Highly Stereoselective Synthesis of Conjugated Polyenes via a Homocoupling Reaction of Unsaturated Silanes

Francesco Babudri, Angela R. Cicciomessere, Gianluca M. Farinola, Vito Fiandanese,
Giuseppe Marchese, Roberta Musio, Francesco Naso,* and Oronzo Sciacovelli

*Centro CNR di Studio sulle Metodologie Innovative di Sintesi Organiche, Dipartimento di Chimica,
Università di Bari, via Amendola 173, 70126 Bari, Italy*

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A new method for the synthesis of conjugated polyenes containing up to eight double bonds with *all-E* configuration is reported. The procedure is based upon a homocoupling reaction of dienyl-, trienyl-, or tetraenylsilanes, promoted by $PdCl_2$ in methanol and in the presence of LiCl and $CuCl_2$. Configurational and conformational assignments were rigorously made on the basis of NMR spectra. The compounds obtained represent a novel interesting class of symmetrically substituted polyenes with potential optical and electrooptical properties. By changing the solvent, the homocoupling process can be switched to the halogenation of the silyl-substituted terminal double bond, thus leading to polyenyl halides.

Introduction

The concept of molecular electronics,[1] i.e. the possibility of performing electronic functions in molecular scale, has led to extensive investigations about electrical[2] and optical[3] properties of organic molecules.

Among the various classes of organic compounds which are of particular importance in these studies, molecules with a long conjugated π-system are envisaged as the most promising materials for future applications in molecular-electronic devices.

Both conjugated polymers and polyenes with a defined length of the π-system are well-known to provide large and fast second-order and third-order nonlinear optical responses.[3a,4] In particular, the third-order nonlinear susceptibility, χ^3, has been determined for α,ω-diphenylpolyenes up to six conjugated double bonds,[5] and an enhancement in the values of χ^3 is expected for bipolaronic states of these and other α,ω-disubstituted polyenes.[6]

Owing to the presence of high polarizable π-electrons, similar molecules should act as connectors permitting electron flow to occur between different elements of a molecular electronic system (molecular wires).[7] Moreover, α,ω-disubstituted polyolefinic systems bearing an electron-accepting group on one end and a donor group on the opposite end, the so-called "push−pull" polyenes, show a preferential one-way electron transfer, and such molecular wires should simulate a rectifying component.[7] Polyenes with a defined length of the π-system are also taken as discrete models of polymeric conjugated materials. For example, the behavior of anionic species generated from α,ω-diphenylpolyenes has been investigated in order to clarify the charge transfer mechanism in *trans*-polyacetylene.[8]

In this framework, the presence of a stereoregular *all-E* structure in the polyenes is of importance. Thus, it is not surprising that considerable efforts have been made to search for stereoselective methods of synthesis of these conjugated systems. The availability of some polyconjugated stereodefined carbonyl compounds, such as crocetin dialdehyde or 2,7-dimethyloctatriendial,[9a] structurally derived from carotenoids, opens the access to carotenoid-like polyenes with a more extended π-system, via Wittig or Wittig-like olefination. Following these synthetic procedures, polyenes which combine the structural features of carotenoids and various terminal groups such as anthryl,[9] naphthyl,[9a] thienyl,[10] pyridyl,[9b,11] and 5,10,15,20-tetraphenylporphyrinyl[9a,d] or push−pull polyenes with a similar structure have been synthesized.[12] However, referring to the stereochemistry of the new double bonds formed, Wittig olefination and related

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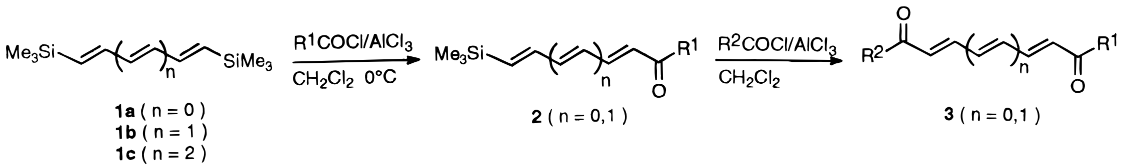
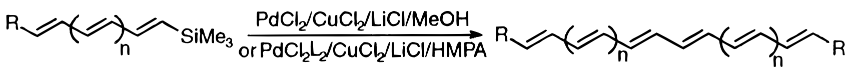
Scheme 1



Scheme 2



2a	R = PhCO	n = 0	**4a**
2b	R = PhCO	n = 1	**4b**
2c	R = $PhCH_2CO$	n = 1	**4c**
2d	R = 4-$CH_3C_6H_4CH_2CO$	n = 1	**4d**
2e	R = 4-n-$C_{10}H_{21}C_6H_4CH_2CO$	n = 1	**4e**
2f	R = PhCO	n = 2	**4f**
2g	R = Ph	n = 0	**4g**

methods often lead to an *E*/*Z* mixture of products, from which the *all-E* isomer has to be isolated.[9a]

Wittig or Horner–Emmons–Wadsworth approaches are also useful for the preparation of symmetrically substituted polyenes with 6–10 double bonds and a variety of terminal groups (such as quinone or hydroquinone,[13] aryl,[14a] alkylthiophenyl,[6a] alkoxyphenyl,[6a] alkoxythienyl,[6a,14c] ferrocenyl[14d–f]) and without angular methyl groups in the polyenic chain. The lack of substituents appears to favor the *all-E* configuration of these polyenes.

The Wittig procedure has been also adopted for the synthesis of both bis([2.2.2]paracyclophanyl)butadiene and hexatriene.[15]

Besides the Wittig procedure other synthetic approaches have attracted attention for the preparation of conjugated polyenes. 6-(Cyclopentadienyl)pentafulvenes[16] with up to five double bonds have been prepared by condensation of sodium cyclopentadienide with vinamidinium salts. Mixture of isomers of *tert*-butyl-capped polyenes containing even or odd numbers of double bonds up to 15 have been obtained by ring-opening methathesis oligomerization of 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]-deca-3,7,9-triene promoted by tungsten catalyst, followed by retro-Diels–Alder reaction.[17] However, a mixture of isomers of various lengths is obtained, and photochemical isomerization is required for inversion to the *all-E* counterpart. *all-E* tetraenedioates and pentaenedioates have been prepared in moderate yields by palladium-catalyzed reaction of vinylic halides with shorter conjugated derivatives.[18] More recently, α,ω-dialkyl-substituted linear polyenes with up to 10 conjugated double bonds have been prepared by Stille coupling of distannylated polyenes with polyenic iodides. Once again photoirradiation of the isomeric final mixture has been used to obtain the required *E* structure.[19]

In our previous studies dealing with the synthesis of stereodefined conjugated polyenes,[20] we reported a synthetic methodology based upon the chemoselective acylation of (1*E*,3*E*)-1,4-bis(trimethylsilyl)-1,3-butadiene **1a** ($n = 0$) (Scheme 1) and (1*E*,3*E*,5*E*)-1,6-bis(trimethylsilyl)-1,3,5-hexatriene **1b** ($n = 1$) to afford, in good yields, *all-E* silylated ketones **2**, or dicarbonyl compounds **3**, with sequential double acylation reactions.[20a]

This methodology was successfully applied to the synthesis of natural products such as ostopanic acid,[20b] a diene cytotoxic fatty acid, β-parinaric acid methyl ester,[20c] with a tetraenic structure, and other trienic compounds of biological interest such as the (6*E*) isomer and a structural analogue of leukotriene B_3,[20b] benzoleukotriene B_3, a LTB_4 antagonist,[20d] and some natural dienic amides.[20e]

In the present work we illustrate the versatility and the efficient synthetic potential of silyl derivatives **1** and **2** for the highly stereoselective preparation of polyenes with more extended conjugated π-systems.

Results and Discussion

Synthesis of Polyenes. Our strategy for the synthesis of polyenes is based upon the homocoupling reactions of unsaturated silanes **2a**–**g** (Scheme 2).

In principle, the reaction is particularly attractive in view of the possibility to *double in one step* the number of conjugated double bonds. Obviously, the critical point of all the process is represented by the stereochemistry, i.e. the preservation of the geometry of the double bonds

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Scheme 3

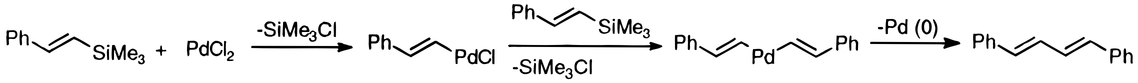

Table 1. Conjugated Polyenes 4a−g via Homocoupling Reaction of Trimethylsilyl Polyenes 2a−g

compd	reaction products (yield, %)[a]	reaction time (h)	catalytic system and solvent
2a	**4a** (50)	3.5	$PdCl_2/CuCl_2/LiCl/MeOH$
2b	**4b** (61)	3	$PdCl_2/CuCl_2/LiCl/MeOH$
2c	**4c** (30)	4	$PdCl_2/CuCl_2/LiCl/MeOH$
2d	**4d** (41)	5	$PdCl_2/CuCl_2/LiCl/MeOH$
2e	**4e** (51)	2	$PdCl_2/CuCl_2/LiCl/MeOH$
2f	**4f** (51)	4	$PdCl_2/CuCl_2/LiCl/MeOH$
2g	**4g** (52)	10	$PdCl_2/CuCl_2/LiCl/MeOH$
2a	**4a** (51)	2	$Pd(MeCN)_2Cl_2/CuCl_2/LiCl/$ HMPA
2b	**4b** (47)	3.5	$Pd(MeCN)_2Cl_2/CuCl_2/LiCl/$ HMPA

[a] Based on isolated materials.

present in the starting silanes and the stereoselectivity in the formation of the new carbon−carbon bond. A reaction of this type has only one precedent in the literature. Indeed, it has been reported that (*E*)-1-phenyl-2-(trimethylsilyl)ethene can be transformed in (1*E*,3*E*)-1,4-diphenyl-1,3-butadiene.[21] This reaction was performed in the presence of palladium dichloride in methanol, and the suggested mechanism (Scheme 3) involves the addition of $PdCl_2$ across the double bond of the vinylsilane, followed by elimination of trimethylsilyl chloride. The addition of the β-styrylpalladium chloride intermediate to a second molecule of vinylsilane, followed by elimination of trimethylsilyl chloride, affords a bis-β-styrylpalladium species which undergoes a reductive elimination of Pd(0) with formation of the diene.

Copper dichloride and lithium chloride are added to reoxidize Pd(0) to Pd(II), and the entire process is made catalytic in palladium. The reported yield in dimerization product was 30%. The cause of the moderate yield was attributed[21] to the proton desilylation of the starting vinylsilane promoted by hydrogen chloride derived from the methanolysis of the trimethylsilyl chloride. In anhydrous conditions and in the presence of 1 equiv of tertiary amine such as dicyclohexylethylamine, the yield rises to 79%. However, under these conditions the reaction is stoichiometric in $PdCl_2$, the $CuCl_2$ being ineffective in reoxidizing Pd(0).

With the aim of applying a similar procedure to more complex systems, we prepared the series of polyenylsilanes **2a**−**g** and investigated their transformation into longer polyenes **4a**−**g** (Table 1).

By performing preliminary experiments in conditions ranging from stoichiometric to catalytic in Pd(II), the best results were obtained by using a 4:1 molar ratio between starting silanes and palladium salt. The presence of a large excess of anhydrous $CuCl_2$, to ensure the reoxidation of Pd(0) to Pd(II), and of LiCl was also necessary to the catalytic system.[22] In our hands, strictly catalytic conditions gave poor results; also the stoichiometric conditions, tested with the silane **2a** in methanol and in the presence of 1 equiv of dicyclohexylethylamine, gave a low yield (27%) of the product **4a**. In an attempt to optimize the yields of these homocoupling products, we tested also a different palladium catalyst, i.e. palladium(II) bis(acetonitrile) dichloride in HMPA, which is effective in promoting the coupling of vinylstannanes to dienes.[23] On applying this procedure to ketones **2a** and **2b**, in the presence of the $CuCl_2$/LiCl couple, which is necessary to reoxidize palladium from the lower oxidation state, the yields in polyenes **4a,b** were nearly the same as those obtained with $PdCl_2/CuCl_2/LiCl$ (Table 1).

The stereochemical aspects of the reaction were investigated. For polyenes **4a**−**f** a complete and detailed NMR study allowed us to ascertain the configuration of all the double bonds of the polyenic chain. The *all-E* configuration and, as a consequence, the stereospecificity of the homocoupling reaction[24] were unambiguously demonstrated (see the following section).

NMR Data for Polyenes 4a−f. The configuration of compounds **4a**−**f** was determined by ^1H NMR spectroscopy. In compound **4a** the analysis of the ^1H-NMR spectrum was straightforward. In compounds **4b-f** the complexity and the extensive overlap of the resonance signals limit the amount of information that can be obtained from single resonance spectra. H(1)/H(1′) protons[25] give origin to a distinct doublet in all the compounds examined, and H(2)/H(2′), H(3)/H(3′), H(4)/H(4′) resonances were assigned by homonuclear decoupling experiments. Chemical shifts and coupling constants of the outer protons, H(1)/H(1′) and H(2)/H(2′), were in all cases obtained directly from ^1H single resonance spectra. For the hydrogen atoms bound to the central carbon atoms, NMR parameters could not be extracted by direct inspection of the spectra, because of second-order effects and extensive overlap of the resonance signals. Even in COSY spectra, cross-peaks originated from second-order effects precluded the possibility to obtain vicinal coupling constants $^3J_{HH}$ reliable enough to assign the configuration at the central double bonds of the polyenic chain. Least-squares analysis of the spectra was the only way to obtain chemical shifts and $^3J_{HH}$ values which permitted the required configurations to be determined unambiguously. Therefore, a modified version of the LAOCN-5[26] program was used. The eight central protons of the polyenic chains in compounds **4b**−**e**, H(3)/H(3′), H(4)/H(4′), H(5)/H(5′), and H(6)/H(6′), were analyzed as an AA′BB′CC′DD′ spin system. The resonances of H(3)/H(3′), H(5)/H(5′), and H(6)/H(6′) are located in a narrow range (50 Hz), and spin-tickling experiments were necessary for a correct

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[24] In order to increase the extent of the conjugated π-system, we transformed the diketo polyenes **4c**, **4d**, and **4e** in α,ω-diphenylhexadecaoctaenes by reduction of the two carbonyl functions and dehydration of the resulting diols. The products were reddish amorphous solids, completely insoluble in all common organic solvents and therefore very difficult to characterize. For the polyene derived from **4c**, a solid state ^1H NMR and ^{13}C NMR analysis confirmed the structure of 1,16-diphenylhexadecaoctaene, but no information about the configuration of the double bonds could be derived.

[25] For the sake of clarity the two carbon atoms at the ends of polyenic chains bound to carbonyl groups (and consequently the two hydrogen atoms bound to them) have been numbered as 1 and 1′. Other hydrogen and carbon atoms have been numbered in increasing order moving toward the center of the chain. This numeration, although differing from IUPAC rules, has been adopted in order to point out the symmetry of these molecules.

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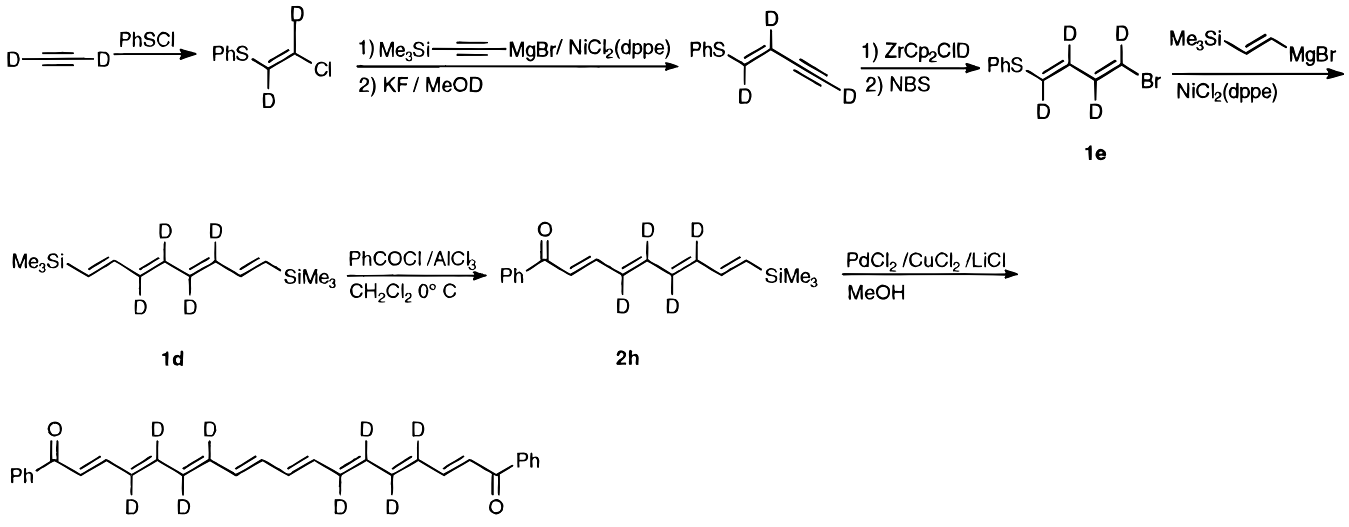
Scheme 4



1e

1d

2h

4h

Table 2. ^{1}H NMR Chemical Shifts[a] and Vicinal Coupling Constants[b] for Polyenes 4a-f

compd	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)
4a	7.07 (14.82)	7.48 (10.74)	6.65 (14.99)	6.76 (11.23)				
4b	6.99 (14.89)	7.48 (11.40)	6.53 (14.80)	6.69 (10.16)	6.43 (14.12)	6.48 (11.95)		
4c	6.23 (15.23)	7.25 (11.39)	6.33 (14.74)	6.65 (10.65)	6.38 (15.12)	6.46 (10.79)		
4d	6.21 (15.28)	7.25 (11.42)	6.33 (14.69)	6.64 (11.19)	6.38 (14.09)	6.45 (11.85)		
4e	6.22 (15.23)	7.26 (11.34)	6.34 (14.78)	6.65 (11.0)	6.38 (14.19)	6.45 (11.09)		
4f	6.97 (14.9)	7.47 (11.5)	6.49 (14.7)	6.72 (11.0)	6.42 (15.0)	6.48 (10.0)	6.43 (14.83)	6.40 (11.40)

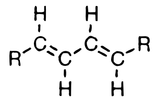
[a] ^{1}H NMR chemical shifts are listed in ppm vs TMS in $CDCl_3$. [b] Vicinal coupling constants of each proton with the following one in the polyenic chain are reported in parentheses (in hertz).

assignment of the experimental frequencies to the calculated transitions. COSY spectra were helpful in estimating the proton chemical shift values used to start the iterative analysis.

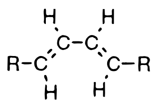
For compound **4f** decoupling of H(4)/H(4′) allowed the H(3)/H(3′) and H(5)/H(5′) resonances to be localized; these resonances strongly overlap with H(6)/H(6′), H(7)/H(7′) and H(8)/H(8′) resonances. Since the signals arising from these 10 protons are located in a range of 90 Hz, it was not possible to carry out the spectral analysis of the spin system H(5)/H(5′), H(6)/H(6′), H(7)/H(7′), and H(8)/H(8′). The stereochemistry of the fragment C(7)−C(8)−C(8′)−C(7′) was determined for the partially and selectively deuterated octaene **4h**, prepared following the same procedure adopted for the nondeuterated analogue, starting from 3,4,5,6-tetradeuterated bis(trimethylsilyl) tetraene **1d** (Scheme 4). This in turn was prepared by nickel-catalyzed cross-coupling reaction of 2 mol of [2-(trimethylsilyl)ethenyl]magnesium bromide with 1-bromo-4-(phenylthio)-1,3-butadiene-*1,2,3,4-d*$_4$ (**1e**) obtained by adapting the procedure described for the light counterpart.[20f]

The ^{1}H-NMR spectrum of the four central protons of **4h** was analyzed as an AA′BB′ spin system. The coupling constants between H(7)/H(7′) and the deuterium atoms on C(6)/C(6′) (~2 Hz) were taken into account as first-order perturbations. In all cases coupling constants over four (−0.58 to −0.87 Hz) and five (+0.32 to +0.69 Hz) bonds were also considered in performing the spectral analysis.

Chemical shifts and vicinal coupling constants are reported in Table 2. Vicinal coupling constants across double bonds are in the range 14.2−15.3 Hz, thus indicating the *all-E* configuration of the conjugated system.[27] The $^3J_{HH}$ values across single carbon−carbon bonds, which are in the range 10.0−11.8, suggest the occurrence of a nearly planar arrangement of the polyenic chains.[27] However, on this basis a distinction between *s-trans* (structure a) or *s-cis* conformation (structure b) was not possible.



(a)



(b)

Conformational Studies on 4a,b and 4f. The conformation of **4a** was fully determined by ^{13}C-NMR and 2D NOESY spectra. The 2D NOESY spectrum shows correlation peaks of significative intensities between the pairs of protons H(1)/H(1′)−H(3)/H(3′) and H(2)/H(2′)−H(4)/H(4′). This suggest an *s-trans* (a) conformation of the polyenic chain. Such a conformation is confirmed also by the $^3J_{(CH)}$ values between C(1)/C(1′) and H(3)/H(3′), 3.8 Hz, and C(2)/C(2′) and H(4)/H(4′), 5.0 Hz.[28]

In the ^{13}C-coupled spectrum, the carbonyl carbon resonance shows a quintet-like multiplicity, which indicates that the couplings over three bonds to H(2)/H(2′) and the aromatic protons in the *ortho* position to the carbonyl group have equal values, about 4.5 Hz, that are

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(27) (a) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*; Pergamon Press: London, 1962. (b) Wernly, J.; Lauterwein, J. *Helv. Chim. Acta* **1983**, *66*, 1576−1587. Wernly, J.; Lauterwein, J. *Magn. Reson. Chem.* **1985**, *23*, 170−176. (c) Harris, R. K.; Cunliffe, A. V. *Org. Magn. Reson.* **1977**, *9*, 483−488.

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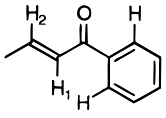
Table 3. Halogenation Reactions of Trimethylsilyl Dienes 2a and 2g to Halo Dienes 5−7

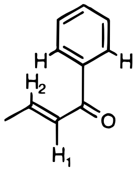
compd	reaction products (yield, %)[a]	E/Z ratio[b]	reaction time (h)	catalytic system and solvent
2a	**5a,b** (76)	50:50	3.5	$PdCl_2/CuCl_2/LiCl/MeCN$
2a	**6a,b** (59)	50:50	1	$Pd(OAc)_2/CuBr_2/LiBr/MeCN$
2a	**5a,b** (45)	61:39	48	$CuCl_2/LiCl/MeCN$
2a	**6a,b** (60)	55:45	1	$CuBr_2/LiBr/MeCN$
2g	**7a,b** (50)	64:36	1	$Pd(OAc)_2/CuBr_2/LiBr/MeCN$
2g	**7a,b** (41)	31:69	1	$CuBr_2/LiBr/MeCN$

[a] Based on isolated materials. [b] Isomers ratio of the isolated materials, determined by ^1H NMR and/or GLC.

in agreement with a nearly planar arrangement of the coupled nuclei.[28] Moreover, the presence in the NOESY spectrum of a quite intense correlation peak between H(1)/H(1′) and the protons in *ortho* position in the aromatic ring suggests that the oxygen atoms are in antiperiplanar position to H(1)/H(1′) (structure c).



(c)



(d)

A further support to this conclusion came from H(1)/H(1′) chemical shift which occurs at 7.0 ppm, compared to the value of 6.3 ppm, predicted on the basis of the substituent effects. This deshielding can be attributed to the diamagnetic anisotropy of the benzene ring. Indeed, a downfield shift of 0.8 ppm has been estimated using Dreiding models and the Johnson and Bovey diagram[29] for H(1)/H(1′) coplanar with the aromatic ring.

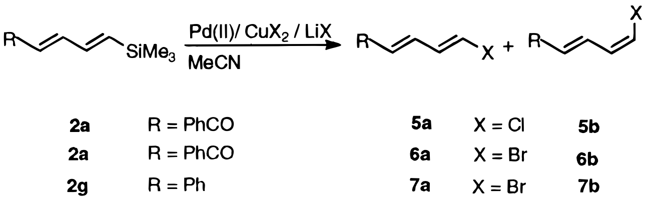
In the case of a syncoplanar conformation, the correlation peak would appear between the hydrogen atom in *ortho* position and H(2)/(H2′) (structure d). Moreover, H(2)/H(2′) would be shifted to lower field by the diamagnetic anisotropy of the benzene ring.

For compound **4b**, the extended *s-trans* conformation of the polyenic chain is suggested from the 2D-NOESY spectrum which shows significant correlation peaks between the pairs of protons H(2)/H(2′)-H(4)/H(4′), H(4)/H(4′)-H(6)/H(6′), H(3)/H(3′)-H(5)/-(5′). The correlation peak between H(1)/H(1′) and protons in the *ortho* positions in the benzene ring and the chemical shift value of H(1)/H(1′) indicate that the conformation at the ends of the conjugated system is the same as in **4a** (i.e. structure c).

It was not possible to obtain the 2D-NOESY and ^{13}C spectra of **4f** because of its very low solubility. However, the values of $^3J_{HH}$ across single bonds and the chemical shifts of protons H(1)/H(1′) suggest that in solution **4f** assumes a conformation similar to those of **4a** and **4b**.

The planar arrangement of the polyenic chain is also supported by AM1[30] calculations performed on **4a**,**b** and **4f** with full geometry optimization. In all the compounds examined, the most stable conformation is very similar to the experimental one with the plane of the aromatic rings rotated of about 30° with respect to the plane containing the polyenic chain and the carbonyl group. According to Dreiding models, this rotation angle is quite consistent with (i) the observed downfield shift of the H(1)/H(1′) resonances and (ii) the intense correlation peak observed in NOESY spectra between H(1)/H(1′) and the two hydrogen atoms in the *ortho* position of the benzene ring.

Scheme 5



Halogenation Reactions of Silyl Polyenes. In our studies directed toward an optimization of the homocoupling reaction of the ketosilane **2a**, we found interesting byproducts, represented by compounds deriving from chlorodesilylation reaction. Since these compounds could represent synthetically useful starting materials in various processes (e.g. cross-coupling reactions), we performed experiments in order to check the possibility of diverting the reaction toward their formation. Indeed, replacing methanol with acetonitrile and starting from ketone **2a** gave the mixture of isomeric chloro derivatives **5a** and **5b** (Scheme 5) as the main product.

With $CuBr_2/LiBr$ and palladium(II) acetate in acetonitrile, a mixture of bromides **6a** and **6b** was obtained. In the same reaction conditions silyl diene **2g** gave the bromides **7a** and **7b** (Table 3).

In order to clarify the role of the different metal salts, we performed the same halogenation reactions without the palladium salt. Chlorination and bromination occurred also in this case. However, lower yields and reaction rates were observed in the case of chlorination of **2a** without Pd(II) salts. The bromination reaction of **2a** and **2g** proceeded at the same rate both in the presence and in the absence of palladium salt, without any marked influence upon the yields of the halogeno derivatives **6a**,**b** and **7a**,**b**. The E/Z ratio in the dienyl halide is somewhat influenced by the presence of palladium(II) salt (Table 3).

Halogenation of vinylsilanes, with substitution of the silyl group, has been performed with various reagents,[31] but copper(II) halides have seldom been employed for such a transformation. In one case the oxidation reaction of alkenyl pentafluorosilicates with copper(II) bromide or chloride to the corresponding alkenyl bromide or chloride with cleavage of the silicon−carbon bond has been reported.[32] On the other hand, chlorination and bromination of alkenes to 1,2-dihalo derivatives promoted

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(30) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.

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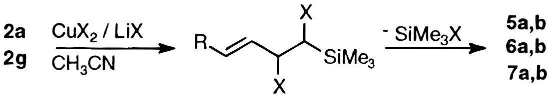
Scheme 6



by copper(II) halides are well documented.[33] This reaction is highly favored in solvents which behave as stabilizing ligands for copper(I), and acetonitrile is the most useful among them.[33c]

In our case addition of halogen to the silicon bearing the double bond promoted by copper(II) halide may be followed by the elimination of trimethylsilyl halide to give the dienyl halide (Scheme 6).

However, at least in the case of chlorination, we cannot rule out the possibility of a parallel route to the polyenyl chloride, involving Pd(0) elimination from an intermediate polyenylpalladium chloride.

Conclusion

Conjugated polyenes **4a**−**g** with an *all-E* configuration of the π-system, as rigorously established by a detailed NMR study, have been obtained following a synthetic procedure based upon an operatively very simple homocoupling reaction of the unsaturated silanes **2a**−**g**. These compounds can be easily derived from bis(trimethylsilyl) polyenes **1a**−**c**. The methodology opens the access to symmetrically substituted polyenes with carbonyl groups at both ends of the conjugated π-system. The influence of two substituents with the same electronic effect on the nonlinear optical properties of various polyenes has been recently addressed. In particular, both electron-donor and electron-acceptor substituents enhance the second hyperpolarizability, γ, of bisaryl and thienyl polyenes.[34] These results show that not only push−pull polyenes but also the symmetrically substituted ones are suitable for providing materials with large nonlinear optical coefficients. With this background, our diketo polyenes represent a new attractive class of compounds, whose potential nonlinear optical behavior is now open to investigation.

Finally, an interesting aspect of our work is the finding of a new method which permits the exchange of the trimethylsilyl group for a halogen atom with formation of polyenyl halides. In principle, these are useful intermediates in the synthesis of more extended conjugated systems *via* cross-coupling reactions.

Experimental Section

Flash chromatography was performed with silica gel (particle size 0.043−0.063 mm). Petroleum ether was the 40−70 °C boiling fraction. GLC analyses were performed with a SPB-1 (methylsilicone 30 m × 0.25 mm i.d.) capillary column. ^{1}H NMR data were measured at 200 and 500 MHz, and ^{13}C NMR data at 50.3 and 125.7 MHz. NMR spectral data were taken in $CDCl_3$ using the residual $CHCl_3$ as the standard for ^{1}H data, and the triplet centered at δ 77.0 as the standard for ^{13}C spectra. GLC/mass spectrometry analyses were performed on a fused silica capillary column SE 30, 30 m. Melting points are uncorrected. (1*E*,3*E*)-1,4-Bis(trimethylsilyl)-1,3-butadiene (**1a**),[35] (1*E*,3*E*,5*E*)-1,6-bis(trimethylsilyl)-1,3,5-hexatriene (**1b**),[36] (1*E*,3*E*,5*E*,7*E*)-1,8-bis(trimethylsilyl)-1,3,5,7-octatetraene(**1c**),[37] (2*E*,4*E*)-1-phenyl-5-(trimethylsilyl)-2,4-pentadien-1-one (**2a**),[20a] (2*E*,4*E*,6*E*)-1-phenyl-7-(trimethylsilyl)-2,4,6-heptatrien-1-one (**2b**),[20a] (3*E*,5*E*,7*E*)-1-phenyl-8-(trimethylsilyl)-3,5,7-octatrien-2-one (**2c**),[20c] and (1*E*,3*E*)-1-phenyl-4-(trimethylsilyl)-1,3-butadiene (**2g**)[40] were prepared as reported in the literature. Copper(II) bromide and copper(II) chloride were commercial products, dried at 150 °C (0.1 mbar) for 2 h, and stored in a nitrogen atmosphere. Palladium(II) chloride, palladium(II) acetate, bis(acetonitrile)palladium(II) chloride, anhydrous lithium chloride, and lithium bromide were commercial products and were used without further purification. Acetonitrile was dried by refluxing on Linde 4 Å molecular sieves and distilled; a second distillation from P_2O_5 was performed immediately prior to use.

(1*E*,3*E*,5*E*,7*E*)-1,8-Bis(trimethylsilyl)-1,3,5,7-octatetraene-*3,4,5,6-d*$_4$ (1d). The synthesis of **1d** required the preliminary preparation of (1*E*,3*E*)-1-bromo-4-(phenylthio)-1,3-butadiene-*1,2,3,4-d*$_4$ (**1e**), following the procedure previously described for the corresponding light compound.[20f] For this purpose acetylene-d_2 was bubbled into a solution of benzenesulfenyl chloride (21.4 g, 148 mmol) in ethyl acetate (150 mL), leading to (*E*)-1-chloro-2-(phenylthio)ethene-1,2-d_2 (8.65 g, 34% yield). GC/MS analysis showed a complete deuteration of the olefinic positions. This compound (8.65 g, 50 mmol) in 105 mL of THF was reacted with [2-(trimethylsilyl)ethynyl]magnesium bromide (0.43 N solution in THF, 118 mL, 51 mmol) in the presence of $NiCl_2$(dppe) (0.79 g, 1.50 mmol). After the usual workup and purification on Florisil column (petroleum ether as eluant), (3*E*)-4-(phenylthio)-1-(trimethylsilyl)-3-buten-1-yne-*3,4-d*$_2$ was obtained as yellow oil (11.36 g, 97% yield). Desilylation reaction of this compound (11.36 g, 48.5 mmol) with KF (27.9 g, 481 mmol) in 103 mL of methanol-d_1 gave, after flash chromatography (elution with petroleum ether), 5.57 g (71% yield) of (1*E*)-1-(phenylthio)-1-buten-3-yne-*1,2,4-d*$_3$ with a complete deuteration. The deuteriozirconation/bromination reactions of this enyne (3.02 g, 18.5 mmol) with zirconocene chloride deuteride (5.30 g, 20.6 mmol) and *N*-bromosuccinimide (3.4 g, 19.11 mmol) in 122 mL of benzene, performed as described,[20f] afforded 2.27 g (50% yield) of **1e**; GC/MS analysis confirmed the full deuteration of the obtained compound. In diene **1e** (1.87 g, 7.63 mmol) in 75 mL of THF both the bromine atom and the phenylthio group were substituted in a cross-coupling reaction with [(*E*)-2-(trimethylsilyl)ethenyl]magnesium bromide (0.38 N solution in THF, 90.5 mL, 34.4 mmol) in the presence of $NiCl_2$(dppe) (0.39 g, 0.74 mmol), at room temperature. After the usual workup and purification of the crude product on Florisil column (elution with petroleum ether), 0.85 g (44% yield) of the tetraene **1d** was obtained as yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.10 (s, 18H), 5.89 (d, $J = 18.3$ Hz, 2H), 6.54 (d, $J = 18.3$ Hz, 2H); GC/MS *m/e* 254 (M^+, 15), 239 (2), 166 (14), 151 (35), 73 (100).

(3*E*,5*E*,7*E*)-1-(4-Methylphenyl)-8-(trimethylsilyl)-3,5,7-octatrien-2-one (2d). The product was prepared following our procedure,[20a] starting from **1b** (1.71 g, 7.62 mmol), 4-methylphenylacetyl chloride (1.42 g, 8.42 mmol), and $AlCl_3$ (1.10 g, 8.25 mmol) in 50 mL of CH_2Cl_2 (1 h reaction time at room temperature). After preliminary purification of the crude product on a Florisil column (elution with 1:1 CH_2Cl_2−petroleum ether) and subsequent distillation with Kugelrohr

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[34] (a) Spangler, C. W.; Havelka, K. O.; Becker, M. W.; Kelleher, T. A.; Cheng, L.-T. A. *Proc. SPIE* **1991**, *1560*, 139−147. (b) Spangler, C. W.; Liu, P.-K.; Kelleher, T. A.; Nickel, E. G. *Proc. SPIE* **1992**, *1626*, 406−414.

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[37] **1c** was prepared by means of Miyaura−Suzuki[38] cross-coupling of (1*E*,3*E*)-1-iodo-4-(trimethylsilyl)-1,3-butadiene and 2-[(1*E*,3*E*)-4-(trimethylsilyl)-1,3-butadienyl]-1,3,2-benzodioxaborole. Both these compounds were obtained from **1a**, adopting our recently reported procedure.[39] Details will be given elsewhere.

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apparatus (ot 165 °C, 2 × 10^{-4} mbar), 0.43 g of a yellow oil was obtained (20% yield): IR (neat) 1681, 1249, 1011, 864, 840 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.23 (s, 9H), 2.45 (s, 3H), 3.92 (s, 2H), 6.27 (d, J = 17.1 Hz, 1H), 6.35 (d, J = 15.3 Hz, 1H), 6.36−6.47 (m, 1H), 6.65−6.75 (m, 2H), 7.22−7.30 (m, 4H), 7.37 (dd, J = 15.3, 11.2 Hz, 1H); MS (70 eV) *m/e* 284 (M^+, 7), 269 (7), 256 (14), 179 (84), 105 (38), 73 (100), 59 (23). Anal. Calcd for $C_{18}H_{24}OSi$: C, 76.00; H, 8.50. Found: C, 76.10; H, 8.60.

(3*E*,5*E*,7*E*)-1-(4-*n*-Decylphenyl)-8-(trimethylsilyl)-3,5,7-octatrien-2-one (2e). The product was prepared following the same procedure described above, starting from **1b** (1.72 g, 7.67 mmol), 4-*n*-decylphenylacetyl chloride[41] (2.27 g, 7.70 mmol), and $AlCl_3$ (1.03 g, 7.73 mmol) in 55 mL of CH_2Cl_2 (reaction time 1.5 h). After the usual workup, the crude product was purified by flash chromatography (elution with 1:1 CH_2Cl_2−petroleum ether); 1.40 g (yield 44%) of a yellow oil was obtained. An analytical sample was obtained by Kugelrohr distillation (ot 225 °C, 2.7 × 10^{-4} mbar): IR (neat) 1682, 1598, 1249, 1010, 773, 726 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.08 (s, 9H), 0.88 (t, J = 6.7 Hz, 3H), 1.15−1.40 (m, 14H), 1.53−1.64 (m, 2H), 2.56 (t, J = 7.7 Hz, 2H), 3.78 (s, 2H), 6.13 (d, J = 17.0 Hz, 1H), 6.21 (d, J = 15.3 Hz, 1H), 6.08−6.32 (m, 1H), 6.50−6.62 (m, 2H), 7.11 (s, 4H), 7.23 (dd, J = 15.3, 11.2 Hz, 1H). Anal. Calcd for $C_{27}H_{42}OSi$: C, 78.95; H, 10.31. Found: C, 78.80; H, 10.45.

(2*E*,4*E*,6*E*,8*E*)-1-Phenyl-9-(trimethylsilyl)-2,4,6,8-nonatetraen-1-one (2f). The product was prepared following the procedure reported above starting from **1c** (2.21 g, 8.83 mmol), benzoyl chloride (1.35 g, 9.60 mmol), and $AlCl_3$ (1.29 g, 9.67 mmol) in 72 mL of CH_2Cl_2 at −20 °C for 20 min. After preliminary purification on a Florisil column (elution with 4:6 CH_2Cl_2-petroleum ether) and subsequent distillation with Kugelrohr apparatus (ot 170 °C, 1 × 10^{-4} mbar), 1.108 g of a yellow oil was obtained (44% yield): IR (neat) 1650, 1607, 1570, 1522, 1278, 1247, 1013, 867, 834, 771, 689; ^1H NMR (500 MHz, $CDCl_3$) δ 0.1 (s, 9H), 6.05 (d, J = 18.2 Hz, 1H), 6.33 (dd, J = 14.8, 10.5 Hz, 1H), 6.41 (dd, J = 14.8, 9.8 Hz, 1H), 6.48 (dd, J = 14.8, 11.5 Hz, 1H), 6.58 (dd, J = 18.2, 9.8 Hz, 1H), 6.69 (dd, J = 14.8, 10.5 Hz, 1H), 6.97 (d, J = 14.8 Hz, 1H), 7.42−7.57 (m, 4H), 7.90−7.95 (m, 2H). Anal. Calcd for $C_{18}H_{22}OSi$: C, 76.54; H, 7.85. Found: C, 76.25; H, 8.18.

(2*E*,4*E*,6*E*,8*E*)-1-Phenyl-9-(trimethylsilyl)-2,4,6,8-nonatetraen-1-one-*4,5,6,7-d*$_4$ (2h). The product was prepared following the same procedure adopted for the synthesis of tetraene **2f**, starting from **1d** (0.850 g, 3.34 mmol), benzoyl chloride (0.510 g, 3.63 mmol), and $AlCl_3$ (0.480 g, 3.60 mmol) in 27 mL of CH_2Cl_2. The crude product was purified on a Florisil column (elution with 7:3 CH_2Cl_2/petroleum ether); 0.36 g of a yellow oil was obtained (yield 38%): ^1H NMR (500 MHz, $CDCl_3$) δ 0.1 (s, 9H), 6.05 (d, J = 18.3 Hz, 1H), 6.58 (d, J = 18.3 Hz, 1H), 6.97 (d, J = 14.9 Hz, 1H), 7.42−7.55 (m, 4H), 7.90−7.95 (m, 2H).

(2*E*,4*E*,6*E*,8*E*)-1,10-Diphenyl-2,4,6,8-decatetraene-1,10-dione (4a). Method A. A solution of silyl ketone **2a** (0.50 g, 2.17 mmol) in 3.5 mL of methanol was added dropwise to a stirred suspension of palladium(II) chloride (0.10 g, 0.56 mmol), lithium chloride (0.07 g, 1.65 mmol), and anhydrous copper(II) chloride (0.60 g, 4.46 mmol) in 4 mL of methanol under a nitrogen atmosphere. The resulting mixture was stirred at room temperature, and the reaction was monitored by capillary GLC analysis. After reaction completion (3.5 h), the solvent was removed at reduced pressure. By means of flash chromatography of the residue (9:1 CH_2Cl_2−petroleum ether) 0.040 g (10% yield) of a mixture of the chloride isomers **5a** and **5b** was eluted first: IR (neat) 1680, 1630, 1020, 780, 725 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.44 (dt, J = 7.2, 0.8 Hz, 1H, **5b**), 6.57 (ddd, J = 10.8, 7.2, 0.7 Hz, 1H, **5b**), 6.65−6.80 (m, 2H, **5a**), 7.00 (d, J = 15.0 Hz, 1H, **5a**), 7.08 (d, J = 15.3 Hz, 1H, **5b**), 7.28−7.38 (m, 1H, **5a**), 7.40−7.65 (m, 3H), 7.80 (ddd, J = 15.3, 10.8, 0.8 Hz, 1H **5b**), 7.90−8.00 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 125.81, 127.39, 128.12, 128.29, 128.35, 128.43, 128.61, 130.37, 132.24, 132.93, 136.53, 137.65, 139.85, 189.91, 190.29; MS (70 eV) *m/e* isomer **5b** 194 (M + 2, 14), 192 (M^+, 39), 157 (100), 129 (38), 105 (30), 77 (58), 51 (58); isomer **5a** 194 (M + 2, 18), 192 (M^+, 53), 157 (100), 129 (55), 105 (48), 77 (72), 51 (69). Anal. Calcd for $C_{11}H_9OCl$: C, 68.58; H, 4.71; Cl, 18.40. Found: C, 68.23; H, 5.18; Cl, 18.15. Further elution gave 0.17 g (50% yield) of compound **4a**: mp 213−214 °C ($CHCl_3$/diethyl ether); IR (KBr) 1656, 1600, 1556, 1019, 772, 697; ^1H NMR (500 MHz, $CDCl_3$) 6.61−6.71 (m, 2H), 6.72−6.81 (m, 2H), 7.07 (d, J = 14.8 Hz, 2H), 7.43−7.61 (m, 8H), 7.92−7.97 (m, 4H); ^{13}C NMR (50.3 MHz, $CDCl_3$, trace DMSO-d_6) δ 126.87, 128.38, 128.64, 132.86, 134.75, 137.98, 140.48, 143.49, 190.12. Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.28; H, 5.66.

Method B. A solution of the silyl ketone **2a** (0.50 g, 2.17 mmol) in 7 mL of HMPA was added dropwise to a stirred solution of $Pd(MeCN)_2Cl_2$ (0.028 g, 0.099 mmol), $CuCl_2$ (0.86 g, 6.39 mmol), and LiCl (0.09 g, 2.12 mmol) in 5 mL of anhydrous HMPA, under nitrogen atmosphere. The solution was warmed to 55 °C, and the reaction, monitored by capillary GLC analysis, was completed after 2 h. The mixture was then diluted with water and extracted with CH_2Cl_2. The organic extracts were washed with aqueous HCl (1 N) and with water, dried over anhydrous sodium sulfate, and concentrated to give the solid product. Recrystallization from CH_2Cl_2/diethyl ether gave 0.175 g (51% yield) of **4a**.

(2*E*,4*E*,6*E*,8*E*,10*E*,12*E*)-1,14-Diphenyl-2,4,6,8,10,12-tetradecahexaene-1,14-dione (4b). Method A. Following the same procedure described for the synthesis of **4a**, compound **4b** was prepared starting from **2b** (0.60 g, 2.34 mmol) and using $PdCl_2$ (0.11 g, 0.62 mmol), $CuCl_2$ (0.72 g, 5.35 mmol), and LiCl (0.087 g, 2.05 mmol) in 10 mL of CH_3OH (3 h reaction time). Concentration of the solvent gave a solid residue which was recrystallized from $CHCl_3$/diethyl ether to give 0.260 g (61% yield) of **4b**: mp 220−222 °C; IR (KBr) 1645, 1575, 1535, 1010, 765, 690 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.43−6.57 (m, 6H), 6.69 (dd, J = 14.8, 10.2 Hz, 2H), 6.99 (d, J = 14.9 Hz, 2H), 7.42−7.62 (m, 8H), 7.90−7.97 (m, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 125.73, 128.35, 128.58, 132.31, 132.58, 134.60, 136.83, 138.44, 141.53, 144.13, 190.24. Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. Found: C, 85.48; H, 6.34.

Method B. The same procedure described for compound **4a** was used starting from **2b** (0.60 g, 2.34 mmol), $Pd(MeCN)_2Cl_2$ (0.03 g, 0.11 mmol), $CuCl_2$ (0.72 g, 5.36 mmol), and LiCl (0.09 g, 2.12 mmol) in 10 mL of HMPA (3.5 h reaction time). After the usual workup, the recrystallization of the residue from CH_2Cl_2/diethyl ether afforded 0.20 g (47% yield) of **4b**.

(3*E*,5*E*,7*E*,9*E*,11*E*,13*E*)-1,16-Diphenyl-3,5,7,9,11,13-hexadecahexaene-2,15-dione (4c). The synthesis of **4c** was performed following the procedure described in method A for compounds **4a** and **4b**, starting from **2c** (0.30 g, 1.11 mmol), $PdCl_2$ (0.05 g, 0.28 mmol), LiCl (0.03 g, 0.71 mmol), and $CuCl_2$ (0.31 g, 2.29 mmol) in 5 mL of CH_3OH (4 h reaction time). After the usual workup, the crude product was purified by flash chromatography (elution with CH_2Cl_2): 0.065 g (30% yield) of a red solid were isolated; mp 190−193 °C (ethanol); IR (KBr) 1636, 1580, 1009, 740, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.82 (s, 4H), 6.23 (d, J = 15.2 Hz, 2H), 6.33 (dd, J = 14.7, 11.4 Hz, 2H), 6.30−6.50 (m, 4H), 6.65 (dd, J = 14.7, 10.7 Hz, 2H), 7.0−7.34 (m, 12H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 48.50, 126.93, 128.59, 128.73, 129.43, 131.89, 134.43, 134.62, 136.72, 141.33, 142.66, 197.09. Anal. Calcd for $C_{28}H_{26}O_2$: C, 85.25; H, 6.64. Found: C, 85.04; H, 6.52.

(3*E*,5*E*,7*E*,9*E*,11*E*,13*E*)-1,16-Bis(4-methylphenyl)-3,5,7,9,11,13-hexadecahexaene-2,15-dione (4d). The synthesis of **4d** was performed following the procedure described above for compound **4a** (method A) starting from **2d** (0.43 g, 1.51 mmol), $PdCl_2$ (0.07 g, 0.39 mmol), LiCl (0.05 g, 1.18 mmol), and $CuCl_2$ (0.42 g, 3.12 mmol) in 7.5 mL of CH_3OH (5 h reaction time). After the usual workup, the crude product was purified by flash chromatography (elution with CH_2Cl_2); 0.130 g (41% yield) of a red solid was isolated: mp 209−211 °C (ethanol);

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[41] This acyl chloride was prepared by a standard procedure starting from the corresponding acid. 4-*n*-Decylphenylacetic acid was prepared following a procedure reported for the synthesis of homologous compounds:[42] mp 74−76 °C (ethyl ether); IR (KBr) 1737, 1712, 1255 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$ + D_2O) δ 0.84 (t, J = 6.8 Hz, 3H), 1.18−1.38 (m, 14H), 1.50−1.63 (m, 2H), 2.57 (t, J = 7.8 Hz, 2H), 3.60 (s, 2H), 7.13 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H). Anal. Calcd for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 78.33; H, 10.12.

[42] Morgan, E. D. *Tetrahedron* **1967**, *23*, 1735−1738.

IR (KBr) 1682, 1640, 1586, 1010, 800; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.30 (s, 6H), 3.75 (s, 4H), 6.21 (d, J = 15.3 Hz, 2H), 6.33 (dd, J = 14.7, 11.3 Hz, 2H), 6.37−6.48 (m, 4H), 6.64 (dd, J = 14.7, 10.6 Hz, 2H), 7.09 (d, J = 8.2 Hz, 4H), 7.12 (d, J = 8.2 Hz, 4H), 7.25 (dd, J = 15.3, 11.4 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 21.02, 48.16, 128.59, 129.29, 129.45, 131.49, 131.93, 134.41, 136.56, 136.66, 141.23, 142.54, 197.34. Anal. Calcd for $C_{30}H_{30}O_2$: C, 85.27; H, 7.16. Found: C, 85.47; H, 7.05.

(3*E*,5*E*,7*E*,9*E*,11*E*,13*E*)-1,16-Bis(4-*n*-decylphenyl)-3,5,7,9,-11,13-hexadecahexaene-2,15-dione (4e). The synthesis of **4e** was performed following the procedure described above for compound **4a** (method A) starting from **2e** (1.25 g, 3.04 mmol), $PdCl_2$ (0.13 g, 0.73 mmol), LiCl (0.10 g, 2.36 mmol), and $CuCl_2$ (0.84 g, 6.24 mmol) in 7.5 mL of CH_3OH (2 h reaction time). After the usual workup, the crude product was purified by flash chromatography (elution with 9:1 CH_2Cl_2−petroleum ether); 0.520 g (51% yield) of a red solid was isolated: mp 169−171 °C (ethanol); IR (KBr) 1679, 1584, 1075, 1009 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (t, J = 6.8 Hz, 6H), 1.20−1.40 (m, 28H), 1.50−1.70 (m, 4H), 2.56 (t, J = 7.8 Hz, 4H), 3.58 (s, 4H), 6.22 (d, J = 15.2 Hz, 2H), 6.34 (dd, J = 14.8, 11.3 Hz, 2H), 6.37−6.48 (m, 4H), 6.65 (dd, J = 14.8, 11.0 Hz, 2H), 7.05−7.15 (m, 8H), 7.26 (dd, J = 15.2, 11.3 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 14.10, 22.67, 29.31, 29.35, 29.49, 29.57, 29.60, 31.43, 31.88, 35.58, 48.17, 128.55, 128.78, 129.25, 131.59, 131.92, 134.43, 136.70, 141.31, 141.65, 142.58, 197.47. Anal. Calcd for $C_{48}H_{66}O_2$: C, 85.40; H, 9.86. Found: C, 85.21; H, 9.64.

(2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*,16*E*)-1,18-Diphenyl-2,4,6,8,-10,12,14,16-octadecaoctaene-1,18-dione (4f). The synthesis of **4f** was performed following the procedure described above for compound **4a** (method A), starting from **2f** (1.10 g, 3.89 mmol), $PdCl_2$ (0.17 g, 0.96 mmol), LiCl (0.13 g, 3.06 mmol), and $CuCl_2$ (1.06 g, 7.90 mmol) in 53 mL of CH_3OH (4 h reaction time). The residue obtained from evaporation of the solvent at reduced pressure and at 0 °C was extracted with CH_2Cl_2 in a Soxhlet apparatus. By partial evaporation of the extraction solvent, a deep red precipitate was obtained (0.411 g, yield 51%). This solid does not melt up to 240 °C and decomposes at this temperature: IR (KBr) 1650, 1561, 1008, 771, 694 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.35−6.55 (m, 10H), 6.72 (dd, J = 14.7, 11.0 Hz, 2H), 6.97 (d, J = 14.9 Hz, 2H), 7.40−7.55 (m, 8H), 7.90−7.94 (m, 4H). Anal. Calcd for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26. Found: C, 85.83; H, 6.00.

(1*E*,3*E*,5*E*,7*E*)-1,8-Diphenyl-1,3,5,7-octatetraene (4g). Tetraene **4g** was prepared following the procedure described in method A for compound **4a**, using diene **2g** (0.30 g, 1.49 mmol), $PdCl_2$ (0.06 g, 0.34 mmol), $CuCl_2$ (0.42 g, 3.12 mmol), and LiCl (0.05 g, 1.18 mmol) in 3 mL of CH_3OH. The residue obtained from evaporation of the solvent at reduced pressure was a yellow solid, which could be crystallized from chloroform; 0.10 g was obtained (52% yield): mp 229−232 °C. The IR and MS spectra were compared with those of an authentic sample.

(2*E*,4*E*,6*E*,8*E*,10*E*,12*E*,14*E*,16*E*)-1,18-Diphenyl-2,4,6,8,-10,12,14,16-octadecaoctaene-1,18-dione-*4,5,6,7,12,-13,14,15-d*$_8$ (4h). Octaene **4h** was prepared following the same procedure described for the nondeuterated analogue **4f**, starting from **2h** (0.12 g, 0.42 mmol), $PdCl_2$ (0.019 g, 0.11 mmol), $CuCl_2$ (0.11 g, 0.82 mmol), and LiCl (0.014 g, 0.33 mmol) in 4 mL of CH_3OH.

The crude product was purified on a Florisil column (eluent 9:1 CH_2Cl_2/petroleum ether) and recrystallized from CH_2Cl_2 to give 0.049 g of a red solid (55% yield): mp 240 °C with decomposition; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.38−6.42 (m, 4H), 6.97 (d, J = 14.9 Hz, 2H), 7.43−7.55 (m, 8H), 7.91−7.95 (m, 4H). Within the limits of the technique, ^{1}H NMR spectroscopy showed full deuteration at the 4,5,6,7,12,13,14,15-positions.

(2*E*,4*E*)- and (2*E*,4*Z*)-1-Phenyl-5-chloro-2,4-pentadien-1-one (5a and 5b). A solution of the silyl ketone **2a** (0.30 g, 1.30 mmol) in 2.5 mL of CH_3CN was added, under a nitrogen atmosphere, to a stirred suspension of $PdCl_2$ (0.05 g, 0.28 mmol), LiCl (0.04 g, 0.94 mmol), and $CuCl_2$ (0.36 g, 2.68 mmol) in 3 mL of freshly distilled CH_3CN. The resulting mixture was stirred at room temperature until the disappearance of the starting compound **2a** (GLC, 3.5 h reaction time). After the usual workup, flash chromatography of the residue (elution with 40:60 CH_2Cl_2−petroleum ether) afforded 0.19 g (76% yield) of a mixture of **5a** and **5b** isomers (*E*/*Z* ratio 50:50 determined by ^{1}H NMR).

The same reaction was performed also in the absence of $PdCl_2$ starting from **2a** (0.40 g, 1.74 mmol), $CuCl_2$ (0.55 g, 4.09 mmol), and LiCl (0.07 g, 1.65 mmol) in 7 mL of CH_3CN (48 h reaction time). In this case 0.15 g (45% yield) of **5a**,**b** was obtained (*E*/*Z* ratio 61:39 determined by ^{1}H NMR).

(2*E*,4*E*)- and (2*E*,4*Z*)-1-Phenyl-5-bromo-2,4-pentadien-1-one (6a and 6b). The bromo derivatives **6a**,**b** were prepared following the same procedure described above for the chloro derivatives **5a**,**b**, starting from **2a** (0.28 g, 1.22 mmol) and $Pd(OAc)_2$ (0.07 g, 0.31 mmol), $CuBr_2$ (0.56 g, 2.52 mmol), and LiBr (0.15 g, 1.73 mmol) in 5 mL of CH_3CN (1 h reaction time). Flash chromatography (elution with 40:60 CH_2Cl_2−petroleum ether) of the crude product gave 0.17 g (59% yield) of a mixture of 4*E* and 4*Z* isomers **6a** and **6b** (*E*/*Z* ratio 50:50 determined by ^{1}H NMR). Further purification by Kugelrohr distillation at 1×10^{-4} mbar was attempted, but the product decomposed at 100 °C (ot): IR (KBr) 1657, 1595, 1019, 990, 759, 689 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.67 (dt, J = 7.2, 1 Hz, 1H, **6b**), 6.88 (d, J = 13.5 Hz, 1H, **6a**), 6.90 (ddd, J = 10.7, 7.2, 1 Hz, 1H, **6b**), 6.96 (dd, J = 13.5, 11.2 Hz, 1H, **6a**), 7.00 (d, J = 15.0 Hz, 1H, **6a**), 7.13 (d, J = 15.2 Hz, 1H, **6b**), 7.30 (dd, J = 15.0, 11.2 Hz, 1H, **6a**), 7.45−7.55 (m, 2H), 7.56−7.60 (m, 1H), 7.71 (ddd, J = 15.2, 10.7, 1 Hz, 1 H, **6b**), 7.92−7.96 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 117.77, 119.00, 125.71, 128.36, 128,44, 128.62, 128.75, 131.26, 132.95, 136.05, 137.64, 137.68, 138.71, 140.87, 190.00, 190.29. Anal. Calcd for $C_{11}H_9OBr$: C, 55.72; H, 3.83; Br, 33.70. Found: C, 55.96; H, 4,06; Br, 33.85.

The same reaction performed in the absence of $Pd(OAc)_2$ afforded 0.17 g (60% yield) of a mixture of isomers (*E*/*Z* ratio 55:45).

(1*E*,3*E*)- and (1*Z*,3*E*)-1-Bromo-4-phenyl-1,3-butadiene (7a and 7b). The same procedure described for the other halo derivatives was followed, starting from silyl diene **2g**, (0.29 g, 1.43 mmol), $Pd(OAc)_2$ (0.04 g, 0.17 mmol), $CuBr_2$ (0.69 g, 3.09 mmol), and LiBr (0.13 g, 1.49 mmol) in 7 mL of CH_3CN. After reaction completion the solvent was evaporated at 0 °C under reduced pressure. The residue was chromatographed on a Florisil column with petroleum ether as eluant. Subsequent distillation of the obtained oil with a Kugelrohr apparatus (ot 150 °C, 1 mbar) afforded 0.15 g (50% yield) of a mixture of 3*E* and 3*Z* isomers **7a** and **7b** (*E*/*Z* ratio 64:36, determined by GLC analysis): IR (neat) 1627, 1570, 971, 770, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.24 (dt, J = 7.1, 1 Hz, 1H, **7b**), 6.43 (d, J = 13.5 Hz, 1H, **7a**), 6.57 (d, J = 15.6 Hz, 1H, **7a**), 6.67 (dd, J = 15.6, 10.6 Hz, 1H, **7a**), 6.75 (d, J = 15.8 Hz, 1H, **7b**), 6.79 (ddd, J = 10.2, 7.1, 1 Hz, 1H, **7b**), 6.88 (dd, J = 13.5, 10.6 Hz, 1H, **7a**), 7.13 (ddd, J = 15.8, 10.2, 1 Hz, 1H, **7b**), 7.25−7.40 (m, 3H), 7.45−7.52 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 108.43, 108.87, 124.40, 126.03, 126.50, 126.81, 128.02, 128.29, 128.69, 132.74, 133.37, 136.12, 136.73, 137.66. Anal. Calcd for $C_{10}H_9Br$: C, 57.44; H, 4.34; Br, 38.22. Found: C, 57.54; H, 4.87; Br, 37.90.

The same reaction performed in the absence of $Pd(OAc)_2$ gave 0.12 g (41% yield) of a mixture of isomers (*E*/*Z* ratio 31:69 GLC).

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