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Oxidative Coupling of Isobutene with Vinylidene Chloride by Palladium (II) Salts

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SUMMARY

Reaction of isobutene and vinylidene chloride with palladium acetate at 60° yields 1,1-dichloro-4-methylpentadienes as well as 2,5-dimethylhexadienes. The reaction is highly dependent on the presence of nitrite, which is essential for the cross-coupling and which suppresses dehydrodimerisation of isobutene.

INTRODUCTION

The oxidative dimerisation of branched olefins by palladium(II) acetate has been rationalised [1] in terms of Markovnikov-like addition of the palladium species to the olefins to give acetoxypalladate intermediates which lack a hydrogen atom β to the palladium. Certain electron deficient olefins, such as vinyl acetate [2], also undergo dehydrodimerisation although they possess hydrogens which would be β to palladium in the proposed intermediates. Since vinylidene chloride is electron deficient and lacks a β-hydrogen, it appears a reasonable candidate for dehydrocoupling even though Pd(II) is known to catalyse nucleophilic displacement of vinylic chloride [3].

1,1-Dichloro-4-methylpenta-1,4-diene (I) and 1,1-dichloro-4-methylpenta-1,3-diene (II) are precursors of an important group of new synthetic pyrethroid insecticides [4]. Previously, I and II have been prepared by a multistage synthesis [5] unsuitable for large scale manufacture. With the aim of devising cheap, single-stage syntheses of I and II, we have found that they are formed directly by the oxidative coupling of isobutene with vinylidene chloride brought about by palladium (II).

EXPERIMENTAL

Materials

Isobutene (Air Products) was dried over calcium chloride. Vinylidene chloride (ICI Mond Division) was dried over 3A molecular sieve. Reagent grade palladous acetate (Johnson Matthey) contained nitrogen (0.57%) but there was no trace metal present at more than 0.01% as revealed by emission spectroscopy. Purer material, which was obtained by recrystallisation from acetic acid or by reaction of palladium sponge [6], contained nitrogen (0.04%) and trace metals at the same concentrations as the reagent grade sample.

Preparation of Standards

1,1,4,4-Tetrachlorobutadiene was prepared from sulpholane [7] and I and II were synthesised from chloral [5].

Reaction Procedure

Typically, $Pd(OAc)_2$ (2 mmol) was dissolved in vinylidene chloride (Table I) and placed in a glass liner within a stainless steel autoclave of 100 ml capacity. The autoclave was purged with nitrogen and liquid isobutene was admitted. After sealing of the

Table 1

Effect of $Pd(OAc)_2$ Purity on the Coupling of Isobutene and Vinylidene Chloride

Reactants (mmol)			Grade of $Pd(OAc)_2$	Temp (°C)	Reaction Period (mins)	Solvent (ml)	Products (mmol)				
Isobutene	Vinylidene Chloride	$Pd(OAc)_2$					Pd^0	I	II	III	IV
100	0	2.0	Reagent	90	60	ϕNO_2 10	1.8	0	0	0.38	0.41
100	0	2.0	Purified	90	60	ϕNO_2 10	1.8	0	0	0.80	0.90
100	0	2.0	Purified	60	60	ϕNO_2 10	1.6	0	0	0.80	0.60
0	360	2.0	Reagent	60	60	-	2.0[†]	0	0	0	0
0	360	2.0	Purified	60	60	-	0.05	0	0	0	0
80	50	2.0	Purified	60	60	DMF 20	0.93	0.005	0	0.55	0.46
80	50	2.0	Reagent	60	60	DMF 20	1.0	0.05	0.01	0.42	0.44
216	2160	2.0	Reagent	60	60	-	0.3	0.03	0.03	0.06	0.14

[†] The only volatile organic product was acetic acid

vessel, the temperature was brought to the desired level and the mixture was stirred throughout the reaction. After the reaction, Pd metal was estimated by weighing and the organic products were determined by GLC at 70° on a 2m column of 10% ββ'-oxydipropionitrile on celite.

Doping of $Pd(OAc)_2$

Recrystallised $Pd(OAc)_2$ was dissolved in acetic acid and an aqueous solution of $NaNO_2$ was added. The mixture was heated under reflux for 10 min and then the solvents were removed under reduced pressure. The solid was extracted with acetone. In every case there was rather less than 1 mol of residual NaOAc for each mol of $NaNO_2$ used. Solvent was removed from the extracts and the doped oxidants were dried *in vacuo*.

Identification of Products

Products were not isolated but were identified on the basis of their GLC-mass spectra. I and II showed a strong parent ion at $^{m}/_{e}$ 150 (2 Cl^{35}) and major fragments, in order of intensity, at $^{m}/_{e}$ 79, 39, 41, 115 (1 Cl^{35}), 99 (1 Cl^{35}) and 135 (2 Cl^{35}). An unidentified chloroacetate, formed on treatment of isobutene and a several fold molar excess of vinylidene chloride with reagent grade $Pd(OAc)_2$, showed major mass peaks at $^{m}/_{e}$ 172 (1 Cl^{35}), 157 (1 Cl^{35}), 129 (1 Cl^{35}); the cracking pattern is consistent with the loss of CH_3 and of CH_3COO from the ion of m/e 172. A product of molecular weight 172 most reasonably corresponds to dehydro-condensation of isobutene with vinylidene chloride, addition of acetic acid and loss of H_2 and HCl. The yield of chloroacetate shown in Fig. 1 is only approximate and supposes that chloroacetate has the same molar glc response as cyclopentanone.

RESULTS AND DISCUSSION

Isobutene reacts with $Pd(OAc)_2$ in polar aprotic solvents such as nitrobenzene to give nearly equal quantities of 2,5-dimethylhexa-1,3-diene (III) and 2,5-dimethylhexa-2,4-diene (IV). The reaction

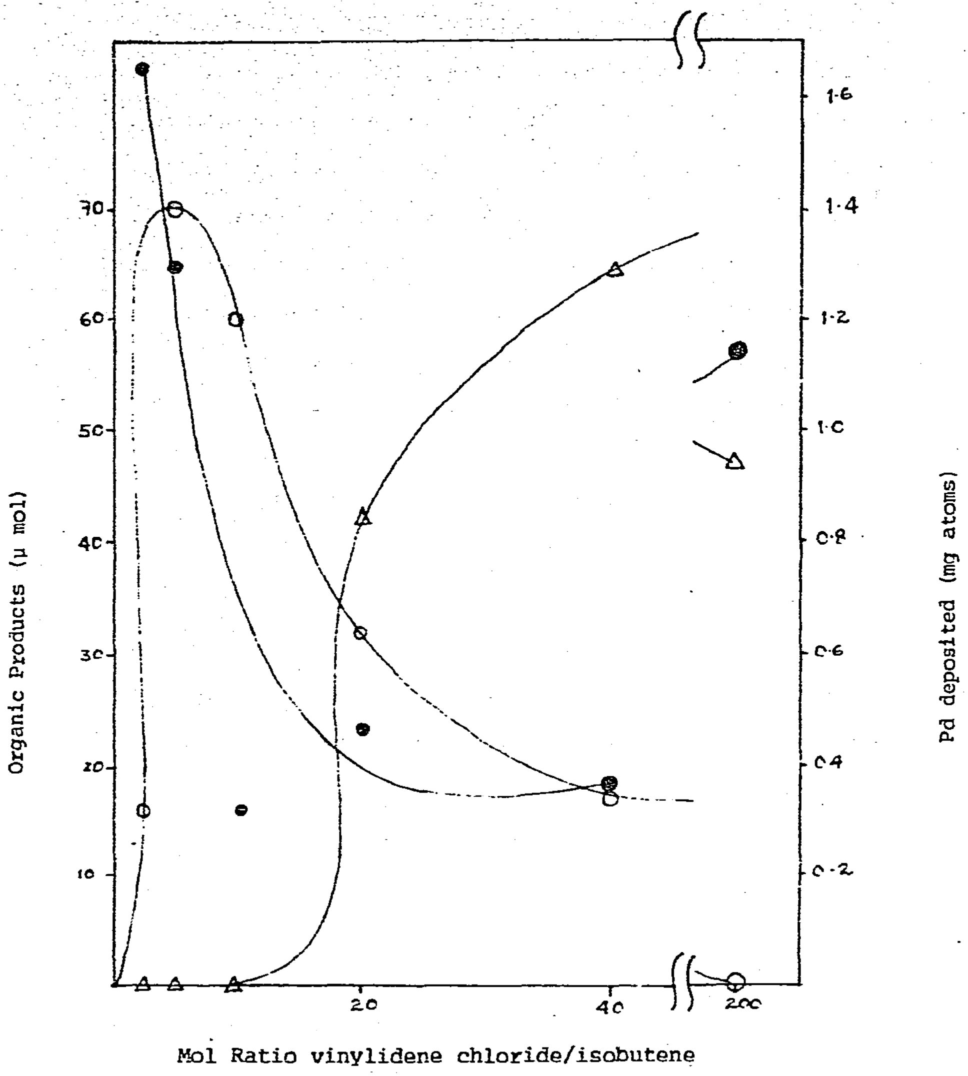

Fig. 1. Effect of Reactant Ratio on Product Distribution with Reagent Grade $Pd(OAc)_2$ (2 mmol)

○ I + II
● Pd metal
Δ Chloroacetate

is not greatly temperature dependent between 60 and 90° (Table I) but higher yields of III and IV, based on metallic palladium deposited, are formed with purified $Pd(OAc)_2$.

Treatment of neat vinylidene chloride with $Pd(OAc)_2$, which dissolves, yields no dehydrodimers and Pd(II) reduction is highly dependent on $Pd(OAc)_2$ purity. With untreated reagent grade $Pd(OAc)_2$, all the Pd(II) is reduced but the only volatile product is acetic acid. In contrast, no volatile products and very little metallic Pd are detected when vinylidene chloride is treated with recrystallised $Pd(OAc)_2$. As expected treatment of mixtures of vinylidene chloride and isobutene with purified $Pd(OAc)_2$ yields dehydrodimers of isobutene but no products derived from vinylidene chloride.

Surprisingly, cross-coupling of isobutene together with vinylidene chloride is accomplished by reagent grade $Pd(OAc)_2$. Reaction of isobutene, in an excess of vinylidene chloride, with unpurified $Pd(OAc)_2$ yields an equimolar mixture of I and II in addition to III and IV. No dimers of vinylidene chloride are produced. The products are formed gradually during about an hour, but the product spectrum remains unchanged throughout the reaction so indicating that each compound is a primary product.

Variation of the reactant ratio has a complex effect on the product yields (Fig. 1). With vinylidene chloride in tenfold molar excess over isobutene, and with reduction of half the initial Pd(II), the combined yield of I and II on Pd^{o} deposited is 20% while that of III and IV is 70%. Selective formation of I and II cannot be achieved merely by increasing the fraction of vinylidene chloride in the reaction mixture because, with high levels of vinylidene chloride, the formation of an unidentified chloroacetate becomes marked. Only a narrow range of conditions favour synthesis of I and II.

In isobutene-vinylidene chloride mixtures, up to half of the reagent grade $Pd(OAc)_2$ added is reduced within an hour, but the remaining Pd(II) remains unreduced even after 16 hours. It seems that III and IV adduct to, and presumably deactivate, the unreacted Pd(II). Thus, the apparent concentrations of III and IV in reaction

Table 2

Effect of Doping with $NaNO_2$

$[NaNO_2]:[Pd(OAc)_2]$*	N(%) in oxidant	$[NO_2]:[OAc]$ in oxidant	Products (mmol)					Yield† (%) I + II	[I + II]: [III + IV]
			I	II	III	IV	Pd^0		
Recrystallised $Pd(OAc)_2$	0.04	1:250	0.005	0	0.55	0.46	0.93	0.5	1:200
Undoped, reagent grade $Pd(OAc)_2$	0.57	1: 18	0.05	0.01	0.42	0.44	1.0	6	1: 14
1:1	4.63	1:2.2	0.02	0.04	0	0.1	0.32	19	1:1.7
2:1	7.25	1:1.2	0.04	0.05	0	0.1	0.31	29	1:1.1
5:1	7.44	1:0.9	0.024	0.03	0	0.05	0.14	40	1:0.9

Reaction mixtures contained isobutene (80 mmol), vinylidene chloride (50 mmol) and Pd(II) (1 mmol) and were heated at 60° for 120 mins.

*Mol ratio of salts from which oxidant was prepared

+Estimated from the N:C ratio

†Yield based on Pd^0 formed.

mixtures, as determined by GLC, increases markedly as the GLC injection block temperature is raised from 110 to 200°.

The chloroacetate, trichloroacetate, benzoate and nitrate of Pd(II) do not promote the olefin dehydrocoupling reactions. Moreover, impurities in commercial $Pd(OAc)_2$, which are removed by recrystallisation, are essential for the production of I and II. On recrystallisation, there is no significant change in the trace metal content of $Pd(OAc)_2$ but the level of nitrogen falls from 0.6 to 0.04%. The presence of nitrogen is attributed to the nitric acid used in the manufacture of $Pd(OAc)_2$ [6]. Doping of purified $Pd(OAc)_2$ with $Pd(NO_3)_2$ produces only a small increase in the selectivity to I and II; the mixture of Pd salts does not yield as much I and II as does unpurified $Pd(OAc)_2$ having an equivalent nitrogen content. Higher nitrate levels depress the yields of coupled products.

Doping of $Pd(OAc)_2$ with nitrite is more effective (Table 2) and I and II can be obtained in 40% yield. The structure of the nitrite-doped samples is not known. The presence of anionic NO_2^- is indicated by an IR band at 835 cm^{-1} which can be attributed to $\delta(NO_2)$ [8]. There are no bands characteristic of other nitrogen containing groups, so it seems likely that all the nitrogen is present as NO_2^-. Elemental analysis does not indicate simple rational compositions. However, the formation of I and II is related to the ratio of nitrite to acetate in the oxidant, as deduced from measured N/C ratios (Table 2), according to Equation 1.

$$\frac{[I + II]}{[III + IV]} = \frac{[NO_2]}{[OAc]} \qquad (1)$$

It is of interest to consider this relationship together with Kikukawa's proposed scheme for oxidative coupling of olefins [1]. In our work, coupling occurs only when isobutene is present. Dimers of vinylidene chloride are never observed, and, with low isobutene/vinylidene chloride ratios the major product appears to be the unidentified chloroacetate. Formation of this chloroacetate is completely supressed by modest quantities of isobutene (Fig. 1). This suggests that the initial reaction leading to I and II is the addition of Pd(II) to isobutene. The adduct or adducts $(CH_3)_2C$ X CH_2 - PdY so formed subsequently react with either vinylidene chloride, to give I and II, or with isobutene, to yield III and IV. The anion dependence (Equ. 1) of this competition suggests that vinylidene chloride is preferred when Y, or perhaps X, is NO_2. The presence of nitrite apparently is essential for the formation of I and II, and high yields of I and II result only at high nitrite levels. However, although Equ. 1 is followed when $|NO_2|:|OAc|$ is varied by a factor of more than 200, the major effect of nitrite is to suppress the formation of III and IV. Thus, conversion to I and II is largely unchanged as the nitrogen content of the oxidant increases from 0.57 to 7.44%. The low conversions to III and IV, which result at high nitrite loadings, suggest that association of one nitrite anion with a Pd(II) ion is sufficient to prevent dehydrodimerisation of isobutene at that centre. Since doping with nitrite markedly lowers the rate at which Pd(II) is consumed, the system is synthetically useless.

As the ratio of vinylidene chloride to isobutene is increased, competition between the two olefins for Pd(II) in the initial addition is expected to increasingly favour vinylidene chloride. Presumably, addition of Pd(II) to vinylidene chloride gives rise to the unidentified chloroacetate which is probably a modified cross-coupled product.

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