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Sequential Pericyclic Reaction of Unsaturated Xanthates. Intramolecular Cycloaddition Selectivity of the 2,4-Alkadienyl 2-Alkenyl Sulfides

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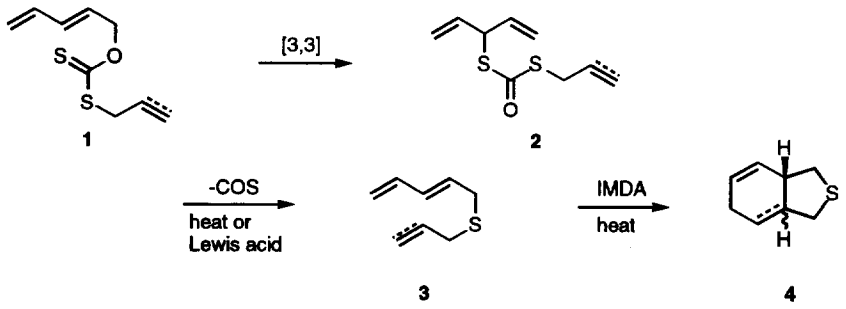
Abstract: Heating of *S*-(1-vinyl-2-alkenyl) *S*-(2-alkenyl or alkynyl) dithiocarbonates (dithiolcarbonates) derived from [3,3]-sigmatropic rearrangement of *O*-(2,4-alkadienyl) *S*-(2-alkenyl or alkynyl) dithiocarbonates (xanthates) gave the 2,4-alkadienyl 2'-(alkenyl or alkynyl) sulfides, which then underwent intramolecular Diels-Alder cycloaddition to give hydrobenzo[c]thiophene derivatives. The thermal cyclizations of *O*-(2,4-pentadienyl) derivatives of xanthate afforded mixtures of the cycloadducts, in which the *cis*-FUSED products slightly predominated over the *trans*-isomers. The selectivity of IMDA reactions is discussed based on the *ab initio* calculation data.

We have previously described a one-pot synthetic method of allylic sulfides.[1] The reaction involves two-step sequential pericyclic reactions; allylic xanthates (**1**) undergo [3,3]-sigmatropic rearrangement to give allylically isomerized dithiolcarbonates (**2**), which decompose into the allylically rearranged sulfides (**3**) with extrusion of carbon oxysulfide (COS) upon heating under more severe reaction conditions.



Scheme 1

The extrusion reaction was enhanced dramatically by use of Lewis acid (*e.g.* $EtAlCl_2$), in which the nature of the concerted reaction mechanism was not changed. Based on *ab initio* [2] MO study, we have concluded that the extrusion reaction falls into category of retro-ene type reaction.[3]

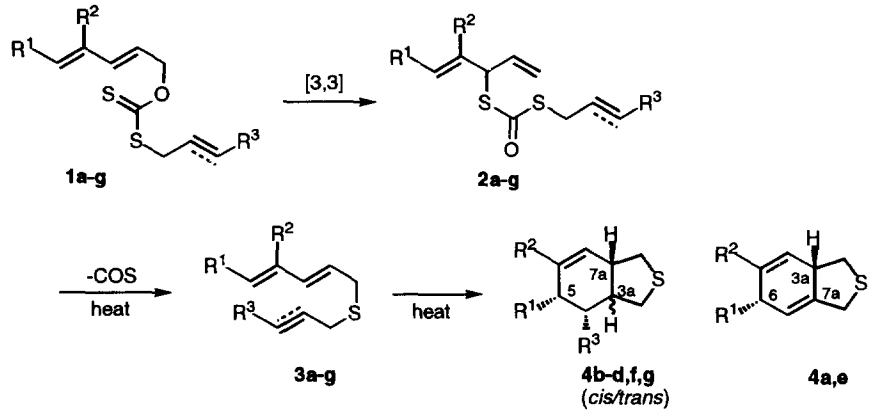
Coupling of this reaction with intramolecular Diels-Alder (IMDA) reaction[4] provides a simple synthetic method of hydrobenzo[*c*]thiophenes (**4**) *via* three-step sequential pericyclic reactions of *O*-(2,4-alkadienyl) *S*-(2-alkenyl) dithiocarbonates (**1**).[5] In order to establish the reaction as a general synthetic method, the stereochemical features must be well studied as the reactivity and selectivity of the reactions strongly depend upon the nature of the substrates.

To show the utility of the sequential reactions, we examined the thermal and Lewis-acid catalyzed cyclizations of newly obtained *O*-(4,5-substituted-2,4-pentadienyl) *S*-(2-alkenyl or 2-alkynyl) dithiocarbonates

(**1a-i**). We also describe herein the results of MO analysis of the IMDA reaction.

RESULTS

Thermolysis of the rearranged product **2a** of *O*-(5-phenyl-2,4-pentadienyl) *S*-propargyl dithiocarbonate (**1a**) in refluxing *o*-dichlorobenzene gave a single product as a colorless oil. The ^{13}C-NMR spectrum showed four sp^3 (two methines and two methylenes) and four sp^2 carbon signals except for phenyl group, indicating that the IMDA reaction had occured to give tetrahydrobenzo[*c*]thiophene **4a**. The ^{1}H-NMR spectrum of **4a** exhibited three olefinic proton signals at 5.53-5.88 ppm.



Scheme 2

Next, heating of *O*-(5-phenyl-2,4-pentadienyl) *S*-allyl dithiocarbonate (**1b**) in refluxing *o*-dichlorobenzene gave a colorless oil with extrusion of COS gas. The ^{13}C-NMR spectrum showed a duplicated signal pattern, suggesting that the product was a mixture of *cis*- and *trans*-FUSED cycloadducts (*cis*-**4b** and *trans*-**4b**). Stereochemistry of the individual cycloadducts was assigned by ^{1}H-NMR and ^{1}H-^{1}H COSY spectra. The spectrum of *cis*-**4b** indicated the presence of a correlation peak (J=4.4 Hz) between 7-H and 7a-H, whereas the correlation peak was not observed in *trans*-**4b**. To ascertain the difference of splitting patterns between *cis*-**4b** and *trans*-**4b**, we estimated the coupling constants between the 7-H and 7a-H on the basis of the dihedral angles (ϕ) of the MNDO-PM3[6] optimized structures of the parent molecules. The ground-state structures of *cis*- and *trans*-FUSED adducts are depicted in Figure 1. The calculated geometry for *trans*-FUSED adduct was approximately in accordance with that of X-ray structure for the sulfone derivative of **4k**.[5] In the case of *cis*-FUSED adduct, the coupling constant was estimated to be *ca.* 3 Hz (ϕ=53.4°) by means of Karplus equation. On the other hand, the coupling constant for *trans*-FUSED adduct was essentially zero (ϕ=92.0°). The observed J value is well consistent with calculated one. The *cis*- and *trans*-3a-methine protons of **4b** resonated at 2.60-2.65 and 1.77-1.80 ppm, respectively. The latter is considerably higher than that observed in the former. This may be due to the shielding effect of the *syn* oriented 5-phenyl group. Therefore, it is apparent that the major product (**4b**) of the IMDA reaction of **3b** possesses *cis* ring fusion. Inspection of 7-H signals indicated that *cis:trans* product ratio was 65:35.

When the extrusion reaction of **2b** was carried out in the presence of $EtAlCl_2$ at 0 °C, the yield of 5-phenyl-2,4-pentadienyl allyl sulfide (**3b**) was only 12%.

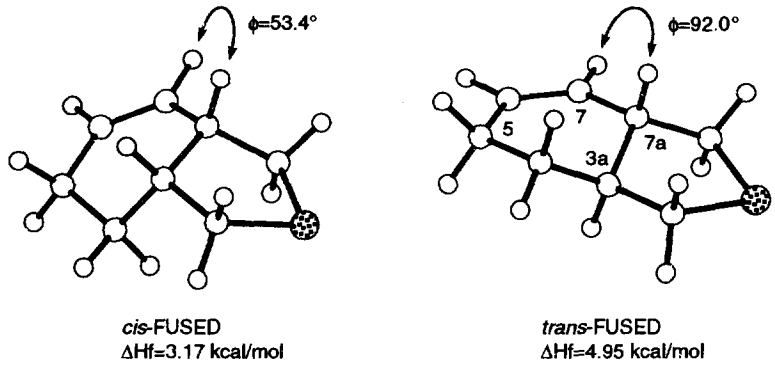


Figure 1 PM3-Calculated Ground-State Structures of *cis*- and *trans*-FUSED IMDA Adducts

In the same way, dithiolcarbonates (**2c-g**) gave the *cis/trans* mixture of FUSED adducts, among which the *cis*-FUSED products predominated slightly (see Table 1). The low selectivity is due to the high reaction temperatures requierd for the present system.

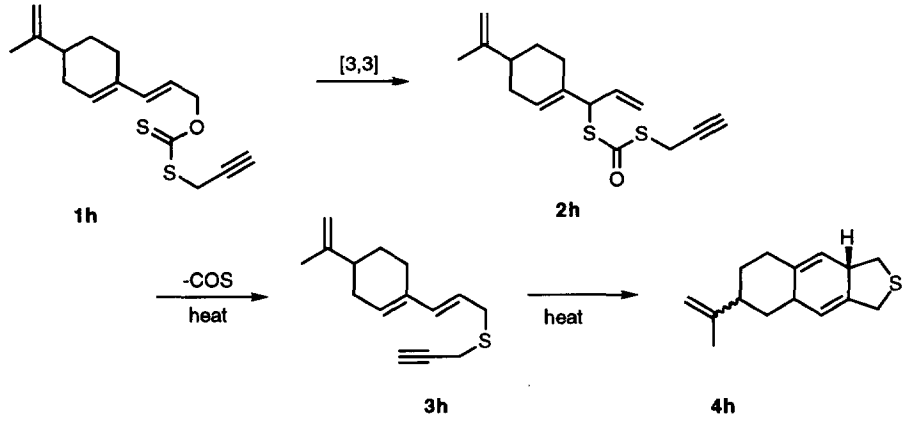
Electron-withdrawing substituents on the terminal carbon atom of dienophilic moiety have a little effect on the stereoselectivity of the uncatalyzed IMDA reaction (see exp. 5 and 11). Especially in **2k**, *trans*-FUSED adduct was formed preferentially (see exp. 15). Lewis acid catalysts dramatically enhanced the *trans* selectivity. The dithiolcarbonate (**2k**) was treated with equimolar amount of $MeAlCl_2$ at room temperature to give a mixture of FUSED adducts in the ratio of *cis* : *trans* being 2 : 98.

Table 1. Products from Sequential Pericyclic Reactions of the *O*-(2,4-Alkadienyl) *S*-(2-Alkynyl and 2-Alkenyl) Xanthates (**1**) with/without Catalyst

Exp. No.	Xanthate (1) R^1	R^2	$(CH_2)_nCH=CHR^3$ or $CH_2C\equiv CH$	Temp. (°C)	Cat. (mol)	Time (h)	Product[a] (Yield %)	*cis:trans* ratio
1	Ph	H	$CH\equiv CCH_2$ - (**1a**)	180[b]		5	**4a** (46)	-
2	Ph	H	CH_2=$CHCH_2$- (**1b**)	180[b]		5	**4b** (46)	65:35
3	Ph	H	CH_2=$CHCH_2$- (**1b**)	0[c]	$EtAlCl_2$(1.0)	5	**3b** (12)	
4	Ph	H	CH_2=$CHCH_2$- (**1b**)	130	PNP(0.5)[d]	1	**4b** (8)	67:33
5	Ph	H	$EtCO_2CH$=$CHCH_2$- (**1c**)[e]	180[b]		5	**4c** (85)	52:48
6	H	Me	CH_2=$CHCH_2$- (**1d**)	200		12	**4d** (28)	80:20
7	Ph	Me	$CH\equiv CCH_2$ - (**1e**)	180[b]		5	**4e** (40)	-
8	Ph	Me	$CH\equiv CCH_2$ - (**1e**)	100	PNP(0.5)[d]	1.5	**4e** (23)	-
9	Ph	Me	$CH\equiv CCH_2$ - (**1e**)	0[c]	$MeAlCl_2$(1.0)	5	**3e** (28)	
10	Ph	Me	CH_2=$CHCH_2$- (**1f**)	180[b]		5	**4f** (65)	65:35
11	Ph	Me	$EtCO_2CH$=$CHCH_2$- (**1g**)[e]	180[b]		5	**4g** (77)	52:48
12	perillyl[f]		$CH\equiv CCH_2$ - (**1h**)	180[b]		5	**4h** (60)	52:48
13	Me	H	CH_2=$CHCH_2CH_2$- (**1i**)	200		1	**3i** (75)	
14[g]	Me	H	CH_2=$CHCH_2$- (**1j**)	200		[h]	**4j** (59)	72:28[i]
15[g]	Me	H	$EtCO_2CH$=$CHCH_2$- (**1k**)[e]	200		[h]	**4k** (60)	43:57
16[g]	Me	H	$EtCO_2CH$=$CHCH_2$- (**1k**)[e]	rt[c]	$MeAlCl_2$(1.0)	4	**4k** (46)	2:98

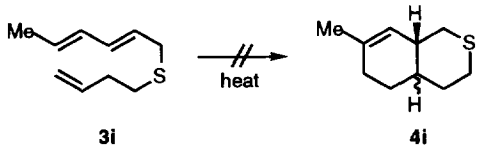
a) Isolated yields. b) Refluxed in *o*-dichlorobenzene. c) In $CHCl_3$. d) *p*-nitrophenol e) *trans* -form
f) $-CH_2CH(i\text{-}C_3H_5)(CH_2)_2$- g) See ref. 4. h) Pyrolyzed under reduced pressure. i) See ref. 7.

For further investigation of the IMDA reaction, the dithiolcarbonate (**2h**), which would form tricyclic ring system, was prepared from the corresponding alcohol (perillyl alcohol) using propargyl bromide (Scheme 3). Exposure of **2h** to refluxing *o*-dichlorobenzene for 5 hr resulted in moderate yield of desired FUSED adduct **4h** as a colorless oil.



Scheme 3

Heating the dithiolcarbonate **2i** at 200 °C caused evolution of COS gas to afford the sulfide (**3i**) in 75 % yield. However, the IMDA reaction of **3i**, which would form six-membered ring, did not occur under the condition tried.



Scheme 4

DISCUSSION

The experimental data showed that the *cis*-FUSED IMDA adducts were formed predominantly under thermolytic conditions except for **2k**. In order to understand the observed stereoselectivity for the IMDA reaction, we carried out MO calculations on possible geometries for the transition states of 2,4-pentadienyl allyl sulfide (**3x**) and its derivatives (**3b**, **3d**, **3j** and **3k**). The results are summarized in Table 2. The *ab initio* and PM3 transition states were located by the TS option, which were characterized by the presence of a single negative Hessian eigenvector. For sulfide **3j**, two possible conformations (*syn-* and *anti*-**TS**) leading to the *cis* and *trans*-FUSED rings are depicted in Figure 2. In RHF/6-31G* calculation of **3x**, the total energy (*E*) of *syn*-**TS** is about 0.3 kcal/mol lower than the *anti*-**TS** leading to *trans*-adduct. For other sulfides (**3b** ,**d** ,**x**), the same trend was observed regardless of the existance of substituents. These results are well in accordance with the observed selectivity (see exp. 2, 6 and 14 in Table 1). However, the PM3 calculation could not reproduce the relative stability, which might be due to neglect of contributions of *3d*-orbitals.[6]

Table 2. Energies (E)[a] and Relative Energies (ΔE)[b] of Transition-States for IMDA Reactions of 4- or 5-Substituted-2,4-pentadienyl Allyl Sulfides

	RHF/3-21G*			RHF/6-31G*			PM3		
Sulfide	*E (syn)*	*E(anti)*	*ΔE*	*E(syn)*	*E(anti)*	*ΔE*	*ΔHf(syn)*	*ΔHf(anti)*	*ΔΔHf*[c]
3b	-932.02421	-932.02380	0.26				99.93	99.39	-0.54
3d				-746.33586	-746.33525	0.38	66.63	66.10	-0.53
3j	-742.57366	-742.57295	0.44	-746.33713	-746.33675	0.24	67.55	66.94	-0.61
3k' [d]	-929.15181	-929.15045	0.85	-933.96507	-933.96566	-0.37	-21.19	-21.25	-0.06
3x				-707.29971	-707.29924	0.30	76.25	75.74	-0.51

a) au b) $\Delta E=E_{(anti\text{-}TS)}-E_{(syn\text{-}TS)}$, kcal/mol c) $\Delta\Delta Hf=\Delta Hf_{(anti\text{-}TS)}-\Delta Hf_{(syn\text{-}TS)}$, kcal/mol d) Free carboxylic acid of **3k**.

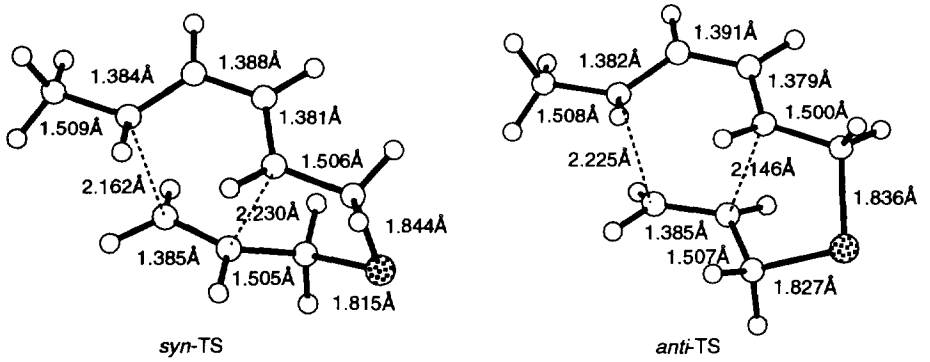


Figure 2 RHF/6-31G* Calculated Transition-State Geometries for IMDA Reaction of Sulfide **3j**.

Introduction of an ethoxycarbonyl group into the terminal carbon of the allylic moiety changed the stereoselectivity of the uncatalyzed IMDA reaction. The RHF/6-31G* optimized TS structures (**3k'**) indicate that the *anti*-**TS** is about 0.4 kcal/mol more stable than the *syn*-**TS**.

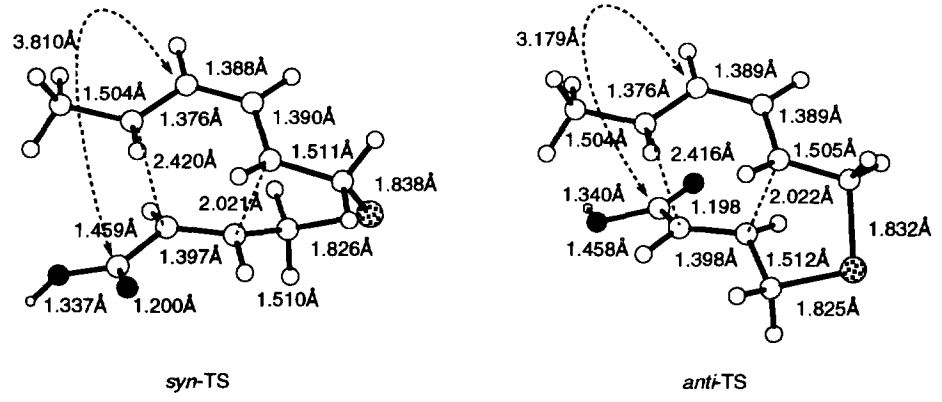


Figure 3 RHF/6-31G* Calculated Transition-State Geometries for IMDA Reaction of Sulfide **3k'**.

The preference of the *anti*-**TS** is considered to be due to the secondary orbital overlap between the carbonyl group and the diene, wherein the nonbonded distance between the C4 and the carbonyl carbon is estimated to be 3.179 Å (Figure 3). Change of substituent on the C5-position of the diene from methyl to phenyl increases a steric interaction between the substituents, which cancels the secondary orbital interaction for the *anti*-**TS**.

In the presence of Lewis acid catalysts, the *trans*-FUSED adducts were formed predominantly (see exp. 16). The orbital interaction of *anti*-**TS** must be intensified by coordination of Lewis acid to the carbonyl group (Figure 4).

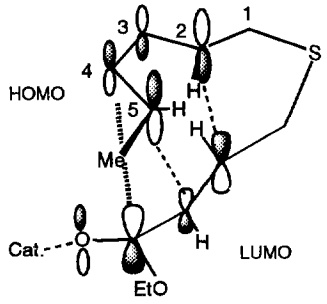


Figure 4 Secondary Orbital Interaction for Sulfide **3k**

Table 3. PM3 Calculated Thermodynamic Parameters for IMDA Reactions of Sulfides

Sulfide	$\Delta H^{\ddagger}$(kcal/mol)	$\Delta S^{\ddagger}$(cal/mol•K)[a]
3x	29.8	-22.6
3i	30.5	-28.1

a) at 300 K

The $\Delta H^{\ddagger}$ for the IMDA reaction of 2,4-pentadienyl 3-butenyl sulfide (**3i**), which would form six-memberd 2-thiaoctalin ring, is estimated to be 30.5 kcal/mol by PM3, 0.7 kcal/mol higher than that for sulfide **3x**, whereas the $\Delta S^{\ddagger}$ is sizably decreased responsible for the decrease of the degrees of freedom of motion (Table 3). These results show that the increase of a methylene unit of the chain connecting the diene and dienophilic moiety results in decrease of the IMDA reactivity.

In summary, the 2,4-alkadienyl sulfides can be prepared by the sequential pericyclic reaction of *O*-(2,4-alkadienyl) xanthates. The thermal IMDA cyclization of the sulfides gave hydrobenzo[*c*]thiophenes, in which *cis*-FUSED isomer was formed predominantly. Introduction of an ester group into the dienophilic moiety resulted in stereoselective formation of the *trans*-FUSED isomers due to the enhanced secondary orbital interaction.

Further use of these sequential pericyclic reactions are currently under investigation.

EXPERIMENTAL

The IR spectra were taken with a Hitachi 270-30 spectrophotometer. The ^{1}H-NMR spectra were taken with JEOL JNM-EX 270 (270 MHz) and GX-400 (400 MHz) spectrometers using TMS as an internal standard and the chemical shifts are expressed in δ values. The coupling constants (*J*) are presented in Hz. High resolution mass spectra (HRMS) were taken with a JEOL JMS-DX303HF spectrometer. MO calculations were performed on a Fujitsu S4/10 and Convex SPP-1000/XA8 engineering workstations.

Preparation of Potassium *O*-(2,4-Alkadienyl) Dithiocarbonates (General Procedure) A suspention of 2,4-alkadienol (0.04 mmol), CS_2 (0.04 mmol) and KOH (0.04 mmol) in acetone (20 ml) was stirred at room temperature until KOH had disappeared. The precipitates were filtered off and washed with Et_2O. The product was pure enough to be used in the sequent reaction.

General Synthesis of *S*-(2-Alkenyl or 2-alkynyl) *S*-(2-Alkenyl) Dithiocarbonates (2)

2-Alkenyl or 2-alkynyl halide (10 mmol) was added to the solution of potassium *O*-(2,4-alkadienyl) dithiocarbonate (10 mmol) in acetone (30 ml). The mixture was stirred at room temperature for 2hr. The mixture was diluted with water and extracted with *n*-hexane. The organic layer was dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure. The oily residue was dissolved in benzene and refluxed for 2 h. Chromatography on silica gel using *n*-hexane-benzene as an eluent afforded *S*-(2-alkenyl or 2-alkynyl) *S*-(2-alkenyl) dithiocarbonate (**2**) as a colorless oil.

***S*-Propargyl *S*-(3-phenyl-1-vinylallyl) dithiocarbonate (2a)**

Colorless oil; yield 25%. IR (KBr) cm^{-1}: 1644 (C=O); ^{1}H-NMR (400MHz, $CDCl_3$): 2.23 (1H, t, *J* 2.56, ≡CH), 3.73 (2H, d, *J* 2.56, S-CH_2C≡), 5.08 (1H, ddd, *J* 1.1, 6.96, 8.06, >CHS-), 5.24 (1H, dd, *J* 1.1, 10.3, CH=C*H*$_2$), 5.35 (1H, dd, *J* 1.1, 16.9, CH=C*H*$_2$), 5.96 (1H, ddd, *J* 6.96, 10.3, 16.9, C*H*=CH_2), 6.25 (1H, dd, *J* 8.1, 15.8, PhCH=C*H*), 6.62 (1H, d, *J* 15.8, Ph-CH=), 7.18-7.40 (5H, m, aromatic H); m/z 274(M^+); HRMS Calcd for $C_{15}H_{14}S_2O$: 274.0486. Found: 274.0469.

***S*-Allyl *S*-(3-phenyl-1-vinylallyl) dithiocarbonate (2b)**

Colorless oil; yield 58%. IR (KBr) cm^{-1}: 1644 (C=O); ^{1}H-NMR (400MHz, $CDCl_3$): 3.64 (2H, d, *J* 6.96, S-C*H*$_2$-CH=), 5.05 (1H, dd, *J* 6.96, 8.06, >CHS-), 5.13 (1H, dd, *J* 1.1, 9.9, SCH_2CH=C*H*$_2$), 5.21-5.23 (1H, m, CH=C*H*$_2$), 5.25 (1H, dd, *J* 1.1, 16.9, SCH_2CH=C*H*$_2$), 5.32 (1H, dd, *J* 1.1, 16.9, CH=C*H*$_2$), 5.80 (1H, ddd, *J* 6.96, 9.9, 16.9, SCH_2-C*H*=), 5.94 (1H, ddd, *J* 6.96, 10.3, 16.9, C*H*=CH_2), 6.23 (1H, dd, J 8.1, 15.8, PhCH=C*H*-), 6.61 (1H, d, *J* 15.8, PhCH=), 7.21-7.39 (5H, m, aromatic H); m/z 276 (M^+); HRMS Calcd for $C_{15}H_{16}S_2O$: 276.0643. Found: 276.0645.

***S*-(3-Ethoxycarbonylallyl) *S*-(3-phenyl-1-vinylallyl) dithiocarbonate (2c)**

Colorless oil; yield 25%. IR (KBr) cm^{-1}: 1642 (C=O), 1722 (ester C=O); ^{1}H-NMR (400MHz, $CDCl_3$): 1.28 (3H, t, *J* 7.33, CH_3), 3.73 (2H, td, *J* 1.47, 6.97, S-C*H*$_2$-CH=), 4.18 (2H, q, *J* 7.33, OCH_2), 5.03 (1H, dt, *J* 1.1, 7.69, >CHS-), 5.24 (1H, d, *J* 10.3, CH=C*H*$_2$), 5.35 (1H, d, *J* 16.9, CH=C*H*$_2$), 5.94-6.05 (2H, m, C*H*=CH_2 and CH=C*H*COO), 6.22 (1H, dd, *J* 7.69, 16.1, PhCH=C*H*), 6.62 (1H, d, *J* 16.1, Ph-CH=), 6.86 (1H, dd, *J* 6.97, 15.4, SCH_2-C*H*=), 7.18-7.39 (5H, m, aromatic H); m/z 348(M^+); HRMS Calcd for $C_{18}H_{20}S_2O_3$: 348.0854. Found: 348.0846.

***S*-Allyl *S*-(2-methyl-1-vinylallyl) dithiocarbonate (2d)**

Colorless oil; yield 32%. IR (KBr) cm^{-1}: 1640 (C=O); ^{1}H-NMR (270MHz, $CDCl_3$): 1.81 (3H, t, *J* 0.99, CH_3), 3.64 (2H, dd, *J* 0.99, 6.93, S-C*H*$_2$-CH=), 4.79 (1H, dd, *J* 0.99, 7.58, >CHS-), 4.94 (1H, dd, *J* 0.99, 1.98, CHC(Me)=C*H*$_2$), 5.02 (1H, dd, *J* 0.99, 1.98, CHC(Me)=C*H*$_2$), 5.11-5.33 (4H, m, 2x CH=C*H*$_2$), 5.75-5.95 (2H, m, 2x C*H*=CH_2); m/z 214(M^+).

***S*-Propargyl *S*-(2-methyl-3-phenyl-1-vinylallyl) dithiocarbonate (2e)**

Colorless oil; yield 59%. IR (KBr) cm^{-1}: 1646 (C=O); ^{1}H-NMR (400MHz, $CDCl_3$): 1.92 (3H, d, *J* 1.1, CH_3), 2.23 (1H, t, *J* 2.56, ≡CH), 3.74 (2H, d, *J* 2.56, S-CH_2C≡), 5.01 (1H, dd, *J* 1.1, 6.96, >CHS-), 5.24 (1H, dd, *J* 1.1, 10.3, CH=C*H*$_2$), 5.37 (1H, dd, *J* 1.1, 16.9, CH=C*H*$_2^{trans}$), 5.98 (1H, ddd, *J* 6.96, 10.3, 16.9, C*H*=CH_2), 6.57 (1H, s, Ph-CH=), 7.19-7.35 (5H, m, aromatic H); m/z 288(M^+); HRMS Calcd for $C_{16}H_{16}S_2O$: 288.0643. Found: 288.0679.

***S*-Allyl *S*-(2-methyl-3-phenyl-1-vinylallyl) dithiocarbonate (2f)**

Colorless oil; yield 56%. IR (KBr) cm^{-1}: 1644 (C=O); ^{1}H-NMR (400MHz, $CDCl_3$): 1.92 (3H, d, *J* 1.1, CH_3), 3.64 (2H, dd, *J* 1.1, 6.96, S-C*H*$_2$-CH=), 4.98 (1H, dd, *J* 1.1, 7.33, >CHS-), 5.13 (1H, ddd, *J* 1.1, 1.1, 10.3, SCH_2CH=C*H*$_2$), 5.23 (1H, dd, *J* 1.1, 10.3, CH=C*H*$_2$), 5.26 (1H, ddd, *J* 1.1, 1.1, 16.9, SCH_2CH=C*H*$_2$), 5.36 (1H, ddd, *J* 1.1, 1.1, 16.9, CH=C*H*$_2$), 5.83 (1H, tdd, *J* 6.96, 10.3, 16.9, SCH_2-C*H*=), 5.99 (1H, ddd, *J* 7.33, 10.3, 16.9, C*H*=CH_2), 6.56 (1H, s, PhCH=), 7.19-7.35 (5H, m, aromatic H); m/z

290(M^+); HRMS Calcd for $C_{16}H_{18}S_2O$: 290.0799. Found: 290.0817.

***S*-(3-Ethoxycarbonylallyl) *S*-(2-methyl-3-phenyl-1-vinylallyl) dithiocarbonate (2g)**

Colorless oil; yield 77%. IR (KBr) cm^{-1}: 2950 (CH), 1726 (C=O); ^{1}H-NMR (270MHz, $CDCl_3$) for *trans*-fused adduct: 1.00 (3H, t, *J* 7.25, CH_3CH_2O), 1.53 (3H, d, *J* 1.65, CH_3), 2.11-2.35 (1H, m, 7a-H), 2.40-2.48 (1H, m, 3-H), 2.59-2.70 (1H, m, 1-H), 2.92 (1H, dd, *J* 6.6, 11.6, 4-H), 3.02-3.18 (3H, m, 1-H, 3-H and 3a-H), 3.78 (2H, q, *J* 7.25, CH_2O), 3.91-4.03 (1H, m, 5-H), 5.77 (1H, brs, 7-H), 7.13-7.59 (5H, m, aromatic H); for *cis*-fused adduct: 0.95 (3H, t, *J* 7.26, CH_3CH_2O), 1.41 (3H, d, *J* 0.99, CH_3), 2.38 (1H, brs, 3a-H), 2.59-2.70 (3H, m, 1-H, 4-H and 3-H), 2.73-2.82 (1H, m, 7a-H), 3.02-3.18 (2H, m, 1-H and 3-H), 3.69-3.85 (1H, m, 5-H), 3.94 (2H, q, *J* 7.26, CH_2O), 5.69 (1H, brs, 7-H), 7.13-7.59 (5H, m, aromatic H); HRMS Calcd for $C_{17}H_{20}SO_2$: 302.1341. Found: 302.1306.

***S*-Propargyl *S*-[1-(4'-isopropenyl-1'-cyclohexenyl)allyl] dithiocarbonate (2h)**

Colorless oil; yield 60%. IR (KBr) cm^{-1}: 1644 (C=O); ^{1}H-NMR (400MHz, $CDCl_3$): 1.72 (3H, s, CH_3), 1.45-2.18 (7H, m, 3 x CH_2 and CH), 2.23 (1H, t, *J* 2.56, ≡CH), 3.74 (2H d, *J* 2.56, SCH_2), 4.69 (1H, d, *J* 0.73, C(Me)=CH_2); 4.72 (1H, d, *J* 0.73, C(Me)=CH_2), 4.79 (1H, d, *J* 8.06, >CHS-), 5.15 (1H, dd, *J* 1.1, 10.3, CH=CH_2), 5.28 (1H, dd, *J* 1.1, 16.9, CH=CH_2), 5.76 (1H, brs, CH_2CH=C<), 5.89 (1H, ddd, *J* 8.06, 10.3, 16.9); m/z 292(M^+); HRMS Calcd for $C_{16}H_{20}S_2O$: 292.0956. Found: 292.0988.

***S*-(3-Butenyl) *S*-(3-methyl-1-vinylallyl) dithiocarbonate (2i)**

Colorless oil; yield 57%. ^{1}H-NMR (400MHz, $CDCl_3$): 1.71 (3H, dd, *J* 0.73, 6.6, CH_3), 2.37 (2H, dt, *J* 6.96, 7.33, SCH_2CH_2), 3.04 (2H, t, *J* 7.33, SCH_2CH_2), 4.80 (1H, dd, *J* 1.1, 7.33, >CHS-), 5.03-5.11 (2H, m, CHCH=CH_2), 5.14 (1H, dd, *J* 1.1, 10.5, SCHCH=CH_2), 5.25 (1H, dd, *J* 1.1, 15.8, SCHCH=CH_2), 5.47-5.54 (1H, m, CH_3CH=C*H*), 5.69-5.92 (3H, m, CH_3-C*H*=CH and 2x C*H*=CH_2); m/z 228(M^+).

General Synthesis of Hydrobenzo[*c*]thiophenes (4) from Dithiolcarbonates (2)

The dithiolcarbonate (**2**) in *o*-dichlorobenzene was refluxed for 5hr. Evaporation of the solvent gave the crude adduct, which was purified by chromatography on silica gel using *n*-hexane-benzene as an eluent to give hydrobenzo[*c*]thiophenes(**4**) as a colorless oil.

6-Phenyl-1,3,3a,6-tetrahydrobenzo[*c*]thiophene (4a)

Colorless oil; yield 46%. ^{1}H-NMR (400MHz, $CDCl_3$): 2.56 (1H, dd, *J* 12.1, 14.3, 3α-H), 3.08-3.13 (2H, m, 3a-H and 3ß-H), 3.38 (1H, d, *J* 12.8, 1-H), 3.61 (1H, d, *J* 12.8, 1ß-H), 3.99 (1H, d, *J* 8.43, 6-H), 5.53 (1H, brs, 7-H), 5.75 (1H, dd, *J* 5.43, 10.3, 5-H), 5.88 (1H, dd, *J* 9.46, 10.3, 4-H), 7.11-7.57 (5H, m aromatic H); m/z 214(M^+); HRMS Calcd for $C_{14}H_{14}S$: 214.0816. Found: 214.0711.

5-Phenyl-1,3,3a,4,5,7a-hexahydrobenzo[*c*]thiophene (4b)

Colorless oil; yield 46%. IR (KBr) cm^{-1}: 3020 (CH); ^{1}H-NMR (400MHz, $CDCl_3$) for *trans*-fused adduct: 1.77-1.80 (1H, m, 3a-H), 1.94 (1H, ddd, *J* 6.6, 12, 12, 4α-H), 1.98 (1H, ddd, *J* 2, 12, 12, 4ß-H), 2.23-2.25 (1H, m, 7a-H), 2.47-2.55 (1H, m, 1α-H), 2.60-2.73 (1H, m, 3-H), 3.03 (1H, dd, *J* 6.6, 9.52, 1α-H), 3.69-3.75 (1H, m, 5-H), 5.74-5.78 (1H, m, 6-H), 6.05 (1H, d, *J* 9.89, 7-H), 7.13-7.59 (5H, m, aromatic H); for *cis*-fused adduct: 1.65 (1H, ddd, *J* 1.47, 11.4, 13.2, 4α-H), 1.80-1.85 (1H, m, 4ß-H), 2.60-2.65 (1H, m, 3a-H), 2.60-2.73 (2H, m, 1α-H and 3α-H), 2.65-2.75 (1H, m, 7a-H), 3.09 (1H, dd, *J* 6.59, 9.52, 3ß-H), 3.20 (1H, dd, *J* 6.59, 10.6, 1ß-H), 3.40-3.46 (1H, m, 5-H), 5.74-5.78 (1H, m, 6-H), 5.92 (1H, ddd, *J* 2.93, 4.39, 9.89, 7-H), 7.13-7.59 (5H, m, aromatic H); ^{13}C-NMR ($CDCl_3$) for *trans*-fused adduct: 34.72 (C4), 34.89 (C1), 35.83 (C3), 40.93 (C3a), 41.74 (C5), 46.92 (7a), 49.15 (C6), 129.26 (C7), 129.89 (C6); for *cis*-fused adduct: 35.26 (C4), 36.15 (C3), 37.56 (C1), 41.63 (C3a), 43.47 (C5), 46.63 (7a), 127.92

(C7), 131.48 (C6); m/z 216 (M^+); HRMS Calcd for $C_{14}H_{16}S$: 216.0973. Found: 216.0896.

Ethyl 5-phenyl-1,3,3a,4,5,7a-hexahydrobenzo[*c*]thiophene-4-carboxylate (4c)

Colorless oil; yield 85%. IR (KBr) cm^{-1}: 2960 (CH), 1730 (C=O); ^{1}H-NMR (400MHz, $CDCl_3$) for *trans*-fused adduct: 1.00 (3H, t, *J* 6.96, CH_3), 2.19-2.23 (1H, m, 7a-H), 2.44-2.49 (1H, m, 3-H), 2.59-2.70 (1H, m, 1-H), 2.97 (1H, dd, *J* 6.96, 11.7, 4-H), 3.06-3.18 (3H, m, 1-H, 3-H and 3a-H), 3.78 (2H, q, *J* 6.96, CH_2CO_2), 3.93-4.03 (1H, m, 5-H), 5.69-5.73 (1H, m, *J* 9.9, 7-H), 6.03 (1H, d, *J* 9.9, 7-H), 7.12-7.42 (5H, m, aromatic H); for *cis*-fused adduct: 0.98 (3H, t, *J* 6.96, CH_3), 2.37 (1H, brs, 3a-H), 2.59-2.70 (3H, m, 1-H, 4-H and 3-H), 2.82-2.89 (1H, m, 7a-H), 3.06-3.18 (2H, m, 1-H and 3-H), 3.64-3.67 (1H, m, 5-H), 4.00 (2H, q, *J* 6.96, CH_2CO_2), 5.69-5.73 (1H, m, *J* 9.9, 6-H), 5.92 (1H, dt, *J* 9.9, 4.0, 7-H), 7.12-7.42 (5H, m, aromatic H); HRMS Calcd for $C_{17}H_{20}SO_2$: 288.1184. Found: 288.1186.

6-Methyl-1,3,3a,4,5,7a-hexahydrobenzo[*c*]thiophene (4d)

Colorless oil; yield 28%. IR (KBr) cm^{-1}: 3928 (CH); ^{1}H-NMR (400MHz, $CDCl_3$) for *trans*-fused adduct: 1.66 (3H, d, *J* 1.1, CH_3), 1.44-1.47 (1H, m, 3a-H), 1.96-2.00 (2H, m, 5-H), 2.09-2.11 (2H, m, 4-H), 2.18 (1H, brs, 7a-H), 2.41-2.50 (2H, m, 1-H and 3-H), 2.89 (1H, dd, *J* 6.6, 9.9, 3-H), 2.93 (1H, dd, *J* 6.6, 9.5, 1-H), 5.46 (1H, s, 7-H); for *cis*-fused adduct: 1.66 (3H, d, *J* 1.1, CH_3), 1.63-1.68 (2H, m, 4-H), 1.96-2.00 (2H, m, 5-H), 2.36-2.40 (1H, m, *J* 4.03, 3a-H), 2.56 (1H, dd, *J* 8.06, 10.3, 1-H), 2.66 (1H, dd, *J* 4.03, 10.3, 3-H), 2.69-2.71 (1H, d, *J* 6.59, 7a-H), 2.98-3.05 (2H, m, 1-H and 3-H), 5.35 (1H, dd, *J* 1.1, 3.67, 7-H); HRMS Calcd for $C_9H_{14}S$: 154.0816. Found: 154.0802.

5-Methyl-6-phenyl-1,3,3a,6-tetrahydrobenzo[*c*]thiophene (4e)

Colorless oil; yield 40%. ^{1}H-NMR (400MHz, $CDCl_3$): 1.49 (3H, s, CH_3), 2.56 (1H, dd, *J* 10.6, 14.3, 3α-H), 3.08-3.13 (2H, m, 3a-H and 3ß-H), 3.35 (1H, d, *J* 12.1, 1α-H), 3.58 (1H, d, *J* 12.1, 1ß-H), 3.79 (1H, brs, 6-H), 5.48 (1H, s, 7-H), 5.65 (1H, s, 4-H), 7.10-7.42 (5H, m, aromatic H); m/z 228(M^+); HRMS Calcd for $C_{15}H_{16}S$: 228.0973. Found: 228.0986.

5-Phenyl-6-methyl-1,3,3a,4,5,7a-hexahydrobenzo[*c*]thiophene (4f)

Colorless oil; yield 65%. IR (KBr) cm^{-1}: 3024-2860 (CH); ^{1}H-NMR (400MHz, $CDCl_3$) for *trans*-fused adduct: 1.59 (3H, d, *J* 1.1, CH_3), 1.72-1.81 (1H, m, 3a-H), 1.88-1.92 (2H, m, 4-H), 2.21-2.24 (1H, m, 7a-H), 2.46 (1H, dd, *J* 1.83, 11.0, 1-H), 2.66-2.74 (2H, m, 3-H), 3.01 (1H, dd, *J* 6.6, 9.16, 1-H), 3.49 (1H, brs, 5-H), 5.80 (1H, s, 7-H), 7.10-7.34 (5H, m, aromatic H); for *cis*-fused adduct: 1.42 (3H, d, *J* 1.1, CH_3), 1.72-1.81 (2H, m, 4-H), 2.26-2.74 (2H, m, 1-H and 7a-H), 2.54-2.59 (2H, m, 3-H and 3a-H), 3.09 (1H, dd, *J* 6.59, 10.6, 3-H), 3.16 (1H, dd, *J* 6.59, 10.6, 1-H), 3.26-3.31 (1H, m, 7-H), 5.68 (1H, brs, 7-H), 7.10-7.34 (5H, m, aromatic H); m/z 230 (M^+); HRMS Calcd for $C_{15}H_{18}S$: 230.1129. Found: 230.1138.

Ethyl 5-phenyl-6-methyl-1,3,3a,4,5,7a-hexahyrobenzo[*c*]thiophene-4-carboxylate (4g)

Colorless oil; yield 38%. IR (KBr) cm^{-1}: 1646 (C=O), 1718 (ester C=O); ^{1}H-NMR (400MHz, $CDCl_3$): 1.28 (3H, t, *J* 6.96, CH_3CH_2O), 1.92 (3H, t, *J* 6.96, CH_3), 3.73 (2H, d, *J* 6.96, S-CH_2-CH=), 4.19 (2H, q, *J* 6.96, OCH_2), 4.99 (1H, d, *J* 7.32, >CHS-), 5.24 (1H, d, *J* 10.3, CH=CH_2), 5.36 (1H, d, *J* 16.9, CH=CH_2), 5.94-6.04 (1H, m, CH=CH_2), 5.99 (1H, d, *J* 15.4, CH=CHCOO), 6.57 (1H, s, Ph-CH=), 6.87 (1H, td, *J* 6.96, 15.4, SCH_2-CH=), 7.15-7.38 (5H, m, aromatic H); m/z 362(M^+); HRMS Calcd for $C_{19}H_{22}S_2O_3$: 362.1010. Found: 362.1001.

7-Isopropenyl-1,3,3a,5,6,7,8,8a-octahydronaphto[2,3-*c*]thiophene (4h)

Colorless oil; yield 76%. ^{1}H-NMR (400MHz, $CDCl_3$): 1.78 (3H, s, CH_3), 1.26-2.23 (7H, m 3 x CH_2 and CH), 2.46 (1H, dd, *J* 12.1, 13.9 3α-H), 2.78 (1H, m, >CH-CH=), 3.00-3.05 (1H, m, 3a-H), 3.02 (1H, dd, *J* 7.33, 12.1, 3ß-H), 3.38 (1H, d, *J* 12.5, 1α-H), 3.55 (1H, d, *J* 12.5, 1ß-H), 4.89 (1H, d, *J* 1.5, =CH_2),

4.97 (1H, d, *J* 1.5, $=CH_2$), 5.36 (1H, s, >CH-C*H*=), 5.43 (1H, d, *J* 2.2, 4-H); m/z 232(M^+); HRMS Calcd for $C_{15}H_{20}S$: 232.1286. Found: 232.1318.

5-Phenyl-2,4-pentadienyl allyl sulfide (3b)

A solution of dithiol ester (**2b**)(0.5 g, 1.8 mmol) and $EtAlCl_2$ (1 M solution, 1.8 ml, 1.8 mmol) in $CHCl_3$ was stirred at 0°C for 4 hr. Water was added to the mixture and $CHCl_3$ layer was separated. The organic layer was dried ($MgSO_4$), filtered, and the solvent was removed under reduce pressure. The residue was purified by chromatography on silica gel using *n*-hexane-benzene as an eluent to give sulfide (**3b**).

Colorless oil; yield 12%. ^{1}H-NMR (400MHz, $CDCl_3$): 3.09 (2H, dd, *J* 1.1, 6.97, SCH_2), 3.17 (2H, d, *J* 7.33. SCH_2), 5.09 (1H, dd, *J* 1.1, 16.1, -CH=C*H*$_2$), 5.10 (1H, dd, *J* 1.1, 10.6, -CH=C*H*$_2$), 5.70-5.82 (2H, m, =C*H*-CH_2SCH_2-C*H*=), 6.22 (1H, tdd, *J* 1.1, 10.3, 15.0, -C*H*=$CHCH_2S$), 6.48 (1H, d, *J* 15.8, PhC*H*=), 6.75 (1H, dd,*J* 10.3, 15.8, PhCH=C*H*-), 7.17-7.41 (5H, m, aromatic H); m/z 216(M^+).

4-Methyl-5-phenyl-2,4-pentadienyl propargyl sulfide (3e)

A solution of dithiol ester (**2e**)(0.5 g, 1.7 mmol) and $MeAlCl_2$ (1 M solution, 1.7 ml, 1.7 mmol) in $CHCl_3$ was stirred at 0°C for 5 hr. Water was added to the mixture and $CHCl_3$ layer was separated. The organic layer was dried ($MgSO_4$), filtered, and the solvent was removed under reduce pressure. The residue was purified by chromatography on silica gel using hexane-benzene as an eluent to give sulfide (**3e**).

Colorless oil; yield 28%. ^{1}H-NMR (400MHz, $CDCl_3$): 2.00 (3H, d, *J* 0.99, CH_3), 2.26 (1H, t, *J* 2.3, ≡CH), 3.19 (2H, d, *J* 2.3, $SCH_2C\equiv$), 3.42 (2H, d, *J* 7.58, SCH_2), 5.73 (1H, dd, J 7.59, 15.5, =C*H*CH_2S), 6.35 (1H, d, *J* 15.5, C*H*=$CHCH_2S$), 6.50 (1H, s, PhC*H*=), 7.18-7.36 (5H, m, aromatic H); m/z 228(M^+); HRMS Calcd for $C_{15}H_{20}S$: 228.0973. Found: 228.0986.

2,4-Hexadienyl 3-butenyl sulfide (3i)

The dithiol ester (**2i**)(0.5 g, 2.2 mmol) was heated at 200°C until evolution of COS had ceased. The pyrolysed product was chromatographed on silica gel to give sulfide (**3i**).

Colorless oil; yield 75%. ^{1}H-NMR (400MHz, $CDCl_3$): 1.75 (3H, d, *J* 6.96, CH_3), 2.31 (2H, dt, *J* 6.96, 7.33, SCH_2CH_2), 2.51 (2H, t, *J* 7.33, SCH_2CH_2), 3.16 (2H, d, *J* 7.33, SCH_2CH=), 5.01-5.09 (2H, m, =C*H*$_2$), 5.51 (1H, m, SCH_2CH=), 5.82 (1H, ddd, *J* 6.96, 10.3, 16.9, C*H*=CH_2), 5.67 (1H, dd, *J* 6.96, 14.3, CH_3-C*H*=), 6.01-6.08 (2H, m, =C*H*-C*H*=); m/z 168(M^+); HRMS Calcd for $C_{10}H_{16}S$: 168.0973. Found: 168.0986.

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7. An error in description of the former report[5] should be corrected.

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