Cobalt-catalysed and -uncatalysed Reactions of Diynes with Activated Alkenes

Zhiming Zhou,[a] Luigi Pietro Battaglia,[b] Gian Paolo Chiusoli,[a] Mirco Costa,[a] Mario Nardelli,[b] Corrado Pelizzi[b] and Giovanni Predieri[b]

[a] *Istituto Chimica Organica Università, Viale delle Scienze, 43100 Parma, Italy*
[b] *Istituto Chimica Generale Università, Viale delle Scienze, 43100 Parma, Italy*

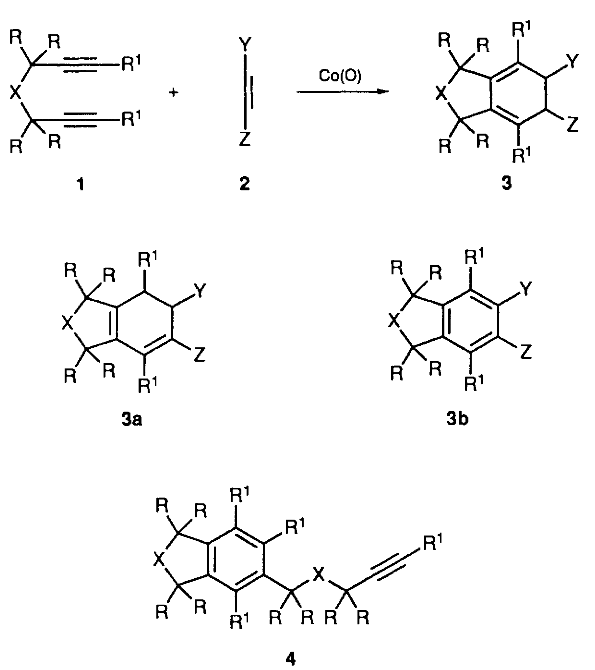
New double annulation reactions of 1,5-diynes with activated alkenes are catalysed by cobalt(0) complexes, and can also occur in the absence of cobalt to give new classes of compounds, containing exocyclic double bonds, if terminal methyl groups are present on the triple bonds.

We report our observations on the remarkable behaviour of 1,5-diynes (**1**; X = NH, NR, CH_2; R,R^1 = H, alkyl) towards activated alkenes (**2**, Y = H, alkyl, aryl, CO_2R, CON–; Z=CO_2R, CON–, *etc.*) such as diethyl fumarate, ethyl acrylate, methyl crotonate, methyl cinnamate and *N*-phenylmaleimide.

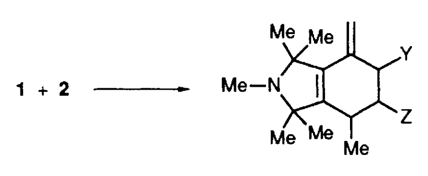
Cobalt(0) complexes, which had previously been shown to catalyse the reaction with C≡C or C≡N triple bonds[1] also proved to be effective for the double annulation reaction of **1** with activated alkenes **2** shown in Scheme 1.

Thus, reaction of **1** (X = NH, R = Me, R^1 = H), 1.6 mmol, with **2** (Y = H, Z = CO_2Et), 25.0 mmol, in the presence of bis(acetonitrile)bis(diethyl fumarate)cobalt(0),[2] 0.16 mmol, at 60 °C for 30 min, gave the corresponding compound **3** in 87% yield. The reaction also occurred with 86% yield at 0 °C, under the same conditions, but with twice the amount of catalyst. Competition for incorporation into the six-membered ring between the activated double bond and the triple bond of **1** led to the formation of a limited amount of compound **4**.[1]

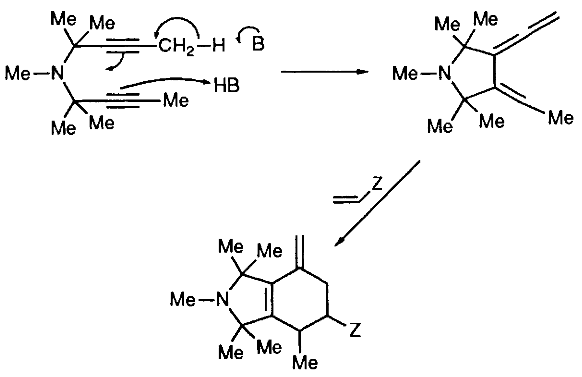
Analogous results were obtained using **2** (Y, Z = *E*-CO_2Et). Isomers resulting from double bond shift, in particular **3a**, were formed in greater quantities at higher temperature or for a longer time, however, so low temperatures (−5 °C) had to be used to obtain **3** as the major product. Aromatization to **3b**[3] also occurred above 120 °C. With **2** (Y, Z = *Z*-CO_2Et) the reaction was slower than with the corresponding *E*-groups and no product was obtained at low temperature. Low yields of **3** and its isomers were obtained at 80 °C, (21% of four GLC peaks, coincident with those



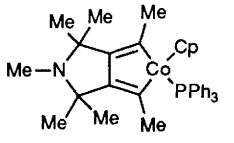
Scheme 1



Scheme 2



Scheme 3



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obtained with the **2** *E*-compound, at 65% conversion in 24 h), together with larger amounts of **4** (24%).

Other activated alkenes required temperatures in the range of 80–100 °C. Bulky R^1 groups such as trimethylsilyl also allowed the reaction to occur at 100 °C (55% yield with Y, Z = *E*-CO_2Et).

The cobalt(0)-catalysed reaction must involve metallacycle formation in accord with the mechanism previously proposed for cobalt(I)-catalysed reactions, on the basis of the isolation of cobalt(III) metallacycles.[4] Whether the mechanism for the subsequent step (alkene incorporation) involves a Diels–Alder type or a stepwise reaction[5] is still to be ascertained.

Although rhodium(I)-catalysed related reactions are known,[6] it is noteworthy that no reaction occurred under the present mild conditions with cobalt(I) cyclopentadienyl complexes such as cyclopentadienylbis(triphenylphosphine)cobalt or cyclopentadienylbis(carbonyl)cobalt.

Complex **5**, the crystal structure of which has been defined by X-ray analysis,[7] was prepared in order to ascertain the reason for the lack of reactivity of this type of complex. Although it reacted with benzonitrile to a low extent to give a condensed pyridine, it did not react with diethyl fumarate. ^1H NMR spectroscopy revealed that there is no interaction between the cobalt complex and the fumarate. This suggests a stepwise mechanism that would require ligand predissociation. Accordingly, the reaction was observed, to occur to a lesser extent (35% of **3**, 12% of its isomers and 4% of **4** with Y, Z = *E*-CO_2Et; 63% of **3** with Y = H, Z = CO_2Et) using (5-methyl-2,6-heptadienyl)(butadiene)cobalt(I)[8] $[(\eta^3\text{-}C_8H_{13})(C_4H_6)Co]$, which has a ligand environment more suitable for coordination of **2** than the cyclopentadienylcobalt derivatives. The reactivity of this complex, which is rather unstable, should be attributed to cobalt(I) catalysis since no sign of disproportion to cobalt(0) and cobalt(II) was observed during the reaction at −5 °C.

Surprisingly, with X = NMe, R^1 = Me and Y, Z = *E*-CO_2Et the reaction readily occurred in the absence of the cobalt complex at 60 °C in 10 h to give compound **6** (85% yield, two stereoisomers in a 78 : 22 ratio). By contrast, the use of **2** (Y, Z = *Z*-CO_2Et), led mainly to polymers together with small amounts of **6** and its isomers.

Interestingly, with Y = H and Z = CO_2Et the reaction also proved to be regioselective, the carboxyl group nearest to the methyl group (**7**, 79% of two stereoisomers in a 1 : 1 ratio). We could also ascertain that in the absence of geminal groups no reaction occurred without the cobalt catalyst. Thus 2,7-nonadiyne (**1**, X = CH_2, R = H, R^1 = Me) did not react in the absence of cobalt, even in the presence of a base (tertiary amine), but gave an 84% yield of **3** with **2** (Y, Z = *E*-CO_2Et) and cobalt(0) as catalyst in 3 h.†

In the presence of the cobalt catalyst both **3** and **6** (X = NMe, R,R^1 = Me, Y, Z = CO_2Et) were obtained. To ascertain whether **6** was formed independently of **3** we used a larger amount of catalyst (1 mol per mol of **1**) and obtained a quantitative yield of **3**. However, no **6** is formed from **3**, so the

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† All new substances exhibited spectroscopic data in accord with the assigned structure. Selected ^1H NMR data ($CDCl_3$, TMS): **3**: (X = NH, R, R′, Y = H, Z = COOEt), δ: 1.24 (s, 6H, 2Me), 1.26 (t, *J* 7.1 Hz, 3H, Me), 1.29 (s, 6H, 2Me), 1.78 (br s, 1H, NH), 2.38–2.56 (m, 2H, CH_2), 3.30 (d of pseudo t, *J* 11.5, 3.2 Hz, 1H, CH), 4.17 (q, *J* 7.1 Hz, 2H, CH_2), 5.37–5.45 (m, 2H, 2CH=); **3a** (X = NH, R = Me, R′ = H, Y, Z = CO_2Et), δ: 1.07 (t, *J* 7.1 Hz, 3H, Me), 1.08, 1.09, 1.13, 1.14 (4s, 12H, 4Me), 1.19 (t, *J* 7.0 Hz, 3H, Me), 1.77 (br s, 1H, NH), 2.32 (dd, *J* 17.6, 7.5 Hz, 1H, CH), 2.70 (dd, 17.6, 3.5 Hz, 1H, CH), 3.69 (dd, *J* 7.5, 3.5 Hz, 1H, CH), 3.99, 4.14 (2q, *J* 7.0, 7.1 Hz, 4H, $2CH_2$), 6.98 (s, 1H, CH); **6**: (X = NMe, R, R′ = Me, Y = H, Z = CO_2Et) (two stereoisomers), first stereoisomer, δ: 1.00 (d, *J* 6.6 Hz, 3H, Me), 1.12, 1.18, 1.25, 1.28 (4s, 12H, 4Me), 1.27 (t, *J* 7.1 Hz, 3H, Me), 2.28 (s, 3H, NMe), 2.54–2.70 (series of m, 4H, CH_2 + 2CH), 4.17 (q, *J* 7.1 Hz, 2H, CH_2), 4.67, 5.03 (2 br s, 2H, CH_2=); second stereoisomer, δ: 1.11–1.29 (series of signals, 18H, 6Me), 2.27 (s, 3H, NMe), 2.43–2.74 (m, 3H, CH_2, CH), 2.89 (ddd or dq, *J* 7.0, 7.0, 3.4 Hz, 1H, CH), 4.05, 4.08, 2q, *J* 7.2 Hz, 2H, CH_2), 4.87, 5.04 (2 br s, 2H, CH_2=).

cobalt(0)-catalysed reaction must follow a completely different pathway from the uncatalysed reaction.

We suggest that a base (B)-catalysed isomerization first takes place, followed by a Diels–Alder type reaction (Scheme 3).

A related nickel–chromium catalysed isomerization of enallenes to cyclic dienes has been recently reported.[9] The conjugated enallene system could not be isolated, but its occurrence is supported by the tendency to polymerize in the presence of maleic anhydride, which has been observed with conjugated systems.[10] Furthermore, electrocyclization of enallenes with alkenes is also known.[11]

In conclusion 1,5-diynes have been shown to react with activated alkenes under the catalytic action of cobalt(0) complexes. The use of cyclopentadienylcobalt(I) complexes gives negative results, probably because coordination of the incoming molecule is hindered. When a base-catalysed isomerization to a cyclic enallene is possible, formation of a cycloaliphatic ring, containing an exocyclic methylene, offers a new pathway, not involving cobalt catalysis.

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