Cycloadditions of Alkynyl Esters and Ethers with 1,2,3-Tri-t-butyl Azete

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Moderately electron-rich alkynes, such as alkynyl carboxylates **2a**, **b**, siloxyalkynes **2c**, **d**, an alkynyl *p*-toluenesulphonate **2e**, and ethoxyacetylene **2f**, add exclusively to the C=N bond of the kinetically stabilized azete **1**; with terminal alkynes **2a**, **f**, a mixture of the regioisomeric 1-Dewar-pyridines **3** and **4** is obtained, whereas addition of internal alkynes results only in 3-oxy-1-Dewar-pyridines **3**.

Siloxyalkynes,[1] as well as alkynyl carboxylates[2] and *p*-toluenesulphonates,[3] are new classes of functionalized acetylenes whose chemistry is just emerging. Whereas the cycloaddition behaviour of the latter two classes of compounds is totally unexplored, siloxyalkynes have recently been found to undergo [2 + 2] cycloaddition to ketene[4] and [2 + 4] cycloaddition to vinylketenes.[1d,4] Phenyl-siloxyalkynes, however, do not react with ketene;[4] furthermore, they are inert as dienophiles in the standard Diels–Alder reaction with dienes such as 2,3-dimethylbutadiene and 1,3-diphenylisobenzofuran, or as dipolarophiles towards nitrile oxides.[5] Thus, siloxyalkynes display the cycloaddition behaviour of moderately electron-rich alkynes, exemplified by alkynyl ethers[6] ('yne-ethers') and characterized by low reactivity and a strong influence of electronic and steric effects on both the reaction rate and the regiochemistry.

We report here that siloxyalkynes, alkynyl ethers, and alkynyl esters undergo a clean cycloaddition to the C=N bond of the kinetically stabilized, but highly reactive azete **1**. This electronically unique hetero-[4]-annulene[7] has been shown to undergo [2 + 2] (or [4 + 2]) cycloaddition reactions with a broad range of π systems, such as alkenes,[8a,b] alkynes,[8a,c,d] nitriles,[8a,c] carbonyl compounds,[8b] a silaethene[8e] and a phosphaalkyne.[8a]

In contrast to the electron-deficient alkenes and alkynes investigated so far, the moderately electron-rich alkynes **2a–f** only slowly add to **1** at room temperature (Table 1). With the disubstituted alkynes **2b–e**, only the 3-oxy-substituted 1-Dewar-pyridines **3b–e** are obtained as products, but with the terminal alkynes **2a**, **f**, the regioisomers **3** and **4** are formed in approximately equal amounts.

The structural assignment of **3** and **4** follows from ^{13}C NMR data.† The presence of four sp^2 ring carbon atoms indicates that the alkynes **2** have added to the C=N rather than the C=C bond of **1**. The signals of the ring carbon atoms bearing Bu^t groups are easily recognized since they are broadened by $^3J_{C,H}$ coupling. The signal of C-6, due to shielding by the adjacent nitrogen atom, appears at a typical low-field position (δ = 162.2–167.3 ppm). If C-2 is deshielded by an OR substituent (**4a**, **f**), its ^{13}C resonance is also found in this region. The absence of such a signal in the 1-Dewar-pyridines **3** clearly indicates that the OR group is now attached to C-3 rather than to C-2.

If the addition of alkynes **2** to **1** was solely controlled by the bond polarity of the reactants, bicyclic products **4** would be expected in all cases. The exclusive formation of regioisomers

Table 1 1-Dewar-pyridines from azete **1** and alkynes **2**[a,b]

2, 3	R^1	R^2	t/h	Yield (%)	
				3	4
a	H	COPh	6	49	34
b	Me	COPh	18	83	0
c	Ph	SiMe$_2$Bu^t	72	40	0
d	Ph	SiPr$^i_3$	72	46	0
e	Bu^t	SO$_2$-C$_6$H$_4$-(4)-CH$_3$	22	79	0
f	H	Et	4	39	34

[a] Synthesis of alkynes **2**: **2a**,[9]; **2b**,[2b]; **2c**, **d**,[1a]; **2e**,[3]; **2f**.[10] [b] In a typical experiment, a solution of azete **1**[8a] (2.3 mmol) and alkyne **2** (2.0 mmol) in pentane (3 ml) is stirred in a Schlenk tube under argon for the time indicated above. The products are isolated by column chromatography (Merck–Lobar columns, LiChroprep Si60, 40–63 µm, eluent ether–light petroleum (40–60 °C) (1 : 10) in the case of **a**, **b–d**, **f**, or by removal of the solvent and washing the residue with a little cold pentane **3e**.†

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† *Physical and spectroscopic data*: All NMR spectra were taken in CDCl$_3$ (TMS as standard) and registered at 90 MHz (^{1}H) or 100.6 MHz (^{13}C), if not stated otherwise.

3a: M.p. 89 °C; IR (KBr) 1732 (C=O), 1615, 1598, 1582 cm^{-1}; ^{1}H NMR δ 1.10, 1.18, 1.22 (3 Bu^t), 6.50 (=CH); ^{13}C NMR δ 27.2, 29.1, 31.6 (3 C*Me*$_3$), 31.8, 33.1, 33.8 (3 *C*Me$_3$), 87.5 (C-4), 128.7, 129.1, 129.7, 130.9 (C-2, d, $^1J_{C,H}$ 201 Hz), 133.5, 138.2 (C-5), 142.3 (C-3), 163.0 (C=O), 165.5 (C-6).

4a: Yellow oil; IR (film) 1742 (C=O), 1610, 1600 cm^{-1}; ^{1}H NMR δ 1.10, 1.23, 1.30 (3 Bu^t), 5.43 (=CH); ^{13}C NMR δ 79.6 (C-4), 100.2 (C-2, d, $^1J_{C,H}$ 193 Hz), 139.8 (C-5), 155.6 (C-2), 162.2 (C-6), 163.0 (C=O).

3b: Viscous oil, b.p. 100 °C/0.04 mbar (Kugelrohr); IR (film) 1736 (C=O), 1640, 1600, 1584 cm^{-1}; ^{1}H NMR δ 1.05, 1.18, 1.21 (Bu^t), 2.04 (2-Me); ^{13}C NMR δ 15.9 (2-Me), 27.2, 30.4, 31.3 (3 C*Me*$_3$), 31.8, 33.3, 33.5 (3 *C*Me$_3$), 83.7 (C-4), 128.6, 129.5, 129.9, 133.3, 136.3 (C-2 or C-3, q, $J_{C,H}$ 6.0 Hz), 138.7 (C-5), 139.9 (C-3 or C-2, q, $J_{C,H}$ 8.2 Hz), 162.4 (C=O), 165.7 (C-6).

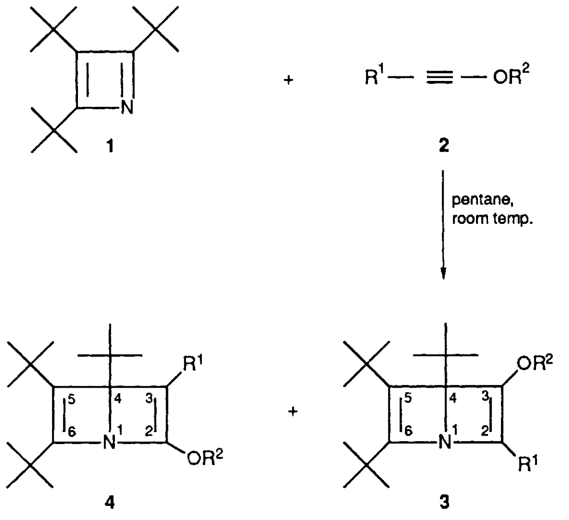
3c: M.p. 51 °C; IR (film) 1620, 1600 cm^{-1}; ^{1}H NMR δ 0.03 (SiMe), 0.22 (SiMe), 1.02, 1.05, 1.20, 1.33 (Bu^t); ^{13}C NMR δ −4.2 (SiMe), −3.8 (SiMe), 18.1 (Si*C*Me$_3$), 25.7, 27.1, 29.9, 31.6 (4 C*Me*$_3$), 31.9, 33.2, 33.6 (3 C-*C*Me$_3$), 84.9 (C-4), 125.9, 127.8, 128.2, 134.0 and 135.0 (C-2 and *ipso*-C), 139.7 (C-5), 142.9 (C-3), 167.1 (C-6).

3d: M.p. 70 °C; IR (nujol) 1662, 1595 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.95, 1.13, 1.26 (3 Bu^t), 0.97, 1.04 (CH*Me*$_2$), *ca.* 1.0 (m, C*H*Me$_2$); ^{13}C NMR δ 13.4 (*C*HMe$_2$), 18.0 and 18.1 (CH*Me*$_2$), 27.3, 29.9, 31.8 (3 C*Me*$_3$), 31.3, 33.0, 33.6 (3 *C*Me$_3$), 84.6 (C-4), 126.8, 127.7, 129.5, 132.4, 135.2, 139.7, 143.1, 167.3 (C-6).

3e: M.p. 142 °C; IR (KBr) 1660, 1595, 1355, 1178 cm^{-1}; ^{1}H NMR δ 0.99, 1.15, 1.22, 1.28 (4 CMe$_3$), 2.45 (Me), 7.29 and 7.83 (AA'BB'); ^{13}C NMR δ 21.6 (Me), 27.1, 28.4, 30.2, 31.6 (4 C*Me*$_3$), 31.1, 33.1, 33.6, 34.2 (4 *C*Me$_3$), 86.3 (C-4), 127.7, 129.5, 131.3, 134.8, 138.9 (C-5), 144.6, 155.9 (C-3), 163.5 (C-6).

3f: B.p. 85 °C/0.05 mbar (Kugelrohr); IR (film) 3080 (=CH), 1625 (C=C) cm^{-1}; ^{1}H NMR δ 1.03, 1.17, 1.20 (3 Bu^t), 1.27 (t), 3.75 (q), 5.69 (=CH); ^{13}C NMR δ 14.5 (OCH$_2$*C*H$_3$), 27.0, 29.1, 31.8 (3 C*Me*$_3$), 28.4, 32.8, 33.7 (3 *C*Me$_3$), 65.2 (OCH$_2$), 87.3 (C-4), 118.0 (C-2, $^1J_{C,H}$ 192 Hz), 138.6 (C-5), 154.2 (C-3), 166.3 (C-6).

4f: B.p. 90 °C/0.05 mbar (Kugelrohr); IR (film) 3090 (=CH), 1623 (C=C) cm^{-1}; ^{1}H NMR δ 1.00, 1.18, 1.20 (3 Bu^t), 1.28 (t), 3.84 (q), 4.55 (=CH); ^{13}C NMR δ 14.3 (OCH$_2$*C*H$_3$), 27.1, 30.1, 30.8, (3 C*Me*$_3$), 30.5, 33.4, 33.8 (3 *C*Me$_3$), 64.6 (OCH$_2$), 76.2 (C-4), 85.1 (C-3, d, $^1J_{C,H}$ 184 Hz), 140.4 (C-5), 163.0 (C-6), 165.1 (C-2).



3b–e favours the idea of a sterically controlled transition-state geometry. Whereas this may be correct for the cycloaddition of disubstituted alkynes **2b–e**, it does not explain why in the case of **2a**, **f**, the adducts **3a**, **f** (the 'wrong' regioisomers with respect to both the polarity and the steric shielding of the C=N bond) are still dominating. Although this apparent contradiction must await an explanation in the context of a thorough analysis of the whole cycloaddition behaviour of this azete, we suggest here that a repulsive interaction between the rather diffuse nitrogen lone pair of **1** and an oxygen lone pair of alkynes **2** destabilizes the transition state leading to 2-oxy-1-Dewar-pyridines **4**.‡

In conclusion, we have presented the first cycloaddition reactions of (moderately) electron-rich alkynes to an azete, and, at the same time, the first cycloadditions of alkynyl carboxylates and an alkynyl *p*-toluenesulphonate. The resulting products, 3- or 2-oxy-1-Dewar-pyridines may serve as precursors to valence-isomeric azaprismanes, pyridine derivatives and 1-Dewar-3- or 2-pyridones.

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‡ According to MNDO calculations, the HOMO-1 of azete is a σ orbital with a large contribution from n(N). By *ab initio* methods (6-31G*//6-31G*), this orbital is calculated as the HOMO. We thank Professor E.-U. Würthwein (Universität Münster) for communicating his MNDO and *ab initio* calculations on azete to us.[11]