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EPOXIDATION WITH MOLECULAR OXYGEN IN THE PRESENCE OF $PdCl(NO_2)(CH_3CN)_2$

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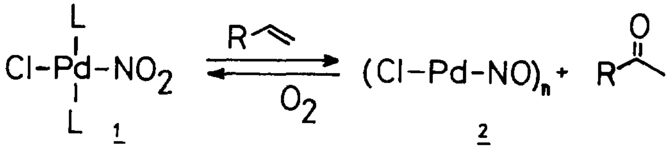
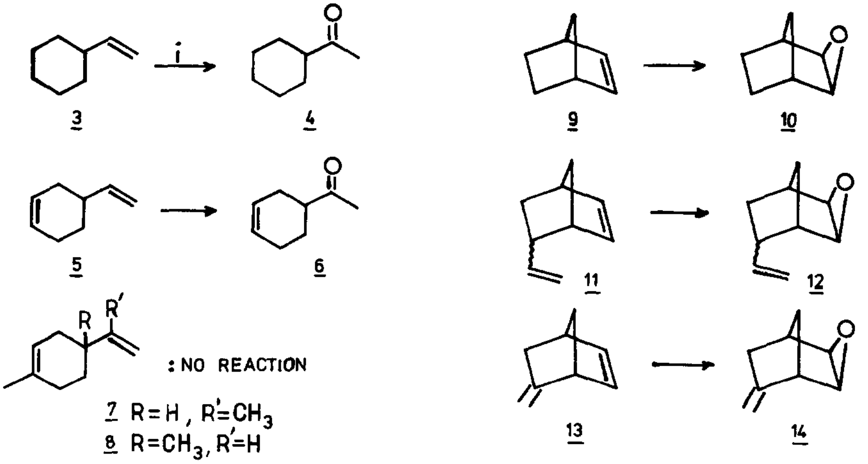
Abstract. Several mono or non conjugated diolefins are submitted to the action of oxygen in presence of catalytic amounts of $PdCl(NO_2)(CH_3CN)_2$. Depending on the olefin structures methylketones or epoxides are obtained.

We report our preliminary results about the oxidation of mono and bicyclic olefins$^{1)}$ in presence of nitro palladium complex 1 ($L=CH_3CN$)$^{2)}$. A redox process is involved in this reaction and an intermediate palladacycle 15 has been postulated$^{2)}$. A modification of the stereochemistry of the latter intermediate should have an influence on the outcome of the oxidation reaction. This is indeed the case as shown by the following reactions$^{3,4)}$:

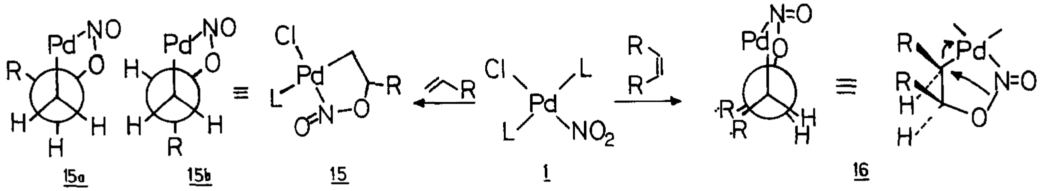




i $PdCl(NO_2)(CH_3CN)_2$ 1 (8mol%), BENZENE, 60°C, yields: 4, 6=50-70%, 10,12,14=30-40%.

The importance of steric factors is emphasized by the difference in the behaviour of vinylcyclohexane 3, which yields a ketone, and norbornene 9 which gives an epoxide. Additionnally the reaction is highly regioselective as shown by the transformation of 4-vinylcyclohexene 5 as well as 5-vinylnorbornene 11 and 5-methylenenorbornene 13.

The formation of epoxides 10, 12, and 14 can be rationalized by a syn elimination mechanism[5] occuring in the intermediary palladacycle 16.



Indeed the steric arrangement observed in this cyclic complex formed with the rigid norbornene skeleton, disfavours the hydrogen migration[2]. However the latter occurs smoothly in conformationnally non rigid olefins where the anti or gauche conformation of the C-H bond relatively to the C-Pd bond can easily be achieved as in 15a or 15b.

This palladium catalyzed epoxidation of norbornene derivatives is the first example of such a reaction using molecular oxygen, which is different from autoxidation[6] and peroxidation[5b,7]. It remains to be shown whether the peculiar structure of norbornene is necessary or not to achieve successfully epoxidations in such conditions.

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3) The ketones and epoxides have been identified by comparison with known products. 4 : E.P.Blanchard, G.Büchi, J.Amer.Chem.Soc., 1963, 85, 955 ; 6 : R.Robinson, G.J.Fray, J.Amer.Chem.Soc., 1961, 83, 249 ; 10 : R.A.Budnik, J.K.Kochi, J.Org.Chem., 1976, 41, 1384 ; 12 : H.K.Wiesse, U.S.P.3,183,249, C.A.1965, 63, P1767d ; 14 : S.W.Tinsley, D.L.MacPeek, U.S.P.3,238,227, C.A.1966, 64, P19557g.

4) In a typical experiment 43,2mg (0,16mmol) of 1 (L=CH$_3$CN) is dissolved in dry benzene (10ml). The olefin (2mmol) is added and the solution stirred at 60°C for 5-7 days. After isolation[2] the ketones (yield 50-70%) or epoxides (yield 30-40%) are identified by means of g.l.c, NMR and IR spectroscopy.

5) a) cf J.Sicher, Angew.Chem.Int.Ed.Engl.1972, 11, 200 ; a similar mechanism has been discussed for the decomposition of peroxymetallacycles : b) H.Mimoun, R.Charpentier, A.Mitschler, J.Fischer, R.Weiss, J.Amer.Chem.Soc., 1980, 102, 1047.

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