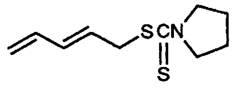
A Novel and General Route to 1-Iodo-2,4(*E*,*E*)-dienes *via* Pentadienyl Dithiocarbamate

Toshio Hayashi,* Kazuo Sasaoka and Takeshi Oishi
The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351, Japan

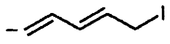
The title compounds were prepared from pentadienyl dithiocarbamate *via* *S*-methylation and by use of the iodide an unsymmetric, all-*trans*-conjugated pentaene was synthesized.

1-Iodo-2,4(*E*,*E*)-dienes **6** are valuable building blocks for the electrophilic introduction of a dienic unit into carbon frames.[1] A conventional method for preparing 1-halodienes consists of the halogenation of the corresponding dienols,[2] which generally are not readily available.[3] Herein we report a new facile method for the synthesis of **5** *via* a five-carbon elongation reaction using pentadienyl dithiocarbamate **1** as an ω-iododienyl anion equivalent **2**.[4] This report constitutes the first synthesis of the iodic counterpart of 1-halo-2,4-dienes, which are much more reactive than the chloro- and bromo-derivatives. Further, we show that the iodides **6** can be easily converted into the corresponding 2,4-dienals **7**. Hence, the reagent **1** can also be considered as a new δ-formyl butadienyl anion equivalent **3**.[5]

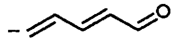
The synthetic process is shown in Scheme 1. ω-Alkylpentadienyl dithiocarbamates **4** were prepared by the alkylation of **1**, followed by the double [3,3]-sigmatropic rearrangement as described before.[4] The procedure for conversion of **5** to the corresponding iodide **6** is straightforward;[6] the reactant **5** was dissolved in a large excess of methyl iodide (*ca.* eight times by weight) and the solution was left to stand in the dark under an argon atmosphere at room temperature for two days. The resulting yellow solids were triturated in pentane and filtered. The filtrate was concentrated and the residue purified by column chromatography over silica gel using hexane–ether (9:1) as eluent. The results are listed in Table 1, with the isomeric ratios.† The iodides are generally unstable. Es-



1



2



3

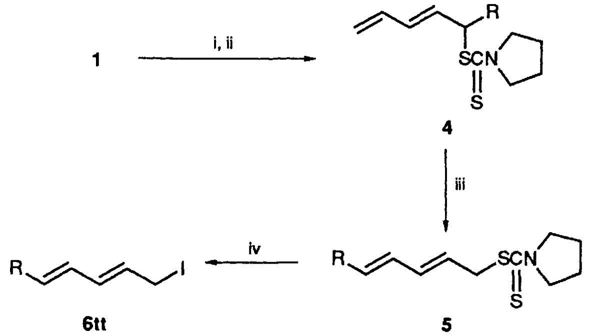
---

† The combustion analysis could not be carried out owing to the instability of the products. The IR spectra (neat) of all the products showed a sharp, characteristic absorption band at 1140 cm^{-1}, which is ascribed to the deformation vibration of the allylic methylene group. The NMR signals (500 MHz, $CDCl_3$) of **5** are located at δ_H 5.79 (1H, dt, *J*/Hz 14.9 and 8.3), 5.80 (1H, dt, *J*/Hz 15.1 and 6.8), 6.00 (1H, dd, *J*/Hz 15.1 and 10.5) and 6.23 (1H, dt, *J*/Hz 14.9 and 10.5) for the alkenic protons.

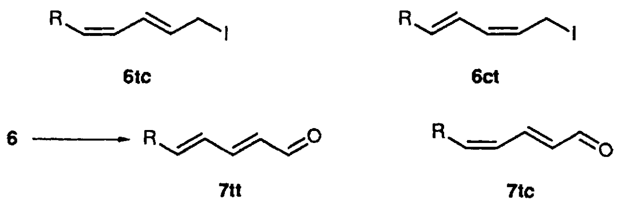
Table 1 Yields and isomeric ratios of 1-iodo-2,4-dienes

Entry	R[a]	Yield (%)[b]	Isomeric ratio[c] **6tt** : **6tc** : **6ct**
1	Me	—[d]	
2	$MeCH_2$	70	94 : 5 : 1
3	$Me(CH_2)_2CH_2$	83	95 : 4 : 1
4	$Me(CH_2)_3CH_2$	81	95 : 4 : 1
5	$Me(CH_2)_4CH_2$	78	94 : 4 : 2
6	$Me(CH_2)_6CH_2$	81	94 : 5 : 1
7	$Me(CH_2)_{13}CH_2$	85	93 : 5 : 2
8	$PhCH_2CH_2$	85	92 : 5 : 3

[a] The structures of the products were confirmed by spectroscopic measurements. [b] Isolated yield. [c] The ratios were determined by the intensities of the nmr signals of the allylic methylene group, which appeared at δ 4.00, *ca.* 4.01–4.03 and 4.08 for **5**, **6** and **7**, respectively. [d] Decomposed.



Scheme 1 *Reagents and conditions*: i, lithium diisopropylamide (LDA); ii, RI; iii, heat; iv, MeI

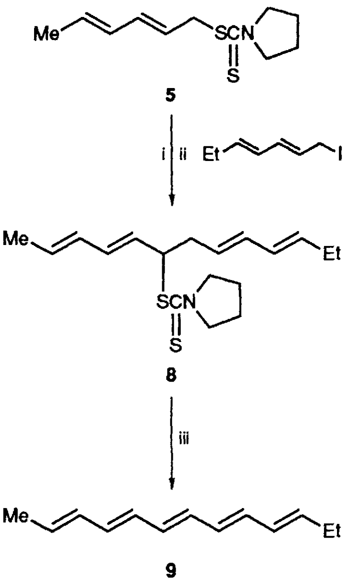


Scheme 2

Table 2 Yields and isomeric ratios of 2,4-dienals

Entry	R[a]	Yield (%)[b]	Isomeric ratio[c] **7tt** : **7tc**
1	$MeCH_2$	70	94 : 6
2	$Me(CH_2)_2CH_2$	80	93 : 7
3	$Me(CH_2)_3CH_2$	74	94 : 6
4	$Me(CH_2)_4CH_2$	70	95 : 5
5	$Me(CH_2)_6CH_2$	70	94 : 6
6	$Me(CH_2)_{13}CH_2$	98	95 : 5
7	$PhCH_2CH_2$	40	96 : 4

[a] The structures of the products were confirmed by spectroscopic measurements. [b] Isolated yield. [c] The ratios were determined by the intensities of the NMR signals of the aldehydic proton, which appeared at δ 9.54 and 9.61 for **11** and **12**, respectively.



Scheme 3 *Reagents*: i, LDA; iii, MeI/CsF/Li_2CO_3 in DMF

pecially, 1-iodohexa-2,4-diene (**1**, R = Me) decomposed explosively when the solvent was removed. The conversion of **6** to **7** was achieved as follows. A solution of **6** and *N*-ethylmorpholine *N*-oxide (4 mol equiv. to **6**) in CH_2Cl_2 was stirred at room temperature under an argon atmosphere for 30 min, then refluxed for 4 h. The solution was washed with water, the solvent was removed and the residue was purified by silica gel column chromatography using hexane–ethyl acetate (7 : 1) as eluent (Scheme 2). The yields are shown in Table 2, with the isomeric ratios.‡ One important application of these iodides is found in the synthesis of unsymmetric, all-*trans*-conjugated pentaenes (Scheme 3). The reaction of the lithium salt of **5** (R = Me) with **6** (R = Et) in tetrahydrofuran (THF) at −78 °C proceeded smoothly to give tetraene **8** in an almost quantitative yield. The treatment of **8** with a mixture of excess MeI, CsF, and Li_2CO_3 in degassed *N*,*N*-dimethylformamide (DMF) in the dark under an argon atmosphere at room temperature[7] produced all-*trans*-pentaene **9** in 78% yield, which was isolated by silica gel column chromatography using hexane as eluent and then recrystallized from petroleum–ethanol to give almost colourless solids having m.p. *ca.* 115–119 °C. The UV spectrum of these solids was in agreement with the literature data.[8] This method offers the most convenient route to pentaene synthesis.

This research was partially supported by grants from the Ministry of Education.

Received, 20th March 1990; Com. 0/01219J

---

‡ We confirmed that dienals (**7**; R = C_4H_9 and C_5H_{11}) which are commercially available from Aldrich, also contained *ca.* 5% of the isomer **7tc**.

References

1 See for example: D. F. Taber, *J. Am. Chem. Soc.*, 1977, **99**, 3514; K. Mori, *Tetrahedron*, 1974, **30**, 3807.
2 E. J. Corey, D. E. Cane and L. Libit, *J. Am. Chem. Soc.*, 1971, **93**, 7016.
3 F. Nat and R. Decorzant, *Helv. Chim. Acta*, 1974, **57**, 1309, and references cited therein.
4 The dithiocarbamates **5** have already been prepared. See: T. Hayashi, I. Hori and T. Oishi, *J. Am. Chem. Soc.*, 1983, **105**, 2909.
5 P. Chabert and C. Mioskowski, *Tetrahedron Lett.*, 1989, **30**, 6031.
6 A. Sakurai, T. Hayashi, I. Hori, Y. Jindo and T. Oishi, *Synthesis*, 1978, 370; A. Sakurai, T. Hayashi and T. Oishi, 1980, 843.
7 T. Hayashi, A. Sakurai and T. Oishi, *Chem. Lett.*, 1977, 413.
8 F. Bohlman, *Chem. Ber.*, 1952, **85**, 386; P. Naylor and M. C. Whiting, *J. Chem. Soc.*, 1955, 3037; R. Kuhn and C. Grundmann, *Chem. Ber.*, 1938, **71**, 442.