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Platinum-Catalysed Cyclopropanation of Olefins with Ethyl Diazoacetate

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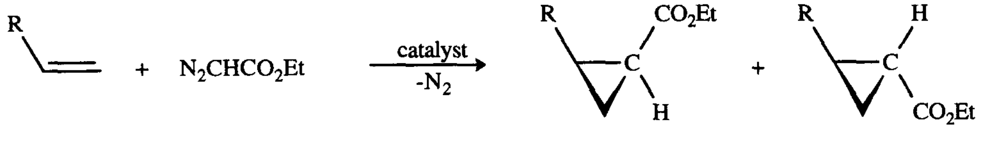
Abstract. The addition of ethyl diazoacetate to olefins in the presence of a catalytic amount of platinum complexes provides the corresponding cyclopropanes in good to excellent yields. © 1997 Published by Elsevier Science Ltd.

Functionalized cyclopropanes provide building blocks of unprecedented synthetic potential. Moreover, natural or synthetic cyclopropanes bearing simple functionalities (hydroxy-, amino-, carboxylic-, 1-hydroxy-carboxylic or 1-aminocarboxylic acids, nucleosides, ...) are endowed with a large spectrum of biological properties, ranging from antibiotic, antiviral, antifungal, insecticidal, hormonal, neurochemical, carcinogenic or antitumoral activities, to plant growth and fruit ripening controls, enzyme and gluconeogenesis inhibitions.[1] The mechanisms responsible for the various biological properties affected by a cyclopropane ring have become clear, only recently.[1]

New methodologies are currently investigated towards the stereoselective synthesis of this attractive class of compounds.[2,3] The direct transfer of carbenes from diazo compounds to alkenes is likely the most straightforward route to cyclopropanes. This reaction is catalysed by transition metals and the use of several metal complexes has been described.[4,5] Palladium complexes including $Pd(OAc)_2$,[6,7] $PdCl_2$,[6] $PdCl_2.2PhCN$,[8] and $Pd(PPh_3)_4$[8,9] have been reported to efficiently catalyse the reaction of diazomethane and of ethyl diazoacetate (eq 1) with both electron-rich and electron-deficient olefins including α,β-unsaturated ketones and esters, strained aryl- and alkyl-substituted alkenes. Despite the periodic relationship of platinum to palladium, -to the best of our knowledge- only two papers report on platinum catalysis in olefin cyclopropanation.



(1)

cis (endo) *trans (exo)*

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In the first example, ethyl vinyl ether was reacted with diazofluorene in the presence of a catalytic amount of $PtCl_2(CH_2{=}CH_2)Py$ to afford the corresponding ethoxy spirocyclopropane derivative in 86% (isolated) yield.[10] In the second example, the formation of cyclopropanes was observed from styrene in the reaction mixture of $Pt(CH_2{=}CH_2)(PPh_3)_2$ with ethyl diazoacetate, in dichloromethane at room temperature (20% yield, *cis/trans* = 0.5).[11] Our interest in the catalytic reactions of diazo compounds with olefins[12] and, especially, in the understanding of the factors that direct the reaction towards carbene transfer or olefin metathesis[13] led us recently to investigate the reaction of ethyl diazoacetate, N_2CHCO_2Et, with olefins in the presence of representative platinum complexes (Table 1).

Table 1. Cyclopropanation of Styrene and Cyclooctene with Ethyl Diazoacetate in the Presence of Representative Platinum Complexes[a]

	Cyclopropanation yield, % (*cis/trans* or *endo/exo* ratio)[b]		
Complex	Styrene, 60 °C	Styrene, 100 °C[c]	Cyclooctene, 100 °C
$Pt(PPh_3)_4$	76 (0.64)	95 (0.64)	42 (0.37)
$PtCl_2$	48 (0.62)	94 (0.64)	39 (0.48)
$[PtCl_2(cyclohexene)]_2$	49 (0.63)	94 (0.64)	54 (0.51)
cis-$PtCl_2(benzonitrile)_2$	47 (0.65)	92 (0.65)	54 (0.53)
cis-$PtCl_2(pyridine)_2$	34 (0.61)	88 (0.63)	22 (0.21)
cis-$PtCl_2(PPh_3)_2$	75 (0.62)	92 (0.62)	29 (0.50)
trans-$PtCl_2(PPh_3)_2$	69 (0.63)	91 (0.62)	33 (0.54)
$PtBr_2$	43 (0.64)[14]	89 (0.65)	29 (0.38)
PtI_2	58 (0.65)	66 (0.64)	54 (0.52)
$PtI_2(NH_3)_2$	67 (0.60)	91 (0.65)	31 (0.36)
$PtCl_4$	79 (0.72)	85 (0.84)	71 (0.56)
$PtBr_4$	54 (0.61)	92 (0.63)	42 (0.37)

[a] Reaction conditions : catalyst, 0.0025 mmol; olefin, 20 mmol; ethyl diazoacetate, 1 mmol diluted by the olefin up to 1 mL; addition time, 4 h. [b] Based on ethyl diazoacetate and determined by GLC analysis. [c] Some polymers were also formed during the cyclopropanation of styrene. At 100 °C : polymer yield, 2-18% (based on styrene) depending on the catalyst and the reaction time; M_n, 95,000-160,000; M_w/M_n, 1.65-2.1.

The model study of cyclopropanation was done on styrene -an activated olefin- and on cyclooctene -a non activated cyclic olefin- with ethyl diazoacetate. The synthesis of the cyclopropanes was performed by dropwise addition of ethyl diazoacetate to neat olefins and 0.25 mol % catalyst over 4 hours. Accelerated addition of the diazoacetate resulted in decomposition of the diazoacetate to higher amounts of carbene dimers (diethyl maleate and diethyl fumarate). In all cases, the successful formation of the ester cyclopropane resulted in a mixture of *cis (endo)* and *trans (exo)* isomers. The results are summarized in Table 1, and in all instances the *trans (exo)* cyclopropane -the most thermodynamically stable stereoisomer- was the major isomer. Quite noteworthy, however, was the lack of stereocontrol provided by the various platinum complexes surveyed for the cyclopropanation of styrene : the *cis/trans* ratio of the cyclopropyl esters ranged from 0.60 to 0.65, except when $PtCl_4$ was used as the catalyst. For the cyclopropanation of cyclooctene, the use of the different platinum

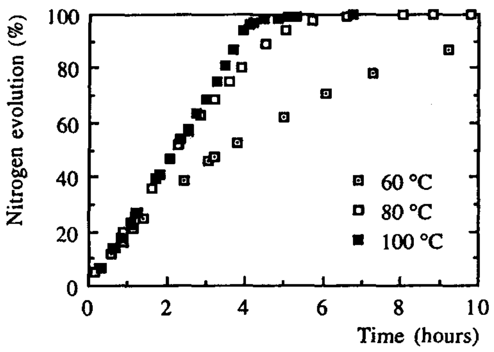

Figure 1. Influence of the temperature on the decomposition rate of ethyl diazoacetate for cyclopropanation of styrene catalysed by $PtCl_4$.

(Reaction conditions same as in Table 1)

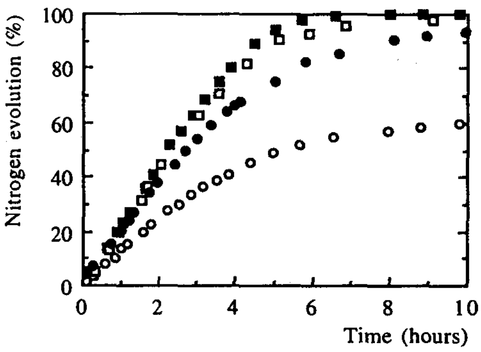

Figure 2. Influence of the substrate on the decomposition rate of ethyl diazoacetate for olefin cyclopropanation catalysed by $PtCl_4$ at 80 °C. (styrene (■); 1-dodecene (□); α-methylstyrene (●); cyclooctene (○)).

resulted in a higher stereocontrol (*endo*/*exo* ratio = 0.2 → 0.55).

Most of the platinum complexes surveyed generally displayed the same reactivity pattern irrespective of the oxidation state of the metal and its ancillary ligands. For all the platinum complexes, the cyclopropane formation exhibited a striking temperature dependence (Table 1 and Figure 1) : the higher the temperature, the higher the cyclopropane yield. The low yields obtained at lower temperature and/or with less reactive substrates can however be enhanced upon addition of a higher amount of the catalyst.[14] In this context, $PtCl_4$ seemed to be the most promising catalyst since, with styrene (60 °C) and cyclooctene (100 °C), the corresponding cyclopropanes were synthesized in reasonable yields. The cyclopropane formation also exhibited a substrate shape preference that may be useful for selective cyclopropanation of polyolefins (Table 2 and Figure 2). Only alk-1-enes and 1,1-disubstituted alkenes reacted efficiently. Thus, 4-substituted styrenes and α-methylstyrene were cyclopropanated efficiently, whereas with cyclooctene diethyl maleate and fumarate were found in higher yield. These coupling products are typically produced when the carbene transfer to the olefin is very slow. With norbornene, 1,3-dipolar addition of ethyl diazoacetate to the substrate was the preferred reaction pathway,[15] whereas with *n*-butyl vinyl ether, polymerisation started upon addition of the substrate to $PtCl_4$.[16]

Table 2. Cyclopropanation of Representative Olefins with Ethyl Diazoacetate in the Presence of $PtCl_4$[a]

Olefin	Cyclopropanation yield, % (*cis*/*trans* or *endo*/*exo* ratio)[b]	Olefin	Cyclopropanation yield, % (*cis*/*trans* or *endo*/*exo* ratio)[b]
Styrene	89 (0.78)	*n*-Butyl vinyl ether	5 (0.53)
4-Methylstyrene	91 (0.75)	1-Octene	68 (0.76)
4-*tert*-Butylstyrene	85 (0.87)	1-Dodecene	72 (0.75)
4-Chlorostyrene	88 (0.76)	Cyclooctene	48 (0.69)
α-Methylstyrene	70 (0.86)	Norbornene[c]	22 (0.25)

[a,b] Reaction conditions same as in Table 1, except the temperature (80 °C). [c] No ring-opening metathesis polymer has been observed upon precipitation of the reaction mixture in technical methanol.[15]

We presume that the active intermediate in these reactions is a platinum carbene species formed by reaction of platinum complexes with ethyl diazoacetate, by analogy to previous work[11-a] in which the $[Pt(CHCO_2Et)(PPh_3)_2]$ species has been detected by fast atom bombardment mass spectrometry. Platinacyclobutanes[17] are also potential intermediates in these reactions as demonstrated by the detection of a carbene-olefin adduct $[Pt(CHCO_2Et)(CH_2{=}CHPh)(PPh_3)_2]$ when the reaction of $Pt(CH_2{=}CH_2)(PPh_3)_2$ with ethyl diazoacetate was carried out in the presence of styrene.[11-a] Work is in progress to extend the scope of these new catalytic systems and to get insights into the mechanism of these reactions.

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14. For cyclopropanation of styrene at 60 °C : 33% yield in the presence of 0.0020 mmol $PtBr_2$; 76% yield in the presence of 0.0043 mmol $PtBr_2$.
15. $[PtCl_2(cyclohexene)]_2$, $PtCl_2(1,5\text{-cyclooctadiene})$, *cis*-$PtCl_2L_2$ (L = triphenylphosphine and pyridine), and $PtBr_2$ have been shown to be inactive for the ring-opening metathesis polymerisation of norbornene, initiated by ethyl diazoacetate or trimethylsilyldiazomethane. For typical reaction conditions, see : Demonceau, A.; Stumpf, A.W.; Saive, E.; Noels, A.F. *Macromolecules* **1997**, *30*, 3127-3136.
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