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Preliminary communication

DIYNE RING CLOSURE INDUCED BY PALLADIUM-CATALYZED CARBONYLATION

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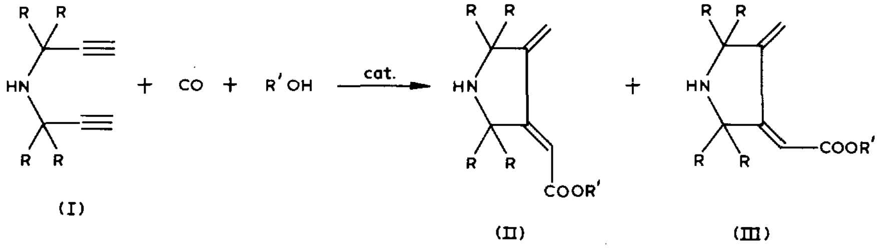
Summary

Reaction of tetraalkyl-substituted dipropargyl amines with carbon monoxide and water or alcohols at room temperature and atmospheric pressure in the presence of PdX_2-thiourea as catalyst (X = Cl, Br, I) leads to pyrrolidine derivatives containing an exocyclic carbonyl group. The results are in accord with an initial attack of the carbomethoxy group on the triple bond.

We report the first palladium-catalyzed ring closure reaction of a 1,6-diyne induced by hydrocarboxylation or hydrocarbalkoxylation with carbon monoxide under mild conditions (room temperature and atmospheric pressure), according to eq. 1 (R = alkyl, R′ = H, alkyl).



(1)

Compounds II and III (R = Me) are obtained in a yield higher than 65%. Their molar ratio is ca. 2/1 at 20°C and 1.26/1 at 13°C.

The reaction is carried out in a very simple way by passing carbon monoxide into a solution of $PdX_2 \cdot 4SC(NH_2)_2$ + $SC(NH_2)_2$ (the latter being added in the

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ratio of 0—10 mol per mol of palladium complex to prevent a too fast deposition of palladium black) in alcohols ROH or in H_2O mixed with an organic solvent such as acetonitrile. So far no other ligand has shown an efficiency comparable to that of thiourea. The presence of H_2O in the alcohol has a beneficial effect on the rate and conversion. About 68 mol of product (II + III) were obtained per mol of complex without optimization.

Compounds II and III (R = Me) were characterized by chemical and spectroscopic methods.

II. mass spectrum; m/z 209 (M^+), 194, 178, 162, 134, 120, 59; IR (film): 3350, 1720, 1640, 1610, 1175, 1020, 900, 870; UV (ethanol): λ_{max} 272—273 nm ϵ = 10380; ^{1}H NMR (100 MHz, $CDCl_3$, δ): 6.06, 5.45, 4.94, (s, 3H, HC=, H_2C=), 3.70 (s, 3H, OMe), 1.80 (brs, 1H, NH), 1.57, 1.33 (s, 12H, Me); ^{13}C NMR, (DMSO, TMS, ppm): 28.1 (Me), 30.5 (Me), 50.8 (OMe) 59.2, 60.5 (CMe_2) 106.3 (CH_2=) 108.3 (CH=), 157.5, 164.5, 164.9 (C=C, C=O).

III. mass spectrum: m/z 209 (M^+) 194, 178, 162, 134, 120, 59; IR (film): 3345—50, 1720, 1640, 1605, 1180, 1020, 920, 860; UV (ethanol): λ_{max} 267 nm, ϵ 6960; ^{1}H NMR (100 MHz, $CDCl_3$, δ): 6.56, 5.7, 5.40 (s, 3H, HC= and H_2C=), 3.70 (s, 3H, OMe), 1.80 (brs, 1H, NH), 1.33 (s, 12H, Me), ^{13}C NMR (DMSO, TMS, ppm): 30.9 (Me), 31.0 (Me), 50.8 (OMe), 59.8, 61.1 (CMe_2) 111.1 (CH_2=), 115.2 (CH=), 152.2, 163.1, 165.8 (s, C=C, C=O). Both compounds II and III give the same semi-hydrogenated and fully hydrogenated products, whose spectroscopic features are in agreement with the expected structures.

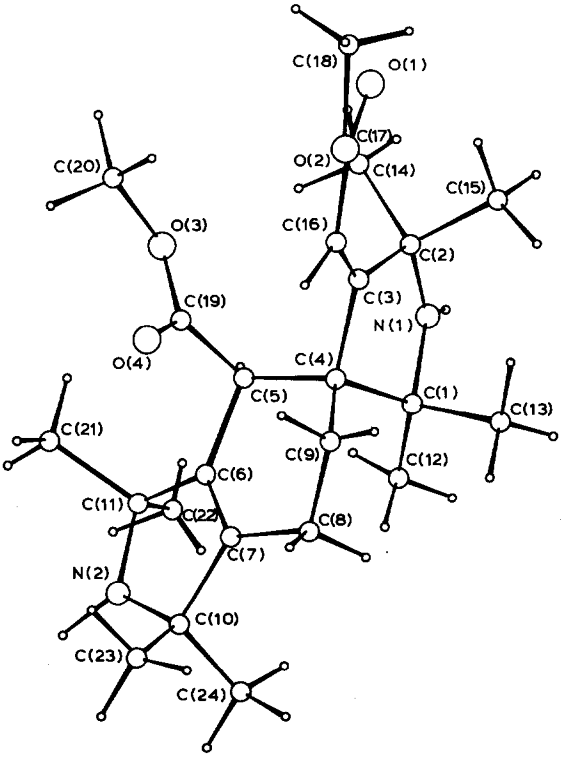
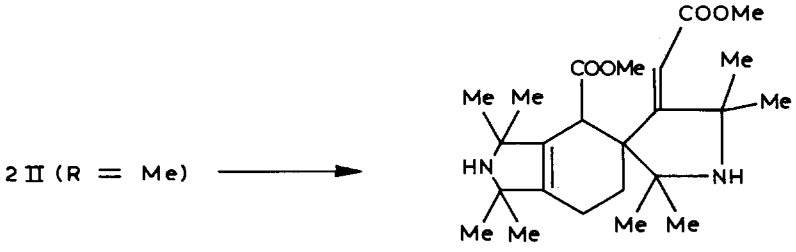


Fig. 1. X-ray structure of the dimer of II [1].

Compound II (R = Me) on standing gives colourless crystals of a Diels—Alder product (predominantly one isomer) whose structure (Fig. 1) has been determined by X-ray methods [1] (eq. 2).

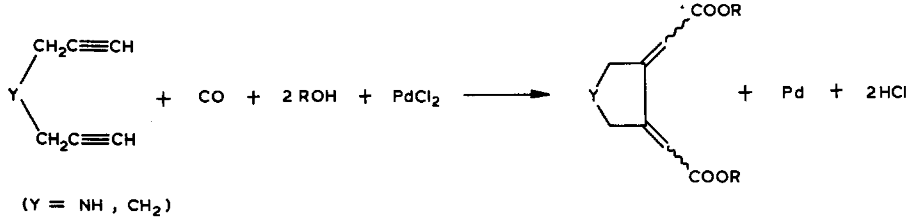


(2)

(IV)

Significant aspects of the results are as follows:

(1) Oxidative carbonylation to a dicarboxylic ester, which could be expected on the basis of the results of the previously reported oxidative carbonylation of acetylene [2] does not occur to any appreciable extent. Only when the alkyl substituents are absent and the nitrogen atom is alkylated (exclusively polymeric products are formed with the simple dipropargylamine) is this reaction observed (eq. 3, Y = NMe) along with the hydrocarboxylation, and the results are poor in terms of molecules converted per molecule of palladium complex. The latter is readily reduced to palladium(0). Analogous results can be obtained if the NMe group is replaced by CH_2 (eq. 3, Y = CH_2):

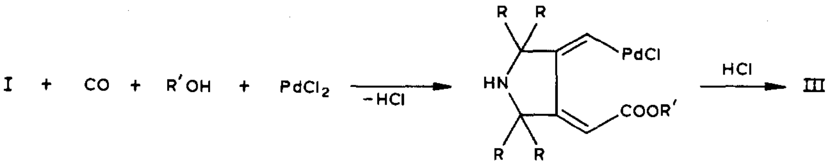


(3)

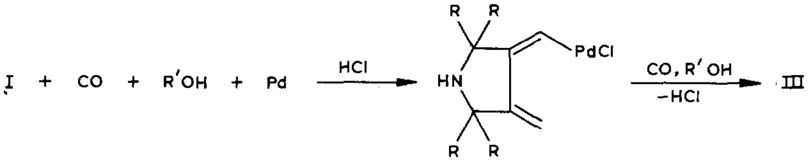
These products are easily identified by formation of their Diels—Alder adducts.

The fact that in the reaction with the $PdCl_2$-thiourea complex the alkyl substituents in the dipropargylamines appear to favor the uptake of a proton or a hydride in preference to the addition of a carbonyl group might be attributable to steric effects which hinder the CO attack. They also prevent a too fast deposition of palladium metal and protect the amino group from reaction with carbon monoxide.

(2) From the mechanistic point of view the reaction can be interpreted either as an attack of the COOR group on one triple bond, followed by ring closure and proton uptake or as a hydride addition followed by ring closure and carbonylation (eq. 4 and 5). A *cis* attack of CO leading to III is assumed in both cases although more complicated patterns are possible.



(4)



(5)

The fact that with less stringent steric requirements (absence of the alkyl groups) the reaction tends to proceed further to dicarboxylic compounds suggests that the reaction begins with the addition of a COOR group and is terminated by a proton [3]. Further experiments are in progress to clarify this point.

(3) The ratio of II to III could correspond to a thermodynamic equilibrium reached by isomerization. The PdX$_2$-thiourea complex can indeed effect the isomerization of II or III (R = Me) toward the 2/1 mixture formed at 20°C, but the reaction appears too slow compared to carbonylation and secondary reactions such as dimerization of II, occur. An alternative mechanism [4] could imply isomerization at the level of an intermediate carbomethoxydienylpalladium. Deuteration experiments with MeOD used as solvent in the reaction with CO, however, showed that compound II (R = Me) incorporates one vinylic H atom (δ 5.45 ppm) predominantly, but with compound III (R = Me) all the three H atoms bonded to unsaturated carbon atoms were involved in the exchange. This suggests that the enolic form of the palladium-bonded precursor of III (eq. 4) undergoes an intramolecular D—H exchange, which is not allowed in the precursor of II, and that compounds II and III do not interconvert significantly during the carbonylation reaction unless more drastic conditions are used. Therefore the process leading to different configurations must occur at an earlier stage.

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