Russian Chemical Bulletin, Vol. 43, No. 8, August, 1994

New synthesis of 3-cyclopentenecarboxylic acid esters by olefin metathesis

N. B. Bespalova,* M. A. Bovina, M. B. Sergeeva, and V. G. Zaikin

A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,
29 Leninsky prosp., 117912 Moscow, Russian Federation.
Fax: +7 (095) 230 2224

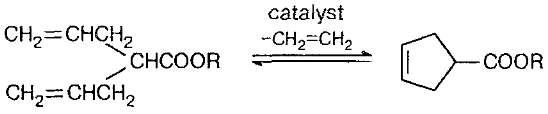
Olefin metathesis of diallylacetic acid esters is proposed for the synthesis of 3-cyclopentenecarboxylic acid esters. WCl_6—organosilicon compounds are used as homogeneous catalysts.

Key words: olefin metathesis, 3-cyclopentenecarboxylic acid esters, homogeneous silicon-containing catalysts.

The olefin metathesis reaction, which was discovered more than thirty years ago, is widely used in organic synthesis. A large number of homogeneous catalysts of metathesis are known, but only a few of them are active in the metathesis of functional derivatives of olefins. As a rule, these are heterogeneous and homogeneous catalytic systems which contain alkyl derivatives of tin and lead.[1,2] The WCl_6—1,1,3,3-tetramethyl-1,3-disilacyclobutane (DSCB) homogeneous system is a highly efficient catalyst for metathesis of functional derivatives of olefins.[3] Moreover, unlike the majority of known catalysts, this system activates the metathesis of substrates in which the multiple bond and functional group are close as, for example, in allylcyanide.[4] It should be noted that organosilicon co-catalysts are less toxic than organotin and organolead compounds.

The goal of the present study is the use of the olefin metathesis reaction for the synthesis of 3-cyclopentenecarboxylic acid esters.

The synthesis of 3-cyclopentenecarboxylic acid esters was carried out by the intramolecular metathesis of diallylacetic acid esters. Homogeneous silicon-containing systems were used as catalysts: tungsten hexachloride—organosilanes (DSCB or dihydrodiphenylsilane (DPS)).



1a,b **2a,b**

R = Me (**a**), R = Et (**b**)

A characteristic feature of this reaction is its unusually high selectivity: linear and cyclic products of the intermolecular metathesis are entirely absent. Table 1 presents data that demonstrate the influence of the substrate/catalyst ratio on the yield of the reaction for two silicon-containing catalytic systems using the metathesis of the ethyl diallylacetate as an example. The optimal yield of the desired product is achieved with the ratio substrate/WCl_6 = 50. The WCl_6—DSCB catalytic system is the more efficient one and allows one to obtain the cyclic ester in 98% yield.

The reaction under consideration is the first example of the use of olefin metathesis for the synthesis of 3-cyclopentenecarboxylic acid esters and can be used for preparative purposes.

Table 1. Metathesis of **1** in the presence of WCl_6 — DSCB and WCl_6 — DPS
(benzene, 10 h, 80 °C; WCl_6 : co-catalyst = 1:2)

Catalyst	**1**/WCl_6	Yield of **2** (%)
WCl_6 — DSCB	25	81
	50	98
	100	71
	150	10
WCl_6 — DPS	25	65
	50	83
	100	52
	150	5

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1503—1504, August, 1994.

Experimental

^1H NMR spectra were recorded with a Bruker MSL 300 instrument, with TMS as the internal standard. Mass spectra were recorded on a Kratos MS-80 instrument at 70 eV. GLC analysis of the reaction mixtures and target products was performed on a Chrom-5 chromatograph equipped with a flame-ionization detector and a glass capillary column (70 m), packed with 8% SE-30 on DMCS on Carbowax W (80/100 mesh) with helium as the carrier gas (60 mL/min), 10 K/min from 60 to 100 °C.

All solvents and starting compounds were freed from moisture and oxygen according to known procedures accepted for work with organometallic compounds and homogeneous catalysts. Organosilicon co-catalysts were produced using reported procedures.[5,6] Methyl and ethyl diallylacetates were obtained from acetoacetic esters and allyl chloride and were dried over P_2O_5. The components of the catalytic systems were used as solutions in benzene and kept in Shlenk vessels under dry argon.

Ethyl 3-cyclopentenecarboxylate (2b). Two g (12 mmol) of **1** were placed into an ampule, which had been evacuated and filled with dry Ar beforehand, then 1 mL (0.24 mmol) of WCl_6 solution in benzene and 2 mL (0.48 mmol) of DSCB solution in benzene were added under a flow of Ar. The contents of ampule were frozen (−196 °C), then the Ar was removed by evacuation at $1\cdot10^{-3}$ Torr. The ampule was sealed and allowed to stand for 10 h at 80 °C, then it was opened, and 1mL of ethanol was added. The liquid was separated and the desired product was isolated by distillation to give 1.6 g (96%) of **2**, b.p. 60—61 °C (10 Torr), n_D^{20} 1.4497, cf. ref[7]. Found (%): C, 71.40; H, 9.49. $C_{10}H_{16}O_2$. Calculated (%): C, 71.43; H, 9.52. MS, m/z (I_{rel} (%)): 140 $[M]^+$ (35), 95 $[M-OC_2H_5]^+$ (25), 67 $[M-COOC_2H_5]^+$ (100), 41$[C_3H_5]^+$ (35).

Methyl 3-cyclopentenecarboxylate (2a) was analogously obtained, b.p. 52—53 °C (12 Torr). MS, m/z (I_{rel} (%)): 126 $[M]^+$ (25), 111 $[M-CH_3]^+$ (13), 95 $[M-OCH_3]^+$ (15), 67 $[M-COOCH_3]^+$ (100), 41 $[C_3H_5]^+$ (38). ^1H NMR spectrum (C_6D_6, ppm): 5.53 (s, 2 H, CH=CH), 3.57 (s, 3 H, OMe), 2.98 (m, 1 H, CH), 2.53 (d, 4 H, CH_2).

References

1. J. C. Mol, *J. Mol. Catal.*, 1982, **15**, 35.
2. J. C. Mol, *J. Mol. Catal.*, 1991, **65**, 799.
3. N. B. Bespalova, M. A. Bovina, *J. Mol. Catal.*, 1992, **76**, 181.
4. N. B. Bespalova, M. A. Bovina, and V. M. Vdovin, *Izv. AN SSSR. Ser, khim.*, 1988, 920 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, 799 (Engl. Transl.)].
5. L. H. Sommer, G. A. Baum, *J. Amer. Chem. Soc.*, 1954, **76**, 5002.
6. D. T. Hard, *J. Amer. Chem. Soc.*, 1945, **67**, 1545.
7. J. Cole, C. Cardoso, *J. Amer. Chem. Soc.*, 1939, **61**, 2350.

Received May 13, 1994