Synthesis of Spiro Dienones from Internal Acetylene and Cyclic 3-Iodo Enones in the Presence of Nickel Bromide and Zinc Powder

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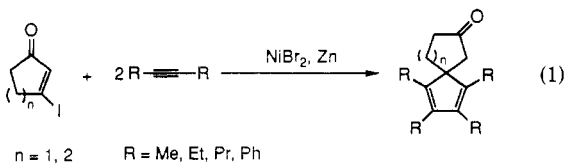
Summary: Five and six-membered cyclic 3-iodo enones undergo spiroannelation with symmetric internal acetylenes RCCR (R = Me, Et, *n*-Pr, and Ph) in the presence of $NiBr_2$ and zinc powder to afford spiro[4.4]nonadienones and spiro[4.5]decadienones in good to excellent yields at temperatures of 60–100 °C. While $NiBr_2$ is a catalyst precursor, zinc powder acts as a reducing agent in the reaction. The observed catalysis is solvent-dependent, and best yields are obtained in acetonitrile or DMF. The addition of PPh_3 to these nickel-catalyzed reactions inhibits the rates and decreases the yields of spirodienone product. Palladium complexes $PdCl_2$ and $PdCl_2{\cdot}PPh_3$ are also active catalyst precursors for the spiroannelation. A mechanism is proposed on the basis of the well-established nickel and palladium chemistry to account for the observed catalysis. The proposed mechanism gains support from the observation that the oxidative-addition adduct of $Pd(PPh_3)_4$ with 3-iodo-2-cyclohexen-1-one reacts with 2 equiv of 3-hexyne to give the corresponding spirodienone in essentially quantitative yield.

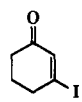
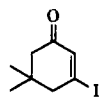
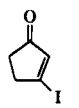
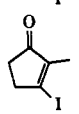
It is known that the spiro framework is an important subunit in a vast number of natural products. While various methods have been developed for spiroannelation, the construction of the subunit is usually the key step in the synthesis of these natural products. In general, particularly designed organic molecules as starting material are required, and multistep sequences are involved in the preparation of the spiro framework.[1] In this paper, we present a one-pot synthesis of polysubstituted spiro dienones from the reaction of cyclic 3-iodo enones with disubstituted acetylenes catalyzed by a nickel system (reaction 1).



n = 1, 2 R = Me, Et, Pr, Ph

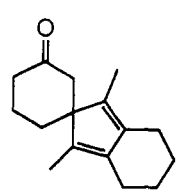
The preparation of spiro dienone from cyclic 3-iodo enone and disubstituted acetylene was carried out in acetonitrile at 60–100 °C on a millimolar scale using $NiBr_2$ as the catalyst precursor and zinc metal powder as the reducing agent. Various iodo enones and acetylenes may be used to prepare the corresponding spiro dienones by this method. The results and detailed reaction conditions are presented in Table I. All the products exhibit spectral data characteristic for the substituted spiro dienone, including a strong absorption at ca. 1710 cm^{-1} for the carbonyl group in the IR spectra and a sp^3 quaternary carbon signal at ca. 60 ppm, two sp^2 quaternary carbon signals at 135–145 ppm (four signals were observed if 3-iodo-2-methyl-2-cyclopenten-1-one was used), and a carbonyl resonance at ca. 215 ppm in the ^{13}C NMR spectra. The mass spectra and the coupling patterns in the ^1H NMR spectra of these products are also fully consistent with the proposed structure.

Table I. Formation of Spiro Dienones from β-Iodo Enones and Disubstituted Acetylenes

β-iodo enone	alkyne	time, h	product	yield, %[a]
	2-butyne	14	1	83
	3-hexyne	20	2	85
	4-octyne	20	3	81
	PhC_2Ph	120	4	71
	2,8-decadiyne	24	5	13
	2-butyne	14	6	85
	3-hexyne	20	7	57
	4-octyne	20	8	53
	2-butyne	14	9	54
	3-hexyne	20	10	87
	4-octyne	20	11	80
	2-butyne	14	12	55
	3-hexyne	20	13	84
	4-octyne	20	14	74

[a] Isolated yields are based on the acetylenes employed. No attempt was made to optimize the yield of each individual reaction.

In the present catalytic reactions, only symmetric internal acetylenes gave single spiro products which were readily characterized. Most of the symmetric acetylenes tested including the sterically hindered diphenylacetylene, gave the expected products in good yields, although a longer reaction time is required for the spiroannelation of the latter acetylene. Interestingly, 2,8-decadiyne also reacts with 3-iodo-2-cyclohexen-1-one under the catalytic conditions to give compound **5**, which contains three rings and a spiro subunit, albeit in low yield (Table I).



5

There is no expected spiro product obtained between bis(trimethylsilyl)acetylene and 3-iodo-2-cyclohexen-1-one. Unsymmetrical internal acetylenes in general lead to the formation of regioisomers which are difficult to separate, while terminal acetylenes presumably yield different types

(1) (a) Marshall, J. A.; Brady, St. F.; Anderson, N. H. *Fortschr. Chem. Org. Naturst.* **1974**, *31*, 283. (b) Krapcho, P. A. *Synthesis* **1974**, 383. (c) Krapcho, P. A. *Synthesis* **1976**, 425. (d) Krapcho, P. A. *Synthesis* **1978**, 77. (e) Vendewalle, M.; DeClercq, P. *Tetrahedron* **1985**, *41*, 1767. (f) Trost, B. M. *Pure Appl. Chem.* **1975**, *43*, 563. (g) Martin, J. D.; Perez, C.; Ravelo, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 7801. (h) Heathcock, C. H.; Graham, S. L.; Pirrung, M. C.; Plavac, F.; White, C. T. In *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley: New York, 1983. (i) Martin, J. D. In *Studies in Natural Products Chemistry*; Atta-ur-Rahman, Ed.; Elsevier: Amsterdam, 1990; Vol. 6. (j) Martin, S. F. *Tetrahedron* **1980**, *36*, 419. (k) Wender, P. A.; White, A. W. *J. Am. Chem. Soc.* **1988**, *110*, 2218. (l) Piers, E.; Lau, C. K.; Nagakura, I. *Tetrahedron Lett.* **1976**, 3233. (m) Piers, E.; Nagakura, I. *Tetrahedron Lett.* **1976**, 3237. (n) Abelman, M. M.; Overman, L. E. *J. Am. Chem. Soc.* **1988**, *110*, 2328. (o) Suzuki, M.; Kurosawa, E. *Tetrahedron Lett.* **1987**, 4805. (p) Suzuki, M.; Furusaki, A.; Kurosawa, E. *Tetrahedron* **1979**, *35*, 823.

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Table II. Effect of the Reducing Agent, Solvent, Catalyst, and Reaction Temperature on the Yield of Spiro Dienone[a]

entry no.	catalyst	reducing agent	solvent	temp, °C	time, h	yield, %[b]
1	$NiBr_2$	Zn	CH_3CN	80	14	98
2	$NiBr_2$·PPh_3	Zn	CH_3CN	80	14	82
3	$NiBr_2$·$2PPh_3$	Zn	CH_3CN	80	14	71
4	$NiBr_2$·$4PPh_3$	Zn	CH_3CN	80	14	49
5	$NiBr_2$·$6PPh_3$	Zn	CH_3CN	80	14	47
6	$NiBr_2$	Mg	CH_3CN	80	40	80
7	$NiBr_2$	$SnCl_2$	CH_3CN	80	14	trace
8	$NiBr_2$	$NaBH_4$	CH_3CN	room temp	14	0
9	$NiBr_2$	Zn	DMF	100	2	96
10[c]	$NiBr_2$	Zn	DMF	100	2	91
11	$NiBr_2$	Zn	toluene	100	14	trace
12	$PdCl_2$	Zn	CH_3CN	60	14	90
13	$Pd(OAc)_2$	Zn	CH_3CN	80	4	18
14	$PdCl_2(PhCN)_2$	Zn	CH_3CN	80	4	15
15	$PdCl_2(CH_3CN)_2$	Zn	CH_3CN	80	4	15
16	$PdCl_2$·PPh_3	Zn	CH_3CN	80	14	85

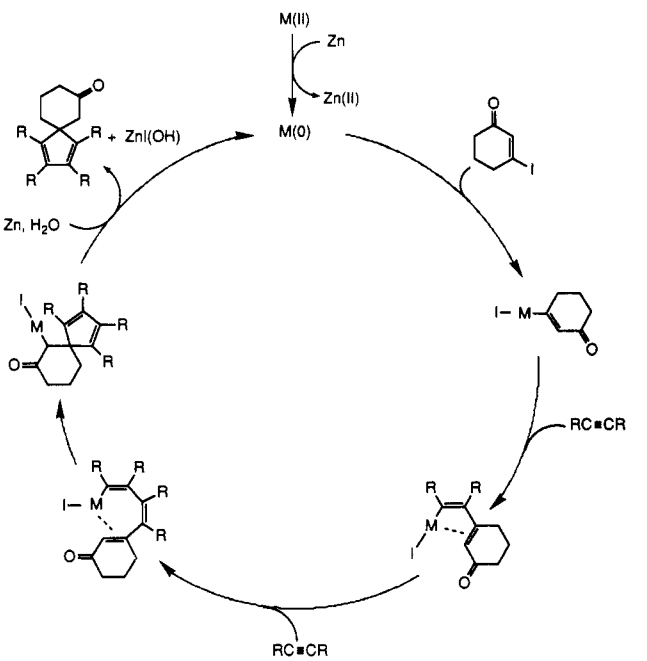
[a] All reaction solutions contain catalyst (0.2 mmol), reducing agent (1.2 mmol), 3-hexyne (2.0 mmol), and 3-iodo-2-cyclohexen-1-one (1.0 mmol) in 0.60 mL of solvent. [b] Determined by the NMR integration method using 1,3,5-trimethylbenzene as the internal standard. [c] 3-Bromo-2-cyclohexen-1-one was used as starting material.

of products, the structures of which have yet to be determined. As indicated in Table I, great selectivities of spiroannelation for most of the six- and five-membered cyclic 3-iodo enones with internal acetylenes were observed. The reactions of 5,5-dimethyl-3-iodo-2-cyclohexen-1-one with 3-hexyne or 4-octyne, however, give lower yields of the expected spiro dienone (Table I). Steric effects of the methyl groups on the iodo enone and the substituents on the alkynes likely play an important role in these cases.

To understand the features of the present reactions, the effect of ligand, solvent, reducing agent, reaction temperature, and metal catalyst on the product yield were studied. In all these investigations, 3-iodo-2-cyclohexen-1-one and 3-hexyne were employed as the substrates, and the results are shown in Table II. As indicated in entries 1–5 of the table, the addition of PPh_3 appears to inhibit the reaction. Both acetonitrile and DMF are suitable as the solvent for the present catalysis, while toluene is not effective, presumably due to the low solubility of $NiBr_2$ in this solvent. Of the four reducing agents tested (entries 1, 6–8), only Zn and Mg gave good yields of the spiro dienone, although a longer reaction time was required for Mg. The use of $SnCl_2$ and $NaBH_4$ in the reaction did not afford the desired product. In acetonitrile and DMF, the reaction time required for the observed catalysis to be completed is greatly reduced when the reaction temperature increases from 60 °C (see Table I) to 100 °C (entries 1 and 9), without significant decrease in the product yield. For example, the reaction time is 20 h at 60 °C and 14 h at 80 °C in acetonitrile and only 2 h at 100 °C in DMF. It is notable that some palladium complexes such as $PdCl_2$ and $PdCl_2$·PPh_3 (entries 12, 16) are also effective catalyst systems for reaction 1. However, $Pd(OAc)_2$, $PdCl_2(PhCN)_2$, and $PdCl_2(CH_3CN)_2$ are not suitable due to the ready decomposition of these complexes to Pd metal under the reaction conditions (entries 13–15).

Although evidence for the presence of the catalytic intermediates is lacking, the catalysis of reaction 1 likely proceeds via well-established steps, i.e. reduction of M(II) (M = Ni, Pd) by zinc powder, oxidative addition of a cyclic 3-iodo enone to a M(0) species to give a M(II) species, and double insertions of acetylenes in the M–carbon bond, followed by an intramolecular olefin insertion into the resulting metal–alkenyl species. Protonation of the final intermediate yields the desired product (Scheme I). The ability of α,β-unsaturated ketones to accept a soft nucleophile at the β-carbon is apparently the driving force for the spiroannelation.[2] Support for the protonation in

Scheme I



the last step comes from the observation that addition of D_2O to the reaction of 3-iodo-2-methyl-2-cyclopenten-1-one with 3-hexyne led to partial deuteration of the final product at the carbon to which the methyl group is attached. The deuterated product is readily distinguished from the protonated product by NMR spectroscopy. In the ^1H NMR spectrum of the product mixture, the methyl group of the deuterated product appears as a singlet at δ 0.56 ppm, while the corresponding resonance of the protonated product occurs as a doublet at δ 0.57 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the signal for the carbon where the methyl group is attached appears as a triplet at δ 48.91 and as a singlet at δ 49.48 ppm for the deuterated and protonated products, respectively. From the relative intensities of the resonances at δ 0.56 (s) and 0.57 (d) ppm for the methyl group in the ^1H NMR spectrum of the product mixture, the ratio of the deuterated to the protonated product is determined to be approximately 1:1. Analysis of the mass spectrum of the product mixture further confirms the presence of the deuterated and pro-

(2) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146.

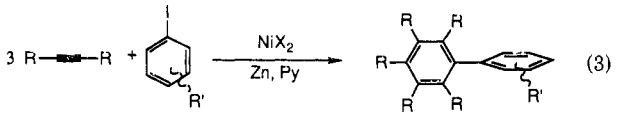
tonated products, the molecular ions of which appear at m/e 261 and 260, respectively.

While attempts to isolate the oxidative-addition product of 3-iodo-2-cyclohexen-1-one with nickel(0) species failed, the reaction of this iodo enone with $Pd(PPh_3)_4$ successfully yielded the oxidative-addition adduct.[3] As a model study, the palladium adduct was allowed to react with 2 equiv of 3-hexyne in THF at 60 °C for 10 h. The NMR spectrum of the solution indicates that the reaction gave the corresponding spiro dienone in essentially quantitative yield (reaction 2). No intermediate was observed from the

(2)

reaction, indicating that the insertion of a alkyne molecule into the palladium–alkenyl bond is slow relative to other steps. The observation gives strong support for the presence of oxidative-addition and alkyne-insertion steps in Scheme I.

It is interesting to compare the difference and similarity between the present nickel-catalyzed reaction and the closely related reaction of aryl iodide with internal acetylene.[4] In the latter, each aryl iodide reacted with three acetylenes to yield an unsymmetrical biaryl (reaction 3),



(3)

while in the former only two acetylenes were consumed for each spiro compound produced. In both reactions, nickel halide–zinc was employed as the catalyst system, and only internal acetylene gave the expected products. To our best knowledge, there is no report in the literature concerning the reaction between vinyl halide and acetylene catalyzed by a nickel system. However, the reaction of 4-*tert*-butyl-1-cyclohexene triflate with (trimethylsilyl)acetylene catalyzed by a palladium complex to give a spiro compound in 49% yield[5] has been presented. Related works on the reactions of vinyl iodides with acetylene to give substituted fulvenes are also known.[5,6]

In summary, we have demonstrated an unusual and efficient method for the synthesis of polyalkylated or polyarylated spiro[4.5] and spiro[4.4]dienones using nickel or palladium species as the catalyst system. The mechanism of the catalytic reactions may be understood on the basis of the well-established nickel and palladium chemistry.

Experimental Section

All reactions were performed under dry nitrogen, and all solvents were dried by standard methods. The ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer at 300 and 75.4 MHz, while infrared spectra were obtained on a Bomem MB-100 instrument. Low-resolution mass spectra were performed on a JEOL JMS-D 100 mass spectrometer. High-resolution mass spectra were recorded on a JEOL JMS-HX 110 instrument.

All chemicals were obtained from commercial suppliers and used without further purification unless otherwise noticed. The following 3-halocycloalken-1-ones were prepared according to the published procedures: 3-iodo-2-cyclohexen-1-one, 5,5-dimethyl-3-iodo-2-cyclohexen-1-one, 3-iodo-2-cyclopenten-1-one, 2-methyl-3-iodo-2-cyclohexen-1-one, and 3-bromo-2-cyclohexen-1-one.[7]

Synthesis of Spiro Dienones from Internal Acetylene and Cyclic 3-Iodo Enones. A typical procedure is as follows. To a mixture of $NiBr_2$ (0.080 g, 0.36 mmol), zinc powder (0.14 g, 2.2 mmol), and 3-iodo-2-cyclohexen-1-one (0.40 g, 1.8 mmol) in acetonitrile (1.0 mL) was added 3-hexyne (0.30 g, 3.6 mmol). The system was then heated under nitrogen at 60 °C with stirring for 20 h. During the course of catalysis, the color of the solution changed from light green to dark red in the first few hours and the color remained the same until the end of the reaction. The acetonitrile solution was then cooled, concentrated, and separated on a silica gel column using hexane–ethyl acetate (10/1, v/v) as the eluent to give the desired product 1,2,3,4-tetraethylspiro-[4.5]deca-1,3-dien-7-one (2) in 85% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 1.04 (t, J = 7.5 Hz, 12 H), 1.70 (t, J = 6.4 Hz, 2 H), 2.09–2.25 (m, 12 H), 2.46 (t, J = 6.6 Hz, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 14.51 (q), 15.01 (q), 18.42 (t), 18.73 (t), 23.24 (t), 29.62 (t), 40.31 (t), 45.67 (t), 59.85 (s), 140.70 (s), 146.75 (s), 213.93 (s). IR (neat): 2971, 2943, 2879, 1712, 1458, 1369, 761 cm^{-1}. HRMS: m/e calcd for $C_{18}H_{28}O$ 260.2141, found 260.2141.

Other spiro dienones were prepared similarly. The detailed reaction conditions and isolated yields are presented in Table I. Important spectral data for these compounds are listed below.

1,2,3,4-Tetramethylspiro[4.5]deca-1,3-dien-7-one (1): ^1H NMR (300 MHz, $CDCl_3$) δ 1.63 (t, J = 6.6 Hz, 2 H), 1.74 (s, 6 H), 1.77 (s, 6 H), 2.10 (s, 2 H), 2.11–2.19 (m, 2 H), 2.43 (t, J = 6.8 Hz, 2 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 10.79 (q), 11.17 (q), 22.66 (t), 29.54 (t), 40.37 (t), 45.48 (t), 58.94 (s), 134.29 (s), 140.54 (s), 213.93 (s); IR (neat) 2936, 2865, 1710, 1446, 1225 cm^{-1}; HRMS m/e calcd for $C_{14}H_{20}O$ 204.1515, found 204.1509.

1,2,3,4-Tetraethylspiro[4.5]deca-1,3-dien-7-one (2): ^1H NMR (300 MHz, $CDCl_3$) δ 1.04 (t, J = 7.5 Hz, 12 H), 1.70 (t, J = 6.4 Hz, 2 H), 2.09–2.25 (m, 12 H), 2.46 (t, J = 6.6 Hz, 2 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 14.51 (q), 15.01 (q), 18.42 (t), 18.73 (t), 23.24 (t), 29.62 (t), 40.31 (t), 45.67 (t), 59.85 (s), 140.70 (s), 146.75 (s), 213.93 (s); IR (neat) 2971, 2943, 2879, 1712, 1458, 1369, 761 cm^{-1}; HRMS m/e calcd for $C_{18}H_{28}O$ 260.2141, found 260.2141.

1,2,3,4-Tetra-*n*-propylspiro[4.5]deca-1,3-dien-7-one (3): ^1H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, J = 7.4 Hz, 12 H), 1.33–1.43 (m, 8 H), 1.67 (t, J = 6.3 Hz, 2 H), 2.00–2.16 (m, 12 H), 2.45 (t, J = 6.6 Hz, 2 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 14.24 (q), 14.64 (q), 23.07 (t), 23.14 (t), 23.75 (t), 27.96 (t), 28.68 (t), 29.86 (t), 40.27 (t), 45.87 (t), 59.73 (s), 139.45 (s), 145.91 (s), 213.90 (s); IR (neat) 2957, 2930, 2872, 1702, 1460, 1096 cm^{-1}; HRMS m/e calcd for $C_{22}H_{36}O$ 316.2767, found 316.2774.

1,2,3,4-Tetraphenylspiro[4.5]deca-1,3-dien-7-one (4): ^1H NMR (300 MHz, $CDCl_3$) δ 1.43–1.52 (m, 2 H), 1.99 (t, J = 6.8 Hz, 2 H), 2.18 (t, J = 6.2 Hz, 2 H), 2.64 (s, 2 H), 6.81 (dd, J = 7.7, 1.9 Hz, 4 H), 6.95–7.03 (m, 6 H), 7.13 (dd, J = 7.7, 1.7 Hz, 4 H), 7.22–7.30 (m, 6 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 20.98 (t), 28.90 (t), 39.47 (t), 44.98 (t), 61.54 (s), 126.40 (d), 127.30 (d), 127.36 (d), 128.37 (d), 130.10 (d), 130.93 (d), 135.22 (s), 137.14 (s), 141.70 (s), 150.72 (s), 212.10 (s); IR (KBr): 3072, 3048, 3020, 2930, 2873, 1710, 1597, 1489, 1440, 1222, 1072, 1027, 783, 731, 689 cm^{-1}; HRMS m/e cald for $C_{24}H_{28}O$ 452.2142, found 452.2140; mp 187 °C.

1,2,3,4,9,9-Hexamethylspiro[4.5]deca-1,3-dien-7-one (6): ^1H NMR (300 MHz, $CDCl_3$) δ 1.06 (s, 6 H), 1.44 (s, 2 H), 1.66 (s, 6 H), 1.68 (s, 6 H), 2.07 (s, 2 H), 2.22 (s, 2 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 10.29 (q), 10.87 (q), 31.40 (q), 37.06 (t), 42.12 (t), 51.75 (t), 55.19 (s), 133.30 (s), 142.28 (s), 214.52 (s); IR (neat) 2951, 2931, 2871, 1704, 1374, 1160, 756 cm^{-1}; HRMS m/e calcd for $C_{16}H_{24}O$ 232.1828, found 232.1828.

9,9-Dimethyl-1,2,3,4-tetraethylspiro[4.5]deca-1,3-dien-7-one (7): ^1H NMR (300 MHz, $CDCl_3$) δ 1.04 (t, J = 7.5 Hz, 6 H), 1.08 (t, J = 7.5 Hz, 6 H), 1.15 (s, 6 H), 1.67 (s, 2 H), 2.10–2.25 (m, 8 H), 2.28 (s, 2 H), 2.32 (s, 2 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) 14.58 (q), 14.97 (q), 18.46 (t), 18.56 (t), 31.37 (s), 31.57 (q), 36.37 (t), 42.39 (t), 51.77 (t), 56.49 (s), 139.72 (s), 148.27 (s), 214.75 (s); IR (neat) 2958, 2930, 2870, 1698, 1458, 1374, 1275, 1180, 1056,

(3) Onishi, M.; Yamamoto, H.; Hiraki, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1856.
(4) Kong, K. C.; Cheng, C. H. *J. Chem. Soc., Chem. Commum.* **1991**, 423.
(5) Lee, G. C. M.; Tobias, B.; Holmes, J. M.; Harcourt, D. A.; Garst, M. E. *J. Am. Chem. Soc.* **1990**, *112*, 9330.
(6) Silverberg, L. J.; Wu, G.; Rheingold, A. L.; Heck, R. F. *J. Organomet. Chem.* **1991**, *409*, 411 and references cited therein.
(7) Piers, E.; Grierson, J. R.; Lau, C. K.; Nagakura, I. *Can. J. Chem.* **1982**, *60*, 210.

759 cm^{-1}; HRMS m/e calcd for $C_{20}H_{32}O$ 288.2454, found 288.2450.

9,9-Dimethyl-1,2,3,4-tetra-*n*-propylspiro[4.5]deca-1,3-dien-7-one (8): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, J = 7.4 Hz, 12 H), 1.24 (s, 6 H), 1.32–1.48 (m, 8 H), 1.66 (s, 2 H), 2.04–2.19 (m, 8 H), 2.27 (s, 2 H), 2.31 (s, 2 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 14.18 (q), 14.67 (q), 23.08 (t), 23.57 (t), 27.95 (t), 28.47 (t), 31.36 (s), 31.52 (q), 36.52 (t), 42.48 (t), 51.78 (t), 56.36 (s), 138.54 (s), 147.34 (s), 214.55 (s); IR (neat) 2950, 2929, 2875, 1702, 1375, 1275, 1158, 759 cm^{-1}; HRMS m/e calcd for $C_{24}H_{40}O$ 344.3081, found 344.3079.

1,2,3,4-Tetramethylspiro[4.4]nona-1,3-dien-7-one (9): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.77 (s, 12 H), 1.91 (t, J = 8.4 Hz, 2 H), 2.17 (s, 2 H), 2.53 (t, J = 8.4 Hz, 2 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 10.08 (q), 10.84 (q), 27.76 (t), 37.64 (t), 43.78 (t), 59.50 (s), 134.38 (s), 139.48 (s), 220.98 (s); IR (neat) 2975, 2929, 1732, 1389, 1144, 755 cm^{-1}; HRMS m/e calcd for $C_{13}H_{18}O$ 190.1358, found 190.1348.

1,2,3,4-Tetraethylspiro[4.4]nona-1,3-dien-7-one (10): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06 (t, J = 7.5 Hz, 12 H), 2.01 (t, J = 8.4 Hz, 2 H), 2.04–2.27 (m, 10 H), 2.52 (t, J = 8.4 Hz, 2 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 14.67 (q), 15.11 (q), 18.29 (t), 18.48 (t), 27.77 (t), 37.70 (t), 44.16 (t), 60.00 (s), 140.69 (s), 145.48 (s), 221.07 (s); IR (neat) 2969, 2935, 2876, 1721, 1459, 1402, 1379, 1158, 1059 cm^{-1}; HRMS m/e calcd for $C_{17}H_{26}O$ 246.1985, found 246.1989.

1,2,3,4-Tetra-*n*-propylspiro[4.4]nona-1,3-dien-7-one (11): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, J = 7.4 Hz, 12 H), 1.35–1.48 (m, 8 H), 1.98 (t, J = 8.4 Hz, 2 H), 2.03–2.20 (m, 8 H), 2.25 (s, 2 H), 2.49 (t, J = 8.4 Hz, 2 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 14.23 (q), 14.56 (q), 14.60 (q), 14.66 (q), 23.20 (t), 23.73 (t), 27.89 (t), 27.98 (t), 28.15 (t), 37.70 (t), 44.33 (t), 60.00 (s), 139.56 (s), 144.52 (s), 221.02 (s); IR (neat): 2960, 2930, 2872, 1733, 1460, 1403, 1377, 1154 cm^{-1}; HRMS m/e calcd for $C_{21}H_{34}O$ 302.2611, found 302.2590.

1,2,3,4,6-Pentamethylspiro[4.4]nona-1,3-dien-7-one (12): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.56 (d, J = 6.7 Hz, 3 H), 1.62 (s, 3 H), 1.62–1.73 (m, 1 H), 1.73 (s, 3 H), 1.75 (s, 3 H), 1.82 (s, 3 H), 2.03–2.15 (m, 1 H), 2.31 (q, J = 6.7 Hz, 1 H), 2.48–2.53 (m, 2 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 7.04 (q), 8.90 (q), 10.48 (q), 11.13 (q), 11.95 (q), 25.23 (t), 35.61 (t), 49.48 (d), 63.54 (s), 135.84 (s), 135.90 (s), 135.98 (s), 137.88 (s), 221.35 (s); IR (neat) 2976, 2935, 2875, 1720, 1381, 1165, 758 cm^{-1}; HRMS m/e calcd for $C_{21}H_{34}O$ 302.2611, found 302.2606.

6-Methyl-1,2,3,4-tetraethylspiro[4.4]nona-1,3-dien-7-one (13): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.57 (d, J = 6.8 Hz, 3 H), 0.98–1.11 (m, 12 H), 1.49–1.62 (m, 1 H), 1.76–1.84 (m, 1 H), 2.14–2.62 (m, 11 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 6.98 (q), 14.78 (q), 14.83 (q), 17.24 (t), 18.11 (t), 18.80 (t), 19.37 (t), 25.33 (t), 35.97 (t), 49.48 (d), 63.96 (s), 142.36 (s), 142.53 (s), 143.39 (s), 221.76 (s); IR (neat) 2976, 2939, 2878, 1723, 1457, 1372, 1137, 757 cm^{-1}; HRMS m/e calcd for $C_{18}H_{28}O$ 260.2141, found 260.2148.

6-Methyl-1,2,3,4-tetra-*n*-propylspiro[4.4]nona-1,3-dien-7-one (14): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.57 (d, J = 7.0 Hz, 3 H), 0.88–0.99 (m, 12 H), 1.36–1.48 (m, 9 H), 1.71–1.79 (m, 1 H), 2.07–2.06 (m, 11 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 7.14 (q), 14.24 (q), 14.53 (q), 14.70 (q), 23.25 (t), 23.53 (t), 23.62 (t), 25.55 (t), 27.23 (t), 27.70 (t), 28.31 (t), 29.22 (t), 36.03 (t), 49.53 (d), 64.00 (s), 141.10 (s), 141.40 (s), 141.70 (s), 142.50 (s), 221.67 (s); IR (neat) 2963, 2876, 1726, 1458, 1375, 1176, 1083, 761 cm^{-1}; HRMS m/e calcd for $C_{22}H_{36}O$ 316.2627, found 316.2759.

6-Deuterio-6-methyl-1,2,3,4-tetraethylspiro[4.4]nona-1,3-dien-7-one (13-*d*): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.56 (s, 3 H), 0.98–1.11 (m, 12 H), 1.49–1.62 (m, 1 H), 1.76–1.84 (m, 1 H), 2.14–2.62 (m, 10 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 6.81 (q), 14.69 (q), 14.76 (q), 17.18 (t), 18.05 (t), 18.74 (t), 19.31 (t), 25.27 (t), 35.93 (t), 48.91 (t, J_{C-D} = 18.5 Hz), 63.84 (s), 142.30 (s), 142.48 (s), 143.31 (s), 221.91 (s); MS m/e 261 ($C_{18}DH_{27}O$).

Compound 5: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.62 (t, J = 6.7 Hz), 1.70 (s, 6 H), 1.71–1.79 (m, 4 H), 2.10 (s, 2 H), 2.10–2.18 (m, 2 H), 2.22–2.30 (m, 4 H), 2.43 (t, J = 6.8 Hz, 2 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 10.99 (q), 22.90 (t), 23.62 (t), 23.85 (t), 29.86 (t), 40.52 (t), 45.74 (t), 59.33 (s), 134.95 (s), 139.50 (s), 214.00 (s); IR (neat) 2960, 2939, 2879, 1710, 1458, 1366, 1101, 760 cm^{-1}; HRMS m/e calcd for $C_{16}H_{22}O$ 230.1672, found 230.1678.

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Registry No. 1, 140110-75-4; 2, 140110-76-5; 3, 140110-77-6; 4, 140110-78-7; 5, 140110-79-8; 6, 140110-80-1; 7, 140110-81-2; 8, 140110-82-3; 9, 140110-83-4; 10, 140110-84-5; 11, 140110-85-6; 12, 140110-86-7; 13, 140110-87-8; 13-*d*, 140110-88-9; 14, 140110-89-0; PhC_2Ph, 501-65-5; $NiBr_2$, 13462-88-9; Zn, 7440-66-6; $NiBr_2$·PPh_3, 25802-21-5; $NiBr_2$·$2PPh_3$, 14126-37-5; $NiBr_2$·$4PPh_3$, 140110-90-3; $NiBr_2$·$6PPh_3$, 140110-91-4; $Pd(OAc)_2$, 301-04-2; $PdCl_2(PhCN)_2$, 14220-64-5; $PdCl_2(CH_3CN)_2$, 14592-56-4; $PdCl_2$·PPh_3, 116694-43-0; Mg, 7439-95-4; $SnCl_2$, 7772-99-8; 3-iodo-2-cyclohexen-1-ol, 56671-82-0; 5,5-dimethyl-3-iodo-2-cyclohexen-1-one, 56671-85-3; 3-iodo-2-cyclopenten-1-one, 61765-46-6; 3-iodo-2-methyl-2-cyclopenten-1-one, 56778-49-5; 2-butyne, 503-17-3; 3-hexyne, 928-49-4; 4-octyne, 1942-45-6; 2,8-decadiyne, 29518-82-9; 3-bromo-2-cyclohexen-1-one, 56671-81-9.

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Stereochemistry of the Dicarbonylation of Olefins Using Styrene as the Model Compound

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Summary: The dicarbonylation reaction of *trans*-β-deuteriostyrene to dimethyl 2-phenylbutanedioate and dimethyl 2,5-diphenyl-4-oxoheptanedioate using Pd(CF$_3$COO)$_2$/2,2′-bipyridine as the catalyst precursor in the presence of 1,4-benzoquinone (i.e., under conditions suitable for the formation of syndiotactic poly(1-phenyl-3-oxotrimethylene)) takes place stereospecifically in a syn fashion. The same stereochemical outcome was found for the dicarbonylation of the same substrate to dimethyl 2-phenylbutanedioate in the presence of (Diop)Pd(CF$_3$COO)$_2$.

The dicarbonylation of olefinic substrates is of interest due to the nature of the products that can be obtained, namely succinic acid derivatives[1] and (2-substituted) poly(1-oxotrimethylenes)[2-4] (compare Scheme I for styrene). The first reaction is carried out in methanol using

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