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An organometallic analogue of the Wittig reaction. A one-pot reaction for C=C bond formation catalyzed by a molybdenum complex

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Abstract

An olefinic bond is formed by the one-pot reaction of an aldehyde, diazoacetate and triphenylphosphine in the presence of a catalytic amount of $MoO_2(S_2CNEt_2)_2$. The mechanism of this reaction is discussed.

Introduction

Olefin synthesis in which organometallic methodologies are used is of current interest [1,2]. Schwartz reported recently that the metalloazine adducts from diazoalkanes and $MoO(S_2CNEt_2)_2$ (**1**) could react with phosphoranes to give olefins in an organometallic variation of the Wittig reaction [2]. Although complex **1** is regenerated in the reaction, olefin synthesis by the reaction between the diazo compound and the phosphorane cannot be catalyzed by **1**, since these reagents react further to give a mixture of by-products. In this paper, we report on the one-pot reaction of aldehydes (**2**), diazoacetate, and triphenylphosphine in the presence of a catalytic amount of $MoO_2(S_2CNEt_2)_2$ (**3**) to give the corresponding olefins (**4**), in what can be regarded as an organometallic analogue of the Wittig reaction.

Results and discussion

A mixture of **2**, diazoacetate and triphenylphosphine in the presence of a catalytic amount of **3** gives the olefins **4** as the main products. The results are shown in Table 1.

$$\underset{(\mathbf{2})}{RCHO} + N_2CHCO_2Et + Ph_3P \xrightarrow[\text{benzene reflux}]{(\mathbf{3})} \underset{(\mathbf{4})}{RCH{=}CHCO_2Et} + Ph_3PO + N_2 \tag{1}$$

It is shown from Table 1 that aromatic aldehydes are better reactants than the

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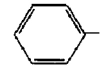
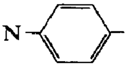
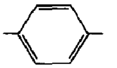
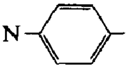
Table 1

Olefin synthesis from aldehydes RCHO and diazoacetate catalyzed by $MoO_2(S_2CNEt_2)_2$ (**3**) [a]

	Aldehyde R	Time (h)	Olefin	Yield [b] (%)	E/Z [c]
2a		5	**4a**	71	93/7
2b	O_2N– 	8	**4b**	7 [d]	
2c	CH_3O– 	5	**4c**	83	93/7
2d	$(CH_3)_2N$– 	9.5	**4d**	62	100/0
2e	Cl– 	10	**4e**	57	93/7
2f	Br– 	6.5	**4f**	20 [e]	
2g	Ph-CH=CH-	7	**4g**	64	(*E*,*E* 100)
2h	$CH_3(CH_2)_3$-	12	**4h**	25	
2i	CH_3CH=CH-	6.5 [f]	**4i**	48	(*E*,*E* 85; *E*,*Z* 15)
2j	$CH_3(CH_2)_8$-	12.5	**4j**	17	

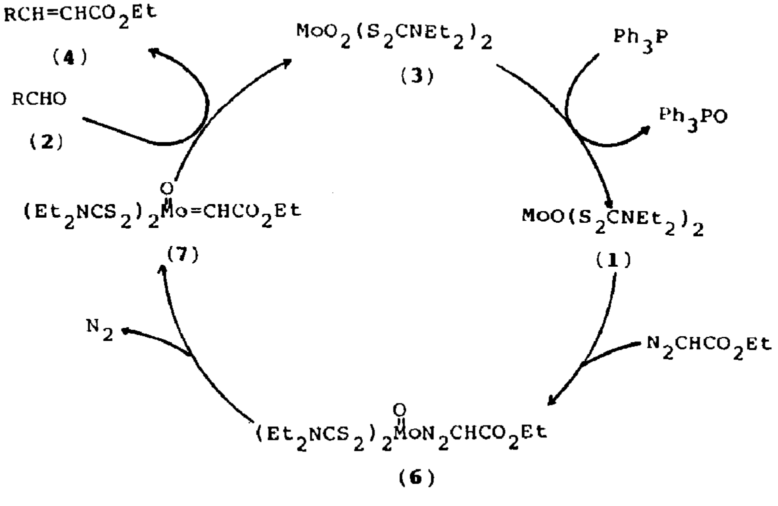
[a] The reaction was carried out at 80 °C using 10 mol% of **3** as catalyst. [b] Isolated yield. [c] Determined by ^1H NMR (200 MHz). [d] O_2N–  –CH=N-N=$CHCO_2Et$ (**5b**) was isolated in 50% yield. [e] Br–  –CH=N-N=$CHCO_2Et$ (**5f**) was isolated in 42% yield. [f] The reaction was carried out at 60 °C.

aliphatic aldehydes. Aromatic aldehydes having an electron-donating group on the benzene ring result in higher yields than aldehydes with an electron-withdrawing group. This order of reactivity is in contrast to that shown in the Wittig reaction. The reactions of **2b** and **2f** yielded the azines **5b** and **5f** (see footnotes *d* and *e* of Table 1), respectively.

A control experiment showed that a mixture of **2a**, ethyl diazoacetate and triphenylphosphine in the absence of the catalyst **3** gave azine **5a** in 83% yield. If triphenylphosphine is absent the reaction does not take place.

$$\mathbf{2a} + N_2CHCO_2Et + Ph_3P \xrightarrow[\text{reflux}]{\text{benzene}} \underset{(\mathbf{5a})}{PhCH{=}N{-}N{=}CHCO_2Et} + Ph_3PO \qquad (2)$$

Two mechanistic pathways are conceivable for this reaction:
(1) Triphenylphosphine may abstract an oxygen atom from **3** to form the tetravalent molybdenum species **1** [3], which in turn reacts with diazoacetate to give the metalloazine **6** as described by Schwartz [2]. It is possible that the metalloazine loses one molecule of dinitrogen to form the active molybdenum–carbene species **7** which



Scheme 1

then reacts with the aldehyde to yield the olefin **4** and the molybdenum complex **3**, so completing a catalytic cycle (Scheme 1). In this mechanism, triphenylphosphine acts only as an oxygen-abstracting agent.

(2) In addition to its reaction with **3** to form **1**, triphenylphosphine reacts mainly with diazoacetate to form the phosphazine **8** [4], which is thought to lose one molecule of dinitrogen by the action of the molybdenum complex **1** to give the ylide **9**, which usually reacts with aldehyde to yield the olefin and triphenylphosphine oxide (Scheme 2). The second pathway is similar to the cuprous chloride-catalyzed reaction of diazomethane and triphenylphosphine in the presence of benzophenone which gives 1,1-diphenylethylene in only 23% yield [5].

For the first mechanistic pathway, a stoichiometric reaction of **1** with ethyl diazoacetate and **2c** was carried out in the absence of triphenylphosphine, **4c** was isolated in only 20% yield together with other by-products and unchanged **2c**, implying that triphenylphosphine plays other important roles in this reaction. It is unlikely that the whole of this reaction proceeds along the pathway as shown in Scheme 1.

In order to confirm that the ylide **9** is found in the reaction, triphenylphosphine was treated with diazoacetate in the presence of a catalytic amount of **3** but in the absence of an aldehyde, to give carbethoxymethylenetriphenylphosphorane **9** in 36% yield. In addition, coupling products, a mixture of by-products, diethyl fumarate and diethyl maleate, was isolated in 23% yield.

$$N_2CHCO_2Et + Ph_3P \xrightarrow{3} \underset{(\mathbf{9})}{Ph_3P{=}CHCO_2Et} + N_2 + EtO_2CCH{=}CHCO_2Et \qquad (3)$$

$$\mathbf{3} + Ph_3P \longrightarrow \mathbf{1} + Ph_3PO$$

$$Ph_3P + N_2CHCO_2Et \longrightarrow \underset{(\mathbf{8})}{Ph_3P{=}N{-}N{=}CHCO_2Et} \xrightarrow[-N_2]{\mathbf{1}} \underset{(\mathbf{9})}{Ph_3P{=}CHCO_2Et}$$

Scheme 2

The formation of **9** from **8** as shown in Scheme 2 was further verified by treating **8** with a catalytic amount of **1** (generated in situ from **3** and triphenylphosphine) to yield **9** in 26% yield, and a mixture of diethyl fumarate and diethyl maleate also in 26% yield.

It is suggested that the more stable ylides are less reactive towards aldehydes and can be more easily isolated. Thus, bis(carbethoxyl)methylene-triphenylphosphorane (**11**) was isolated in 67% yield when diethyl diazomalonate (**10**) was treated with triphenylphosphine and a catalytic amount of **3** even in the presence of the aldehyde **2c**. The recovery of **2c** implies that the ylide **11** is very stable and remains intact during the reaction.

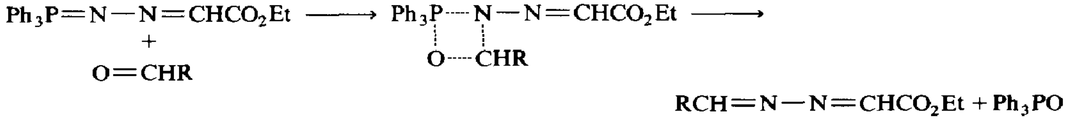
$$\underset{(\mathbf{10})}{N_2C(CO_2Et)_2} + Ph_3P \xrightarrow{3} \underset{(\mathbf{11})}{Ph_3P{=}C(CO_2Et)_2} \qquad (4)$$

Further evidence that the second pathway is followed is provided by the reaction of **8** with benzaldehyde in the presence of a catalytic amount Ph_3P and **3**. Compound **4a** was obtained as the main reaction product in 52% yield and **5a** as a by-product in 21.6% yield.

In conclusion, the second pathway seems to be the main pathway of this reaction, but the first pathway cannot be excluded because of the results of the stoichiometric reaction of **1**, **2c** and diazoacetate to form **4c** in 20% yield in the absence of Ph_3P. It is reasonable to suggest that reactions (1) and (2) are in competition. In the absence of the catalyst, phosphazine **8** forms first and then the nitrogen atom attacks the carbonyl group to form **5** and triphenylphosphine oxide as shown in Scheme 3:

In the presence of the catalyst, the reactions of diazoacetate with **1** and with Ph_3P are competitive. The diazoacetate reacts with Ph_3P to form the phosphazine **8** as in Scheme 2. The metalloazine **6** that forms either evolves dinitrogen to give metallocarbene complex **7** and so completes the catalytic cycle, as shown in Scheme 1, or reacts with Ph_3P also to yield the phosphazine **8**. The latter generates dinitrogen under catalysis by **1**. The evolution of dinitrogen is regarded as an important step. Thus, for the more reactive aldehydes (aldehydes with an electron-withdrawing group on the benzene ring), the attack of nitrogen atom on the carbonyl group would be faster than the evolution of dinitrogen, and azines **5** are obtained as the main products (from aldehydes **2b** and **2f**). For the less reactive aldehydes (aldehydes with an electron-donating group on the benzene ring), the dinitrogen is evolved first and as a result of attack by the carbon atom on the carbonyl group, olefins **4** are formed as the main products as shown in Scheme 4.

Further applications of this reaction are being investigated in this laboratory.



$$\begin{matrix} Ph_3P{=}N{-}N{=}CHCO_2Et \\ + \\ O{=}CHR \end{matrix} \longrightarrow \begin{matrix} Ph_3P \cdots N{-}N{=}CHCO_2Et \\ \vdots \quad\ \vdots \\ O \cdots CHR \end{matrix} \longrightarrow RCH{=}N{-}N{=}CHCO_2Et + Ph_3PO$$

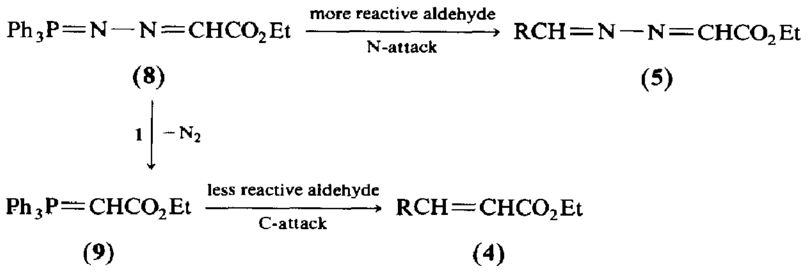
(5)

Scheme 3

Table 2

Spectral and analytical data for the novel compounds

Compound	^1H NMR CCl$_4$, 60 MHz) (ppm), *J*(Hz)	IR (KCl) (cm^{-1})	Molecular formula	MS (*m/e*)	m.p. (°C)	Elementary Analysis (Found (Calc) (%))			
						C	H	N	Br
5a	1.40(t, *J* 7, 3H) 4.32(q, *J* 7, 2H) 7.36–8.00(m, 6H) 8.52(s, 1H)	1740 1620 1580 1550 1200	$C_{11}H_{12}O_2N_2$ (204.24)	205(M^+ + 1)	41–42	64.69 (64.26	5.92 5.89	13.72 13.48)	
5b	1.45(t, *J* 7, 3H) 4.40(q, *J* 7, 2H) 7.75–8.55(m, 6H)	1720 1625 1600 1525 1345 1275	$C_{11}H_{11}O_4N_3$ (249.33)	250(M^+ + 1)	106–107	52.96 (52.80	4.41 4.41	16.85 16.14)	
5f	1.39(t, *J* 7, 3H) 4.30(q, *J* 7, 2H) 7.50–7.80(m, 5H) 8.44(s, 1H)	1720 1640 1600 1500 1315 1180	$C_{11}H_{11}O_2N_2Br$ (283.12)	285(M^+ + 2) 283(M^+)	74–75	46.67 (46.61	3.92 3.86	9.89 9.94	28.22 28.16)



Scheme 4

Experimental

All reactions were carried out under prepurified nitrogen by Schlenk techniques. Benzene was freshly distilled under nitrogen from sodium and benzophenone immediately before use. All the starting materials were purified either by distillation under nitrogen or by recrystallization. Starting materials and products were characterized by comparing their boiling points or melting points, IR, ^{1}H NMR and MS with published data. ^{1}H NMR spectra were recorded on Varian EM-360A (60 MHz) or Varian XL-200 (200 MHz) spectrometer using CCl_4 or $CDCl_3$ solution containing tetramethylsilane as internal standard. Infrared spectra were recorded as liquid film or KCl disc using a Shimadzu IR-440 spectrometer. Mass spectra were obtained on a Finnigan 4021 GC-MS instrument. GLC was carried out with a 2 m column (10% OV-101 supported on 102 silanized white support, 60–80 mesh).

The following reagents were prepared by standard procedures: ethyl diazoacetate[6], diethyldiazomalonate[7], $MoO_2(S_2CNEt_2)_2$ (**3**) [8], $MoO(S_2CNEt_2)_2$ (**1**) [9] and $Ph_3P{=}N{-}N{=}CHCO_2Et$ (**8**) [4].

Typical procedure for the reaction of aldehyde, ethyl diazoacetate, triphenylphosphine and a catalytic amount of 3

A mixture of *p*-anisaldehyde (**2c**, 136 mg, 1.0 mmol), ethyl diazoacetate (150 mg, 1.3 mmol), Ph_3P (320 mg, 1.2 mmol) and **3** (40 mg, 0.09 mmol) in benzene (5ml) was refluxed for 5 h. After removal of the solvent, the residue was chromatographed on silica gel with petroleum ether/ethyl acetate (8/1) as the eluent. The product was isolated on removing the solvent under vacuum and identified as ethyl *p*-methoxycinnamate (**4c**) by IR, ^{1}H NMR and MS spectra, 170 mg, yield: 83%. The results are shown in Table 1.

Reaction of 4-bromobenzaldehyde (2f), ethyl diazoacetate and triphenylphosphine in the presence of a catalytic amount of 3

A mixture of **2f** (185 mg, 0.1 mmol), ethyl diazoacetate (170 mg, 1.5 mmol), Ph_3P (300 mg, 1.1 mol) in benzene (5ml) was refluxed for 6.5 h. The reaction mixture was concentrated under vacuum and separated by column chromatography with petroleum ether/ethyl acetate (15/1) to (8/1) as eluent. The products were identified as **4f** and **5f**. Yield **4f**: 20% and **5f**: 42%. A similar procedure was used for the reaction of **2b**.

Reaction of benzaldehyde, ethyl diazoacetate and triphenylphosphine in the absence of the catalyst 3

A mixture of benzaldehyde (100 mg, 0.94 mmol), ethyl diazoacetate (150, 1.3 mmol), Ph_3P (300 mg, 1.1 mmol) in benzene (5 ml) was refluxed for 5 h. After removal of the solvent, the residue was separated by column chromatography with petroleum ether/ethyl acetate (4/1) as eluent. The product was characterized by ^1H NMR, IR, MS and elementary analysis as **5a**, 160 mg, yield: 83%.

Stoichiometric reaction of p*-anisaldehyde (2c), ethyl diazoacetate and 1 in the absence of triphenylphosphine*

A mixture of *p*-anisaldehyde (**2c**, 170 mg, 1.25 mmol), ethyl diazoacetate (150 mg, 1.3 mmol) and **1** (400 mg, 0.98 mmol) in benzene (6 ml) was refluxed for 8 h. Most of **2c** remained intact as shown by GLC. The mixture was filtered, the filtrate was concentrated under vacuum and the residue was separated by column chromatography with petroleum ether/ethyl acetate (8/1) as the eluent. The product **4c**, 41 mg, was obtained in 20% yield.

Reaction of carbethoxymethylenetriphenylphosphazine (8) and benzaldehyde in the presence of a catalytic amount of Ph_3P and 3

A mixture of **8** (380 mg, 1 mmol), **2a** (150 mg, 1.3 mmol), Ph_3P (40 mg, 0.15 mmol) and **3** (40 mg, 0.09 mmol) in benzene (5 ml) was refluxed for 5 h. After removal of the solvent under vacuum, the residue was chromatographed on silica gel with petroleum ether/ethyl acetate (8/1) as eluent. **4a** was isolated in 51% yield and **5a** was isolated in 22% yield.

Reaction of triphenylphosphine, ethyl diazoacetate and a catalytic amount of 3 in the absence of an aldehyde

A mixture of Ph_3P (870 mg, 3.3 mmol), ethyl diazoacetate (400 mg, 3.5 mmol) and **3** (80 mg, 0.19 mmol) in benzene (5 ml) was refluxed for 5 h. After removal of the solvent, the residue was separated by column chromatography with petroleum ether/ethyl acetate (20/1) as eluent. A mixture of diethyl fumarate and diethyl maleate, 123 mg, was obtained in 23% yield as determined by GLC analysis by comparison with an internal standard. The column was further eluted with ethyl acetate and the product was identified as **9**, 380 mg, in 36% yield; m.p. 123–125°C (lit[10]: m.p. 125–127.5°C); ^1H NMR(δ, CCl_4, 60 MHz, TMS): 1.07(t, J 9 Hz, 3H), 3.85(q, J 9 Hz, 2H), 7.2–7.85(m, 16H); IR(KCl, cm^{-1}): 1607(m), 1187(m), 1120(m), 722(m), 695(m); MS(m/e): 348 (M^+), 277, 183, 77.

Reaction of carbethoxymethylenetriphenylphosphazine (8), a catalytic amount of Ph_3P and 3 in the absence of an aldehyde

A mixture of **8** (380 mg, 1 mmol), Ph_3P (80 mg, 0.3 mmol) and **3** (40 mg, 0.09 mmol) in benzene (5 ml) was refluxed for 5 h. The procedure for the isolation of the products was the same as above experiment. A mixture of diethylfumarate and diethyl maleate, 44 mg, was obtained in 26% yield, and compound **9**, 100 mg, was isolated in 26% yield.

Reaction of triphenylphosphine, diethyl diazomalonate (10) and 2c in the presence of a catalytic amount of 3

A mixture of Ph_3P (300 mg, 1.1 mmol), **2c** (160 mg, 1.2 mmol) **10** (270 mg, 1.7

mmol) and **3** (40 mg, 0.09 mmol) in benzene (5 ml) was refluxed for 5h. The procedure used for the isolation of the products was the same as above. The product was identified as **11**, 280 mg, 67%, m.p. 104–105 °C (lit[11]: 106–107 °C); ^{1}H NMR (δ, CCl_4, 60 MHz, TMS), 0.96(t, J 9 Hz, 6H), 3.80(q, J 9.8 Hz, 4H), 7.16–7.90 (m, 15H); IR(KCl, cm^{-1}): 1705(m), 1295(m), 1055(m); MS(m/e): 420(M^+), 348, 275, 183.

Data for the new compounds **5a**, **5b** and **5f** are listed in Table 2.

Acknowledgement

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