

Aqueous Diels-Alder Reactions of Cyclopentadiene with Symmetric Diester of Fumarate or Maleate

Guang Dian HAN^{1,*}, Zhao Yang MA², Guo Sen HE²

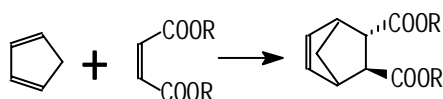
¹Institute of Materia Medica, Peking Union Medical College, Chinese Academy of Medical Sciences, Beijing 100050

²Institute of Occupational Health, Chinese Academy of Preventive Medicine, Beijing 100050

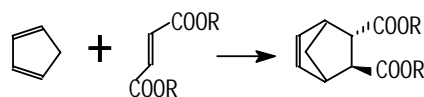
Abstract : Symmetric diesters of *cis*- or *trans*- bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylate were prepared by aqueous Diels-Alder reaction of cyclopentadiene with symmetric diester of fumarate or maleate.

Keywords: Aqueous Diels-Alder reaction, diester of bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylate, diester of fumarate and maleate, cyclopentadiene.

Cis- or *trans*- dimethyl and diethyl ester of bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylate (**2** or **4**) were used as pesticides¹⁻⁴ in the forties and fifties of the century to prevent or kill mosquito, fly and flea. The *cis*-dimethyl ester **2a** was also added to cosmetics for the same purpose⁵. The diethyl and dipropyl esters (**2b** and **2c**) could be used to make rubber and elastomers^{6,7}. Besides, this kind of compounds are important intermediates for synthesis of some drugs.



1a	R=Me	2a	R=Me
b	R=Et	b	R=Et
c	R=Pr	c	R=Pr



3a	R=Me	4a	R=Me
b	R=Et	b	R=Et
c	R=Pr	c	R=Pr

The Diels-Alder reaction of cyclopentadiene with dienofiles **1** or **3** is the most simplest method for preparing adducts **2** or **4**. These methods are usually carried out in

organic solvent, most of them need catalyst. If the catalyst is absent, the reaction is sluggish⁸.

In 1980, Breslow reported an aqueous Diels-Alder reaction of cyclopentadiene with buten-2-one and revealed that the Diels-Alder reaction was accelerated by the hydrophobic effect of water⁹. We have now tried the possibility of the aqueous Diels-Alder reaction of the symmetric diester of maleate (**1**) and fumarate (**2**) with cyclopentadiene. The reaction proceeded smoothly in an aqueous mixed solvent (water : acetone=3 : 2). The yields range from 74.7% to 94% after vacuum distillation.

Experimental

Typical procedure is exemplified by the following reaction.

17.2 g (0.1 mol) of diethyl fumarate and 12.3 g (0.2 mol) of freshly distilled cyclopentadiene were added to 50 mL of solvent described above and the mixture was refluxed about 12 h. After separating the organic layer, the aqueous layer was extracted 3 times with petroleum ether, the combined organic phase were washed with water, dried over anhydrous magnesium sulphate, and evaporated. The residue was purified by vacuum distillation to give 21.18 g (89%) of product (**4b**), b.p. 106~108 °C/1 mm¹⁰.

Acknowledgment

We thank the Ministry of Health for the financial support.

References and notes

1. J. P. Linduska, J. H. Cochran, F. A. Morton, *J. Econ. Entomol.*, **1946**, 39, 767.
2. C. N. Smith, M. M. Cole, E. A. Jones, *J. Econ. Entomol.* **1949**, 42, 716.
3. C. N. Smith, D. Burnett, Jr. *J. Econ. Entomol.*, **1949**, 42, 439.
4. R. M. Altman, C. N. Smith, *J. Econ. Entomol.*, **1955**, 48, 67.
5. W. G. McAllister, *Soap, Perfumery and Cosmetics*, **1949**, 22, 716.
6. *CA*, **1969**, 71, 71703h; (*Fr.*, 1556215, **1969**).
7. *CA*, **1970**, 73, 46421y; (*Fr. Addn.*, 94672, **1969**).
8. H. Koch, *Monatsh*, **1962**, 93, 1343.
9. D. C. Rideout, R. Breslow, *J. Am. Chem. Soc.*, **1984**, 102, 7816.
10. **2a**, b. p. 94~96°C/2mm, yield 81.5%; **2b**, b. p. 120°C/3mm, yield 86.2%; **2c**, b. p. 127~129°C/3mm, yield 87.5%; **4a**, b. p. 100~105°C, yield 94%; **4b**, b. p. 106 ~ 108°C/1mm, yield 89%; **4c**, b. p. 122~128°C/1mm, yield 74.7%.

Received 1 September 1999