CHEMISTRY LETTERS, pp. 1031-1034, 1989.

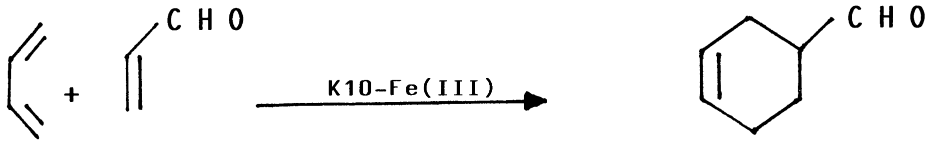
Catalysis of Diels-Alder Reactions with Acrolein as Dienophile by Iron(III)-Doped Montmorillonite

Pierre LASZLO* and Hélène MOISON
Laboratoire de Chimie Fine, Biomimétique et aux Interfaces,
Ecole Polytechnique,
91128 Palaiseau Cédex, France

Acrolein is improved as a dienophile in the presence of the K10 montmorillonite exchanged with iron(III). Cycloaddition occurs with a number of dienes at room temperature and in high yield. Dienes tested include butadiene, isoprene, cyclopentadiene, cyclohexadiene, 1-methoxycyclohexadiene, anthracene.

Acrolein is a choice dienophile for Diels-Alder cycloadditions with normal electron demand : an electron-rich diene (HOMO) combining with an electron-poor (LUMO) dienophile. It gives access to numerous functionalized cyclic olefins. Lewis acids catalyze the reaction.1,2) They lower the dienophile LUMO, thus decreasing the energy gap between the frontier orbitals of the reaction partners.

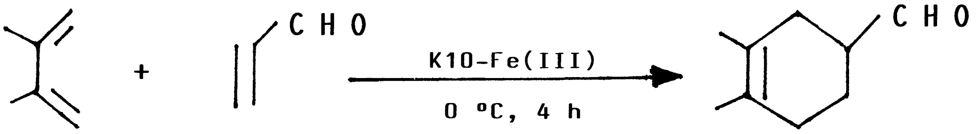
Another way to speed-up the reaction takes advantage of Le Chatelier's principle : since the Diels-Alder reaction has a negative volume of activation, increasing the pressure reduces the energy barrier. Indeed, reticent furan dienes can be coerced into cycloaddition by application of pressures of ca. 15 kbars.3) We have shown in an earlier study4) that such Diels-Alder reactions involving furans are performed efficiently at ambient pressure, using as a catalyst the K10 montmorillonite ion-exchanged with ferric ions.4)



The same catalytic system proved more generally its worth for Diels-Alder reactions between unactivated hydrocarbon partners;5) and it gave, in organic solvents such as methylene chloride, impressive stereoselectivities6) comparable to those achieved by aqueous Diels-Alder reactions.7) It remains to define optimum reaction conditions for a normal electron demand Diels-Alder reaction catalyzed by K10-Fe(III); this is the goal of the present study, in which we react acrolein with a number of dienes.

Why choose acrolein? Because of its industrial importance. And also because it is liable to polymerization : which makes a high yield Diels-Alder cycloaddition more of a challenge to achieve. Thus success in meeting such a goal would carry the more general significance of catalysis of the normal-electron demand Diels-Alder, a reaction of crucial importance in organic synthesis.

We started by focussing once more on the test reaction below. We had already explored its promise :5)



Preliminary runs at 0 °C in methylene chloride5,6) gave these useful indications :

i. When the liquid reactants are impregnated on the modified clay without solvent, homopolymers of acrolein and of the diene predominate. Conversely, high dilutions (concentration below decimolar) produce selectively the desired cycloadduct. An interpretation is preferential solvatation of Brønsted acidic sites leaving Lewis acidic sites free to catalyze the cycloaddition. Under such high dilution conditions, methylene chloride gives better yields than benzene, 1,4-dioxane, ether or acetonitrile.

ii. Addition of 10% (w/w) 4-t-butylphenol increases the yield and the chemiselectivity. The phenol acts as a co-catalyst : under the same conditions a polymerisation inhibitor, hydroquinone, leads to the same selectivity but with a lower yield. The role of the phenol is believed to be the production of radical cations when adsorbed onto a clay.8) Radical cations are now known to catalyze Diels-Alder reactions, those between unactivated hydrocarbon partners in particular.9)

The attempted cycloreversion on the tetrahydrobenzaldehyde product at 0 °C and at 20 °C in the joint presence of the K10-Fe(III) catalyst and of either maleic anhydride, as a diene trap, or of hexachlorocyclopentadiene, as a dienophile trap, did not occur.

Accordingly, we proceeded with a Simplex optimization,10) a standard procedure in our laboratory,11) on the same test reaction (Eq.1). A 90% yield was obtained for the reaction during four hours at 20 °C with 1.8 g of K10-Fe(III) and 0.13 g of 4-*t*-butylphenol for an equimolar mixture of the reaction partners (15 mmol each) in 75 mL of methylene chloride.

Table 1. Diels-Alder Reaction of Acrolein with Different Dienes in the Presence of the K10-Fe(III) Catalyst.

Diene	Temperature °C	Time h	Yield %
Butadiene	20	6	83
Isoprene	40	2.5	70
2,3-Dimethylbutadiene	20	4	90[a)]
Cyclopentadiene	20	1	97
Cyclohexadiene	20	24	55
Anthracene	20	24	96

a) Addition of 0.13 g 4-*t*-butylphenol.

These conditions have been extended to other dienes (Table 1). The phenol co-catalyst is a mixed blessing, since it can induce the competitive cycloaddition of the diene on itself;[9)] and we have been able to dispense with it in most cases, except for the test reaction itself. The reaction conditions defined in the present study are a compromise between reaction temperature, time and selectivity. For instance, isoprene does not add acrolein immediately at room temperature and after 24 h side reactions take place. Moderate heating activates the reaction which should be stopped early enough to prevent polymerization or degradation of the cycloadduct.

The observed stereoselectivities are similar to those obtained with Lewis acid catalysis, whereas the yields are higher,[12)] close to the ones reached under much drastic conditions, at high temperature and pressure.[13,14)]

Thus, Diels-Alder cycloaddition with normal electronic demand, a reaction central to organic chemistry, can be performed efficiently under mild conditions.

Experimental procedure is as follow : K10-Fe(III) :[15)] To 1 L of a stirred aqueous solution (1 M) of $FeCl_3$, 80 g of K10 clay are added. Stirring is maintained for 24 h. The clay suspension is centrifuged, and the supernatant solution is discarded. The clay catalyst is washed with distilled water (suspension, stirring, centrifugation), and the washing cycles are repeated untill disappearance of Cl^- ions from the discarded water. The clay, after drying overnight in an oven at 120 °C, is finely ground in a mortar.

To the equimolar mixture of 15 mmol of the reactants in 50 mL or 75 mL of CH_2Cl_2 is added 1,8 g of K10-Fe(III). The catalyst is dried overnight at 120 °C prior to use. The suspension is stirred for a reaction time adapted to the reactants as listed in Table 1. The clay is filtered off rapidly, whashed twice with 10 mL of CH_2Cl_2 and the solvent is then evaporated. The residual oil or solid is then analysed by NMR spectrometry (Bruker AC 200). We thank ATOCHEM (Elf Aquitaine group) and CNRS for their joint support of this research. We thank Süd-Chemie (Munich) for the gift of the K10 sample.

References

1) P. Yates and P. Eaton, J. Am. Chem. Soc., 82, 4436 (1960).
2) S. Danishefsky and M. Bednarski, Tetrahedron Lett., 26, 2507 (1985).
3) W.G. Dauben and H.O. Krabbenhoft, J. Am. Chem. Soc., 98, 1992 (1976).
4) P. Laszlo and J. Lucchetti, Tetrahedron Lett., 25, 4387 (1984).
5) P. Laszlo and J. Lucchetti, Tetrahedron Lett., 25, 1567 (1984); J. Cabral, P. Laszlo and M.T. Montaufier, ibid., 29, 547 (1988).
6) P. Laszlo and J. Lucchetti, Tetrahedron Lett., 25, 2147 (1984).
7) D.C. Rideout and R. Breslow, J. Am. Chem. Soc., 102, 7816 (1980); R. Breslow, O. Maitra,and D. Rideout, Tetrahedron Lett. 24, 1901 (1983).
8) H.E. Doner and M.M. Mortland, Science, 166, 1406 (1969); M.M. Mortland and T.J. Pinnavaia, Nature (London), 229, 75 (1971); J. Phys. Chem.;, 75, 3957 (1971); J.P. Rupert, J. Phys. Chem., 77, 784 (1973); D. Fenn, M.M. Mortland, and T.J. Pinnavaia, Clays Clay Miner., 21, 315 (1973); T.J.Pinnavaia, P.L. Hall, S.S. Cady, and M.M. Mortland, J. Phys. Chem., 78, 994 (1974); M.M. Mortland and L.J. Halloran, Proc. Soil Sci. Soc. Am., 40, 367 (1976); P.J. Isaacson and B.L. Sawhey, Clay Miner., 18, 253 (1983).
9) N.L. Bauld, D.J. Bellville, B. Harirchian, K.T. Lorenz, R.A. Pabon, D.W. Reynolds, D.D. Wirth, H.S. Chiou, and B.K. March, Acc. Chem. Res., 20, 371 (1987).
10) S.N. Deming and D.M. Morgan, Anal. Chem., 45, 278A (1973).
11) J. Florkin and P. Laszlo, Actualité Chimique, 1985, September, 53.
12) G.I. Fray and R. Robinson, J. Am. Chem. Soc., 83, 249 (1961); E.F. Lutz and G.M. Bailey, ibid., 86, 3899 (1964).
13) J.P. Schirmann, G. Bonnard, and F. Weiss, Bull. Soc. Chim. Fr., 3326 (1968).
14) B.A. Arbuzov, A.I. Konovalov, and Yu. Yu. Samitov, Dokl. Akad. Nov. SSSR, 143, 109 (1961); Chem. Abstr., 57, 4521c (1962).
15) P. Laszlo and A. Mathy, Helv. Chim. Acta, 70, 577 (1987).

(Received February 17, 1989)