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OXIDATION OF OLEFINS BY OXYGEN WITH A MIXED PALLADIUM/SILVER NITRITE CATALYST IN ALCOHOLS.

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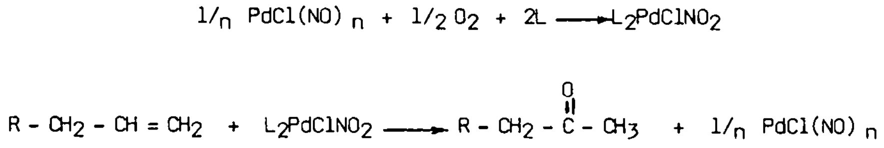
Summary. Selective oxidation of a terminal olefin by a mixed catalytic system comprising $Pd(dba)_2$ and silver nitrite gives a methyl ketone. A WACKER type mechanism is proposed, in which organic nitrites derived from the alcoholic solvent used are involved.

The use of molecular oxygen or air for converting olefins into epoxides or carbonyl derivatives is of special interest to industry for manufacturing products such as acetaldehyde, propylene and ethylene oxide. Efforts have been made in the past to design catalytic systems able to bind and transfer molecular oxygen (1). Among them, those using transition metals (mainly palladium(0) and rhodium(I)) lead to the most active systems. However, in most cases the catalytic activities obtained are inadequate for industrial development and, very often, the parallel oxidation of a cosubstrate such as triphenylphosphine or alcohol (2) is required for maintaining catalytic cyles.

Recently, a new approach has been introduced by ANDREWS (3) and MARES (4) who showed that oxygen transfer could be achieved by the nitroso ligand of a transition metal complex according to scheme 1. The first step is a bimolecular reaction leading to a clean partition of the diatomic oxygen molecule into two resulting nitro species which can then transfer one oxygen atom regenerating the starting nitrosyl species. Although only limited turnover numbers of catalysts were reported, (up to 12), this approach in principle appears to be potentially efficient and attractive since no oxidation of a cosubstrate is required for catalytic activity.



$$1/_n\ PdCl(NO)_n + 1/_2\ O_2 + 2L \longrightarrow L_2PdClNO_2$$

$$R-CH_2-CH=CH_2 + L_2PdClNO_2 \longrightarrow R-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 + 1/_n\ PdCl(NO)_n$$

Scheme 1

This led us to investigate whether catalytic systems associating a palladium complex, bis(dibenzylidenacetone) palladium(0) (5) and the commercially available silver nitrite would be capable of generating in situ nitro/nitrosyl species.

Among the numerous reaction solvents tried (including toluene, acetonitrile, acetic acid or dimethylformamide) only alcohols proved to be efficient in promoting significant olefin oxidation under molecular oxygen (Table). In every case the methylketone was the sole olefin oxidation product detected ; other products were the isomerized olefins, mainly as the 2-alkene isomer (about 80% of the olefinic fraction). Improvement in both yield and olefin conversion could be obtained when triphenylphosphine was added to the catalytic system in a one to one molar ratio relative to the palladium complex (compare entries 1 and 3) but no additional improvement was observed when diversely substituted trialkyl or triarylphosphines were used in this ratio.

Therefore all further experiments were carried out with a catalytic system comprising a $PPh_3/Pd(dba)_2$ ratio of one (and a $AgNO_2$/"Pd" ratio of 10).

The involvement of molecular oxygen in the reaction process is shown in the table : under oxygen (entry 3) the activity of the system is increased by a factor of five compared to that reaction run under an argon atmosphere (entry 2).

The influence of alcoholic solvents on reaction yield was then examined (entries 3 to 7). Primary alcohols were the most efficient, a secondary alcohol (entry 4) leading to lower yield ; with a tertiary (entry 5) only trace amounts of ketone were formed. Most interesting was the effect of increasing steric hindrance around the primary alcohol functionality (entries 6 and 7) since the ketone yield was greatly improved because the olefin isomerization was lowered to a large extent. It would therefore seem that the alcohol is involved during this isomerization step but experiments run in totally deuterated alcohols (methanol and cyclohexanol) did not lead to any labelling of the products (ketone and isomeric alkenes). This observation rules out the possibility that the palladium hydride species arising from the reduction of a palladium complex by the alcohol is responsible for isomerization as has been proposed by BREGEAULT et al (6).

At this point we tried to determine the mechanism of the ketone oxidation ; there were three possibilities i) transfer of oxygen in a way similar to the nitro/nitrosyl system shown by ANDREWS (3) and MARES (4), ii) a cooxidation mechanism as often encountered in alcoholic solvents (2) iii) a more conventionnal WACKER type process (7). In favour of (i) is the recent result of Feringa (8) in which he proposed a nitro/nitrosyl type mechanism for a mixed catalytic system associating, in tertiobutanol, a nitro complex of palladium and a copper salt under molecular oxygen (8).

Accordingly, the behaviour of the nitrites introduced in the form of silver salts in the catalytic system was examined. At the end of reaction, titration (9) showed that 60% of them were still present in the reaction mixture as nitrites. Infra-red analysis of the vapor phase revealed the presence of n-propyl nitrite, while silver was quantitatively recovered in metallic form. This result suggests that the oxygen transfered onto the olefin was derived mainly from the molecular oxygen consumed and not from the oxygen bound to the nitrite.

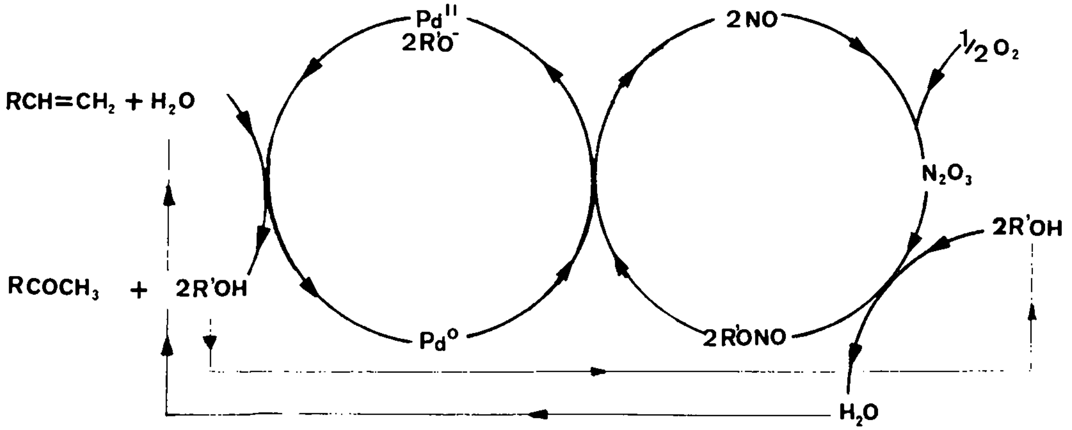
We then attempted to establish the relationship between the oxygen consumed and the oxidation products formed during the reaction. Beside oxidation of the olefin into methyl ketone, analysis showed that the alcohol (propanol-1 in this experiment) was oxidized into propanaldehyde acetal and that water was consequently formed (10). The ratio of molecular oxygen uptake / methyl ketone obtained was 0.65 (corresponding to entry 3) which is not in favour of a cooxidation type process where this ratio has to be close to one. As the oxidation of alcohol occuring during the reaction gives rise to the formation of water in the reaction medium, we checked the influence of water on the kinetics of the reaction. Addition (10%) accelerated ketone formation at the beginning of the reaction but the overall yield was not changed. On the contrary, addition of a water scavenger (dimethoxypropane, 10%) (11) had a marked effect : kinetics was slowed down and yield was lowered. These results indicate that a WACKER type mechanism, where the transfered oxygen is coming from the nucleophilic action of a water molecule on a palladium / olefin complex, is certainly the major pathway by which olefins are oxidized in our system.

We propose that a WACKER type mechanism initiated by the water coming from oxidation of the alcoholic solvent is taking place. In agreement with this is the observation that in a non oxidizable alcohol such as tertiobutanol, no olefin oxidation was detected (entry 5). As could be expected, when tertiobutanol containing 10% water was used as the solvent reaction, oxidation of

Table : Oxidation of 1-dodecene in alcoholic solvents

entry	$Pd(DBA)_2$ %	PPh_3 %	Co-catalyst %	solvent	olefin conversion %	ketone yield (selectivity)% %	Turn over
1	1.1	0.0	$AgNO_2$ 11	1-Propanol	42	29	17
2*	1.1	1.1	"	1-Propanol	27	21	5
3	1.1	1.1	"	1-Propanol	80	33	23
4	1.1	1.1	"	2-Propanol	50	32	14
5	1.1	1.1	"	t-Butanol	3	-	2
6	1.1	1.1	"	2-Methyl-1 butanol	65	43	25
7	1.1	1.1	"	2,2-dimethyl-1-propanol	36	73	23
8	1.1	1.1	"	t-Butanol/H_2O(10%)	64	76	43
9	1.1	1.1	tBuONO 11	t-Butanol/H_2O(10%)	57	40	20
10	1.1	1.1	tBuONO 11 + $AgOCOCF_3$ 1.1	t-Butanol/H_2O(10%)	45	45	30
11	1.1	1.1	HNO_3 0.55 + $AgNO_2$ 0.55	t-Butanol/H_2O(10%)	80	81	60

Conditions : solvent 10 ml, 50°C under 1 atmosphere of oxygen (* except entry 2 run under argon). Molar percent of catalyst and conversion are given relative to the initial olefin introduced (9.1 millimoles) ; yields are relative to the transformed olefin and turn over is defined as the ratio ketone/Palladium. Analyses were performed by VPC using the internal standard technic. Reactions were conducted until no evolution could be noticed (from 20 to 30 hours at 50°C)



Scheme 2

the olefin took place but in this case even better yields and turnover were obtained (entry 8). In an attempt to improve this result we tried to identify the agent responsible for the reoxidation of the palladium. This was essential for explaining the role of alcohol since no oxidation could be detected with our system in dimethyl formamide/water which is the usual "WACKER" solvent. Results mentioned above show that part of the nitrites were present in the form of alkylnitrite derived from the alcoholic solvent. Further, the reoxidation of zerovalent palladium by such nitrites has been described in catalytic carbonylation processes (12). Catalytic oxidation of olefins into acetals by an alkyl nitrite / palladium system in an alcoholic solvent has also been reported (13). Based on these arguments, alkyl nitrites appear to be the agent responsible for the catalytic oxidation. We therefore propose that the catalytic cycle shown in scheme 2 is the primary mechanism responsible for olefin oxidation.

When using tertiobutyl nitrite in the presence of a palladium complex (entry 9), the yield was lower than that obtained when using silver nitrite, but it was increased on the addition of silver ions (entry 10). We tried to obtain even better yield and olefin conversion using a combination of silver nitrite and nitric acid in tertiobutanol/water solvent which gives rise in situ to tertiobutyl nitrite in the presence of silver ions. Results are given in entry 11 : the yield was raised to 81% (turnover number of palladium : 60) with a high olefin conversion. This compares favorably with other catalytic systems reported in the literature (14).

We are currently trying to understand the reasons why catalytic activity stops in order to further improve our system.

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14. Other catalytic systems can give a higher turnover number with a lower selectivity (Ref.6 : T.O. = 96 ; selectivity 60 %) or, on the contrary, a better selectivity with a lower turnover number (Ref.11 : selectivity > 99 % ; T.O. = 40).

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