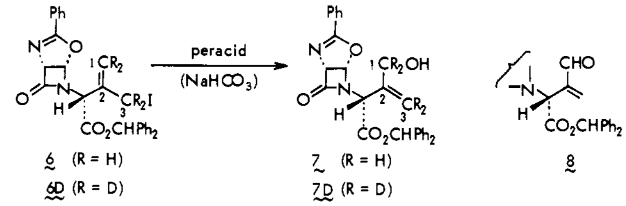
Table I. Peracid Oxidation of Allylic Iodide **6** to Allylic Alcohol **7**

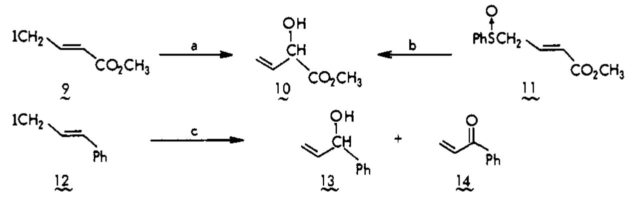
peracid equiv[a]	inorg base (equiv)	solvent	temp, °C	time, h	yield, %
m-CPBA (4.0)	$NaHCO_3$ (2.0)	EtOAc-H_2O (2:1)	rt	2	88[b]
m-CPBA (4.0)	$NaHCO_3$ (2.0)	CH_2Cl_2-H_2O (2:1)	5–10	1	82[b]
$PhCO_3H$ (4.5)	$NaHCO_3$ (2.0)	EtOAc-H_2O (2:1)	rt	3	88[c]
o-$HO_2CC_6H_4CO_3H$ (5.0)	$NaHCO_3$ (2.0)	EtOAc-H_2O (tr)	rt	2.5	84[c]
CH_3CO_3H[d] (6.0)	$NaHCO_3$ (2.0)	EtOAc-H_2O (1:1)	rt	17	93[c]
CH_3CO_3H[d] (6.0)	$NaHCO_3$ (2.0)	CH_2Cl_2-H_2O (1:1)	rt	7	93[c]

[a] Excess amounts of peracid were used to overcome their competing decomposition catalyzed with the base. [b] Isolated yield. [c] Determined by HPLC analysis. [d] Commercially available 40% peracetic acid was used.

Scheme I



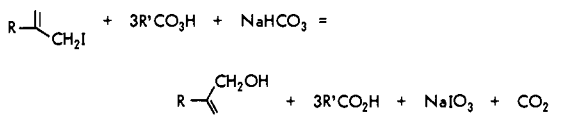
Scheme II



[a] *m*-CPBA, EtOAc or CH_2Cl_2/aqueous Na_2CO_3, 5–20 °C, 1 h. [b] Ph_3P, CH_3OH-C_6H_6, reflux, 7 h. [c] *m*-CPBA, $CHCl_3$, $HO(CH_2)_2OH$/aqueous Na_2CO_3, −13 to −17 °C.

are necessary for the saturated system, at least 3 equiv (4–6 equiv in practice) of peracid are necessary for the allylic system.[8] Moreover, evidence against carbonium ion intermediacy postulated for the oxidation of alkyl iodides,[4] but support for possible incorporation of an allylic rearrangement in the present oxidation was obtained by a rigorously performed deuterium-scrambling experiment.[7] Thus, while the double bond at C_1–C_2 in **6D**[7] was shifted to C_2–C_3 in **7D**, the deuterium contents[7] of 15–17% and 25–27%, respectively, at C_1 and C_3 were retained throughout the reaction. Direct evidence for this view was obtained from the following examples, which demonstrate also the general applicability of the present reaction. Oxidation of methyl *trans*-γ-iodocrotonate (**9**)[9] afforded the rearranged, deconjugated allylic alcohol **10**[10] in 65–67% yield[11,12] (Scheme II). Remarkably, no isomeric methyl γ-hydroxycrotonate was detected in the products. Cinnamyl iodide (**12**)[13] was also oxidized, at a lower temperature of -13 to -17 °C, to give 63%[11] of phenylvinylcarbinol (**13**)[14] and 10%[11] of phenyl vinyl ketone (**14**).[15] Again, no cinnamyl alcohol was formed in this reaction.

On the basis of these findings, we propose the following tentative reaction pathway (eq 1) and stoichiometry (eq 2) for the present



(2)

reaction. In this pathway, initially formed unstable iodoso compound **2** is assumed to rearrange to hypoiodite **3** in a [2,3] sigmatropic manner by analogy with the structurally related selenoxide.[3a] Intermediate **3** undergoes further oxidation to give iodate **4**, which is finally hydrolyzed to allylic alcohol **5** and iodate anion.

Finally, the efficiency of the present reaction was compared with the well-known Mislow[2a,b]–Evans[2c,d] reaction. Methyl γ-phenylthiocrotonate *S*-oxide (**11**)[7] was heated with triphenylphosphine in methanol and benzene. In both reactions, the rearranged alcohol **10** was formed in comparable yields, but the Mislow–Evans reaction required the very drastic condition of 7-h refluxing in contrast with the 1-h standing at 5–20 °C in our process.

Acknowledgment. We sincerely appreciate the discussions of the NMR studies by the late Dr. K. Tori and J. Nishikawa and the mass spectrum analyses done by Dr. Y. Nakagawa and H. Iwatani.

Registry No. **6**, 67977-89-3; **7**, 67977-88-2; **9**, 65495-78-5; **10**, 5837-73-0; **12**, 59625-54-6; **13**, 4393-06-0.

Supplementary Material Available: Spectral and combustion data for **8** and **11**, deuterium distribution data for **6D** and **7D**, and data for preparation of **6D** and **11** (2 pages). Ordering information is given on any current masthead page.

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(8) More recently Davidson and Kropp[4d] observed that the number of molar equivalents of oxidant for complete oxidation depends on the substrate system.

(9) Gershon, H.; Shanks, L.; Gawiak, D. E. *J. Med. Chem.* **1976**, *19*, 1069–1072.

(10) Palm, R.; Ohse, H.; Cherdron, H. *Ang. Chem., Int. Ed. Engl.* **1966**, *5*, 994–1000.

(11) As determined by GC analysis.

(12) In a typical procedure, aqueous Na_2CO_3 (4.68 g, 44.2 mmol, in 100 mL of H_2O) was added to a stirred solution of **9** (10.0 g, 44.2 mmol) in CH_2Cl_2 (200 mL). To this mixture was added *m*-CPBA (35.9 g, 0.177 mol) portionwise at 5 °C under stirring and nitrogen stream (slightly exothermic reaction). The reaction mixture was further stirred vigorously at room temperature for 1 h. $NaIO_3$ (8.7 g, 99%) was removed by filtration. After the usual workup, the product containing 67% (GC) of **10** was distilled at 58–66 °C (12–13 mmHg) to give 2.59 g (51%) of pure **10**.

(13) Kaiser, C.; Burger, A.; Zirngibl, L.; Davis, C. S.; Zirkle, C. L. *J. Org. Chem.* **1962**, *27*, 768–773.

(14) Duveen, D. I.; Kenyon, J. *J. Chem. Soc.* **1939**, 1697–1701.

(15) Franzen, V. *Ann. Chem.* **1957**, *602*, 199–208.

Pentadienyl Dithiocarbamate as a 1,5-Dianion Equivalent. Versatile Reagent for Polyene Synthesis[1]

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The Institute of Physical and Chemical Research (RIKEN)
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Received December 29, 1982

Although thioallylic anions have become recognized as an increasingly important tool in synthetic aliphatic chemistry,[2] thiopentadienyl anions are as yet much less explored for organic

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(1) Presented in part at the 45th Annual Meeting of the Chemical Society of Japan, Apr 1982, Tokyo, and at the 4th International Congress on Organic Synthesis, IUPAC, Aug 1982, Tokyo, Japan.

(2) Biellman, J. F.; Ducey, J. B. *Org. React.* **1982**, *27*, 1.

Scheme I

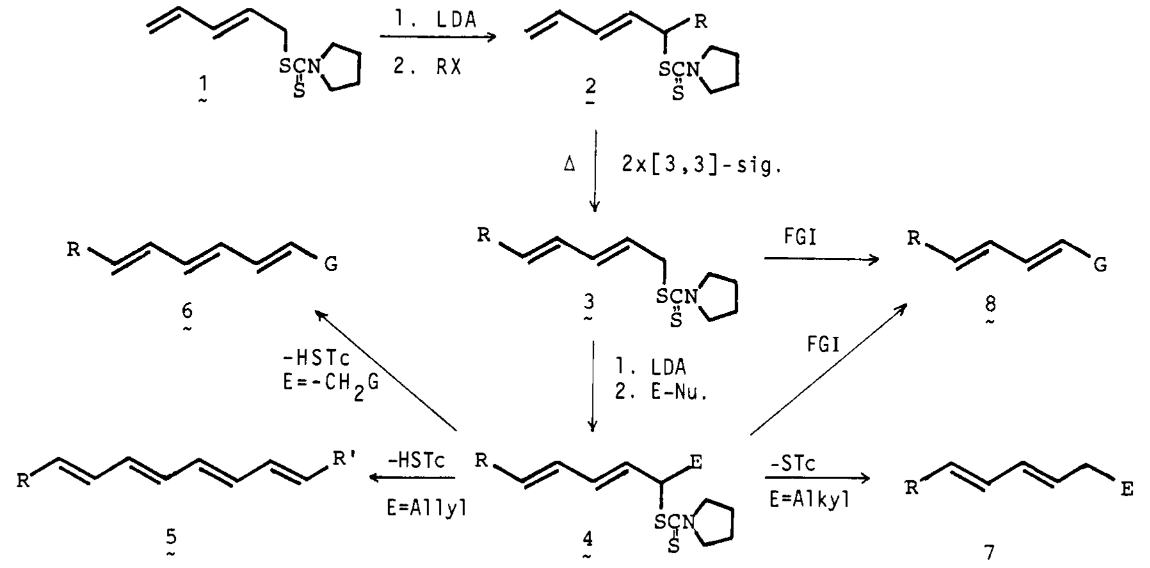
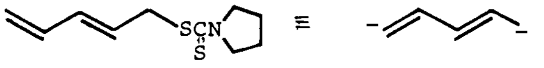


Table I. First Alkylation of 1 and Regioselectivity

			regioisomeric ratio, %[b,c]			
entry	RX	total[a] yield, %	α-trans	γ-trans	γ-cis	ε-trans
1	MeI	98	97.0	3.0		
2	EtI	98	94.5	3.3		2.2
3	*n*-PrI	96	91.2	4.6	2.8	1.4
4	*n*-BuI	96	89.1	5.7	3.6	1.6
5	*n*-PenI	95	85.1	10.5	2.6	1.8
6	$PhCH_2CH_2I$	95	75.6	15.5	6.5	2.4
7	*i*-PrI	94	58.6	30.3	8.0	3.2

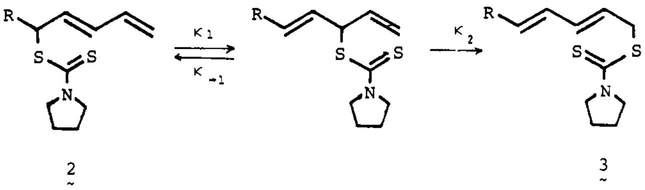
[a] In all cases, the yields are reported on chromatographed material whose regioisomeric composition is noted in the subsequent column. [b] Analytical HPLC was performed on a Waters 600 instrument with a 300 mm × 8 mm column packed with nucleosil 50-5, with hexane-EtOAc (9:1) as the mobile phase at a flow rate of 1.0 mL/min. [c] All products were isolated pure and completely characterized (see supplementary material).

synthetic use.[3,4] We describe herein the use of pentadienyldithiocarbamate **1**[5] as a 1,5-dianion equivalent, which can be effectively used for the diene, triene, and tetraene synthesis. Our strategy is conceptualized in Scheme I.



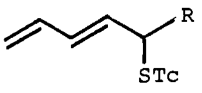
1 1,5-dianion

Scheme II

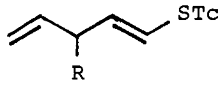


The present studies have focused on a new rearrangement of α-alkylated substrates **2** to **3** with 100% trans selectivity,[6] which has been followed by the realkylation, allylation, or functional group interconversion (FGI) at the newly created α-methylene group.

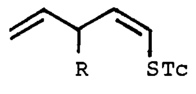
The alkylation of **1** was achieved in quantitative yields as follows. LDA (1.0 equiv) in hexane was added to a solution of **1** (1.0–1.1 equiv) in THF at −78 °C under nitrogen. The addition of an alkyl iodide resulted in the immediate discharge of the intense red. After warming to 0 °C and quenching with NH_4Cl solution, the reaction mixture gave **2**. HPLC and ^1H NMR analysis revealed that **2** consisted of four regioisomers: α-trans as the major product and γ-trans, γ-cis, and ε-trans isomers as the minor products. The results are summarized in Table I.



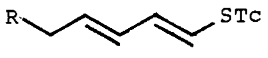
α-*trans*



γ-*trans*



γ-*cis*



ε-*trans*

It should be noticed that in contrast to the low level of α-selectivity observed in the alkylation of pentadienyl anion itself,[3] the alkylation of **1** afforded a very high level of α-selectivity. Evidently, the introduction of the thiocarbamoylthio group (denoted as STc in the schemes) at the terminal position of pentadiene enhances the selectivity drastically. Table I also shows that the selectivity decreases gradually with an increase in the length of

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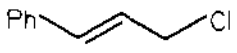
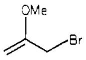
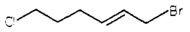
(3) For the studies on the pentadienyl anion itself, see: (a) Bates, R. B.; Beavers, W. A.; Greene, M. G.; Klein, J. H. *J. Am. Chem. Soc.* **1974**, *96*, 5640. (b) Bates, R. B.; Gosselink, D. W.; Kaczynski, J. A. *Tetrahedron Lett.* **1976**, 205. (c) Bates, R. B.; Cole, C. M.; Davidson, E. W.; Forsythe, G. D.; McCombs, D. A.; Roth, A. S. *J. Am. Chem. Soc.* **1973**, *95*, 926. (d) Schlosser, M.; Rauschwalbe, G. *Ibid.* **1978**, *100*, 3258. (e) Ford, W. T.; Newcomb, M.; *Ibid.* **1974**, *96*, 309. (f) Kloosterziel, H.; Van Drunen, J. A. A. *Recl. Trav. Chim. Pays-Bas*, **1969**, *88*, 1471. (g) Schlosser, M. *Helv. Chim. Acta* **1974**, *57*, 2261. (h) Oppolzer, W., Burford, S. C.; Marazza, F. *Ibid.* **1980**, *63*, 555. (i) Oppolzer, W.; Briner, P. H.; Snowden, R. *Ibid.* **1980**, *63*, 976. (j) Yasuda, H.; Yamauchi, M.; Nakamura, A.; Sei, T.; Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1089. (k) Seyferth, D.; Pornet, J. *J. Org. Chem.* **1980**, *45*, 1721.

(4) During the preparation of this paper, an application of pentadienylphenyl sulfide to the synthesis of a dienal via double [2,3] sigmatropic rearrangement has appeared: Corey, E. J.; Hoover, D. J.; *Tetrahedron Lett.* **1982**, *23*, 3463.

(5) Pentadienyldithiocarbamate **1** or 1-(penta-2(*E*),4-dienyl)-1-pyrrolidinecarbodithioate was easily prepared from pentadienyl bromide and sodium 1-pyrrolidinecarbodithioate. The thiocarbamoyl group is denoted as Tc in the schemes.

(6) The [3,3] sigmatropic rearrangement of allyl dithiocarbamate was reported by us and others: (a) Hayashi, T. *Tetrahedron Lett.* **1974**, 339. (b) Hayashi, T.; Midorikawa, H. *Synthesis*, **1974**, 100. (c) Nakai, T.; Shono, H.; Okawara, M.; *Tetrahedron Lett.* **1974**, 3625.

Table II. Second Alkylation of **3** and Regioselectivity

entry	R	E-Nu	major product **4** R	 E	compd no.	total[a] yield, %	α:γ[b,c] ratio
8	Me	*n*-PrI	Me	*n*-Pr	4a	97	96.9:3.1
9	Me	*n*-PenI	Me	*n*-Pen	4b	99	96.4:3.6
10	Me	$PhCH_2CH_2I$	Me	$PhCH_2CH_2$	4c	99	95.2:4.8
11	Me	$PhCH_2I$	Me	$PhCH_2$	4d	97	88.5:11.5
12	Me	$THPO(CH_2)_6I$	Me	$THPO(CH_2)_6$	4e	99	96.1:3.9
13	Et	$THPO(CH_2)_5I$	Et	$THPO(CH_2)_5$	4f	99	95.0:5.0
14	Et	$THPO(CH_2)_7I$	Et	$THPO(CH_2)_7$	4g	98	95.7:4.3
15	*n*-Pr	$THPO(CH_2)_4I$	Et	$THPO(CH_2)_4$	4h	96	95.0:5.0
16	Me	crotyl Br	Me	$CH_3CH{=}CHCH_2$	4i	99	90.0:10.0
17	Me		Me	$PhCH{=}CHCH_2$	4j	97	91.9:8.1
18	Me		Me	CH_3COCH_2	4k	84	85.4:14.6
19	Et		Et	$Cl(CH_2)_3CH{=}CHCH_2$	4l	99	82.6:17.4

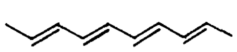
[a] In all cases, the yields are reported on chromatographed material, whose regioisomeric ratio is noted in the last column. [b] All products were purified chromatographically and characterized by IR, 400-MHz ^{1}H NMR, and either high-resolution mass spectroscopy or combustion analysis. [c] Regioisomeric ratios were determined by the same method as described in Table I.

the alkyl chain and rapidly with the branching of it.[7] An appreciable amount of the γ-cis isomer was always detected in the product mixture **2**.[8]

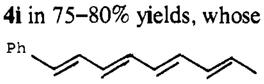
2-α-Trans substances, which have been isolated pure by preparative HPLC, easily undergo double [3,3] sigmatropic rearrangement (toluene, 2 h, reflux), to yield **3** in the ratio **3**:**2** = 20:1. HPLC analysis demonstrated that **3** is the sole product of this rearrangement (Scheme II), whose geometry has been assigned *E*,*E* about the two double bonds.[9] The driving force of the rearrangement may be attributed to stabilization by internalization of the diene unit.[4] Kinetic studies demonstrated that the rearrangement follows the first-order kinetics ($k = 6.1 \times 10^{-4}$ s^{-1} mol^{-1}, $t_{1/2}$ = 18.5 min at 111.5 °C in toluene; $k = 2.1 \times 10^{-4}$ s^{-1} mol^{-1}, $t_{1/2}$ = 61.5 min at 99.5 °C in isooctane).[10]

An attractive feature of this procedure is that the rearrangement leads to the formation of a new methylene group at the terminal position of the pentadienyl moiety, which can be again alkylated or allylated according to the same procedure as used in the first alkylation. Table II summarized the results of the second alkylation and allylation. It is noted that an alkyl substituent at the terminal position increases the level of α-selectivity substantially in the alkylation but less effectively in the reactions with allylic halides, which are softer nucleophiles, and that it depresses the yields of the γ-cis and ϵ isomers to a negligible extent.

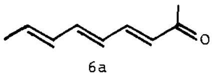
The synthesis of tetraenes having all-trans geometry can be achieved by treating allylated substrates **4** with a mixture of MeI, LiF, and Li_2CO_3 suspended in DMF under argon in the dark at room temperature for 24 h.[11] Thus, *all-trans*-2,4,6,8-decatetraene (**5a**, R = R′ = Me) was prepared from **4i** in 75–80% yields, whose UV spectrum was in agreement with the reported values.[12]



5a



5b



6a

Similarly, *all-trans*-1-phenyl-1,3,5,7-nonatetraene (**5b**, R = Ph, R′ = Me) and 3,5,7-nonatrien-2-one (**6a**, R = Me, G = COMe) were obtained from **4j** and **4k** in 80% and 81% yields. The UV and IR data agreed with the reported values.[13] Other spectral data also supported the structures of **6a**.[14] Furthermore, this methodology has the possibility of synthesizing diene derivatives by regiocontrolled reductive desulfurization of alkylated substrates **4** or functional group conversion of **3**.

In summary, the procedures described are very general, convenient, and stereoselective, and far wider applications than described above are possible. We are currently investigating (1) application to the synthesis of natural polyolefinic compounds, (2) the synthesis of insect sex pheromones having a diene unit, (3) highly stereo- and regioselective preparation of 1,3,5-trienes, (4) the interconversion of the functionality, and (5) an extension to the synthesis of pentaenes.

Registry No. 1, 85235-54-7; *α-trans*-**2** (R = Me), 85235-55-8; *α-trans*-**2** (R = Et), 85235-56-9; *α-trans*-**2** (R = Pr), 85235-57-0; *α-trans*-**2** (R = Bu), 85235-58-1; *α-trans*-**2** (R = Pen), 85235-59-2; *α-trans*-**2** (R = $PhCH_2CH_2$), 85235-60-5; *α-trans*-**2** (R = *i*-Pr), 85235-61-6; *γ-trans*-**2** (R = Me), 85235-62-7; *γ-trans*-**2** (R = Et), 85235-63-8; *γ-trans*-**2** (R = Pr), 85235-64-9; *γ-trans*-**2** (R = Bu), 85235-65-0; *γ-trans*-**2** (R = Pen), 85235-66-1; *γ-trans*-**2** (R = $PhCH_2,CH_2$), 85235-67-2; *γ-trans*-**2** (R = *i*-Pr), 85235-68-3; *γ-cis*-**2** (R = Pr), 85235-69-4; *γ-cis*-**2** (R = Bu), 85235-70-7; *γ-cis*-**2** (R = Pen), 85235-71-8; *γ-cis*-**2** ($PhCH_2CH_2$), 85235-72-9; *γ-cis*-**2** (R = *i*-Pr), 85235-73-0; *ϵ-trans*-**2** (R = Et), 85235-74-1; *ϵ-trans*-**2** (R = Pr), 85235-75-2; *ϵ-trans*-**2** (R = Bu), 85235-76-3; *ϵ-trans*-**2** (R = Pen), 85235-77-4; *ϵ-trans*-**2** (R = $PhCH_2CH_2$), 85235-78-5; *ϵ-trans*-**2** (R = *i*-Pr), 85235-79-6; **3** (R = Me), 85235-80-9; **3** (R = Et), 85235-81-0; **3** (R = Pr), 85235-82-1; **3** (R = Bu), 85235-83-2; **3** (R = Pen), 85235-84-3; **3** (R = $PhCH_2CH_2$), 85235-85-4; **3** (R = *i*-Pr), 85235-86-5; **4a**, 85235-87-6; **4b**, 85293-62-5; **4c**, 85235-88-7; **4d**, 85235-89-8; **4e**, 85235-90-1; **4f**, 85235-91-2; **4g**, 85235-92-3; **4b**, 85235-93-4; **4i**, 85235-94-5; **4j**, 85235-95-6; **4k**, 85235-96-7; **4l**, 85235-97-8; **5a**, 64550-72-7; **5b**, 85235-98-9; **6a**, 16326-91-3; MeI, 74-88-4; EtI, 75-03-6; PrI, 107-08-4; BuI, 542-69-8; *n*-PenI, 628-17-1; $PhCH_2CH_2I$, 17376-04-4; *i*-PrI, 75-30-9; $PhCH_2I$, 620-05-3; $THPO(CH_2)_6I$, 65785-44-6; $THPO(CH_2)_5I$, 55305-32-3; $THPO(CH_2)_7I$, 65785-43-5; $THPO(CH_2)_4I$, 41049-30-3; (*E*)-$PhCH{=}CHCH_2Cl$, 21087-29-6; (*E*)-$Cl(CH_2)_3CH{=}CHCH_2Br$, 85235-99-0; crotyl bromide, 4784-77-4; 2-methoxyallyl bromide, 26562-24-3.

Supplementary Material Available: Spectral and physical data for **1–6** (15 pages). Ordering information is given on any current masthead page.

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(7) These regioselectivities may be interpreted in terms of the combined effects of HSAB and steric factors: Baba, H.; Hayashi, T.; Oishi, T. *Chem. Pharm. Bull.* **1982**, *30*, 3852.

(8) The formation of the γ-cis isomers suggests the presence of the torsional isomers in the anion solution, as depicted below.

exo-W type

endo-W type

(9) The assignment of the *E*,*E* configuration to the two double bonds was supported by the vicinal coupling constants, $J_{2,3}$ = 15.6 Hz and $J_{4,5}$ = 15.6 Hz, in the proton-decoupled 400-MHz ^{1}H NMR spectra.

(10) The first-order kinetics of the rearrangement can be explained by assuming that $(k_{+1} + K_{-1}) \ll k_2$.

(11) Hayashi, T.; Sakurai, A.; Oishi, T. *Chem. Lett.* **1977**, 1483.

(12) UV_{max} (hexane) 282 nm, 283, 295, and 309.5 with the 295-nm maximum the most intense (lit.: Blout, E. R.; Fields, M. *J. Am. Chem. Soc.* **1948**, *70*, 189).

(13) Kroner, M. *Chem. Ber.* **1967**, *100*, 3172.

(14) Trienes and tetraenes are extremely sensitive to the atmospheric oxygen and light. Therefore, care should be exercised to avoid exposure of the products to air and light. When an electron-withdrawing group is attached to the conjugated position, however, they seem to become much less sensitive to oxygen.