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Heteroannulation of α, β-Unsaturated Carbene Complexes. [3+2] Dipolar Cycloaddition of Methoxy(α, β-alkynyl)tungsten Carbene Complexes with 1,3-Thiazolium-4-olates

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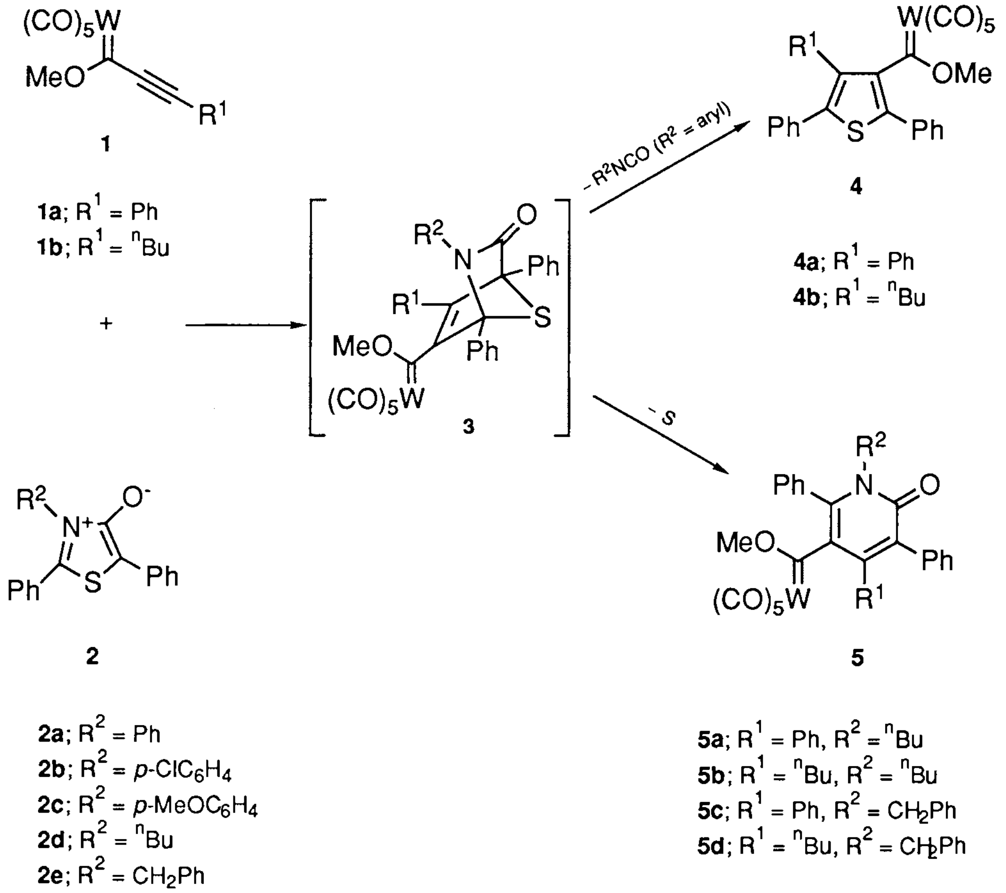
A novel [3+2] dipolar cycloaddition of methoxy(α, β-alkynyl)tungsten carbene complexes with 1,3-thiazolium-4-olates, synthetic equivalents of thiocarbonyl ylide affords methoxy(thienyl)tungsten carbene complexes or methoxy(pyridyl)tungsten carbene complexes depending on the electronic nature of a substituent at N-3 on the 1,3-thiazole nucleus.

There has been a rapid growth in the chemistry of Fisher-type carbene complexes which are known to react as metal-turned carbonyl compounds.1) For instance, α,β-unsaturated carbene complexes, analogs of α, β-unsaturated esters enjoy a [4+2] cycloaddition and have provided a great possibility in building natural and non-natural products.1,2) [3+2] dipolar cycloaddition of alkynyl carbene complexes with 1,3-dipoles could provide valuable routes to a various type of the polysubstituted heterocycles of five membered ring. Nevertheless, their reactions with 1,3-dipoles have scarcely been investigated.3) In the course of our contineous research program related to polyheterocyclic compounds with potential biological activities,4) we were interested in synthetic method to *o*-alkoxyphenol fused to heterocycle of five or six membered ring5) *via* the [3+2] dipolar cycloaddition of alkoxy(α, β-alkynyl)metal carbene complexes with masked 1,3-dipoles followed by a photo-irradiated electrocyclization reaction.6) Mesoionic compounds are attractive masked 1,3-dipoles because of easy preparation, wide application as synthetic intermediates leading to a variety of polysubstituted heterocycles of five membered ring.7)

We have succeeded in [3+2] dipolar cycloaddition of methoxy(α, β-alkynyl)tungsten carbene complexes **1a** or **1b** with 1,3-thiazolium-4-olates **2a-d** or **2e**,8) synthetic equivalents of thiocarbonyl ylide, and obtained highly substituted derivatives of thiophene and pyridone.

Our preliminary results are given in Scheme 1 and Table 1. The primary 1:1 adduct **3** was not isolated. The reaction products9) were those derived from the adduct **3** by the extrusion of sulfur or aryl isocyanate. The outcome of the product formation is governed by the substituent at N-3 in 1,3-thiazole nucleus. Thus, the reactions of carbene complex **1a** or **1b** with an equimolar amount of 3-aryl-2,5-diphenyl-1,3-thiazolium-4-olates **2a**, **2b** or **2c** in dry toluene at 60 °C for 1-5 h afforded the corresponding derivatives of methoxy(thienyl)tungsten carbene complexes **4a** or **4b**, *via* the adduct **3** in moderate yields. The carbene complex **1a** or **1b** also underwent a cycloaddition with 3-alkyl-2,5-thiazolium-4-olate **2d**, or **2e** in dry toluene at 60 °C for 1- 4.3 h. However, in these cases the derivatives of methoxy(pyridyl)tungsten carbene complexes

5a-d were formed in moderate yields by the extrusion of sulfur atom from the primary adduct **3**. The reactions of n-butylacetylene substituted carbene complex **1b** with 1,3-thiazolium-4-olates **2b-d** or **2e** were faster than those of phenylacetylene substituted carbene complex **1a**. As described for most Fischer carbene complexes[10)] the mass spectra of complexes **4** and **5** showed molecular ions and successive CO losses. The ^1H NMR and ^{13}C NMR spectra of complexes **4** and **5** were unique. In the ^1H NMR of complexes **4** and **5**, the resonances for methoxy (except for **5a**) and methylene protons of alkyl chain were unusually broad. The half height width of methoxy signals ($\Delta\nu_{1/2}$) was 5 -36 Hz. Moreover, the line broadening for the proton resonances of alkyl chain gradually increases as getting nearer to a heterocyclic nucleus. In ^{13}C NMR of complexes **5**, signal of cis carbonyls of tungsten was devided into three peaks and trans into one or two. These may indicate the existence of rotamers or the limitation of free rotation imposed by the steric congestion of a highly substituted heterocycle. The full spectral behavior is under investigation.



Scheme 1.

In the previously reported case for [3+2] dipolar cycloaddition of 1,3-thiazolium-4-olates with acetylenic dipolarophiles,[8b,c)] mechanistic difference for the formation of the derivatives of thiophene and pyridone was ascribed to the steric effect of substituents on the 1,3-thiazole nucleus. Our results, however, suggest that the electronic effect of substituent at N-3 on the 1,3-thiazole nucleus plays an important role rather than the steric effect in transition state of the thermal decomposition of the adduct **3**. 3-Aryl-2,5-diphenyl-1,3-thiazolium-4-olate **1a** or **1b** gives the methoxy(thienyl)tungsten carbene complexe **4a** or **4b** due to stabilizing interaction of aromatic

π-orbital with p-orbital at N-2 of the adduct **3** in the transition state of extrusion. To our knowledge, this is the first example of a [3+2] dipolar cycloaddition of Fischer-type carbene complexes with masked 1,3-dipoles.

Table 1. [3+2] Dipolar Cycloaddition of Methoxy(α, β-alkynyl)tungsten Carbene Complexes with 1,3-Thiazolium-4-olates

Entry	Reactant a)		t/h b)	Product			
	Complex	1,3-Dipole		Compound		mp/°C c)	Yield/% d)
1	**1a**	**2a**	1.5	**4a**	red needles	137.5 (dec)	17
2	**1b**	**2a**	3	**4b**	orange needles	84.5 - 85.5	70
3	**1a**	**2b**	5	**4a**			43
4	**1b**	**2b**	2.5	**4b**			32
5	**1a**	**2c**	2.5	**4a**			7
6	**1b**	**2c**	1	**4b**			45
7	**1a**	**2d**	2.5	**5a**	dark red needles	133 - 135	41
8	**1b**	**2d**	2	**5b**	dark red solid	56 (dec)	38
9	**1a**	**2e**	4.3	**5c**	dark red solid	120 -123	23
10	**1b**	**2e**	1	**5d**	dark red solid	57.5 - 59	40

a) Complex/1,3-Dipole (molar ratio): 1:1; b) Reaction temperature/solvent: 60 °C/dry toluene; c) Uncorrected; d) After usual workup and chromatographic purification (silica gel, finer than 230 mesh).

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9) All new compounds were characterized by spectroscopy and microanalysis. Spectroscopic data: for **4a**: IR (KBr-disc) 2080, 2000, 1960, 1920 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.60 (br s, 3 H, OCH$_3$, $\Delta\nu_{1/2}$ = 10 Hz), 7.16 - 7.40 (m, 15 H, 3 Ph); ^{13}C NMR (100 MHz, CDCl$_3$) δ 328.3 (C$_{\text{carbene}}$), 203.8 (WCO$_{\text{trans}}$), 195.5 (WCO$_{\text{cis}}$), 68.9 (OCH$_3$); m/z (%) 678 (M^{+}, 7), 650 (M^{+} - CO, 11) 594 (M^{+} - 3 CO, 63), 538 (M^{+} - 5 CO, 15). for **4b**: IR (KBr-disc) 2080, 1990, 1950, 1920 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.80 (t, 3 H, CH$_3$), 1.23 (m, 2 H, -CH$_2$), 1.56 (br m, 2 H, -CH$_2$), 2.32 and 2.67 (br m + br m, 2 H, -CH$_2$), 4.71 (br s, 3 H, OCH$_3$, $\Delta\nu_{1/2}$ = 36 Hz), 7.29-7.49 (m, 10 H, 2 Ph); ^{13}C NMR (100 MHz, CDCl$_3$) δ 330.4 (C$_{\text{carbene}}$), 203.8 (WCO$_{\text{trans}}$), 196.3 (WCO$_{\text{cis}}$), 69.3 (OCH$_3$); m/z (%) 658 (M^{+}, 8), 630 (M^{+} - CO, 4), 574 (M^{+} - 3 CO, 68), 518 (M^{+} - 5 CO, 16). for **5a**: IR (KBr-disc) 2090, 1970, 1940, 1920, 1640 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.70 (t, 3 H, CH$_3$), 1.08 (sextet, 2 H , CH$_2$), 1.58 (br m, 2H, CH$_2$), 3.67 and 3.83 (br m + br m, 2H, NCH$_2$), 4.25 (s, 3 H, OCH$_3$), 6.98 - 7.50 (m, 15 H, 3 Ph); ^{13}C NMR (100 MHz, CDCl$_3$) δ 327.8 (C$_{\text{carbene}}$), 202.7 (WCO$_{\text{trans}}$), 196.9, 196.3 and 195.6 (WCO$_{\text{cis}}$), 161.2 (CO$_{\text{pyridyl}}$), 68.6 (OCH$_3$); m/z (%) 745 (M^{+}, 2), 717 (M^{+} - CO, 3), 661 (M^{+} - 3 CO, 40), 605 (M^{+} - 5 CO, 18). for **5b**: IR (KBr-disc) 2090, 1980, 1930, 1645 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.65 and 0.71 (t + t, 6 H, 2 CH$_3$), 1.08 - 1.60 (m, 8 H, 4 CH$_2$), 2.23 and 2.59 (br m + br m, 2 H, =CCH$_2$), 3.72 (br m, 2 H, NCH$_2$), 4.46 (br s, 3 H, OCH$_3$, $\Delta\nu_{1/2}$ = 5 Hz), 7.16 - 7.48 (m, 10 H, 2 Ph); ^{13}C NMR (100 MHz, CDCl$_3$) δ 330.5 (C$_{\text{carbene}}$), 203.6 and 202.8 (WCO$_{\text{trans}}$), 197.5, 196.6 and 195.6 (WCO$_{\text{cis}}$), 161.5 (CO$_{\text{pyridyl}}$), 69.2 (OCH$_3$); m/z (%) 723 (M^{+}, 1), 639 (M^{+} - 3 CO, 19), 611 (M^{+} - 4 CO, 1), 583 (M^{+} - 5 CO, 8). for **5c**: IR (KBr-disc) 2070, 1960, 1910, 1640 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.23 (s, 3 H, OCH$_3$, $\Delta\nu_{1/2}$ = 8 Hz), 5.13 and 5.21 (br s + br s, 2 H, NCH$_2$), 6.86 - 7.38 (m, 20 H, 4 Ph); ^{13}C NMR (100 MHz, CDCl$_3$) δ 327.3 (C$_{\text{carbene}}$), 202.7 (WCO$_{\text{trans}}$), 197.0, 196.2 and 195.8 (WCO$_{\text{cis}}$), 161.6 (CO$_{\text{pyridyl}}$), 68.5 (OCH$_3$); m/z (%) 779 (M^{+}, 1), 751 (M^{+} - CO, 1), 695 (M^{+} - 3 CO, 3), 639 (M^{+} - 5 CO, 2.4). for **5d**: IR (KBr-disc) 2070, 1960, 1920, 1640 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.66 (t, 3 H, CH$_3$), 1.06 (m, 2 H, CH$_2$), 1.20 (m, 2 H, CH$_2$), 2.24 and 2.62 (br m + br m, 2 H, =CCH$_2$), 4.43 (br s, 3 H, OCH$_3$, $\Delta\nu_{1/2}$ = 5 Hz), 5.08 (br s, 2 H, NCH$_2$), 6.85 - 7.80 (m, 15 H 3 Ph); ^{13}C NMR (100 MHz, CDCl$_3$) δ 330.0 (C$_{\text{carbene}}$), 203.5 and 202.7 (WCO$_{\text{trans}}$), 197.0, 196.4 and 195.8 (WCO$_{\text{cis}}$), 161.9 (CO$_{\text{pyridyl}}$), 69.2 (OCH$_3$); m/z (%) 758 (M^{+}, 1), 673 (M^{+} - 3 CO, 3), 617 (M^{+} - 5 CO, 1). The regiostructures of methoxy(thienyl)tungsten carbene complexes **4a**, **b** and methoxy(pyridyl)tungsten carbene complexes **5a** - **d** are tentatively assigned on the basis of the fact that C-5 atom of 1,3-thiazolium-4-olate attacks β-position of carbene complex owing to the delocalization of the exocyclic negative charge to the C-5 position of thiazole nucleus. For the regiochemistry of cycloaddition of mesoionic compounds, see: W. E. McEwen, K. B. Kanktkar, and W. M. Hung, *J. Am. Chem. Soc.*, **93**, 4484 (1971).

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