Studies on Seven-Membered Heterocycles. XXXV.¹⁾ Synthesis of the Group 16 1-Benzoheteroepines Involving the First Examples of 1-Benzotellurepine and 1-Benzoselenepine Rings

Haruki SASHIDA, Koichi ITO, and Takashi TSUCHIYA*

Faculty of Pharmaceutical Sciences, Hokuriku University, Kanagawa-machi, Kanazawa 920–11, Japan.

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Novel 2-alkyl-1-benzotellurepines (**11**) and 2-alkyl-1-benzoselenepines (**12**) were obtained by sodium borohydride reduction of di[*o*-(1-buten-3-ynyl)phenyl] ditellurides (**8**) and diselenides (**9**), together with 2-alkylidene-2*H*-tellurachromenes (**13**) and 2-alkylidene-2*H*-selenachromenes (**14**), respectively, via the phenyltellurol and phenylselenol intermediates (**10**). The dimers (**8**, **9**) were readily prepared from the 4-alkyl-1-(*o*-bromophenyl)-1-buten-3-ynes (**7**) by successive treatment with *tert*-butyllithium, tellurium or selenium powder, and potassium ferricyanide in one pot. The 2-alkyl-1-benzothiepine (**16**) were obtained directly from the enynes (**7**) by successive treatment with *tert*-butyllithium, sulfur powder, and ethanol in one pot. To examine the chemical behavior of the novel tellurepine ring, several reactions of 2-*tert*-butyltellurepine (**11c**) were carried out.

Keywords 1-benzotellurepine; 1-benzoselenepine; 1-benzothiepine; 2-alkylidene-2*H*-tellurachromene; 2-alkylidene-2*H*-selenachromene; 1-(*o*-bromophenyl)-1-buten-3-yne

The synthesis of new fully unsaturated seven-membered heterocyclic rings (heteroepines) containing a heavier element other than nitrogen or oxygen has recently received increasingly intensive study and a variety of monocyclic and fused heteroepines containing Group 14 (Si,²⁾ Ge,³⁾ Sn^{3,4)} and Group 15 (P,^{1,5–7)} As,^{1,8)} Sb^{8,9)} elements have been prepared. With regard to Group 16 heteroepines, several thiepine have been reported,^{10–12)} but they are relatively thermally unstable. Heteroepines containing a heavier element such as tellurium or selenium have been predicted¹³⁾ to be more thermolabile than thiepine, and only a limited number of examples of tellurepines and selenepines are known. Monocyclic 4,5-diethoxycarbonyl-2,7-di-*tert*-butylselenepine (**1**)¹³⁾ was prepared by ring-expansion of a 4*H*-selenopyran derivative and dibenzo[*b, f*]selenepine (**2**)¹⁴⁾ was obtained from 2-(phenylseleno)benzoic acid via eight steps. More recently, we have described the synthesis of 3-benzotellurepine (**3**)¹⁵⁾ from *o*-diethynylbenzene as the first

example of tellurepines. In connection with our studies on 1-benzoheteroepines (**4**: M=Si, Ge, Sn, P, As),^{1,8)} we report here on the synthesis of Group 16 1-benzoheteroepines (**4**: M=Te, Se, S)¹⁶⁾; the 1-benzotellurepines and 1-benzoselenepines are novel heterocyclic ring systems.

It is known that simple thiepine and selenepines are thermally unstable owing to ready extrusion of the hetero elements, but the stability of the heteroepine rings can be enhanced by introduction of bulky groups in the α -positions.^{12,13)} For example, the half-life of 2-methyl-1-benzothiepine is more than twice as long as that of the parent 1-benzothiepine ($t_{1/2}$ = 58 min at 47°C).¹²⁾ This finding on thiepine suggests that only 1-benzotellurepines and 1-benzoselenepines having at least one bulky group at the 2-position could be isolated. Therefore, we examined the synthesis of 2-substituted 1-benzoheteroepines.

(*Z*)- β -*o*-Dibromostyrene (**5**), prepared from *o*-bromobenzaldehyde via four steps according to the reported procedure,¹⁷⁾ was coupled¹⁸⁾ with various alkylacetylenes (**6a–g**) in benzene–piperidine (1 : 1) in the presence of a catalytic amount of a mixture of bis(triphenylphosphine)-palladium dichloride and copper(I) iodide to give the corresponding 4-alkyl-1-(*o*-bromophenyl)-1-buten-3-ynes (**7**) in 80–90% yields. The enynes (**7**) were lithiated with *tert*-butyllithium in anhydrous tetrahydrofuran (THF) at –80°C and then treated with tellurium or selenium powder, followed by oxidation with potassium ferricyanide, giving rise to the ditelluride dimers (**8a–f**) and diselenide dimers (**9a–f**) in one pot in yields ranging from 53% to 85%, except for the 4-phenyl derivative (**7g**), which did not give the dimers (**8g, 9g**).

Treatment of the dimers (**8, 9**) with sodium borohydride in THF–ethanol resulted in ring closure to give the desired 1-benzotellurepines (**11**) and 1-benzoselenepines (**12**), together with the 2-alkylidenetellurachromenes (**13**) and 2-alkylideneselenachromenes (**14**) in the yields shown in Table I. In the case of the methyl diselenide (**9a**), neither the selenepine (**13a**) nor the selenachromene (**14a**) could be isolated, probably because of their thermal instability.

Chart 1

Chart 2

Chart 3

TABLE I. Cyclization of the Dimers (8, 9) to the Heteroepines (11, 12) and Heterochromenes (13, 14)

Dimer	R	Product ^{a)} (yield, %) ^{b)}	
8a	Me	11a (8)	13a (5)
8b	<i>n</i> -Bu	11b (22)	13b (13)
8c	<i>t</i> -Bu ^{c)}	11c (48)	13c (15)
8d	<i>n</i> -Hex	11d (22)	13d (24)
8e	<i>c</i> -Hex ^{d)}	11e (20)	13e (51)
8f	<i>n</i> -Oct	11f (19)	13f (11)
9a	Me	12a (—)	14a (—)
9b	<i>n</i> -Bu	12b (12)	14b (10)
9c	<i>t</i> -Bu ^{c)}	12c (31)	14c (45)
9d	<i>n</i> -Hex	12d (13)	14d (17)
9e	<i>c</i> -Hex ^{d)}	12e (11)	14e (66)
9f	<i>n</i> -Oct	12f (18)	14f (10)

^{a)} All products (11—14) are red or orange viscous oils, except for **13e** (mp 83—85°C) and **14e** (mp 50—52°C), which are yellow prisms (from MeOH-Et₂O).
^{b)} Isolated yields. ^{c)} *tert*-Butyl. ^{d)} Cyclohexyl.

This ring closure reaction may proceed *via* the phenylheterol intermediates (10), which might undergo intramolecular cyclization *via* two competing paths; path a gives the seven-membered ring products (11, 12) and path b affords the six-membered ring products (13, 14), as shown in Chart 2. It is known¹⁹⁾ that treatment of phenyllithium with tellurium powder initially affords the unisolable phenyltellurol, which on treatment with an appropriate oxidizing agent gives the stable diphenyl

ditelluride. Therefore, in the present transformation from the enynes (7) to the dimers (8), the mixture before oxidation can be assumed to contain the key intermediate (10). Thus, the mixture was treated with sodium borohydride and ethanol without oxidation to afford the tellurepines (11) and tellurachromenes (13), but in very low yields (3—8%, 1—4%).

2-Alkyl-1-benzothiepine (16a—f) were also obtained from 7 by using sulfur powder instead of tellurium or selenium powder. However, the disulfide dimers (M=S in the structures 8 or 9) were not formed. Therefore, the reaction mixture obtained by the reaction of 7 with *tert*-butyllithium and sulfur powder, without oxidation, was treated with ethanol at 55°C, resulting in the formation of the thiepine (16) in 5—25% yields, presumably *via* the thiophenol intermediates (15), but the thiachromenes (17) could not be isolated. Although the yields are relatively low, the present result provides a new synthetic route to 1-benzothiepine.

All the 1-benzoheteroepines (11, 12, 16) and 2-alkylidene-2H-heterochromenes (13, 14) thus obtained are new compounds except for 2-methyl-1-benzothiepine (16a),¹²⁾ and were characterized mainly on the basis of high-resolution mass spectral (HR-MS) and ¹H-NMR spectral analyses (Tables II, III). The ¹H-NMR spectra of the novel heteroepine ring systems (11, 12) are essentially similar to those of known 1-benzoheteroepines such as 1-benzoxepines,¹⁰⁾ 1-benzothiepine,¹²⁾ and various 1-

TABLE II. Spectral Data for the 1-Benzoheteroepines (**11**, **12**, **16**)

Compd. No.	Formula	HR-MS Calcd (Found)	3-H	¹ H-NMR (400 MHz) (CDCl ₃) 4-H (dd) ^{a)}	5-H (d) ^{b)}	Ar-H		R-H
11a	C ₁₁ H ₁₀ Te	271.9845 (271.9819)	6.22 (dq) ^{c)}	6.05	6.73	6.08—7.17 (3H, m), 7.01 (1H, d) ^{d)}	Me	2.14 (d)
11b	C ₁₄ H ₁₆ Te	314.0314 (314.0302)	6.51 (dt) ^{c)}	6.25	6.93	7.14—7.29 (3H, m), 7.68 (1H, dd) ^{d)}	<i>n</i> -Bu	0.88 (3H, t), 1.25—1.52 (4H, m), 2.56 (2H, dt)
11c	C ₁₄ H ₁₆ Te	314.0314 (314.0310)	6.58 (d)	6.33	6.99	7.19—7.30 (3H, m), 7.76 (1H, dd)	<i>t</i> -Bu ^{e)}	1.21 (9H, s)
11d	C ₁₆ H ₂₀ Te	342.0627 (342.0636)	6.52 (br d)	6.27	6.95	7.16—7.30 (3H, m), 7.69 (1H, dd)	<i>n</i> -Hex	0.86 (3H, t), 1.20—1.51 (8H, m), 2.56 (2H, br t)
11e	C ₁₆ H ₁₈ Te	340.0478 (340.0473)	6.56 (d)	6.29	6.96	7.15—7.30 (3H, m), 7.70 (1H, d)	<i>c</i> -Hex ^{f)}	1.50—1.80 (10H, m), 2.18 (1H, m)
11f	C ₁₈ H ₂₄ Te	370.0947 (370.0954)	6.52 (br d)	6.27	6.95	7.17—7.29 (3H, m), 7.69 (1H, d)	<i>n</i> -Oct	0.87 (3H, t), 1.20—1.60 (12H, m), 2.56 (2H, t)
12b	C ₁₄ H ₁₆ Se	264.0417 (264.0415)	6.30 (br d)	6.28	6.94	7.15—7.26 (3H, m), 7.43 (1H, dd)	<i>n</i> -Bu	0.88 (3H, t), 1.25—1.58 (4H, m), 2.44 (2H, br t)
12c	C ₁₄ H ₁₆ Se	264.0417 (264.0407)	6.39 (d)	6.37	6.99	7.15—7.26 (3H, m), 7.43 (1H, dd)	<i>t</i> -Bu ^{e)}	1.22 (9H, s)
12d	C ₁₆ H ₂₀ Se	292.0730 (292.0739)	6.33 (br d)	6.22	6.93	7.17—7.31 (3H, m), 7.48 (1H, dd)	<i>n</i> -Hex	0.85 (3H, t), 1.20—1.50 (8H, m), 2.45 (2H, t)
12e	C ₁₆ H ₁₈ Se	290.0574 (290.0585)	6.30 (d)	6.32	6.96	7.17—7.28 (3H, m), 7.45 (1H, dd)	<i>c</i> -Hex ^{f)}	1.20—1.84 (10H, m), 2.21—2.29 (1H, m)
12f	C ₁₈ H ₂₄ Se	320.1043 (320.1056)	6.41 (d)	6.27	6.97	7.19—7.29 (3H, m), 7.46 (1H, dd)	<i>n</i> -Oct	0.89 (3H, t), 1.18—1.66 (12H, m), 2.47 (2H, t)
16a	C ₁₁ H ₁₀ S	174.0503 (174.0521)	6.18 (dq)	6.33	6.97	7.24—7.37 (4H, m)	Me	2.14 (3H, d)
16b	C ₁₄ H ₁₆ S	216.0973 (216.0970)	6.16 (br d)	6.35	6.98	7.15—7.34 (4H, m)	<i>n</i> -Bu	0.88 (3H, t), 1.20—1.60 (4H, m), 2.36 (2H, br t)
16c	C ₁₄ H ₁₆ S	216.0973 (216.0954)	6.26 (d)	6.45	7.04	7.19—7.37 (4H, m)	<i>t</i> -Bu ^{e)}	1.24 (9H, s)
16d	C ₁₆ H ₂₀ S	244.1286 (244.1302)	6.17 (d)	6.37	7.00	7.16—7.35 (4H, m)	<i>n</i> -Hex	0.87 (3H, t), 1.29—1.57 (8H, m), 2.35 (2H, t)
16e	C ₁₆ H ₁₈ S	242.1130 (242.1133)	6.17 (d)	6.40	7.00	7.14—7.34 (4H, m)	<i>c</i> -Hex ^{f)}	1.19—1.96 (10H, m), 2.14—2.26 (1H, m)
16f	C ₁₈ H ₂₄ S	272.1599 (272.1614)	6.19 (d)	6.39	7.01	7.16—7.39 (4H, m)	<i>n</i> -Oct	0.88 (3H, t), 1.20—1.56 (12H, m), 2.36 (2H, t)

a) $J_{3,4} = 5.5\text{--}5.9\text{ Hz}$. b) $J_{4,5} = 11.5\text{--}12.5\text{ Hz}$. c) $J_{3,2\text{-CH}} = 0\text{--}1.5\text{ Hz}$. d) $J_{8,9} = 6.5\text{--}7.5$, $J_{7,9} = 0\text{--}1.5\text{ Hz}$. e) *tert*-Butyl. f) Cyclohexyl.

TABLE III. Spectral Data for the Tellurachromenes (**13**) and Selenachromenes (**14**)

Compd. No.	Formula	HR-MS Calcd (Found)	3-H (d) ^{a)}	¹ H-NMR (400 MHz) (CDCl ₃) 4-H (d)	1'-H	Ar-H		R-H
13a	C ₁₁ H ₁₀ Te	271.9845 (271.9833)	5.65	6.35	6.17 (q) ^{b)}	7.09—7.15 (3H, m), 7.23 (1H, d) ^{c)}	Me	1.65 (3H, d)
13b	C ₁₄ H ₁₆ Te	314.0314 (314.0326)	5.75	6.12	6.15 (t)	6.91—7.05 (3H, m), 7.33 (1H, d)	<i>n</i> -Bu	0.91 (3H, t), 1.31—1.51 (4H, m), 1.87 (2H, dt)
13c	C ₁₄ H ₁₆ Te	314.0314 (314.0304)	5.75	6.12	6.32 (s)	6.93—7.05 (3H, m), 7.33 (1H, d)	<i>t</i> -Bu ^{d)}	1.15 (9H, s)
13d	C ₁₆ H ₂₀ Te	342.0627 (342.0635)	5.77	6.15	6.17 (t)	6.93—7.07 (3H, m), 7.35 (1H, d)	<i>n</i> -Hex	0.89 (3H, t), 1.25—1.50 (8H, m), 1.87 (2H, dt)
13e	C ₁₆ H ₁₈ Te	340.0478 (340.0497)	5.75	6.15	6.01 (d)	6.93—7.06 (3H, m), 7.34 (1H, d)	<i>c</i> -Hex ^{e)}	1.10—1.80 (11H, m)
13f	C ₁₈ H ₂₄ Te	370.0947 (370.0950)	5.77	6.14	6.17 (t)	6.95—7.07 (3H, m), 7.35 (1H, d)	<i>n</i> -Oct	0.88 (3H, t), 1.20—1.53 (12H, m), 1.86 (2H, dt)
14b	C ₁₄ H ₁₆ Se	264.0417 (264.0400)	6.06	6.21	5.73 (t)	7.00—7.11 (3H, m), 7.23 (1H, d)	<i>n</i> -Bu	0.95 (3H, t), 1.36—1.67 (4H, m), 1.88 (2H, dt)
14c	C ₁₄ H ₁₆ Se	264.0417 (264.0418)	6.00	6.14	5.77 (s)	6.98—7.04 (3H, m), 7.17 (1H, d)	<i>t</i> -Bu ^{d)}	1.19 (9H, s)
14d	C ₁₆ H ₂₀ Se	292.0730 (292.0699)	6.10	6.22	5.71 (t)	7.02—7.14 (3H, m), 7.25 (1H, d)	<i>n</i> -Hex	0.90 (3H, t), 1.23—1.55 (8H, m), 1.93 (2H, dt)
14e	C ₁₆ H ₁₈ Se	290.0574 (290.0977)	6.04	6.23	5.60 (d)	6.99—7.13 (3H, m), 7.23 (1H, d)	<i>c</i> -Hex ^{e)}	1.05—1.92 (11H, m)
14f	C ₁₈ H ₂₄ Se	320.1043 (320.1048)	6.05	6.20	5.77 (t)	6.98—7.13 (3H, m), 7.20 (1H, d)	<i>n</i> -Oct	0.89 (3H, t), 1.20—1.60 (12H, m), 1.84—1.90 (2H, m)

a) $J_{3,4} = 11.4\text{--}11.7\text{ Hz}$ for **13**; $10.6\text{--}10.8\text{ Hz}$ for **14**. b) $J_{1',1\text{'-CH}} = 7.0\text{ Hz}$. c) $J_{7,8} = 6.5\text{--}7.5\text{ Hz}$. d) *tert*-Butyl. e) Cyclohexyl.

benzometallopines.^{1,8)} In the $^1\text{H-NMR}$ spectra of the chromenes (**13**, **14**), nuclear Overhauser effect (NOE) was observed between 3-H and the exocyclic methylene proton (1'-H), indicating that the methylene moiety has the (*Z*)-stereochemistry. Phenyltellurol, generated *in situ* by sodium borohydride reduction of diphenyl ditelluride, is known to undergo stereospecific intermolecular *trans*-addition to phenylacetylene, forming (*Z*)-phenyl styryl telluride.²⁰⁾ This result clearly supports not only the present final cyclization reaction proceeding *via* the intermediate (**10**), but also the (*Z*)-structure of the 2-alkylidenechromenes (**13**, **14**).

As expected, the 2-alkylheteroepines (**11c**, **12c**, **16c**) having the bulkiest *tert*-butyl group are stable and can be kept for several weeks at room temperature without decomposition in solution, whereas the 2-methyl derivatives (**11a**, **12a**, **16a**) are unstable and gradually decomposed even during isolation, analogously with 1-⁶⁾ and 3-benzophosphepines,⁷⁾ 1-benzarsepines,¹⁾ and 3-benzotellurepines.¹⁵⁾ Such decomposition would account for the low isolated yields and the failure to isolate the 2-methylselenepine (**12a**). The heterochromenes (**13**, **14**) are also thermolabile and gradually decompose to give complex mixtures.

Recently, the tellurium chemistry involving application of tellurium reagents in organic synthesis and chemical transformation of organotellurium compounds has been widely studied.²¹⁾ Therefore, we next examined several reactions of the new tellurepine ring using the most stable compound, 2-*tert*-butyltellurepine (**11c**), as a representa-

tive compound.

Flash vacuum pyrolysis (FVP)¹⁾ of **11c** at 650 °C (1.0×10^{-5} mmHg) resulted in extrusion of Te to give 1-*tert*-butylnaphthalene (**18**) in 88% yield, by analogy with 1-benzosilepines and 1-benzophosphepine 1-oxides,¹⁾ which are thermally stable and remain unchanged even when heated at 180 °C in solvents, but undergo decomposition to naphthalene on FVP at 550–580 °C. Treatment of **11c** with a halogenating reagent (SO_2Cl_2 , Br_2 , or I_2) in hexane afforded the corresponding 1,1-dihalogenotellurepines (**19A–C**) (70–90% yields), which were dehalogenated on treatment with sodium sulfide, reverting to **11c** in high yields. Oxidation of **11c** with *m*-chloroperbenzoic acid (*m*-CPBA) gave the telluroxide (**20**), which was also obtained in high yield by treatment of **11c** with *N*-chlorosuccinimide (NCS) or *tert*-butyl hypochlorite (*tert*-BuOCl) followed by alkaline hydrolysis; similar oxidation of several alkyl aryl ditellurides has been reported.²²⁾ The deoxygenation of the oxide (**20**) was achieved by treatment with sodium methoxide in methanol, affording **11c**, probably *via* the unisolable 1,1-dimethoxy derivative. In addition, acetylation of the oxide (**20**) with acetic anhydride gave the 1,1-diacetoxy compound (**21**).

Treatment of **11c** with 2.2 mol eq of butyllithium in THF at –80 °C followed by addition of water or deuterium oxide produced (1*Z*,3*E*)-5,5-dimethyl-1-phenyl-1,3-hexadiene (**22**) or its *o*,4-dideuterio derivative (**22-D**) in high yield *via* the initial tellurium–lithium exchange reaction.²³⁾ On the basis of this result, methyl iodide was

Chart 4

used as an electrophile instead of water in the above reaction, with the aim of obtaining alkylative ring opening products, but only the elimination product, (Z)-5,5-dimethyl-1-phenyl-1-hexen-3-yne (**24**), was formed in 44% yield, presumably *via* the intermediate (**23**), and the expected dimethyl compound (**25**) was not obtained. However, alkylative ring opening²⁴ was achieved by the reaction of **11c** with methylmagnesium iodide in the presence of 1,3-bis(diphenylphosphino)propanenickel dichloride (NiCl₂ dppp), giving rise to the desired (1Z, 3E)-4,5,5-trimethyl-1-tolyl-1,3-hexadiene (**25**) in *ca.* 60% yield; its stereostructure was confirmed by NOE experiments.

Experimental

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. IR spectra were determined with a Hitachi 270-30 spectrometer. Mass spectra (MS) and HR-MS were recorded on a JEOL JMS-DX300 instrument. NMR spectra were determined with a JEOL PMX-60SI (60 MHz) or JEOL JNM-GSX 400 (400 MHz) spectrometer in CDCl₃ using tetramethylsilane as an internal standard unless otherwise stated, and spectral assignments were confirmed by spin-decoupling experiments. Microanalyses were performed in the Microanalytical Laboratory of this Faculty by Mrs. R. Igarashi and Miss K. Yakubo.

(Z)-4-Alkyl-1-(o-bromophenyl)-1-buten-3-yne (7a–g) General Procedure: Bis(triphenylphosphine)palladium dichloride (350 mg, 0.5 mmol) and copper(I) iodide (200 mg, 1.05 mmol) were added to a stirred mixture of (Z)-β-o-dibromostyrene (**5**)¹⁷ (13.1 g, 50 mmol) and an alkylacetylene (**6**) (60 mmol) in benzene–piperidine (1:1) (100 ml) at room temperature, and the mixture was heated at 50–60 °C with stirring. In the case of gaseous methylacetylene, a steady stream of this gas, generated *in situ* by treatment of 1,2-dibromopropane with potassium hydroxide, was passed through the mixture during the period of the reaction. The reaction was followed in terms of the disappearance of the spot of the starting **5** on TLC and was complete in 8–10 h. After cooling, cold water (100 ml) was added to the reaction mixture with stirring. The layers were separated and the aqueous layer was extracted with benzene (70 ml × 3). The combined organic layer was successively washed with water (100 ml × 3), 5% H₂SO₄ (100 ml × 2), saturated aqueous NaHCO₃ (100 ml × 2), and brine, then dried over MgSO₄ and concentrated *in vacuo*. The resulting reddish yellow oily residue was vacuum-distilled to give **7a–g** as pale yellow oils.

7a (4-Methyl): 77% yield, bp 98–100 °C (3 mmHg). IR (neat): 2204 (C≡C) cm⁻¹. ¹H-NMR (60 MHz) δ: 1.97 (3H, d, *J* = 2 Hz, 4-Me), 5.77 (1H, dq, *J* = 12, 2 Hz, 2-H), 6.87 (1H, d, *J* = 12 Hz, 1-H), 7.05–7.66 (3H, m, Ar-H), 8.33 (1H, dd, *J* = 7, 2 Hz, Ar-H). HR-MS *m/z*: M⁺ Calcd for C₁₁H₉Br: 219.9888, 221.9867. Found: 219.9868, 221.9843.

7b (4-*n*-Butyl): 94% yield, bp 126–128 °C (4 mmHg). IR (neat): 2204 (C≡C) cm⁻¹. ¹H-NMR δ: 0.87, 1.10–1.70, 2.33 [3H (t, *J* = 6 Hz), 4H (m), 2H (dt, *J* = 6, 3 Hz), 4-*n*-Bu], 5.81 (1H, dt, *J* = 12, 3 Hz, 2-H), 6.92 (1H, d, *J* = 12 Hz, 1-H), 6.90–7.65 (3H, m, Ar-H), 8.48 (1H, dd, *J* = 7, 2 Hz, Ar-H). HR-MS *m/z*: M⁺ Calcd for C₁₄H₁₅Br: 262.0357, 264.0337. Found: 262.0351, 264.0289.

7c (4-*tert*-Butyl): 93% yield, bp 108–110 °C (2 mmHg). IR (neat): 2208 (C≡C) cm⁻¹. ¹H-NMR δ: 1.27 (9H, s, 4-*tert*-Bu), 5.82 (1H, d, *J* = 12 Hz, 2-H), 6.92 (1H, d, *J* = 12 Hz, 1-H), 7.06–7.73 (3H, m, Ar-H), 8.42 (1H, dd, *J* = 7, 2 Hz, Ar-H). HR-MS *m/z*: M⁺ Calcd for C₁₄H₁₅Br: 262.0357, 264.0337. Found: 262.0352, 264.0328.

7d (4-*n*-Hexyl): 78% yield, bp 140–144 °C (2 mmHg). IR (neat): 2205 (C≡C) cm⁻¹. ¹H-NMR δ: 0.89, 1.10–1.77, 2.37 [3H (t, *J* = 5 Hz), 8H (m), 2H (dt, *J* = 6, 3 Hz), 4-*n*-Hex], 5.82 (1H, dt, *J* = 12, 3 Hz, 2-H), 6.91 (1H, d, *J* = 12 Hz, 1-H), 7.07–7.74 (3H, m, Ar-H), 8.38 (1H, dd, *J* = 7, 2 Hz, Ar-H). HR-MS *m/z*: M⁺ Calcd for C₁₆H₁₉Br: 290.0670, 292.0650. Found: 290.0666, 292.0627.

7e (4-Cyclohexyl): 93% yield, bp 148–150 °C (2 mmHg). IR (neat): 2200 (C≡C) cm⁻¹. ¹H-NMR δ: 1.0–2.0, 2.48–2.57 [10H (m), 1H (m), 4-cyclo-Hex], 5.78 (1H, dd, *J* = 12, 2 Hz, 2-H), 6.86 (1H, d, *J* = 12 Hz, 1-H), 7.10–7.70 (3H, m, Ar-H), 8.37 (1H, dd, *J* = 7, 2 Hz, Ar-H). HR-MS *m/z*: M⁺ Calcd for C₁₆H₁₇Br: 288.0514, 290.0493. Found: 288.0530, 290.0515.

7f (4-*n*-Octyl): 89% yield, bp 160–163 °C (2 mmHg). IR (neat): 2200 (C≡C) cm⁻¹. ¹H-NMR δ: 0.89, 1.08–1.81, 2.38 [3H (t, *J* = 6 Hz), 12H (m), 2H (dt, *J* = 6, 3 Hz), 4-*n*-Oct], 5.82 (1H, dt, *J* = 12, 3 Hz, 2-H), 6.90 (1H, d, *J* = 12 Hz, 1-H), 7.04–7.74 (3H, m, Ar-H), 8.38 (1H, dd, *J* = 7, 2 Hz, Ar-H). HR-MS *m/z*: M⁺ Calcd for C₁₈H₂₃Br: 318.0983, 320.0963. Found: 318.0969, 320.0970.

7g (4-Phenyl): 80% yield, bp 163–165 °C (3 mmHg). IR (neat): 2200 (C≡C) cm⁻¹. ¹H-NMR δ: 6.03 (1H, d, *J* = 12 Hz, 2-H), 7.05 (1H, d, *J* = 12 Hz, 1-H), 7.12–7.72 (8H, m, Ar-H), 8.43 (1H, dd, *J* = 8, 2 Hz, Ar-H). HR-MS *m/z*: M⁺ Calcd for C₁₆H₁₁Br: 282.0044, 284.0024. Found: 282.0026, 284.0022.

Di[o-(1-buten-3-ynyl)phenyl] Ditellurides (8a–f) General Procedure: A *tert*-butyllithium hexane solution (1.5 M, 14.7 ml, 22 mmol) was added dropwise over a 15 min period to a stirred solution of **7** (10 mmol) in anhydrous THF (50 ml) at –80 °C under an argon atmosphere, and the mixture was stirred for 1 h at the same temperature. The reaction mixture was allowed to warm to –40 °C and tellurium powder (1.27 g, 10 mmol) was added in one portion, then the mixture was warmed to room temperature over a 1 h period with stirring. Stirring was continued for an additional 1 h, then an aqueous solution (120 ml) of potassium ferricyanide (4.0 g, 12 mmol) was added to the reaction mixture. The whole was stirred for 30 min and extracted with ether (100 ml × 3). The combined extract was washed with brine, dried, and concentrated *in vacuo*. The residue was chromatographed on silica gel with hexane–benzene (1:1) to give the ditellurides (**8a–f**) as fed viscous oils.

8a (R = Me): 64% yield. IR (neat): 2200 (C≡C) cm⁻¹. ¹H-NMR (60 MHz) δ: 1.97 (6H, d, *J* = 2 Hz, Me × 2), 5.64 (2H, dq, *J* = 12, 2 Hz, 2-H × 2), 6.74 (2H, d, *J* = 12 Hz, 1-H × 2), 6.80–7.80 (8H, m, Ar-H). HR-MS *m/z*: M⁺ Calcd for C₂₂H₁₈Te₂: 541.9547. Found: 541.9561.

8b (R = *n*-Bu): 63% yield. IR (neat): 2200 (C≡C) cm⁻¹. ¹H-NMR δ: 0.91, 1.18–1.71, 2.18–2.55 [6H (t, *J* = 6 Hz), 8H (m), 4H (m), *n*-Bu × 2], 5.65 (2H, dt, *J* = 12, 3 Hz, 2-H × 2), 6.80 (2H, d, *J* = 12 Hz, 1-H × 2), 6.98–7.45 (4H, m, Ar-H), 7.88–8.18 (4H, m, Ar-H). HR-MS *m/z*: M⁺ Calcd for C₂₈H₃₀Te₂: 626.0486. Found: 626.0482.

8c (R = *tert*-Bu): 83% yield. IR (neat): 2200 (C≡C) cm⁻¹. ¹H-NMR δ: 1.24 (18H, s, *tert*-Bu × 2), 5.66 (2H, d, *J* = 12 Hz, 2-H × 2), 6.81 (2H, d, *J* = 12 Hz, 1-H × 2), 7.01–7.23 (4H, m, Ar-H), 7.89–8.21 (4H, m, Ar-H). HR-MS *m/z*: M⁺ Calcd for C₂₈H₃₀Te₂: 626.0486. Found: 626.0470.

8d (R = *n*-Hex): 62% yield. IR (neat): 2208 (C≡C) cm⁻¹. ¹H-NMR δ: 0.88, 1.06–1.79, 2.12–2.59 [6H (t, *J* = 6 Hz), 16H (m), 4H (m), *n*-Hex × 2), 5.65 (2H, dt, *J* = 12, 3 Hz, 2-H × 2), 6.79 (2H, d, *J* = 12 Hz, 1-H × 2), 6.96–7.37 (4H, m, Ar-H), 7.89–8.11 (4H, m, Ar-H). HR-MS *m/z*: M⁺ Calcd for C₃₂H₃₈Te₂: 682.1112. Found: 682.1132.

8e (R = cyclo-Hex): 69% yield. IR (neat): 2200 (C≡C) cm⁻¹. ¹H-NMR δ: 0.73–2.13, 2.30–2.81 [20H (m), 2H (m), cyclo-Hex × 2), 5.67 (2H, dd, *J* = 12, 2 Hz, 2-H × 2), 6.80 (2H, d, *J* = 12 Hz, 1-H × 2), 7.00–7.39 (4H, m, Ar-H), 7.90–8.16 (4H, m, Ar-H). HR-MS *m/z*: M⁺ Calcd for C₃₂H₃₄Te₂: 678.0799. Found: 678.0800.

8f (R = *n*-Oct): 55% yield. IR (neat): 2200 (C≡C) cm⁻¹. ¹H-NMR δ: 0.88, 1.02–1.58, 2.15–2.55 [6H (t, *J* = 5 Hz), 24H (m), 4H (m), *n*-Oct × 2], 5.67 (2H, dt, *J* = 12, 3 Hz, 2-H × 2), 6.79 (2H, d, *J* = 12 Hz, 1-H × 2), 7.00–7.40 (4H, m, Ar-H), 7.91–8.14 (4H, m, Ar-H). HR-MS *m/z*: M⁺ Calcd for C₃₆H₄₆Te₂: 738.1738. Found: 738.1744.

Di(o-1-buten-3-ynylphenyl) Diselenides (9a–f) The title compounds (**9**) were prepared from **7** (10 mmol) in a similar manner to that described for **8** using selenium powder (0.8 g, 10 mmol) instead of tellurium powder, and are reddish orange viscous oils except for **9e**.

9a (R = Me): 20% yield. IR (neat): 2200 (C≡C) cm⁻¹. ¹H-NMR (60 MHz) δ: 1.96 (6H, d, *J* = 2 Hz, Me × 2), 5.68 (2H, dq, *J* = 12, 2 Hz, 2-H × 2), 6.62 (2H, d, *J* = 12 Hz, 1-H × 2), 7.01–7.69 (2H, m, Ar-H), 7.69–8.10 (6H, m, Ar-H). HR-MS *m/z*: M⁺ Calcd for C₂₂H₁₈Se₂: 441.9738. Found: 441.9747.

9b (R = *n*-Bu): 85% yield. IR (neat): 2200 (C≡C) cm⁻¹. ¹H-NMR δ: 0.91, 1.14–1.73, 2.20–2.58 [6H (t, *J* = 6 Hz), 8H (m), 4H (m), *n*-Bu × 2], 5.67 (2H, dt, *J* = 12, 2 Hz, 2-H × 2), 6.78 (2H, d, *J* = 12 Hz, 1-H × 2), 7.02–7.40, 7.58–7.80, 8.04–8.30 [4H (m), 2H (m), 2H (m) Ar-H]. HR-MS *m/z*: M⁺ Calcd for C₂₈H₃₀Se₂: 526.0677. Found: 526.0651.

9c (R = *tert*-Bu): 68% yield. IR (neat): 2208 (C≡C) cm⁻¹. ¹H-NMR δ: 1.28 (18H, s, *tert*-Bu × 2), 5.74 (2H, d, *J* = 12 Hz, 2-H × 2), 6.98 (2H, d, *J* = 12 Hz, 1-H × 2), 7.11–7.44, 7.67–7.89, 8.17–8.38 [4H (m), 2H (m), 2H (m) Ar-H]. HR-MS *m/z*: M⁺ Calcd for C₂₈H₃₀Se₂: 526.0677. Found: 526.0666.

9d (R = *n*-Hex): 59% yield. IR (neat): 2205 (C≡C) cm⁻¹. ¹H-NMR

δ : 0.89, 1.07—1.74, 2.17—2.57 [6H (t, $J=5$ Hz), 16H (m), 4H (m), n -Hex $\times$ 2], 5.59 (2H, dt, $J=12$, 2 Hz, 2-H $\times$ 2), 6.81 (2H, d, $J=12$ Hz, 1-H $\times$ 2), 7.11—7.47, 7.67—7.87, 8.12—8.34 [4H (m), 2H (m), 2H (m), Ar-H]. HR-MS m/z : M^+ Calcd for $C_{32}H_{38}Se_2$: 582.1303. Found: 582.1303.

9e (R=cyclo-Hex): 68% yield, yellow prisms (from EtOH), mp 54—55°C. MS m/z : 578 (M^+). 1H -NMR δ : 0.69—2.12, 2.25—2.85 [20H (m) and 2H (m), cyclo-Hex $\times$ 2], 5.69 (2H, dd, $J=12$, 2 Hz, 2-H $\times$ 2), 6.90 (2H, d, $J=12$ Hz, 1-H $\times$ 2), 7.05—7.29, 7.60—7.85, 8.11—8.39 [4H (m), 2H (m), 2H (m), Ar-H]. Anal. Calcd for $C_{32}H_{34}Se_2$: C, 66.42; H, 5.93. Found: C, 66.41; H, 6.11.

9f (R= n -Oct): 53% yield. IR (neat): 2200 ($C\equiv C$) cm^{-1} . 1H -NMR δ : 0.89, 1.09—1.67, 2.22—2.50 [6H (t, $J=5$ Hz), 24H (m), 4H (m), n -Oct $\times$ 2], 5.71 (2H, dt, $J=12$, 2 Hz, 2-H $\times$ 2), 6.93 (2H, d, $J=12$ Hz, 1-H $\times$ 2), 7.10—7.46, 7.64—7.86, 8.12—8.32 [4H (m), 2H (m), 2H (m), Ar-H]. HR-MS m/z : M^+ Calcd for $C_{36}H_{46}Se_2$: 638.1929. Found: 638.1939.

Treatment of the Ditellurides (8) with Sodium Borohydride: Formation of the 1-Benzotellurepines (11) and 2-Alkylidene-2H-tellurachromenes (13) General Procedure: $NaBH_4$ (200 mg, ca. 5 mmol) was added in small portions to a stirred solution of **8** (1 mmol) in THF-EtOH (1:1) (20 ml) at room temperature under an argon atmosphere, and then the solution was heated at 55—60°C with stirring. The reaction was followed in terms of the disappearance of the starting **8** on TLC and was complete in 5—10 h. After cooling, ice-water (50 ml) was added to the reaction solution and the whole was extracted with hexane (50 ml $\times$ 3). The combined extract was washed with brine, dried, and concentrated *in vacuo*. The residue was chromatographed on silica gel with hexane to give **11** and **13** successively, in the yields given in Table I. HR-MS and 1H -NMR spectral data for **11a—f** and **13a—f** are listed in Tables II and III, respectively.

Treatment of the Diselenides (9) with Sodium Borohydride: Formation of the 1-Benzoselenepines (12) and 2-Alkylidene-2H-selenachromenes (14) The diselenides (**9**) (1 mmol) were treated with $NaBH_4$ and worked up as described for **8** to give **12** and **14**, except for the methyl-substituted diselenide (**9a**), which afforded a complex mixture, and neither benzoselenepine (**12a**) nor selenachromene (**14a**). Yields and spectral (HR-MS and 1H -NMR) data for **12b—f** and **14b—f** thus obtained are listed in Tables I, II, and III.

1-Benzothiepinines (16) General Procedure: A *tert*-butyllithium pentane solution (1.5 M, 14.7 ml, 22 mmol) was added dropwise to a stirred solution of **7** (10 mmol) in anhydrous THF (40 ml) at $-80^\circ C$ under an argon atmosphere and the mixture was stirred for 1 h at the same temperature. After addition of sublimed sulfur powder (320 mg, 10 mmol), the mixture was allowed to warm to room temperature over a 2 h period with stirring, and then EtOH (10 ml) was added to the mixture. The mixture was heated at 55°C with stirring for 2—4 h, and then poured into ice water (100 ml) and the whole was extracted with ether (100 ml $\times$ 3). The combined extract was washed with brine, dried, and concentrated *in vacuo*. The residue was chromatographed on silica gel with hexane to give **16** in the following yields: **16a**: 5%; **16b**: 16%; **16c**: 25%; **16d**: 18%; **16e**: 15%; **16f**: 18%. HR-MS and 1H -NMR spectral data for **16** are listed in Table II. In the reaction, no thiachromene derivatives (**17**) could be isolated.

Flash Vacuum Pyrolysis of 11c Compound **11c** (50 mg) was vaporized under reduced pressure (1.0×10^{-5} mmHg) and pyrolyzed¹¹ through a hot zone (quartz tube: i.d. = 1 cm, l = 20 cm) heated at 650°C in a pyrolysis furnace. The pyrolyzate was collected in a trap cooled with liquid N_2 and chromatographed on silica gel with hexane to give 1-(*tert*-butyl) naphthalene (**18**):²⁵ 26 mg, 88% yield.

1,1-Dihalogeno-2-*tert*-butyl-1-benzotellurepines (19A—B) General Procedure: A 1.1 mol eq amount of SO_2Cl_2 (30 mg), Br_2 (36 mg), or I_2 (56 mg) was added to a solution of **11c** (63 mg, 0.2 mmol) in hexane (30 ml) with stirring in an ice bath, and the mixture was stirred for 1—2 h at 0—5°C. The resulting precipitates were collected by filtration, washed with hexane, and recrystallized from hexane-benzene (1:1) to give **19**.

19A (1,1-Dichloro): 62 mg, 90% yield, pale yellow prisms, mp 155—158°C. 1H -NMR (400 MHz) δ : 1.59 (9H, s, *tert*-Bu), 6.27 (1H, dd, $J=13.9$, 9.2 Hz, 4-H), 6.73 (1H, d, $J=13.9$ Hz, 5-H), 7.19 (1H, d, $J=9.2$ Hz, 3-H), 7.43—7.53 (3H, m, Ar-H), 7.79 (1H, d, $J=7$ Hz, 9-H). Anal. Calcd for $C_{14}H_{16}Cl_2Te$: C, 43.93; H, 4.21. Found: C, 44.17; H, 4.21.

19B (1,1-Dibromo): 75 mg, 79% yield, yellow prisms, mp 173—176°C. 1H -NMR (400 MHz) δ : 1.60 (9H, s, *tert*-Bu), 6.23 (1H, dd, $J=13.9$,

9.2 Hz, 4-H), 6.71 (1H, d, $J=13.9$ Hz, 5-H), 7.12 (1H, d, $J=9.2$ Hz, 3-H), 7.39—7.54 (3H, m, Ar-H), 7.92 (1H, dd, $J=7.7$, 1.5 Hz, 9-H). Anal. Calcd for $C_{14}H_{16}Br_2Te$: C, 35.65; H, 3.42. Found: C, 35.70; H, 3.39.

19C (1,1-Diodo): 77 mg, 68% yield, red prisms, mp 140—142°C. 1H -NMR (400 MHz) δ : 1.30 (9H, s, *tert*-Bu), 6.38 (1H, dd, $J=13.2$, 6.2 Hz, 4-H), 6.79 (1H, d, $J=13.2$ Hz, 5-H), 7.04 (1H, d, $J=6.2$ Hz, 3-H), 7.32—7.47 (3H, m, Ar-H), 7.74 (1H, dd, $J=7.7$, 1.5 Hz, 9-H). Anal. Calcd for $C_{14}H_{16}I_2Te$: C, 29.73; H, 2.85. Found: C, 30.00; H, 2.91.

Dehalogenation of 19 with Sodium Sulfide General Procedure: A 2% aqueous Na_2S solution (5 ml) was added to a solution of **19** (20 mg) in hexane (5 ml) with vigorous stirring in an ice bath. After stirring for a further 10 min, water (10 ml) was added to the reaction mixture, and the whole was extracted with CH_2Cl_2 (20 ml $\times$ 3). The combined extract was dried and concentrated *in vacuo*. The residue was chromatographed on silica gel with hexane to give 2-*tert*-butyl-1-benzotellurepine (**11c**). From **19A**: 14 mg, 86% yield. From **19B**: 12 mg, 91% yield. From **19C**: 11 mg, 97% yield.

2-*tert*-Butyl-1-benzotellurepine 1-Oxide (20) i) Reaction of **11c** with *m*-CPBA: *m*-CPBA (54 mg, 0.42 mmol) was added to a stirred solution of **11c** (63 mg, 0.2 mmol) in CH_2Cl_2 (10 ml) at room temperature. After having been stirred for 6 h, the reaction mixture was successively washed with saturated aqueous $NaHCO_3$ and brine, then dried and concentrated to dryness *in vacuo*. The resulting solid residue was recrystallized from CH_2Cl_2 -hexane to give **20**: 59 mg, 90% yield, colorless prisms, mp 142—145°C (dec.). 1H -NMR (400 MHz) δ : 1.35 (9H, s, *tert*-Bu), 6.44 (1H, dd, $J=12.5$, 5.5 Hz, 4-H), 6.56 (1H, d, $J=5$ Hz, 3-H), 7.14 (1H, d, $J=12.5$ Hz, 5-H), 7.40—7.66 (3H, m, Ar-H), 8.02 (1H, d, $J=7.7$ Hz, 9-H). MS m/z : 330 (M^+). Anal. Calcd for $C_{14}H_{16}OTe$: C, 51.28; H, 4.92. Found: C, 51.21; H, 4.81.

ii) Reaction of **11c** with NCS: NCS (28 mg, 0.21 mmol) was added to a stirred solution of **11c** (63 mg, 0.2 mmol) in CH_2Cl_2 -MeOH (1:1) (6 ml) and the mixture was stirred for 1 h in an ice bath. After addition of CH_2Cl_2 (20 ml) and 10% aqueous NaOH (1 ml), the mixture was stirred for 20 min at room temperature, and then washed with brine, dried, and concentrated to dryness *in vacuo*. The solid residue was recrystallized from CH_2Cl_2 -hexane to give **20**: 61 mg, 92% yield.

iii) Reaction of **11c** with *tert*-Butyl hypochlorite: *tert*-BuOCl (24 mg, 0.22 mmol) was added to a stirred solution of **11c** (63 mg, 0.2 mmol) in CH_2Cl_2 -MeOH (1:1) (6 ml) and the mixture was stirred for 1 h in an ice bath. After addition of 10% aqueous NaOH (1 ml) and CH_2Cl_2 (15 ml), the mixture was stirred for 15 min at room temperature, then washed with brine, dried, and evaporated to dryness *in vacuo*. The solid residue was recrystallized from CH_2Cl_2 -hexane to give **20**: 64 mg, 96% yield.

Reaction of 20 with Acetic Anhydride A mixture of **20** (66 mg) and Ac_2O (5 ml) was stirred for 15 h at room temperature, and then evaporated to dryness *in vacuo*. The resulting solid residue was recrystallized from Et_2O -hexane to give 1,1-diacetoxy-2-*tert*-butyl-1-benzotellurepine (**21**): 82 mg, 95% yield, colorless prisms, mp 150—153°C (dec.). IR (KBr): 1634 ($C=O$) cm^{-1} . 1H -NMR (400 MHz) δ : 1.46 (9H, s, *tert*-Bu), 1.92 (6H, s, OAc), 6.17 (1H, dd, $J=13.9$, 8.4 Hz, 4-H), 6.67 (1H, d, $J=13.9$ Hz, 5-H), 7.17 (1H, d, $J=8.4$ Hz, 3-H), 7.41—7.50 (3H, m, Ar-H), 8.09 (1H, d, $J=7.5$ Hz, 9-H). Anal. Calcd for $C_{18}H_{22}O_4Te$: C, 55.28; H, 5.16. Found: C, 50.40; H, 5.02.

Treatment of 11c with Butyllithium and H_2O (or D_2O) A butyllithium hexane solution (1.66 M, 0.66 ml, 1.1 mmol) was added to a solution of **11c** (156 mg, 0.5 mmol) in anhydrous THF (4 ml) with stirring at $-80^\circ C$ under an argon atmosphere and the mixture was stirred for 30 min at the same temperature. The reaction mixture was allowed to warm to room temperature over a 1 h period with stirring, then H_2O or D_2O (0.5 ml) was added to the mixture. After having been stirred for 30 min, the mixture was diluted with hexane (20 ml), then washed with brine, dried, and concentrated *in vacuo*. The residue was chromatographed on silica gel with hexane to give (1Z,3E)-5,5-dimethyl-1-phenyl-1,3-hexadiene (**22**) or its *o*,4-dideuterio compound (**22-D**) as a colorless oil.

22: 65 mg, 70% yield. MS m/z : 186 (M^+). 1H -NMR (400 MHz) δ : 1.05 (9H, s, *tert*-Bu), 5.90 (1H, d, $J=15.4$ Hz, 4-H), 6.21 (1H, dd, $J=11.4$, 11.4 Hz, 2-H), 6.32 (1H, d, $J=11.4$ Hz, 1-H), 6.57 (1H, dd, $J=15.4$, 11.4 Hz, 3-H), 7.21—7.34 (5H, m, Ar-H). HR-MS m/z : M^+ Calcd for $C_{14}H_{18}$: 186.1408. Found: 186.1412.

22-D: 85 mg, 86% yield. MS m/z : 188 (M^+ for $C_{14}H_{16}D_2$). 1.04 (9H, s, *tert*-Bu), 6.20 (1H, dd, $J=11.4$, 11.4 Hz, 2-H), 6.32 (1H, d, $J=11.4$ Hz, 1-H), 6.55 (1H, d, $J=11.4$ Hz, 3-H), 7.24—7.31 (4H, m, Ar-H).

Treatment of 11c with Butyllithium and Methyl Iodide Compound

11c (156 mg, 0.5 mmol) was treated with BuLi (1.1 mmol) and worked up as described for the formation of **22** from **11c** using MeI (0.5 ml, 8 mmol) instead of H₂O to give (*Z*)-5,5-dimethyl-1-phenyl-1-hexen-3-yne (**24**): 40 mg, 44% yield, colorless oil. IR (neat): 2208 (C≡C) cm⁻¹. ¹H-NMR (60 MHz) δ: 1.30 (9H, s, *tert*-Bu), 5.73 (1H, d, *J* = 12 Hz, 2-H), 6.55 (1H, d, *J* = 12 Hz, 1-H), 7.1–7.4 (3H, m, Ar-H), 7.8–8.0 (2H, m, Ar-H). HR-MS *m/z*: M⁺ Calcd for C₁₄H₁₆: 184.1252. Found: 184.1253.

Treatment of 11c with Methylmagnesium Iodide A solution of MeMgI, prepared from Mg (802 mg, 33 mmol) and MeI (4.26 g, 30 mmol) in a usual manner, in anhydrous THF (25 ml) was added dropwise to a mixture of **11c** (94 mg, 0.3 mmol) and NiCl₂ dppp [NiCl₂(Ph₂PCH₂CH₂CH₂PPh₂)] (16.2 mg, 0.03 mmol) in anhydrous benzene (20 ml) with stirring at ca. 70 °C, and then the mixture was refluxed for 6 h. After the mixture had cooled, water (30 ml) was added to it and the whole was extracted with hexane (50 ml × 3). The combined extract was washed with brine, dried, and concentrated *in vacuo*. The residue was chromatographed on silica gel with hexane to give (1*Z*,3*E*)-4,5,5-trimethyl-1-tolyl-1,3-hexadiene (**25**): 36 mg, 56% yield, colorless oil. ¹H-NMR (400 MHz) δ: 1.04 (9H, s, *tert*-Bu), 1.84 (3H, d, *J* = 1.1 Hz, 4-Me), 2.28 (3H, s, Ph-Me), 6.27 (1H, dq, *J* = 11.0, 1.1 Hz, 3-H), 6.34 (1H, d, *J* = 11.4 Hz, 1-H), 6.53 (1H, dd, *J* = 11.0, 11.4 Hz, 2-H), 7.15–7.29 (4H, m, Ar-H). HR-MS *m/z*: M⁺ Calcd for C₁₆H₂₂: 214.1721. Found: 214.1715.

References and Notes

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