by the molecule. The program was modified to allow a variable-point density and averaging of a series of volume calculations. The point density used and the number of averaged calculations gave a reproducibility better than ±1%. The van der Waals radii used were those reported by Kitaigorodsky[37] derived from X-ray crystallographic data.

Acknowledgment. Support of this research by the National Science Foundation and NIH Grant GM07487 is gratefully acknowledged. The synthetic portions were supported by the National Institutes of Health while the mechanistic aspects were supported by NSF.

Supplementary Material Available: ORTEP drawings and tables of positional parameters, interatomic distances, bond angles, anisotropic temperature factors, and isotropic temperature factors for 2,2-dicyano-5,5-dimethyl-3,3-diphenylbicyclo[2.1.0]pentane, **1-5**, **17**, **23**, **24c**, **26**, **25**, **28**, **29a**, **29b**, **29c**, **33**, **35**, **39**, **40**, and **42** (105 pages). Ordering information is given on any current masthead page.

Preparation of *tert*-Butyl-Capped Polyenes Containing up to 15 Double Bonds

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Contribution from the Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received February 28, 1989

Abstract: 7,8-Bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (TCDT) can be ring-opened in a controlled manner by $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ (Ar = 2,6-C_6H_3-*i*-Pr_2) to give living oligomers from which the metal can be removed in a Wittig-like reaction with pivaldehyde or 4,4-dimethyl-*trans*-2-pentenal. Heating the oligomer yields a distribution of *tert*-butyl-capped polyenes, $(t\text{-Bu})(CH{=}CH)_n(t\text{-Bu})$, where *n* is odd if pivaldehyde is used in the cleavage reaction or even if 4,4-dimethyl-*trans*-2-pentenal is used. Mixtures of odd and even polyenes have been analyzed by reversed-phase HPLC methods, and those having as many as 13 double bonds have been isolated by column chromatography on silica gel under dinitrogen at -40 °C and characterized by ^1H and ^{13}C NMR and UV-vis studies. The 17-ene has been observed by HPLC. Polyenes containing more than 17 double bonds are relatively unstable under the reaction and subsequent isolation conditions; those containing between 11 and 15 double bonds decompose thermally progressively more readily. The initial isomer in the odd-ene series has largely the trans(cis,trans)$_x$ geometry as a result of stereospecific trans initiation, stereoselective trans propagation, stereospecific trans cleavage, and stereospecific cis retro-Diels-Alder reactions. The even-ene series is more complex since the Wittig-like reaction involving 4,4-dimethyl-*trans*-2-pentenal is not selective. UV-vis and ^{13}C and ^1H NMR data have been collected and analyzed in detail for the trans(cis,trans)$_x$ isomers for $x = 1$-5 (up to 11 double bonds) and for the odd and even all-trans forms containing up to nine double bonds. Extrapolation of a plot of the energy of the $^1B_u \leftarrow {}^1A_g(0\text{-}0)$ transition versus $1/n$ (for up to the 13-ene) predicts that the HOMO-LUMO gap will be 1.79-1.80 eV for an infinite *all-trans*-polyene; in carbon disulfide it will be 1.56 eV. For the trans(cis,trans)$_x$ forms the $^1B_u \leftarrow {}^1A_g(0\text{-}0)$ energy gap is predicted to be 1.95 eV for an infinite polyene in a mixture of acetonitrile, dichloromethane, and water (90:5:5). The ease of thermal cis-to-trans isomerization (ultimately to the all-trans form) correlates directly with chain length, isomerization to the all-trans form being especially facile for the 13-ene and beyond. The *all-trans*-polyenes are significantly less soluble than forms that contain one or more cis double bonds, although cross-linking cannot be ruled out as a contributor to insolubility for polyenes longer than the 13-ene. The retro-Diels-Alder reaction in the first unit away from the metal in living polyTCDT is accelerated 10 times relative to that in the second unit away from the metal. Heating polyTCDT gives living polyenes that are stable at 50 °C for 45 min in solution; no benzene is formed.

Conjugated polyene chains are important components of natural products[1] and are a key feature of polyacetylene.[2] Isoprenoid polyenes containing up to 19 double bonds in the backbone are known,[3] but no polyene having an unsubstituted backbone longer than a 10-ene appears to have been prepared.[4] Since evidence is accruing that relatively short conjugated sequences can sustain a soliton,[5] it would be of fundamental interest to prepare well-defined unsubstituted polyenes that contain 10-20 double bonds.

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(1) (a) Birge, R. *Annu. Rev. Biophys. Bioeng.* **1981**, *10*, 315. (b) Honig, B. *Annu. Rev. Phys. Chem.* **1978**, *29*, 31. (c) Zechmeister, L. *Cis-trans Isomeric Carotenoids, Vitamins A and Arylpolyenes*; Springer: Wien, 1962. (d) For proceedings of the International Symposium on Carotenoids see: *Pure Appl. Chem.* **1985**, *57*; **1979**, *51*; **1976**, *47*; **1973**, *35*; **1969**, *20*; **1967**, *14*.

(2) (a) Chien, J. C. W. *Polyacetylene Chemistry, Physics and Material Science*; Academic Press: New York, 1984. (b) Skotheim, T. A., Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986. (c) Kuzmany, H., Mehring, M., Roth, S., Eds. *Electronic Properties of Conjugated Polymers*; Springer Series in Solid State Sciences; Springer: New York, 1988; Vol. 76. (d) Bowden, M .J., Turner, S. R., Eds. Electronic and Photonic Applications of Polymers. *Adv. Chem. Ser.* **1988**, *218*. (f) Proceedings of the International Conference on the Physics and Chemistry of Low-Dimensional Synthetic Metals. *Synth. Met.* **1987**, *17*; *Mol. Cryst. Liq. Cryst.* **1985**, *117*, 118. (g) Wegner, G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 361. (h) Baughman, R., Bredas, J.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* **1982**, *82*, 209. (i) Simionescu, C. I.; Perec, V. *Prog. Polym. Sci.* **1982**, *8*, 133.

(3) β-Carotene, one of the longest and most important of the naturally occurring polyenes, is an 11-ene isoprenoid.[1] The longest synthetic isoprenoid is dodecapreno-β-carotene, a 19-ene, obtained by derivatizing natural isoprenoids; see: Karrer, P.; Eugstler, C. H. *Helv. Chim. Acta* **1951**, *34*, 1805.

(4) A number of reviews are available.[4a-e] The longest well-characterized polyenes containing an unsubstituted backbone are 10-enes.[4c] Longer polyenes (e.g., the diphenyl-capped 15-ene[4a]) have been claimed,[4a,f] but no data are available that would allow one to confirm that this material is not cross-linked. Di-*tert*-butyl-capped poly*enynes* containing up to 30 carbon atoms have been reported.[4g] The synthesis of polyenes with up to eight double bonds having functionalized aryl end groups has been reported.[4h,i] (a) Kuhn, R. *Angew. Chem.* **1937**, *34*, 703. (b) Yanovskaya, L. A. *Russ. Chem. Rev.* **1967**, *36*, 400. (c) Hudson, B. S.; Kohler, B. E.; Schulten, K. In *Excited States*; Lim, E. C., Ed.; Academic: New York, 1982. (d) Bohlmann, F.; Mannhardt, H.-J. *Chem. Ber.* **1956**, *89*, 1307. (e) Sondheimer, F.; Ben-Efraim, D. A.; Wolovsky, R. *J. Am. Chem. Soc.* **1961**, *83*, 1675. (f) Nayler, P.; Witing, M. C. *J. Chem. Soc.* **1955**, *3037*. (g) Wudl, F.; Bitler, S. P. *J. Am. Chem. Soc.* **1986**, *108*, 4685. (h) Spangler, C. W.; Nickel, E. G.; Hall, T. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 219. (i) Spangler, C. W.; Sapochuk, L. S.; Struck, G. E.; Gates, B. E.; McCoy, R. K. *Ibid.* **1987**, *28*, 219.

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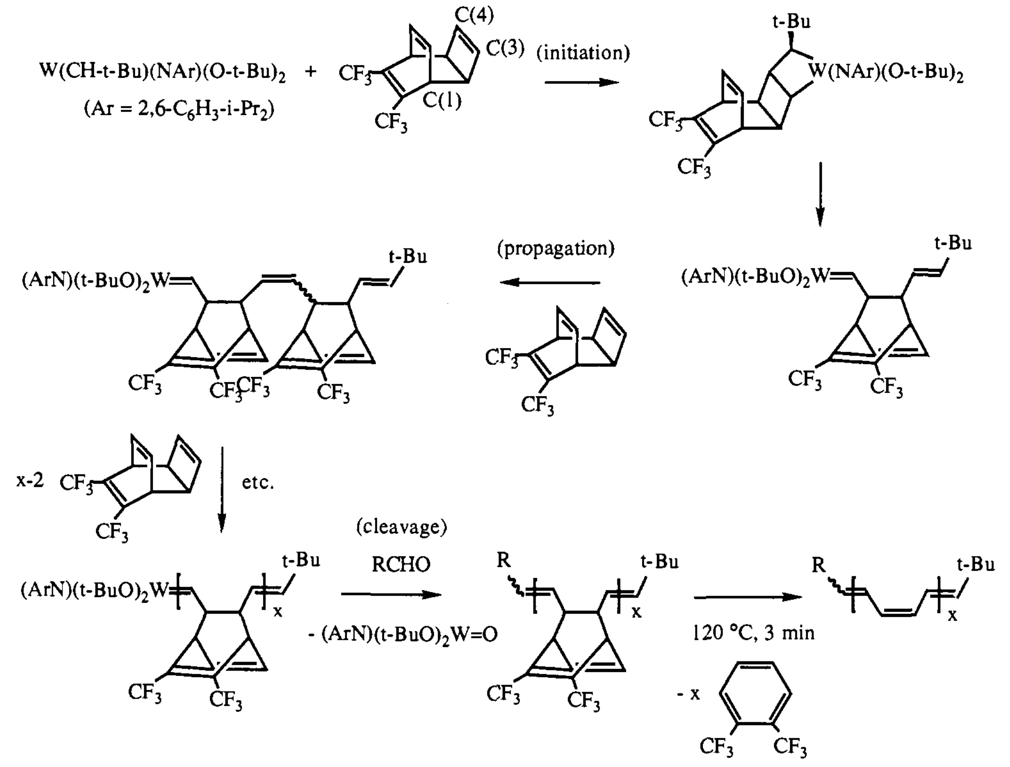
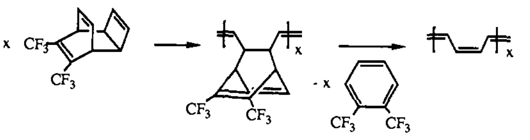
Scheme I. General Method for Preparing Polyenes



Preparation of polyenes in a controlled fashion is also highly desirable to prepare materials for potential third-order nonlinear optical applications.[6] Potentially interesting materials would contain oriented polyenes of a given chain length or tight distribution of chain lengths in host matrices or polyenes as part of diblock or triblock copolymers.[7]

Feast[8] discovered that tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-trienes (e.g., the 7,8-bis(trifluoromethyl) derivative) and related molecules can be ring-opened by classical olefin metathesis catalysts[9] to give a polymer from which an arene is ejected upon heating to give polyacetylene (eq 1). This method was an important breakthrough in polyacetylene research since it could be employed to prepare oriented polyacetylene films by stretching the precursor polymer film before the retro-Diels–Alder reaction,[10] a significant advantage over classical "Ziegler–Natta" methods of preparing polyacetylene.[2] However, the nature of classical metathesis catalysts in general is not well-understood at a molecular level. Therefore their activity cannot be controlled to yield polymers with a relatively tight distribution of predictable molecular weights or block copolymers.



(1)

Recently it has been discovered that well-characterized catalysts of the type M(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (M = Mo or W; Ar = 2,6-C$_6$H$_3$-*i*-Pr$_2$)[11] will ring-open-polymerize norbornenes in a controlled manner.[12] (Three other well-characterized catalysts based on Ti,[13] Ta,[14] and W[15] will also ring-open-polymerize norbornenes.) We have found that the M(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ catalysts also can be used to ring-open-polymerize (more accurately oligomerize) 7,8-bis(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene in a controlled manner,[16] thereby making it possible to prepare a distribution of polyenes whose lengths differ by four carbon atoms. We report here full details of this method of preparing and characterizing *tert*-butyl-capped polyenes containing up to 15 double bonds.

Results

General Preparative Methods. The general method for preparing polyenes is shown in Scheme I. The technique is based on the selective formation of a tungstacyclobutane ring employing the cyclobutene double bond in 7,8-bis(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (TCDT), presumably through the exo

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(5) (a) Bredas, J. L.; Street, G. B. *Acc. Chem. Res.* **1985**, *18*, 309. (b) Reid, R. D.; Schug, J. C.; Lilly, A. C.; Dwyer, R. W. *J. Chem. Phys.* **1988**, *88*, 2049, and references therein.

(6) Herrmann, J. P.; Ducuing, J. *J. Appl. Phys.* **1974**, *45*, 5100. (b) Rustagi, K. C.; Ducuing, J. *J. Opt. Commun.* **1974**, *10*, 258.

(7) Well-defined block copolymers containing a polyene unit might be of particular interest for making Langmuir–Blodgett films. See ref 2c, pp 53, 243, 297.

(8) (a) Bott, D. C.; Brown, C. S.; Edwards, J. H.; Feast, W. J.; Parker, D.; Winter, J. N. *Mol. Cryst. Liq. Cryst.* **1985**, *117*, 9. (b) Edwards, J. H.; Feast, W. J.; Bott, D. C. *Polymer* **1984**, *25*, 395. (c) Feast, W. J.; Winter, J. N. *J. Chem. Soc., Chem. Commun.* **1985**, 202.

(9) (a) Ivin, K. J. *Olefin Metathesis*; Academic: London, 1983. (b) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring-opening Polymerization of Cyclo-Olefins*, 2nd ed.; Wiley-Interscience: New York, 1985.

(10) (a) Kahlert, H.; Leising, G. *Mol. Cryst. Liq. Cryst.* **1985**, *117*, 1. (b) Montaner, A.; Rolland, M.; Sauvajol, J. L.; Galtier, M.; Almairac, R.; Ribet, J. L. *Polymer* **1988**, *29*, 1101. (c) Perego, G.; Lugli, G.; Pedretti, U. *Mol. Cryst. Liq. Cryst.* **1985**, *117*, 59.

(11) (a) Schrock, R. R. *J. Organomet. Chem.* **1986**, *300*, 249. (b) Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771. (c) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373. (d) Schrock, R. R.; DePue, R.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423.

(12) (a) Schrock, R. R.; Feldman, J.; Grubbs, R. H.; Cannizzo, L. *Macromolecules* **1987**, *20*, 1169. (b) Schrock, R. R.; Krouse, S. A.; Knoll, K.; Feldman, J.; Murdzek, J. S.; Yang, D. C. *J. Mol. Catal.* **1988**, *46*, 243. (c) Murdzek, J. S.; Schrock, R. R. *Macromolecules* **1987**, *20*, 2640.

(13) (a) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733. (b) Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1988**, *21*, 1961. (c) Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1488.

(14) (a) Wallace, K. C.; Schrock, R. R. *Macromolecules* **1987**, *20*, 448. (b) Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4964.

(15) (a) Kress, J.; Osborn, J.; Greene, R. M. E.; Ivin, K. J.; Rooney, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 899. (b) Kress, J.; Osborn, J. A.; Amir-Ebrahimi, V.; Ivin, K. J.; Rooney, J. J. *J. Am. Chem. Soc., Chem Commun.* **1988**, 1164. (c) Kress, J.; Aguero, A.; Osborn, J. A. *J. Mol. Catal.* **1986**, *36*, 1.

(16) (a) Knoll, K.; Krouse, S. A.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4424. (b) Krouse, S. A.; Schrock, R. R. *Macromolecules* **1988**, *21*, 1885.

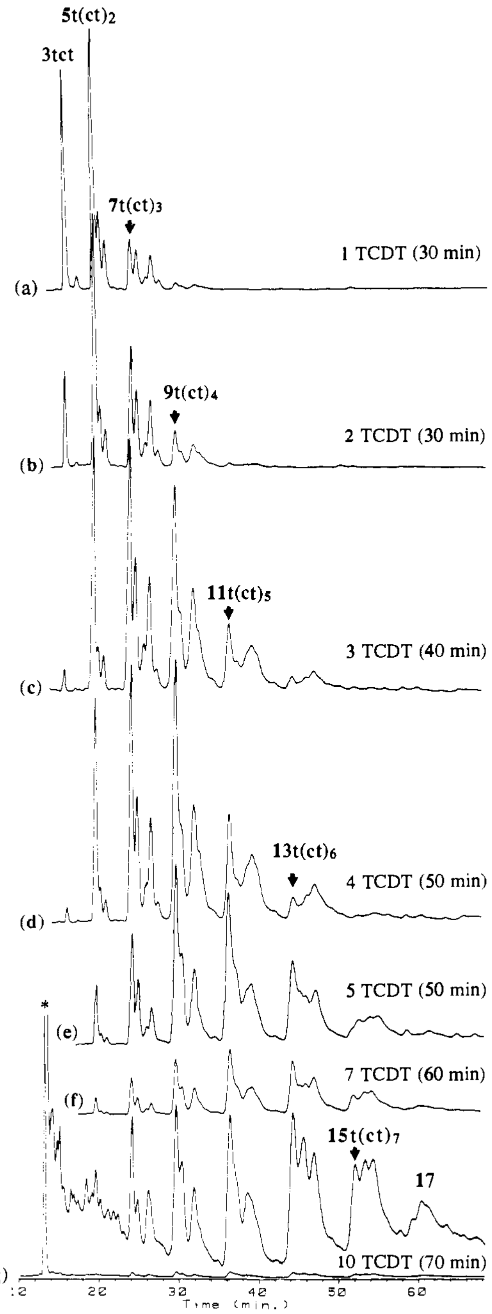


Figure 1. HPLC traces of odd polyenes prepared under standard conditions (120 °C/3 min retro-Diels–Alder reaction) employing from 1 to 10 equiv of TCDT (asterisk = guaiazulene internal standard; times in parentheses are reaction times before quenching).

face of the C(3)–C(4) double bond. No intermediate tungstacyclobutane complex has ever been observed. Metallacycles also have not been observed in the case of norbornene polymerization with catalysts of this general type,[12] although tungstacycles made from norbornene *have* been observed[15a,b] in related tungsten catalyst systems.[15c] In this system the *tert*-butyl group in the initial metallacycle must be almost exclusively trans to the norbornane ring system since this initial tunstacyclobutane complex rearranges to form a new alkylidene complex (the "first insertion product") that has a trans terminal double bond (Scheme I). The new alkylidene complex can then react with another equivalent of TCDT to give a new tungstacyclobutane complex, etc., until a living polymer results that contains on the average x equiv of TCDT in ring-opened form. Each of the propagation steps can produce either a cis or a trans double bond, although trans propagation dominates. The reaction period varies from 15 min to 1 h, depending on concentration and number of equivalents of TCDT. The organic oligomer is then cleaved from the metal in a Wittig-like reaction between the W=C bond and an aldehyde. The last step is a retro-Diels–Alder (retro-DA) reaction that generates hexafluoroorthoxylene. The reaction mixture is then filtered through silica gel to remove $W(O)(NAr)(O\text{-}t\text{-}Bu)_2$ and unreacted aldehyde. If pivaldehyde is used in the Wittig-like reaction, the result is a series of "odd" polyenes containing $2x + 1$ double bonds. If 4,4-dimethyl-*trans*-2-pentenal is used, then a series of "even" polyenes containing $2x + 2$ double bonds is formed. The total yield of the crude mixture of odd polyenes generated by using 3–4 equiv of TCDT is high (>90% by weight) under "standard" conditions (retro-DA conditions of 3 min at 120 °C).

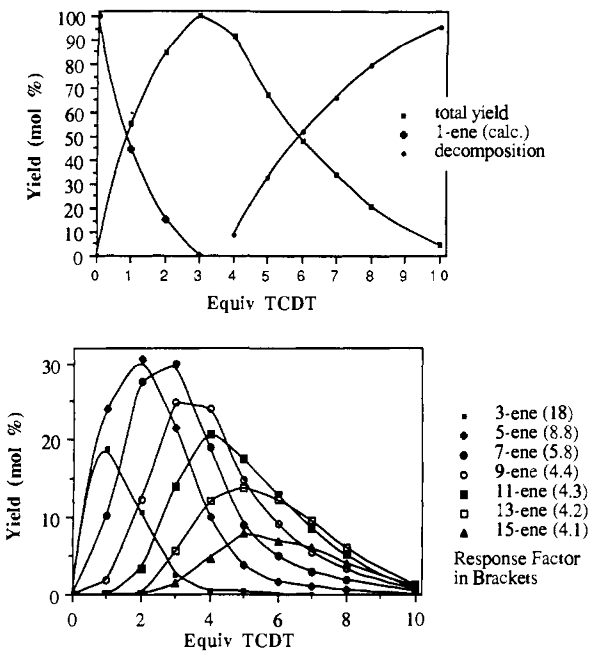
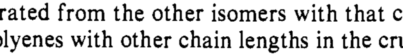


Figure 2. Absolute yields of odd polyenes (mixture of initial isomers; *trans*-di-*tert*-butylethylene excepted) under standard conditions: individual polyenes (bottom); total polyenes (top). (See Experimental Section for an explanation of how absolute yields were determined.)

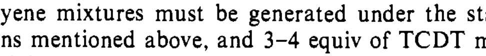
An essential analytical tool for analyzing polyenes and polyene mixtures is reversed-phase HPLC in conjunction with a UV–vis diode array detector in the range 240–600 nm using guaiazulene as an internal standard. The solvent is initially a 90:5:5 mixture of acetonitrile, dichloromethane, and water. After 30 min, water is removed over a period of 30 min and substituted with acetonitrile. Complete UV–vis spectra are accumulated every 1.6 s and correlated with the various peaks in the HPLC trace. Although the extinction coefficients of the various length polyenes and the different isomeric forms differ significantly, relative yields of polyenes can be determined in this manner by integration, and many isomers can be identified by their absorption spectra. Many polyenes could be isolated relatively pure by adsorption chromatography on silica at −40 °C under dinitrogen and identified by exhaustive NMR and UV–vis studies and correlated with HPLC studies of complex mixtures. Full experimental details can be found in the Experimental Section.

Polyenes Having an Odd Number of Double Bonds. HPLC results for odd polyenes prepared under standard conditions employing from 1 to 10 equiv of TCDT are shown in Figure 1. Under these conditions the odd polyenes of different chain lengths (but still mixtures of isomers) are separated cleanly from one another. The distribution of chain lengths shifts to longer chains as more TCDT is employed. It is important to note (i) that the maximum length polyene observable under these conditions appears to be the 17-ene and (ii) that the total yield employing 10 equiv of TCDT is very low (Figure 1g), even though the patterns of the distribution of observable polyenes is virtually the same as when fewer equivalents of TCDT are employed. The absolute yields of any given length polyene are plotted versus the number of equivalents of TCDT employed in Figure 2 (bottom) and the total yield in Figure 2 (top). (Note that the 3-, 5-, and 7-enes absorb more weakly than the longer polyenes; response factors are provided that will convert a given area to an area equivalent to standard guaiazulene.) We can conclude first that for x equiv of TCDT the polyene with the maximum yield has a length greater than $2x + 1$, approximately $2x + 3$. For example, the yield of the 11-ene maximizes by using only 4 equiv of TCDT. These results suggest that the rate of propagation is slightly faster than the rate of initiation, so that polyenes that are slightly longer than one would otherwise predict are formed. Note that the total yield maximizes when 3 equiv of TCDT have been added. The drop in polyene yield and the failure to observe any polyenes longer than the 17-ene are likely to be the consequence of the same phenomenon. One possibility is that the relatively long polyenes decompose progressively more readily beyond ~15 double bonds, under the conditions employed at one point (120 °C, 3 min). The nature of this decomposition will be discussed in detail later.

A major polyene isomer of a given length (up to the 11-ene) can be separated from the other isomers with that chain length and from polyenes with other chain lengths in the crude mixture by adsorption chromatography on silica gel at −40 °C under dinitrogen by using mixtures of pentane and dichloromethane. The polyene mixtures must be generated under the standard conditions mentioned above, and 3–4 equiv of TCDT must be employed for the best total yields. (Some loss of total yield is necessary to prepare the longer polyenes.) The isomer that is formed in largest amounts for the 3-, 5-, 7-, 9-, and 11-ene and the one that elutes first by reversed-phase HPLC for all chain lengths (see Figure 1) also happens to be the one that elutes first in macroscale column chromatography. It is the trans(cis,trans)$_x$ or t(ct)$_x$ or "alternating form" having either C_{2h} symmetry (e.g., **9t(ct)$_4$**) or C_{2v} symmetry (e.g., **11t(ct)$_5$**). Yields of the isolated alternating form is as high as 60% (for shorter polyenes). Another isomer or two of **5** and **7** could be identified by proton and carbon NMR as a small fraction in this leading cut. The number of isomers was too great for **13** and the yields also too low for **13** and **15** to identify any but the alternating form by its UV–vis spectrum in HPLC studies. Other isomers of a given chain length from macroscale column chromatography could be accumulated and each transformed into intermediate trans-rich isomers and ultimately the all-trans isomers as described later.



9t(ct)$_4$



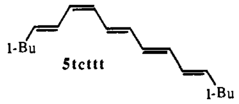
11t(ct)$_5$

Let us turn to a more detailed stepwise examination of preparation and analysis of the odd polyenes. Pivaldehyde reacts relatively slowly with W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (2 h with 1.5 equiv at a concentration of ~0.1 M in W) to give *trans-tert*-butylethylene virtually quantitatively. The reaction must be slow for steric reactions, since 4,4-dimethyl-2-pentenal reacts relatively quickly with W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (see later). There is no evidence for *cis*-di-*tert*-butylethylene (<1%) by NMR or GLC methods. This result confirms that a complex that contains the *neopentylidene* ligand reacts with pivaldehyde to give the trans Wittig-like product stereoselectively.

When 1 equiv of TCDT is added to W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ followed after 30 min by the standard workup (addition of pivaldehyde followed by the retro-DA reaction), a mixture is obtained whose HPLC trace is shown in Figure 1a. (*trans*-Di-*tert*-butylethylene is also present in the mixture, since W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ is not completely consumed by 1 equiv of TCDT (Figure 2, top), but it is not shown in this HPLC trace.) The major isomer of **3** was shown by a variety of ^{1}H and ^{13}C NMR techniques to be **3tct**, the isomer that is to be expected if initiation and cleavage (Scheme I) proceed stereospecifically trans. The only other possible isomer, the all-trans isomer **3t$_3$**, is a minor component of this particular mixture; it cannot be a *primary* product if the reaction proceeds as shown in Scheme I, since the central double bond is formed in the retro-DA reaction and therefore must be cis. Therefore **3t$_3$** must form by a more involved process than that shown in Scheme I. This important subtlety is discussed in the next section. The amount of **3** decreases steadily as more TCDT is employed; very little **3** is present if 3 (Figure 1c) or more equiv of TCDT are employed.

Three isomers of **5** form as primary products, assuming that no two elute at the same time. The one that elutes first, and the major isomer, is **5t(ct)$_2$**. The other isomer that could logically be formed as a primary product is **5tccct**, the result of a cis propagation step. **5tcttt** and **5t$_5$** also are logical products of cis-to-trans double-bond isomerization of **5t(ct)$_2$** and **5tcttt**, respectively, but **5t$_5$** can be shown to elute much later. **5tccct** has been identified by NMR in mixtures containing largely **5t(ct)$_2$** that have been isolated by adsorption chromatography. Therefore we propose that the third isomer is **5tcttt**, a proposal that is corroborated by studies to be described in the next section. What can be stated at this juncture on the basis of these data is that the propagation step appears to be ~75% trans selective, roughly the same as the approximately 2:1 trans selectivity in the propagation step in the ring-opening of norbornene by this tungsten catalyst.[12] Note that the relative amounts of the three 5-enes does not change greatly as additional TCDT is employed (Figure 1a–f).

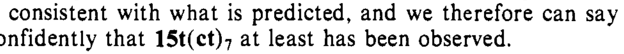
5tccct



5tcttt

The mixture of isomers of **7** formed when 2–5 equiv of TCDT are employed consists of **7t(ct)$_3$** (Figure 1) and at least four other isomers (two major and two minor are visible). Since two double bonds now can be either cis or trans in the initial polyene as a result of the propagation step, there is a higher probability that either the third or the fifth double bond in the chain will be cis instead of trans, thus giving rise to **7tccctct** instead of **7tctctct**. Complete identification of these isomers depends upon experiments to be described in the next section. The all-trans form (**7t$_7$**) again is not found in this isomer mixture.

Although **9t(ct)$_4$** can be identified in a typical reaction mixture (Figure 1), it now becomes much more difficult to be certain of the number and identity of isomers that elute after **9t(ct)$_4$**. The situation becomes even more complicated for **11**, **13**, and **15**, although the isomer that elutes first in each case has a UV–vis spectrum that is totally consistent with it being the alternating form, and relatively pure **9t(ct)$_4$** and **11t(ct)$_5$** could be isolated on a preparative column. **15** could be isolated in small amounts by using 5 equiv of TCDT, but **15t(ct)$_7$** could not be separated into pure form. The mixture of isomers of **17** can be observed (Figure 1f,g), but the yield was always too low to isolate any material by preparative column chromatography. It is also likely that **17** is simply too unstable to isolate by these techniques. Since the alternating isomer of **17** is not observable, we actually cannot be absolutely certain that the 17-enes are formed. However, the UV–vis spectrum of **15t(ct)$_7$** (recorded in an HPLC experiment) is consistent with what is predicted, and we therefore can say confidently that **15t(ct)$_7$** at least has been observed.



15t(ct)$_7$

The polyene mixtures that result if the retro DA reaction is carried out on polyTCDT (5 equiv of TCDT) at progressively higher temperatures are shown in Figure 3. The fact that isolated **11** behaves similarly upon heating confirms that these results can be ascribed to thermal instability of the polyenes rather than any reaction involving excess aldehyde or W(O)(NAr)(O-*t*-Bu)$_2$. It is no longer possible to observe **15** if the retro-DA reaction is carried out at 135 °C, and **13t(ct)$_6$** and other closely related forms isomerize at this temperature to trans-rich forms that elute later under these HPLC conditions (Figure 3b). Higher temperatures are required to isomerize **11t(ct)$_5$**, and even higher temperatures are required to isomerize **9t(ct)$_4$**; some **9t(ct)$_4$** is still visible in

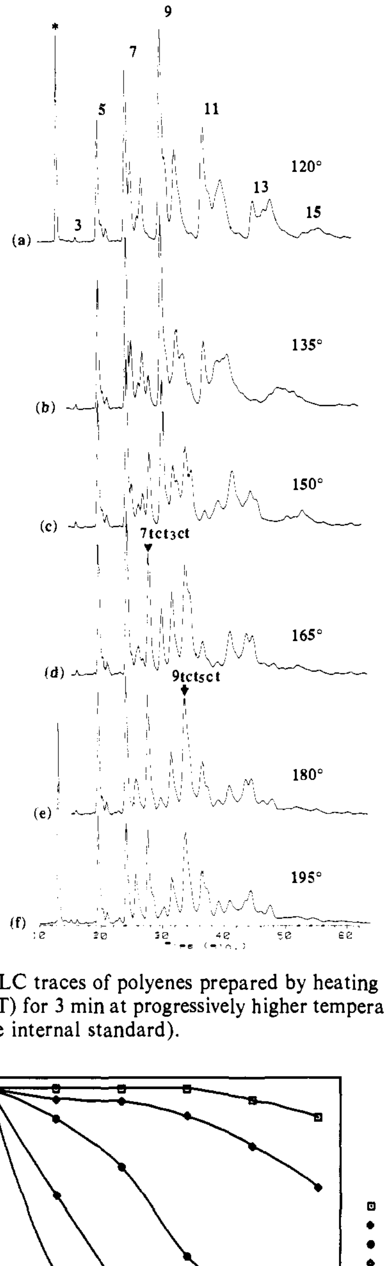


Figure 3. HPLC traces of polyenes prepared by heating polyTCDT (5 equiv of TCDT) for 3 min at progressively higher temperatures (asterisk = guaiazulene internal standard).

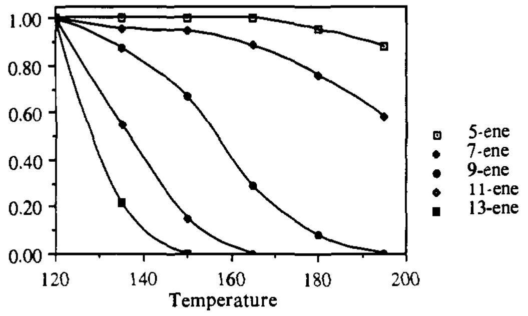


Figure 4. Decay of the alternating forms in the HPLC studies shown in Figure 3.

Figure 3e. The amount of **7t(ct)$_3$** in Figure 3f is somewhat less than what it is in Figure 3a, while the amount of **5t(ct)$_2$** changes only slightly between Figure 1a and 1f. The major isomer of **7** that is formed upon heating the mixture is proposed to be **7tct$_3$ct** (Figure 3d), while that for **9** is proposed to be **9tct$_5$ct** (Figure 3e), on the basis of past findings that internal cis bonds isomerize most readily and those near the end most slowly,[1c,17a,b] and our finding that NMR analysis of the mixture of 7-enes shown in Figure 3d or 3e (see later) is consistent with **7t(ct)$_3$** and **7tct$_3$ct** being the major isomers present.

Disappearance of the alternating forms upon heating is shown graphically in Figure 4. It also should be noted that the total yield decreases significantly. We propose that **15** isomerizes to trans-rich forms immediately and then (or concurrently) decomposes rapidly (Figure 3b vs 3a). The rate of decomposition of **13** is significantly less than that of **15**, and **11** less than that of **13**, etc. The yield of **9** and shorter polyenes does not appear to decrease drastically upon heating for 3 min at 195 °C.

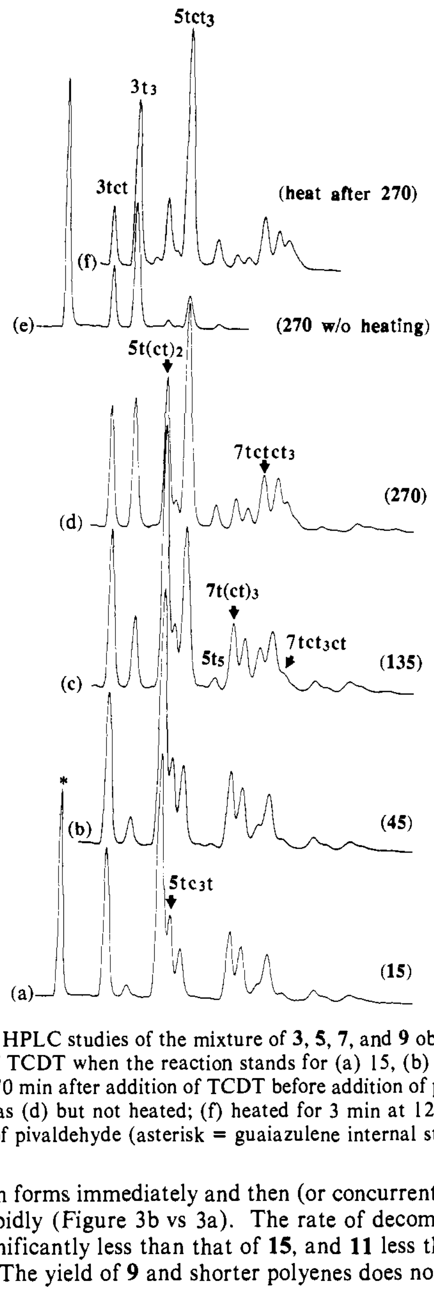
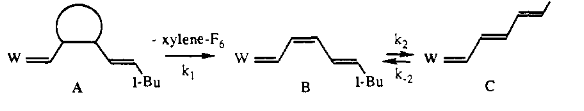


Figure 5. HPLC studies of the mixture of **3**, **5**, **7**, and **9** obtained from 1 equiv of TCDT when the reaction stands for (a) 15, (b) 45, (c) 135, and (d) 270 min after addition of TCDT before addition of pivaldehyde; (e) same as (d) but not heated; (f) heated for 3 min at 120 °C *before* addition of pivaldehyde (asterisk = guaiazulene internal standard).

Formation of Vinylalkylidene Complexes and "Living Polyenes". We noted earlier that formation of **3t$_3$** is inconsistent with the mechanism shown in Scheme I. In this section we offer an explanation of this and related findings.

In Figure 5 are shown HPLC analyses of polyene mixtures generated from 1 equiv of TCDT under a variety of conditions, most of them (Figure 5a–d) involving simply waiting for up to 270 min before adding pivaldehyde to the living polyTCDT and heating the mixture to promote the retro-DA reaction. Upon waiting for 270 min at 24 °C befor e adding pivaldehyde to the living polyTCDT, the amount of **3t$_3$** formed upon cleavage increases to ~50% of total **3** (Figure 5d). We propose that this isomerization is possible under conditions where no *thermal* isomerization of *isolated* **3tct** to **3t$_3$** takes place because of an accelerated retro-DA reaction near the metal followed by a facile isomerization of the first C=C bond (eq 2). Subsequent reaction



(2)

of C with pivaldehyde would give **3t$_3$**. In Figure 5e is shown the result of analyzing the product mixture after standing living

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(17) (a) Ohmine, I.; Morokuma, K. *J. Chem. Phys.* **1980**, *73*, 1907. (b) Malrieu, J. P.; Nebot-Gil, I.; Sanchez-Morin, J. *Pure Appl. Chem.* **1984**, *56*, 1241. (c) Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187.

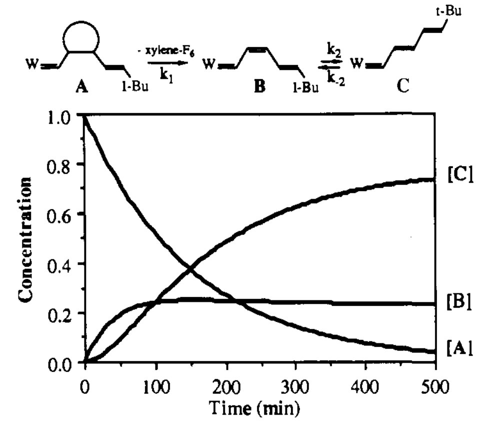
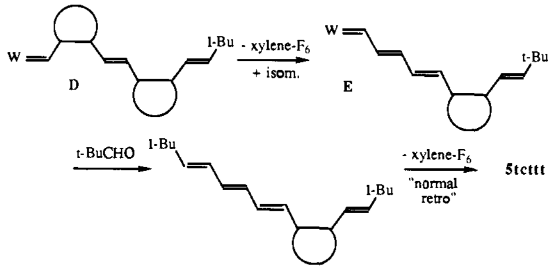


Figure 6. Modeling the retro-Diels–Alder reaction and subsequent cis/trans isomerization using data shown in Figure 5: found $k_1 = 6.5 \times 10^{-3}$ min^{-1}, $k_2 = 1.7 \times 10^{-2}$ min^{-1}, $k_{-2} = 5.1 \times 10^{-3}$ min^{-1} at 24 °C. (See Experimental Section for details.)

polyTCDT for 270 min and cleaving with pivaldehyde, but *without* subsequently heating the sample. Virtually only **3** is observed, since the only significant retro-DA reaction occurs in the first TCDT unit away from the metal, but only the reaction shown in eq 2 produces an actual polyene. For example, the sequence shown in eq 3 (or related sequences) would not yield a polyene



(3)

until the mixture is heated to 120 °C, where the "normal" retro-DA reaction occurs. Note that the overall yield of **3** in Figure 5e is less than that in Figure 5d, since the "accelerated" retro-DA reaction is not yet complete after 270 min at 24 °C, i.e., some A (eq 2) remains. If the reaction mixture is heated to 120 °C for 3 min *before* pivaldehyde is added, then the greatest amount of **3t$_3$** is formed, along with other polyenes that result from normal retro-DA reactions (Figure 5f; cf. Figure 5a). The approximately 2:1 ratio of **3t$_3$** to **3tct** in Figure 5e increases to approximately 3:1 in Figure 5f, because (we propose) that the equilibrium between B and C shown in eq 2 is not reached until the living polymer is heated to 120 °C for 3 min, i.e., the rate of the "accelerated" retro-DA reaction and the rate of the cis-to-trans isomerization shown in eq 2 are approximately the same. The overall yields of **3** and **5** in Figure 5e should be compared with the yields in Figure 5d and/or 5f. (The amount of **3** is approximately 80% of the maximum in Figure 5e, the amount of **5** only ~10% of the maximum.)

If we assume that the sequence of reactions that give **3tct** and **3t$_3$** is that shown in eq 2 and that B and C are in equilibrium, then it is possible to extract k_1, k_2, and k_{-2} by modeling the reaction with use of the data shown in Figure 5a–e (see Experimental Section). The best fit is shown in Figure 6, and the extracted values (at 24 °C) are $k_1 = 6.5 \times 10^{-3}$ min^{-1}, $k_2 = 1.7 \times 10^{-2}$ min^{-1}, and $k_{-2} = 5.1 \times 10^{-3}$ min^{-1}. Note that the rate of isomerization is approximately twice that of the accelerated retro-DA reaction. It is also possible to determine the rate of the retro-DA reaction in the second TCDT unit away from the metal (e.g., in E in eq 3) by following the appearance of **5** (see Experimental Section for details). The rate constant for this retro reaction is approximately 6×10^{-4} min^{-1}. Therefore the retro-DA reaction in the first TCDT unit away from the metal is about 10 times faster than in the second TCDT unit. We assume for now that the rate of the retro-DA reaction in the second TCDT unit away from the metal is virtually the same as that further out in the chain or in a system free of metal. Further and more accurate studies will be required to confirm these proposals.

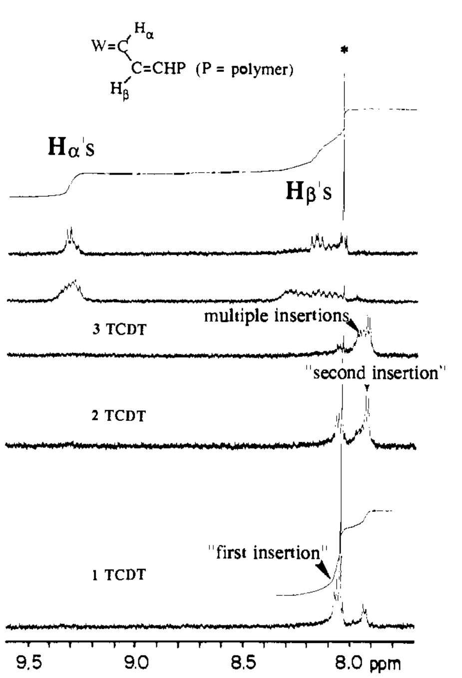


Figure 7. The 500-MHz ^{1}H NMR spectra of the alkylidene region in samples of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ after addition of (a) 1 equiv, (b) 2 equiv, and (c) 3 equiv of TCDT. Spectra d and e were obtained after heating samples that had spectra c and a, respectively, to 50 °C for 45 min. The solvent is benzene-d_6. Asterisk = neopentylidene Hα.

Other consequences of the accelerated retro-DA reaction near the metal followed by cis-to-trans isomerization of that double bond are also observed in Figure 5. After pivaldehyde is added and the normal retro-DA reaction carried out, the result is an isomer with a trans,trans,trans sequence at the end. This is most obvious when the **5t(ct)$_2$** form largely disappears and is replaced by the "third isomer" alluded to and proposed above, namely, **5tct$_3$** (eq 3 and Figure 5d,f). A small amount of **5t$_5$** is also formed. (**5t$_5$** is formed only by thermal isomerization at high temperatures; Figure 3.) The origin of **5t$_5$** is not known, but we have noted what appears to be an anomalously rapid isomerization of **5t(ct)$_2$** to **5t$_5$** via **5tct$_3$** in isolated samples of **5t(ct)$_2$** that we believe are catalyzed by byproducts of the workup procedure. Therefore we do not want to attach any special significance to the small amounts of **5t$_5$** formed here. Similar reasoning allows us to identify **7tctct$_3$** as the isomer of **7** that increases in Figure 5a–d as **7t(ct)$_3$** decreases.

The 500-MHz proton NMR studies of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ plus 1, 2, or 3 equiv of TCDT are shown in Figure 7. An internal standard that was present in all cases allowed us to conclude that virtually no material was lost over the course of these studies. Addition of 1 equiv of TCDT to W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ converts about half of it to an approximately 1:1 mixture of the "first insertion" product (A, eq 2) and the "second insertion" product (D, eq 3), plus a small amount of higher oligomers, on the basis of the intensities of the alkylidene proton resonances around 8 ppm (Figure 7a). The doublet at ~8.08 ppm can be ascribed to that for the alkylidene proton in the first insertion product on the basis of the fact that it decreases upon addition of a second equivalent of TCDT (Figure 7b). The doublet at ~7.93 ppm must be due to the alkylidene proton in the second insertion product. Resonances for alkylidene protons in higher oligomers begin to fall on top of one another between 7.9 and 8.0 ppm (Figure 7c). Note that virtually all of the W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ initiator is consumed upon addition of 3 equiv of TCDT (Figure 7c), good evidence that propagation is not a great deal faster than initiation and consistent with the finding that the total yield of polyenes maximizes by using 3 equiv of TCDT (Figure 2).

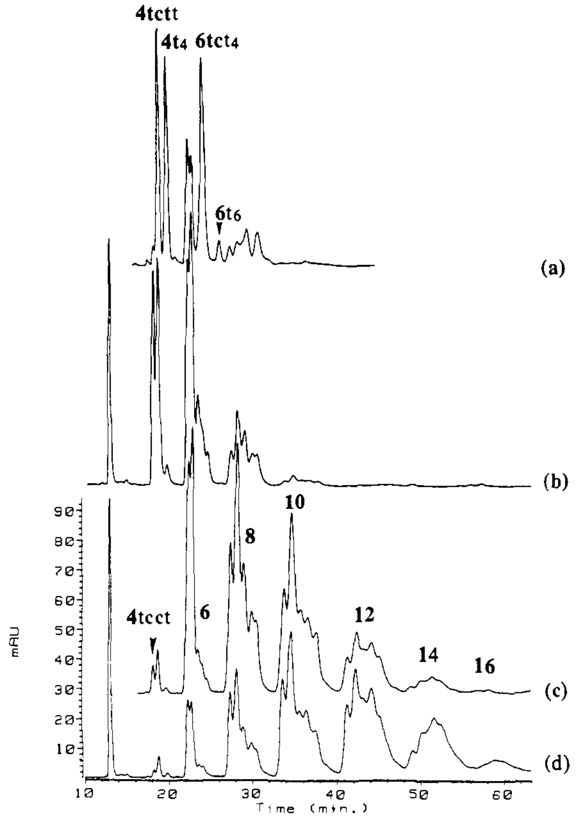


Figure 8. HPLC data for even polyenes prepared by using (a) 1 equiv of TCDT and heating before addition of 4,4-dimethyl-*trans*-2-pentenal; (b) 1 equiv, (c) 3 equiv, and (d) 5 equiv of TCDT followed by addition of 4,4-dimethyl-*trans*-2-pentenal and heating.

When the sample whose spectrum is shown in Figure 7a is heated to 50 °C for 45 min, the spectrum shown in Figure 7e is obtained. On the basis of recent studies in which vinylalkylidene complexes (W=CHCH=CHR) have been prepared,[18] we can confidently assign the resonances at ~9.35 ppm to alkylidene α protons in "living polyenes" and the more complex set of resonances between 8 and 8.2 ppm to β protons in "living polyenes". The alkylidene α-proton resonance seem to be less sensitive to the C_β=C_γ bond configuration than the β-proton resonance and primarily consists of two doublets, the major one being ascribable to that for W=C*H*(CH=CH)$_2$(*t*-Bu), the ultimate product of insertion of 1 equiv of TCDT, and the minor one to W=C*H*(CH=CH)$_4$(*t*-Bu) (cf. Figure 7a). The total area of the resonance at 9.35 ppm represents the amount of conversion of initiator to a living oligomer, here of the type W=C*H*(CH=CH)$_{2x+2}$(*t*-Bu) (where x = 0, 1, 2, ...). If we assume that all propagation rates are strictly the same, then it is possible to obtain an expression that relates γ ($=k_p/k_i$) to the amount of initial initiator (I_0), remaining initiator (I if $I \neq 0$), and initial monomer (M_0):[19] $M_0/I_0 + \gamma \ln (I/I_0) + (1 - \gamma)(I/I_0 - 1) = 0$. The group of resonances at ~9.3 ppm is approximately as intense as that for the initiator so that $I/I_0 = 0.5$, $M_0/I_0 = 1$, and therefore $\gamma = k_p/k_i = 2.6$. Since the resonance for the initiator overlaps that for the β protons, the accuracy of the value for k_p/k_i probably is not high, but it is of approximately the magnitude we expected. The fact that the rate of propagation is only 2–3 times the rate of initiation is consistent with the relatively bulky nature of the propagating alkylidene formed by opening TCDT.

If the sample whose spectrum is shown in Figure 7c is heated to 50 °C for 45 min, a more complex set of resonances that those shown in Figure 7c are found, because a relatively large number of different chain lengths are present (a_{avg} in W=C*H*(CH=CH)$_{2x+2}$(*t*-Bu) is 3 with a range of 1–6). The initiator has now been virtually completely consumed, and areas of the two patterns centered at ~9.3 ppm (H_α protons) and that at ~8.2 ppm (H_β protons) are equal. Resonances for olefinic protons further out the chain are found further upfield in the general region where protons in pure polyenes are found.

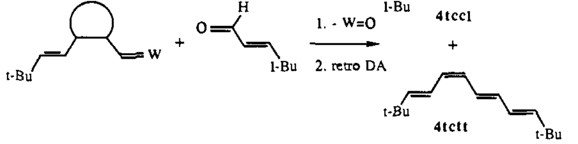
Table I. Retention Times of all Di-*tert*-butyl-Capped Polyenes Identifiable in HPLC Studies

compd	time, min	compd	time, min
guaiazulene	13.02	**7t(ct)$_3$**	23.42
3tct	15.88	**7tctct$_3$**	25.09
3t$_3$	17.35	**7tct$_3$ct**	26.84
4tcct	17.92	**7t$_7$**	29.30
4tctt	18.48	**8t$_8$**	33.27
4t$_4$	19.46	**9t(ct)$_4$**	28.59
5tctct	19.22	**9tctct$_3$ct**	30.44
5tc$_3$t	19.84	**9t(ct)$_3$tt**	30.84
5tct$_3$	20.53	**9tct$_5$ct**	32.59
5t$_5$	22.37	**9tct$_7$**	35.18
6tcttct	21.92	**9t$_9$**	37.67
6tctcct	21.95	**10t$_{10}$**	42.41
6tctctt	22.35	**11t(ct)$_5$**	34.82
6tct$_4$	23.69	**13t(ct)$_6$**	42.42
6t$_6$	25.66	**15t(ct)$_7$**	49.80

All that we have presented in this section is fully consistent with an "accelerated" retro-DA reaction in the first TCDT unit away from the metal at a rate about 10 times that of a retro-DA reaction in the second TCDT unit and (we assume) "normal" retro DA reaction further out the chain. But what we found equally surprising is that the resulting vinylalkylidene complexes (or living polyene complexes if the normal retro-DA reaction occurs throughout the chain) appear to be much more stable than a typical *n*-alkylidene complex, e.g., a propylidene complex.[11c] Since it is likely that the reactivity of a vinylalkylidene complex or living polyene will be significantly different from that of a living TCDT oligomer, the details of chain growth could be complex under conditions where the accelerated retro-DA reaction becomes competitive with chain growth. The subject of vinylalkylidenes and living polyenes is a large and complex one that will be addressed fully in future publications.

Preparation of Polyenes Containing an Even Number of Double Bonds. 4,4-Dimethyl-*trans*-2-pentenal (1.5 equiv) reacts cleanly with W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (~0.1 M) in ~1 h to give W(O)(NAr)(O-*t*-Bu)$_2$ and a mixture of **2tt** (91%) and **2tc** (9%) virtually quantitatively. The Wittig-like cleavage reaction is less trans selective than it is in the case of pivaldehyde, presumably because 4,4-dimethyl-*trans*-2-pentenal is considerably less bulky than pivaldehyde near the carbonyl group.

Addition of 1 equiv of TCDT to W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ followed after 15 min by 4,4-dimethyl-*trans*-2-pentenal and standard workup gives a mixture whose HPLC is shown in Figure 8b. The first two peaks have been ascribed to a 1:1 mixture of **4tcct** and **4tctt** on the basis of isolation on a macroscale and identification by NMR methods. The predominant 4-ene should be **4tctt** if the Wittig-like reaction and the first ring-opening step proceed selective trans, as they do in the case of forming the odd polyene series. Formation of ~50% **4tcct** implies that the Wittig-like reaction is virtually completely nonselective (eq 4).



(4)

Lack of selectivity again can be ascribed to the considerably smaller steric bulk of 4,4-dimethyl-*trans*-2-pentenal compared to pivaldehyde, a difference that was hinted at in the reaction involving W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ noted above. The next group of peaks in Figure 8b can be assigned to isomers of **6**, and the third and fourth groups of peaks to isomers **8** and **10**, respectively.

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[18] Crowe, W. E.; Schrock, R. R., unpublished results.

[19] (a) We thank G. Bazan for pointing out this approach.[19b] (b) Gold, L. *J. Chem. Phys.* **1958**, *28*, 91.

Table II. ^{13}C and ^{1}H NMR Data for *all-trans*-Polyenes[a]

	1[b]	2	3	4	5	6	7	8	9	*C*Me$_3$	C*Me*$_3$
1	135.70 (5.30)									32.31	29.93 (0.95)
2t$_2$	143.62 (5.62)	125.42 (5.93)								33.03	29.61 (1.01)
3t$_3$	145.22 (5.66)	125.28 (5.96)	131.40 (6.09)							33.20	29.59 (1.01)
4t$_4$	145.90 (5.70)	125.46 (5.99)	132.72 (6.14)	131.10 (6.15)						33.33	29.55 (1.01)
5t$_5$	146.37 (5.72)	125.47 (6.00)	133.29 (6.17)	131.14 (6.17)	132.35 (6.19)					33.39	29.53 (1.01)
6t$_6$	146.59 (5.73)	125.50 (6.01)	133.65 (6.18)	132.37 (6.21)	132.91 (6.22)					33.42	29.51 (1.02)
7t$_7$	146.74 (5.74)	125.52 (6.02)	133.85 (6.19)	131.14 (6.18)	132.36 (6.22)	132.92 (6.24)	133.26 (6.23)			33.43	29.51 (1.02)
8t$_8$	146.83 (5.74)	125.53 (6.02)	133.98 (6.19)	131.13 (6.18)	132.37 (6.23)	132.90 (6.25)	133.26 (6.24)	133.45 (6.24)		33.44	29.51 (1.02)
9t$_9$	146.86 (5.75)	125.56 (6.02)	134.06 (6.19)	131.14 (6.18)	132.36 (6.24)	132.90 (6.26)	133.23 (6.25)	133.45 (6.25)	133.57 (6.25)	33.44	29.51 (1.02)

[a] NMR data are listed in ppm vs TMS in CDCl$_3$. ^{1}H NMR data are those in parentheses. $^{3}J_{HH}$ is 15.3 Hz in each case. [b] This number refers to the olefinic carbon atom or proton in the chain with the carbon atom to which the *tert*-butyl group is bound being defined as 1.

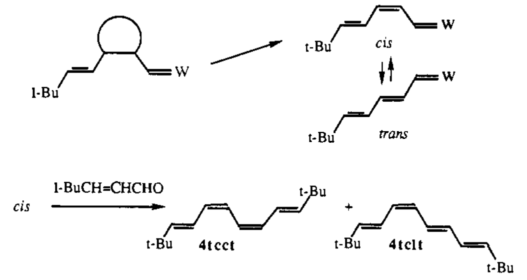
Table III. ^{13}C and ^{1}H NMR Data for the Alternating Isomers of Di-*tert*-butyl-Capped Polyenes[a]

	1[b]	2	3	4	5	6	7	8	9	10	11	*C*Me$_3$	C*Me*$_3$
3tct	146.44 (5.71) [+0.05][c]	120.35 (6.39) [+0.43]	128.22 (5.85) [−0.24]									33.40	29.55 (1.04)
5t(ct)$_2$	147.51 (5.76) [+0.04]	120.58 (6.44) [+0.44]	130.48 (5.96) [−0.21]	127.73 (5.99) [−0.18]	128.31 (6.66) [+0.47]							33.55	29.51 (1.05)
7t(ct)$_3$	147.87 (5.78) [+0.04]	120.56 (6.44) [+0.42]	131.06 (5.99) [−0.20]	127.64 (5.99) [−0.19]	128.24 (6.69) [+0.47]	129.18 (6.70) [+0.46]	129.84 (6.11) [−0.12]					33.59	29.49 (1.05)
9t(ct)$_4$	148.01 (5.78) [+0.03]	120.56 (6.44) [+0.42]	131.25 (5.99) [−0.20]	127.62 (5.98) [−0.20]	128.21 (6.69) [+0.45]	129.12 (6.73) [+0.47]	129.75 (6.09) [−0.16]	130.39 (6.12) [−0.13]	129.48 (6.71) [+0.46]			33.60	29.48 (1.05)
11t(ct)$_5$	148.05 (5.79)	120.55 (6.45)	131.32 (6.00)	127.61 (6.00)	128.19 (6.70)	129.05 (6.74)	129.70 (6.10)	130.29 (6.12)	129.41 (6.75)	129.58 (6.72)	130.57 (6.14)	33.61	29.48 (1.05)
type			α/β	α/β	β/γ	β/γ	α/β	α/β	β/γ				

[a] NMR data are listed in ppm vs TMS in CDCl$_3$; ^{1}H NMR data are in parentheses. $^{3}J_{HH}$ is 15.3 Hz in each case. [b] This number refers to the olefinic carbon atom or proton along the chain with the carbon atom bound to the *tert*-butyl group being defined as carbon atom 1. [c] Number in brackets refers to the change in chemical shift relative to that for the corresponding proton in the respective *all-trans*-polyene (Table II).

Use of 3 (Figure 8c) and 5 (Figure 8d) equiv of TCDT yields peaks characteristic of isomers of **12**, **14**, and **16**.

If the living TCDT oligomer prepared from 1 equiv of TCDT (Figure 8b) is heated before adding 4,4-dimethyl-*trans*-2-pentenal, then the result shown in Figure 8a is obtained. On the basis of what we discussed above for the odd polyenes the isomers in Figure 8a should now be largely **4tctt** and **4t$_4$** (eq 5–7). Note that **4tctt** is formed by both reaction pathways (eq 6 and 7). The second peak in Figure 8a can be identified as **4t$_4$** by its characteristic UV–vis spectrum. Therefore the isomer of **4** that elutes first in Figure 8a (second in Figure 8b) must be **4tctt**, and the isomer that elutes first in Figure 8b must be **4tcct**. Note that very little **4tcct** remains in Figure 8a, as if the all-cis form (eq 5) were converted to the trans form. We know that the cis and trans forms are in equilibrium (see eq 2 and Discussion), so perhaps the Wittig reaction shown in eq 6 yields little **4tcct**. The "conversion" of **4tcct** in Figure 8b to **4t$_4$** in Figure 8a therefore is not real, only circumstantial.



(5)

(6)

$$trans \xrightarrow{\text{t-BuCH=CHCHO}} 4tctl + 4t_4 \qquad (7)$$

The two primary initial isomers of **6** that are observed in Figure 8b (and 8c and 8d) must be **6tctctt** and **6tctcct**. If the living TCDT oligomers are heated first, then **6tct$_4$** and **6tcttct** should form. Only one "new" isomer of **6** is observed in Figure 8a. The "new" isomer is assigned as **6ctct$_4$** according to its UV–vis spectrum. However, UV–vis spectra suggest also that **6tctcct** in Figure 8b is replaced by another isomer in Figure 8a. We assign it as **6tcttct** on the basis of its UV–vis spectrum. Apparently **6tctcct** and **6tcttct** simply elute at approximately the same time under these HPLC conditions (Table I). After NMR studies of the t(ct)$_x$ isomers (Table III), the all-trans isomers (Table II), and several others (Table SI in the supplementary material (see the paragraph at the end of the paper)) were complete, it was possible at least to show that the ^{13}C NMR spectrum of the initial mixture of isomers of the 6-ene was consistent with the presence of comparable amounts of **6tctctt** and **6tctcct**, plus smaller amounts of **6tcttct** and **6tct$_4$**, among other as yet unidentified isomers.

Characterization of the initial mixture of isomers of the even-numbered polyenes by HPLC or NMR methods was not possible for any containing more than six double bonds.

Preparation of *all-trans*-Polyenes. When the retro-Diels–Alder reaction is carried out for 3 min at temperatures progressively higher than 120 °C, then more complex mixtures are obtained that contain a lower total yield of polyenes, and more isomers that contain trans double bonds, as we discussed above (Figures 3 and 4). **13t(ct)$_6$** disappears quickly. In contrast, little **5t$_5$** forms in 3 min at 180 °C. The two major and two minor isomers of **7** are likely to be cis-rich forms since they appear to isomerize to **7t(ct)$_3$** as **7t(ct)$_3$** begins to isomerize to **7tct$_3$ct**, a relatively stable isomer that builds up in the reaction mixture (Figure 3). **7tct$_3$ct** isomerizes slowly to **7t$_7$**. **9tctct$_3$ct** and **9tct$_5$ct** are formed sequentially when **9t(ct)$_4$** isomerizes thermally or photochemically; **9tct$_5$ct** also builds up in reaction mixtures because it only slowly isomerizes to **9t$_9$**. We should note that the conditions used for a typical retro-DA reaction are too mild for electrocyclic reactions[17c] to proceed to any significant extent.

The best method of isomerizing the initial mixture of isomers of **5**, **7**, and **9** to all-trans forms is by irradiating them in pentane by using a medium-pressure mercury lamp. For **5** and **7** the Pyrex glass of the Schlenk tube (~290-nm cutoff) is sufficient as a short-wavelength filter, while a Schott WG 345 filter (~50% absorption at 345 nm) gave good results in the case of **9**. On a preparative scale (30–40 mg in 300 mL of pentane) the photochemical isomerization process required up to 15 h, even when using a focused 500-W medium-pressure lamp, to obtain a mixture that consists of ~90% of the all-trans form of a given polyene. The process can be followed conveniently by ^{1}H NMR, UV–vis, or HPLC. In each case solutions containing ≥90% of the all-trans form were prepared with no significant loss of material. **5t$_5$** was prepared 95% pure by this method; it was not purified further. **7t$_7$** was crystallized from pentane at −80 °C, while **9t$_9$** crystallized out of pentane solution as it formed. **3t$_3$** was readily accessible by irradiation of **3tct** in the presence of a trace of iodine in pentane with >300-nm light. **3t$_3$** is obtained ~80% pure.

Photochemical isomerization of **11** and **13** was not successful. However, because of the low solubility of **11t$_{11}$** and **13t$_{13}$** and the relative ease of thermally isomerizing the initial isomers that contain cis linkages, **11t$_{11}$** and **13t$_{13}$** can be prepared by heating solutions of the initial isomer mixtures to 180 °C in toluene for 30–90 min. They crystallize out directly as fine shiny plates, red-purple in the case of **11t$_{11}$** and blue-purple in the case of **13t$_{13}$**. They are both soluble enough in pentane, toluene, dichloromethane, and carbon disulfide to record UV–vis spectra, but not soluble enough to obtain ^{13}C NMR spectra, even in 10-mm tubes at high field. Solid-state visible spectra show some significant changes with time, a fact that leads us to speculate that irreversible changes take place in the solid state with time under dinitrogen in the dark. **11t$_{11}$** and **13t$_{13}$** become increasingly insoluble, and intensity shows up in the solid-state absorption spectrum in the region characteristic of shorter polyenes. We do not yet know to what extent this process is influenced by light or traces of oxygen. We hope to elucidate this "aging" of **11t$_{11}$** and **13t$_{13}$** in the solid state in the future. For now the characterization of **11t$_{11}$**, and especially **13t$_{13}$**, in the solid state must be said to be incomplete, even though UV–vis spectra of soluble material from freshly prepared samples are totally consistent with the **11t$_{11}$** and **13t$_{13}$** formulations. We should also state that while hypothetical "pristine" *all-trans*-polyenes containing more than 13 double bonds may indeed be too insoluble to be detected by using the HPLC conditions we have employed, on the basis of results described later we believe that "insolubility" ultimately must be ascribed to oligomerization (cross-linking) of polyenes.

Even polyenes can be isomerized by analogous methods. (**2t$_2$** is obtained ~91% pure, as noted earlier.) **4t$_4$** is readily accessible by irradiation of mixtures of **4tcct** and **4tctt** in the presence of a trace of iodine in pentane with >300-nm light. **4t$_4$** is obtained >95% pure. The initial mixtures of **6** and **8** each can be photolyzed to yield **6t$_6$** and **8t$_8$**, respectively, in good yield, in a manner analogous to that described above for preparing **7t$_7$** and **9t$_9$**.

A convenient and the preferred method for preparing **9t$_9$**, **10t$_{10}$**, **11t$_{11}$**, and **12t$_{12}$** is to isomerize **9**, **10**, **11**, and **12** with a trace of iodine. Details can be found in the Experimental Section. Isomerization is rapid between 25 and 50 °C, and the products crystallize readily from the reaction solution. The easiest to isomerize by this method are **10t$_{10}$** and **11t$_{11}$**. The method fails for **13t$_{13}$**, we believe because the oxidation of **13t$_{13}$** to the radical cation (where isomerization is rapid) is not reversible under these conditions.

We should point out that thermal, photochemical, and catalytic oxidative isomerizations all have been used for decades to isomerize a wide variety of relatively short polyenes having an unsubstituted backbone or longer carotenoids.[1c]

All polyenes that we have identified in HPLC studies are listed in Table I according to their retention times under the HPLC conditions we routinely employed for analysis of the crude product mixtures (90:5:5 acetonitrile/dichloromethane/water).

NMR Data for Polyenes. NMR data were gathered through extensive homonuclear correlation (COSY) and heteronuclear correlation (HETCOR) experiments[20] on a 500-MHz instrument starting with the simplest polyene in a given series (the two most complete being the all-trans series and the alternating series) and

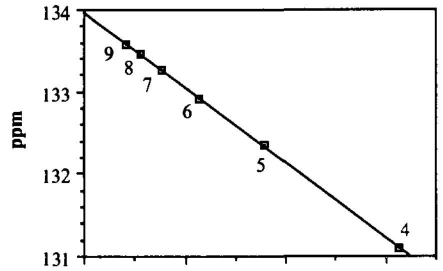


Figure 9. Plot of the chemical shift of the innermost carbon atom in the *all-trans*-polyenes containing n double bonds vs $1/n^{2.5}$ (R^2 = 1.000, intercept = 133.95 ppm, slope = −90.996).

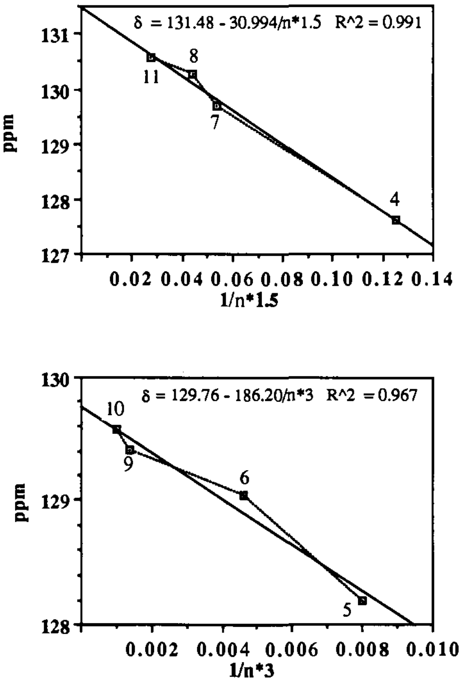


Figure 10. Plot of δ_C for the carbon atoms in cis olefinic bonds 4–11 in **11t(ct)**$_5$ vs $1/n^{1.5}$ (top) and δ_C for the carbon atoms in trans olefinic bonds 5–10 in **11t(ct)**$_5$ vs $1/n^3$ (bottom).

working up to the longest characterizable polyene in that series. The data were checked and cross-checked until a totally consistent picture emerged. $^3J_{HH}$ across a trans double bond was found to be 15.2–15.3 Hz, across a cis double bond 12.1 Hz, and across a single bond 10.6–11.4 Hz.[21] Proton and ^{13}C NMR data for the *all-trans*-polyenes up through the 9-ene are shown in Table II. NMR data for the t(ct)$_x$ series are shown in Table III. NMR data for several other isomers are listed in Table SI and parameters for calculating carbon chemical shifts are given in Table SII (supplementary material). NMR studies for *cis*- and *trans*-di-*tert*-butylethylene have been reported[21a] as have studies of some dienes[21b–d] and carotenoids.[21e] However, this is the first extensive series of polyenes that has been available and therefore the first time that such a complete set of data has been accumulated.

For the *all-trans*-polyenes the proton chemical shifts converge on a value of 6.25–6.26 ppm as the proton moves toward the center of the chain and as the polyene becomes longer (Table II). The chemical shift of H(1) in **1** starts at 5.30 ppm and quickly approaches the limit of 5.75 ppm in **9t**$_9$. The chemical shift of H(2) ranges from 5.93 in **2t**$_2$ to 6.02 ppm in **9t**$_9$. Beyond the 6-ene the protons' chemical shifts vary little with increasing chain length. H(6) in **9t**$_9$ has the lowest field shift by a small margin (0.01 ppm). The shifts can be described by the equation $\delta_n = \delta_\infty - k/n^{1.5}$, where k = 1.04 and δ_∞ = 6.29, the chemical shift predicted for a proton in a hypothetical infinitely long *all-trans*-polyene. The chemical shift of the protons in the *tert*-butyl group changes little.

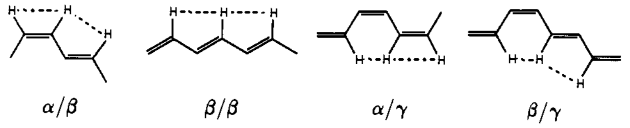
Table IV. Proton Shift Increments (in ppm) for Protons in All Isomers in All Environments Relative to Those in the All-Trans Form (β/β)

type	$\Delta\delta_H$(avg)	range	no of examples
α/β	−0.20	12–24	23
β/β	+0.04	0–9	10
α/γ	+0.18		1
β/γ	+0.46	44–48	13

In the ^{13}C NMR spectra of the *all-trans*-polyenes the chemical shifts of C(1) and C(3) vary significantly with chain length, while those for C(2) and C(4) or greater do not change. In polyenes longer than **4t**$_4$ the chemical shift of the innermost carbon atom begins to increase smoothly. If these data for **4t**$_4$ and longer polyenes are plotted by using the relationship $\delta = \delta_\infty - k/n^{2.5}$ (where δ is the shift in ppm of the innermost carbon atom of the n-ene and δ_∞ the chemical shift of the innermost carbon atom in a hypothetical polyene with an infinite chain length) an excellent straight line is obtained with R^2 = 1.000, δ_∞ = 133.95 ppm, and k = 90.996 (Figure 9). The predicted chemical shift of 133.95 ppm for a hypothetical polyene of infinite chain length should be compared with the observed chemical shift of 137–139 ppm for the carbon atoms in *trans*-polyacetylene (in the solid state).[22] (The chemical shift for the carbon atoms in *cis*-polyacetylene has been observed to be 128 ppm.[23]) Chemical shifts can be calculated for both olefinic and *t*-Bu carbon atoms by using the equation $\delta_n = \delta_\infty - k/n^x$ (where x can vary between 1 and 3) with the parameters listed in Table SII (supplementary material).

The trends in the chemical shifts of the carbon atoms in the alternating polyenes (Table III) parallel those observed in the *all-trans*-polyenes. $\delta_{C(1)}$ through $\delta_{C(3)}$ again behave relatively uniquely compared to the chemical shifts of carbon atoms further toward the center of the chain. If one plots δ_C for the carbon atoms in cis-olefinic bonds 4–11 in **11t(ct)**$_5$ versus $1/n^{1.5}$ and δ_C for the carbon atoms in trans-olefinic bonds 5–10 in **11t(ct)**$_5$ versus $1/n^3$, straight lines are obtained (Figure 10) with δ_∞ values of 131.48 and 129.76 ppm, respectively.

There are four types of environments for a proton in a polyene that contains only transoid single bonds (which is what we will assume here). The β/β variety is that found in the *all-trans*-polyenes. The chemical shift of protons in the three other environments may be referenced to $\delta_H(\beta/\beta)$ in the corresponding *all-trans*-polyene to yield values for $\Delta\delta_H$ for a proton in any given environment. In Table III $\Delta\delta_H$ for the protons in **3tct**, **5t(ct)**$_2$, **7t(ct)**$_3$, and **9t(ct)**$_4$ (i.e., δ_H relative to $\delta_H(\beta/\beta)$ in **3t**$_3$, **5t**$_5$, **7t**$_7$, and **9t**$_9$) are shown in brackets, and the type of environment is shown at the bottom of the table. H(3) is the first to fall into one of the four categories (since the *tert*-butyl group is present), so only protons at the 3 position and further along the chain can be assigned to a one of the four types of environments. In the alternating polyenes $\Delta\delta_H(\beta/\gamma)$ averages +0.45 ppm and $\Delta\delta_H(\alpha/\beta)$



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(20) For a recent review of 2D NMR techniques see: Kessler, H.; Gehrke, M.; Griesinger, C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 490.

(21) (a) Garratt, D. G.; Tidwell, T. *Org. Magn. Reson.* **1974**, *6*, 87. (b) Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem.* **1971**, *36*, 2757. (c) Bacon, M.; Maciel, G. E. *Mol. Phys.* **1971**, *21*, 257. (d) Albriktsen, P.; Cunliffe, A. V.; Harris, R. K. *J. Magn. Reson.* **1970**, *2*, 150. (e) Wernly, J.; Lauterwein, J. *Magn. Reson. Chem.* **1985**, *23*, 170.

(22) (a) Maricq, M. M.; Waugh, J. S.; MacDiarmid, A. G.; Shirakawa, H.; Heeger, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 7729. (b) Gibson, H. W.; Pochan, J. M.; Kaplan, S. *J. Am. Chem. Soc.* **1981**, *103*, 4619. (c) Mehring, M.; Weber, H.; Miller, W.; Wegner, G. *Solid State Commun.* **1983**, *45*, 1079.

(23) Gibson, H. W.; Pochan, J. M.; Kaplan, S. *J. Am. Chem. Soc.* **1981**, *103*, 4619.

Table V. UV–vis Data for *all-trans*-Polyenes[a]

	$1^1B_u \leftarrow 1^1A_g$				$3^1A_g \leftarrow 1^1A_g$		$2^1B_u \leftarrow 1^1A_g$
	0–0	0–1	0–2	0–3	0–0	0–1	0–0
2t$_2$	237.2 (0.688)	227.8 (1.00)	219.8 (0.948)				
3t$_3$	275.6 (0.766)	264.8 (1.00)	255.6 (0.779)				
4t$_4$	311.4 (0.897)	297.4 (1.00)	284.8 (0.683)	274.6 (0.369)			
5t$_5$	343.0 (0.991)	325.8 (1.00)	311.0 (0.615)	297.8 (0.294)	237.8 (0.062)		
6t$_6$	371.2 (1.00)	351.0 (0.931)	334.2 (0.558)	319.0 (0.258)	258.2 (0.037)	250.0 (0.032)	
7t$_7$	396.2 (1.00)	373.6 (0.906)	355.6 (0.520)	338.0 (0.239)	277.6 (0.035)	267.8 (0.026)	
8t$_8$[b]	418.8 (1.00)	394.0 (0.869)	374.0 (0.531)	354.2 (0.254)	296.4 (0.046)	285.6 (0.033)	239.0 (0.123)
9t$_9$[c]	438.8 (1.00)	411.2 (0.921)	390.2 (0.574)	371.8 (0.290)	313.6 (0.080)	301.8 (0.059)	253.0 (0.179)
10t$_{10}$	456.4 (0.977)	427.8 (1.00)	405.2 (0.638)	382.6 (0.310)	330.8 (0.099)	317.6 (0.056)	267.8 (0.165)
11t$_{11}$	468.8 (0.921)	439.4 (1.00)	414.4 (0.657)	393.4 (0.340)	346 (0.106)	330 (0.071)	282 (0.159)
13t$_{13}$	494 (0.921)	462 (1.00)	438 (0.757)	412 (0.450)	370 (0.214)	352 (0.143)	306 (0.186)
8t$_8$	450.4 (1)	423.2 (0.953)	400.0 (0.571)				
9t$_9$[d]	473.0 (1)	444.2 (0.982)	418.8 (0.582)	397.6 (0.292)			
10t$_{10}$[d]	493.2 (1)	462.2 (0.977)	435.2 (0.611)	414 (0.303)			
11t$_{11}$[d]	510.2 (0.867)	476.4 (1)	449.0 (0.702)	422 (0.403)			
13t$_{13}$[d]	540.2 (0.871)	504.6 (1)	474.4 (0.726)	447 (0.427)			

[a] UV–vis data are listed in nanometers. Relative extinction coefficients are listed in parentheses. The solvent is *n*-pentane, unless otherwise noted. The assignments of transition 2 and transition 3 (last three columns) are tentative. [b] In dichloromethane the first three transitions (ϵ in L mol^{-1} cm^{-1}) are 432 (111 000), 406 (103 000), and 384 (64 300). [c] In dichloromethane the first three transitions (ϵ in L mol^{-1} cm^{-1}) are 452 (114 000), 424 (101 000), and 402 (65 000). [d] In carbon disulfide.

Table VI. UV–vis Data for Alternating Polyenes[a]

	$1^1B_u \leftarrow 1^1A_g$			$3^1A_g \leftarrow 1^1A_g$	$2^1B_u \leftarrow 1^1A_g$
	0–0	0–1	0–2	0–0	0–0
3tct	275[b] (0.732)	266.2 (1)	258[b] (0.834)		
5t(ct)$_2$	343.6 (0.866)	326.8 (1)	312.0 (0.676)	247 (0.05)	
7t(ct)$_3$	394.0 (0.888)	372.4 (1)	353.8 (0.669)	283.4 (0.053)	
9t(ct)$_4$	432.0 (0.851)	406.6 (1)	385.2 (0.703)	317.4 (0.082)	262.4 (0.220)
11t(ct)$_5$	459.2 (0.797)	432.2 (1)	409.0 (0.737)	346.6 (0.141)	286.6 (0.246)
13t(ct)$_6$	480.0 (0.752)	451.6 (1)	427.2 (0.779)	374 (0.268)	309.8 (0.268)
15t(ct)$_7$	494.6 (0.737)	462.4 (1)	441.8 (0.861)	396 (0.355)	330.6 (0.324)

[a] UV–vis data are listed in nanometers. Relative extinction coefficients are listed in parentheses. The solvent is acetonitrile/dichloromethane/water (90:5:5). The assignments of transition 2 and transition 3 (last two columns) are tentative. [b] Shoulder.

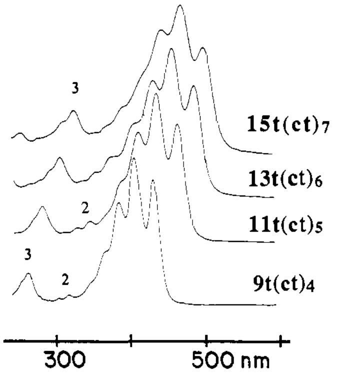

Figure 11. UV-vis spectra of the longer alternating polyenes. (The numbers 2 and 3 refer to transitions 2 and 3 as discussed in the text and Tables V and VI.)

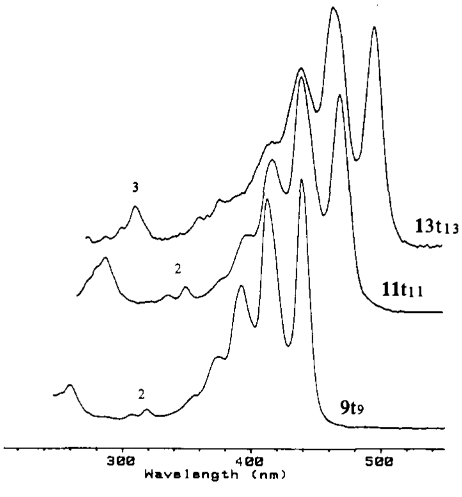

Figure 12. UV-vis spectra of the longer odd *all-trans*-polyenes. (The numbers 2 and 3 refer to transitions 2 and 3 as discussed in the text and Tables V and VI.)

averages −0.18 ppm. ($\Delta\delta_H(\beta/\beta)$ is not represented in this series of polyenes.)

The trends in chemical shifts appear to hold for protons in other isomers that have been identified by NMR methods (Table SI) since configurations that can be assigned on this basis are consistent with the expected isomerization sequences or alternative stereochemical outcomes.

The averages of all $\Delta\delta_H$ values for protons in all environments in all isomers are shown in Table IV. The range is smallest for $\Delta\delta_H(\beta/\gamma)$. On the whole the variations are relatively consistent and should be of some value in assigning the configuration of an unknown isomer. One result that stands out is that protons that give rise to resonances at >6.4 ppm must be in the β/γ environment. Therefore the stereochemical purity of the *all-trans*-polyenes can be checked easily since isolated cis double bonds in an otherwise *all-trans*-polyene create β/γ environments.

UV-vis Studies. UV-vis spectra of the longer alternating odd polyenes in a mixture of acetonitrile, dichloromethane, and water are shown in Figure 11 and the longer all-trans odd polyenes in pentane in Figure 12. Complete UV-vis data for the all-trans isomers can be found in Table V and for the alternating forms in Table VI. These UV-vis spectra are fully in accord with what has been observed for many other polyenes in the past. For example, in the standard 90:5:5 HPLC solvent mixture the absorption spectrum of **9t$_9$** is shifted by 11.6 nm relatively to the spectrum of **9t(ct)$_4$**. Typical solvent effects are also observed. For example, the spectrum of **13t$_{13}$** in highly polarizable carbon disulfide (Table V) is shifted by 46 nm relative to the spectrum in pentane. In the spectra of the longer polyenes (both alternating and all-trans) two additional higher energy transitions can be

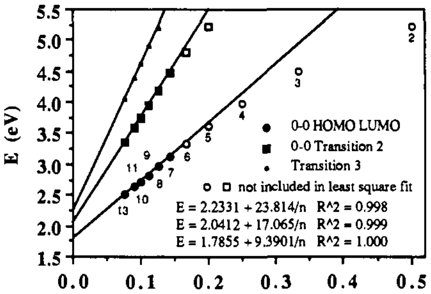

Figure 13. Plot of E_n vs $1/n$ for all the *all-trans*-polyenes having between 5 and 13 double bonds (in pentane).

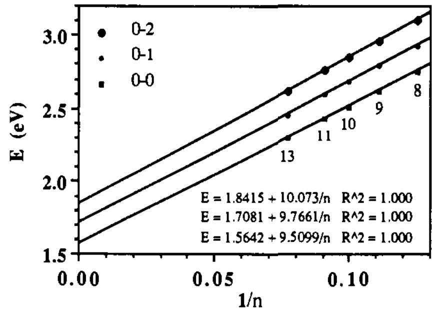

Figure 14. Plot of E_n vs $1/n$ for $\mathbf{8t_8}$, $\mathbf{9t_9}$, $\mathbf{10t_{10}}$, $\mathbf{11t_{11}}$, and $\mathbf{13t_{13}}$ in carbon disulfide.

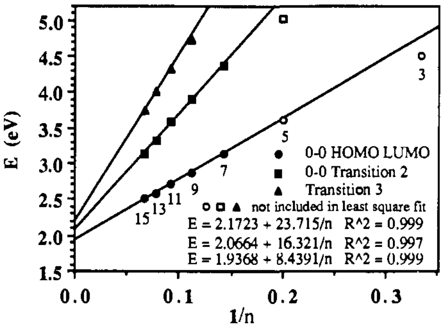

Figure 15. Plot of E_n vs $1/n$ for the alternating polyenes in a mixture of acetonitrile, dichloromethane, and water (90:5:5).

observed. The first ("transition 2") is what has been called the "cis band" in the literature.[1c] The second ("transition 3") is one that has been observed only in rather different types of polyenes, never in a sufficiently extensive homologous series of polyenes. If these transitions were to be assigned according to what has been proposed in the literature,[24a,b] appropriate assignments would be $3^1A_g \leftarrow 1^1A_g$ (weak and formally forbidden for centrosymmetric polyenes) for transition 2 and $2^1B_u \leftarrow 1^1A_g$ (allowed) for transition 3.

The formula usually used to describe the relationship between the number of double bonds and the energy of the $^1B_u \leftarrow {}^1A_g$ (0–0) transition of an *all-trans*-polyene in solution is $E_n = E_\infty + k/n$, where E_∞ is the HOMO–LUMO gap of a hypothetical infinite polyene, E_n is the HOMO–LUMO gap of an *n*-ene, and *k* is an experimentally determined constant.[24b,d] A plot of E_n vs $1/n$ shows that the values for $\mathbf{10t_{10}}$, $\mathbf{11t_{11}}$, and $\mathbf{13t_{13}}$ fit well on the line containing the data for $\mathbf{5t_5}$–$\mathbf{9t_9}$ and gives E_∞(pentane) = 1.80 eV with $k = 9.125$. If only the data for $\mathbf{7t_7}$–$\mathbf{13t_{13}}$ are used in the plot for the $^1B_u \leftarrow {}^1A_g$ (0–0) transition and data for transition 2 and transition 3 are included in separate plots, the result is shown in Figure 13 (intercepts at 1.79, 2.03, and 2.23 eV, respectively). If the $1/n$ extrapolation to 0 is valid and accurate, then these data show that the three electronic states that give rise to these transitions are distinct in a hypothetical conjugated polyene of infinite length.

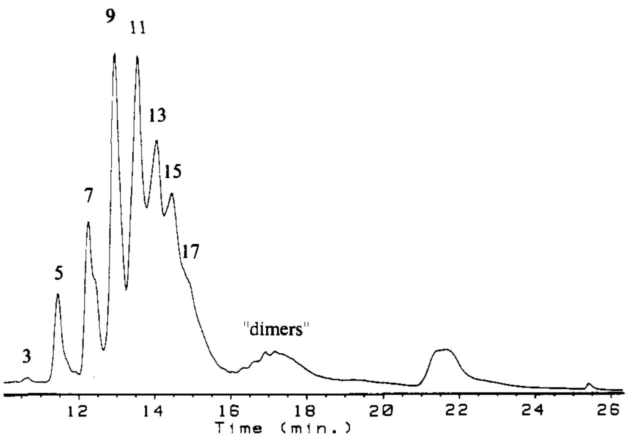

Figure 16. HPLC study of all dichloromethane-soluble material produced employing 5 equiv of TCDT.

Plots of the UV–vis data for the values for the 0–0, 0–1, and 0–2 branches of the $^1B_u \leftarrow {}^1A_g$ transition in $\mathbf{8t_8}$, $\mathbf{9t_9}$, $\mathbf{10t_{10}}$, $\mathbf{11t_{11}}$, and $\mathbf{13t_{13}}$ in carbon disulfide are shown in Figure 14. The extrapolated value for the 0–0 transition in a hypothetical infinite polyene in carbon disulfide is 1.56 eV.

Similar plots of the data for the alternating forms ($\mathbf{3tct}$–$\mathbf{15t(ct)_7}$) in a mixture of acetonitrile, dichloromethane, and water (90:5:5; the standard HPLC solvent mixture) are shown in Figure 15. Here the energies of the $1^1B_u \leftarrow 1^1A_g$ (0–0) and two other transitions extrapolate to similar values for the infinite polyene by using data for $\mathbf{7t(ct)_3}$ and higher polyenes.

Solid-state spectra of the *all-trans*-polyenes are relatively broad, and the maxima dramatically red-shifted by as much as 100 nm in the case of $\mathbf{13t_{13}}$ with a long absorption tail to low energy, perhaps in part because of light scattering by the polyene crystallites. Since at this stage we cannot prove that the potentially more interesting relatively long *all-trans*-polyenes are *not* irreversibly altered in the solid state (see comments above and in the Discussion), it is premature to attempt to explain these results. For similar reasons solid-state spectra should be used with great care to infer the length of conjugation of the backbone. These and related issues will be addressed in future studies.

Evidence for Cross-Linking. A crude mixture of polyenes prepared from 5 equiv of TCDT was examined under different HPLC conditions (Figure 16). The sample was filtered through 3 cm of silica gel after the retro-DA reaction, and this silica gel was extracted with dichloromethane. Only an insignificant amount of brown powder remained on the silica gel. The solvent system in this HPLC study was initially a 90:10 mixture of acetonitrile and dichloromethane that was changed in a gradient to 100% dichloromethane after 30 min. The mixtures of isomers of **3**–**17** now elute relatively early and are not well-separated. The important point is that apparently higher molecular weight polyene-like material elutes at ~17 and 21.5 min and perhaps also at ~19, ~23, and ~25.5 min. The yield of these "decomposition products" should be ~30% (Figure 2), a sensible figure on the basis of a rough comparison of the peak areas shown in Figure 16. The peak that elutes between 16 and 18 min can be divided in roughly three parts: The UV–vis spectrum of the material that elutes first (16.7 min in Figure 17) shows the typical pattern of a 9-ene with some 7-ene as minor component. The middle section (16.9 and 17.2 in Figure 17) is composed largely of 9-enes and 11-enes in similar amounts, while the third section (17.5 and 17.9 in Figure 17) also contains some 13-enes. The material that elutes at 21.5 min appears to consist of an approximately 1:1:1 mixture of 7-, 9-, and 11-enes. Since decomposition under the reaction conditions becomes significant only for polyenes with more than 15 double bonds, we propose that the higher molecular weight material consists of oligomers (those eluting at ~17 min are

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(24) (a) Dale, J. *Acta Chem. Scand.* **1957**, *11*, 265. (b) Dale, J. *Acta Chem. Scand.* **1954**, *8*, 1235. (c) Hudson, B.; Kohler, B. *Synth. Met.* **1984**, *9*, 241. (d) Szabo, A.; Langlet, J.; Malrieu, J.-P. *Chem. Phys.* **1976**, *13*, 173.

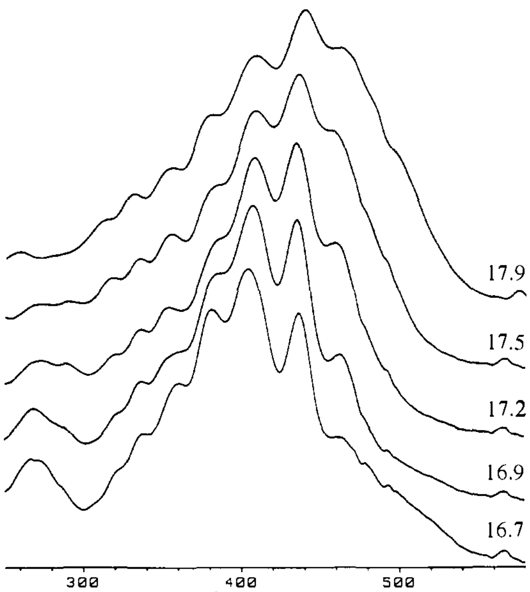

Figure 17. UV–vis spectra of the "dimers" at various elution times between 16 and 18 min in Figure 16.

perhaps dimers of the higher polyenes), and that the conjugated chain length in each case is approximately halved as a consequence of the cross-linking reaction. According to these data, it appears that the cross-linking involves one or more double bonds close to the middle of the polyene chain and that the remaining polyene chromophores contain largely an *odd* number of double bonds. An apparent preference for odd conjugated sequences also was observed in triblock polymers ABA where A was polynorbornene and B was a polyene segment obtained by polymerization of TCDT.[16b] If we assume that at least one double bond per original chain is destroyed or taken out of conjugation in the process of cross-linking, then two 17-enes could generate a dimer containing largely 7-enes, depending upon exactly what the cross-linking reaction is in detail. Although it seems unlikely that polyenes with the same chain length couple only with each other, there does seem to be a tendency for long polyenes to couple relatively selectively with other long polyenes. Studies aimed at elucidating the nature of these apparently cross-linked materials will form the basis of future studies.

Discussion

Two methods of preparing material that resembles classical polyacetylene by ring-opening reactions have been reported recently, one employing benzvalene[25] and one employing cyclooctatetraene.[26] That employing benzvalene is potentially also a means of preparing well-defined polyenes, since the most successful catalyst was also found to be W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$. The disadvantage is that benzvalene is not as easily prepared and handled as TCDT, and polybenzvalene was found to cross-link readily, presumably by opening of the bicyclic ring system. The method involving cyclooctatetraene requires a catalyst that is relatively active for metathesis of ordinary olefins, since cyclooctatetraene will not react readily with W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$. Therefore although "polyacetylene" can be prepared from cyclooctatetraene in this manner, ring-opening is not completely controlled and therefore should not be as amenable to preparation of well-defined polyenes or block copolymers as is the approach that employs TCDT or a similar precursor.[16b]

The key property of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ that makes it possible to prepare living polymers is that the W=C double bond will react *readily* only with strained double bonds such as that in the cyclobutene ring in TCDT. However, under some circumstances ordinary olefins are attacked, especially when the alkylidene is relatively small (e.g., a propylidene), or the olefin is terminal, or (especially) if the olefin is ethylene.[27] The reactivity of vinylalkylidene complexes or living polyenes of the type described here is unknown.

Of the three types of double bonds in the living polyTCDT (Scheme I), one is substituted by two CF_3 groups and therefore should be completely inert. Another (in the polymer backbone) should be relatively unreactive because of the bulk of the cyclopentyl substituents. (The rate of reaction between W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and *cis*-2-pentene is extremely slow.[11d]) The last is what was the C(9)–C(10) double bond in TCDT. Cross-linking would result if this double bond were attacked, a problem that would become more serious as more monomer is employed, and one that therefore could account for the observed limit to polyene chain length. We think that this double bond is *not* attacked during the course of a typical polymerization reaction for several reasons. First, the yields of polyenes employing 3–4 equiv of TCDT are high, and there is no significant product loss if living polyTCDT is left in solution for more than 4 h. Second, the cyclobutene ring is most likely attacked on the exo face, and therefore one face of the C(9)–C(10) double bond is protected by the bulk of the catalyst, while the other side is protected to a large extent by the two trifluoromethyl groups. Third, analogous reactions involving tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene itself *do* give relatively low yields of polyenes, a result that we attribute to cross-linking that involves the now unprotected double bonds in the bicyclic cyclohexadiene ring.[28] Finally, cross-linking was suspected when tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene was polymerized with classical catalysts, but no significant cross-linking was observed employing TCDT.[8b] Therefore we are relatively confident that polyene chain length is not limited by cross-linking during preparation of polyTCDT or by some other quirk of the synthetic method.

Another potential problem that could in theory limit the effectiveness of this synthetic method is decomposition of the living TCDT by some process (e.g., coupling of alkylidene ligands) that is inherent to alkylidene complexes of the type described here. W(CHR)(NAr)(O-*t*-Bu)$_2$ catalysts are unstable if the alkylidene is small, and decomposition appears to be bimolecular.[11d] Dilute conditions encountered in a typical metathesis reaction of ordinary olefins therefore are ideal for catalyst longevity, but high concentrations could be problematic. Typical concentrations in reactions in which living polyTCDT is prepared are *not* especially dilute, but the alkylidene *is* relatively bulky as evidenced by the fact that propagation is only 2–3 times faster than initiation. Therefore decomposition of living polyTCDT by a reaction characteristic of complexes that contain a smaller alkylidene ligand would not appear to be a significant problem, and indeed the data shown in Figure 5 do not reveal any evidence of decomposition of living polyTCDT over a period of more than 4 h.

An unexpected result of this investigation is the accelerated retro-DA reaction in the first unit away from the metal compared to the retro-DA reaction in the second unit away from the metal and presumably also elsewhere in the chain. We hesitate to propose why the retro-DA reaction is accelerated in the absence of data for other tricyclodecatrienes and other catalyst systems (e.g., analogous Mo catalysts[11c]), and a lack of knowledge of the intimate structure of the "living polyenes". (It is not clear, for example, that such an alkylidene is strictly η^1 bound.) The mechanism of the subsequent isomerization of the C=C bond formed in the accelerated retro-DA reaction also remains to be probed and could very likely be closely connected with structure. But new questions now arise concerning the reactivity of vinylalkylidene complexes in general. One might presume that vinylalkylidene complexes will be less reactive than ordinary alkylidene complexes (if steric effects are excluded) because of delocalization

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(25) Swager, T. M.; Dougherty, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2973.

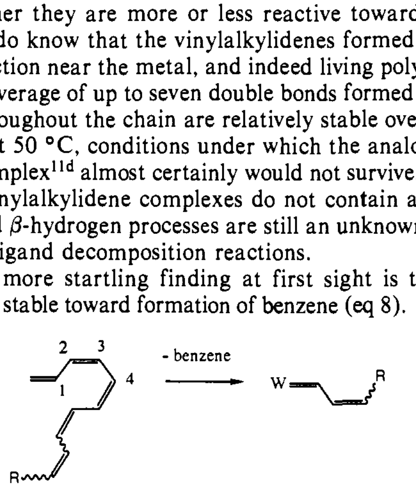
(26) (a) Korshak, Y. V.; Korshak, V. V.; Kanischka, F.; Hoecker, H. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 685. (b) Klavetter, F. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7807.

(27) Feldman, J.; Schrock, R. R., submitted.

(28) Park, L. Y.; Schrock, R. R., unpublished results.

of the negative charge on C_α of the alkylidene ligand and perhaps especially unreactive if they are η^3 bound. However, if they are strictly η^1 bound, the fact that vinylalkylidene ligands are relatively flat could be an important determinant of their reactivity in a sterically crowded environment. Although we do not know at this stage whether they are more or less reactive toward ordinary olefins, we do know that the vinylalkylidenes formed in the retro-DA reaction near the metal, and indeed living polyenes containing an average of up to seven double bonds formed by a retro reaction throughout the chain are relatively stable over a period of 45 min at 50 °C, conditions under which the analogous propylidene complex[11d] almost certainly would not survive. It is also true that vinylalkylidene complexes do not contain aliphatic β protons, and β-hydrogen processes are still an unknown factor in alkylidene ligand decomposition reactions.

An even more startling finding at first sight is that living polyenes are stable toward formation of benzene (eq 8). However, formation of benzene requires cis configurations at C(2) and C(4), a circumstance that seems unlikely in view of the approximately 3:1 preference for a trans configuration at C(2) (formed in the accelerated retro-DA reaction) and at C(4) (formed in a propagation step). The likelihood of both a cis configuration at C(2) and a cis configuration at C(4) then becomes very small (approximately 5%). Although it is not especially surprising (in spite of the lack of data concerning the reactivity of dienes, trienes, etc.) that the W=C bond in living polyenes does not react readily with C=C bonds in other polyene chains, it is not clear why an intramolecular version would not be dramatically accelerated (if the configuration at C(2) and C(4) were cis). Ultimately the bulky nature of the catalyst center, in combination with a generally reduced activity of the metal toward ordinary olefins, is likely to be the most important factor in limiting the amount of "backbiting" to give benzene. It must be stressed that studies such as those shown in Figure 5 do not begin to touch on questions concerning stability of living polyenes that contain more than ca. seven double bonds on the average or the relative stability of cis-rich vs trans-rich or all-trans living polyenes. We presume at this stage that the factors that lead to an instability of the longer polyenes themselves also will destabilize the longer living polyenes.



(8)

An important question is why polyenes longer than 17 cannot be observed and why those longer than 15 could not be isolated. The evidence we have presented would seem to limit explanations to those based on the properties of the polyenes themselves, rather than side-reactions during polymerization of TCDT or complications during the retro-Diels–Alder reaction. One possibility is that polyenes that contain 15 or more double bonds simply isomerize readily to all-trans forms, and those all-trans forms are too insoluble to observe by using the techniques we have employed. Although very long *all-trans*-polyenes might indeed be quite insoluble, as many have assumed in the past,[1,4] they are still hypothetical, since no one to our knowledge has shown definitively that *solid* "*all-trans*-polyenes" are not cross-linked. The detection of what appears to be relatively high molecular weight materials by HPLC that have UV–vis spectra characteristic of relatively short conjugation lengths (Figure 16 and 17) augurs *against* the possibility that long *all-trans*-polyenes are going undetected and *for* dimerization and more extensive cross-linking reactions between polyenes beyond a certain chain length. It has long been noted that substitution either on the backbone (as in carotenoids) or at the end of a polyene enhances its stability. Both types of substitution would slow bimolecular reactions. Almost certainly the fact that *tert*-butyl groups are present in the polyenes we have prepared enhances their stability, and that alone might be the reason they apparently are the most stable polyenes having an unsubstituted backbone that have been prepared to date.

Preliminary studies of polynorbornene/polyene block copolymers have demonstrated that beyond a certain polyene length (~20 double bonds) the macromolecules "aggregate" to give high molecular weight species that contain between 10 and 30 of the macromolecules and that large polynorbornene capping groups in triblocks retard formation of aggregates.[16b] The "aggregates" we think are formed by cross-linking between the fraction of molecules that contain the longest polyene chains. If the cross-linking proposal is correct, then it should be possible to stabilize relatively long polyenes if they are diluted in a host polymer. Preliminary studies along these lines suggest that this is the case.[29]

It has long been assumed that a given cis-double bond in a polyene (including one in polyacetylene) isomerizes to trans via formation of a pair of delocalized radicals. It makes sense that a minimum number of double bonds are required to delocalize and thereby stabilize *each* radical. Since it is currently believed that only five to seven double bonds are necessary to stabilize an uncharged radical (soliton),[5] isomerization of a central cis bond should become especially facile around the 15-ene, as we have observed. Although we can observe some alternating 15-ene, we cannot observe the alternating form for the 17-ene, a fact that is also consistent with the above statement. One might also suspect that such biradicals should be able to couple intermolecularly or to attack another polyene that is capable of stabilizing a radical and thereby serve as a method of dimerizing or trimerizing polyenes containing between 15 and ~25 double bonds and polymerizing polyenes containing more than 30 or 40 double bonds. The data shown in Figure 3 do suggest that the polyenes longer than **11** are largely those that are consumed upon heating 180 °C, consistent with the proposal that cross-linking is not a random process. There is evidence in the literature that cross-linking does occur in polyacetylene in the process of isomerizing the cis to the trans form.[2] There are many reactions (Diels–Alder-like, radical chains, etc.) that a priori one should consider as the means by which polyenes longer than **11** are consumed. We are hoping that at least the so-called dimerization reaction is relatively well-defined and will attempt to more completely define this reaction in future studies.

Experimental Section

Starting Materials and General Procedures. W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ was prepared either as described in the literature[11d] or by an improved route to be reported elsewhere. Pivaldehyde was purchased commercially, filtered through a 10-cm column packed with anhydrous alumina, and distilled at 1 atm (bp 77–78 °C). 4,4-Dimethyl-*trans*-2-pentenal was prepared by a procedure analogous to the preparation of *n*-PrCH=CHCHO.[30] The product must be purified by spinning band distillation (bp$_{50}$ 90 °C; yield on 1-mol scale = 48%). Solvents were dried under dinitrogen by standard procedures noted elsewhere.[11d] The toluene used for polymerization reactions was stored over Na/K alloy.

Reaction of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ with Aldehydes. The reaction between W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and 1.5 equiv of pivaldehyde in pentane takes at least 2 h to go to completion at 25 °C. The reaction can be accelerated by refluxing the solution for 45 min. In each case the color changes slightly from yellow to lemon yellow. The reaction between W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and 4,4-dimethyl-*trans*-2-pentenal is much faster at 25 °C (ca. 1 h) and also can be accelerated (20 min) by refluxing the reaction mixture. The reaction mixture was filtered through silica gel to remove W(O)(NAr)(O-*t*-Bu)$_2$ and excess aldehyde, and the solvent was removed in vacuo to yield the pure olefin products.

Reaction of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ with TCDT. Addition of 1 equiv of TCDT (46 mg, 0.174 mmol) in 1 mL of toluene to a stirred solution of 100 mg (0.174 mmol) of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ in 5

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(29) Preliminary experiments with 95:5 blends of poly(benznorbornadiene) (187 equiv) and diblocks of poly(benznorbornadiene) (187 equiv) and polyTCDT (5, 10, 15, 20, 30, 40, 50 equiv) show that polyenes with up to ~80 conjugated double bonds can be obtained for 50 equiv of TCDT (the most abundant polyenes have 30–40 conjugated double bonds), when the retro-Diels–Alder reaction is carried out in a precast, unoriented film. Between n = 5 and 20 equiv of TCDT the UV–vis spectra are those expected for polyenes with $2n + 1$ double bonds. Additional TCDT leads to a broadening of the absorption without a significant red shift. If the retro-DA reaction is carried out in solution before the film is cast, then polyenes no longer than 17-enes are observed. Further studies of this general nature are under way.

(30) Wittig, G.; Suchanek, P. *Chem. Ber.* **1967**, *100*, 347.

mL of toluene yielded a deeper yellow solution. After 15 min, 17 mg of pivaldehyde or 22 mg of 4,4-dimethyl-2-pentenal, respectively (1.1-fold excess), was added. The solution turned lemon yellow. It was heated to 125 °C for 5 min and chromatographed at −40 °C on silica gel. Eluting with pentane yielded **1** (10 mg) and **2** (10 mg), respectively; pentane/dichloromethane (50/1) yielded **3** (6 mg) and **4** (8 mg); pentane/dichloromethane (30/1) yielded **5** (8 mg) and **6** (10 mg); pentane/dichloromethane (15/1) yielded **7** (5 mg) and **8** (5 mg).

Employing 1.75 equiv of TCDT (81 mg) in a similar preparation gave **3** (9 mg), **4** (11 mg), **5** (14 mg), **6** (14 mg), **7** (11 mg), and **8** (12 mg).

The reaction between W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and 5 equiv of TCDT is best carried out on a 1-g scale of catalyst in toluene. A solution of TCDT (2.31 g, 8.69 mmol) in toluene (20 mL) was added dropwise to a rapidly stirred solution of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (1 g, 1.73 mmol) in toluene (50 mL). After 15 min 298 mg of pivaldehyde or 388 mg of 4,4-dimethyl-*trans*-2-pentenal, respectively (3.46 mmol), was added to the solution. After 15 min the pale yellow solution was diluted with toluene to a total volume of 200 mL and transferred to two Fischer–Porter bottles, each of which contained 1 drop of anhydrous hydrazine. The bombs were placed in a 125 °C oil bath and allowed to reach equilibrium (a constant pressure of ca. 10 psi). The solution was heated for an additional 4–5 min and then rapidly cooled to room temperature. It was filtered through a bed of Celite (2 cm) layered with silica gel (2 cm) to give a dark red–orange filtrate. Removal of solvent in vacuo gave a mixture of polyenes as a dark red cake (630 mg, 91% odd enes, and 600 mg, 81% even enes). The polyene mixtures were chromatographed on a silica gel column (3 × 40 cm, Merck Grade 60, dried at 150 °C in vacuo) at −40 °C using a pentane/dichloromethane gradient (95% pentane to 70% pentane by volume) to yield **5** (25 mg), **7** (60 mg), **9** (95 mg), **11** (90 mg), **13** (85 mg), and **15** (75 mg) in the odd series and **6** (30 mg), **8** (65 mg), **10** (95 mg), **12** (90 mg), and **14** (75 mg) in the even series. **15** was the most difficult to isolate in pure form because of its great sensitivity to air and to cross-linking. Mass spectra of **6**–**13** were totally consistent with their formulation, but C and H analyses were low and irreproducible, presumably because of incomplete combustion.

Another experiment was designed to serve as a basis for determining absolute yields by HPLC. A solution of TCDT (5 equiv, 1.155 g) in 5 mL of toluene was added dropwise over 1 min to a stirred solution of 500 mg of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ in 5 mL of toluene. After 10 min 300 μL of pivaldehyde was added to the now red solution; 15 min later 20 mL of toluene was added, and the solution was divided between four vials, which were heated to 120 °C for 3 min in a preheated oil bath and rapidly cooled in a water bath afterward. Polyenes in the following yields were obtained after chromatographic workup: **7** (25 mg, 9.7%); **9** (39 mg, 12.9%); **11** (51 mg, 14.7%); **13** (35 mg, 8.9%); **15** (21 mg, 4.8%). Four vials were employed to mimic the conditions used to prepare HPLC samples and to ensure rapid heating and cooling and therefore an accurate reaction time and temperature. The results vary considerably if reaction time and temperature are not accurately controlled.

Photochemical Isomerizations. The 5-, 6-, 7-, 8-, and 9-enes were isomerized on a preparative scale. To find the proper conditions, a pentane solution was made up such that the absorbance was 0.4–0.6. This solution was irradiated in a water bath while being stirred. At regular intervals a UV–vis spectrum was run to monitor the extent of isomerization. When a solution containing mostly the all-trans isomer had formed, irradiation of the 0–0 peak did *not* induce back-isomerization to cis-rich forms, even after prolonged irradiation of the final product mixture. This observation implies that cutting off light of wavelengths shorter than that whose energy corresponds to the $^1B_1 \leftarrow {}^1A_g$ transition is sufficient to prevent photochemical degradation. The photochemical procedure works well for all polyenes up to the 9-ene. It was not tested for the 10-, 11-, and 12-ene. It seems to fail for the 13-ene, since after an initial change of the UV–vis spectrum toward the pattern characteristic of **13t$_{13}$**, the sample decomposed rapidly to give what apparently are polyenes with shorter conjugation lengths, according to their UV–vis spectra. These results may be indicative of photochemically induced backbiting reactions. For shorter polyenes equilibrium is reached after ca. 210 min. On a preparative scale (ca. 300 mL of pentane, 30–40 mg of compound) the irradiation requires more time by a factor 4–5. Initially the UV–vis spectrum red-shifts rapidly to give the peaks expected for the all-trans forms after ca. 90 min. The intensity of the spectrum then grows steadily (the extinction coefficient for the 0–0 transition tripling, that for the 0–1 transition doubling) until the spectrum for the all-trans form is attained. For the 5-ene to 7-ene the Pyrex glass of the Schlenk tube is sufficient (cutoff 290 nm). For the 8- and 9-ene a Schott WG 345 filter was employed (50% cutoff at 345 nm). The 3- and 4-enes, which absorb below 300 nm, can be isomerized in the presence of iodine within 20 min upon irradiation with >300-nm light. **3t$_3$** is ~80% pure, **4t$_4$** > 98% pure.

Thermal Isomerizations in the Presence of Iodine. **9** (20 mg) was dissolved in 10 mL of pentane. A pentane solution (0.5 mL) containing about 0.1 mg of iodine was added and the solution was heated to 50 °C in a sealed vial. **9t$_9$** precipitates as a yellow powder essentially quantitatively. **10** or **11** (20 mg) were dissolved in 10 mL of dichloromethane and 0.1 mg of iodine in 0.1 mL of dichloromethane was added. Orange **10t$_{10}$** or bright red **11t$_{11}$** precipitated immediately and virtually quantitatively as powders. The preparation of **12t$_{12}$** was the same as that for **11t$_{11}$** except the solution had to be heated to 40 °C. Red–purple **12t$_{12}$** precipitated quantitatively.

HPLC Studies. HPLC experiments were done on a Hewlett-Packard 1090 liquid chromatograph (with a diode array detector operating in the range 240–600 nm) in connection with an HP ChemStation. A 250-mm C18 reversed-phase analytical column (Econosil) from Alltech Associates, Inc., was employed. All runs were done at 30 °C and a flow rate of 0.5 mL min^{-1}. The initial mobile phase was usually a mixture of acetonitrile, dichloromethane, and water in the ratio 90:5:5. The column was equilibrated for at least 2 h prior to use; 30 min after injection the solvent mixture was changed in a 30-min gradient to acetonitrile and dichloromethane (95:5). UV–vis spectra were recorded between 240 and 600 nm every 1.6 s so that each HPLC peak was described by at least 15 spectra. Final spectra were obtained by combining individual spectra. Guaiazulene was employed as an internal standard.

Catalyst, TCDT, and Guaiazulene were taken from freshly prepared toluene stock solutions with an Eppendorf pipet. Approximately 5 mg of catalyst was employed. The TCDT solution was added at 24 °C dropwise to a stirred solution of catalyst in a vial. After a given time (15 min or longer) the aldehyde (~5-fold excess) was added. The vial was sealed and heated in a preheated oil bath for 3 min and rapidly cooled in water. The solution was filtered through 3 cm of silica gel, which was then washed with 5 mL of toluene. Guaiazulene (0.25 mg) was added to the combined filtrates, and all solvent was removed in vacuo. The residue was dissolved in dichloromethane (0.5 mL), and the solution was diluted to 2 mL with acetonitrile. A portion of this sample was injected into the HPLC.

Experiments in Figure 1. TCDT (*n* equiv, 2.314 × *n* mg) in *n*/2 mL of toluene was added to catalyst (5 mg) in 1 mL of toluene. The end of the polymerization reaction was indicated by a color change from yellow to orange (formation of vinylalkylidene complexes): equivalents (time in minutes); 1 (30); 2 (30); 3 (40); 4 (50); 5 (50); 6 (60); 7 (60); 8 (70); 10 (70). The living polymers were quenched with 5 μL of pivaldehyde and worked up as already described.

Experiments in Figure 8. TCDT (1, 3, or 5 equiv, 2.314 × *n* mg) in *n*/5 mL of toluene was added to catalyst (5 mg) in 0.375 mL of toluene. The living polymers were quenched after 15 min with 10 μL of 4,4-dimethyl-*trans*-2-pentenal and worked up as already described. For Figure 8a the living polymer was heated to 120 °C for 3 min, quenched with 10 μL of 4,4-dimethyl-*trans*-2-pentenal, and worked up as already described.

Experiments in Figure 5. TCDT (1 equiv, 2.314 mg) in 0.2 mL of toluene was added to catalyst (5 mg) in 0.375 mL of toluene. The living polymers were quenched with 5 μL pivaldehyde after 5, 15, 45, 135, and 270 min and worked up as already described. For Figure 5e the living polymer was capped with 5 μL of pivaldehyde after 270 min and worked up as quickly as possible as already described. For Figure 5f the living polymer was heated to 120 °C for 3 min, quenched with 5 μL of pivaldehyde, and worked up as already described.

Determination of Rate Constants. The necessary data were provided by two experiments. In one experiment the living oligomer formed by adding 1 equiv of TCDT to the tungsten catalyst was heated to 120 °C for 3 min to induce the complete retro-DA reaction and cis/trans equilibration of the first C═C bond. After 30 min the living polyene was quenched with pivaldehyde and analyzed by HPLC. If we assume that (i) the extinction coefficients for **3tct** and **3t$_3$** are the same in the wavelength range employed (240–600 nm), (ii) all reactions are first order, and (iii) no significant decomposition occurs, we can obtain the total yield of **3** relative to the standard and the equilibrium constant of the cis/trans isomerization. In a second experiment the living polymer was kept at 24 °C for 270 min, quenched with pivaldehyde, and quickly analyzed by HPLC without further heating. This experiment yields directly the amount of **3tct**, **3t$_3$**, and **5** formed in 270 min. In the first experiment the resulting standardized areas are 0.2642 for **3tct**, 0.9000 for **3t$_3$**, and 2.2815 for total **5**. The second experiment gives 0.2810 for **3tct**, 0.6838 for **3t$_3$**, and 0.2946 for total **5**.

Determination of k_1 and K. We will assume that A is transformed into B with rate constant k_1 and that B and C equilibrate with rate constants k_2 and k_{-2} (eq 2 in text). Therefore $[A] = [A]_0 \exp(-k_1 t)$, $[A]_0 = [A] + [B] + [C]$, and $[A]_0 = [B]_\infty + [C]_\infty$. From the first experiment we get $[B]_\infty = 0.2642$ and $[C]_\infty = 0.9000$, and therefore $[A]_0 = 1.1642$. The second experiment yields $[B]_{270} = 0.2810$ and $[C]_{270} = 0.6838$, and consequently $[A]_{270} = 0.1994$ and $k_1 = 6.5 \times 10^{-3}$ min^{-1}. $K = [B]_\infty/[C]_\infty = k_{-2}/k_2 = 0.294$.

Determination of k_2 and k_{-2}:

$$d[B]/dt = k_1[A] - k_2[B] + k_{-2}[C] \qquad (1')$$

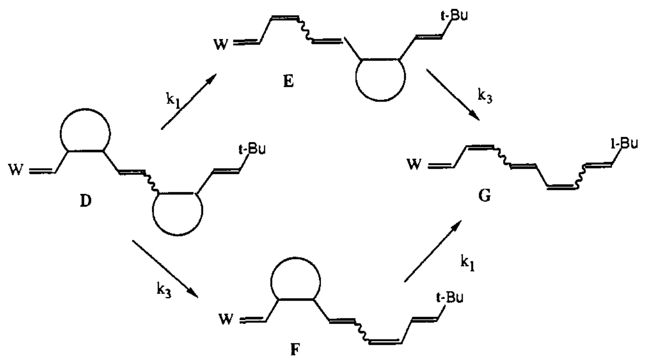
$$[C] = [A]_0 - [A] - [B] \qquad (2')$$

Substituting $[A] = [A]_0 \exp(-k_1 t)$ and eq 2′ into eq 1′ and solving yield

$$[B] = [A]_0\left[\frac{k_{-2}}{k_2 + k_{-2}} + \left\{\frac{k_1 - k_{-2}}{k_2 + k_{-2} - k_1}\right\}\exp(-k_1 t) - \left\{\frac{k_1 - k_{-2}}{k_2 + k_{-2} - k_1} + \frac{k_{-2}}{k_2 + k_{-2}}\right\}\exp\{-(k_2 + k_{-2})t\}\right]$$

If one sets $k_{-2} = k_2 K$ and uses $K = 0.294$, $k_1 = 6.5 \times 10^{-3}$ min^{-1}, $[A]_0 = 1.164$, and $[B]_{270} = 0.281$, one finds by graphical solution that $k_2 = 1.7 \times 10^{-2}$ min^{-1} and hence $k_{-2} = 5.1 \times 10^{-3}$ min^{-1}.

To determine the rate of the retro-DA reaction in the second unit we will assume that two pathways to G are possible, viz.



For the sake of simplicity we will assume that the rates of the reactions D → E and F → G are identical and that the rates of the reactions D → F and E → G are identical. We will also assume that the rates of all retro reactions are independent of chain length, i.e., k_1 is the same in a precursor to **5** (D or F) as it is in a precursor to **3** (A).

Determination of k_3:

$$[G] = [D]_0 - [D] - [E] - [F] \qquad (3')$$

$$d[D]/dt = -k_1[D] - k_3[D] \quad \text{or} \quad [D] = [D]_0 \exp(-(k_1 + k_3)t) \qquad (4')$$

$$d[E]/dt = k_1[D] - k_3[E] \qquad (5')$$

$$d[F]/dt = k_3[D] - k_1[F] \qquad (6')$$

Solving eq 5′ and 6′ gives eq 7′ and 8′:

$$[E] = [D]_0 \{\exp(-k_3 t)\}(1 - \exp(-k_1 t)) \qquad (7')$$

$$[F] = [D]_0 \{\exp(-k_1 t)\}(1 - \exp(-k_3 t)) \qquad (8')$$

Substituting eq 4′, 7′, and 8′ into eq 3′ and rewriting give

$$[G] = [D]_0\{1 + \exp(-(k_1 + k_3)t) - \exp(k_1 t) - \exp(k_3 t)\} \qquad (9')$$

Substituting $[G]_{270} = 0.2976$, $[D]_0 = 2.2815$, and $k_1 = 6.5 \times 10^{-3}$ min^{-1} into eq 9′ gives $k_3 = 6.3 \times 10^{-4}$ min^{-1}.

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Registry No. 1, 558-37-2; **2**$\mathbf{t_2}$, 22430-49-5; **3tct**, 122093-75-8; **3**$\mathbf{t_3}$, 81380-18-9; **4tcct**, 122170-12-1; **4tctt**, 122170-13-2; **4**$\mathbf{t_4}$, 121987-85-7; **5tctct**, 122170-14-3; **5tc**$_3$**t**, 122170-15-4; **5tct**$_3$, 122170-16-5; **5t**$_5$, 121987-86-8; **6tcttct**, 122170-17-6; **6tctcct**, 122170-18-7; **6tctctt**, 122170-19-8; **6tct**$_4$, 122170-20-1; **6t**$_6$, 121987-87-9; **7t(ct)**$_3$, 122170-21-2; **7tctct**$_3$, 122170-22-3; **7tct**$_3$ct, 122170-23-4; **7t**$_7$, 121987-88-0; **8**t$_8$, 121987-89-1; **9t(ct)**$_4$, 122170-24-5; **9tctct**$_3$ct, 122170-25-6; **9t(ct)**$_3$tt, 122170-26-7; **9tct**$_5$**ct**, 122170-27-8; **9tct**$_7$, 122170-28-9; **9t**$_9$, 121987-90-4; **10t**$_{10}$, 122093-76-9; **11t(ct)**$_5$, 122093-77-0; **13t(ct)**$_6$, 122093-78-1; **13t**$_{13}$, 122170-29-0; **15**t(ct)$_7$, 122093-79-2; (*E*)-*t*-BuCH═CHCHO, 22597-46-2; W(CH-*t*-Bu)(NC$_6$H$_3$-2,6-*i*-Pr$_2$)(O-*t*-Bu), 107440-84-6; pivaldehyde, 630-19-3; guaiazulene, 489-84-9.

Supplementary Material Available: Tables of proton NMR data for other identified polyenes and parameters for calculating carbon chemical shift in *all-trans-* or alternating polyenes (3 pages). Ordering information is given on any current masthead page.

Communications to the Editor

Direct Polymerization of Acetylene To Give Living Polyenes

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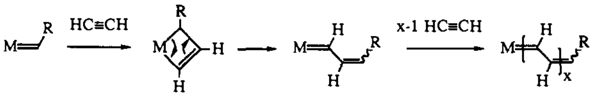
Polyacetylene has been of great interest in the past decade as (inter alia) a potential organic conductor,[1] but so far it has not been possible to prepare polyacetylene or shorter oligomers in a controlled polymerization of acetylene. There is good evidence that this should be possible under the right circumstances by using an alkylidene complex (eq 1).[2,3] We report here the preparation of living polyenes of moderate length and block copolymers containing polyene sequences by this method.



(1)

Addition of up to 60 equiv of acetylene[4] to a solution of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (Ar = 2,6-C$_6$H$_3$-*i*-Pr$_2$)[5] in pentane yields a black, intractable precipitate of what appears to be a form of polyacetylene on the basis of its solid-state ^{13}C NMR spectrum (broad singlet at 135 ppm).[6] However, if W(CH-*t*-Bu)-

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(1) (a) Chien, J. C. W. *Polyacetylene Chemistry, Physics and Material Science*; Academic Press: New York, 1984. (b) Skotheim, T. A., Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986. (c) Kuzmany, H., Mehring, M., Roth, S., Eds. *Electronic Properties of Conjugated Polymers*; Springer Series in Solid State Sciences; Springer: New York, 1988; Vol. 76. (d) Bowden, M. J., Turner, S. R., Eds. Electronic and Photonic Applications of Polymers. *Adv. Chem. Ser.* **1988**, *218*. (e) Proceedings of the International Conference on the Physics and Chemistry of Low-Dimensional Synthetic Metals. In *Synth. Met.* **1987**, *17*; *Mol. Cryst. Liq. Cryst.* **1985**, *117*, 118. (f) Wegner, G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 361. (g) Baughman, R.; Bredas, J.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* **1982**, *82*, 209. (h) Simionescu, C. I.; Perec, V. *Prog. Polym. Sci.* **1982**, *8*, 133. (i) Frommer, J.; Chance, R. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1986; p 462.

(2) (a) Masuda, T.; Higashimura, T. *Adv. Polym. Sci.* **1986**, *81*, 121. (b) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422. (c) Han, C.-C.; Katz, T. J. *Organometallics* **1985**, *4*, 2186. (d) Katz, T. J.; Hacker, S. M.; Kendrick, R. D.; Yannoni, C. S. *J. Am. Chem. Soc.* **1985**, *107*, 2182. (e) Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737.

(3) Wallace, K. C.; Liu, A. H.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 644.

0002-7863/89/1511-8004$01.50/0