134.3, 133.8, 133.7, 129.5, 129.4, 128.9, 128.8, 128.3, 67.9. Anal. Calcd for $C_{14}H_{11}N_3O$ (237.26): C, 70.87; H, 4.67; N, 17.71. Found: C, 71.29; H, 4.70; N, 17.92.

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Supplementary Material Available: Copies of ^{13}C NMR spectra of **1b,c,j,k** and a copy of the ^{1}H NMR spectrum of **1e** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.