7429-44-9; 2-(trifluoromethyl)cyclohexanone, 56734-74-8; 2-bromocyclohexanone, 822-85-5; 2,6-dimethylcyclohexanone, 2816-57-1; 2-chloro-2,6-dimethylcyclohexanone, 84928-32-5; oxygen, 7782-44-7.

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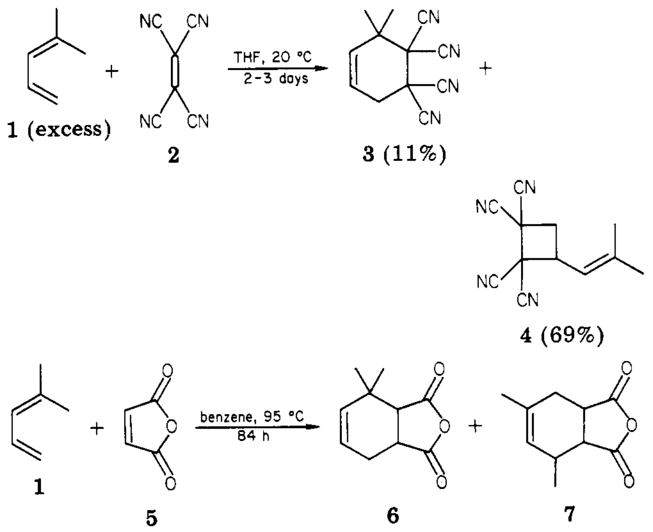
Synthesis and Diels-Alder Reactions of Allylidenecyclopropane

Summary: Allylidenecyclopropane, readily available from 1-lithio-1-(phenylthio)cyclopropane, reacts with a large variety of electrophilic olefins and produces functionalized spirooctenes. The reactions are, in most cases, highly regioselective but lead mainly to the unexpected regioisomers.

Sir: Despite the wide applicability of the Diels-Alder[1] reaction, there remain cases for which the cycloaddition cannot be achieved due to the lack of reactivity of one of the two partners. This is the case, among others, of 1,1-disubstituted butadienes.[1-5] For example, 4-methyl-1,3-pentadiene (1) is known to react very sluggishly with reactive dienophiles such as tetracyanoethylene[3] and maleic anhydride,[4,5] leading to various cycloadducts 4 and 7 besides the expected ones, 3 and 6 (Scheme I).

We report our results concerning the reactivity of allylidenecyclopropane (**10**) toward some electrophilic olefins. Although it is a member of the 1,1-dialkyl-substituted family, it is expected to be far more reactive than 1 due to the strain present in the alkylidenecyclopropane moiety. This should provide a very direct access to the spiro[2.5]octene system, present as a substructure in some natural products (i.e., illudins[7]) and that could also serve as a precursor of 1,1-dimethylcyclohexanes.[8]

Scheme I



1 (excess)

2

3 (11%)

4 (69%)

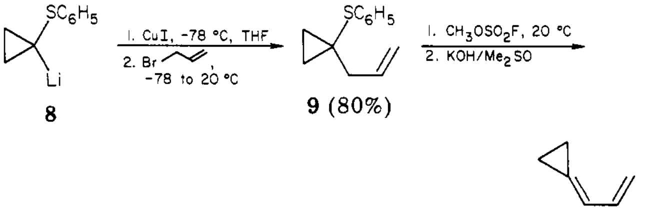
1

5

6

7

Scheme II



8

9 (80%)

10 (70%)

Allylidenecyclopropane (**10**) was efficiently synthesized[9] (Scheme II) in two steps from 1-lithio-1-(phenylthio)cyclopropane (**8**).[10] The first step requires the allylation of **8**. This was achieved successfully, and for the first time, in 80% yield by using allyl bromide (2 molar equiv, -78 to 20 °C) provided that cuprous iodide (0.5 molar equiv) was present in the reaction medium. The second step was accomplished in one pot and 70% overall yield, by methylation of **9** (CH_3OSO_2F (1.5 molar equiv), neat, 20 °C, 0.5 h, then trituration with pentane to remove the excess of magic methyl) and further treatment of the resulting sulfonium salt with base (powdered KOH (4 equiv) in Me_2SO, 20 °C, 15 h). The diene **10** was isolated by flash distillation from the reaction medium (20-40 °C (200-15 mmHg) receiver cooled in liquid nitrogen). It is oxygen sensitive and must be stored under inert gas (argon) at -20 °C.

As expected, allylidenecyclopropane (**10**) exhibits a much higher reactivity than **1** toward dienophiles. It reacts at room temperature with dienophiles possessing two or more activating groups such as tetracyanoethylene, maleic anhydride, and *p*-benzoquinone (Table I). Its reaction with dimethyl acetylene dicarboxylate, dimethyl fumarate, and dimethyl maleate require more drastic conditions (80, 110, 150 °C, respectively). These reactions and others reported in this paper have been performed under argon in sealed glass tubes, and only 1 equiv of the diene **10** was normally used. Monoactivated dienophiles also react with **10** (Table II), but the presence of an alkyl substituent on the dienophile dramatically lowers the yield if it is branched at the α-position or almost completely inhibits the reaction if it is located in the β-position of the activating group (see Table II, entry 7). In these specific cases, the temperature at which these reactions were performed was found to be critical. 100 °C was found to be the best compromise since

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[1] March, J. "Advanced Organic Chemistry: Reactions, Mechanisms and Structure"; McGraw-Hill Kogakusha: Tokyo, 1977; p 761.

[2] Wollweber, H. *Methoden Org. Chem. (Houben-Weyl), 4th ed.* **1970**, *5*, 1019.

[3] (a) Stewart, C. A. *J. Org. Chem.* **1963**, *28*, 3320. (b) Stewart, C. A. *J. Am. Chem. Soc.* **1962**, *84*, 1117.

[4] (a) Slobodin, Y. M.; Grigoreva, V. I.; Schmulyakovskii, Y. E. *Zh. Obshch. Khim.* **1958**, *23*, 1873. (b) Goldman, N. L. *Chem. Ind. (London)* **1963**, 1036. (c) Ichikizaki, I.; Avai, A. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 432 and references cited.

[5] Erratic results have been reported for that specific reaction which produces under similar conditions but depending on the authors: (a) polymers,[4a] (b) the normal Diels-Alder adduct **6**,[4b] or a mixture of adducts **6** and **7**.[4c] We have repeated this reaction using an excess of the diene **1** and a small amount of hydroquinone, performing the reaction under argon in a sealed glass tube at 100 °C for 72 h. We obtained a 20:80 mixture of **6**/**7** if the maleic anhydride contains some diacid. However, if carefully purified[6] maleic anhydride is used, the **6**/**7** ratio increased to 50:50. Omission of hydroquinone results in polymer formation.

[6] Vogel, A. I. "Practical Organic Chemistry"; Longman: London, 1970; p 376.

[7] Matsumoto, T.; Shirahama, H.; Ichihara, A.; Shin, H.; Kagama, S.; Saken, F.; Miyano, K. *Tetrahedron Lett.* **1971**, 2049.

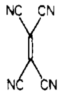
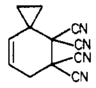
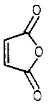
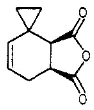
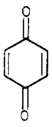
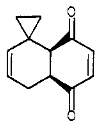
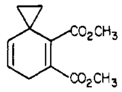
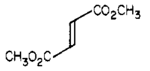
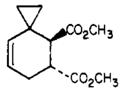
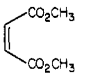
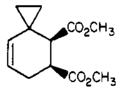
[8] See, for example: Wender, P. A.; Eck, S. L. *Tetrahedron Lett.* **1982**, 1871.

[9] (a) For a previous synthesis of **10**: Binger, P.; Germer, A. *Chem. Ber.* **1981**, 114, 3325. (b) Three other routes to **10** have been devised in our laboratory. They imply 1-lithio-1-(methylseleno)cyclopropane or its phenylseleno analogue as the starting material. The last route uses a strategy we previously described. They will be reported later. (c) Halazy, S.; Krief, A. *Tetrahedron Lett.* **1981**, 1836, 2135.

[10] Trost, B. M.; Keeley, D.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 3068.

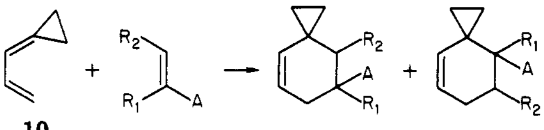
0022-3263/83/1948-1135$01.50/0

Table I

entry	dienophile	conditions	isolated product	yield of isolated product, %
1		1 equiv, CCl_4, 20 °C, 16 h	 **11a**	77
2		0.75 equiv,[a] benzene, 20 °C, 16 h	 **11b**	77[b]
4		0.9 equiv,[a] CH_2Cl_2, 20 °C, 16 h	 **11c**	56
4		1 equiv, 1. benzene, 20 °C, 16 h; 2. benzene, 80 °C, 16 h	 **11d**	05; 54
5		1 equiv, toluene, 110 °C, 16 h	 **11e**	75
6		1 equiv, toluene, 150 °C, 16 h	 **11f**	20

[a] In these cases a slight excess of diene was used to ensure complete reaction of the dienophile. The presence of remaining dienophile makes purification of the adducts **11b** and **11c** difficult. [b] Yield determined on corresponding diester (**11f**), obtained by methanolysis, followed by diazomethane treatment.

Table II



10 **12** **13**

entry	A	R_1	R_2	conditions		yield, %		yield, %
1	$COOCH_3$	H	H	toluene, 70 °C, 18 h, 3 equiv dienophile	**12a**	25		
				toluene, 100 °C, 18 h, 3 equiv dienophile	**12a**	68[a]		
2	$COCH_3$	H	H	toluene, 100 °C, 18 h, 3 equiv dienophile	**12b**	80		
3	CHO	H	H	toluene, 100 °C, 18 h, 5 equiv dienophile	**12c**	53	**13c**	06
4	NO_2	H	H	toluene, 110 °C, 16 h, 1 equiv dienophile	**12d**	51	**13d**	21
5	$COOCH_3$	CH_3	H	toluene, 100 °C, 17 h, 5 equiv dienophile	**12e**	38[b]		
6	CHO	CH_3	H	toluene, 100 °C, 16 h, 5 equiv dienophile	**12f**	39[b]		
7	CHO	H	CH_3	toluene, 150 °C, 15 h, 3 equiv dienophile	**12g**	12[c]		

[a] Gas chromatographic analysis of the reaction product **12a** reveals a minor impurity (5%), which is probably the ortho adduct **13a**. [b] These adducts can be purified only with great difficulty because of the presence of several minor contaminants (maybe including the ortho adducts). [c] 3:1 mixture of regioisomers (whose structures have not yet been assigned).

spiro derivatives were obtained in low yield both at lower temperature (~75 °C) and at much higher temperature (150 °C). In the latter case, the dimerization of the diene was observed[11], especially with nonreactive dienophiles.

While the reported reactions show the stereospecificity usually observed in the Diels–Alder reaction,[1,2] (see Table I, entries 5 and 6), their regioselectivity was significantly different from the one usually reported for 1-substituted dienes, which are known to give predominantly the "ortho adduct".[1,2] In the case of allylidenecyclopropane, a reversed tendency was found and the "meta adduct" **12** was mainly formed. Regioselectivity is high in the case of α,β-unsaturated esters, ketones, and aldehydes, somewhat

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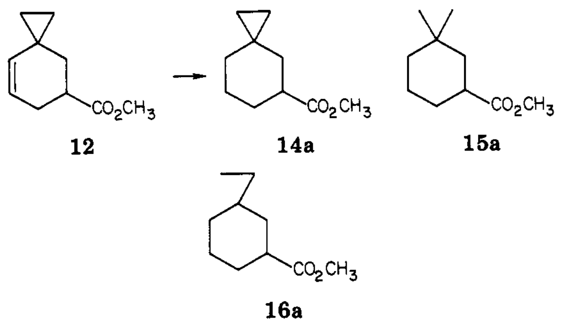
[11] The interconversion of these dimers and the determination of their structures is actually investigated in our laboratory.

[12] Eisenstein, O.; Lefour, J. M.; Nguyen Trong, Anh; Hudson, R. F. *Tetrahedron* 1970, *33*, 523.

J. Org. Chem. 1983, 48, 1137-1139

Scheme III



	combined yield, %	14a	15a	16a
a, $[(C_6H_5)_3P]_3RhCl$, benzene	84	100		
b, PtO_2/AcOH	93		97	03
c, 10% Pd/C, THF, H_2O	92	16		84

less pronounced with nitroethylene (Table II).

The structure of each adduct was proven by ^1H NMR analysis.[13] Moreover, the structure of the adduct obtained from acrylate has been proven beyond doubt by comparison of the NMR and IR spectra of the derived acid with the spectra of an authentic sample prepared by a totally different route by Yates et al.[14]

We have found that the vinylcyclopropane system present in the spirooctene derivatives can serve as precursor of spirooctanes, of *gem*-dimethylcyclohexanes, or of ethylcyclohexanes. Our results on the acrylate adduct **12a** are herein reported. Thus we found that the carbon–carbon double bond in **12a** can be selectively (100%) reduced by hydrogen if the reaction is performed in the presence of a rhodium catalyst ($[(C_6H_5)_3P]_3RhCl$, 0.1 molar equiv, benzene, 20 °C, 10 h; **14a**, 84% yield) (Scheme III). However, the nature of the product(s) formed critically depends upon the nature of the catalyst used.[15] For example, the dimethylcyclohexane **15a** resulting from the concomittant reduction of the double bond and of the cyclopropane ring was quite exclusively formed (**15a**/**16a** = 97:3) if platinum is used (Pt, 0.3 molar equiv, CH_3CO-OH, 20 °C, 4 h, 93% yield), while the ethylcyclohexane **16a** formally formed through a 1,5-reduction was obtained (**16a**/**14a** = 84:16) if the reaction is conducted over palladium (Pd/C 10%, 20% (w/w), THF/H_2O (1:1), 20 °C, 4 h, 92% yield). Further work on more substituted dienes will be reported in due course.

Registry No. 2, 670-54-2; 5, 108-31-6; 8, 41596-88-7; 9, 84864-32-4; 10, 80119-20-6; **11a**, 84864-33-5; **11b**, 84864-34-6; **11c**, 84864-35-7; **11d**, 84864-36-8; **11e**, 84864-37-9; **11f**, 84864-38-0; **12a**, 84864-39-1; **12b**, 84864-40-4; **12c**, 84864-41-5; **12d**, 84864-42-6; **12e**, 84864-43-7; **12f**, 84864-44-8; **12g** (isomer 1), 84864-45-9; **12g** (isomer 2), 84864-46-0; **13c**, 84864-47-1; **13d**, 84864-48-2; **14a**, 84864-49-3; **15a**, 84864-50-6; **16a**, 84864-51-7; *p*-benzoquinone, 106-51-4; dimethyl acetylenedicarboxylate, 762-42-5; dimethyl fumarate, 624-49-7; dimethyl maleate, 624-48-6; methyl acrylate, 96-33-3; 3-buten-2-one, 78-94-4; 2-propenal, 107-02-8; nitroethene, 3638-64-0; methyl methacrylate, 80-62-6; 2-methyl-2-propenal, 78-85-3; (*E*)-2-butenal, 123-73-9.

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(13) NMR of the acrylate adduct **12a** (Jeol MH 100, 100 MHz, CCl_4, Me_4Si as internal standard): δ 5.49 (dt, J = 10.0, 3.5 Hz, 1 H), 4.92 (br d, J = 10 Hz, 1 H), 3.57 (s, 3 H), 2.60 (m, $\sum J$ = 28 Hz, 1 H), 2.22 (m, 2 H), 1.92 (dd, J = 12, 10 Hz, 1 H), 1.35 (dd, J = 12.0, 3 Hz, 1 H), 0.52 (s, 4 H).

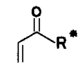
(14) (a) We thank Prof. Peter Yates for providing us with the IR and NMR data of that compound.[14b] (b) Yates, P.; Fenwick, J. D. *J. Am. Chem. Soc.* 1971, *93*, 4618.

(15) Rylander, P. N. "Catalytic Hydrogenation in Organic Synthesis"; Academic Press: New York, 1979; Chapter 14, p 251.

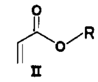
Asymmetric Diels–Alder Reaction: Design of Chiral Dienophiles

Summary: An asymmetric Diels–Alder reaction between cyclopentadiene and a new chiral dienophile is described. Excellent diastereofacial selectivity can now be achieved even in the *absence* of a catalyst. The stereochemical result of this reaction has been rationalized on the basis of a rigid hydrogen-bonded cisoid conformation of the ketol-type dienophile.

Sir: The use of a chiral dienophile or enophile[1] in the Diels–Alder reaction effects (single)[2] asymmetric induction, the degree of which is expressed by the diastereofacial selectivity[3] of either chiral reactant. This asymmetric Diels–Alder chemistry, pioneered by Korolev and Mur[4] and Walborsky et al.,[5] has received renewed interest in recent years,[6] and, indeed, *with the aid of a Lewis acid catalyst*, some reactions now proceed with very high and sometimes near-perfect diastereoselection.[7] After a close review of this development, our attention has been directed to the design of chiral dienophiles in which a chiral auxiliary is attached one atom closer to the three-carbon enone unit (type I) than in those (type II) often used earlier.[6,7] The outcome brought about by this simple design change is significant, and even *in the absence of an external catalyst* (*vide supra*), a new dienophile described below attains a diastereofacial selectivity as high as >100:1. To our best knowledge, the highest ratio thus far recorded for the *uncatalyzed* reaction has been 80:20.[8]



I



II

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(1) Chiral Lewis acids also effect asymmetric induction: Hashimoto, S.; Komeshima, N.; Koga, K. *J. Chem. Soc., Chem. Commun.* 1979, 437.

(2) The phase "single asymmetric induction" is used when only one chiral reactant participates in a reaction. Similarly, multiple (double, triple...) asymmetric induction is defined.

(3) For the definition of this phrase, see (a) Masamune, S.; Lu, L.D.-L.; Jackson, W. P.; Kaiho, T.; Toyoda, T. *J. Am. Chem. Soc.* 1982, *104*, 5523 (footnote 16). For a detailed discussion, see (b) Masamune, S.; Choy, W. *Aldrichimica Acta* 1982, *15*, 47.

(4) Korolev, A.; Mur, V *Dokl. Akad. Nauk. SSSR* 1948, *59*, 251; *Chem. Abstr.* 1948, *42* 6776*f*.

(5) Walborsky, H. M.; Barash, L.; Davis, T. C. *J. Org. Chem.* 1961, *26*, 4778.

(6) For a recent review, see: Mori, Y. *J. Syn. Org. Chem.* (Yuki Gosei Kagaku) 1982, *40*, 321. Also see (b) Oppolzer, W. "Diastereo- and Enantioselective Cycloaddition of the Ene Reactions in Organic Synthesis" presented at the Fourth International Conference on Organic Synthesis, Tokyo, 1982.

(7) For an enophile, see (a) Trost, B. M.; O'Krongly, D.; Belletire, J. L. *J. Am. Chem. Soc.* 1980, *102*, 7595. For a dienophile, see: (b) Oppolzer, W.; Chapuis, C.; Dao, G. M.; Reichlin, D.; Godel, T. *Tetrahedron Lett.* 1982, *23*, 4781.

(8) (a) Helmchen, G.; Schmierer, R. *Angew, Chem., Int. Engl.* 1981, *20*, 205. A claim of high asymmetric induction was made: (b) Horton, D.; Machinami, T. *J. Chem. Soc., Chem. Commun.* 1981, 88. However, their reported specific rotation for the *R* enantiomer of the methyl ester of 8 was "$[\alpha]_D$ −10°, $CHCl_3$", which was compared with $[\alpha]^{25}_D$ −10.2° (*c* 1.8, 95% EtOH) recorded for the same ester obtained through partial resolution (estimated optical purity, 35%, see ref 11) by (c) Berson, J. A.; BenEfraim, D. A. *J. Am. Chem. Soc.* 1959, *81*, 4083.

0022-3263/83/1948-1137$01.50/0