SPIRO[4.5]DECA-2,7-DIENE-1,6-DIONE AND SPIRO[5.5]UNDECA-2,8-DIENE-1,7-DIONE. SYNTHESIS, REDUCTIONS AND PALLADIUM-CATALYZED ALLYLIC SUBSTITUTIONS

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Received May 17, 2001
Accepted October 17, 2001

Dedicated to Professor Kjell Undheim on the occasion of his 70th birthday.

Spiro[4,5]deca-2,7-diene-1,6-dione (**2a**) and spiro[5,5]undeca-2,8-diene-1,7-dione (**2b**) were prepared by a direct synthesis starting from diethyl malonate. The two-step 1,2-reductions ($NaBH_4/CeCl_3$) of the diones gave *cis*/*trans*-diols, which could be easily transformed into diacetates. Both diacetates were subjected to Pd(0)-catalyzed allylic alkylations, in which the relative stereochemistry was retained.

Keywords: Spirodecane; Spiroundecane; Spirocyclic compounds; Spiranes; Reductions; Allylic substitutions; Cyclic allyl alcohols.

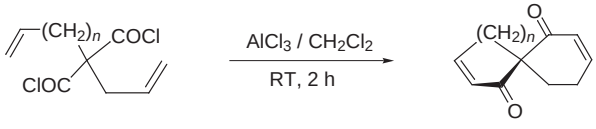
The spiro-systems, in wich two rings are interconnected through a common ring atom are rigid. The two rings have an orthogonal relationship. The functional groups in the same relative position in the two rings will also have a pseudo-orthogonal relationship. Te conformational freedom in acyclic structures is gone, as well as various degrees of flexibility in ring structures. Hence, functional groups in the spiro-rings are highly directed in space. Stereochemical features and chiroptical properties of substituted spiro-systems have been the focus of several studies. In this context, successful chiral resolutions of those systems have been reported[1–6]. Appropriately functionalized spiro-systems can be used for the control of interactions in biological systems, between a bioreceptor and functional or pharmacophoric groups in a particular spirane[7,8]. Thus, the construction and stereoselective substitutions in spiranes could be used to provide rigid skeletons for explorations in medicinal chemistry.

Due to their rigidity, spiranes can also be constructed as ligands for organometallic complexes. Simple symmetrical systems such as the

spiro[4.4]nonane system have been studied in connection with their C_2-symmetry and chiroptical properties[1,3,6,9].

Spirocyclic structural units are present in a number of natural products. Therefore, several approaches have been developed for the synthesis of cyclospiranes, as intermediates in total synthesis of natural products[10,11].

We have initiated work on the preparation and palladium mediated transformations of spirocycles. In a previous paper[12], we reported results from studies on substitutions and stereoselectivities in reactions in the spiro[4.4]nona-2,7-diene-1,6-dione[13]. We have extended our investigations on the preparation and substitutions in simple spiro-systems, to two new substrates, spiro[4.5]deca-2,7-diene-1,6-dione (**2a**) and spiro[5.5]undeca-2,8-diene-1,7-dione (**2b**) (Scheme 1). We report here the synthesis of these new unsaturated spiro compounds and studies on their selective 1,2-reductions and palladium mediated allylation reactions.



1a, n = 1
1b, n = 2

2a, n = 1, 43%
2b, n = 2, 30%

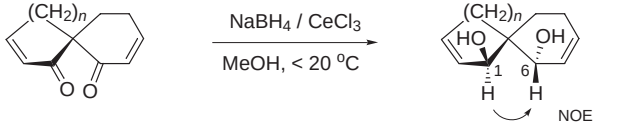
SCHEME 1

RESULTS AND DISCUSSION

The title compounds **2a** and **2b** were prepared by intramolecular Fridel–Crafts acylations of allyl(but-3-en-1-yl)malonyl dichloride (**1a**) and di(but-3-en-1-yl)malonyl dichloride (**1b**)[14]. The acid chlorides **1a** and **1b** were added slowly to a solution of aluminium chloride, nitromethane and dichloromethane at 0 °C, to give spiro[4.5]deca-2,7-diene-1,6-dione (**2a**) and spiro[5.5]undeca-2,8-diene-1,7-dione (**2b**), in yields 43 and 30%, respectively. The ^{1}H and ^{13}C NMR spectra were in accordance with the structure of the products **2a** and **2b**; the correct assignment of the signals was made using the two-dimensional (H, C)-correlated NMR spectroscopy (COSY).

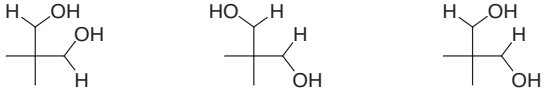
For the selective 1,2-reduction of the spirodiketones **2a** and **2b**, we used sodium borohydride and cerium(III) chloride in methanol. Four sets of enantiomeric pairs of diols can be formed[10] (Scheme 2), but by keeping the temperature below 20 °C, the reduction could be controlled to almost exclusive formation of the *cis*/*trans*-spiro[4.5]deca-2,7-diene-1,6-diol (**3a**) and *cis*/*trans*-spiro[5.5]undeca-2,8-diene-1,7-diol (**3b**), which were isolated in 78

and 83% yields, respectively (Scheme 2). At higher temperatures, mixtures of the stereoisomers were formed. Flash chromatography allowed the separation of the main *cis*/*trans* isomers **3a** and **3b** from the mixture of the other isomers. For simplicity, for a compound with three stereogenic centers, and particularly for a spirane, the relative configuration is designated using the *cis*/*trans*-system, generally adopted (Scheme 2).



2a, *n* = 1
2b, *n* = 2

3a, *trans/cis*, *n* = 1, 78%
3b, *cis/trans*, *n* = 2, 89%



cis/cis *trans/trans* *cis/trans*

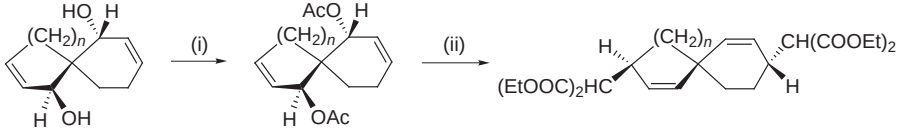
SCHEME 2

The structure assignment of the diol **3b** was based on ^{1}H and ^{13}C NMR data. The *cis*/*cis* and *trans*/*trans* isomers have the C_2-symmetry and hence the NMR signals from both rings coincide. In the *cis*/*trans* isomer **3b**, however, the hydrogens as well as the carbons in the two rings are all magnetically nonequivalent. Hence, there is a set of signals from each ring, unless there is some partial overlapping of the signals.

The mechanism of the reduction of the two carbonyl groups, which is a two-step process, was studied and presented in our previous paper[12]. The structure assignment for the *cis*/*trans*-diol **3a** was made using the 1D and 2D NMR spectra ^{1}H, ^{13}C, (H-H)-COSY, (H-C)-COSY and NOE NMR spectra. In the ^{13}C NMR spectra, the signals for the carbons bearing the hydroxy groups (COH) have a specific position and cannot be confused. The (H-C)-COSY spectra, allowed assignment of the signals for the hydrogen atoms bonded to the carbon atoms bearing the hydroxyl groups (C**H**OH), for the five- and six-membered rings. NOE experiment was carried out saturating the signal of hydrogen C(1)**H**OH (δ 4.90) from the five-membered ring. The difference spectra showed an increase in the intensity of the hydrogen signal from the six-membered ring C(6)**H**OH (δ 3.70). This proves that the stereoisomer **3a** have a *trans*-structure at the alcohol from the five-

membered ring and a *cis*-structure at the alcohol from the six-membered ring. For all other stereoisomers, the hydrogen atoms bonded to the same carbon like the hydroxyl groups are situated too far from each other to produce a NOE effect.

We continued our investigations on the properties of the newly prepared spiro compounds by studying their abilities to participate in palladium-catalyzed allylic substitutions. The acetates are known as good leaving groups in these reactions. Therefore, the *cis*/*trans*-diols **3a** and **3b** were transformed into their corresponding diacetates, **4a** and **4b**. Using DMAP and acetic anhydride in dichloromethane, *cis*/*trans*-1,6-diacetoxyspiro-[4.5]deca-2,7-diene (**4a**) and *cis*/*trans*-1,7-diacetoxyspiro[5.5]undeca-2,8-diene (**4b**) were obtained in 84 and 85% yields, respectively (Scheme 3). The diacetates were subjected to Pd(0)-catalyzed allylic substitutions in the presence of the soft nucleophile sodium diethyl malonate. The catalyst was generated *in situ* from $Pd_2(dba)_3 \cdot CHCl_3$ and 1,2-bis(diphenylphosphino)ethane (dppe). The allylation reactions with the diacetates **4a** and **4b** proceeded with the formation of tetraethyl *cis*/*trans*-spiro[4.5]deca-1,6-diene- 3,8-diyl-dimalonate (**5a**) and tetraethyl *cis*/*trans*-spiro[5.5]undeca-1,7-diene-3,9-diyl-dimalonate (**5b**), as the only isomers, in the yields of 60 and 68%, respectively (Scheme 3).



3a, *n* = 1
3b, *n* = 2

4a, *n* = 1, 84%
4b, *n* = 2, 85%

5a, *n* = 1, 60%
5b, *n* = 2, 68%

(i) Ac_2O, DMAP, CH_2Cl_2, 0 °C, 2 h; (ii) $Pd_2(dba)_3$, dppe, $NaCH(COOEt)_2$, THF, 20-50 °C, 1-2 h

SCHEME 3

The allylic substitutions were initiated by metal coordination to the double bond from the opposite side of the acetate group, before the acetate becomes a leaving group and the π-allylic complex is formed. The nucleophilic attack of sodium malonate takes place at the less substituted or less shielded allylic terminal carbon of the π-allylic system, from the opposite side of the palladium atom. After two inversions, the product is formed with the retention of the relative configuration. The reactions were followed by GC. In the case of diacetate **4a**, in the first step, two new peaks appeared, corresponding to the two monosubstituted products. Then, they

disappeared and a new peak was formed, corresponding to the disubstituted product. After work up and purification, we have obtained the product **5a** as only isomer. The assignment of structure of this product was made by 1D and 2D NMR. The NOESY spectra shows a cross peak between the hydrogen signal from the malonate C**H**$(COOEt)_2$ from the five-membered ring and a hydrogen atom bonded to C(6) from the six-membered ring. This corresponds to a *trans*-structure, so the reaction occurred with the retention of the relative configuration of the starting material **4a**. The NOESY spectra also shows a cross peak between the hydrogen signal from the malonate C**H**$(COOEt)_2$ from the six-membered ring and a hydrogen signal from the double bond. The NOE effect between these hydrogen atoms proves that the substituent from the six-membered ring has a *cis*-structure, corresponding also to a retention of configuration of the starting material.

In the case of diacetate **4b**, the GC shows the initially formation of only one intermediary corresponding to the monosubstituted product, and then the formation of the product **5b** as only isomer. The assignment of the relative configuration of this compound as *cis*/*trans* was made by ^{1}H and ^{13}C NMR. The spectra show a set of signals for each ring, that corresponds to an unsymmetrical molecule. The only stereoisomer that can give different signals for each ring is the one with a *cis*/*trans*-structure. Here again, the results were consistent with retention of relative configuration of the *cis*/*trans* starting material **4b**.

In conclusion, we have successfully prepared two new unsaturated spirodiketones **2a** and **2b** and reduced them 1,2-selectively, in the presence of cerium(III) chloride. We prepared the allylic acetates for both substrates, which were successfully used for Pd(0)-catalyzed allylic substitutions with sodium diethyl malonate.

EXPERIMENTAL

Melting points were determined on a Boetius block and are uncorrected. The NMR spectra were recorded in $CDCl_3$ on a Bruker DPX 250 spectrometer operating at 250 (^{1}H) and 62.5 MHz (^{13}C). Chemical shifts are reported in ppm (δ-scale) using residual $CHCl_3$ (7.24 ppm) and $CDCl_3$ (77.00 ppm) as references, coupling constants (*J*) in Hz. The COSY experiments were carried out using the pulse sequence and the program provided by the manufacturer. The mass spectra under electron impact conditions (EI) were recorded at 70 eV ionizing potential; methane was used for chemical ionization (CI). The spectra are presented as *m/z* (rel.%).

Solvents were degassed by bubbling them with argon. Dry dichloromethane was distilled from CaH_2 under argon. Dry THF was distilled from sodium and benzophenone under argon.

Procedure for Cyclization of Malonyl Dichloride Derivatives

In a three-necked 250 ml flask, dry CH_2Cl_2 (60 ml) was mixed under nitrogen with $AlCl_3$ (10 g, 75 mmol) and nitromethane (2 ml), and the flask was cooled to 0 °C. Then, malonyl dichloride (**1a** or **1b**) (30 mmol) was added dropwise to the mixture. The resulting brown solution was stirred at room temperature for 2 h, then it was cooled again to 0 °C and a 10% aqueous NH_4Cl solution (10 ml) was added. The precipitate was filtered off and the green filtrate was washed with 5% aqueous HCl (10 ml) and water (3 ×). The organic layer was dried over $MgSO_4$, filtered, and the solvent evaporated. The residue was subjected to flash chromatography on silica gel.

Spiro[4.5]deca-2,7-diene-1,6-dione (**2a**). Flash chromatography on a 10 cm diameter column, using hexane–ethyl acetate (2 : 1) as eluent, afforded the title compound (**2a**) (2.07 g, 43%) as a white solid with m.p. 51 °C (CH_2Cl_2). If the reaction time was increased or the mixture was heated, the yield dropped. For $C_{10}H_{10}O_2$ (162.0) calculated: 74.0% C, 6.10% H; found: 74.12% C, 6.18% H. HRMS (*m/z*): 162.0680. Calculated for $C_{10}H_{10}O_2$: 162.0678. ^{1}H NMR: 2.04–2.11 m, 1 H (CH_2); 2.18–2.23 m, 1 H (CH_2); 2.27–2.34 m, 1 H (CH_2); 2.37 dt, J = 19, J = 2.5, 1 H (CH_2); 2.79–2.88 m, 1 H (CH_2); 3.32 dt, J = 19, J = 2.5, 1 H (CH_2); 6.01–6.06 m, 2 H (C**H**=CHCO); 7.05–7.09 m, 1 H (CHCO); 7.71–7.74 m, 1 H (CHCO). ^{13}C NMR: 22.7 (CH_2); 31.1 (CH_2); 40.3 (CH_2); 57.8 (C); 128.5 (CH=); 132.4 (CH=); 152.3 (CH=); 164.5 (CH=); 195.4 (CO); 206.8 (CO). EI MS (*m/z*, rel.%): 162 (M^+, 52), 161 (17), 145 (21), 144 (22), 133 (42), 119 (12), 105 (15), 91 (27), 77 (13), 68 (100), 51 (14), 39 (41), 27 (15).

Spiro[5.5]undeca-2,8-diene-1,7-dione (**2b**). Flash chromatography on a 7.5 cm diameter column using hexane–ethyl acetate (1 : 1) as eluent, gave the title compound (**2b**) (1.58 g, 30%) as colorless oil. HRMS (*m/z*): 176.2150. Calculated for $C_{11}H_{12}O_2$: 176.2146. ^{1}H NMR: 1.95–2.07 m, 2 H (CH_2); 2.09–2.18 m, 2 H (CH_2); 2.26–2.38 m, 2 H (CH_2); 2.71–2.86 m, 2 H (CH_2); 5.95–6.10 m, 2 H (CH=); 6.98–7.12 m, 2 H (CH=). ^{13}C NMR: 22.9 (CH_2); 31.4 (CH_2); 58.2 (C); 128.7 (CH=); 152.4 (CH=); 198.8 (CO). EI MS (*m/z*, rel.%): 176 (M^+, 24), 159 (17), 158 (29), 147 (42), 119 (12), 94 (12), 82 (100), 51 (17), 27 (21).

cis/*trans*-Spiro[4.5]deca-2,7-diene-1,6-diol (**3a**)

$NaBH_4$ (77.3 mg, 2.0 mmol) was added in portions to a solution of **2a** (300 mg, 1.85 mmol) and $CeCl_3 \cdot H_2O$ (1.4 g, 3.8 mmol) in methanol (25 ml) at 15–20 °C. The solution was cooled in an ice bath, to keep the temperature inside the flask below 20 °C while $NaBH_4$ was added. The solution was then stirred at ambient temperature for 1.5 h. The progress of the reaction was followed by TLC. When the reaction was finished, water was added and methanol was evaporated. The product was extracted from the obtained solution with ethyl acetate (3 ×). The combined solutions were dried over $MgSO_4$ and evaporated. The crude product was purified by flash chromatography on silica gel, using a 3 cm diameter column and eluting with hexane–ethyl acetate (1 : 1 then 1 : 2). The pure product **3a** (242 mg, 78%) was obtained as a white solid with m.p. 110 °C (CH_2Cl_2). For $C_{10}H_{14}O_2$ (166.0) calculated: 72.28% C, 8.43% H; found: 72.37% C, 8.55% H. ^{1}H NMR: 1.49–1.62 m, 1 H (CH_2); 1.72–1.97 m, 2 H (CH_2); 2.05–2.27 m, 3 H (CH_2); 3.70 s, 1 H (C**H**OH); 4.90 s, 1 H (C**H**OH); 5.71–5.89 m, 4 H (CH=). ^{13}C NMR: 20.3 (CH_2); 23.2 (CH_2); 38.7 (CH_2); 48.4 (C); 71.2 (CHOH); 80.8 (CHOH); 127.5 (CH=); 130.9 (CH=); 131.4 (CH=); 132.1 (CH=). CI MS (*m/z*, rel.%): 166 (M^+, 0.39), 165 (0.81), 148 (56), 130 (30), 120 (76), 107 (96), 96 (98), 91 (48), 79 (100), 77 (43), 70 (46), 41 (41), 39 (44).

cis/*trans*-Spiro[5.5]undeca-2,8-diene-1,7-diol (**3b**)

Using the same procedure as described above for the product **3a** and 1 h reaction time, we have obtained from spiro[5.5]undeca-2,8-diene-1,7-dione (**2b**) (300 mg, 1.70 mmol) the compound (**3b**) (272 mg, 89%) as a white solid, m.p. 94 °C (CH_2Cl_2). HRMS (*m/z*): 180.2468. Calculated for $C_{11}H_{16}O_2$: 180.2462. ^{1}H NMR: 1.45–1.56 m, 2 H (CH_2); 1.59–1.76 m, 2 H (CH_2); 1.84–1.89 m, 2 H (CH_2); 2.21–2.38 m, 2 H (CH_2); 2.44 s, 1 H (C**H**OH); 3.31 s, 1 H (C**H**OH); 5.69–5.91 m, 4 H (CH=). ^{13}C NMR: 23.2 (CH_2); 32.6 (CH_2); 57.2 (C); 69.8 (CH); 74.2 (CH); 127.8 (CH=); 130.9 (CH=); 134.5 (CH=); 136.4 (CH=). CI MS (*m/z*, rel.%): 180 (M^+, 2), 162 (42), 144 (37), 134 (66), 107 (42), 96 (100), 86 (52), 79 (22), 68 (72), 39 (34), 28 (17).

cis/*trans*-1,6-Diacetoxyspiro[4.5]deca-2,7-diene (**4a**)

Ac_2O (184.3 mg, 1.8 mmol) in dry CH_2Cl_2 (3 ml) was added dropwise to a solution of diol **3a** (120 mg, 0.72 mmol) and DMAP (220.5 mg, 1.8 mmol) in dry dichloromethane (15 ml) under argon at 0 °C. The solution was stirred at 0 °C for 2 h, washed with aqueous $CuSO_4$ (3 ×), aqueous $NaHCO_3$ (2 ×) and brine, dried ($MgSO_4$) and evaporated. The crude product was purified by flash chromatography, eluting with ethyl acetate–hexane 2 : 1. We have obtained the product **4a** (150 mg, 84%) as a colorless oil. For $C_{14}H_{18}O_4$ (250.2) calculated: 67.12% C, 7.19% H; found: 67.25% C, 7.27% H. HRMS (*m/z*): 250.2910. Calculated for $C_{14}H_{18}O_4$: 250.2812. ^{1}H NMR: 1.62–1.71 m, 1 H (CH_2); 1.75–1.85 m, 1 H (CH_2); 2.0 d, 6 H (CH_3); 2.05–2.19 m, 3 H (CH_2); 2.41 dd, 1 H (CH_2); 4.85 d, 1 H (CHOAc); 5.62–5.80 m, 3 H (CH=); 5.92–6.01 m, 2 H (CH and CH=). ^{13}C NMR: 21.2 d (CH_3); 23.4 (CH_2); 24.5 (CH_2); 40.4 (CH_2); 46.2 (C); 72.1 (CH); 81.3 (CH); 124.4 (CH=); 128.9 (CH=); 134.0 (CH=); 135.3 (CH=); 160.5 (CO); 161.1 (CO). EI MS (*m/z*, rel.%): 250 (M^+, 2), 228 (15), 191 (6), 189 (2), 172 (60), 148 (80), 147 (69), 131 (39), 95 (67), 91 (36), 79 (40), 55 (42), 43 (100).

cis/*trans*-1,7-Diacetoxyspiro[5.5]undeca-2,8-diene (**4b**)

Using the procedure described above for the diacetate **4a**, we have obtained from diol **3b** (180 mg, 0.72 mmol), diacetate **4b** (161 mg, 85%) as a colorless oil. HRMS (*m/z*): 264.3211. Calculated for $C_{15}H_{20}O_4$: 264.3206. ^{1}H NMR: 1.58–1.65 m, 2 H (CH_2); 1.71–1.84 m, 2 H (CH_2); 2.01 d, 6 H (CH_3); 2.05–2.19 m, 4 H (CH_2); 4.83 d, 1 H (CH); 5.01 d, 1 H (CH); 5.72–5.88 m, 2 H (CH=); 5.98–6.12 m, 2 H (CH=). ^{13}C NMR: 21.3 (CH_3); 23.4 (CH_2); 24.7 (CH_2); 45.2 (C); 70.9 (CH); 75.1 (CH); 124.2 (CH=); 126.7 (CH=); 133.8 (CH=); 134.7 (CH=); 160.4 (CO). EI MS (*m/z*, rel.%): 264 (M^+, 1), 221 (34), 220 (18), 204 (52), 194 (14), 178 (29), 124 (41), 98 (12), 70 (19), 60 (100), 54 (27), 44 (87), 43 (68).

Tetraethyl *cis*/*trans*-Spiro[4.5]deca-1,6-diene-3,8-diyldimalonate (**5a**)

Pd_2dba_3 (51.7 mg, 0.05 mmol) was added to dppe (39.8 mg, 0.1 mmol) in THF (1 ml). The mixture was stirred under argon at ambient temperature for 10 min and then added to a solution of **4a** (0.25 ml, 1 mmol) in THF (5 ml). After stirring for 10 min, a solution of sodium malonate was added. The sodium diethyl malonate solution was prepared from NaH (55% in oil; 157 mg, 3.6 mmol) and diethyl malonate (0.48 ml, 3 mmol) in THF (5 ml). The resulting solution was stirred at ambient temperature for 1 h, and at 50 °C for 1 h, when GC showed the reaction to be complete. Water and diethyl ether was added to the cold reaction

mixture, the ether layer was collected, the water layer extracted with ether, the combined ether solutions were dried ($MgSO_4$), and evaporated. The product was purified by Kugelrohr distillation (200 °C/40 Pa); yield 270 mg (60%) of colorless oil. For $C_{24}H_{34}O_8$ (450.2) calculated: 63.96% C, 7.55% H; found: 64.11% C, 7.72% H. HRMS (*m/z*): 450.2258. Calculated for $C_{24}H_{34}O_8$: 450.2253. ^{1}H NMR: 1.25 t, 12 H (CH_3); 1.31–1.36 m, 1 H (CH_2); 1.48–1.52 m, 2 H (CH_2); 1.73–1.76 m, 1 H (CH_2); 2.01–2.06 m, 2 H (CH_2); 2.85 m, 1 H (C**H**CH_2); 3.15 dd, 2 H (CHCO); 3.42–3.46 m, 1 H (C**H**CH_2); 4.15 q, 8 H (CH_2); 5.41–5.47 m, 2 H (CH=); 5.58–6.03 m, 2 H (CH=). ^{13}C NMR: 17.2 (CH_3); 26.4 (CH_2); 30.5 (CH_2); 36.1 (CH); 43.0 (CH); 45.4 (CH_2); 50.6 (C); 57.2 (CH); 58.3 (CHCO); 62.0 (CH_2CH_3); 125.1 (CH=); 130.0 (CH=); 135.5 (CH=); 139.2 (CH=); 168.2 (CO). EI MS (*m/z*, rel.%): 450 (M^+, 3), 393 (5), 302 (10), 291 (36), 290 (100), 217 (27), 216 (55), 171 (14), 161 (48), 131 (66), 130 (89), 29 (23).

Tetraethyl *cis*/*trans*-Spiro[5.5]undeca-1,7-diene-3,9-diyldimalonate (**5b**)

The reaction was run under the same conditions as above. From diacetate **4b** (264 mg, 1 mmol) we have obtained, after purification by Kugelrohr distillation, the product **5b** (180 mg, 68%) as a colorless oil (b.p. 210 °C/40 Pa). HRMS (*m/z*): 464.5551. Calculated for $C_{25}H_{36}O_8$: 464.5546. ^{1}H NMR: 1.18 t, 12 H (CH_3); 1.38–1.43 m, 2 H (CH_2); 1.51–1.68 m, 4 H (CH_2); 1.84–2.04 m, 2 H (CH_2); 2.83 m, 2 H (CH); 3.04 dd, 2 H (CHCO); 4.06 q, 8 H (CH_2CH_3); 5.35–5.51 m, 4 H (CH=). ^{13}C NMR: 15.3 (CH_3); 26.3 (CH_2); 30.1 (CH_2); 35.6 d (CH); 49.7 (C); 58.4 d (CHCO); 62.4 (CH_2CH_3); 124.3 d (CH=); 135.1 d (CH=); 168.4 (CO). EI MS (*m/z*, rel.%): 464 (M^+, 2), 437 (14), 392 (17), 348 (24), 304 (100), 261 (43), 217 (32), 190 (18), 145 (87), 79 (31), 60 (18), 27 (29).

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