

Cyclopropanation reactions catalysed by copper(II)-exchanged clays and zeolites. Influence of the catalyst on the selectivity

J. M. Fraile, J. I. García and J. A. Mayoral*†

Departamento de Química Orgánica, Instituto de Ciencia de Materiales de Aragón, C.S.I.C.—Universidad de Zaragoza, Facultad Ciencias, E-50009 Zaragoza, Spain

The reaction of ethyl diazoacetate with styrene is catalysed by Cu^{II}-exchanged clays and zeolites; the *trans/cis* selectivity strongly depends on the nature of the catalyst and when using Cu^{II}-K10 montmorillonite the normal selectivity in solution is reversed and the *cis*-cyclopropane is the major product. The tendency of this catalyst to increase the amount of the product less favoured in solution is confirmed in other reactions.

The development of new methods for the efficient and selective preparation of cyclopropanes is of great interest in organic chemistry due to the frequent existence of these structures in biologically active compounds¹ and their role as valuable synthetic intermediates.² The direct transfer of carbene from diazo compounds to alkenes, which is the most straightforward route to cyclopropanes, is catalysed by transition metals and the use of several metal complexes has been described.^{3,4}

In the reactions of diazo esters, copper catalysts generally provide a high *trans*-selectivity, which is reduced with rhodium and palladium catalysts. To the best of our knowledge there is only one catalyst, the rhodium *meso*-tetraphenylporphyrin complex (RhTPPI), that gives reversed stereoselectivity in reactions of ethyl diazoacetate with certain alkenes.⁵ For instance, when the reaction of ethyl diazoacetate with styrene is catalysed by Cu(acac)₂ a ratio of *trans/cis* = 2.6 is obtained, whereas the reaction catalysed by RhTPPI leads to a ratio of *trans/cis* = 0.88.

During the last few years a great deal of effort has been devoted to the development of heterogeneous systems able to promote organic reactions.⁶ With regard to cycloadditions it has been reported that clays,^{7,8} zeolites⁹ and Lewis acids supported on inorganic solids¹⁰ are able to promote Diels–Alder reactions. The use of clays⁸ and zeolites¹¹ in some [2 + 2] cycloadditions has also been reported.

Copper bronze is a traditional catalyst for cyclopropanation reactions,¹² but the only reference about copper-exchanged clays and zeolites is the use of zeolite NaCuX in the reactions of ethyl diazoacetate with several alkenes.¹³

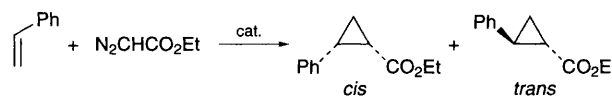
In view of this we tested several clays and zeolites exchanged with Cu^{II} in the benchmark reaction of styrene with ethyl diazoacetate (Scheme 1 and Table 1). The selectivity in diazoacetate was low and did not depend on the catalyst, but the alkene was usually used in a large excess to avoid the dimerisation and polymerisation of the diazoacetate. We also carried out the reactions using equimolar amounts of both reagents. In fact, when a 2:1 excess of styrene was used (Table 2) the selectivity in diazoacetate noticeably increased.

The selectivity in styrene depends on the acidity of the catalyst, given that acid catalysts are able to promote the cationic polymerisation of this reagent. Therefore, the selectivity was increased when the catalyst was modified to reduce the acidity, as is clearly shown in the case of the K10 montmorillonite calcined at 550 °C and end-capped by silylation with Me₃SiCl.⁸

Catalytic activity does not depend on the content of copper and on the previous treatment of the catalyst. Thus, Cu^{II}-exchanged K10 montmorillonite led to similar yields as other clays in spite of the very low amount of copper contained in the clay. Zeolite Y was less active than clays and does not promote the reaction at room temperature. Finally, calcination under dry air reduced the catalytic activity.

The most interesting result was that the *trans/cis* selectivity depended on the nature of the catalyst, so that the Cu^{II}-exchanged K10 montmorillonite was the only copper catalyst able to reverse the normal *trans* preference. This result had only previously been obtained with the expensive RhTPPI.

It is very difficult to propose an explanation for this behaviour, but the role of several factors can be analysed. First of all, the influence of shape-selectivity must be discarded given



Scheme 1

Table 1 Results of the cyclopropanation of styrene with ethyl diazoacetate using several Cu^{II}-exchanged catalysts in CH₂Cl₂^a

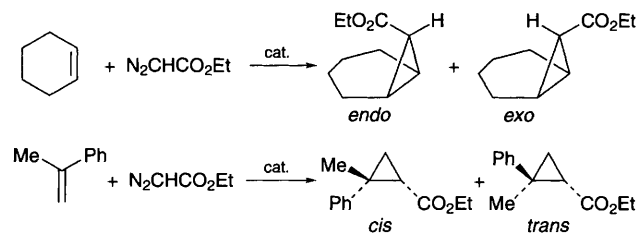
Catalyst (pre-treatment temp./°C)	T/°C	t/h	Styrene (% conv.) ^b	Styrene (% select.) ^b	Diazoacetate (% select.) ^b	<i>trans/cis</i> ^b
Cu ^{II} -K10 (120) ^c	25	0.67	50	44	22	0.8
Cu ^{II} -bentonite (120) ^d	25	0.67	38	61	23	1.8
Cu ^{II} -laponite (120) ^e	25	0.67	43	47	20	1.4
Cu ^{II} -K10 (550)	50	0.67	61	44	27	1.0
Cu ^{II} -K10-EC ^f	50	0.67	38	72	27	1.0
Cu ^{II} -bentonite (550)	25	10	36	77	28	1.3
Cu ^{II} -laponite (550)	25	10	35	79	28	1.4
Cu ^{II} -Y (120) ^g	50	0.67	19	74	14	2.0
Cu ^{II} -Y (550)	50	0.67	38	72	27	1.7

^a Using 30 mg of catalyst mmol⁻¹ of styrene and a 1:1 molar ratio of reagents, the diazoacetate is added in two fractions. ^b Determined by gas chromatography using decane as internal standard. ^c 0.09 mmol Cu g⁻¹, determined by plasma emission spectroscopy. ^d 0.70 mmol Cu g⁻¹. ^e 0.72 mmol Cu g⁻¹. ^f The clay is silylated by treatment with Me₃SiCl (ref. 8). ^g 0.57 mmol Cu g⁻¹.

Table 2 Results of the cyclopropanation of alkenes with ethyl diazoacetate using a 2:1 excess of alkene at 25 °C in CH₂Cl₂^a

Catalyst	Alkene	Alkene (% conv.) ^b	Alkene (% select.) ^b	Diazoacetate (% select.) ^b	<i>trans/cis</i> ^b	<i>endo/exo</i> ^b
Cu ^{II} -K10	styrene	29	80	47	0.8	—
Cu ^{II} -bentonite	styrene	27	89	49	1.8	—
Cu ^{II} -K10	cyclohexene	40	53	42	—	1.6
Cu ^{II} -bentonite	cyclohexene	28	79	44	—	3.6
Cu ^{II} -K10	α -methylstyrene	31	84	52	0.7	—
Cu ^{II} -bentonite	α -methylstyrene	31	98	60	1.2	—

^a Using 30 mg of catalyst mmol⁻¹ of alkene. Catalysts pretreated at 120 °C. The diazoacetate is added dropwise. The catalyst is previously activated by heating at 50 °C for 10 min with a small amount of diazoacetate. ^b Determined by gas chromatography using decane as internal standard.

**Scheme 2**

that the *trans*-cyclopropane is bigger than the *cis*-cyclopropane and the higher *trans* preference was observed with the zeolite Y whereas the solid with the largest pores, namely the K10 montmorillonite, led to a *cis*-cyclopropane preference.

It may be suggested that changes in selectivity originated from catalytic sites in the solid different from the exchanged copper, for instance Fe^{III} of bentonite or K10 montmorillonite. However, the solids without copper do not catalyse the reaction.

It may also be speculated that the formation of small particles of copper oxide is responsible for the changes in the selectivity observed. In order to test this hypothesis we used this solid as a catalyst in the same reaction. As expected, it was less active than the Cu^{II}-exchanged catalysts and it led to *trans/cis* = 2.3, therefore it was not responsible for the unexpected *cis*-preference obtained with Cu^{II}-exchanged K10 montmorillonite.

In view of the above discussion it is difficult to offer an explanation for the changes in selectivity observed. We suggest that changes in the dimensionality of the solid and/or more probably the isolation of the catalytic sites are responsible for this behaviour, taking into account that Cu^{II}-exchanged K10 montmorillonite contains the lowest amount of copper and copper oxide leads to the higher *trans*-preference.

In order to test if the selectivity changes are also observed with other alkenes, we carried out the reactions of ethyl diazoacetate with cyclohexene and with α -methylstyrene (Scheme 2). The results obtained (Table 2) show that the use of Cu^{II}-exchanged K10 montmorillonite as a catalyst favours the formation of the product less favoured in solution, which is also the most sterically hindered.

This work was made possible by the generous financial support of the Comisión Interministerial de Ciencia y Tecnología (Project MAT93-0224).

Footnote

† E-mail: gas@qorg.unizar.es

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Received, 25th March 1996; Com. 6102039I