Stereochemistry of the [4 + 2] Cycloaddition of Diarylselenoketones with Conjugated Dienes

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Received July 13, 1995[⊗]

Abstract: The ylides $Ph_3P{=}CAr^1Ar^2$ **1a−g** (Ar = C_6H_5, *p*-C_6H_4Cl, *p*-C_6H_4F, *m*-$C_6H_4CF_3$, *p*-$C_6H_4OCH_3$, *p*-C_6H_4-CH_3) were treated with elemental selenium (~80 °C) to give the corresponding selenoketones $Se{=}CAr^1Ar^2$ **2** by Staudinger-chalcogenation. Their reaction with *trans,trans*-2,4-hexadiene proceeds completely stereospecifically to yield the 2,2-diaryl-3,6-dihydro-*cis*-3,6-dimethyl-2*H*-selenapyrans **3**. In contrast, the reactions of the selenoketones **2** with *cis,trans*-2,4-hexadiene proceeds stereoselectively, *also* giving the dihydro-*cis*-dimethyl-2*H*-selenapyrans **3** as the major products, now admixed with small amounts of the dihydro-*trans*-dimethyl-2*H*-selenapyran isomers **4**. The [4 + 2] cycloaddition of **2** with *cis,trans*-2,4-hexadiene proceeds stereospecifically, however, when carried out at a pressure of 12 kbar, now yielding **4** as the major products along with the corresponding tetraarylethenes **8**. Along with the results of additional mechanistic studies (determination of solvent and substituent effects) it can be concluded that diarylselenoketones are likely to react by means of a concerted [4 + 2] cycloaddition with very reactive conjugated dienes (such as *trans,trans*-2,4-hexadiene), whereas a stepwise mechanism, resulting in diene *cis/trans*-isomerization with subsequent mechanistic "leakage" to the concerted pathway, appears to be preferred when a much less reactive conjugated diene such as *cis,trans*-2,4-hexadiene is employed. The reaction of the corresponding diarylthioketones **5a−g** with *trans,trans*- and *cis,trans*-2,4-hexadiene, respectively, shows an analogous behavior.

Introduction

Thio-, seleno-, and telluroketones and -aldehydes are the reactive heavy homologues of the ubiquitous carbonyl compounds in organic chemistry. Their much increased reactivity originates from an elevated energy content of the C=X π-orbital (and to a lesser extent of the chalcogene lone pairs) and lowered C=X π^*-orbital energies. The higher HOMO and lower LUMO make the usually deeply colored chalcogenacarbonyl compounds more nucleophilic and at the same time more electrophilic as compared to ordinary ketones and aldehydes.[1]

Thiocarbonyl chemistry is well established and has found much application in organic synthesis. Much less is known about selenoketones and -aldehydes.[2] There are a few examples of stable, isolable selenoketones, mostly kinetically stabilized by adjacent bulky substituents,[3] and there are a few examples of electronically stabilized $R_2C{=}Se$ compounds.[4] Only very little is known about persistent selenoaldehydes.[5] The majority of selenoketones and -aldehydes known so far has a fleeting existence under standard conditions.[6−8] Some can be studied as stable species in solution, but evade their isolation as pure compounds by, e.g., dimerization. Selenobenzophenone and some substituted analogues show such behavior.[7]

Many selenoketones and -aldehydes are so reactive that they even cannot be observed in dilute solution. Knowledge about their intermediate generation usually comes from trapping experiments. The $R^1R^2C{=}Se$ species is formed by a variety of specific synthetic procedures in the presence of a suitable scavenger. Then the stable addition product is isolated, and its structural characterization and the knowledge about the general reaction pathway leading to its formation allows for the interpretative identification of the nature of the in situ generated selenocarbonyl species.

A variety of trapping reactions has been used, but the majority of in situ generated selenoketones and -aldehydes has been added to conjugated dienes yielding various differently substituted 3,6-dihydro-2*H*-selenapyran systems. Often cyclic (e.g., cyclopentadiene) or internally substituted 1,3-dienes have been used. In a few instances conjugated dienes bearing substituents at the diene termini have also been employed.[6] The [4 + 2]

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1995.

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0002-7863/95/1517-10922$09.00/0

cycloaddition between a selenoketone or -aldehyde and these conjugated dienes has mostly been inferred to as a concerted hetero-Diels–Alder-type reaction and regio- and stereochemical preferences (the latter mostly referring to exo/endo-selectivities) have quite uniformly been interpreted accordingly.[6,9,10] However, to our knowledge there has not been a single systematic study aimed at identifying the stereochemical outcome of any of these selenocarbonyl plus 1,3-diene [4 + 2] cycloaddition reactions, although knowing that the stereochemistry introduced by a pair of, e.g., suitably 1,4-substituted conjugated diene reagents being retained during the addition reaction and consequently reflected in the obtained substituted 2*H*-selenapyran products would be a *necessary* condition for describing these trapping reactions as concerted.[11] We have, therefore, treated a series of substituted diarylselenoketones (and, for comparison, their diarylthioketone analogues as well) each with *trans,trans*- and *cis,trans*-2,4-hexadiene and characterized the stereochemistry of the 2,2-diaryl-3,6-dihydro-3,6-dimethyl-2*H*-selenapyran product formation under various reaction conditions.[12] This led to the surprising result that is described and interpreted in the following account.

Results and Discussion

The diarylseleno- and -thioketones employed in this study were all generated by means of the *Staudinger-chalcogenation* method.[12,13] In this reaction the respective ylide $Ph_3P{=}CAr^1Ar^2$ was treated with elemental selenium or sulfur, respectively, in toluene solution at elevated temperature. In a few cases the diarylthio- or -selenoketone was obtained as a monomer; most diarylselenoketones dimerized upon isolation as solid products. These systems reconverted to their respective monomers when brought back into solution, as was previously described.[14] In most experiments carried out in this series of studies the

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Table 1. Selected ^{1}H NMR Chemical Shifts of the Dihydro-2*H*-selenapyrans **3**[a]

compd	3-H	4-H	5-H	6-H	3-CH_3	6-CH_3
3a	2.85	5.61	5.98	2.90	0.91	1.38
3b	2.72	5.57	5.88	2.83	0.83	1.33
3c	2.73	5.55	5.90	2.80	0.84	1.34
3d	2.80	5.58	5.92	2.82	0.83	1.34
3e	2.71	5.52	5.88	2.81	0.83	1.32
3f	2.62	5.59	5.88	2.88	0.81	1.33
			5.87		0.80	1.32
3g	2.80	5.56	5.92	2.80	0.87	1.36
			5.91		0.85	1.35

[a] In $CDCl_3$, δ-scale.

Table 2. ^{1}H NMR Coupling Constants (in Hz) of the 2,2-Diaryl-3,6-dihydro-*cis*-3,6-dimethyl-2*H*-selenapyrans **3**

	5-H			4-H		3-H	6-H
compd	$^3J_{H5/H4}$	$^3J_{H5/H6}$	$^4J_{H5/H3}$	$^3J_{H4/H3}$	$^4J_{H4/H6}$	$^3J_{H3/3\text{-}CH_3}$	$^3J_{H6/6\text{-}CH_3}$
3a	10.9	5.4	2.7	1.8	1.8	6.6	7.4
3b	10.9	5.4	2.7	1.8	1.8	6.6	7.3
3c	10.8	5.3	2.7	1.8	1.8	6.6	7.3
3d	10.9	5.6	2.8	1.7	1.7	6.7	7.4
3e	10.9	5.3	2.6	1.6	1.6	6.6	7.4
3f	10.9	5.3	2.8	1.7	1.7	6.7	7.4
3g	10.9	5.4	2.6	1.7	1.7	6.7	7.4

Table 3. Selected ^{13}C NMR Data of **3**[a]

compd	C-2	C-3	C-4	C-5	C-6	3-CH_3	6-CH_3
3a	58.6	38.2	130.7	135.4	28.8	18.1	19.9
3b	57.1	38.1	130.7	134.8	29.2	19.3	19.9
3c	57.1	38.5	129.6	135.0	29.3	19.2	19.8
3d	57.4	38.0	128.8	134.8	29.4	19.2	19.8
3e	57.7	38.6	130.6	135.5	29.0	19.4	20.0
3f, 3f'	58.5	38.2	131.2	135.3	28.9	19.4	20.0
			130.7	135.2			
3g, 3g'	57.9	38.2	130.8	135.1	29.2	19.3	19.9
	55.6	38.0	130.5		28.9	19.2	

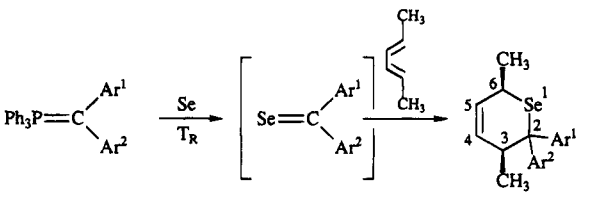
[a] In $CDCl_3$, δ-scale.

diarylseleno- and diarylthioketones were generated in situ in the presence of the conjugated diene trapping reagents and the corresponding substituted 2,2-diaryl-3,6-dihydro-2*H*-chalcogenapyrans isolated and characterized.

Reaction of Diarylchalcogenoketones with the 2,4-Hexadiene Isomers. The ylides **1a−g** were prepared as previously described and converted to the selenoketones **2a−g** by Staudinger-chalcogenation.[14] The selenoketones **2a−g** were trapped in situ by an added excess of *trans,trans*-2,4-hexadiene. The corresponding 2,2-diaryl-3,6-dihydro-*cis*-3,6-dimethyl-2*H*-selenapyrans **3a−g** were formed nearly quantitatively and isolated after chromatographic purification in high yield as oils (see Table 1). Only a single product was obtained in each of the reactions of the symmetrically substituted diarylselenoketones **2a−e**. All these products exhibit a *cis*-stereochemistry of the methyl groups at positions 3 and 6 of the dihydro-2*H*-chalcogenapyran-ring system: The stereochemistry of the *trans,trans*-2,4-hexadiene reagent has been retained in the product formation. The unsymmetrically substituted diarylselenoketones **2f** and **2g** give rise to the formation of two diastereoisomeric products each. This is due to the additional stereogenic center at C2 of the dihydro-2*H*-selenapyran-ring. In each case both products exhibit *cis*-3,6-dimethyl substitution as is evident from a comparison of their very typical NMR data (see Tables 1−3).

We next treated the diarylselenoketones **2a−g** with *cis,trans*-2,4-hexadiene. Again, 2,2-diaryl-3,6-dihydro-3,6-dimethyl-2*H*-selenapyran formation took place, and the corresponding products were isolated in high yield. In each case, a mixture

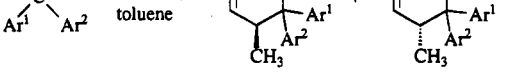
Scheme 1



1 **2** **3**

product	Ar^1	Ar^2	T_R (°C)	rxn time (h)	yield (% isolated)
3a	C_6H_5	C_6H_5	85	6	87
3b	pC_6H_4Cl	pC_6H_4Cl	80	10	89
3c	pC_6H_4F	pC_6H_4F	85	2	74
3d	$mC_6H_4CF_3$	$mC_6H_4CF_3$	85	12	67
3e	$pC_6H_4OCH_3$	$pC_6H_4OCH_3$	85	6	54
3f, 3f'	C_6H_5	$pC_6H_4CH_3$	85	24	64
3g, 3g'	C_6H_5	pC_6H_4Cl	85	2	71

Scheme 2



2a - g X = Se **3a - g** **4a - g**

5a - g X = S **6a - g** **7a - g**

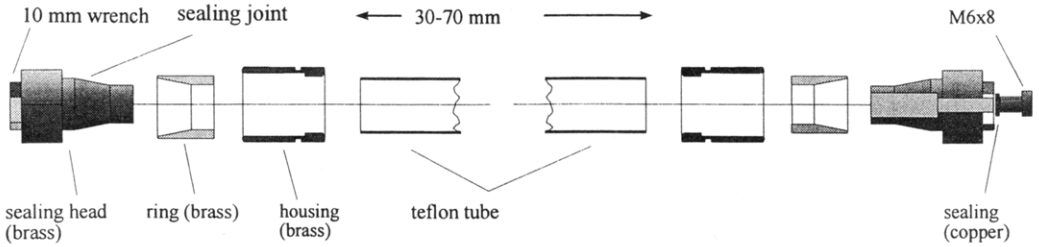
[Ar^1 and Ar^2 are as given in Scheme 1]

educt	rxn temp (°C)	rxn time (h)	yield (% isolated)	**3** : **4** or **6** : **7** ratio
2a	80	8	86	97 : 3
2b	90	6	80	80 : 20
2c	80	8	86	91 : 9
2d	80	12	68	59 : 41
2e	80	16	68	> 98 : 2
2f	80	30	80	> 98 : 2
2g	80	8	71	85 : 15
5a	80	28	80	> 98 : 2
5b	80	26	74	> 98 : 2
5c	80	28	68	> 98 : 2
5d	80	36	70	> 98 : 2
5e	80	46	68	> 98 : 2
5f	80	30	70	94 : 6
5g	80	30	53	> 98 : 2

of *cis*- and *trans*-3,6-dimethyl derivatives was formed with the *cis*-isomer **3** always being the dominating product over the *trans*-isomer **4** (characteristic spectroscopic data of **4** are given later). The product ratio was monitored by ^{1}H NMR spectroscopy of an aliquot of the crude reaction mixture; it stayed constant during the chromatographic workup. We noted that the ratio of *cis*- and *trans*-product isomers in the case of the reaction of **2b** varied with the reaction temperature. A maximum **4b**:**3b** value was obtained at 75 °C, whereas lower as well as higher temperatures led to smaller **4b**:**3b** ratios. For the other examples the **3**:**4** product ratio (see Scheme 2) varied much less with the reaction conditions, so that a conclusive explanation of this slightly different behavior of the **2b**/*cis,trans*-2,4-hexadiene reaction system cannot be given at present.

It appears that the reaction between the diarylselenoketones

Scheme 3



2 with *cis,trans*-2,4-hexadiene predominantly leads to the same stereoisomeric [4 + 2] cycloadducts as with *trans,trans*-2,4-hexadiene, namely the 2,2-diaryl-3,6-dihydro-*cis*-3,6-dimethyl-2*H*-selenapyran system **3**: the stereochemistry of the *cis,trans*-2,4-hexadiene reagent is thus not retained in this product formation. An energetic evaluation of the products employing a PM3 calculation has revealed that the stereoisomers **3a** and **4a** are almost identical in energy (the calculated heats of formation are 30.6 and 30.4 kcal mol^{-1}, respectively[15]); thus the predominant formation of the *cis*-dimethyl compounds **3** from **2** and the *cis,trans*-hexadiene isomer is very likely to be kinetically controlled.

The preference for 2,2-diaryl-3,6-dihydro-*cis*-3,6-dimethyl-2*H*-chalcogenapyran formation is even more pronounced when the respective diarylthioketones (**5a**−**g**, analogously generated) are treated with *cis,trans*-2,4-hexadiene. The [4 + 2] cycloaddition requires longer reaction times at 80 °C because the thioketones are less reactive, but most yields were acceptable (see Scheme 2) and the products were almost the pure **6a**−**g** isomers (the corresponding data of the *trans*-isomers **7a**−**g** are given later).

Reactions at High Pressure. The reaction of the diarylchalcogenoketones (**2** and **5**) with *cis,trans*-2,4-hexadiene did not proceed with a conservation of the stereochemistry of the reagent and thus has apparently taken a course other than concerted. The concerted Diels−Alder reaction and its heteroanalogous relatives can often be made advantageous by performing them under high pressure conditions.[16] We, therefore, have performed the [4 + 2]addition reactions of the diarylseleno- and -thioketones **2a**−**g** and **5a**−**g**, respectively, with *cis,trans*-2,4-hexadiene in toluene solution at a pressure of 12 kbar.

Handling the reactive chalcogenoketones and treating them under defined conditions at high pressure required the construction of a new reaction cell (see Scheme 3), that was inserted into a commercial 12 kbar autoclave, and a special technique to keep the mixture of very reactive reagents inert until the defined high pressure regime was reached.

The reaction cell was constructed from a flexible piece of Teflon tubing that was connected to two metal stoppers, one of which was equipped with a small inlet, through which the reagents and solvent could be introduced, and that was later sealed by a metal screw cap. Even very sensitive selenocarbonyl compounds could be handled with this device without the formation of hydrolysis products. Solutions of the chalcogenoketones **2** and **5** were generated by Staudinger-chalcogenation in toluene at 80 °C. The highly colored solutions were concentrated to a volume of ca. 2−4 mL. The solution of the chalcogenoketone was introduced into the Teflon reagent chamber and cooled to −78 °C. Then pure toluene solvent was carefully added through the inlet, taking good care that the two liquids did not mix. The mixture was allowed to attain the temperature of the cooling bath. Then the "sandwich" of educt (**2**/**5**), toluene solvent, and trapping reagent was completed by carefully adding a layer of *cis,trans*-2,4-hexadiene in toluene until the reaction chamber was filled. It was cooled, sealed, and transferred to the high pressure autoclave system, taking care that the layers did not become mixed. The system was pressurized to 12 kbar, and the reagents were then allowed to diffuse together[17] and react during a period of 12 to 24 h. Conventional workup at normal pressure then gave the reaction products.

In all cases the product mixtures have contained the two dihydrodimethyl-2*H*-selenapyran isomers **3** and **4**, but now the formation of the *trans*-3,6-dimethyl isomer (**4**) is predominant, i.e., the [4 + 2] cycloaddition proceeds with retention of the stereochemistry. The stereochemical assignment taken is internally consistent and is based on a comparison of the characteristic NMR data of the pairs of stereoisomeric products (see Tables 1−3 for the *cis*-3,6-dimethyl series **3**, Tables 6−8 for the *trans*-series **4**). It is in accord with an inspection of

Table 4. Selected ^{1}H NMR Data of the Dihydro-2*H*-thiapyran Systems **6a**−**g**[a]

compd	3-H	4-H	5-H	6-H	3-CH_3	6-CH_3
6a	3.08	5.53	5.95	2.66	0.82	1.23
6b	2.98	5.54	5.92	2.67	0.82	1.23
6c	2.99	5.53	5.92	2.65	0.81	1.23
6d	3.08	5.56	5.97	2.63	0.83	1.25
6e	2.98	5.52	5.92	2.68	0.82	1.22
6f, 6f′	3.05	5.53	5.96	2.67	0.83	1.23
			5.94		0.82	1.22
6g, 6g′	3.39	5.49	5.91	2.99	0.80	1.20
				2.93	0.78	1.18

[a] In $CDCl_3$, chemical shifts in ppm, δ-scale.

Table 5. Selected ^{13}C NMR Data of **6a**−**g**[a]

compd	C-2	C-3	C-4	C-5	C-6	3-CH_3	6-CH_3
6a	59.2	36.8	130.5	133.5	33.7	18.5	19.5
6b	58.3	36.8	131.3	132.5	33.9	18.5	19.4
6c	58.2	37.3	131.1	135.0	34.0	18.6	19.4
6d	58.8	36.8	130.5	132.6	34.0	18.4	19.5
6e	58.4	36.3	130.1	133.6	33.9	18.7	19.6
6f, 6f′	59.0	37.0	132.1	133.5	33.8	18.6	19.7
			131.9	132.3			19.5
6g, 6g′	58.9	37.0	130.3	133.2	33.9	18.6	19.5
		35.8	130.2	131.5	33.8		

[a] In $CDCl_3$, chemical shifts in ppm, δ-scale.

(15) Würthwein, E.-U. unpublished results: PM3 method: Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209; 221.

(16) *Organic High Pressure Chemistry*; le Noble, W. J., Ed.; Elsevier: Amsterdam, 1988. Klärner, F.-G. *Chem. Unserer Zeit* **1989**, *23*, 53. van Eldik, R.; Asano, T.; le Noble, W. J. *Chem. Rev.* **1989**, *89*, 549. Isaacs, N. S. *Tetrahedron* **1991**, *47*, 8463. For selected specific examples, see: Branchadell, V.; Sodupe, M.; Ortuno, R. M.; Oliva, A.; Gomez-Pardo, D.; Guingant, A.; d'Angelo, J. *J. Org. Chem.* **1991**, *56*, 4135. Tietze, L. F.; Hübsch, T.; Oelze, J.; Ott, C.; Tost, W.; Wörner, G.; Buback, M. *Chem. Ber.* **1992**, *125*, 2249. Klärner, F.-G.; Krawczyk, B.; Ruster, V.; Deiters, U. K. *J. Am. Chem. Soc.* **1994**, *116*, 7646.

(17) This special "sandwich-technique" had to be used in order to obtain reproducible stereochemical results. Direct mixing of the cold reagent solutions followed by pressurization of the homogeneous reaction mixtures resulted in a range of deviating diastereomeric product ratios in any series of experiments due to ill defined actual reaction pressure conditions.

Table 6. Selected ^{1}H NMR Data of the 2,2-Diaryl-3,6-dihydro-*trans*-3,6-dimethyl-2*H*-selenapyrans **4a−g**[a]

compd	3-H	4-H	5-H	6-H	3-CH_3	6-CH_3
4a	3.15	5.85	5.55	3.33	0.90	0.94
4b	3.03	5.86	5.60	3.40	0.92	1.03
4c	3.12	5.90	5.59	3.39	0.92	1.02
4d	3.18	5.86	5.60	3.38	0.94	1.00
4e	3.16	5.86	5.57	3.37	0.94	1.05
4f, 4f′	3.20	5.89	5.59	3.38	0.953	1.04
	3.19	5.88	5.57	3.37	0.951	1.00
4g, 4g′	3.19	5.86	5.57	3.39	0.93	1.04
	3.13				0.91	0.98

[a] In $CDCl_3$, chemical shifts in ppm, δ-scale.

Table 7. ^{1}H NMR Coupling Constants (in Hz) of **4a−g**

	5-H			4-H		3-H	6-H
compd	$^3J_{H5/H4}$	$^3J_{H5/H6}$	$^4J_{H5/H3}$	$^3J_{H4/H3}$	$^4J_{H4/H6}$	$^3J_{H3/3\text{-}CH_3}$	$^3J_{H6/6\text{-}CH_3}$
4a	11.0	3.9	2.0	4.6	2.1	7.1	7.4
4b	11.0	3.9	2.0	4.4	2.3	7.2	7.4
4c	11.0	3.9	2.0	4.7	2.1	7.1	7.4
4d	10.9	3.9	2.0	4.7	2.1	7.0	7.4
4e	11.0	3.7	2.1	4.3	2.1	7.0	7.4
4f, 4f′	11.0/10.9	*a*	*a*	4.7/4.6	2.2/2.1	7.3/7.2	7.7
4g, 4g′	*a*	*a*	*a*	*a*	*a*	7.3/6.9	7.7/7.3

[a] Not determined.

Table 8. Selected ^{13}C NMR Data of **4a−g**[a]

compd	C-2	C-3	C-4	C-5	C-6	3-CH_3	6-CH_3
4a	55.5	40.0	129.5	134.4	30.3	18.1	21.1
4b	*b*	40.9	130.7	135.6	31.6	19.0	22.3
4c	55.8	40.2	129.6	134.0	30.6	18.0	21.2
4d	54.9	39.7	*b*	*b*	30.7	18.0	21.2
4e	55.6	40.7	129.6	134.6	30.5	18.0	21.2
4f, 4f′	56.27	40.6	129.3	134.8	30.6	18.41	21.5
	56.22	40.4			30.3	18.35	21.2
4g, 4g′	55.5	40.3	129.4	134.3	30.6	18.2	21.4
	55.2	39.6		134.0	30.3	27.9	21.0

[a] In $CDCl_3$. [b] Not located.

molecular models based on the result of X-ray structure determinations of the parent compounds[14,18] that the 2,2-diaryl-3,6-dihydro-*cis*-3,6-dimethyl-2*H*-selenapyrans **3** each exhibit a pair of very different ^3J(3-H,4-H) and ^3J(5-H,6-H) coupling constants (~1.8 and 5.4 Hz, respectively), whereas the analogous ^{1}H NMR ^3J(H,H) coupling constants in the *trans*-3,6-dimethyl-isomers **4** are closer in magnitude at $^3J \approx 4.5$ and 3.9 Hz. The magnitude of the respective coupling constants was determined by simulation of the ^{1}H NMR spectra (using the PANIC program package). A typical example is shown in Figure 1. The 6-CH_3 resonance was unambigously assigned by means of its ^{77}Se satellites and used as an internal reference.

We had previously shown that selenobenzophenone is only stable up to ca. 90 °C and slowly begins to decompose at higher temperatures to yield tetraphenylethene.[12,13b] In a separate experiment we have now shown that the diarylselenoketones also appear to slowly decompose at 12 kbar under the conditions applied here. Keeping compound **2c** at 12 kbar under the reaction conditions gave a mixture containing ca. 50% tetra(4-fluorophenyl)ethene (**8c**, isolated and identified by an X-ray crystal structure analysis[19]), 25% of remaining diarylselenoketone **2c**, and 25% of a mixture of as yet unidentified decomposition products. Therefore, it was not surprising that the respective tetraarylethenes were also formed during the [4 + 2] cycloaddition reaction of the diarylselenoketones **2a−g** with *cis,trans*-2,4-hexadiene at 12 kbar. In some of these reactions, the respective tetraarylethene competition product was by far the major component of the product mixture (see Scheme 4). The reactions of the diarylthioketones **5a−g** with *cis,trans*-2,4-hexadiene at 12 kbar gave very similar product mixtures with **7a−g** being the dominating cycloaddition products.

(18) Fröhlich, R.; Grehl, M.; Wilker, S.; Erker, G.; Mazerolles, P.; Laurent, C. *Z. Naturforsch.* **1994**, *49b*, 1397.

(19) Compound **8c** was characterized by X-ray diffraction from a crystal that contained the bis(4-fluorophenyl)selenoketone-dimer and tetra(4-fluorophenyl)ethene in a 1:1 mixture. Fröhlich, R.; Grehl, M. unpublished results. Details of this X-ray crystal structure analysis are given in the supporting information.

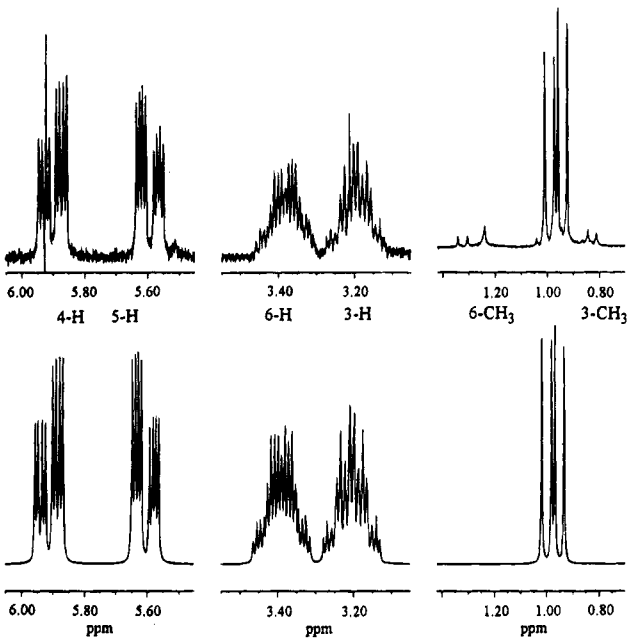
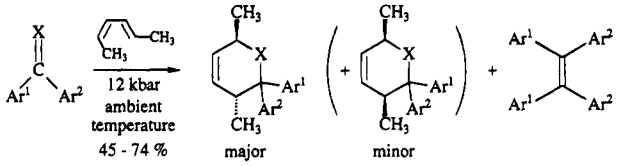


Figure 1. Comparison of Observed and Calculated Selected ^{1}H NMR Resonances of **4a**

Scheme 4



2a - g X = Se **4a - g** **3a - g** **8**

5a - g X = S **7a - g** **6a - g**

educt	trans-/cis- (4 : 3 or 7 : 6)	% 8	educt	trans-/cis- (4 : 3 or 7 : 6)	% 8
2a	95 : 5	20	**5a**	96 : 4	60
2b	75 : 25	90	**5b**	85 : 15	20
2c	92 : 8	40	**5c**	92 : 8	13
2d	75 : 25	80	**5d**	80 : 20	23
2e	84 : 16	30	**5e**	-	-
2f	84 : 16	40	**5f**	77 : 23	50
2g	80 : 20	36	**5g**	79 : 21	31

Solvent and Substituent Dependence of the Reaction Rates. The stereochemical course taken indicates that the reaction of **2** (and **5**) with *cis,trans*-2,4-hexadiene at normal pressure is not following a concerted pathway. Therefore, it was necessary to determine the solvent polarity dependence of the reaction rate of the dihydro-2*H*-chalcogenapyran formation of a representative example using the *cis,trans*-hexadiene trapping reagent. Rate determining involvement of ionic or dipolar intermediates would be revealed by very large k_{rel} values using sufficiently different solvent polarities.[11]

For this investigation we chose as a typical example the reaction of bis(4-fluorophenyl)selenoketone (**2c**) with *cis,trans*-

Scheme 5

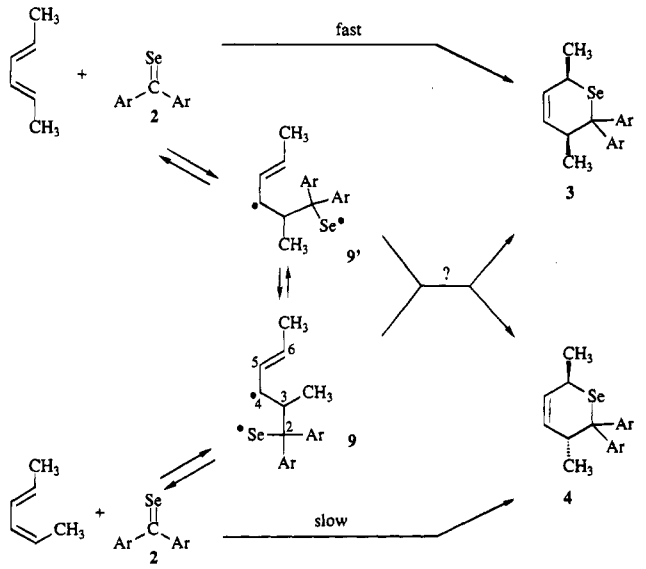


Table 9. Selected ^{1}H NMR Chemical Shifts (ppm, δ-scale) of the 2,2-Diaryl-3,6-dihydro-*trans*-3,6-dimethyl-2*H*-thiapyrans **7a–d,f,g**[a]

compd	3-H	4-H	5-H	6-H	3-CH_3	6-CH_3
7a	3.09	6.00	5.64	3.17	0.83	0.93
7b	3.13	5.97	5.65	3.20	0.92	0.95
7c	3.09	5.93	5.61	3.16	0.85	0.90
7d	3.20	5.86	5.60	3.20	0.81	0.92
7f, 7f'	3.16	5.96	5.61	3.16	0.87	0.94
		5.95			0.84	0.93
7g, 7g'	3.17	5.94	5.62	3.39	0.86	0.92
	3.13				0.83	0.90

[a] In $CDCl_3$.

Table 10. ^{1}H NMR Coupling Constants (in Hz) of **7a–d,f,g**

	5-H			4-H		3-H	6-H
compd	$^3J_{H5/H4}$	$^3J_{H5/H6}$	$^4J_{H5/H3}$	$^3J_{H4/H3}$	$^4J_{H4/H6}$	$^3J_{H3/3\text{-}CH_3}$	$^3J_{H6/6\text{-}CH_3}$
7a	10.7	3.3	1.5	4.4	1.9	7.0	7.3
7b	10.6	3.6	1.9	4.7	2.2	7.1	7.4
7c	10.7	3.5	2.0	4.6	2.2	7.0	7.3
7d	10.9	3.9	2.0	4.7	2.1	7.1	7.3
7f, 7f'	10.7	3.3	1.6	4.1	2.1	7.1	7.2/7.3
7g, 7g'	*a*	*a*	*a*	*a*	*a*	7.1	7.2/7.5

[a] Not determined.

2,4-hexadiene. For these experiments the selenoketone was isolated. The monomer/dimer mixture was dissolved in the respective (deuterated) solvent and then kept at 60 °C until the dimer to monomer conversion was complete (as judged by ^{1}H NMR spectroscopy). Then an ca. 10-fold excess of the *cis,trans*-2,4-hexadiene trapping reagent was added, and the cycloaddition reaction was carried out in a thermostated bath at 67 °C. The time dependent decrease of the concentration of **2c** was monitored by ^{1}H NMR spectroscopy and the pseudo-first-order rate constants at 67 °C calculated. The relative reaction rates were almost the same in acetone-d_6 (k_{rel} = 1), toluene-d_8 (k_{rel} = 1.25), and tetrahydrofuran-d_8 (k_{rel} = 1.35). The reaction is only slightly faster in dichloromethane-d_2 (k_{rel} = 2.65) and acetonitrile-d_3 (k_{rel} = 8.0, see Table 12).

Under analogous conditions (tetrahydrofuran-d_8, 67 °C, 10-fold excess of *cis,trans*-2,4-hexadiene) the substituent dependence of the reaction rate of the diarylselenoketone plus *cis,trans*-hexadiene cycloaddition was determined under kinetic pseudo-first-order conditions employing the chalcogenocarbonyls **2c** [bis(4-fluorophenyl)selenoketone], **2a** [selenobenzophenone], and **2e** [bis(4-methoxyphenyl)selenoketone]. The pseudo-first-order rate constants of the formation of the respective dihydro-2*H*-selenapyran systems (**3**/**4**-mixtures similar as given in Scheme 2) are almost identical starting from these three differently substituted diarylselenoketones at 2.74 × 10^{-5} s^{-1} (**2c**), 2.68 × 10^{-5} s^{-1} (**2a**), and 2.42 × 10^{-5} s^{-1} (**2e**). Thus, there is almost no substituent dependence on the rate of this trapping reaction. Consequently, the linear Hammett plot using these data and standard σ-substituent constants gave a ρ-value (+0.08) close to zero.

Table 11. Selected ^{13}C NMR Data of **7a–d,f,g**[a]

compd	C-2	C-3	C-4	C-5	C-6	3-CH_3	6-CH_3
7a	57.4	39.2	128.3	132.8	35.3	17.6	20.8
7b	56.4	39.0	129.2	132.2	34.4	18.5	20.9
7c	56.3	39.4	128.6	132.0	35.4	17.6	20.8
7d	56.8	38.8	128.1	133.2	35.3	17.5	20.8
7f, 7f'	57.3	39.5	128.6	132.9	35.3	17.7	20.8
		39.3	128.2				
7g, 7g'	57.0	39.3	128.5	131.8	33.9	17.6	21.0
	56.6	38.7	128.3	131.0	33.8	17.5	20.6

[a] In $CDCl_3$.

Table 12. Dependence of the Pseudo-First-Order Rate Constant of the Bis(4-fluorophenyl)selenoketone (**2c**) Plus *cis,trans*-2,4-Hexadiene Cycloaddition Reaction from the Solvent Polarity (at 67 °C)[a]

solvent:	toluene	THF	dichloromethane	acetone	acetonitrile
$k \cdot 10^5$ [s^{-1}]	2.5	2.7	5.3	2.0	16.0
E_t[b]	34.4	37.4	41.1	42.2	46.0

[a] Measured in deuterated solvents. [b] Values from ref 26.

Conclusions

The key for understanding the stereochemical features of the addition reactions of the chalcogenocarbonyl compounds **2** and **5** with the 2,4-hexadiene isomers to give the *cis*- and *trans*-dimethyl substituted dihydro-2*H*-chalcogenapyran systems lies in the fact that *trans,trans*-2,4-hexadiene is about 1000 times more reactive in common (concerted) Diels–Alder reactions than the *cis-trans*-2,4-hexadiene isomer.[20] Therefore, it is likely that the stereospecific reactions of the diarylselenocarbonyl compounds **2a–g** with *trans,trans*-2,4-hexadiene to give the 2,2-diaryl-3,6-dihydro-*cis*-3,6-dimethyl-2*H*-selenapyrans **3a–g** (and the analogous formation of **6a–g** from **5a–g** and *trans,trans*-2,4-hexadiene as well) have to be regarded as concerted thermally induced hetero-Diels–Alder reactions.

The course of the cycloaddition reaction of the chalcogenoketones with the much less reactive *cis,trans*-2,4-hexadiene isomer is more complicated. At normal pressure the reaction is clearly not one step concerted, because this would lead to stereospecific formation of the dihydro-*trans*-3,6-dimethyl-2*H*-selenapyran system **4**. Therefore, we have to assume a stepwise reaction mechanism, i.e., a situation where only one new bond is formed at a time and the reaction "rests" at the stage of an intermediate. However, in this case the intermediate involved seems not to be placed on a direct route to the formation of the final six-membered ring products since such a direct two step mechanism would probably result in an unselective formation of a near to equimolar mixture of the close to isoenergetic *cis*- and *trans*-product isomers **3** and **4**. Just this is not observed experimentally. Instead, the reaction of **2** with *cis,trans*-2,4-hexadiene leads to the *stereoselective* formation of the *cis*-product isomer **3**. Therefore, it has to be assumed that the intermediate formed in the first step from **2** and *cis,trans*-2,4-hexadiene does not

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predominantly undergo ring closure but rather prefers cleavage to re-form **2** and 2,4-hexadiene. The simple reverse reaction would lead back to *cis,trans*-2,4-hexadiene, but the alleged intermediate can probably conformationally equilibrate and then liberate **2** plus the very reactive isomerized diene, *trans,trans*-2,4-hexadiene. Since this is so much more reactive than the *cis,trans*-2,4-hexadiene starting material, it is not accumulated in the reaction mixture but very effectively consumed by **2** with the observed stereoselective formation of **3**.

Such a stepwise 1,4-disubstituted 1,3-diene isomerization that is competing with a concerted [4 + 2] cycloaddition is not unprecedented in the literature. Singlet oxygen addition to *cis,trans*- and *trans,trans*-2,4-hexadiene[21] or the reaction of the 1,4-(*N,N*-dimethylamino)butadienes with 1,2-dicyanoethylene[22] are typical examples. Ionic pathways through dipolar intermediates are the favored diene isomerization mechanisms in such reactions but that seems to be different with the reaction of a diarylselenoketone with *cis,trans*-2,4-hexadiene. The marginal rate dependence of this reaction on solvent polarity is contradictious to a formulation of the dominating pathway proceeding through a polar intermediate.[11] We assume a mechanism involving a diradical intermediate.[23] Remains the question whether this is formed by carbon−carbon or carbon−selenium bond formation. In principle this may potentially be decided by evaluating the influence of arene substituents on the rate of the reaction between differently substituted diarylselenoketones and *cis,trans*-2,4-hexadiene, although the Hammett behavior of radical reactions is sometimes complicated.[24] A complete absence of an arene substituent rate effect as observed here, is, however, probably a strong indication that one of the radical centers is chalcogene centered, i.e., we assume that the diradical intermediate **9** (see Scheme 5) is formed in the reaction of **2** with *cis,trans*-2,4-hexadiene. This can then be conformationally equilibrated with **9′** by rotation about the C3−C4 single bond, followed by C2−C3 bond cleavage to give *trans,trans*-2,4-hexadiene, that is then effectively trapped by **2** to give **3**. In principle there could be some "mechanistical leakage" from **9**/**9′** to the products **3** and **4**, but the observed **3**:**4** ratios clearly show that this alternative pathway is in most cases not significant here. Finally, the concerted pathway can eventually compete with the stepwise "isomerization" route when the reaction of the selenoketones (and thioketones) with *cis,trans*-2,4-hexadiene is carried out under high pressure conditions at 12 kbar.

From our study on these specific systems one can probably draw the general conclusion that most trapping reactions of the reactive in situ generated chalcogenocarbonyl compounds reported in the literature are indeed concerted [4 + 2] cycloadditions, especially when the reactive s-*cis*-oriented conjugated dienes are employed. Only when less reactive hetero-Diels−Alder trapping reagents are used, one has to take more complicated stepwise mechanistic pathways into account, which are then likely to become dominant.

Experimental Section

The ylides and thio- and selenoketones were prepared and handled in an inert atmosphere (argon) using Schlenk-type glassware or a glovebox. All solvents were dried and distilled under argon prior to use. The ylides were prepared as previously described;[14] *trans,trans*- and *cis-trans*-2,4-hexadiene were available commercially and also prepared according to a literature procedure.[25] The ^{1}H NMR characterization (^{1}H NMR at 200, 300, or 360 MHz, ^{13}C NMR at 50, 75, or 90 MHz) of most diaryldihydro-2*H*-chalcogenapyran products included NOE- and decoupling experiments and PANIC spectrum simulation. The ^{13}C NMR characterization mostly included a DEPT experiment, often the spectra were recorded gated decoupled to allow for the $^1J_{CH}$ determination. Reactions at 12 kbar were performed using a hydropneumatic autoclave system (Hofer, A. Mülheim a. d. Ruhr, Germany).

Trapping Reaction of the Diarylselenoketones with *trans,trans*-2,4-Hexadiene. General Procedure. One molar equiv of the ylide **1** was dissolved in toluene. Two molar equivs of elemental selenium were added and seven molar equivs of *trans,trans*-2,4-hexadiene. The red reaction mixture was kept for several hours at 75−85 °C with stirring and then cooled to room temperature. Excess selenium was removed by filtration and the solvent and the residual conjugated diene were distilled in vacuo into a cold trap. The diene was analyzed by GPC. The residue was taken up in pentane and filtered. The filtrate was concentrated. Usually an aliquot was evaporated to dryness and analyzed by ^{1}H NMR. The major portion of the pentane extract was chromatographed with pentane at silica gel to give the 2,2-diaryl-3,6-dihydro-*cis*-3,6-dimethyl-2*H*-selenapyrans **3** as colorless, sometimes slightly yellow oils. The ^{1}H- and ^{13}C NMR data of the products are given in Tables 1−3. Additional information is provided with the supporting information.

3,6-Dihydro-*cis*-3,6-dimethyl-2,2-diphenyl-2*H*-selenapyran, 3a. The ylide **1a** (2.70 g, 6.29 mmol) was treated with 0.99 g (12.6 mmol) of selenium and 2.88 g (35.1 mmol) of *trans,trans*-2,4-hexadiene in 150 mL of toluene for 6 h at 85 °C to give 1.92 g (94%) of crude **3a**; after chromatography 1.79 g (87%) of **3a** was obtained as a slightly yellow oil. For characterization see ref 10.

2,2-Bis(4-chlorophenyl)-3,6-dihydro-*cis*-3,6-dimethyl-2*H*-selenapyran, 3b. Reaction of 2.39 g (4.80 mmol) of the ylide **1b** with 0.77 g (9.75 mmol) of selenium and 2.88 g (35.1 mmol) of *trans,trans*-2,4-hexadiene in 150 mL of toluene for 10 h at 80 °C gave 1.37 g (89%) of **3b**.[10]

2,2-Bis(4-fluorophenyl)-3,6-dihydro-*cis*-3,6-dimethyl-2*H*-selenapyran, 3c. Treatment of 0.50 g (1.07 mmol) of the ylide **1c** with 0.17 g (2.14 mmol) of selenium in the presence of 0.61 g (7.49 mmol) of *trans,trans*-2,4-hexadiene for 2 h at 85 °C in 30 mL of toluene gave 0.34 g (89%) of crude **3c**, 0.28 g (74%) after chromatography (oil). Anal. Calcd for $C_{19}H_{18}F_2Se$ (363.3): C, 62.81; H, 4.91. Found: C, 63.21; H, 5.08.

2,2-Bis[3-(trifluoromethyl)-3,6-dihydro-*cis*-3,6-dimethyl-2*H*-selenapyran, 3d. Reaction of 0.40 g (0.71 mmol) of the ylide **1d** with 0.11 g (1.42 mmol) of selenium and 0.41 g (4.79 mmol) of *trans,trans*-2,4-hexadiene for 12 h at 85 °C in 70 mL of toluene gave 0.29 g (88%) of crude **3d**, after chromatography 0.22 g (67%) as a slightly yellow oil. Anal. Calcd for $C_{21}H_{18}F_6Se$ (463.2): C, 54.44; H, 3.92. Found: C, 55.08; H, 3.79.

3,6-Dihydrobis(4-methoxyphenyl)-*cis*-3,6-dimethyl-2*H*-selenapyran, 3e. Reaction of 0.50 g (1.02 mmol) of the ylide **1e** with 0.16 g (2.04 mmol) of selenium and 0.59 g (7.16 mmol) of *trans,trans*-2,4-hexadiene for 6 h at 85 °C in 30 mL of toluene gave 0.28 g (72%) of crude **3e**, 0.21 g (54%) (colorless oil) after chromatography. Anal. Calcd for $C_{21}H_{24}O_2Se$ (387.4): C, 65.11; H, 6.24. Found: C, 65.35; H, 6.07.

3,6-Dihydro-*cis*-3,6-dimethyl-2-(4-methylphenyl)-2-phenyl-2*H*-selenapyran, 3f. Treatment of 0.50 g (1.12 mmol) of the ylide **1f** with 0.18 g (2.25 mmol) of selenium and 0.65 g (7.91 mmol) of *trans,trans*-

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2,4-hexadiene for 24 h at 85 °C in 30 mL of toluene yielded 0.33 g (85%) of crude 1:1 mixture of the diastereomeric products **3f** and **3f'**, 0.25 g (64%) after chromatography (colorless oil). Anal. Calcd for $C_{20}H_{22}Se$ (341.1): C, 70.37; H, 6.44. Found: C, 70.30; H, 6.69.

2-(4-Chlorophenyl)-3,6-dihydro-*cis*-3,6-dimethyl-2-phenyl-2*H*-selenapyran, 3g. Treatment of 1.00 g (2.16 mmol) of the ylide **1g** with 0.34 g (4.31 mmol) of selenium and 1.23 g (15.1 mmol) of *trans,trans*-2,4-hexadiene for 2 h at 85 °C in 30 mL of toluene gave 0.69 g (88%) of a viscous oil, 0.58 g (71%) of a 1:1 mixture of **3g** and **3g'** after chromatography. Anal. Calcd for $C_{19}H_{19}ClSe$ (361.8): C, 63.08; H, 5.29. Found: C, 63.42; H, 4.82.

Trapping of the Diarylselenoketones with *cis,trans*-2,4-Hexadiene at Normal Pressure. These reactions were performed similarly as the *trans,trans*-2,4-hexadiene trapping reactions described above; here all reactions were carried out at 80 °C. It was assured by ^{1}H NMR spectroscopy that the *cis/trans*-diastereomeric ratio (**3**:**4**) was almost identical before and after the chromatographic workup. The reisolated *cis,trans*-2,4-hexadiene was checked by GPC (and in one case also by ^{1}H NMR) and found to be isomerically unchanged. For spectroscopic and physical characterization of the products **4** see Tables 6−8 and the details given below. Each experiment was carried out several times. The following experimental data are representative.

3a:**4a** = 97:3, 0.81 g (77%) was isolated (after chromatography) from 1.00 g (2.30 mmol) of **1a**, 0.37 g (4.60 mmol) of selenium, and 1.08 g (12.0 mmol) of *cis,trans*-2,4-hexadiene (reaction carried out for 8 h at 80 °C in 75 mL of toluene). **3c**:**4c** = 91:9, 0.67 g (86%) was isolated from the reaction of 1.00 g (2.15 mmol) of **1c** with 0.34 g (4.30 mmol) of selenium and 1.23 g (15.1 mmol) of *cis,trans*-2,4-hexadiene in 75 mL of toluene (8 h, 80 °C). **3d**:**4d** = 59:41, 0.29 g (68%) was isolated from the reaction of 0.50 g (0.89 mmol) of **1d** with 0.14 g (1.7 mmol) of selenium and 0.50 g (6.2 mmol) of *cis,trans*-2,4-hexadiene in 75 mL of toluene (12 h, 80 °C). **3e**:**4e** = >98:2, 0.27 g (68%) was isolated from the reaction of 0.50 g (1.02 mmol) of **1e** with 0.16 g (2.04 mmol) of selenium and 0.59 g (7.16 mmol) of *cis,trans*-2,4-hexadiene in 75 mL of toluene (16 h, 80 °C). **3f**:**4f** = >98:2 (**3f**:**3f'** = 1:1), 0.48 g (80%) was isolated from the reaction of 0.80 g (1.81 mmol) of **1f** with 0.28 g (3.62 mmol) of selenium and 1.03 g (12.6 mmol) of *cis,trans*-2,4-hexadiene in 150 mL of toluene (30 h, 80 °C). **3g**:**4g** = 85:15 (**3g**:**3g'** = 1:1 and **4g**:**4g'** = 1:1), 0.55 g (71%) was isolated from the reaction of 1.00 g (2.16 mmol) of **1g** with 0.34 g (4.3 mmol) of selenium and 1.23 g (15.1 mmol) of *cis,trans*-2,4-hexadiene in 75 mL of toluene (8 h, 80 °C). The trapping reaction of the selenoketone **2b** with *cis,trans*-2,4-hexadiene was exceptional as here the **3b**:**4b** ratio turned out to be remarkably dependent on the reaction temperature. Withing a range of ± 5% the following **3b**:**4b** ratios were observed when the trapping reaction was carried out analogously as described above: 83:17 (60 °C), 80:20 (70 °C), 62:38 (75 °C), 74:26 (80 °C), 80:20 (90 °C), and 81:19 (100 °C); single experiments where the reaction conditions were further changed (e.g., other concentrations used) gave an even larger variation around these typical **3b**:**4b** ratios. The smallest product diastereomer ratio reached within this series of experiments starting from isomerically pure *cis,trans*-2,4-hexadiene was **3b**:**4b** = 58:42.

Kinetics of the 3c + 4c Formation in Five Different Solvents. Samples of ca. 10 mg (ca. 0.035 mmol) of the selenoketone **2c** (monomer/dimer mixture) were dissolved in toluene-d_8, THF-d_8, acetone-d_6, dichloromethane-d_2, and acetonitrile-d_3 (ca. 0.5 mL each), respectively, and then kept at 60 °C until no dimer could be detected by ^{1}H NMR. Then 0.19−0.38 mmol of *cis,trans*-2,4-hexadiene was added, and the probes were sealed in 5 mm NMR tubes. The thermolyses were carried out in a thermostated bath at 67 °C, and the progress of the reaction was monitored at given times by means of ^{1}H NMR spectroscopy at 300 K (integration of the *o*-phenyl hydrogen signals of **2c** and the 6-CH_3 resonance of the dihydrodimethyl-2*H*-selenapyran). From these time dependent concentration changes the *k*-values given in Table 12 were obtained (the observed experimental data are provided with the supporting information).

Kinetics of the Reaction of the Selenoketones 2a, 2c, and 2e with *cis,trans*-2,4-Hexadiene. The first-order rate constants were determined analogously as described above (67 °C); the experimental data are listed in the supporting information.

High Pressure Trapping Reactions of the Diarylselenoketones with *cis,trans*-2,4-Hexadiene. General Procedure. The ylide **1** was dissolved in toluene, the solution charged with 2 molar equivs of selenium, and the mixture was kept for several hours at 75 °C with stirring. The reaction mixture was then cooled to room temperature and filtered. The green filtrate was concentrated in vacuo to a volume of ca. 2 mL and then transferred to the high pressure reaction vessel (see Scheme 3). The sample was cooled to −78 °C (15 min), and then toluene was added with taking good care that a two layer system was obtained. The two layer system was cooled, and then the "sandwich construction" completed by carefully adding without mixing a final layer containing ca. 7 molar equivs of *cis,trans*-2,4-hexadiene dissolved in toluene. The reaction vessel was cooled again, then sealed, and transferred to the high pressure system. The system was pressurized to 12 kbar while the sample inside the reaction vessel was still cold, then the system was allowed to stand at 12 kbar at ambient temperature for a period of 24 h. The system was depressurized and the product mixture removed from the reaction vessel. Volatiles were removed in vacuo (excess *cis,trans*-2,4-hexadiene analyzed by GPC), the residue taken up in pentane and filtered from triphenylphosphine selenide. The product ratio (**3**:**4**:**8**) was determined by ^{1}H NMR spectroscopy from an aliquot of the solution, and then the product purified by chromatography (silica gel/pentane). In most cases the obtained products **4** still contained some quantities of the corresponding tetraarylethenes which were not completely removed. Usually the characterization of the dihydro-*trans*-dimethyl-2*H*-pyrans **4** were carried out using these substantially enriched product mixtures. The tetraarylethenes **8** were in most cases obtained pure in variable yield by chromatography. Selected ^{1}H and ^{13}C NMR data of the complexes **4** are given in Tables 6−8; additional information and the spectroscopic data of the tetraarylethenes **8** is given in the supporting information.

3,6-Dihydro-*trans*-3,6-dimethyl-2,2-diphenyl-2*H*-selenapyran, 4a. Reaction of 0.30 g (0.70 mmol) of **1a** with 0.11 g (1.39 mmol) of selenium and 0.40 g (4.90 mmol) of *cis,trans*-2,4-hexadiene gave 0.16 g (71%) of a slightly yellow oil containing the products **4a** and **3a** in a 95:5 ratio (**4a**:**8a** = 80:20); 0.12 g (52%) of **4a** was isolated after chromatography. Anal. Calcd for $C_{19}H_{20}Se$ (327.3): C, 69.7; H, 6.16. Found: C, 69.25; H, 5.79.

2,2-Bis(4-chlorophenyl)-3,6-dihydro-*trans*-3,6-dimethyl-2*H*-selenapyran, 4b. Reaction of 0.30 g (0.60 mmol) of **1b** with 95 mg (1.20 mmol) of selenium and 0.34 g (4.20 mmol) of *cis,trans*-2,4-hexadiene gave 193 mg (84%) of the crude product, 0.17 g (74%) after chromatography (9:1 pentane/toluene), **4b**:**3b** = 75:25, **4b**:**8b** = 8:92.

2,2-Bis(4-fluorophenyl)-3,6-dihydro-*trans*-3,6-dimethyl-2*H*-selenapyran, 4c. Reaction of 0.40 g (0.86 mmol) of **1c** with 0.14 g (1.7 mmol) of selenium and 0.49 g (6.0 mmol) of *cis,trans*-2,4-hexadiene gave 0.21 g (67%) of a yellow oil, 0.18 g (58%, based on the transferred Ar_2C-units) after chromatography (10:1 pentane/ethanol), **4c**:**3c** = 92:8, **4c**:**8c** = 59:41. A second fraction of pure **8c** (60 mg) was obtained from the chromatographic separation. The compound **8c** was characterized by an X-ray crystal analysis (for details see the supporting information). HRMS of **4c** calcd for $C_{19}H_{18}F_2Se$ 364.0543, found 364.0555.

2,2-Bis[3-(trifluoromethyl)phenyl]-3,6-dihydro-*trans*-3,6-dimethyl-2*H*-selenapyran, 4d. Reaction of 0.40 g (0.82 mmol) of **1d** with 0.11 g (1.42 mmol) of selenium and 0.41 g (4.90 mmol) of *cis,trans*-2,4-hexadiene gave 0.26 g (81%) of a yellow solid, 0.22 g (69%) after chromatography (9:1 pentane/toluene), **4d**:**3d** = 75:25, **4d**:**8d** = 18:82.

3,6-Dihydro-2,2-bis(4-methoxyphenyl)-*trans*-3,6-dimethyl-2*H*-selenapyran, 4e. Reaction of 0.40 g (0.82 mmol) of **1e** with 0.13 g (1.6 mmol) of selenium and 0.46 g (5.60 mmol) of *cis,trans*-2,4-hexadiene gave 0.25 g (80%) of a green viscous oil, 0.15 g (45%) (colorless oil) after chromatography (20:1 pentane/ethanol), **4e**:**3e** = 84:16, **4e**:**8e** = 69:31. A second fraction (50 mg) of pure **8e** and a third fraction of unreacted selenoketone **2e** was obtained. HRMS of **4e** calcd for $C_{21}H_{24}O_2Se$ 388.0943, found 388.0931.

3,6-Dihydro-*trans*-3,6-dimethyl-2-(4-methylphenyl)-2-phenyl-2*H*-selenapyran, 4f. Reaction of 0.30 g (0.67 mmol) of **1f** with 0.11 g (1.40 mmol) of selenium and 0.38 g (4.70 mmol) of *cis,trans*-2,4-hexadiene gave 0.14 g (65%) of a yellow oil, 0.10 g (45%) after chromatography (pentane), **4f**:**4f'** = 1:1, (**4f** + **4f'**):(**3f** + **3f'**) = 84:16,

(**4f** + **4f'**):(**8f** + **8f'**) = 60:40. HRMS of **4f** calcd for $C_{20}H_{22}Se$ 342.0888, found 342.0879.

2-(4-Chlorophenyl)-3,6-dihydro-*trans*-3,6-dimethyl-2-phenyl-2*H*-selenapyran 4g. Reaction of 0.30 g (0.65 mmol) of **1g** with 0.10 g (1.30 mmol) of selenium and 0.37 g (4.55 mmol) of *cis,trans*-2,4-hexadiene gave 0.17 g (77%) of a slightly yellow oil, 0.11 g (48%) after chromatography (20:1 pentane/ethanol), **4g**:**4g'** = 1:1, (**4g** + **4g'**):(**3g** + **3g'**) = 80:20, (**4g** + **4g'**):(**8g** + **8g'**) = 64:36. HRMS of **4g** calcd for $C_{19}H_{19}ClSe$ 400.0786, found 400.0772.

Trapping of Diarylthioketones with *cis,trans*-2,4-Hexadiene at Normal Pressure. In these experiments the diarylthioketones (**5**) were not isolated but generated in situ by means of the Staudinger-chalcogenation method. The ylide **1** was dissolved in toluene. Sulfur (2 molar equivs) and *cis,trans*-2,4-hexadiene (ca. 7 molar equivs) were added. The mixture was kept for several hours at 80 °C with stirring, then cooled to room temperature, and filtered. Volatiles were removed in vacuo and collected in a cold trap (isomeric purity of reisolated *cis,trans*-2,4-hexadiene was established by GPC) An aliquot of the solid or oily residue was investigated by ^1H NMR (**6**:**7** ratio), and then the product was purified by chromatography (silica gel/pentane). Only the dihydro-*cis*-3,6-dimethyl-2*H*-pyran products **6** were obtained unless noted otherwise. For selected ^1H and ^{13}C NMR data of the obtained products see Tables 4 and 5; for additional data see the supporting information; the spectral assignment was done in analogy to the corresponding selenium containing heterocycles.

3,6-Dihydro-*cis*-3,6-dimethyl-2,2-diphenyl-2*H*-thiapyran, 6a. The reaction of 0.50 g (1.17 mmol) of the ylide **1a** with 74 mg (2.34 mmol) of sulfur and 0.67 g (8.19 mmol) of *cis,trans*-2,4-hexadiene for 28 h at 80 °C in 75 mL of toluene gave 0.39 g (83%) of a yellow oil, 0.38 g (80%) of a solid, mp 54−55 °C[10] after recrystallization from ether/pentane.

2,2-Bis(4-chlorophenyl)-3,6-dihydro-*cis*-3,6-dimethyl-2*H*-thiapyran, 6b. Reaction of 0.50 g (1.00 mmol) of **1b** with 64 mg (2.01 mmol) of sulfur and 0.57 g (7.0 mmol) of *cis,trans*-2,4-hexadiene in 75 mL of toluene (26 h at 80 °C) gave 0.30 g (85%) of a viscous oil, 0.26 g (74%) (colorless oil) after chromatography. HRMS of **6b** calcd for $C_{19}H_{18}Cl_2S$ 348.0506, found 348.0499.

2,2-Bis(4-fluorophenyl)-3,6-dihydro-*cis*-3,6-dimethyl-2*H*-thiapyran, 6c. Reaction of 1.00 g (2.20 mmol) of **1c** with 0.12 g (4.40 mmol) of sulfur and 1.26 g (15.4 mmol) of *cis,trans*-2,4-hexadiene in 75 mL of toluene (28 h at 80 °C) gave 0.52 g (74%) of a yellow oil, 0.48 g (68%) of pure **6c** as a colorless solid after chromatography (ether/pentane 20:80), mp (DSC) 71 °C. Anal. Calcd for $C_{19}H_{18}F_2S$ (316.4): C, 72.12; H, 5.73. Found: C, 71.70; H, 5.43.

2,2-Bis(3-trifluorophenyl)-3,6-dihydro-*cis*-3,6-dimethyl-2*H*-thiapyran, 6d. Reaction of 0.50 g (0.89 mmol) of **1d** with 57 mg (1.77 mmol) of sulfur and 0.51 g (6.32 mmol) of *cis,trans*-2,4-hexadiene in 75 mL of toluene (36 h at 80 °C) gave 0.31 g (84%) of a dark yellow oil, 0.26 g (70%) after chromatography, slightly yellow oil. HRMS of **6d** calcd for $C_{21}H_{18}F_6S$ 416.1034, found 416.1043.

3,6-Dihydro-2,2-bis(4-methoxyphenyl)-*cis*-3,6-dimethyl-2*H*-thiapyran, 6e. Reaction of 0.50 g (1.02 mmol) of **1e** with 65 mg (2.04 mmol) of sulfur and 0.58 g (7.2 mmol) of *cis,trans*-2,4-hexadiene in 75 mL of toluene (46 h at 80 °C) gave 0.28 g (82%) of a yellow oil, 0.23 g (68%) after chromatography, yellow oil. Anal. Calcd for $C_{21}H_{24}O_2S$ (340.5): C, 74.08; H, 7.11. Found: C, 73.90; H, 6.71.

3,6-Dihydro-*cis*-3,6-dimethyl-2-(4-methylphenyl)-2-phenyl-2*H*-thiapyran, 6f. Reaction of 0.50 g (1.13 mmol) of **1f** with 72 mg (2.26 mmol) of sulfur and 0.65 g (7.9 mmol) of *cis,trans*-2,4-hexadiene in 150 mL of toluene (30 h, 80 °C) gave 0.27 g (81%) of a very viscous yellow oil, 0.23 g (70%) after chromatography (ether/pentane 10:90), **6f**:**6f'** = 1:1. In this case a small amount of the isomers **7f**/**7f'** and the olefins **8f**,**8f'** were also present: (**6f** + **6f'**):(**7f** + **7f'**) = 94:6, (**6f** + **6f'**):(**8f** + **8f'**) = 66:34. HRMS of **6f** calcd for $C_{20}H_{22}S$ 294.1442, found 294.1450.

2-(4-Chlorophenyl)-3,6-dihydro-*cis*-3,6-dimethyl-2-phenyl-2*H*-thiapyran, 6g. Reaction of 0.50 g (1.10 mmol) of **1g** with 69 mg (2.16 mmol) of sulfur and 0.62 g (7.6 mmol) of *cis,trans*-2,4-hexadiene in 80 mL of toluene (30 h, 80 °C) gave 0.29 g (85%), 0.18 g (53%) after chromatography, colorless oil, **6g**:**6g'** = 1:1, (**6g** + **6g'**):(**8g** + **8g'**) = 75:25. HRMS of **6g** calcd for $C_{19}H_{19}ClS$ 314.0896, found 314.0904.

Reactions of the Diarylthioketones with *cis,trans*-2,4-Hexadiene at High Pressure. The reactions of the thioketones **5** with *cis,trans*-2,4-hexadiene at 12 kbar were performed analogously as described for the diarylselenoketones. The thioketones were also directly prepared by treatment of the ylides **1** with excess chalcogene at 75 °C and reacted without isolating them with *cis,trans*-2,4-hexadiene at 12 kbar and ambient temperature. Selected NMR data of the products **7** are given in Tables 9 and 10. For additional data see the supporting information.

3,6-Dihydro-*trans*-3,6-dimethyl-2,2-diphenyl-2*H*-thiapyran, 7a. Reaction of 0.40 g (0.93 mmol) of **1a** with 63 mg (2.02 mmol) of sulfur (at 75 °C and normal pressure) and then with 0.76 g (9.50 mmol) of *cis,trans*-2,4-hexadiene at 12 kbar (ambient temperature, 3 days) gave 0.15 g (58%), 0.12 g (51%) after chromatography (silica gel, pentane), **7a**:**6a** = 96:4, **7a**:**8a** = 40:60. HRMS of **7a** calcd for $C_{19}H_{20}S$ 280.1286, found 280.1280.

2,2-Bis(4-chlorophenyl)-3,6-dihydro-*trans*-3,6-dimethyl-2*H*-thiapyran, 7b. Reaction of 0.40 g (0.80 mmol) of the ylide **1b** with 51 mg (1.59 mmol) of sulfur and then with 0.66 g (8.00 mmol) of *cis,trans*-2,4-hexadiene at 12 kbar gave 0.21 g (75%), 0.19 g (68%) after chromatography, **7b**:**6b** = 85:15, **7b**:**8b** = 80:20. HRMS of **7b** calcd for $C_{19}H_{18}Cl_2S$ 348.0506, found 348.0499.

2,2-Bis(4-fluorophenyl)-3,6-dihydro-*trans*-3,6-dimethyl-2*H*-thiapyran, 7c. Reaction of 0.30 g (0.65 mmol) of **1c** with 42 mg (1.31 mmol) of sulfur and then with 0.53 g (6.50 mmol) of *cis,trans*-2,4-hexadiene at 12 kbar gave 0.11 g (53%) of the crude product containing **7c** and **6c** in a 92:8 and **7c** and **8c** in a 87:13 ratio. The **7c**/**6c** mixture (92:8) could be obtained free from the tetraarylethene by chromatography, yield 92 mg (45%), mp (DSC) 105 °C. Anal. Calcd for $C_{19}H_{18}F_2S$ (316.4): C, 72.12; H, 5.73. Found: C, 71.70; H, 5.43.

2,2-Bis(3-fluorophenyl)-3,6-dihydro-*trans*-3,6-dimethyl-2*H*-thiapyran, 7d. Reaction of 0.30 g (0.53 mmol) of **1d** with 34 mg (1.06 mmol) of sulfur and then with 0.43 g (5.3 mmol) of *cis,trans*-2,4-hexadiene at 12 kbar gave 0.20 g (91%), 0.18 g (82%) after chromatography, **7d**:**6d** = 80:20, **7d**:**8d** = 77:23. HRMS of **7d** calcd for $C_{21}H_{18}F_6S$ 416.1034, found 416.1043.

3,6-Dihydro-*trans*-3,6-dimethyl-2-(4-methylphenyl)-2-phenyl-2*H*-thiapyran, 7f. Reaction of 0.30 g (0.68 mmol) of **1f** with 41 mg (1.36 mmol) of sulfur and then with 0.53 g (6.5 mmol) of *cis,trans*-2,4-hexadiene at 12 kbar gave 0.13 g (60%), 0.10 g (48%) after chromatography, **7f**:**7f'** = 1:1; (**7f** + **7f'**):(**6f** + **6f'**) = 77:23, (**7f** + **7f'**):(**8f** + **8f'**) = 51:49. HRMS of **7f** calcd for $C_{20}H_{22}S$ 294.1442, found 294.1450.

2-(4-Chlorophenyl)-3,6-dihydro-*trans*-3,6-dimethyl-2-phenyl-2*H*-thiapyran, 7g. Reaction of 0.33 g (0.72 mmol) of **1g** with 50 mg (1.55 mmol) of sulfur and then with 1.02 g (12.3 mmol) of *cis,trans*-2,4-hexadiene at 12 kbar gave 0.12 g (53%), **7g**:**7g'** = 1:1; (**7g** + **7g'**):(**6g** + **6g'**) = 79:21, (**7g** + **7g'**):(**8g** + **8g'**) = 69:31. HRMS of **7g** calcd for $C_{19}H_{19}ClS$ 314.0896, found 314.0904.

Acknowledgment. Financial support from the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, and the Alfried Krupp von Bohlen und Halbach-Stiftung is gratefully acknowledged. We thank W. Beineke for his great technical help with carrying out the high pressure experiments, E.-U. Würthwein for helping us with the calculations of the dihydro-dimethyl-2*H*-selenapyran isomers, and R. Fröhlich and M. Grehl for the X-ray crystal structure analysis of **8c**.

Supporting Information Available: Experimental and spectroscopic details and X-ray crystal structural data of **8c** (32 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA9522948