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Preliminary communication

Annulation of aryl rings and formation of pyrones involving depalladation of organometallic compounds *

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Abstract

The depalladation of various organopalladium compounds, derived from cyclopalladated complexes in which two alkynes have been inserted into their Pd–C bonds, affords organic products containing six-membered rings. The latter are obtained either by de-alkylation of an ester group or by annulation of an aryl ring, the ester and the aryl units being substituents on the alkynes used in the synthesis of the starting materials.

We [1] and others [2] have shown that cyclometallated compounds serve as useful synthetic precursors when treated with alkynes. In several instances heterocyclic compounds have been produced via intramolecular nucleophilic addition of amine functions to activated alkene units [1a,b,e,f,2a,b]. This subject needs to be thoroughly investigated, however, in order to define the scope and limitations of the processes that have been discovered to date. It is particularly important to establish with which type of alkyne substituents the formation of heterocycles might take place. We present here a selection of examples which emphasise this particular aspect of chemistry, since the depalladation of organometallic intermediates leads to intramolecular formation of various C–C or C–O bonds in what may be regarded as side reactions to the expected formation of heterocycles.

The synthesis of the starting compounds (obtained through the insertion of alkynes into the Pd–C bond of either cyclopalladated 8-methylquinoline or dimethylaminomethylphenyl (dmba) ligands) has been discussed previously [1a,1c]. Heating a solution of compound **1** [1c] in chlorobenzene at reflux temperature affords, after work-up, variable yields (20–50%) of compound **2** as pale yellow crystals.

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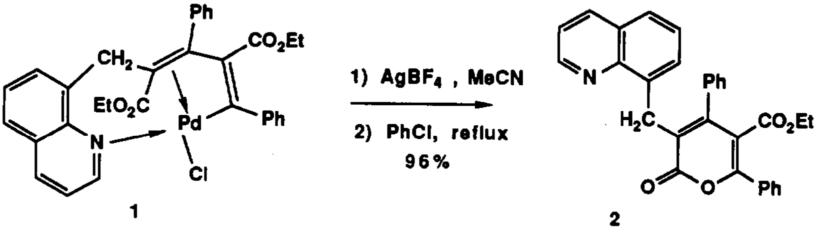
* Dedicated to Professor P.L. Pauson on the occassion of his retirement.

Better yields of this compound were obtained by treating **1** with a silver salt, thus generating *in situ* a cationic organopalladium compound which is then thermally depalladated in refluxing chlorobenzene. The ^1H NMR spectrum of **2** shows a singlet for the CH_2 group and indicates the absence of one of the ethyl groups [*]. Its molecular structure has been determined by means of an X-ray diffraction study [**] (see Fig. 1).



(1)

In a previous study [1a] it was suggested that the depalladation reaction of compound **1** could afford zwitterionic heterocyclic compounds via formation of a C–N bond between the nitrogen atom of the starting materials and one of the carbon atoms of the butadienyl chain η^3-bonded to the palladium atom. In light of the present results this assumption can be seen to be erroneous. Pyrones related to **2** were obtained by treating the neutral cyclopalladated compounds **3** and **5** [1a] with a large excess (up to 5 equivalents) of maleic anhydride. After work-up, however, **4** and **6** were isolated as maleic or fumaric acid adducts [*].

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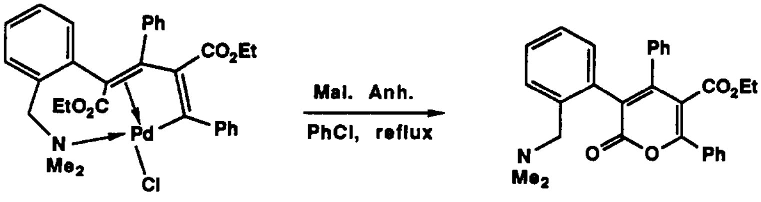
[*] *Selected ^1H NMR data* (200 MHz, $CDCl_3$, 293 K), δ in ppm, J in Hz: **2**: 8.79 (dd, 1H, H_o, $^4J(H_oH_p)$ 1.8, $^3J(H_oH_m)$ 4.2); 8.08 (dd, 1H, H_p, $^3J(H_pH_m)$ 8.3); 7.34 (dd, 1H, H*m*); 4.44 (s, 2H, CH_2); 3.79 (q, 2H, CH_2 of Et); 0.79 (t, 3H, CH_3, $^3J(HH)$ 7.1) (H_o, H_m and H_p are the protons *ortho*, *meta* and *para* to the N atom of the quinoline unit, respectively). **4**: 7.73–6.93 (m, 14H, Ar); 6.26 (s, 2H, HC=CH of maleic acid); 4.05 and 3.81 (2d (AB spin system), NCH_2, $^2J(HH)$ 14); 3.83 (q, 2H, CH_2 of Et); 2.71 (s, 6H, NMe_2); 0.8 (t, 3H, CH_3 of Et, $^3J(HH)$ 7.2). **6**: 7.77–7.16 (m, 14H, Ar); 6.54 and 5.88 (2d, 2H, HC=CH of fumaric acid, $^3J(HH)$ 12.1); 6.24 (s, 2H, HC=CH of maleic acid); 4.14 and 4.04 (2d, CH_2, $^2J(HH)$ 13.8); 3.17 (s, 3H, OCH_3); 2.69 (s, 6H, NMe_2) (the corresponding compound **6** free of acids can be obtained as an oil by increasing the reaction time from ca 0.5 h to 3h: 7.56–7.13 (m, 14H, Ar); 3.47 and 3.63 (2d, 2H, CH_2, $^2J(HH)$ 15); 3.16 (s, 3H, OCH_3); 2.24 (s, 6H, NMe_2)). **8**: 7.03 and 6.69 (2s, HC3 and HC6 (see Fig. 2)); 5,94 (d, 2H, OCH_2O); 3.02 and 2.90 (2d, 2H, CH_2N, $^2J(HH)$ 14.2); 2.05 (s, 6H, NMe_2).

[**] *Crystal data*: $C_{30}H_{23}NO_4$ (**2**), $M = 461.52$, triclinic, space group $P\bar{1}$ (No. 2), a 9.190(3), b 11.522(3), c 12.817(3) Å, α 71.72(2), β 74.28(2), γ 78.44(2)°, V 1230.6 Å^3, $Z = 2$, ρ(calc) 1.24 g cm^{-3}, $F(000) = 484$, μ 0.8 cm^{-1}, Enraf-Nonius CAD-4 diffractometer, λ 0.71073 Å. 4526 independent $\pm h, \pm k, l$ reflections were measured ($2° < \theta < 25°$) at 20 °C for which 2640 reflections with $I > \sigma(I)$ were treated as observed. $R(F) = 0.059$, $R_w(F) = 0.078$. $C_{38}H_{31}NO_2$ (**8**), $M = 533.68$, monoclinic, space group, $P2_1/c$ (No. 14), a 13.140(3), b 18.489(4), c 12.953(3) Å, β 117.89(2)°, V 2781.4 Å^3, $Z = 4$, ρ(calc) 1.274 g cm^{-3}, μ 5.709 cm^{-1}, Philips PW1100/16 diffractometer, λ 1.5418 Å. 2869 independent $\pm h,k,l$ reflections were measured ($3° < \theta < 48°$) at −100 °C for which 1874 reflections with $I > 3\sigma(I)$ were treated as observed. $R(F) = 0.039$, $R_w(F) = 0.049$, GOF = 1.62.
The structures were solved with MULTAN [3]. All non-hydrogen atoms were found by difference-Fourier syntheses. Hydrogen atoms were placed at calculated positions (C–H 0.95 Å, $B(H) = 1.3\ B_{eq}(C)$ Å^2 for **8** and $B(H) = 5$ Å^2 for **2**) and not refined. No absorption corrections were applied owing to the low value of the linear absorption coefficient. Further details of the structural investigations are available from the authors (G.l.B. for compound **2**, A. d. C. and J. F. for compound **8**). Tables of atomic coordinates and lists of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. They may be obtained on request from the director by citing the full literature reference for this communication.



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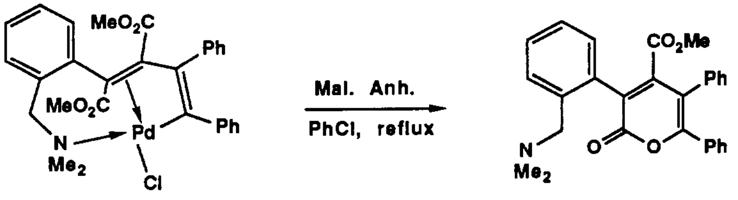

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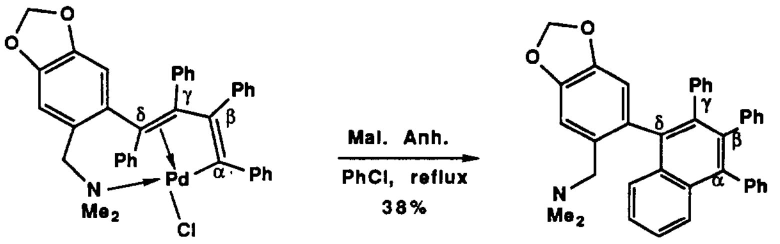
(3)

Maleic anhydride is also an efficient reagent for promoting the depalladation reactions of related organopalladium complexes having no ester group on the butadienyl chain. Thus, under the conditions depicted in eq. 4 compound **7** (obtained by a procedure similar to that used for the synthesis of the corresponding dmba analogue [1a]) leads to an organic product **8** in acceptable yields *.



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(4)

The existence of a tetrasubstituted naphthyl unit resulting from the annulation of the aryl ring at the carbon δ from Pd on the η^3-butadienyl fragment has been unequivocally established by a single-crystal X-ray diffraction study **. This result is in contrast to those observed in previous studies [2d] which established that thermal depalladation of the cationic derivative of a compound related to **7** (containing a non-substituted dmba aryl ring) leads to a fulvene derivative via annulation of the phenyl group attached to the carbon γ with respect to Pd. We detected in reaction 4 non-isolable traces of an additional isomer of **8** which may also contain such a fulvene unit.

The structures of compounds **6** and **8** differ markedly from those compounds obtained in related reactions with the same substituents on the butadienyl moiety and in which the dmba ligands were replaced by a 8-methylquinolyl unit: heterocyclic compounds have thus been obtained via addition of the quinoline N atom on the carbon δ [1b] or γ [1a] of the butadienyl chain. The non-occurrence of C–N bond formation in reactions 3 and 4 may be a consequence of the greater flexibility of the $ArCH_2NMe_2$ unit in **5** and **7** that prevents the N atom remaining in the

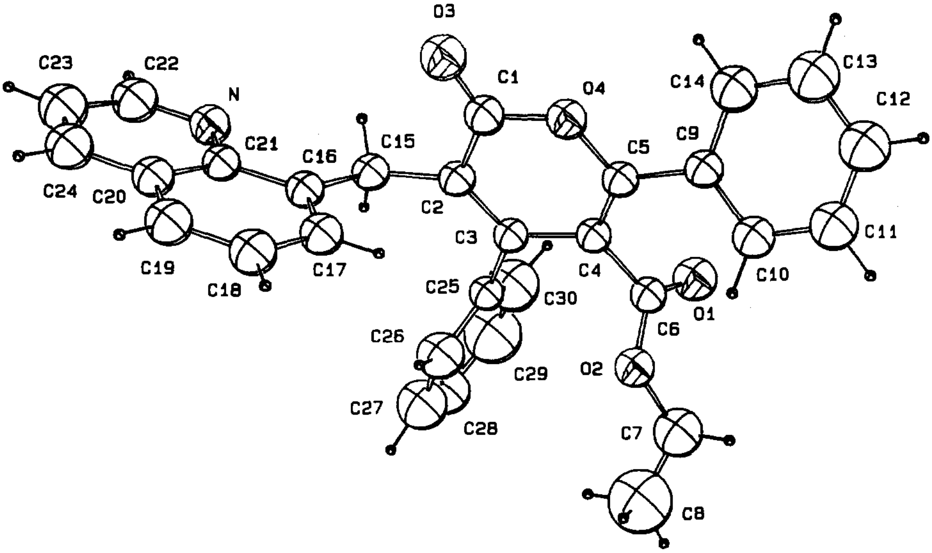

Fig. 1. ORTEP view of compound 2.

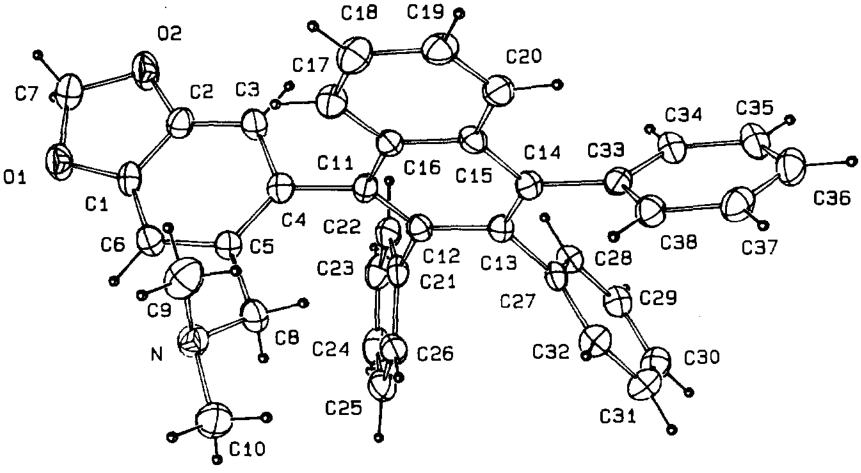

Fig. 2. ORTEP view of compound 8.

coordination sphere of the palladium, so that a nucleophilic attack by the NMe_2 group on the activated alkene cannot take place [4].

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