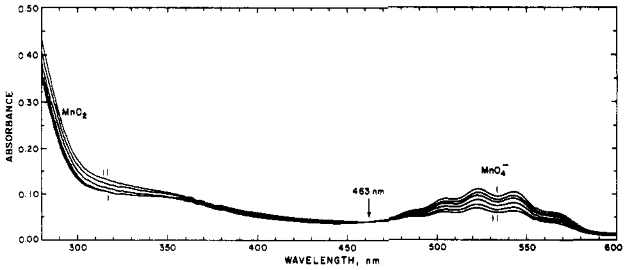


Figure 1. Successive ultraviolet–visible spectra (overall 11 scans; chart speed 10 nm s^{-1}) for disappearance of permanganate ion (4.00×10^{-5} M) and formation of manganese dioxide during the oxidation of 2,3-dimethyl-2-butenoate (**13**, 4.00×10^{-5} M) in 0.20 M KH_2PO_4–Na_2HPO_4 (pH 6.83, $\mu = 0.80$, isosbestic point 463 nm). The reference cell contained 0.20 M buffers.

Reduction of Manganese. A typical ultraviolet–visible change for the permanganate ion oxidation of α,β-unsaturated carboxylate ions is shown in Figure 1. Corresponding to the disappearance of the permanganate ion peak at 526 nm is the appearance of the characteristic spectrum of manganese dioxide. Excellent isosbestic points in the 465-nm region suggest a reaction with no buildup of an intermediate. Spectrophotometric and titritmetric analyses have shown this manganese species to be of oxidation state 4 (MnO_2).[1,6-8,19b,22,23]

Acknowledgment is made to the National Science Foundation for the purchase of the stopped-flow spectrometer (CHE 77-04970) and for financial assistance toward the purchase of the NMR spectrometers.

Registry No. **5**, 13095-94-8; **6**, 17263-38-6; **7**, 10344-93-1; **8**, 54467-93-5; **9**, 20224-66-2; **10**, 18358-13-9; **11**, 19342-43-9; **12**, 18358-40-2; **13**, 101225-65-4; **13** (protonated acid), 4411-97-6; **14**, 101225-66-5; **14** (protonated acid), 16666-45-8; **15**, 2964-00-3; **16**, 142-44-9; **17**, 142-42-7; **18**, 66482-37-9; **19**, 101225-67-6; **20**, 101225-68-7; **20** (protonated acid), 14378-06-4; $CH_3CHBrCO_2Et$, 535-11-5; CH_3COCH_3, 67-64-1; t-BuCHO, 630-19-3; $Ph_3P{=}CHCO_2Et$, 1099-45-2; (E)-t-BuCH=CHCO$_2$Et, 87995-20-8; PhCHO, 100-52-7; $CNCH_2CO_2H$, 372-09-8; MnO_4^-, 14333-13-2; etyhl 2,3-dimethyl-2-butenoate, 13979-28-7.

---

^{77}Se NMR. 2.[1] The Basis for Application of J_{Se-Se} and J_{Se-H} in Structure Assignments of Mono-, Di-, and Triseleno-Substituted Alkenes

Ib Johannsen,* Lars Henriksen, and Hanne Eggert*

Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

Received January 6, 1986

Series of isomeric mono-, di-, and triseleno-substituted alkenes have been synthesized and subjected to ^{77}Se NMR analysis. In di- and triseleno-substituted alkenes stereochemical assignments were obtained by measurements of ^{77}Se–^{77}Se coupling constants. Values between 117–77 Hz for cis $^3J_{Se-Se}$, 55–19 Hz for $^2J_{Se-Se}$, and 12–2 Hz for trans $^3J_{Se-Se}$ were found. A large body of vinylic ^{77}Se–^{1}H coupling constants has been obtained in di- and trisubstituted ethenes. This parameter also shows a stereochemical dependence, i.e., trans $^3J_{Se-H} \sim$ 1–4 Hz, cis $^3J_{Se-H} \sim$ 6–10 Hz, and $^2J_{Se-H} \sim$ 11–26 Hz. The stereochemistry of the base-catalyzed reaction of 1-alkynes with diselenides and the addition of benzeneselenol to alkynyl selenides are discussed in terms of the ^{77}Se NMR based structural assignments.

Introduction

In the field of synthetic organic chemistry, organoselenium compounds including alkenyl selenides have proved to be valuable synthetic precursors.[2,3]

In order to utilize selenium compounds as synthons, it is of major importance to have efficient analytical methods available. Standard spectroscopic methods (IR, ^{1}H NMR, ^{13}C NMR, MS) provide some information about the structure of these compounds, but in particular the identification of structural isomers causes severe problems. This is especially a problem within the synthetically important group of alkenylic selenides. Apart from cases where the presence of a vinylic proton–proton coupling constant can reveal the stereochemistry, no methods of general applicability are available for isomer assignments in selenium-substituted alkenes.

Several features make ^{77}Se NMR the ideal tool for solving the above mentioned problems. The relatively high receptivity of the ^{77}Se spin $^1/_2$ nucleus (three times better than ^{13}C)[4] allows easy measurements even on low-field instruments of not only chemical-shift values but also ^{1}H–^{77}Se coupling constants. The large spread in shielding of ^{77}Se ($\sim$3000 ppm) combined with narrow lines ($\Delta\nu_{1/2} \lesssim 1$ Hz normally) result in well-resolved lines and coupling patterns even when mixtures of several configurational isomers are studied. Moreover, if the molecule contains two or more nonequivalent selenium atoms, ^{77}Se–^{77}Se coupling constants can be measured. This very useful parameter is obtainable from the selenium satellites in the proton-noise-decoupled ^{77}Se NMR spectra. However, ^{77}Se NMR can not be applied efficiently in structure elucidation due to the lack of a sufficient body of relations between ^{77}Se NMR parameters and molecular structure.

In a previous paper[1] we established a relationship between the vicinal coupling constant $^3J_{Se-Se}$ and the cis/trans orientation of the selenium atoms in selenium-substituted alkenes. These promising results have led us to undertake a systematic ^{77}Se NMR study of selenium-substituted alkenylic systems. Within this group of com-

---

(1) Johannsen, I.; Eggert, H. *J. Am. Chem. Soc.* **1984**, *106*, 1240.

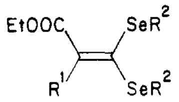
(2) For some general reviews see: Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049. Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22. Liotta, D. *Acc. Chem. Res.* **1984**, *17*, 28.

(3) Comasseto, J. V. *J. Organomet. Chem.* **1984**, *253*, 131.

(4) Harris, R. K. In "NMR and the Periodic Table"; Harris, R. K.; Mann, B. E., Eds.; Academic Press: London, 1978; p 4.

0022-3263/86/1951-1657$01.50/0

Table I. ^{77}Se–^{77}Se Coupling Constants (Hz) and ^{77}Se Chemical Shifts (ppm) of Geminal Diseleno-Substituted Alkenylic Compounds



compd	R^1	R^2	$^2J_{\text{Se-Se}}$	δ ^{77}Se^a
1a	$-COCH_3$	$-CH_2CH_2-$	55	606; 639
1b	$-COCH_3$	$-CH_2CH_2CH_2-$	34	399; 455
1c	$-COCH_3$	$PhCH_2-$, $PhCH_2-$	20	462; 515
1d	$-CN$	$-CH_2CH_2-$	53	593; 615
1e	$-CN$	$-CH_2CH_2CH_2-$	35	401; 487
1f	$-CN$	$PhCH_2-$, $PhCH_2-$	30	462; 615

^{a}The chemical shifts are relative to $(CH_3)_2Se$ (see Experimental Section) and are not assigned.

pounds three types of ^{1}H–^{77}Se and three types of ^{77}Se–^{77}Se coupling constants are possible (gem $^2J_{\text{Se-H}}$, cis $^3J_{\text{Se-H}}$, trans $^3J_{\text{Se-H}}$, gem $^2J_{\text{Se-Se}}$, cis $^3J_{\text{Se-Se}}$ and trans $^3J_{\text{Se-Se}}$). In this paper we present a complete basis for application of these parameters in structure assignments of selenium-substituted alkenes.

The work presented is organized as follows. First the size-range for the geminal ^{77}Se–^{77}Se coupling constants is determined using appropriate model compounds of known structure. The results from this and our previous study are then applied in order to determine the structure and the stereochemistry of the products from the addition reactions of diselenides and selenols to alkynes. This extended set of compounds with a well-established stereochemical structure is then used to provide a large body of vinylic ^{77}Se–^{1}H coupling constants. It is also shown that this parameter is related to the structure and the stereochemistry of the alkenyl selenides. A discussion of the stereochemical course of the addition reactions on the basis of the products formed is given at the end of the paper.

Results and Discussion

^{77}Se Chemical Shifts. The ^{77}Se chemical shifts of the compounds studied are given in Tables I and III. The spectra of the compounds presented in Table III were recorded from the crude reaction mixtures (see Experimental Section). The large spread in shielding for these products (200–600 ppm) resulted in resolved lines and coupling patterns even for mixtures of several closely related structures. Signal connectivities for the di- and triseleno-substituted alkenes were established on the basis of ^{77}Se–^{77}Se coupling constants obtained from the selenium satellites in the ^{77}Se NMR spectra. These satellites arise from molecules containing two ^{77}Se isotopes (^{77}Se natural abundance: 7.6%). The two ^{77}Se nuclei in the present compounds are nonequivalent; consequently they will give rise to a satellite AB spectrum due to a ^{77}Se–^{77}Se coupling. Within each compound, assignment of the ^{77}Se signals followed from the multiplicity of the signals in the proton-coupled ^{77}Se NMR spectra and the value of the vinylic $J_{\text{Se-H}}$ coupling constants (see below).

^{77}Se–^{77}Se Coupling Constants. Literature values regarding ^{77}Se–^{77}Se coupling constants in organic compounds are sparse. Besides our previous study on $J_{\text{Se-Se}}$ in tetraselenafulvalenes and our paper[5] on one- and two-bond ^{77}Se–^{77}Se coupling constants in dialkyl polyselenides a few other studies[6-9] have reported on $J_{\text{Se-Se}}$ coupling constants.

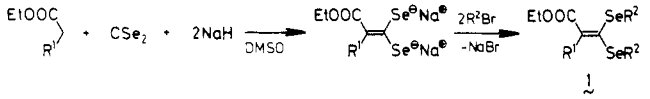


Figure 1. Preparation of 1,1-diseleno-substituted ethylenes (1).

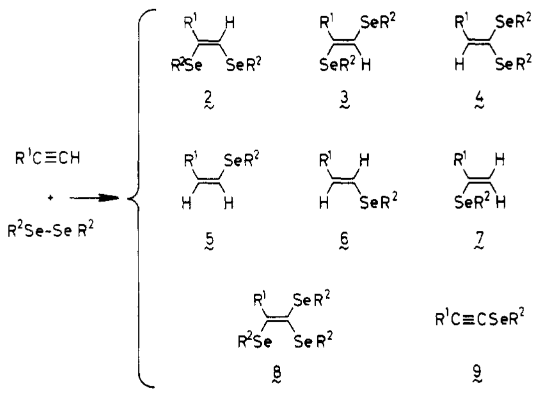


Figure 2. Reaction A. Possible reaction products in the base-catalyzed reaction between acetylenes and diselenides.

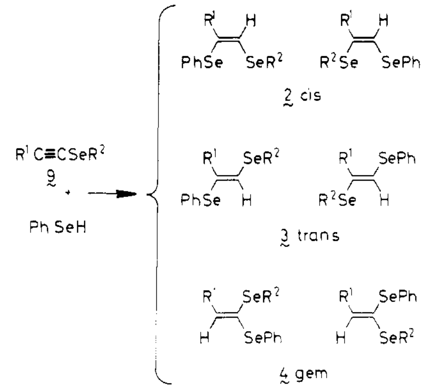


Figure 3. Reaction B. Possible reaction products in the reaction between 9 and benzeneselenol.

In these studies[6-9] only the $^1J_{\text{Se-Se}}$ has been measured and the reported numerical values range from 2–36 Hz. The detection of $^2J_{\text{Se-Se}}$ and $^3J_{\text{Se-Se}}$ in the ^{77}Se NMR spectra of 2- and 3-seleno-substituted selenophene derivatives was attempted, but no satellites due to ^{77}Se–^{77}Se couplings were observed. These coupling constants were therefore assumed to be less than the line width (2 Hz).[7]

Three types of homonuclear ^{77}Se couplings are possible in selenium substituted alkenes: gem $^2J_{\text{Se-Se}}$, cis $^3J_{\text{Se-Se}}$, and trans $^3J_{\text{Se-Se}}$. In the previous study[1] we measured $^3J_{\text{Se-Se}}$ and reported upon the relation of this parameter to dihedral bond angles. Large coupling constants (83–100 Hz) are observed for cis orientation of the atoms, while trans arrangement gives rise to numerically much smaller values (12–23 Hz). In this study we have obtained values for $^2J_{\text{Se-Se}}$ from the ^{77}Se NMR spectra of a series of geminal diseleno-substituted alkenes. The structural identity of these model compounds is unambiguous due to the synthetic procedure as outlined in Figure 1. The numerical values of the geminal ^{77}Se–^{77}Se coupling constants measured range from 20–55 Hz (Table I). This range is well separated from the range of cis $^3J_{\text{Se-Se}}$ but there is a small overlap between the numerical ranges of trans and geminal $J_{\text{Se-Se}}$.

In order to test the applicability of the results given above for $J_{\text{Se-Se}}$ we examined the course of the two reactions shown in Figures 2 and 3, i.e., the base catalyzed

---

[5] Eggert, H.; Nielsen, O.; Henriksen, L. *J. Am. Chem. Soc.*, in press.

[6] McFarlane, W. *J. Chem. Soc. A* **1969**, *670*.

[7] Granger, P.; Chapelle, S.; Paulmier, C. *Org. Magn. Reson.* **1980**, *14*, 240.

[8] Gombler, W. *J. Magn. Reson.* **1983**, *53*, 69.

[9] Anderson, J. A.; Odom, J. D.; Zozulin, A. J. *Organometallics* **1984**, *3*, 1458.

Table II. $^{77}Se-^{77}Se$ **Coupling Constants (Hz) and Structure Assignments in the Products of Reactions A and B of Figures 2 and 3**

			J_{Se-Se} measured				
R^1	R^2	cond[a]	cis	trans	gem	structure assigned[b]	other products formed[b]
				Reaction A			
-Ph	-Ph	a	80			**2a** (80)	**5a** 10), **9a** (10)
-Ph	$-CH_2Ph$	a	77			**2c** (40)	**9c**[c] (40)[c]
-Ph	-EAc[d]	a	91			**2d** (60)	**5c** (20), **9d** (20)
-Ph	$-CH_3$	a	96			**2b** (30)	**5b** (30), **9b** (10)
				12		**3a** (30)	
-COOEt	-Ph	a			47	**4a** (40)	**5d** (40), **6a** (10), **9e** (10)
-COOEt	$-CH_2Ph$	a			45	**4b** (70)	**6b** (10), **9f**[c] (5)[c]
-COOEt	-EAc[d]	a			41	**4c** (30)	**5e** (30), **6c** (10), **9g** (3)
$-(CH_2)_3CH_3$	-Ph	a	85			**2e** (70)	**9h** (30)
$-(CH_2)_3CH_3$	-Ph	b	117	2	25	**8a** (50)	**9h** (50)
				Reaction B			
$-(CH_2)_3CH_3$	-Ph	c	85			**2e** (70)	–
					19	**4e** (30)	
-Ph	$-CH_3$	c		9		**3b** (20)	–
				2		**3c** (20)	
					27	**4d** (60)	

[a] Reaction conditions: (a) 0.25 equiv of NaOEt, EtOH, room temperature → reflux. (b) 0.25 equiv of $NaOC(CH_3)_2C_2H_5$, THF, reflux. (c) 1 equiv of PhSeH, THF, reflux. [b] Approximate product distribution in percent are given in parenthesis. [c] Several minor byproducts formed due to the acidity of the benzylic protons. [d] -EAc is $-CH_2CH(OEt)_2$.

addition of diselenides to terminal acetylenes (reaction A) and the addition of selenols to selenium substituted acetylenes (reaction B). As shown in the figures several products are a priori possible in each reaction. ^1H noise decoupled ^{77}Se NMR spectra of the various reaction mixtures revealed that in most cases more than one product was formed. Observation of selenium satellites in the ^{77}Se NMR spectra of the reaction mixtures gave the $^{77}Se-^{77}Se$ coupling constants for di- and triseleno-substituted alkenes and identified those signals arising from the same isomer. In Table II are given the measured values of J_{Se-Se} together with the structure assignments of the products. For all compounds except **4d**, **4e**, and **8a**, the numerical values of J_{Se-Se} are found far from the overlapping region between J_{gem} and J_{trans}. Therefore the structure of these compounds can be assigned directly on the basis of the ranges given above. **4d** and **8a** with J_{Se-Se} values of 27 and 25 Hz respectively can both be assigned to a geminal diseleno-substituted structure as the alternative trans arrangements are already identified by very small $^{77}Se-^{77}Se$ coupling constants (2–9 Hz). This is not the case for **4e**. The geminal assignment for J_{Se-Se} = 19 Hz in **4e** is obtained from measurement of the vinylic $^1H-^{77}Se$ coupling constants as described below. The material for J_{Se-Se} presented in Table II shows that this parameter in general can be used in structure assignment of di- and triseleno-substituted alkenes. Within this group of compounds the numerical value of J_{Se-Se} falls into three separated ranges (117–77 Hz, 55–19 Hz, and 12–2 Hz) corresponding to a cis, a geminal, or a trans location of the coupling ^{77}Se nuclei. The larger trans coupling constants (19–23 Hz) are measured only in the completely flat highly conjugated systems of tetraselenafulvalenes.[1]

Coupling constants are most often rationalized in terms of the Pople–Santry expression for Fermi contact interaction.[10] The expressions for the other two coupling mechanisms are rarely mentioned although the total dominance of Fermi contact interaction is established only for couplings involving protons.[11] The extent of Fermi contact dominance is not known for couplings between heavy nuclei such as ^{77}Se.

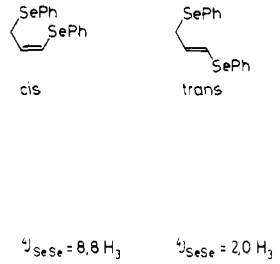


Figure 4. Homoallylic $^{77}Se-^{77}Se$ coupling constants.

The experimental set of $^{77}Se-^{77}Se$ coupling constants now available provide a basis for a test of the different theoretical approaches. Although an extensive interpretation of the data will not be attempted, certain trends are apparent. The observed pattern indicates that selenium p-orbital overlap is involved in the transmission of the perturbation. From an examination of the variation in geminal $^{77}Se-^{77}Se$ coupling constants for the series **1a–c** and **1d–f** (Table I) it is seen that the numerically largest geminal coupling constants are found in the almost planar five-membered cyclic systems **1a** + **1d** having the p-orbitals aligned for maximum interaction. Moving away from planarity and p-orbital alignment, as in the six-membered rings **1b** + **1e**, the coupling constants decrease and the lowest values are found in noncyclic systems **1c** and **1f**.

The $^3J_{Se-Se}$ coupling constant is sensitive to the geometrical relationship of the two spin coupled selenium nuclei but in a different way from that of the $^1H-^1H$ coupling. Thus for homonuclear selenium-77 coupling the cis coupling constants are very large (77–117 Hz) while the trans orientation of the coupling nuclei gives small coupling constants, sometimes at the limit of detection. In the cis isomer, the lone pair p-orbitals of the spatially proximate selenium atoms are positioned for a favorable interaction. Such a large interaction is not possible in the trans isomer. Homoallylic $^4J_{Se-Se}$ coupling constants of the compounds shown in Figure 4 also show a stereochemical dependence. Again the cis isomer, having the possibility of selenium p-orbital overlap, show a coupling constant much larger than the trans isomer.

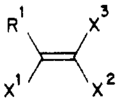
The very low values of $^1J_{Se-Se}$ reported have previously been commented upon.[6,9] However, the situation becomes much more interesting in view of the much larger coupling constants now reported for coupling between selenium-77

---

[10] Pople, J. A.; Santry, D. P. *Mol. Phys.* **1964**, *8*, 1.

[11] Kowalewski, J. In "Annual Reports on NMR Spectroscopy"; Webb, G. A., Ed.; Academic Press, London, 1982; chapter 2.

Table III. ^{77}Se Chemical Shifts (ppm) and ^{77}Se–^{1}H, ^{77}Se–^{77}Se, and ^{1}H–^{1}H Coupling Constants (Hz) of Alkenyl Selenides[a]



					δ ^{77}Se[c]			alkenylic J_{Se-H}			
	R^1	X^1	X^2	X^3	Se-1	Se-2	Se-3	^2J	cis ^3J	trans ^3J	J_{H-H} (J_{Se-Se})[d]
2a	–Ph	–SePh	–SePh	–H	443	397		14		4	(80)
2b	–Ph	$-SeCH_3$	$-SeCH_3$	–H	219	204		15		4	(96)
2c	–Ph	$-SeCH_2Ph$	$-SeCH_2Ph$	–H	380	364		12		4	(77)
2d	–Ph	–SeEAc[b]	–SeEAc[b]	–H	285	250		14		4	(91)
2e	–Butyl	–SePh	–SePh	–H	402	391		16		4	(85)
3a	–Ph	$-SeCH_3$	–H	$-SeCH_3$	285		223	11	7		(12)
3b	–Ph	$-SeCH_3$	–H	–SePh	319		422	11	7		(9)
3c	–Ph	–SePh	–H	$-SeCH_3$	489		256	13	9		(2)
4a	–COOEt	–H	–SePh	–SePh		588	511		10	2	(47)
4b	–COOEt	–H	$-SeCH_2Ph$	$-SeCH_2Ph$		514	417		8	4	(45)
4c	–COOEt	–H	–SeEAc[b]	–SeEAc[b]		440	336		10	4	(41)
4d	–Ph	–H	–SePh	$-SeCH_3$		511	218		8	4	(27)
4e	–Butyl	–H	–SePh	–SePh		459	374		8	4	(19)
5a	–Ph	–H	–H	–SePh			387	16		3	10
5b	–Ph	–H	–H	$-SeCH_3$			186	16		1	10
5c	–Ph	–H	–H	–SeEAc[b]			237	14		3	10
5d	–COOEt	–H	–H	–SePh			497	11		4	9
5e	–COOEt	–H	–H	–SeEAc[b]			354	14		2	9
6a	–COOEt	–H	–SePh	–H		422		25	7		16
6b	–COOEt	–H	$-SeCH_2Ph$	–H		365		26	7		16
6c	–COOEt	–H	–SeEAc[b]	–H		273		25	6		18
8a	–Butyl	–SePh	–SePh	–SePh	495	502	477				*e*

[a] The chemical shifts are relative to $(CH_3)_2Se$ (see Experimental Section). [b] –SeEAc is $-SeCH_2CH(OEt)_2$. [c] The selenium atom numbering follows the X numbering. [d] Values in parenthesis are alkenylic ^{77}Se–^{77}Se coupling constants. [e] Three values: 25, 117, and 2 Hz (see Table II for assignments).

nuclei separated with two and three bonds. Thus, the vinylic cis $^3J_{Se-Se}$ and the $^2J_{Se-Se}$ measured in dialkyl polyselenides (112–117 Hz)[5] are all much larger than the one bond coupling constants reported. The $^1J_{Se-Se}$ coupling constants reported are all measured for diselenides where the p orbitals are close to orthogonal. However, we have found that $^1J_{Se-Se}$ rises to 3–400 Hz if the lone pair dihedral angle is reduced to the value found in a cyclic five-membered diselenide.[12] This fact strongly supports the proposal of selenium p-orbital overlap involvement in transmission of ^{77}Se–^{77}Se coupling.

^{77}Se–^{1}H Coupling Constants. ^{77}Se–^{1}H coupling constants are easily obtained from proton-coupled ^{77}Se NMR spectra; alternatively they may be determined from the ^{77}Se satellites in the ^{1}H NMR spectrum. Selenium satellites in ^{1}H NMR spectra are generally used to locate selenium-coupled protons but only a few reports relating J_{Se-H} to structure and stereochemistry have appeared.[1,13,14]

Table III lists the numerical values of the ^{77}Se–^{1}H coupling constants measured. All ^{77}Se–^{1}H coupling constants within the substituents X^1 to X^3 (Table III) agree with reported values and are not given. The proton-coupled ^{77}Se NMR spectra of the compounds included in this study are all amenable to first-order analysis.

On the basis of J_{Se-Se}, the relative stereochemical orientation of the selenium atoms have already been established for the diseleno-substituted products **2a** to **4d** (Table III). The vinylic hydrogen atom in these structures will couple to each of the two different selenium atoms. The cis structures **2a–e** have the vinylic hydrogen atom placed trans to one and geminal to the other selenium atom. All examples of this general structure (**2**) show one selenium signal with a small (4 Hz) and one with a larger (12–16 Hz) coupling to the vinylic hydrogen atom. In the trans isomers **3a–c**, the vinylic hydrogen atom will couple with a geminal $^2J_{Se-H}$ to one of the selenium atoms and a cis $^3J_{Se-H}$ to the other. The spectra of **3a–c** all show vinylic ^{77}Se–^{1}H couplings with values 11–13 Hz and 7–9 Hz respectively. In the geminal diseleno-substituted isomers **4a–d** a trans and a cis vinylic ^{77}Se–^{1}H coupling are present. A small coupling constant (2–4 Hz) and a somewhat larger one (8–10 Hz) are found in each example. Comparison of the results of J_{Se-H} for cis, trans, and geminal diseleno-substituted alkenes gives the assignment of the small J_{Se-H} (2–4 Hz) as the trans coupling, the intermediate (7–10 Hz) as the cis $^3J_{Se-H}$, and the larger (11–16 Hz) as the geminal $^2J_{Se-H}$.

Compounds of general types **5** and **6** are monoseleno-substituted alkenes and two vinylic hydrogen atoms are present. The value of $^3J_{H-H}$ (Table III) determine **5** to be *cis*- and **6** to be *trans*-alkenes. In the structures of type **5** the selenium resonance shows both a two-bond and a trans three-bond ^{77}Se–^{1}H coupling, 11–16 Hz and 1–4 Hz, respectively, assigned in accordance with the results above. The type **6** structures have a cis $^3J_{Se-H}$ and a $^2J_{Se-H}$ vinylic coupling. The ranges found are 25–26 Hz and 6–7 Hz. The last range of values agree well with that found for cis $^3J_{Se-H}$, while 25–26 Hz are much larger than the values above for $^2J_{Se-H}$. Even larger values of vinylic $^2J_{Se-H}$ are known: In selenophene this coupling constant is 47 Hz[15] and in tetraselenafulvalenes values of 53–56 Hz[1] have been measured. Apparently, planarity of the systems strongly influence the size of this coupling constant.

In conclusion, the vinylic J_{Se-H} values of Table III establish the following stereochemical relationships: trans $^3J_{Se-H}$ = 1–4 Hz, cis $^3J_{Se-H}$ = 6–10 Hz, and gem $^2J_{Se-H}$ > 11 Hz. The ranges are well separated and provide a basis

---

(12) Eggert, H.; Nielsen, O.; Henriksen, L., unpublished results.

(13) Rodger, C.; Sheppard, N.; McFarlane, C.; McFarlane, W. In "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds. Academic Press: London, 1978; p 409.

(14) McFarlane, H. C. E.; McFarlane, W. In "NMR of Newly Accessible Nuclei"; Laszlo, P. Ed.; Academic Press: London, 1983; p 285.

(15) Christiane, L.; Piette, J.-L.; Laitem, L.; Baiwir, M.; Denoel, J.; Llabres, G. *Org. Magn. Reson.* **1976**, *8*, 354.

for the use of $^1H-^{77}Se$ coupling constants in determining the stereochemistry of alkenylic selenides. The method complements the use of $^{77}Se-^{77}Se$ coupling constants in this class of materials as it is applicable also to alkenes with only one selenium group attached.

The $^1H-^{77}Se$ coupling constants for trans orientation of the coupling nuclei are smaller than for the cis orientation as found for $^{77}Se-^{77}Se$ coupling. However, it should be noted that the range for trans $^3J_{Se-H}$ found in this work is restricted to the general case of di- and trisubstituted alkenes. In the special case of monosubstituted alkenes such as ethenyl phenyl selenide a value of 21.6 Hz has been reported.[16]

We have applied the results obtained for J_{Se-H} to determine the structure of compound **4e** (Table III). A value of 19 Hz for J_{Se-Se} for **4e** did not a priori allow distinction between trans or geminal diseleno substitution (see above). The two vinylic J_{Se-H} coupling constants for **4e** are 8 and 4 Hz corresponding to a cis and a trans $^3J_{Se-H}$ coupling constant. This determines **4e** as a geminal diseleno-substituted structure.

In reaction B (figure 3) for $R^2 \neq Ph$ two isomers of each cis, trans, or geminal case become possible. Thus, in the example where $R^2 = CH_3$, two isomeric trans (**3b** and **3c**) and one (**4d**) of the two possible geminal isomers are formed (Table II). Examining the vinylic J_{Se-H} coupling constants allows determination of specific isomeric structures. In **3b** the phenyl-substituted selenium atom shows a geminal $^{77}Se-^1H$ coupling (11 Hz) while the methyl-substituted selenium atom has a cisoid coupling (7 Hz) to the vinylic hydrogen atom. In **3c** the coupling constants are 13 and 9 Hz but interchanged between the two types of selenium atoms. In **4d** the methyl-substituted selenium atom is trans coupled (4 Hz) and the phenyl-substituted selenium atom cis coupled (8 Hz) to the vinylic hydrogen atom. These four examples show how efficiently J_{Se-H} coupling constants can be applied in direct stereochemical assignment.

Preparative Methods and Reaction Pathways. The primary goal of the preparative work was to make available the various selenium substituted alkenes needed for establishing the NMR parameters. Accordingly little effort was directed toward mechanistic studies. Nevertheless some implications regarding reaction pathways go forth from the product distributions under the varying reaction conditions.

Reaction A. The base-catalyzed reaction of terminal acetylenes with diselenides[17] may give rise to four types of product: (a) alkynyl selenides (**9**) corresponding to substitution of the acetylenic proton by an organoselenium ion (RSe^+), (b) alkenyl selenides (**5**, **6**) corresponding to the addition of a selenol over the triple bond, (c) bis(organoseleno)alkenes formally corresponding to the addition of a diselenide to the triple bond without (**2**) or with (**4**) accompanying rearrangement, (d) tris(organoseleno)alkenes (**8**) formally corresponding to a combination of reactions a and c.

The distribution among these four types of product from various substrates and under varying conditions of reaction is summarized in Table II. These product distributions can be rationalized in terms of the competing pathways depicted in Figure 5. The main conclusion inherent in this figure is that the key step is the attack of the acetylide ion on the diselenide with formation of the alkynyl selenide (**9**) and a selenolate ion. The final, vinylic products arise by subsequent nucleophilic additions with varying regio- and stereospecificity of the liberated selenolate ion to the triple bonds of either the parent acetylene or **9**. The experimental evidence strongly supports this conclusion. First, the reaction leading to the final, vinylic products normally proceeds over a period of 24 h with about 0.25 equiv of sodium ethanolate in refluxing ethanol. If, however, the reaction mixture is investigated after a 30-min period extensive formation of **9** and selenolate but very little of the vinylic products are seen. Secondly the treatment of phenylacetylene with 1 equiv of a strong base under aprotic conditions (sodium 2-methyl-2-butanolate in toluene) followed by 1 equiv of diphenyl diselenide led to an almost quantitative conversion into **9a** and benzeneselenolate ion. On subsequent addition of a proton donor (ethanol) a clean conversion of **9a** to **2a**, without competing formation of **5a**, was observed. Incidently this procedure constitutes an excellent synthetic route to **2** (R = Ph, Bu) but it cannot be used for **4** ($R = CO_2Et$) since propynoic esters tend to polymerize rather than add to diselenides under these strongly basic conditions. The reaction of 1-hexyne with diphenyl diselenide under these conditions resembled that of phenylacetylene in that **9h** was formed cleanly at room temperature, and under protic conditions (ethanol) further heating afforded the diseleno-substituted product (**2e**). If, however, the reaction was conducted under aprotic conditions a new type of reaction, not observed for phenylacetylene, took place. In this case on subsequent heating with an excess of the diselenide the tris(organoseleno) alkene (**8a**) was formed. We suggest that this product is formed by addition of benzeneselenolate ion to **9h** followed by trapping of the resulting Se-stabilized anion by its reaction with the diselenide.

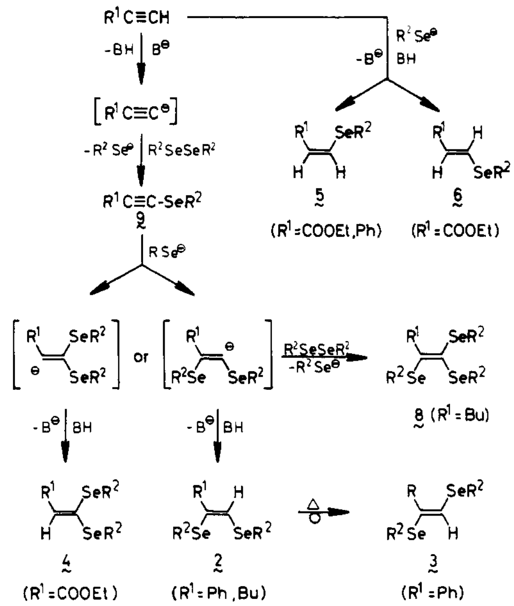


Figure 5. Outline of the base-catalyzed reaction between terminal acetylenes and diselenides.

In the addition of selenols to **9** the regioselectivity differs from R = Ph to $R = CO_2Et$. The former gives a 1,2- and the latter a 1,1-diseleno-substituted alkene. This difference should, in our adopted reaction pathway, reflect the difference in stabilization of the intermediary anion in accord with the order of anion-stabilizing power: $CO_2Et > SeR > Ph$.[18]

---

(16) Kushnarev, D. F.; Kalabin, G. A.; Marnatov, T. G.; Mullin, V. A.; Larin, M. F.; Pestunovich, V. A. *Zh. Org. Khim.* **1976**, *12*, 1482.

(17) Katayeva, L. M.; Katayev, E. G.; Ya Idiyatullina, D. *Zh. Strukt. Khim.* **1966**, *7*, 380. Dipole moment studies give some indications of cis addition of diselenides to acetylenes.

(18) Bordwell, F. G.; Van der Puy, M.; Vanier, N. R. *J. Org. Chem.* **1976**, *41*, 1883, 1885.

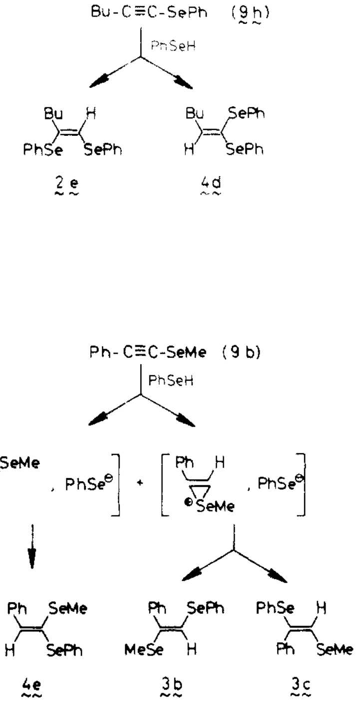


Figure 6. Outline of the reactions between seleno-substituted acetylenes and benzeneselenol.

It should be noted that in the 1,2-diseleno-substituted products the cis isomer (**2**) is completely dominating. The formation of the cis product corresponds to a formal *trans* addition of R^2SeH to **9**. The trans isomer is seen only in one case (**3a**), and it probably arises from a partial isomerization of the corresponding cis isomer (**2b**). The expected[3] trans addition of R^2SeH is predominant also in the competing reaction with the parent acetylenes, although both cis and trans addition is seen in the reaction with ethyl propiolate.

Reaction B. We have investigated the addition of benzeneselenol to phenylethynyl methyl selenide (**9b**)[19] and to 1-hexynyl phenyl selenide (**9h**). The last compound was obtained by reacting sodium butylacetylide with diphenyl diselenide in toluene (see Experimental Section). Formally, these addition reactions correspond to the addition step in Figure 5, but differences in the product distribution arise from the change of medium from strongly basic (RO^-) to acidic (RSeH). The presence of additional, strong acid had little consequence on the product distribution. Therefore it is unlikely that a competition between nucleophilic and electrophilic substitution is determining the product distribution; only the latter pathway seems of importance. The products and our suggestion of their mode of formation are summarized in Figure 6.

In the reaction of 1-hexynyl phenyl selenide, (**9h**) both the 1,2-diseleno compound (**2e**) and the 1,1-diseleno compound (**4e**) may arise from an expected trans addition of benzeneselenole.[3] A more complicated pattern is found in the reaction between phenylethynyl methyl selenide and benzeneselenol. In this case no trans addition products are seen. Instead, the two isomeric 1,2-(*E*)-diseleno-substituted alkenes **3b** and **3c** together with a 1,1-diseleno isomer **4d** corresponding to a formal cis addition of benzeneselenol appear. The formation of **3b** requires a 1,2-migration of the methylseleno group. In contrast to 1-hexynyl phenyl selenide, methyl phenylethynyl selenide apparently forms rather stable cationic intermediates on protonation. Protonation may occur α to selenium forming a selenirenium ion[20] upon cyclization or β to selenium giving the delocalized carbonium ion shown in Figure 6. These cationic intermediates are stablized by both the phenyl group and the alkylseleno group. The fact that selenium migration takes place in the methyl—but not in the phenyl selenide—may be attributed to the enhanced selenirenium ion stabilization by alkyl substituents as it is seen in the reaction between selenyl halides and alkynes.[21] The cationic intermediates are then attacked by benzeneselenoate to give the diseleno-substituted products **3b**, **3c**, and **4d**.

Experimental Section

^{77}Se NMR. The ^{77}Se NMR spectra were recorded at 17.04 MHz on a JEOL FX90Q NMR instrument equipped with a broadband probe. All spectra were obtained on $CDCl_3$ solutions. Chemical shifts are referenced to external dimethyl selenide in $CDCl_3$ (1 M) (resonance frequency 48701.5 Hz) by frequency difference calculations. The probe temperature was held between 29–30 °C for all measurements. Chemical shifts and coupling constants were determined with a maximum of 0.49 Hz per data point. The ^{77}Se chemical shifts of the compounds studied show a sizeable temperature variation. Heating from the decoupler causes thermal inhomogeneity of the sample. With high decoupling power the temperature gradient in the sample is sufficiently large (~ 1 °C) to prevent the observation of selenium satellites due to line broading of the mother peaks and loss of S/N.[5] By carefully reducing the decoupler power to the minimum amount necessary, line widths $\Delta\nu_{1/2} \leq 1$ Hz could usually be obtained.

All reactions were performed under dry nitrogen cover. Reagent grade reagents were used unless otherwise specified. Phenylacetylene was distilled prior to use. Literature procedures were used preparing dimethyl diselenide,[22] dibenzyl diselenide,[22] bis(2,2-diethoxyethyl) diselenide,[22] (1,3-bis(phenylseleno)propene,[23] phenyl trimethylsilyl selenide,[24] methylphenylethynyl selenide,[19] and the type **1** compounds.[25] Sodium ethanolate (1 M in ethanol) and sodium 2-methyl-2-butanolate (1.8 M in toluene) were prepared by reacting sodium with the appropiate alcohols.

Reaction of Diselenides with Terminal Acetylenes. Typical Procedure: A solution of diselenide (5 mmol), phenylacetylene (6 mmole), and sodium ethanolate (1.5 mmol) in 25 ml of ethanol was heated under reflux until complete conversion of the diselenide was observed. (TLC, silica gel CH_2Cl_2–Pentane, 1:5). Then the mixture was diluted with water and extracted with toluene. The organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The resulting yellow oil was subjected to ^{77}Se NMR without further separation. Product distributions are given in Table II and NMR data (except for **9**) are given in Table II and III. Structure **9** was assigned from ^{77}Se and ^{13}C NMR spectra, and ^{77}Se and acetylenic ^{13}C chemical shift values (ppm) are as follows [**9**, $\delta(^{77}Se)$, $\delta(^{13}C)$, $\delta(^{13}C)$]: **9a**, 280, 69.5, 102.9; **9b**, 150, 71.5, 98.0; **9c**, 259, 71.5, 101.4; **9d**, 133, 71.5, 101.4; **9e**, 284, 74.2, 94.7; **9f**, 257, 77.3, 95.0; **9g**, 136, 76.9, 92.5; **9h**, 275, 57.7, 104.5). In a few cases to obtain the vinylic $^3J_{H-H}$ of the type **5** and **6** compounds it was necessary to separate the products. This was effected using column chromatography and preparative TLC (silica gel, pentane containing 0 to 10% dichloromethane). Due to undesired side reactions (polymerisation) in the reactions with propynoic acid ethyl ester, it was necessary to add up to 100% excess of the acetylene. In this case the reactants were mixed at 0 °C and stirred for 1 h before heating to reflux. The polymeric byproducts formed were removed by passing the product mixture through a short column (silica gel,

---

[19] Bradsma, L.; Wijers, H. E.; Arens, J. F. *Rec. Trav. Chim. Pays-Bas* **1962**, *81*, 583.

[20] Stable selenirenium ions have been reported: Schmid, G. H.; Garrett, D. *Tetrahedron Lett.* **1975**, 3991.

[21] Johannsen, I., unpublished results.

[22] Syper, L.; Mtochowski, J. *Synthesis* **1984**, 439.

[23] Reich, H. J.; Clark, M. C.; Willis, W. W., Jr., *J. Org. Chem.* **1982**, *47*, 1618.

[24] Miyoshi, N.; Ishii, H.; Kondo, K.; Murai, S.; Sonoda, N. *Synthesis* **1979**, 300.

[25] Jensen, K. A.; Henriksen, L. *Acta Chem. Scand.* **1970**, *24*, 3213.

dichloromethane–pentane, 2:5).

Reaction of Diphenyl Diselenide with 1-Hexyne (Aprotic). A solution of 1-hexyne (5 mmol), diphenyl diselenide (5 mmol), and sodium 2-methyl-2-butanolate (2 mmol) in 25 mL of benzene was heated under reflux for 24 h. Precipitated sodium benzeneselenolate was removed by filtration. The filtrate was diluted with 100 mL of water and extracted with toluene. The yellow oil (0.6 g) obtained by removal of the solvent under reduced pressure was subjected to ^{77}Se NMR spectroscopy without further purification. Apart from the products **8a** and **9h** mentioned in Table II it contained about 25% unreacted diphenyl diselenide.

Synthesis of *cis*-1-Phenyl-1,2-bis(phenylseleno)ethene. To a stirred solution of phenylacetylene (10 mmol) in 50 mL of dry THF was added sodium 2-methyl-2-butanolate (10 mmol) and 5 min later diphenyl diselenide (10 mmol). The solution became colorless and white crystals of sodium benzeneselenolate precipitated. At this stage the reaction mixture could be filtered and the filtrate worked up to give an almost quantitative yield of **9a**. In order to obtain **2a** 20 mL ethanol was added to the above reaction mixture, and it was refluxed overnight (16 h), diluted with 5 volumes of water, and extracted with toluene. The organic phase was washed with water, dried over $MgSO_4$, and evaporated under reduced pressure to yield **2a** as a slightly yellow oil 3.95 g (92%). ^{1}H NMR δ 7.0–7.8 (multiplet). ^{77}Se NMR data are given in Table III. The product contained no impurities judged from TLC and ^{77}Se NMR.

Phenyl 1-Hexynyl Selenide (9h). To a stirred solution of 1-hexyne (20 mmol) in 25 mL of dry toluene was added sodium 2-methyl-2-butanolate (20 mmole). After 5 min diphenyl diselenide (20 mmol) was added whereupon the reaction mixture was stirred for 15 min at room temperature, then poured out into 100 mL of deoxygenated water. The water phase was extracted with 50 mL of toluene, and the combined organic phase was washed with water, dried over $MgSO_4$, and evaporated. A slightly yellow oil (4.6 g) was obtained. It contained **9h** together with a little diphenyl diselenide (less than 5%) and was used without further purification in the addition reaction (^{77}Se NMR, δ 275 ppm ($CDCl_3$)). The water phase containing benzeneselenolate was acidified and air-oxidized to give an almost quantitative recovery of $^1/_2$ equiv of diphenyl diselenide.

Addition of Benzeneselenol to Seleno-Substituted Acetylenes (9b and 9h). The substituted alkyne **9b** or **9h** (10 mmol) was added to a THF solution of benzeneselenol prepared from phenyl trimethylsilyl selenide and slight excess of methanol or acetic acid.[24] The reaction mixture was refluxed overnight, whereupon the solvent was evaporated, and the crude product mixture was subjected to ^{77}Se NMR analysis. (Data given in Tables II and III.)

Summary

In this paper we give a general method for differentiation between isomeric alkenes substituted with two or more organo selenium groups. It is based on the homonuclear ^{77}Se coupling which gives rise to a satellite pattern at the foot of each selenium-77 line: 117–77 Hz coupling constants are found for cis $^3J_{Se-Se}$, 55–19 Hz for gem $^2J_{Se-Se}$, and 12–2 Hz for trans $^3J_{Se-Se}$.

Furthermore, an extended set of assigned J_{Se-H} coupling constants is presented. These provide a basis for using ^{1}H–^{77}Se coupling constants to determine the stereochemistry of selenium-substituted alkenes including those with only one selenium group attached.

It is shown that the base-catalyzed reaction between diselenides and terminal acetylenes proceed via a substitution of the acetylenic proton followed by an addition of a selenolate ion. Under aprotic conditions the reaction may proceed to give a triseleno-substituted alkene. The addition of benzeneselenol to alkylseleno-substituted acetylenes gives rise to products with 1,2-migrated alkyl seleno groups probably via a selenirenium ion like intermediate.

Registry No. **1a**, 32847-07-7; **1b**, 32847-15-7; **1c**, 32846-96-1; **1d**, 32847-03-3; **1e**, 32847-12-4; **1f**, 32846-91-6; **2a**, 7392-13-4; **2b**, 7392-17-8; **2c**, 101316-22-7; **2d**, 101316-23-8; **2e**, 101349-67-1; **3a**, 101316-24-9; **3b**, 101349-68-2; **3c**, 101316-25-0; **4a**, 101316-26-1; **4b**, 101316-27-2; **4c**, 101316-28-3; **4d**, 101316-29-4; **4e**, 101316-30-7; **5a**, 60466-30-0; **5b**, 101316-31-8; **5c**, 101316-32-9; **5d**, 94848-67-6; **5e**, 101316-33-0; **6a**, 94848-68-7; **6b**, 101316-34-1; **6c**, 101316-35-2; **8a**, 101316-36-3; **9a**, 30665-96-4; **9b**, 19859-24-6; **9c**, 101349-66-0; **9d**, 101349-69-3; **9e**, 81699-91-4; **9f**, 101316-37-4; **9g**, 101316-38-5; **9h**, 68001-64-9; ^{77}Se, 14681-72-2; PhSeH, 645-96-5; $PhC\equiv CH$, 536-74-3; $EtOCOC\equiv CH$, 623-47-2; $CH_3(CH_2)_3C\equiv CH$, 693-02-7; PhSeSePh, 1666-13-3; $PhCH_2SeSeCH_2Ph$, 1482-82-2; AcESeSeAcE, 101316-39-6; $CH_3SeSeCH_3$, 7101-31-7.

Photochemistry of 2-Vinylstilbene, 1,2-Distyrylbenzene, and 2,2′-Distyrylbiphenyl Absorbed on Silica Gel. Influence of Ground-State Conformers on Formation of Photoproducts

Arie J. W. Tol and Wim H. Laarhoven*

Department of Organic Chemistry, Catholic University of Nijmegen, Toernooiveld,
6525 Ed Nijmegen, The Netherlands

Received September 11, 1985

Irradiation of 2-vinylstilbene (**1**) absorbed on silica gel gives rise to several products. In addition to *exo*- and *endo*-5-phenylbenzobicyclo[2.1.1]hex-2-enes (**2** and **3**) (the sole products formed in solution) derivatives of naphthalene and of indene are formed. The formation of these products has been ascribed to variation in the photoreactivities of the distinct conformers of **1** and to the reduced mobility of the intermediate biradicals leading to **2** (and **3**) when they are absorbed on silica gel. 1,2-Distyrylbenzene (**22**) absorbed on silica gel forms upon irradiation not only dimers (nearly the sole photoproducts in solution) but also *exo*-5,*endo*-6-diphenylbenzobicyclo[2.1.1]hexene (**25**), a product analogous to **2**, and an indene derivative (**26**). Irradiation of 2,2′-distyrylbiphenyl (**28**) absorbed on silica gel and in solution gives the two photoproducts **29** and **30** in the same ratio. The results are discussed in terms of the NEER principle and the absorption of parts of the molecules to the silica gel surface.

The photochemistry of compounds absorbed on silica gel is still a rather unexploited field.[1] In the course of our photochemical studies we became familiar with several compounds for which different ground-state conformers seemed to lead to different photoproducts. According to the NEER principle[2] (nonequilibration of excited rotamers) the photoproduct composition of such compounds should depend on the rotamer equilibrium in the ground

---

(1) For literature see ref 1 in: Bauer, R. K.; de Mayo, P.; Okada, K.; Ware, W. R.; Wu, K. C. *J. Phys. Chem.* **1983**, *87*, 460.

(2) Jacobs, H. J. C.; Havinga, E. *Adv. Photochem.* **1979**, *11*, 305.

0022-3263/86/1951-1663$01.50/0