

Figure 1. Rate of VPL ring opening as a function of time. Conditions: 25 °C in CH₂Cl₂ with a ratio Pd(OAc)₂: VPL 0.02.

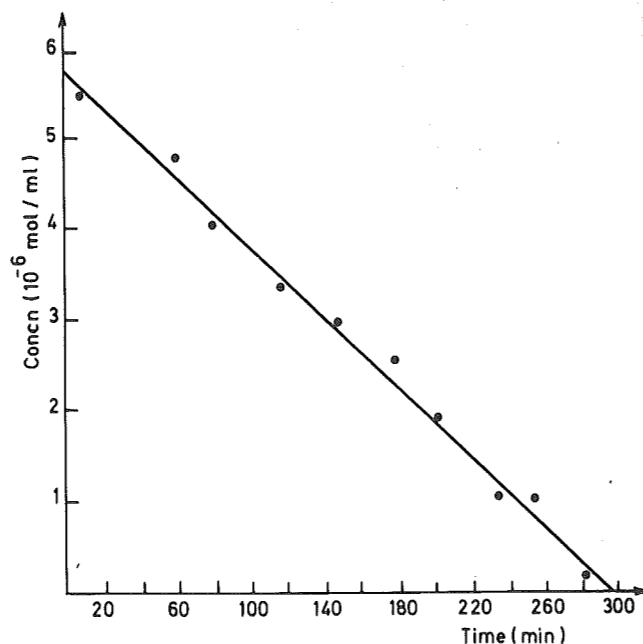
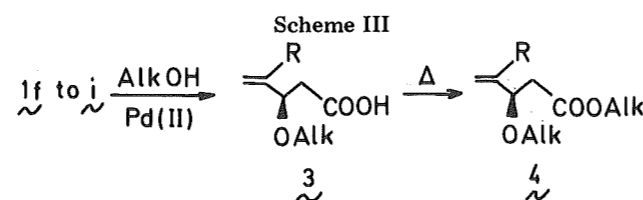
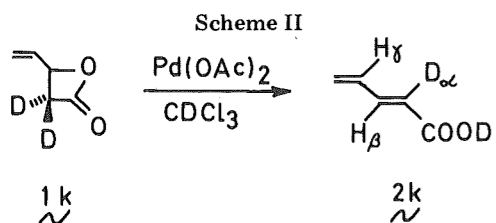


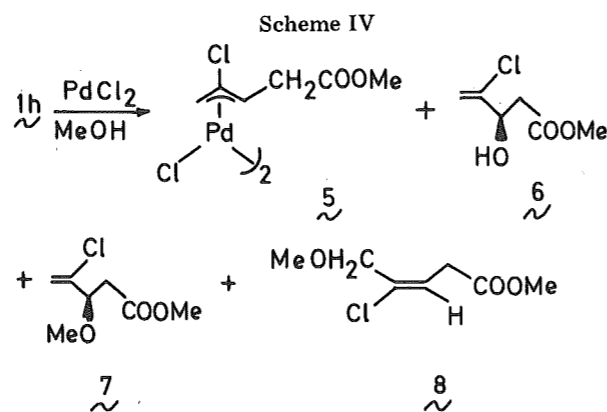
Figure 2. Same as Figure 1 but after addition of trimethyl phosphite (TMP). Conditions: 0 °C in CH₂Cl₂, ratio Pd(OAc)₂: VPL 0.02 and TMP: Pd(II) 4.



takes place and the overall process constitutes an easy synthetic route to the polyfunctional molecules 4.

Isolation of the acid 3 renders a further esterification non-catalytic in palladium and a precipitation of Pd(0) is then observed. Thus it seems that metal complexation is different in the crude mixture and in a solution of previously isolated 3, where a competition between esterification and formation of η^3 -allylic species probably occurs. It was checked that under the same catalytic conditions, neither was 3 nor 4 formed when 2f was reacted with methanol at 25 or at 60 °C. In the latter case, 2f methyl ester is formed (as identified by comparison with an authentic sample). That allows the ruling out of 2f as being an intermediate in the formation of 3.

Deactivation of the vinyl function in 1h is reflected by a poor reactivity at room temperature and by a competitive ring opening with breaking of either C-alkyl or C-acyl-oxygen bonds and formation of 6 and 7 in about 35 and 45% yields, respectively, at 50 °C (Scheme IV).



H _{α} (doublet in the protonated molecule, δ 5.91 ppm, $^3J = 15.8$ Hz) nor any acidic proton present. After the addition of a drop of water, the last one shows up at about 11.5 ppm.

No isotopic effect was observed when equimolecular mixtures of 1f and 1k were submitted to ring-opening conditions.

2. Effects of Ligands on the Catalysis. The addition of tertiary phosphines or phosphites to the system causes a significant increase in the reaction rate (see kinetics) as well as major changes in the nature of the compounds formed.

For instance, if r represents the molar ratio of the added ligand to Pd(OAc)₂, the addition of n -Bu₃P, with $r = 1$, to a methylene chloride solution of VPL leads to an important evolution of CO₂ with formation of polymers ($\approx 50\%$) whereas polymerization prevails ($>80\%$) when $2 < r < 4$. It is of definite preparative interest that the addition of trimethyl phosphite (TMP) leads to an almost quantitative isomerization into 2f when $3 < r < 4$; when $r < 3$, the loss of CO₂ remains important (20–50%).

Other ligands (triphenylphosphine, phosphite, or -arsine) gave intermediate results of those described above, although no straightforward correlation appears between basicity or bulkiness of the ligands and the products formed. 2f and a catalytic amount of triphenyl phosphite do not appreciably react in methylene chloride, as checked by VPC. However, a further addition of palladium acetate to the mixture yields reaction products whose concentration is proportional to the amount of added salt. The relatively high ratio of phosphite to metal is thus probably due to a partial neutralization of the former by the acid formed from the catalyst.

3. Reactions in Protic Solvents. At room temperature in methanol or ethanol, in the presence of a catalytic amount of PdCl₂, the ring opening of the unsaturated lactones 1f–i smoothly takes place with the formation of ether acids 3 (Scheme III). The yield of 3 is above 80%. If the crude mixture of 3 is refluxed for a few hours, a quantitative esterification

In addition, about half of the metal is recovered as a η^3 -allylic species 5, and an estimated 7–10% of 8 is identified as a product of the reaction.

In the same conditions, no alcohol ester corresponding to 6 is ever observed with 1f or 1g; that rules out a possible formation of 6 by a reaction of 1h with the water resulting from esterification of the acid. It was checked that under the conditions used, 6 was neither transformed into 7 nor was 7 into 8 in an appreciable amount. Moreover, 5 is not a catalyst for the ring opening of β -lactones.

4. Kinetics of the Reaction. The rate of the VPL ring opening in CH₂Cl₂ under the influence of Pd(OAc)₂ has been studied at 25 °C with no added ligand (Figure 1), and at 0 °C after the addition of TMP, $r = 4$ (Figure 2). In both experiments the ratio of Pd(II) to VPL was 0.02. An induction period of several hours is observed when the Pd(II) salt alone is used but not if any TMP is added to the sample.

In both cases (but only after an induction time of about 7 h at 25 °C), the disappearance of the lactone is independent of its concentration in the solution. Such an observation is characteristic of a process with a rate-controlling active catalytic species. Any determination of the reaction order with respect to the metal was hampered by solubility problems. Nevertheless, the above results also show that the reaction is not autocatalytic in the sense that the products formed have little influence on the reaction rate. Furthermore, the initially added 2 (alone, with PdCl₂ or as a Pd(II) salt) has no influence on the induction time and thus 2 is not a co-catalyst. After consumption of the initial lactone, isomerization of some freshly added monomer immediately starts again although at a slightly different rate.

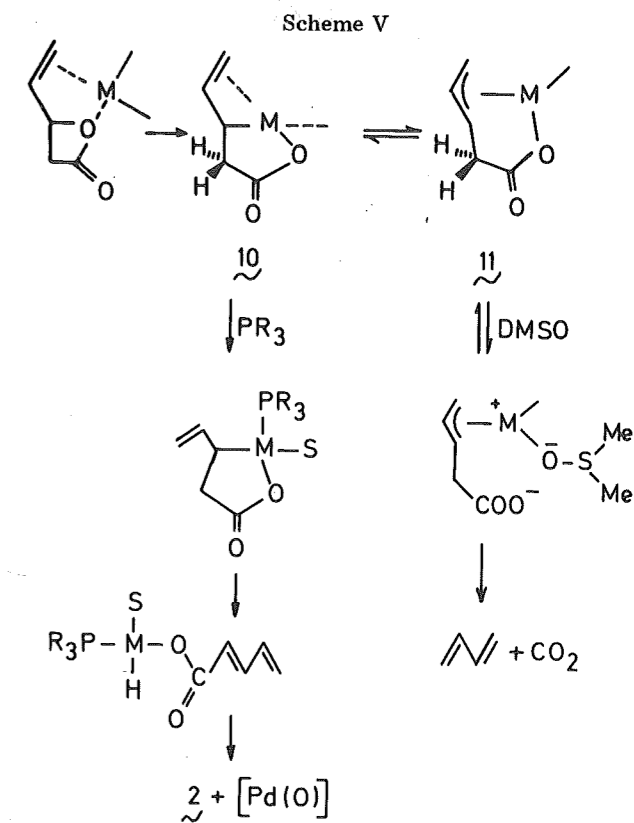
Discussion

The experimental data indicate that we are dealing with a true catalytic process and that an unsaturated vinyl group β to the carbonyl is necessary for its observation. Its replacement by a chain containing a heteroatom susceptible to assist the ring opening⁸ such as in 1j leads to an inert compound as far as our catalytic system is concerned.

On the other hand, it is well known that palladium derivatives form reactive π complexes with olefins.⁹ The examination of molecular models of VPL (1f) strongly favors a bidentate type of complexation with the endocyclic oxygen acting as the second site of coordination. The complexation of the endocyclic oxygen is also substantiated by the finding that ring opening of β -lactones on aluminum alkoxide catalysts takes place through coordination of the same oxygen to the Lewis acid site.¹⁰ Thus, it is reasonable to propose on the basis of favorable steric factors a bidentate type of complexation of the monomer.

The induction period observed could be explained by a slow reduction of the catalyst by the olefinic lactone to a palladium(0) complex which then reacts with another lactone molecule by oxidative addition to give 10 or 11. The latter quickly stabilize to either an unsaturated acid 2 or a polymer or loses CO₂, depending upon the experimental conditions (Scheme V).

Examples are known where π -allyls possessing an α activated methylene are easily transformed into conjugated molecules when bases (e.g., amines) are added to the system.¹¹ Not only does the opening of the lactone cycle ipso facto generate a base (the carboxylate anion) but it does so close to the activated methylene. The abstraction of one hydrogen liberates an acyldiene which obviously, if the reaction is to proceed catalytically, does not effectively compete with the pure lactone for coordination to the metal. We have indeed confirmed that 2f reacts more slowly than the lactone itself



with the catalysts and mostly forms insoluble oligomers after several days.

The proposed mechanism is supported by the stability to our catalysts of the otherwise reactive acetylenic lactone 1i; the spatial factors for a favorable coordination (bidentate) and the possibility of formation of π -allylic derivatives both lack in this case. The deep red color immediately observed after the addition of the highly reactive 1,5-cyclooctadienenickel(0) to a benzene solution of VPL is also characteristic of a π -allyl path. Although then another reactional pathway (mostly polymerization) is favored over the formation of 2f ($\approx 10\%$), it clearly hints that the ability to form such species could be determinant.

Moreover, the precipitation in some frozen-out samples of a highly unstable black compound which quickly evolves CO₂ upon handling is consistent with a structure such as 10. Since no isotopic effect was observed, the insertion step with the breaking of the lactone cycle and the formation of 10 is probably rate determining.

The quantitative evolution of CO₂, observed in good coordinating aprotic solvents (DMF, Me₂SO) is explained by a poor solvation of the carboxylate anion, and that promotes reaction through the carboxylate (evolution of CO₂).

Alcohols, which stabilize the developing positive charge when the cycle opens up, predominantly give nucleophilic substitution products (ether acids 3). The influence of phosphites or phosphines is less clear. They surely compete for coordination, as indicated by the various colorations observed with different ratios of metal to ligands, and significantly reduce the induction time; such an effect has previously been noted.¹² However, the competition for coordination (e.g., between an olefinic bond and the phosphorus atom) should also promote rearrangement through the σ -allyl and/or stabilize some metal hydride intermediate. The formation of allylic cations such as those previously proposed as reactive intermediates in nucleophilic substitutions¹³ of η^3 -allyl enhances the electrophilic character of the species; that would favor an attack of the carboxylate ion on a methylenic proton¹⁴ and thus cannot be ruled out.

