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Preliminary communication

AN EFFICIENT PALLADIUM(II) BASED CATALYTIC SYSTEM FOR THE DIMERIZATION OF METHYL ACRYLATE PROMOTED BY SILVER TETRAFLUOROBORATE AND *p*-BENZOQUINONE

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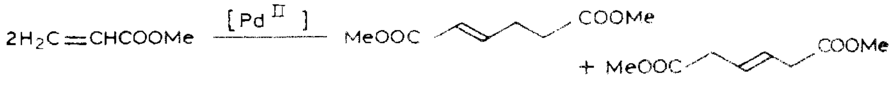
Summary

Dimerization of methyl acrylate to (E)-Δ^2-dimethyl dihydromuconate has been improved by a catalyst containing palladium(II), silver tetrafluoroborate and *p*-benzoquinone which gave satisfactory turnover numbers (up to 340) and high selectivity (94–96%).

The linear dimerization of acrylic acid esters by means of catalytic systems containing palladium [1], rhodium [2] or nickel complexes [3] opens up an attractive route to the derivatives of dehydroadipic acid, the cyclization products of which are interesting intermediates for the synthesis of natural cyclopentanoid compounds [4]. In a recent paper [5] in which homogeneous palladium and rhodium catalysts were critically compared, Nugent and Hobbs concluded that rhodium-based catalysts were the more efficient system in the above-mentioned dimerization. Here we demonstrate that Pd^{II} in combination with $AgBF_4$ and *p*-benzoquinone may be even more efficient and selective than Rh^{III} catalysts, and thus useful for the synthesis on a preparative scale.



(1) (2)

With dichloro-bis(benzonitrile)-palladium(II) as catalyst the products (E)-Δ^2-dimethyl dihydromuconate (**1**) and (E)-Δ^3-dimethyl dihydromuconate (**2**) are formed in a ratio of about 1 : 1 [6]. Adding *p*-benzoquinone in catalytic amounts gave a system with improved stability and efficiency, but had very little influence on selectivity [7]. In contrast, activation of the palladium catalyst by $AgBF_4$, led to high activities and high selectivities for the generation of **1** but only a limited lifetime (turnover number ~ 80 mol acrylate/mol [Pd^{II}]) [6]. Much better results with

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TABLE 1

CATALYTIC DIMERIZATION [a] OF METHYL ACRYLATE [b] BY MEANS OF SYSTEMS CONTAINING PALLADIUM(II) COMPLEXES, SILVER TETRAFLUOROBORATE AND *p*-BENZOQUINONE

Entry	$[Pd^{II}]$ (mol%) [c]	$AgBF_4$ (mol%)	Quinone (mol%)	Conditions	Conversion (%)	Turnover numbers (mol monomer/mol$[Pd^{II}]$) GC (isolated)	**1** (%)
1	[a] 0.33	1.0	1.67	r.t. → 50 °C(30 min)	56	169 (145)	94
2	[a] 0.33	1.0	1.0	r.t. → 50 °C(30 min)	54	163 (137)	94
3	[a] 0.33	1.0	1.67	r.t. (24 h)	64	224 (194)	95
4	[a] 0.17	0.5	0.83	r.t. (20 h)	47	284 (268)	96
5	[a] 0.1	0.3	0.5	r.t. (20 h)	34	340 (290)	94
6 [d]	[a] 0.1	0.3	0.5	r.t. (18 h)	–	–	–
7	[a] 0.17	0.5 [e]	0.83	r.t. (18 h), 50 °C (2 h)	3.5	21	94
8	[b] 0.17	1.0	1.67	60 °C (16 h)	57 [f]	173 (130)	96
9	[b] 0.08	0.5	0.83	60 °C (18 h)	28 [f]	168 (146)	95
10	[c] 0.08	0.5	0.83	60 °C (12 h)	3.5 [f]	21 (21)	96
11 [g]	[a] 0.2	0.6	1.0	r.t. (18 h)	26	134 (116)	93

[a] *p*-Benzoquinone, $[Pd^{II}]$, and finally the silver salt were placed in a double-walled glass flask and were heated, with magnetic stirring, and circulating water. All experiments were performed under argon. For conditions see body of table. [b] Methanol was not detected (< 0.05% by GC; OV-101 capillary). [c] a = $PdCl_2(C_6H_5CN)_2$; b = $[Ph_3PPdCl_2]_2$; c = $[n\text{-}Bu_3PPdCl_2]_2$. [d] 1 mol% methanol added. [e] AgO_3SCF_3 instead of $AgBF_4$. [f] Catalytic system still active. [g] Containing 50%(v) methyl propionate.

respect to activity, selectivity and stability were obtained by the addition of *p*-benzoquinone and silver tetrafluoroborate to the palladium complex.

A selection of our results is summarized in Table 1. In this work the optimum composition of the catalytic system was found to be $[Pd^{II}]:3[AgBF_4]:5$[benzoquinone].

The catalyst to substrate ratio was less than 1 : 100 in all cases, with 1 : 1000 as the minimum. We observed the highest turnover numbers at the lowest concentrations of the catalytic system, probably owing to monomer/dimer competition with the palladium catalyst during complex formation. As a matter of fact a brown precipitate was separated from the reaction mixture, and treated with bis(diphenylphosphino)ethane (dppe) it gave $PdCl_2$(dppe) and (*E*)-Δ^2-dimethyldihydromuconate (**1**) and a small amount of benzonitrile. This reaction is presumably the result of displacement of the π-bonded dimer by the chelating phosphine. In an earlier paper [8] the action of $AgBF_4$ was explained as the substitution of the covalently-bonded chloride in $PdCl_2(C_6H_5CN)_2$ by the less-coordinating BF_4 anion, but a comparison of the experiments (entries 4 and 7) shows that silver triflate influenced only the selectivity and not the efficiency. It is well known that trifluoromethanesulfonate is one of the best leaving groups in organic [9] and inorganic [10] chemistry, but examples of strong coordination are also known [11]. The reason for the different behaviour of $AgBF_4$ and AgO_3SCF_3 could be due to a difference in the solubilities of the active species, all the more because we observed precipitation a short time after starting the reaction.

The purity of the substrate also seems to be very important. Starting from a technical grade methyl acrylate, different methods of purification were tried;
(1) tandem drying with anhydrous magnesium sulfate, phosphorus pentoxide,

(2) filtration through a column with activated alumina (alkaline, activity 1),
(3) storing over a molecular sieve, A4 (freshly activated at 180°C, in a vacuum, in the presence of phosphorus pentoxide),
(4) distillation under normal pressure, twice and the use of the fraction collected at exactly 79°C,
(5) redistillation of methyl acrylate from catalytic experiments.
The best results were achieved by method 4.

Nugent [5] demonstrated the necessity of a very low methanol content in methyl acrylate for successful catalytic action (approx. equimolar to palladium). We determined the amount of methanol in all fractions of methyl acrylate by capillary GC (OV 101) and found only traces ($\ll 0.1\%$). Adding 5 to 10 moles of methanol per mole of complexed palladium immediately stopped the catalytic reaction (entry 6). Some experiments were performed in the presence of 50% (v) methyl proprionate as solvent, but with clearly lower yields (entry 11). Palladium-phosphine complexes like $[PPh_3PdCl_2]_2$ give a suitable catalytic system in the presence of $AgBF_4$ and *p*-benzoquinone. This system works well at elevated temperatures (50-60°C) and shows the highest selectivity with respect to the Δ^2-ester, **1**. Yields are comparable with those of $PdCl_2(C_6H_5CN)_2$ (see entries 4 and 9).

However, the dimer dichloro(tri-n-butylphosphine)palladium(II) gave no satisfactory results because the phosphine-palladium bond is more stable than in dichlorotriphenylphosphinepalladium(II).

At present, it is not possible to explain the role of *p*-benzoquinone in our systems. Some observations have been previously published [7]. A detailed investigation of the reactions of quinone in methyl acrylate will be discussed in a subsequent paper.

It should be noted, that in the catalytic dimerization of methyl methacrylate [12] quinone is less active as a promoter.

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