

## Regioselective Hydrochlorination of Olefins Is Favored by an Acidic Solid Catalyst

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*Abstract* : With thionyl chloride  $\text{SOCl}_2$  as HCl precursor, 1-methylcyclohexene is hydrochlorinated. In the absence of a solid catalyst, between half and two-thirds of the product mixture are the anti-Markovnikov adduct, trans 1-chloro-2-methyl cyclohexane. Catalysis by the ZF 520 zeolite or the K10 montmorillonite makes the reaction selective. It then affords a quantitative yield of (10:1) Markovnikov adduct 1-chloro-1-methylcyclohexane.

A recent communication by Kropp *et al.*<sup>1</sup> on the use of suspended alumina or silica to speed-up and render stereoselective the addition of hydrogen halides to olefins prompts us to disclose our complementary exploratory work in this area. We opted to study hydrochlorination, known to be less brutal a reaction than hydrobromination, from thionyl chloride  $\text{SOCl}_2$  as a convenient precursor of HCl. We chose 1-methylcyclohexene as the test olefin. To obtain authentic samples of the adducts, 1-chloro-1-methylcyclohexane, and the diastereoisomeric 1-chloro-2-methyl cyclohexanes *cis* and *trans*, we converted the corresponding alcohols into the chlorides, a tricky procedure for which conflicting and sometimes difficult to duplicate reports have appeared<sup>2-12</sup>.

Our first impulse was to try and emulate our earlier success with the zeolites 13NaX and ZF520 in favoring either the radical or the ionic chlorination, respectively, of aromatic hydrocarbons from sulfuryl chloride  $\text{SO}_2\text{Cl}_2$ <sup>13</sup>. The ionic addition would be promoted, we felt, by catalysts having a strong Brønsted acidity, such as the K10 montmorillonite or, better yet, a zeolite with a high silicon-to-aluminum ratio, such as ZF520 that is characterized with a silicon-to-aluminum ratio of about 20<sup>13</sup>. For comparison's sake we tried also two common chromatographic adsorbents, alumina and silica ; and together with this the war horse from our stable the K10 montmorillonite<sup>14</sup> a kaolinite<sup>15</sup>. For comparison's sake we ran a control reaction in the absence of any solid catalyst (run 1) and we performed also a reaction under classical conditions for a

radical process, with benzoyl peroxide as an initiator, which we complemented with UV irradiation (run 2).

**Typical procedure :**

In a 25 mL flask purified<sup>16</sup> 1-methylcyclohexene (0.9617 g; 10 mmol ) is introduced together with 10 mL of dry methylene chloride and together with 1 g of a) no additive; b) recrystallized benzoyl peroxide ; c) alumina p.a. Merck ; d) NaX zeolite, Aldrich molecular sieve 13X; e) ZF520 zeolite, Zéocat; f) silicagel for chromatography, Janssen; g) K10 montmorillonite, Süd-Chemie; h) kaolinite, B.E.T. specific surface 19 m<sup>2</sup>.g<sup>-1</sup>, Kaolins d'Arvor. The suspension is cooled in an ice bath prior to addition of freshly distilled thionyl chloride (1.784 g, 15 mmol) and of dry methylene chloride (5 mL). One adds yet *n*-nonane (1 mL) as a GC internal standard prior to analysis of the reaction mixture. Stirring is maintained and sampling is done repeatedly at two-hourly intervals, with the reaction mixture thermostatted at 0°C. The suspension returns to ambient temperature after six hours of reaction at 0°C, and a last GC injection is done after 21 h of reaction. The GC results, because of the poor sensitivity of the flame ionization detector to chloro compounds, and because of the questionable purity of the 1-chloro-1-methylcyclohexane used for normalization, are good only to +/- 3%.

A first result is the coexistence of only two products. Together with 1-chloro-1-methylcyclohexane (that arises from the Markovnikov electrophilic addition), only *trans* 1-chloro-2-methylcyclohexane (from a radical mechanism with anti-Markovnikov orientation) is formed.

Table 1 - Yields and Regioselectivities (1,1/ *trans*-1,2) in the Hydrochlorination of 1-Methylcyclohexene.as a Function of Reaction Time.

Run/Catalyst	2h	4h	6h	21h
1. ----	25 (44/56)	16(48/52)	16 (60/40)	20 (72/28)
2. BzOOBz,hv <sup>a</sup>	63 (26/74)	67 (31/69)		43 (74/26)
3. alumina	20 (70/30)	20 (82/18)	22 (80/20)	33 (77/23)
4. NaX zeolite	15 (45/55)	28 (40/60)	26 (64/36)	68 (89/11)
5. ZF520 zeolite	89 (96/4)	87 (97/3)	98 (92/8)	98 (92/8)
6. silica	84 (89/11)	88 (89/11)	93 (88/12)	89 (95/5)
7. K10	98 (91/9)	97 (89/11)	92 (92/8)	100 (91/9)
8. kaolin	56 (78/22)	63(66/34)	61 (69/31)	70 (83/17)

<sup>a</sup> a UV lamp 5 cm from the Pyrex flask irradiated the reaction mixture during the first four hours.

The uncatalyzed reaction (Table 1) displays the rivalry between the two modes, radical and ionic; non-selective in the early stages, it slowly establishes a marked but far from total dominance of the latter. Such an isomerization is far from unprecedented. It

is well known that hydrohalogenation of olefins is a reversible process. One way to prevent it (run 2) is initiation of a free-radical chain reaction and its maintenance using UV irradiation. When such illumination is removed, the isomerization resumes (run 2, 21h). Yields furthermore remain very low and impractical. Two of the solids that were tried, alumina and the 13NaX zeolite are devoid in our hands of any useful effect. The attendant results (runs 3 and 4) are close to those obtained on the control (run 1).

Four solids have an effect, relatively minor with kaolinite, but spectacular with silica, with the K10 montmorillonite, and with the zeolite ZF520. With all these, highly regioselective ionic addition is observed. In terms of selectivity, better results stem from the use of the zeolite (run 5; an average value of 94:6) than with silica<sup>1</sup> (88:12). *One can thus recommend using this zeolite or the K10 montmorillonite together with a reaction time of two to six hours to combine a high, quantitative yield, with a high regioselectivity.* The K10 montmorillonite (90:10) and kaolinite (an average value of 76:24) indeed also perform well. Rather than just an empirical finding, it was entirely predictable that the more acidic catalysts, K10 and ZF520, should give the best results: rational design proved its worth once again !

Thus another reaction important for organic chemistry gets to be renovated. It illustrates one of these standard cases in which teaching is too remote from reality. We teach our undergraduate students the ease of addition of hydric acids to olefins. We fail to warn them that the reaction takes place, in actual practice, only with special, activated olefins such as norbornene. In more "normal" cases, elevated reaction temperatures and prolonged reaction times are mandatory. The solution we submit here, if it is of general applicability, brings very mild conditions to bear on hydrochlorination.

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12. The *cis* methyl-2-cyclohexanol (0.1 mol) is converted into chloro-1-methyl-1-cyclohexane by SOCl<sub>2</sub> (0.2 mol) in the presence of pyridine (0.1 mol) at ambient temperature in 1.5 h. [ Botteron and Shulman reported having prepared *cis* 1-chloro-2-methyl-cyclohexane from the corresponding alcohol using thionyl chloride in pyridine<sup>9</sup>, in contrast to these findings ]. The *trans* methyl-2-cyclohexanol (80 mmol) when treated by HCl (37 %, 20 mL) at reflux for 3 h gives 27 % of chloro-1-methyl-1-cyclohexane together with 56 % of *trans* chloro-1-methyl-2-cyclohexane, 8 % of the *cis* diastereoisomer and 9 % of chloro-2-ethylcyclopentane. [ This is another procedure of Botteron and Shulman<sup>9</sup> in which they have claimed exclusive formation of the *trans* 1-chloro-2-methylcyclohexane ]. By distillation on a rotary band column, we could enrich a fraction enough in the *trans* isomer (> 65 %, T<sub>eb</sub> 36-40° C/13mm) to record its pmr spectrum<sup>11</sup> and to identify it securely in the gas chromatograms. However, the purity of this compound was insufficient for a reliable normalization of the chromatograph.
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16. Dried on anhydrous MgSO<sub>4</sub> prior to distilled under reduced pressure (T<sub>eb</sub> 20-21°C/22 mm) in the presence of LiAlH<sub>4</sub>, and stored in a refrigerator.

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