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EASY FORMATION OF DIELS-ALDER CYCLOADDUCTS BETWEEN FURANS AND α,β-UNSATURATED ALDEHYDES AND KETONES AT NORMAL PRESSURE.

Pierre Laszlo* and Jean Lucchetti
Institut de Chimie Organique
Université de Liège au Sart-Tilman
4000 Liège, Belgium.

Abstract : The K-10 bentonite clay doped with Fe^{III} or, even better $AlCl_3$ alone catalyse the Diels-Alder reaction between furan or dimethyl-2,5-furan and either acrolein or methyl- vinylketone. The cycloadducts are obtained with isolated yields in the range 20-81%.

CENTRAL to organic theory[1] and practice[2], the Diels-Alder reaction still presents several challenges : hence, much recent work has striven to make it more generally applicable than to the usual prescription of electron-rich dienes and electron-poor dienophiles. Radical-cation catalysis has been applied successfully to unactivated dienes and dienophiles[3-4]. In another important breakthrough, recourse to water rather than organic solvents as reaction medium has also led to considerable improvements in reaction times and stereoselectivities[5-7].

Use of furans as dienes is another sector where effort is clearly needed. True, some (4+2) cycloadditions have been forced into a measure of success by application of huge pressures, 15,000 atm typically[8,9]. We report here alternative conditions to make such reactions go under very mild conditions. Our tactics builds on earlier reports of Lewis-acidic catalysis for such reactions[10,11]. However, when these procedures[10,11] are applied with acrolein or with methylvinylketone as dienophile, polymers or furan ring substitution products are obtained[10].

Hence, and in order to bypass cycloreversion which occurs at room temperature or above, we have opted for Lewis acid catalysis (0.1 g/mmol reactant Fe^{III}-doped K-10 bentonite clay = procedure A; 15 mol % $AlCl_3$ = procedure B) at low temperature (-43°C) in methylene chloride. The methodology introduced here commends itself, we feel, by its greater ease of implementation as well as by somewhat superior results. It will greatly facilitate the access to the 7-oxabicyclo (2.2.1) heptane system, which features in a number of important natural products, which have been targets of synthetic efforts.

Diene	Dienophile	Conditions	Isolated yield (%)	exo/endo[a]	Reference
furan	methylvinylketone	15,000 atm; 4 h	48	ca. 1	8
furan	methylvinylketone	A; 6 h	60	2.2	this work
furan	methylvinylketone	B; 15 mn	81	1.3	this work
furan	acrolein	15,000 atm; 4 h	53	ca. 1	8
furan	acrolein	A; 5 h	24	10	this work
furan	acrolein	B; 15 mn	65	5	this work
dimethyl-2,5-furan	methylvinylketone	15,000 atm; 4 h	36	ca. 1	8
dimethyl-2,5-furan	methylvinylketone	A; 5 h	65	0,6	this work
dimethyl-2,5-furan	methylvinylketone	B; 15 mn	19	0,7	this work
dimethyl-2,5-furan	acrolein	15,000 atm; 4 h	42	ca. 1	8
dimethyl-2,5-furan	acrolein	A; 5 h	40	1	this work
dimethyl-2,5-furan	acrolein	B; 30 mn	< 5	-	this work

[a] determined by ^1H nmr (Bruker AM 300 WB)

Note : it is important to remove the catalyst (A or B) before work-up at ambient temperature, otherwise the retro Diels-Alder reaction is immediate; $AlCl_3$ is eliminated by addition of an aqueous saturated solution of K_2CO_3 at -43°C, contact for 5 mn and return to room temperature.

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