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A NOVEL PALLADIUM CATALYSED OXYCARBONYLATION OF DIENONES : A CONVENIENT METHOD FOR CONSTRUCTION OF CYCLIC ACETALS

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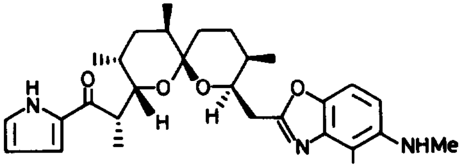
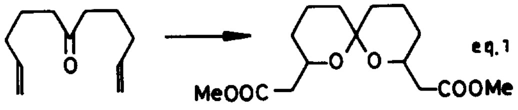
Abstract A new palladium catalysed intramolecular double cyclisation of dienones to cyclic acetals in a single reaction has been described.

In connection with a programme on synthesis of ionophores[1] in general and calcimycin (1) in particular, there was a need to have a convenient method for the preparation of bifunctional spiroacetals. They constitute a part structure of several biologically active molecules such as ionophores[1], pheromones[2] and anti-parasitic agents like avermectins and milbemycins[3] etc. Spiroacetals are commonly prepared by intramolecular ketalisation of suitably substituted dihydroxyketones and more recently via organoselenium[4] or organomercury[5] routes. Herein we wish to report a simple, practical and new method for the construction of spiroacetals by palladium catalysed double cyclisation of dienones with concomitant introduction of two carbomethoxy groups in the side chains using CO, methanol and trimethylorthoformate (TMOF) as other reactants, in a single operation[6] (eq. 1).



1



2 3

Thus dienone **2a** was subjected to carbonylation by $PdCl_2$, CO, MeOH and TMOF to yield spiroketal **3a** in good yield. The reaction was further exemplified by **2b**[7a] and **2c**[7b] which gave the spiroketals **3b** and **3c** respectively[8] (Table 1). The product formation is believed to have taken place through in situ formed dimethyl acetals of dienones.[9]

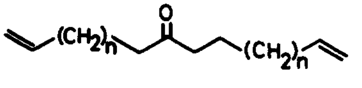
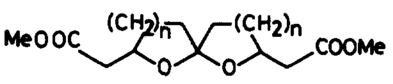
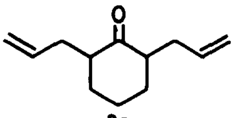
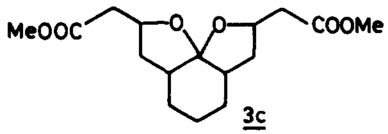
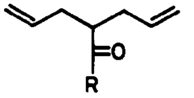
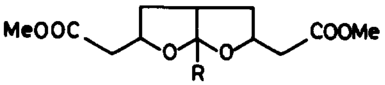
Consequent to the success of obtaining spiroketals, attention was focussed on α,α-dialkenyl ketones, which could give furo [2,3b] furans, a structural units of insect antifeeding agents such as clerodin[10a], and aflatoxins.[10b] The reactant dienones **2d** and **2e** gave the fused furans **3d** and **3e** respectively under similar reaction conditions mentioned above.

In summary, a simple and convenient method to prepare bifunctional spiroketals and fused furans from dienones is described which would undoubtedly be useful in the synthesis of several natural products of biological interest. Further work on the application of these routes will be reported elsewhere.

Typical experimental procedure

A mixture of dienone (1 mmol), $PdCl_2$ (0.3 mmol) and anhydrous $CuCl_2$ (3 mmol) in methanol (5 ml) and trimethylorthoformate (5 ml) was placed in a 50 ml two-necked flask attached with a balloon filled with CO and was stirred at an ambient temperature for 20 hr. Solvents were removed and the residue was triturated with petroleum ether and filtered. Evaporation of solvent followed by filtration through a short silica gel column (pet. ether) gave the products.

Table 1 Preparation of cyclic acetals (3)

Entry	Dienone (2)	Products(3)	Yield (%)
1	 2a, n = 2	 3a, n = 2	85
2	2b, n = 1	3b, n = 1	50
3	 2c	 3c	75
4	 2d, R = CH_3	 3d, R = CH_3	54
5	2e, R = Ph	3e, R = Ph	90

References and footnotes

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8. All new compounds gave satisfactory spectral data.
9. In fact, a sample of dimethyl acetal of dienone **2a** gave the spiroketal **3a** under the same reaction conditions.
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