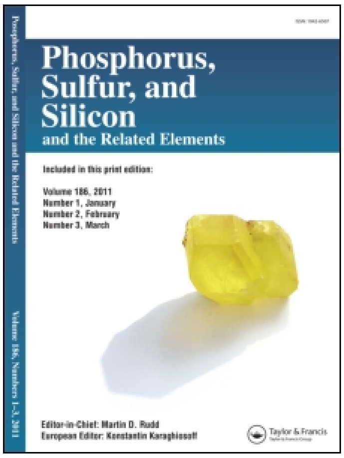

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REACTIVITY AND STEREOSELECTIVITY IN THE DIELS-ALDER REACTIONS BETWEEN CYCLOPENTADIENE AND SOME α,β-UNSATURATED THIOESTERS.

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Abstract Some new norbornene thioester derivatives of endo configuration are sinthesized. Proofs are provided that thioester group has more preference for endo configuration than the ester group.

The stereoselectivity of the Diels-Alder reaction between cyclopentadiene and electron deficient dienophiles has been subject of much interest from the synthetic[1] as well as mechanistic[2,3] side. The Alder endo rule showed to be more effective in the catalysed reactions. Thus, the increase of the endo selectivity was reported for the reaction of some α,β-unsaturated esters, using as Lewis catalyst aluminum chloride[4]. Recently[5], catechol boron bromide was employed, with success, for the Diels-Alder reaction between cyclopentadiene and some vinyl-aldehydes, vinyl-ketones, α,β-unsaturated esters and vinyl-nitriles, leading to the corresponding adducts preponderantly endo.

The investigation of the stereoselectivity of the reaction of cyclopentadiene with α,β-unsaturated thioesters of E configuration, obtained in our laboratory by thermolysis of the α-sulfinyl-thioesters[6], seemed to be desirable due to the difference in size and electronic character between thioester and ester group$^{7-10}$.

Table I shows the endo:exo ratio for the adducts from the α,β-unsaturated thioesters studied (1a,2a,3a,4a and 5), in the presence of Lewis acid catalysts, such as aluminum chloride and catechol boron bromide, at 30°C and -70°C, respectively, compared with those for the corresponding esters (1b,2b,3b and 4b). In the presence of aluminum chloride the percentages of the endo isomers for the α,β-unsaturated thioesters were higher (89-99%) than those for the correesponding esters (60-94%). However, in the presence of a more effective Lewis acid catalyst, such as catechol boron bromide, 100% of endo adduct is observed for both series. Methyl thiocynnamate (4a), as well as the corresponding ester (4b), did not react with cyclopentadiene in the presence of aluminum chloride. However, in the presence of catechol boron bromide, 4a and not 4b showed to be reactive to give the corresponding adduct 87% endo. Interesting result was obtained for the methyl monothiofumarate (5) which afforded endo:exo ratio of 50:50 in the uncatalysed reaction, 65:35 in the presence of aluminum chloride and 81:19 in the presence of catechol boron bromide. These results are in line with those for the aluminum chloride catalysed reaction of α,β-unsaturated thioesters and esters and indicate that the thioester group has more preference for endo configuration than the ester group.

It seemed reasonable to admit that the increase of the endo selectivity in the case of α,β-unsaturated thioesters, in comparison with the corresponding esters, could be due to a more effective complexation of the carbonyl group by acid Lewis catalyst, in the former species. In fact, the ^{13}C NMR chemical shifts for the coordinated carbonyl groups, in the

TABLE I Yields[a] and endo:exo ratio[b] for the adducts[c] of catalysed reactions of cyclopentadiene with α,β-unsaturated thioesters and esters.

Dienophiles H C=C R' R Y			A[d] endo:exo	B[e] endo:exo
1a	R=R'=H	Y=COSMe	99:1	100:0
1b		CO_2Me	94:6[f]	100:0[h]
2a	R=Me R'=H	COSMe	97:3	100:0
2b		CO_2Me	93:7[f]	100:0
3a	R=H R'=Me	COSMe	89:11	100:0
3b		CO_2Me	60:40[f]	100:0
4a	R=Ø R'=H	COSMe	-	87:13
4b		CO_2Me	-	-
5	R=CO_2Me R'=H	COSMe	65:35[g]	81:19[g]

[a] Isolated products. [b] Calculated from the relative intensities of the ^1H NMR SMe, OMe or C_6H_5 isomers signals and confirmed by g.l.c. [c] All were new compounds and were fully characterized by elemental analysis and ^1H NMR and IV Spectroscopy. [d] $AlCl_3$. [e] Catechol boron bromide. [f] Reference 4. [g] COSMe:CO_2Me. [h] Reference 5.

presence of catechol boron bromide for the monothiofumarate (5), compared with the corresponding values for the uncoordinated carbonyl groups in the same compound and in some α,β-unsaturated thioesters (1a),(2a) and the corresponding esters (1b),(2b), confirmed our supposition (Table II).

It may be seen that a larger deshielding effect due to complexation (approx. 7ppm) occurs for the thioester group than for the ester group (approx. 4ppm).

The reported results are unique examples of α,β-unsatu-

TABLE II ^{13}C NMR[a] CO chemical shifts (ppm) for some α,β-unsaturated thioesters and esters.

Entry	Thioester group	Entry	Ester group
1a	190.1	1b	166.5[c]
2a	188.9	2b	166.1[d]
4a	190.0	4b	167.1
5	189.2	5	165.5[e]
	196.0[b]		169.4[b]

[a] Bruker AC-200 spectrometer, in chloroform. [b] CO coordinated with catechol boron bromide. [c] The Sadtler Collection, spectrum No. 2813. [d] Ibid, spectrum No.1959. [e] Ibid, spectrum No. 4624.

rated thioesters as dienophiles. They open the synthetic possibilities for other norbornene derivatives of endo configuration.

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