CAPTO-DATIVE SUBSTITUENT EFFECTS. 12<sup>1</sup> - NEW KETENE EQUIVALENTS FOR DIELS-ALDER CYCLOADDITIONS

Lucien Stella<sup>\*</sup> and Jean-Luc Boucher

Laboratoire de Chimie Organique B, associé au CNRS, Faculté des Sciences St-Jérôme - 13397 Marseille Cedex 13 (France)

Summary : We describe the use of "capto-dative" olefins <u>1</u> as novel ketene equivalents which behave as efficient dienophiles in the Diels-Alder process.

The intrinsic instability of ketene and its tendency to form 2+2 cycloadducts are well known<sup>2</sup> Although some geminally disubstituted olefins have been used as ketene equivalents<sup>3</sup>, their general synthetic applicability is frequently reduced either because of their sluggishness in the 4+2 cycloaddition reaction step or due to the drastic conditions and/or lengthy work-up necessary for the further transformation of the adducts to ketones As a part of our interest in the field of *capto-dative* substituent effects<sup>4</sup> in organic chemistry, we investigated the aptitude of *capto-dative* olefins <u>1</u> for performing 4+2 cycloadditions with conjugated dienes<sup>5</sup> Some recent reports<sup>6</sup> prompt us to publish our first promising results



 $\alpha$ -Morpholino acrylonitrile<sup>7</sup> <u>la</u>,  $\alpha$ -methylthioacrylonitrile<sup>8</sup> <u>lb</u> and methyl  $\alpha$ -methylthioacrylate<sup>9</sup> <u>lc</u> are easily prepared and handled They react with conjugated dienes to afford oroducts of Diels-Alder addition in good yield. Several examples, along with reaction conditions used are given in the Table. The cycloadditions do not occur in refluxing solvents such as ether, benzene, chlorobenzene or dimethylformamide, but they can be brought about by heating the neat diene-dienophile mixture to 140-160°C. With isoprene <u>2a</u> and cyclohexadiene <u>2c</u> only 4+2 cycloadditions occur. Cyclopentadiene <u>2b</u> leads also to 4+2 cycloadducts but an

	2)				Reaction conditions				
Dienophile <u>1</u>	11e Diene <sup>d)</sup> <u>2</u>	Adducts	Overal yıeld	Isomer ratıo a/b	Diene (Dienophile)	Lewis acid	(Lewis acid) (Dienophile)	temp (°C)	tıme (hr)
<u>1a</u>	<u>2a</u>	<u>3</u> a,b	62	d)	3			160	6
<u>1a</u>	<u>2b</u>	<u>6</u> a,b	92	50/50	3			160	6
<u>1a</u>	<u>2b</u>	<u>6</u> a,b	32 <sup>b)</sup>	50/50	5			160	6
<u>1a</u>	<u>2c</u>	<u>9</u> a,b	92	30/70	15			160	6
<u>1b</u>	2a	<u>4</u> a,b	62	96/4	2			140	4
<u>1b</u>	<u>2b</u>	<u>7</u> a,b	57	50/50	15			140	6
<u>1b</u>	<u>2b</u>	<u>7</u> a,b	44 <sup>c)</sup>	50/50	3			160	4
<u>1b</u>	<u>2c</u>	<u>10</u> a,b	50	23/77	15			160	4
<u>1b</u>	2 <u>a</u>	<u>4</u> a,b	81	97/3	5	A1C1 <sub>3</sub>	05	20	6
<u>1b</u>	<u>2b</u>	<u>7</u> b	60	0/100	2	A1C1 <sub>3</sub>	02	20	0 25
<u>1b</u>	<u>2b</u>	<u>7</u> b	88	0/100	5	Cu(BF <sub>4</sub> ) <sub>2</sub>	05	20	6
<u>1b</u>	<u>2c</u>	<u>10</u> a,b	72	17/83	5	A1C1 <sub>3</sub>	05	20	6
<u>1c</u>	<u>2a</u>	<u>5</u> a,b	84	97/3	5	A1C1 <sub>3</sub>	0.5	20	4
<u>1c</u>	<u>2b</u>	<u>8</u> b	77	0/100	5	A1C1 <sub>3</sub>	05	20	4
<u>1c</u>	<u>2c</u>	<u>11</u> b	81	0/100	5	A1C1 <sub>3</sub>	05	20	4

a)  $\underline{2a}$  = 1soprene,  $\underline{2b}$  = cyclopentadiene,  $\underline{2c}$  = cyclohexadiene

b) together with 48% of  $\underline{12}$  , c) together with 36% of  $\underline{13}$ 

d) not determined





increase of its relative concentration leads to the competition between the Diels-Alder 4+2 process and the 2+2 cycloaddition with dicyclopentadiene<sup>10</sup> The addition of a Lewis acid to the reaction mixture leads to the decomposition of  $\underline{la}^{11}$  but accelerates the reaction of  $\underline{lb}$  and  $\underline{lc}$  so that it proceeds even at room temperature in benzene solution. The ratio of isomers is determined by NMR analysis for the adducts  $\underline{6}$  and 9 and by NMR and GC analysis for the other ones. Except for  $\underline{3}$  and 6, the mixtures of isomers are readily separated by means of column chromatography on silica gel<sup>12</sup>. It is noteworthy that in the case of cyclopentadiene  $\underline{2b}$ , for example, the thermic reactions lead to a 50/50 mixture of the two isomers  $\underline{7a}$  and  $\underline{7b}$ , while in the presence of Lewis acid at room temperature no *endo*-CN isomer  $\underline{7a}$  can be detected and the *exo*-CN isomer 7b is formed exclusively.

Concerning further transformation of the adducts it is of interest to note that

 $\alpha$ -dialkylamino nitriles<sup>13</sup> and  $\alpha$ -alkylthio esters<sup>14</sup> can be converted to ketones by mild and simple means. All these facts place the *capto-dative* olefins, especially the  $\alpha$ -alkylthio-acrylates, among the best ketene equivalents hitherto studied. Further systematic investigations of largest series of *capto-dative* olefins and conjugated dienes are in progress to illustrate the possibilities, limitations and features of this mild reaction process.

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## REFERENCES AND NOTES

- 1- Capto-dative substituent effects, Part 11 A, De Mesmaeker, L Vertommen, R Merényi, and H.G. Viehe, Tetrahedron Lett., in print
- 2- W.T. Brady, Synthesis, 415 (1971), H. Ulrich, "Cycloaddition Reactions of Heterocumulenes" p. 38-121, Academic Press, Inc., New York, 1967; R.S. Ward and W.T. Brady, in "The Chemistry of Ketenes, Allenes ans Related Compounds", (S Patai, ed.), Part 1, Chap. 7 and 8, Wiley (interscience), New York, 1980.
- 3- S. Ranganathan, D Ranganathan and A.K Mehrotra, Synthesis, 289 (1977)
- 4- H.G. Viehe, R. Merényi, L. Stella and Z. Janousek, Angew. Chem Int. Ed. Engl, <u>18</u>, 917 (1979).
- 5- The spontaneous and reversible (2+2) cyclodimerisation of olefin <u>1b</u> to cyclobutane derivate<sup>15</sup> has been interpreted<sup>4</sup> as the result of the proradical nature of captodatively substituted carbon atoms.
- 6- I. Alfaro, W Ashton, K.L. Rabone and N A.J Rogers, Tetrahedron, <u>30</u>, 559 (1974),
  J Quick and R. Jenkins, J. Org Chem., <u>43</u>, 2275 (1978); J. Tamariz and P. Vogel,
  Helv Chim. Acta, <u>64</u>, 188 (1981), H. Horikawa, T. Nishitani, T Iwasaki, Y Mushika,
  I. Inoue and M Miyoshi, Tetrahedron Lett, 4101 (1980), S Knapp, R Lis and P. Michna,
  J. Org. Chem., <u>46</u>, 624 (1981), R J Ardecky, F A J Kerdesky and M P. Cava, *ibid*,
  46, 1483 (1981).
- 7- S.C. Temin, J Org. Chem., 22, 1714 (1957)
- 8- K.D. Gundermann and R Thomas, Chem. Ber, 89, 1263 (1956).
- 9- K.D. Gundermann and H. Schulze, *ibid*, 94, 3254 (1961)
- 10- We are extending our study with other simplest olefinic systems to help us gain a better understanding of this unexpected (2+2) cycloaddition.
- 11- In the case of  $\underline{1a}$ , the effect of AlCl<sub>3</sub>, SnCl<sub>4</sub>, Cu(BF<sub>4</sub>)<sub>2</sub> and CuBr<sub>2</sub> has been studied
- 12- Structural assignment of the adducts is supported by infrared, <sup>1</sup>H and <sup>13</sup>C magnetic resonance and mass spectral data
- 13- G. Buchi, P.H. Liang and H. Wuest, Tetrahedron Lett., 2763 (1978).
- 14- B M Trost and Y Tamaru, J Am Chem Soc , 99, 3101 (1977)
- 15- K D Gundermann and E Rohrl, Justus Liebigs Ann Chem , 1661 (1974).
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