Intramolecular Electron Transfer in 9-(Arylseleno)bicyclo[4.2.1]nona-2,4,7-trien-9-yl and -bicyclo[4.2.1]nona-2,4-dien-9-yl Carbanions Promoted by the Aryl Ligands

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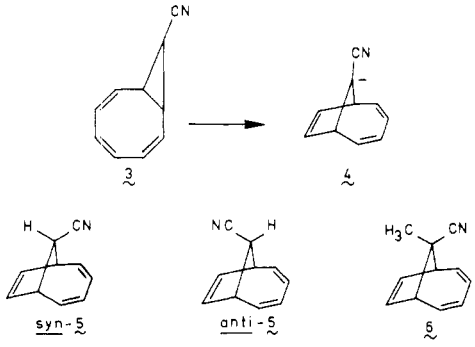
The reaction of 9,9-bis(arylseleno)bicyclo[4.2.1]nona-2,4,7-trienes (**7**) and 9,9-bis(*p*-tolylseleno)bicyclo-[4.2.1]nona-2,4-diene (**24**) with *n*-butyllithium in tetrahydrofuran produces the C_9 carbanions **31** and **39**. Quenching at −78 °C directly after carbanion formation affords C_9-substituted derivatives. The preference of soft electrophiles to attack *anti*-**31** and -**39** is attributed to stereoelectronic control consequent on the involvement of a bis-homoaromatic interaction. Low-temperature addition of electrophiles at a later point in time affords products formed via electrophilic aromatic substitution. This result is interpreted in terms of a complete stereospecific isomerization of the strongly activated C_9 carbanions to the more stable aryllithium intermediates **32** and **40**. In this process electrons are transferred from C_9 to the ortho position of the aromatic ring via intramolecular proton exchange. Room-temperature quenching leads in the case of the triene selenoketals **7** to the exclusive formation of tetracyclic compounds. The parent tetracyclic allylic intermediates **33** are formed by a further electron transfer from the aryllithium compounds **32** to the butadiene moiety. The allylic carbanions **33** are identified with the aid of ^1H NMR spectroscopy.

In recent years a number of studies have been reported concerning the homo- and bicycloaromatic[1] properties of the bicyclo[4.2.1]nona-2,4,7-trien-9-yl cation **1**.[2] In dis-

1 **2**

agreement with the prediction this cation turned out to be destabilized.[3] The corresponding carbanion **2** is expected to be stabilized according to Goldstein's prerequisite for longicyclic stabilization.[1] However, until now, reports concerning the preparation and properties of the unsubstituted carbanion **2** are almost completely lacking.[3a,4]

Recently the 9-carbonitrile-substituted bicyclo[4.2.1]-nona-2,4,7-trien-9-yl carbanion **4** was prepared in an in-



3 **4**

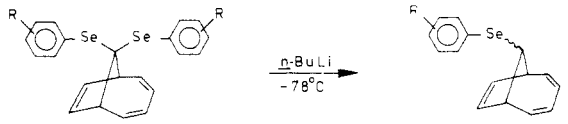
syn-**5** *anti*-**5** **6**

direct manner by the rearrangement of the 9-carbonitrilo-*cis*-bicyclo[6.1.0]nona-2,4,6-trien-9-yl carbanion **3**.[5] Carbanion **4** reacted in a nonstereospecific way with HCl to produce the protic epimers *syn*- and *anti*-**5**. Quenching with methyl iodide gave 9-methylbicyclo[4.2.1]nona-2,4,7-triene-9-*syn*-carbonitrile (**6**).

Direct generation of negative charge at C_9 can only be achieved by the introduction of heteroatoms which can be cleaved from carbon readily. From modern organoselenium chemistry it is known that selenoketals are excellent precursors for the production of α-seleno-substituted carbanions.[6] Therefore, selenoketals of the bicyclo[4.2.1]nonane series were investigated.

In the studies documented below, reactions of carbanions generated from these selenoketals are described. The initially C_9 carbanions are strongly activated intermediates. In the *inter*molecular reactions of the C_9 trienyl and dienyl carbanions with various electrophiles, homoaromatic interactions play a role. However, much more important is the *intra*molecular transfer of negative charge from C_9 to the aryl ring via proton exchange. This process proceeds with 100% stereospecificity. The resulting aryllithium compounds can react further *intra*molecularly with the diene moiety of the systems, which leads to stable allylic carbanions.

Quench Results of 9-Arylseleno-Substituted Carbanions. The triene selenoketals **7a-c** reacted with *n*-butyllithium in tetrahydrofuran at −78 °C via C–Se bond cleavage to produce α-seleno-substituted carbanions **31**.



7 a-c **31** a-c

a R = H b R = *p*-CH_3 c R = *o*-CH_3

Direct quenching after carbanion formation leads to C_9-substituted derivatives (Table II). Deuterium oxide (or methanol-d_4) afforded the C_9-deuterated epimers **13b** and **14b** in approximately equal amounts. Methyl iodide gave predominantly 9-methyl-*anti*-9-(*p*-tolylseleno)bicyclo-[4.2.1]nona-2,4,7-triene (**14c**) together with the substituted aromatic compound **15c** (Scheme I).

Products like **15c**, attributable to electrophilic substitution in the aromatic ring, were formed in all reactions

(1) (a) M. J. Goldstein, *J. Am. Chem. Soc.*, **89**, 6357 (1967); (b) M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971).

(2) (a) T. A. Antkowiak, D. C. Sanders, G. B. Trimitsis, J. B. Press, and H. Shechter, *J. Am. Chem. Soc.*, **94**, 5366 (1972); (b) D. C. Sanders and H. Shechter, *ibid.*, **95**, 6858 (1973); (c) A. F. Diaz, J. Fulcher, M. Sakai, and S. Winstein, *ibid.*, **96**, 1264 (1974); (d) A. F. Diaz and J. Fulcher, *ibid.*, **96**, 7954 (1974); (e) W. Kirmse and G. Voigt, *ibid.*, **96**, 7598 (1974); (f) A. F. Diaz and J. Fulcher, *ibid.*, **98**, 798 (1976).

(3) (a) P. Schipper, Thesis, Eindhoven University of Technology, Eindhoven, The Netherlands; (b) P. Schipper and H. M. Buck, *J. Am. Chem. Soc.*, **100**, 5507 (1978).

(4) (a) T. V. Rajan Babu, D. C. Sanders, and H. Shechter, *J. Am. Chem. Soc.*, **99**, 6449 (1977); (b) M. Kato, T. Chikamoto, and T. Miwa, *Bull. Chem. Soc. Jpn.*, **50**, 1083 (1977).

(5) G. Boche and D. Martens, *Chem. Ber.*, **112**, 175 (1979).

(6) (a) D. Seebach and N. Peleties, *Chem. Ber.*, **105**, 511 (1972); (b) D. Seebach and A. K. Beck, *Angew. Chem., Int. Ed. Engl.*, **13**, 806 (1974); (c) W. Dumont, P. Bayet, and A. Krief, *ibid.*, **13**, 804 (1974).

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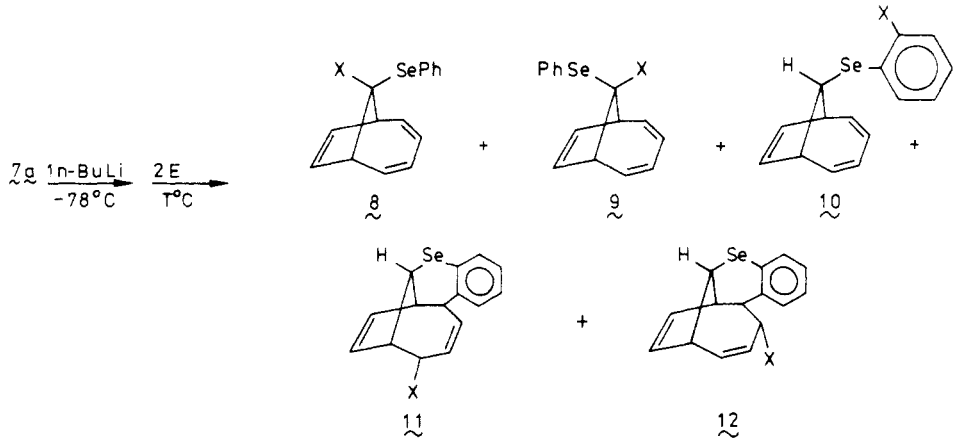
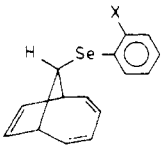
Table I. Products of the Reaction of Selenoketal 7a with *n*-BuLi and Electrophiles



E	X	time[a]	temp, °C	yield, %[b]	products (%)[c]				
H_2O	H	30	−78	92.5	**8a** (81.4)	**9a** (18.6)	**10a**	**11a**	**12a**
		60	20	76.4				**11a** (100)	
D_2O	D	30	−78	90.6	**8b** (30.8)[e]	**9b** (24.1)	**10b** (45.1)[e]	**11b**	**12b**
CH_3I	CH_3	30	−78	96	**8c**	**9c** (15)	**10c** (85)	**11c**	**12c**
		60	20	84.4				**11c** (27)[f]	**12c** (73)[g]
PhC(O)H	PhC(OH)H	30	−78	87	**8d**	**9d** (48.1)	**10d** (51.9)	**11d**	**12d**
$Ph_2C(O)$	$Ph_2C(OH)$	30	−78	84.5	**8e**	**9e** (16)	**10d** (84)	**11e**	**12e**
DMF	C(O)H	30	−78	81	**8f**	**9f** (40)[e]	**10e** (60)[e]	**11f**	**12f**
CO_2	C(O)H	30	−78	90	**8g**	**9g**	**10g** (17.6)[d]	**11g**	**12g**

[a] In minutes after the addition of *n*-BuLi. [b] Calculated from isolated *n*-butyl phenyl selenide. [c] Calculated from isolated products. [d] Total yield of isolated product. [e] Calculated from ^1H NMR integrals. [f] Endo:exo ratio 7:3. [g] Methyl substituent 100% endo.

when the electrophiles were added 0.5 h after carbanion generation (Tables I and II). The phenyl selenoketal **7a** produced predominantly substituted aromatic compounds **10** (Table I).



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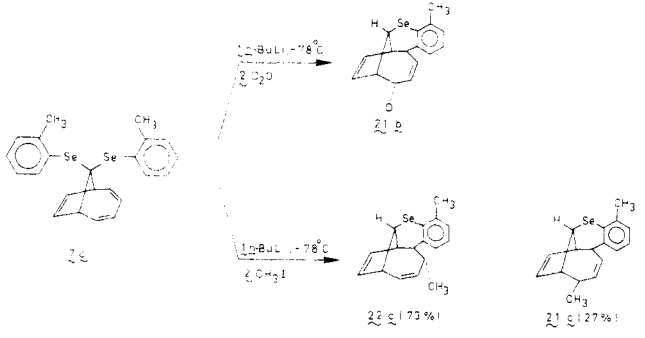
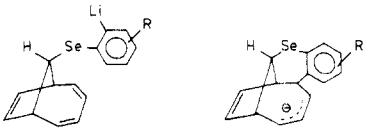
The *o*-tolyl selenoketal **7c** afforded a third product. Tetracyclic derivatives **21** and **22** were isolated together



with C_9-substituted compounds **18** and **19** and substituted aromatic products **20** (Table III). Deuterium oxide (and methanol-d_4) gave the C_5-substituted tetracyclic compound **21b**. Methyl iodide produced predominantly the C_3 endo methylated derivative **22c**.

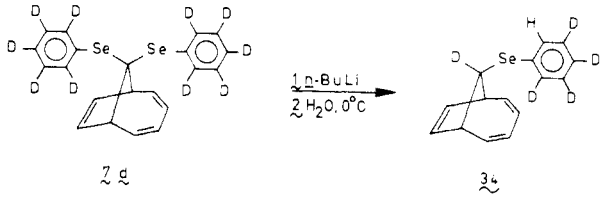
All triene selenoketals **7a–c** gave exclusively tetracyclic derivatives when the electrophile was added to the anionic solution at room temperature.

The isolation of products formed via electrophilic aromatic substitution indicated that the initially formed C_9 carbanions **31** isomerize stereospecifically to aryllithium compounds **32**. These in turn rearrange *intra*molecularly to tetracyclic allylic carbanions **33** (vide infra).



32 **33**

So, the intermediate aryllithium compound **32** plays a crucial role in the reactions of the triene selenoketal. This raised the question about the origin of the proton at C_9 in the intermediate **32**. Therefore the labeled selenoketal **7d** was synthesized. This selenoketal was reacted with

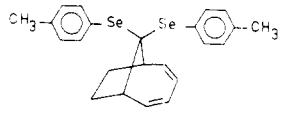


7d **34**

n-BuLi and subsequently with water. A product, **34**, was isolated with deuterium at C_9 and with hydrogen in the aromatic ring (singlet at 7.2 ppm).

Thus, the proton at C_9 in **32** resulted from a complete stereospecific electron transfer from C_9 to the ortho position of the aromatic ring via *intra*molecular proton exchange (vide infra). In order to learn more about possible homo- and/or bicycloaromatic properties in the arylseleno-substituted trienyl carbanions **31**, the reactions of the diene selenoketal **24** and the saturated selenoketal **25** with *n*-BuLi and electrophiles were investigated.

The diene selenoketal **24** reacted somewhat slower with *n*-BuLi at −78 °C than the triene selenoketal **7b**. Reaction with an electrophile at this temperature gave three products: C_9-substituted derivatives, products formed via electrophilic aromatic substitution, and *syn*-9-(*p*-tolyl-



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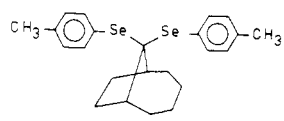

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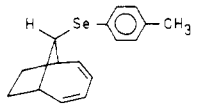
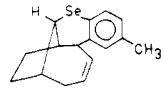
seleno)bicyclo[4.2.1]nona-2,4-diene (**26a**) (Table IV).



26 a

Deuterium oxide (and methanol-d_4) afforded directly after carbanion formation mainly syn 9-deuterated product **27b**. This contrasts with the behavior of the triene selenoketal **7b** which produced both C_9-deuterated epimers in approximately equal amounts (vide supra). The dienyl carbanions gave with deuterium oxide at a later point in time predominantly *syn*-9-*p*-tolylseleno derivatives **26a,b** and **28b** (Table IV). At room temperature the main product of the reaction of the anionic solution with water was **26a**. Tetracyclic compound **29a** was isolated in very



29 a

low yield (less than 7%). A remarkable difference between the diene selenoketal **24** and the triene selenoketal **7b** was the formation of **26a** in all quench reactions. Apparently, C_9 dienyl carbanions are more basic than C_9 trienyl carbanions. Presumably, the C_9 dienyl carbanions reacted partly with THF (vide infra).

The saturated selenoketal **25** reacted very sluggishly with *n*-BuLi. After 1.5 h at 0 °C, quenching with water afforded a mixture which still contained 40% starting material. Therefore, no further experiments were performed.

Structural Assignment of the Quench Products. The stereochemistry of the bicyclic protic quench products was assigned on the basis of their ^{1}H NMR spectra which exhibited a triplet for H_9 of the syn compounds (**8a**, **13a**, **18a**, **26a**), whereas a singlet was observed for the anti compounds (**9a**, **14a**, **19a**, **27a**).[2a] The configuration of the C_9-deuterated products followed from a comparison of their ^{1}H NMR spectra with those of the corresponding protic syn and anti compounds (Table V).

The syn disposition of the seleno moiety in the aromatic substituted products (**10**, **15**, **20**, **28**) was established on the basis of the triplets for H_9. Ortho substitution in the aromatic ring was evident from ^{1}H and ^{13}C NMR spectral data (Tables VI and VIII). The configuration of the methylated derivatives **9c**, **14c**, **19c**, and **27c** was tentatively assigned on the basis of product formation similar to that in other quench reactions (vide infra). NOE experiments did not provide further structural information. The stereochemistry of the benzylic alcohols **9d**, **13d**, and **14d** could be established on the basis of their spectral properties (Tables V and VII). The diastereotopic ring carbons all absorbed at different field positions. The compounds **9d** and **14d** displayed large ^{13}C NMR shift differences between the diene carbons whereas the chemical shift difference between the monoene carbons was small. For the alcohol **13d** the situation was reversed. The spectral data are consistent with a syn disposition of the benzylic alcohol, with respect to the diene bridge, in **9d** and **14d** whereas the alcohol function in **13d** has anti stereochemistry. Additional structural information of

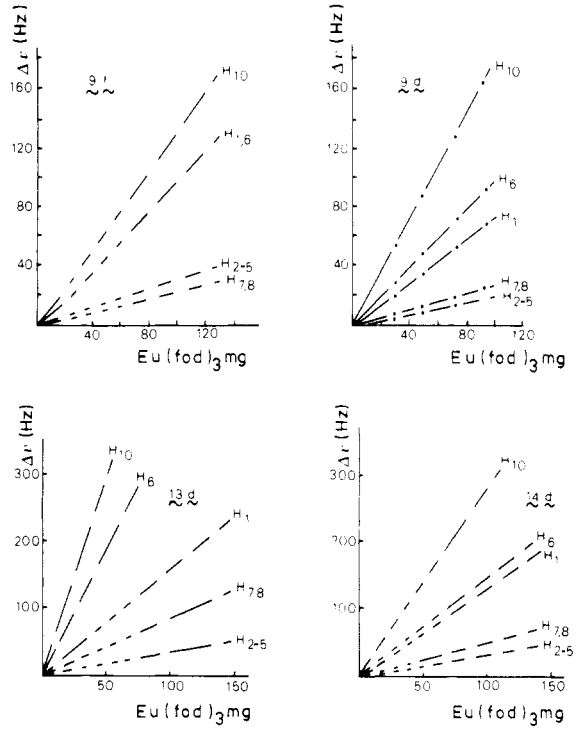
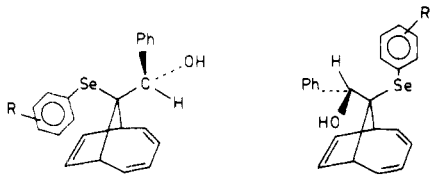


Figure 1. Plot of the chemical shift induced by shift reagent, $\Delta\nu$, vs. the amount of added shift for protons of **9d**, **9f**, **13d**, and **14d**.

compounds **9d–f**, **13d**, and **14d** was obtained by using lanthanide shift reagents. Addition of Eu(fod)$_3$ to the benzylic alcohols caused marked nonequivalent downfield shifts of the bridgehead protons, the effect being most pronounced for the alcohol **13d** (Figure 1). The results point to a time-averaged positioning of the hydroxyl function out of the plane bisecting the bridgehead–bridgehead axis. Dreiding models reveal that in **13d** one bridgehead proton is pointing toward the hydroxyl group, whereas in **9d** and **14d** the corresponding bridgehead proton is pointing away. This explains why in **13d** the bridgehead protons shifted faster than those in **9d** and **14d** and confirms the assigned stereochemistry. In spite of the syn disposition of the benzylic alcohol group in **9d** and **14d**, the downfield shift of the monoene protons was somewhat larger than those of the diene protons. This indicated that europium was located closer to the monoene bridge. Inspection of Dreiding models revealed that this mode of complexation could be realized. The downfield shift of the monoene protons of **13d** was, as expected, significantly larger than that of the diene protons, which confirmed the assigned stereochemistry.

For the diphenyl carbinol **9e** europium-induced shifts were very small, due to the crowded position of the hydroxyl function. Therefore, no extra structural information could be obtained. The application of Eu(fod)$_3$ was more successful with **9f** which has a more approachable aldehyde functionality. The downfield shift of the diene protons was larger than that for the monoene protons, which confirms the syn configuration of the aldehyde group with respect to the diene bridge (Figure 1).

In the syn benzylic compounds **9d** and **14d** the monoene protons were respectively shifted 0.6 and 0.4 ppm upfield with respect to the corresponding selenoketals **7a,b** whereas in **13d** the monoene protons were shifted slightly downfield (Table V). Due to the large steric interactions between the benzylic alcohol function and the seleno moiety, the latter is positioned time averaged above the monoene protons in **9d** and **14d**, causing a shielding of



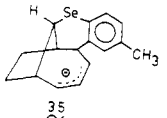
9, 14 d 13 d

these protons. In the benzylic alcohol **13d** these large interactions do not occur.

The monoene protons of the diphenyl carbinol **9e** displayed a 0.9-ppm upfield shift. Thus, the alcohol function in **9e** was assigned the syn configuration with respect to the diene moiety. The structure and stereochemistry of the tetracyclic products were obtained from 90-MHz ^1H NMR decoupling experiments. ^1H NMR spectral data for these compounds are displayed in Table IX.

Direct ^1H NMR Observation of Anionic Solutions. The reaction of the triene selenoketal **7a** with *n*-BuLi in THF-d_8 was investigated with the aid of ^1H NMR spectroscopy. The structure of one carbanionic intermediate could be elucidated by 90-MHz decoupling experiments. This intermediate was formed at approximately −45 °C. It was stable for several days at room temperature. Quenching with water afforded tetracyclic derivative **11a** as the sole product. The intermediate had the tetracyclic structure **33a** (Figure 2).

At temperatures below −45 °C other intermediates were present. However, we were unable to identify these because of the fast *intra*molecular reactions that occurred (vide infra). No intermediate of the reaction of the diene selenoketal **24** with *n*-BuLi in THF-d_8 could be identified. An allylic carbanion **35**, comparable with **33**, was not observed.



35

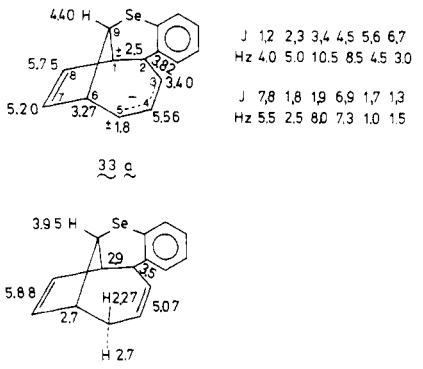
Discussion

The reaction of 9,9-bis(arylseleno)bicyclo[4.2.1]nona-2,4,7-trienes **7a–c** with *n*-butyllithium in tetrahydrofuran proved to be an efficient method to generate seleno-substituted carbanions. High yields of products were isolated after quenching with electrophiles. Three different compounds were formed: C_9-substituted products, substituted aromatic compounds, and tetracyclic derivatives (vide supra). The composition of the product mixture appeared to be dependent on time, temperature, and electrophile. An acceptable mechanism for the product formation is offered in Figure 3.

The triene selenoketals **7** react with *n*-BuLi to produce the equilibrating anions *anti*- and *syn*-**31**. The latter is thermodynamically unstable and rearranges to the aryllithium compound **32**. This intermediate reacts *intra*molecularly with the diene bridge to generate the stable allylic carbanion **33**. Carbanion **33** was characterized with the aid of ^1H NMR spectroscopy. The other intermediates are proposed on the basis of the structure of the isolated products.

The hard electrophiles water, deuterium oxide, methanol, and methanol-d_4 react in a nonstereospecific way with both C_9 carbanions. Other electrophiles, even bulky ones like benzaldehyde, prefer to attack *anti*-**31**, although this carbanion is sterically the most hindered one.

The carbonitrile-substituted carbanion **4** reacts with methyl iodide at the sterically least hindered side (vide supra).[5] However, C_9 in the carbanion **4** is sp^2 hybridized,



J 1,2 2,3 3,4 4,5 5,6 6,7
Hz 4.0 5.0 10.5 8.5 4.5 3.0

J 7,8 1,8 1,9 6,9 1,7 1,3
Hz 5.5 2.5 8.0 7.3 1.0 1.5

33 a

Figure 2. Spectral data for the carbanion **33a** and for its quench product **11a**.

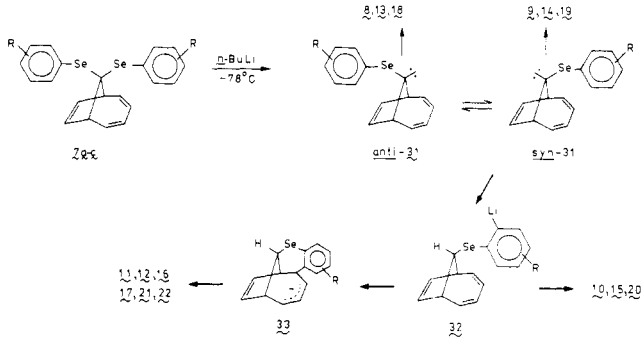
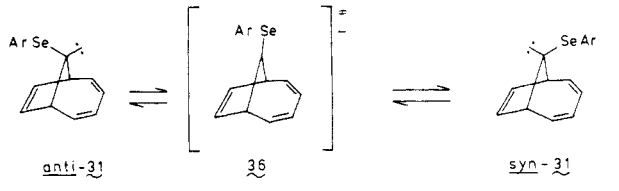


Figure 3. Mechanism for the reaction of *n*-BuLi with selenoketals **7a–c**.

due to the strong electron-withdrawing effect of the substituent. There is no need for bishomo- or bicycloaromatic stabilization. The stereochemistry of the reaction of carbanion **4** with soft electrophiles like methyl iodide is controlled by steric interactions.[2a,7] In the 9-seleno-substituted carbanions **31**, C_9 is sp^3 hybridized. The carbanions equilibrate via the activated complex **36**. Soft elec-



anti-31 36 syn-31

trophiles attack predominantly *anti*-**31** because of the preferred localization of electron density at the butadiene side of the carbanion. This can be attributed to a bishomoaromatic-stabilizing 6-π-electron interaction in this intermediate. This stabilizing interaction is not possible in *syn*-**31**. Presumably, this carbanion is a contact ion pair with the lithium cation very closely associated to the lone pair at C_9. This lowers the approachability of *syn*-**31** for electrophiles.

To the syn carbanions an alternative reaction path is available which leads to a more stable intermediate. Via a stereospecific process, the syn carbanions isomerize to aryllithium compounds **32**. These compounds react with electrophiles to produce substituted aromatic compounds.

Substituted aromatic compounds have already been reported.[8] When phenyl vinyl selenide was reacted with *n*-BuLi in ether at room temperature and subsequently quenched with methyl iodide, a mixture of hexyl tolyl selenides was isolated. Apparently, selenium-substituted aryllithium compounds are more stable than α-seleno-substituted carbanions.

(7) W. Todd Wipke and P. Gund, *J. Am. Chem. Soc.*, **98**, 8107 (1976).
(8) M. Sevrin, G. N. Denis, and A. Krief, *Angew. Chem.*, **90**, 550 (1978).

Scheme I

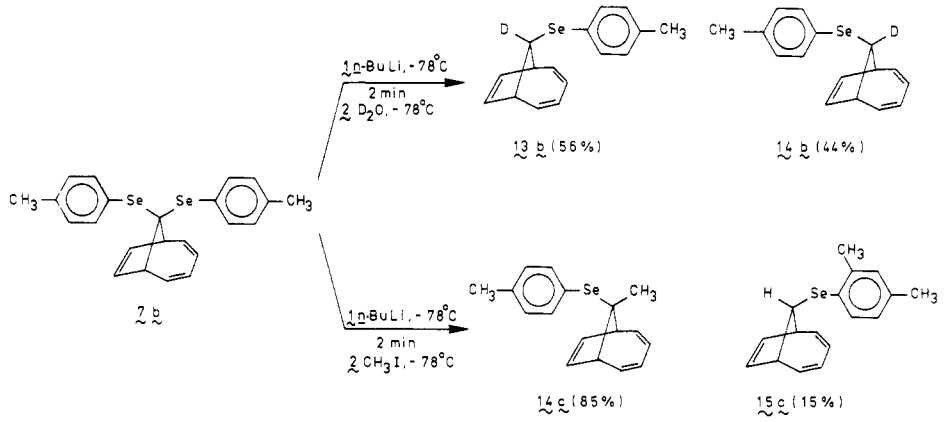
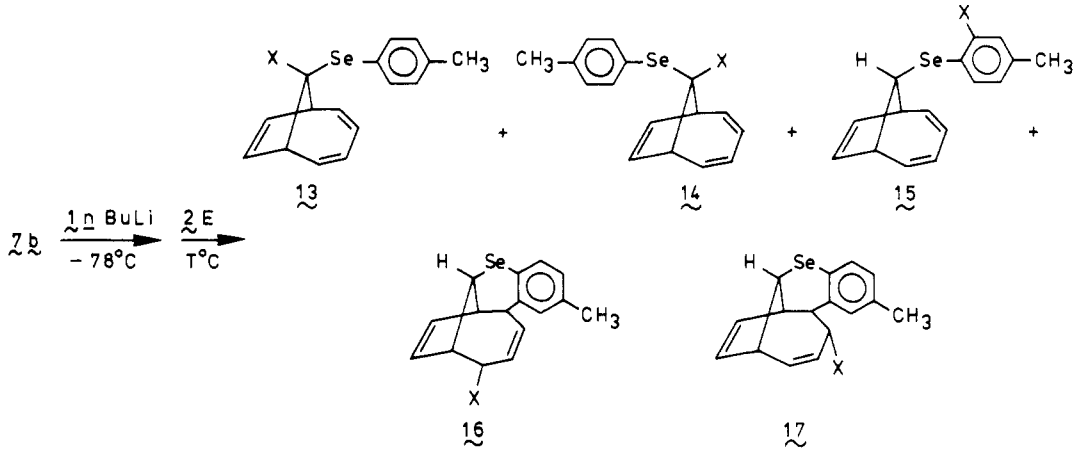


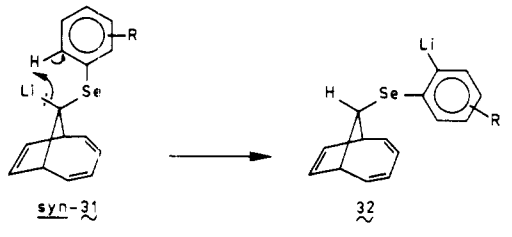
Table II. Products of the Reaction of Selenoketal 7b with *n*-BuLi and Electrophiles



E	X	time[a]	temp, °C	yield, %[b]	products (%)[c]				
H_2O	H	2	−78	80.4	13a (56)	14a (44)	15a	16a	17a
		30	−78	94.4	13a (65)	14a (35)			
		60	20	70				16a (100)	
D_2O	D	2	−78	80.4	13b (56)	14b (44)	15b	16b	17b
		30	−78	94.4	13b (19.3)	14b (35.8)[d]	15b (44.9)[d]		
CH_3I	CH_3	2	−78	88.3	13c	14c (85)	15c (15)	16c	17c
		30	−78	98.4		14c (72.1)	15c (27.9)		
PhC(O)H	PhC(OH)H	30	−78	84.4	13d (23)	14d (59)	15d (18)	16d	17d

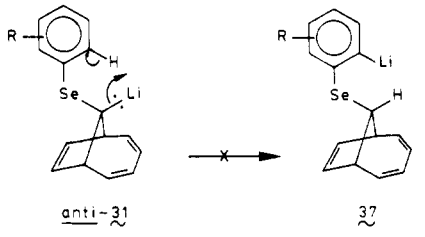
[a] In minutes after the addition of *n*-BuLi. [b] Calculated from isolated *n*-butyl *p*-tolyl selenide. [c] Calculated from isolated products. [d] Calculated from ^1H NMR integrals.

In our experiments only ortho-substituted products are formed, implying that the negative charge is generated exclusively at the ortho position. Dreiding models show that in the rigid carbanions *syn*-**31** the ortho proton ap-



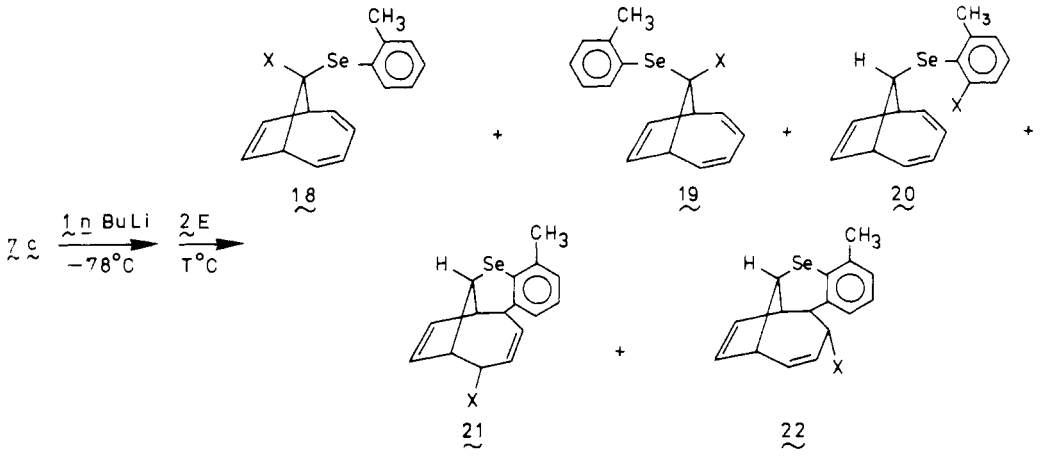
proaches the negative charge at C_9 very closely. *Intra*molecular electron transfer via proton exchange leads to the aryllithium compounds **32**. This was established by the use of the perdeuterio selenoketal **7d** which afforded product with deuterium at C_9, anti with respect to the butadiene bridge (vide supra). *Inter*molecular proton transfer can be ruled out on the basis of steric hindrance and the absence of compounds **8a**, **13a**, and **18a** in the quench reactions with aprotic electrophiles.

The isomerization of C_9 carbanions **31** to aryllithium compounds is a 100% stereospecific process. No product attributable to a rearrangement of *anti*-**31** to aryllithium compound **37** was observed. Apparently the bishomo-



aromatic interactions in *anti*-**31** decrease the basicity at C_9 and disfavor *intra*molecular proton exchange. This homoaromatic stabilization does, however, not overcome the driving force to generate the more stable aryllithium intermediates **32** via prior equilibration of the C_9 carbanions. The *p*-tolyl selenoketal **7b** gives under identical experimental conditions less substituted aromatic product than the phenyl selenoketal **7a**. The *p*-methyl substituent has no effect on the steric interactions at C_9. Therefore,

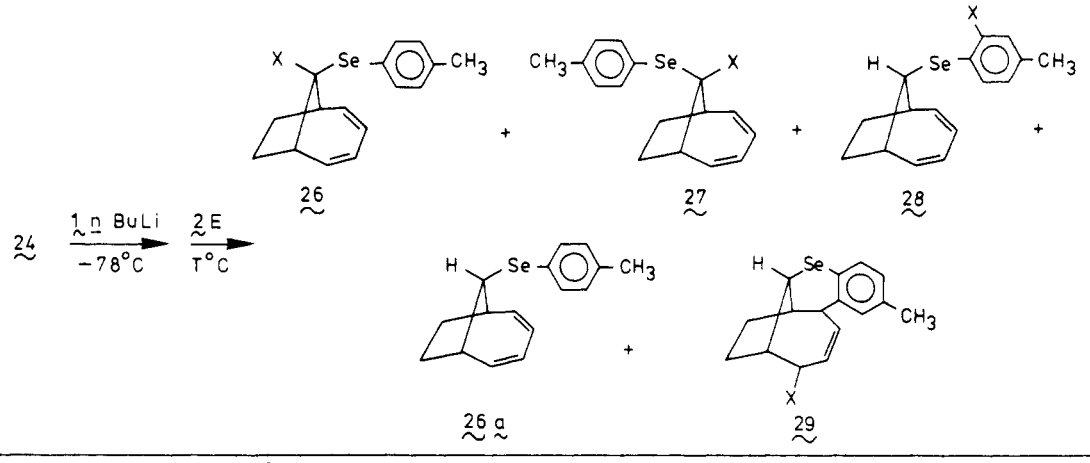
Table III. Products of the Reaction of Selenoketal 7c with *n*-BuLi and Electrophiles



E	X	time[a]	temp, °C	yield, %[b]	products (%)[c]				
H_2O	H	30	−78	86.4	**18a** (68.5)	**19a** (14)	**20a**	**21a** (17.5)	**22a**
		60	20	95				**21a** (100)	
D_2O	D	30	−50	92.4	**18b** (9.2)[d]	**19b**	**20b** (12.8)[d]	**21b** (78)[e]	**22b**
CH_3I	CH_3	30	−78	92	**18c**	**19c** (39.4)	**20c** (9.9)	**21c** (13.7)[f]	**22c** (37)[g]

[a] In minutes after the addition of *n*-BuLi. [b] Calculated from isolated *n*-butyl *o*-tolyl selenide. [c] Calculated from isolated products. [d] Calculated from ^1H NMR integrals. [e] Predominantly (90–95%) endo deuterium. [f] Endo:exo ratio 7:3. [g] Methyl substituent endo.

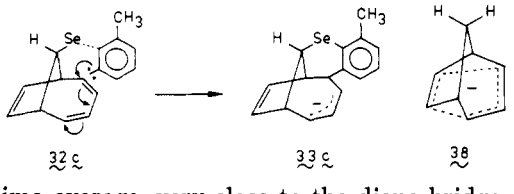
Table IV. Products of the Reaction of the Selenoketal 24 with *n*-BuLi and Electrophiles



E	X	time[a]	yield, %[b]	products (%)[c]				
H_2O	H	2	56.2	**26a** (20)	**27a** (80)	**28a**		**29a**
		30	84	**26a** (70)	**27a** (30)			
		60	81	**26a** (30.1)[d]				**29a** (7)[d]
D_2O	D	2	56.2	**26b** (8)	**27b** (80)	**28b** + **26a** (12)		**29b**
		30	70	**26b** (6.2)	**27b** (38.4)	**28b** + **26a** (55.4)		
CH_3I	CH_3	30	64.3	**26c**	**27c** (42)	**28c** (20)	**26a** (38)	**29c**

[a] In minutes after the addition of *n*-BuLi. [b] Calculated from isolated *n*-butyl *p*-tolyl selenide. [c] Calculated from isolated products. [d] Total yield of isolated products.

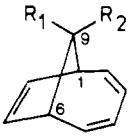
the lower tendency to isomerize has to be attributed to the electron-donating effect of the substituent. The *o*-methyl function in **31c** exercises the same electronic effect. Once proton exchange has occurred, the steric requirements of the *o*-methyl substituent bring the negative charge in **32c**,



on a time average, very close to the diene bridge. The allylic carbanion **33c** is then formed via direct *intra*molecular electron transfer. The other aryllithium compounds **32a,b** produce tetracyclic carbanions at higher temperature.

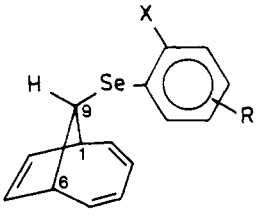
The allylic carbanions **33** are the most stable intermediates in the reaction pathway. The carbon atom C_5 has the highest electron density as is revealed by the high upfield shift of the H_5 proton in the ^1H NMR spectrum (vide supra). Water and deuterium oxide react exclusively at C_5. Methyl iodide shows a preference to attack C_3. A possible explanation for these results is that **33** exists as contact ion pairs in THF with the lithium cation associated to endo C_5. Deuterium oxide and water displace the metal

Table V. ^{1}H NMR Spectral Data for C_9-Substituted Products



prod	R_1	R_2	$H_{1,6}$	H_{2-5}	$H_{7,8}$	H_9	H_{ar}	H_{others}
8a	H	PhSe	3.27 (t)	6.03 (m)	5.27 (d)	3.77 (t)	7.53-6.87 (m)	
9a	PhSe	H	3.20 (d)	5.90 (m)	5.23 (d)	3.47 (s)	7.53-6.87 (m)	
8b	D	PhSe	3.3 (d)	6.1 (m)	5.33 (d)	3.77 (t)	7.53-6.87 (m)	
9b	PhSe	D	3.20 (d)	5.90 (m)	5.23 (d)		7.53-6.87 (m)	
9c	PhSe	CH_3	2.87 (m)	6.07 (m)	5.07 (d)		7.67-6.87 (m)	1.33 (s)
9d	PhSe	PhC(OH)H	2.97 (m)	6.07 (m)	4.53 (d)		7.70-6.70 (m)	3.53 (s)
			3.43 (m)					4.33 (s)
9e	PhSe	$Ph_2C(OH)$	3.93 (m)	5.90 (m)	4.23 (d)		7.70-6.70 (m)	3.40 (s)
9f	PhSe	C(O)H	3.30 (m)	6.13 (m)	5.20 (d)		7.60-6.70 (m)	9.07 (s)
13a	H	*p*-tolSe	3.17 (t)	5.9 (m)	5.13 (d)	3.57 (t)	7.36-6.73 (AB)	2.33 (s)
14a	*p*-tolSe	H	3.10 (d)	5.78 (m)	5.08 (d)	3.27 (s)	7.36-6.73 (AB)	2.27 (s)
13b	D	*p*-tolSe	3.2 (d)	5.9 (m)	5.13 (d)		6.37-6.7 (AB)	2.27 (s)
14b	*p*-tolSe	D	3.10 (d)	5.80 (m)	5.13 (d)		7.4-6.77 (AB)	2.30 (s)
14c	*p*-tolSe	CH_3	2.82 (m)	6.03 (m)	5.07 (d)		7.47-6.77 (AB)	2.28 (s), 1.3 (s)
14d	*p*-tolSe	PhC(OH)H	2.97 (m)	6.08 (m)	4.52 (d)		7.60-6.73 (m)	3.53 (s), 2.3 (s)
			3.53 (m)					4.33 (s)
13d	PhC(OH)H	*p*-tolSe	3.2 (m)	6.09 (m)	5.09 (m)		7.67-6.67 (m)	2.55 (s), 2.28 (s)
			2.55 (m)					4.48 (s)
18a	H	*o*-tolSe	3.33 (t)	6.33 (m)	5.4 (d)	3.8 (t)	7.7-6.9 (m)	2.33 (s)
19a	*o*-tolSe	H	3.17 (d)	5.83 (m)	5.17 (d)	3.37 (s)	7.4-6.73 (m)	2.33 (s)
18b	D	*o*-tolSe	3.33 (d)	6.33 (m)	5.4 (d)		7.7-6.9 (m)	2.33 (s)
18c	*o*-tolSe	CH_3	2.87 (m)	6.00 (m)	5.02 (d)		7.5-6.7 (m)	2.42 (s), 1.22 (s)

Table VI. ^{1}H NMR Spectral Data for Compounds Formed via Electrophilic Aromatic Substitution



prod	R	X	$H_{1,6}$	H_{2-5}	$H_{7,8}$	H_9	H_{ar}	H_{others}
10b	H	D	3.30 (t)	6.10 (m)	5.33 (d)	3.77 (t)	7.53-6.87 (m)	
10c	H	CH_3	3.23 (t)	6.00 (m)	5.23 (d)	3.66 (t)	7.53-6.73 (m)	2.37 (s)
10d	H	PhC(OH)H	3.13 (t)	5.90 (m)	5.13 (d)	3.50 (t)	7.70-6.70 (m)	6.1 (s), 2.8 (s)
10e	H	$Ph_2(OH)$	3.07 (t)	5.90 (m)	5.20 (d)	3.52 (t)	7.60-6.70 (m)	5.67 (s)
10f	H	C(O)H	3.30 (t)	6.03 (m)	5.30 (d)	3.77 (t)	7.60-6.70 (m)	10.20 (s)
10g	H	C(O)OH	3.40 (m)	6.00 (m)	5.37 (d)	3.83 (t)	8.67-7.00 (m)	
15b	*p*-CH_3	D	3.20 (m)	5.90 (m)	5.13 (d)	3.57 (t)	7.37-6.70 (m)	2.27 (s)
15c	*p*-CH_3	CH_3	3.17 (t)	5.97 (m)	5.20 (d)	3.53 (t)	7.40-6.73 (m)	2.33 (s), 2.22 (s)
15d	*p*-CH_3	PhC(OH)H	3.50 (t)	5.98 (m)	5.18 (d)	3.70 (t)	7.67-6.73 (m)	2.28 (s), 2.9 (s), 6.18 (s)
20b	*o*-CH_3	D	3.33 (t)	6.33 (m)	5.40 (d)	3.80 (t)	7.70-6.90 (m)	2.43 (s)
20c	*o*-CH_3	CH_3	3.20 (t)	6.00 (m)	5.18 (d)	3.60 (t)	7.50-6.70 (m)	2.33 (s)

cation to form deuterium and hydrogen-bonded carbanions which rapidly collapse.[9,10] On these precedents endo protonation and deuteration at C_5 is to be expected. Conversely, it is probable that quenching with methyl iodide occurs without the involvement of hydrogen bonding. The preference to attack C_3 from the endo side has to be explained by steric hindrance of the lithium cation associated to C_5. In the allylic carbanion **33** a stabilizing bishomoaromatic interaction is possible between the allylic anion part and the proximate double bond. This kind of interaction has already been reported for the bicyclo[3.2.1]octa-2,6-dienyl anion **38**.[11] Definite proof for the bishomocyclopentadienide character of **38** came from ^{1}H NMR observations. Direct ^{1}H NMR investigations of carbanion **33** under long-life conditions did not, however, provide conclusive evidence for stabilizing 6-π-electron interactions.

The mechanism for product formation out of the diene selenoketal **24** is almost the same as that encountered for the triene selenoketals **7a–c**. The selenoketal reacts with *n*-BuLi in THF to produce *syn*- and *anti*-**39** via C–Se bond cleavage. The soft electrophile methyl iodide attacks exclusively the homoaromatic-stabilized anti carbanion (vide

(9) Y. Pocken and S. H. Exner, *J. Am. Chem. Soc.*, **90**, 6764 (1968).
(10) W. D. Kollmeyer and D. J. Cram, *J. Am. Chem. Soc.*, **90**, 1784 (1968).

(11) (a) J. M. Brown and J. L. Occolowitz, *Chem. Commun.*, 376 (1965); (b) J. M. Brown, *ibid.*, 638 (1967); (c) J. M. Brown and J. L. Occolowitz, *J. Chem. Soc. B*, 411 (1968); (d) J. M. Brown and E. L. Caine, *J. Am. Chem. Soc.*, **92**, 3821 (1970); (e) S. Winstein, M. Ogliarusso, M. Sakai, and J. M. Nicholson, *ibid.*, **89**, 3656 (1967).

Table VII. ^{13}C NMR Spectral Data for C_9-Substituted Products[a]

prod	R_1	R_2	$C_{1,6}$	$C_{2,5}$	$C_{3,4}$	$C_{7,8}$	C_9	C_i	C_o	C_m	C_p	others
8a	H	PhSe	49.10	135.32	127.22	125.10	42.13	132.41	130.0	134.41	129.87	
8b	PhSe	H	51.33	136.31	125.37	122.54	41.95	131.90	130.17	134.10	128.10	
9b	PhSe	D	51.33	136.31	125.37	122.54	41.95	131.90	130.17	134.10	128.10	
9c	PhSe	CH_3	55.63	135.69	127.35	121.93	46.76	129.03	129.56	137.85	129.56	29.30
9d	PhSe	PhC(OH)H	47.11	134.19	128.63	119.63	76.09	128.37	130.04	136.92	129.64	63.70
			51.08	135.51	127.44	120.16						
9e	PhSe	$Ph_2C(OH)$	51.12	135.34	127.22	117.56	68.99	128.94	126.75	129.25	129.95	84.73
13a	H	*p*-tolSe	48.79	134.89	127.22	124.62	42.26	128.76	130.39	134.89	137.1	22.14
14a	*p*-tolSe	H	51.39	136.00	125.23	122.19	46.80	128.19	130.66	134.63	137.32	22.19
14b	*p*-tolSe	D	51.39	136.00	125.23	122.19	46.80	128.19	130.66	134.63	137.22	22.19
14c	*p*-tolSe	CH_3	55.49	135.03	127.48	121.57	46.10	126.38	130.09	137.98	137.98	22.28, 29.73
13d	PhC(OH)H	*p*-tolSe	53.95	135.69	127.31	123.34	73.76	126.25	130.22	139.09	139.61	22.28
			52.05		126.56	122.06						66.17
14d	*p*-tolSe	PhC(OH)H	50.99	134.23	127.57	120.07	76.01	124.62	130.92	137.06	139.19	22.36
			46.89	135.64	128.10	119.59						63.52
18a	H	*o*-tolSe	48.92	135.12	127.26	124.70	40.94	133.57	140.63	127.44	127.70	23.86
									134.37	130.62		
19a	*o*-tolSe	H	51.26	136.04	125.41	122.32	45.39	133.30	140.14	127.31	127.44	23.42
									132.42	130.79		
18c	*o*-tolSe	CH_3	58.58	135.04	127.27	121.76	58.32	131.20	138.65	126.79	129.13	23
									134.82	130.54		27.09

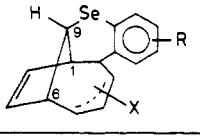
[a] See Table V for structure and numbering scheme.

Table VIII. ^{13}C NMR Spectral Data for Compounds Formed via Electrophilic Aromatic Substitution[a]

prod	R	X	$C_{1,6}$	$C_{2,5}$	$C_{3,4}$	$C_{7,8}$	C_9	C_{ar}				others
10b	H	D	49.10	135.32	127.22	125.10	42.13	132.41	130.00	134.41	129.87	
10c	H	CH_3	48.92	135.12	127.26	124.70	40.94	133.57	140.63	127.44	127.70	23.86
								134.37	130.62			
10d	H	PhC(OH)H	48.79	135.47	127.22	124.88	43.10	146.85	144.47	136.62	131.63	67.23
								129.25	128.45			
10e	H	$Ph_2C(OH)$	48.53	135.42	127.46	124.92	44.05	150.38	148.13	138.64	131.23	84.00
								129.73	128.90	127.62		
10g	H	C(O)OH	48.41	136.08	127.28	125.04	37.55	139.66	133.90	132.50	130.80	169.20
								130.56	125.71			
15b	*p*-CH_3	D	48.79	134.89	127.22	124.62	42.26	128.76	130.39	134.89	137.10	22.14
15c	*p*-CH_3	CH_3	48.96	134.98	127.18	124.62	41.24	140.94	137.98	131.45	127.88	23.87, 21.96
								135.16	125.71			
20b	*o*-CH_3	D	48.92	135.12	127.26	124.70	40.94	133.57	140.63	127.44	127.70	23.86
								134.37	130.62			

[a] See Table VI for structure and numbering scheme.

Table IX. ^1H NMR Spectral Data for Tetracyclic Compounds

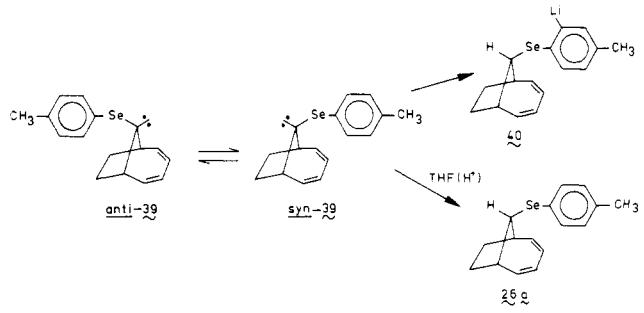


prod	R	X	$H_{1,6}$	H_2	H_3	$H_{3,4}$	$H_{4,5}$	H_5	$H_{7,8}$	H_{ar}	others
11a	H	5-H	2.85 (m)	3.50 (m)		5.07 (d)		2.85 (m)	5.88 (t)	7.40-6.70 (m)	
								2.30 (m)			
12c	H	3-CH_3	2.80 (m)	2.15 (m)	2.47 (q)		5.45 (m)		6.10 (t)	7.40-6.67 (m)	1.15 (d)
			2.15 (m)								
16a	*p*-CH_3	5-H	2.75 (m)	3.50 (m)		5.13 (d)		2.75 (m)	5.93 (t)	7.30-6.67 (m)	2.06 (s)
								2.06 (m)			
21a	*o*-CH_3	5-H	2.53 (m)	3.50 (m)		5.00 (d)		2.53 (m)	5.90 (t)	7.20-6.90	2.30 (s)
								2.30 (m)			
21b	*o*-CH_3	5-D	2.88 (m)	3.60 (m)		5.20 (d)		2.30 (m)	6.10 (t)	7.20-6.80 (m)	2.30 (s)
22c	*o*-CH_3	3-CH_3	3.25 (m)	3.25 (m)	2.40 (q)		5.10 (m)		6.17 (t)	7.06-6.70 (m)	2.27 (s)
			3.03 (m)								1.20 (d)

supra). The syn carbanion appears to be more unstable than the corresponding trien-9-yl carbanion **31**. It reacts with THF, or acidic impurities in THF, to produce *syn*-9-(*p*-tolylseleno)bicyclo[4.2.1]nona-2,4-diene (**26a**). It partly isomerizes to the aryllithium compound **40** via *intra*molecular electron transfer.

Tetracyclic carbanion **35** is formed in only minor amounts, as is evident from the low yield of isolated tetracyclic compound **29a** (vide supra). In part the low yield can be attributed to the side reaction of *syn*-**39** with THF. However, electronic effects may play an important role too.

From all these results it is evident that the behavior of 9-arylseleno-substituted bicyclo[4.2.1]nona-2,4,7-trien-9-yl (**31**) and bicyclo[4.2.1]nona-2,4-dien-9-yl carbanions **39** is dominated by the availability of a unique stereospecific reaction path in which electrons are transferred from C_9



to the aryl ring via *intra*molecular proton exchange. The driving force for this isomerization is the formation of a more stable aryllithium compound out of the "hot" C_9 carbanions. Further electron transfer to the butadiene segment via an *intra*molecular cyclization leads in the case of the triene system to the formation of a stable tetracyclic anion **33**.

Experimental Section

^{1}H NMR spectra were recorded with Varian EM-360A, Varian T-60A, and Bruker HX-90R instruments using Me_4Si as internal standard. ^{13}C spectra were taken on a Varian HA-100 spectrometer equipped with a Digilab FTS-NMR-3. Mass spectra were obtained with a Finnigan 4000 GS/MS instrument at an ionization potential of 70 eV. Preparative high-pressure LC separations were accomplished on a Jobin Yvon Chromatospac Prep 100. All separations were performed on silica H (type 60, Merck). Microanalyses were carried out in our laboratories by Messrs. P. v. d. Bosch and H. Eding. Melting points are uncorrected. Bicyclo[4.2.1]nona-2,4,7-trien-9-one (**41**),[2a] bicyclo[4.2.1]nonan-9-one (**43**),[2a] benzeneselenol (**44a**),[12] *p*-tolueneselenol (**44b**),[12] *o*-tolueneselenol (**44c**),[12] and benzene-d_5-selenol (**44d**)[12] were prepared according to the literature.

9,9-Bis(phenylseleno)bicyclo[4.2.1]nona-2,4,7-triene (7a). A stream of dry hydrogen chloride gas was passed through a solution of ketone **41** (7.8 g, 0.059 mol) and benzeneselenol (**44a**; 15.6 g, 0.099 mol) in dry diethyl ether (30 mL) at 0 °C during 15 min. The resulting mixture was poured into saturated sodium bicarbonate solution and extracted with ether. The organic layers were washed with water, 7% aqueous potassium hydroxide, and water, dried ($MgSO_4$), and concentrated. High-pressure LC with benzene–hexane (10/90) gave 11.3 g (53%) of **7a**: ^{1}H NMR (CCl_4) δ 7.9–6.8 (m, 10), 6.1 (m, 4), 5.3 (d, 2), 3.1 (m, 2); ^{13}C NMR (CCl_4) δ 56.02 ($C_{1,6}$), 134.22 ($C_{2,5}$), 128.01 ($C_{3,4}$), 122.23 ($C_{7,8}$), 57.22 (C_9), 132.11 and 131.28 (C_i), 129.60 (C_o), 134.10 and 138.42 (C_m), 129.60 (C_p).

9,9-Bis(*p*-tolylseleno)bicyclo[4.2.1]nona-2,4,7-triene (7b). Selenoketal **7b** was prepared in the same way as **7a**. High-pressure LC followed by recrystallization gave pure ketal in 55.7% yield: mp 79–80 °C; ^{1}H NMR (CCl_4) δ 7.6–6.67 (m, 8), 5.93 (m, 4), 4.92 (d, 2), 3.00 (m, 2), 2.53 (s, 3), 2.30 (s, 3); ^{13}C NMR (CCl_4) δ 55.80 ($C_{1,6}$), 134.01 ($C_{2,5}$), 127.97 ($C_{3,4}$), 121.97 ($C_{7,8}$), 57.26 (C_9), 127.84 and 128.94 (C_i), 130.17 (C_o), 138.77 and 139.09 (C_m), 138.47 and 137.98 (C_p), 22.54 (CH_3).

Anal. Calcd for $C_{23}H_{22}Se_2$: C, 60.53; H, 4.86. Found: C, 60.72; H, 4.91.

9,9-Bis(*o*-tolylseleno)bicyclo[4.2.1]nona-2,4,7-triene (7c) was prepared and isolated as for **7b**: yield 30.5%; mp 82–83 °C; ^{1}H NMR (CCl_4) δ 7.77–6.67 (m, 8), 5.93 (m, 4), 4.83 (d, 2), 3.37 (m, 2), 2.40 (s, 3), 2.27 (s, 3); ^{13}C NMR (CCl_4) δ 57.08 ($C_{1,6}$), 134.19 ($C_{2,5}$), 127.66 ($C_{3,4}$), 121.62 ($C_{7,8}$), 56.95 (C_9), 134.01 and 133.0 (C_i), 139.57, 136.48, 143.01, and 143.76 (C_o), 130.97, 130.62, 126.51, and 126.60 (C_m), 129.12 and 129.78 (C_p), 24.57 and 24.66 (CH_3).

Anal. Calcd for $C_{23}H_{22}Se_2$: C, 60.53; H, 4.86. Found: C, 60.76; H, 4.91.

9,9-Bis(phenyl-d_5-seleno)bicyclo[4.2.1]nona-2,4,7-triene (7d) was prepared and isolated as for **7a**: yield 45%; ^{1}H NMR (CCl_4) δ 5.9 (m, 4), 4.87 (d, 2), 3.03 (m, 2).

Bicyclo[4.2.1]nona-2,4-dien-9-one (42). The nickel boride catalyst[13] used was prepared under nitrogen in the hydrogenation flask by adding dropwise a solution of sodium borohydride (0.033 g, 0.87 mmol in 20 mL of ethanol) to a stirred solution of nickel(II) acetate tetrahydrate (0.23 g, 0.92 mmol in 20 mL of ethanol). Ketone **41** dissolved in 20 mL of ethanol was introduced into the reaction flask, and 169 mL of H_2 was taken up under stirring. The resulting mixture was poured into 100 mL of saturated sodium bicarbonate solution, filtered, and extracted with ether. The water phase was stripped from the ethanol and subsequently extracted with ether. The combined ether layers were washed with water, dried ($MgSO_4$), and concentrated, yielding 0.87 g (86%) of ketone **42**: ^{1}H NMR (CCl_4) δ 5.44 (m, 4), 2.42 (m, 2), 2.00 (m, 4); mass spectrum *m/e* 134.

9,9-Bis(*p*-tolylseleno)bicyclo[4.2.1]nona-2,4-diene (24). To a solution of ketone **42** (0.5 g, 3.7 mmol) and *p*-tolueneselenol (**44b**; 1.09 g, 6.4 mmol) in 5 mL of dry diethyl ether was added 0.2 mL of concentrated H_2SO_4.[14] After being stirred for 1 h at room temperature under a nitrogen atmosphere, the reaction mixture was poured into a saturated sodium bicarbonate solution and extracted into ether. The organic layers were washed with water, 10% aqueous sodium hydroxide, and water, dried ($MgSO_4$) and concentrated. High-pressure LC with benzene–hexane (10/90), followed by recrystallization from hexane, gave 0.47 g (32%) of pure selenoketal **24**, mp 95.2–95.7 °C; ^{1}H NMR (CCl_4) δ 7.72–6.33 (m, 8), 5.73 (m, 4), 2.38 (s, 6), 2.4 (m, 4); ^{13}C NMR (CCl_4) δ 51.26 ($C_{1,6}$), 135.60 ($C_{2,5}$), 127.13 ($C_{3,4}$), 41.55 ($C_{7,8}$), 63.87 (C_9), 128.50 and 127.84 (C_i), 130.26 and 130.57 (C_o), 137.81 (C_m), 139.26 and 139.88 (C_p), 22.45 (CH_3).

Anal. Calcd for $C_{23}H_{24}Se_2$: C, 60.26; H, 5.28. Found: C, 60.07; H, 5.35.

9,9-Bis(*p*-tolylseleno)bicyclo[4.2.1]nonane (25) was prepared in the same way as selenoketal **24**: yield 25%; mp 93–94 °C; ^{1}H NMR δ 7.67–6.9 (m, 8), 2.6–1.23 (m, 12), 2.3 (s, 6).

Anal. Calcd for $C_{23}H_{28}Se_2$: C, 59.74; H, 6.10. Found: C, 59.95; H, 6.18.

General Procedure for the Quench Reactions. A solution of 1 g of triene selenoketal **7a–d** in 10 mL of dry THF was treated with 2 mL of *n*-BuLi (15% in hexane) at −78 °C under a nitrogen atmosphere. In the direct quench experiments the electrophiles were added 2 min after carbanion formation. In the other low-temperature quench reactions the anionic solution was stirred 0.5 h prior to the addition of electrophile. For the room-temperature experiments the triene selenoketals were reacted 0.5 h with *n*-BuLi at −78 °C and 0.5 h at room temperature. After being quenched, the reaction mixtures were allowed to warm to room temperature, poured into water, and extracted into ether or chloroform. The organic layers were washed with water, dried ($MgSO_4$), and concentrated. The products were isolated with the aid of high-pressure LC. For ^{1}H and ^{13}C NMR spectral data see Tables V–IX. Some products were solid: **8g** (mp 213–214 °C); **13d** (mp 156–158 °C); **14d** (mp 122–123 °C); **16a** (mp 113–114 °C); **21a** (mp 89–91 °C); **22c** (mp 115–119 °C). All these compounds gave satisfactory microanalyses. The products of the reaction of triene selenoketals **7** with *n*-BuLi and water, deuterium oxide, and methyl iodide were examined with GLC/MS. All derivatives gave the expected molecular ions.

Reactions with Diene Selenoketal 24. The procedure was the same as that described for the triene selenoketals **7** (vide supra). Reaction with water afforded **26a** and **27a**.

26a: mass spectrum *m/e* 290; ^{1}H NMR δ 7.50–6.73 (AB, 4), 5.70 (m, 4), 3.85 (t, 1), 2.77 (m, 2), 1.92 (m, 4), 2.27 (s, 3); ^{13}C NMR δ 45.13 ($C_{1,6}$), 136.31 ($C_{2,5}$), 126.60 ($C_{3,4}$), 40.19 ($C_{7,8}$), 46.00 (C_9), 129.42 (C_i), 130.44 (C_o), 135.16 (C_m), 137.10 (C_p), 22.19 (CH_3).

27a: mass spectrum *m/e* 290; ^{1}H NMR δ 7.47–6.78 (m, 4), 6.03–5.27 (m, 4), 3.93 (s, 1), 2.57 (d, 2), 2.27 (s, 3), 2.07 (m, 4); ^{13}C NMR δ 46.76 ($C_{1,6}$), 137.85 ($C_{2,5}$), 124.93 ($C_{3,4}$), 39.52 ($C_{7,8}$), 50.86 (C_9), 128.19 (C_i), 130.66 (C_o), 134.89 (C_m), 137.37 (C_p), 22.19 (CH_3).

Reaction with deuterium oxide afforded **26a**, **26b**, **27b**, and **28b**.

26b and 28b: mass spectrum *m/e* 291; ^{1}H and ^{13}C NMR as for **26a**.

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(13) C. A. Brown, *Chem. Commun.*, 600 (1969).

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27b: mass spectrum m/e 291; ^{1}H NMR δ 7.47–6.73 (AB, 4), 6.03–5.10 (m, 4), 2.60 (m, 2), 2.27 (s, 3), 2.06 (m, 4); ^{13}C NMR as for **27a**.

Reaction with methyl iodide afforded **26a**, **27c**, and **28c**.

27c: mass spectrum m/e 304; ^{1}H NMR δ 7.60–6.93 (AB, 4), 5.87 (m, 4), 2.50 (m, 2), 2.43 (s, 3), 2.13 (m, 4), 1.43 (s, 3); ^{13}C NMR δ 22.78 and 29.73 (CH_3), 39.66 ($C_{7,8}$), 50.20 (C_9), 51.21 ($C_{1,6}$), 126.47 ($C_{3,4}$), 136.39 ($C_{2,5}$).

28c: mass spectrum m/e 304; ^{1}H NMR δ 7.60–6.70 (m, 3), 5.74 (m, 4), 3.54 (t, 1), 2.70 (m, 2), 2.23 (s, 3), 2.23 (s, 3), 2.00 (m, 4).

Reaction of 25 with *n*-BuLi and Water. This reaction afforded starting material and a mixture of *n*-butyl *p*-tolyl selenide (m/e 228), *syn*-9-(*p*-tolylseleno)bicyclo[4.2.1]nonane (m/e 294; 3.5 ppm, t, H_9), and *anti*-9-(*p*-tolylseleno)bicyclo[4.2.1]nonane (m/e 294; 3.6 ppm, s, H_9) which could not be separated by high-pressure LC.

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Registry No. **7a**, 72065-39-5; **7b**, 72065-40-8; **7c**, 72065-41-9; **7d**, 72065-42-0; **8a**, 72065-43-1; **8b**, 72065-44-2; **8c**, 72065-45-3; **8d**, 72065-46-4; **8e**, 72065-47-5; **8f**, 72065-48-6; **8g**, 72065-49-7; **9a**, 72065-50-0; **9b**, 72065-51-1; **9c**, 72065-52-2; **9d**, 72065-53-3; **9e**, 72065-54-4; **9f**, 72065-55-5; **9g**, 72065-56-6; **10b**, 72065-57-7; **10c**, 72065-58-8; **10d**, 72065-59-9; **10e**, 72065-60-2; **10f**, 72065-61-3; **10g**, 72065-62-4; **11a**, 72065-63-5; **11b**, 72065-64-6; *endo*-**11c**, 72065-65-7; *exo*-**11c**, 72065-66-8; **11d**, 72065-67-9; **11e**, 72065-68-0; **11f**, 72065-69-1; **11g**, 72065-70-4; **12a**, 72065-71-5; **12b**, 72065-72-6; **12c**, 72065-73-7; **12d**, 72065-74-8; **12e**, 72065-75-9; **12f**, 72065-76-0; **12g**, 72065-77-1; **13a**, 72065-78-2; **13b**, 72065-79-3; **13c**, 72065-80-6; **13d**, 72065-81-7; **14a**, 72065-82-8; **14b**, 72065-83-9; **14c**, 72065-84-0; **14d**, 72065-85-1; **15b**, 72065-86-2; **15c**, 72065-87-3; **15d**, 72065-88-4; **16a**, 72065-89-5; **16b**, 72065-90-8; **16c**, 72065-91-9; **16d**, 72065-92-0; **17a**, 72065-93-1; **17b**, 72065-94-2; **17c**, 72065-95-3; **17d**, 72065-96-4; **18b**, 72065-97-5; **18c**, 72065-98-6; **19a**, 72065-99-7; **19b**, 72066-00-3; **19c**, 72066-01-4; **20b**, 72066-02-5; **20c**, 72066-02-5; **21a**, 72066-03-6; **21b**, 72066-04-7; *endo*-**21c**, 72120-56-0; *exo*-**21c**, 72066-05-8; **22a**, 72066-06-9; **22b**, 72066-07-0; **22c**, 72066-08-1; **24**, 72066-09-2; **25**, 72066-10-5; **26a**, 72066-11-6; **26b**, 72066-12-7; **26c**, 72066-13-8; **27a**, 72066-14-9; **27b**, 72066-15-0; **27c**, 72066-16-1; **28a**, 72066-11-6; **28b**, 72066-17-2; **28c**, 72066-18-3; **29a**, 72066-19-4; **29b**, 72066-20-7; **29c**, 72066-21-8; **41**, 34733-74-9; **42**, 52902-51-9; **44a**, 645-96-5; **44b**, 37773-23-2; CH_3I, 74-88-4; PhCHO, 100-52-7; Ph_2CO, 119-61-9; DMF, 68-12-2; CO_2, 124-38-9; H_2O, 7732-18-5; D_2O, 7789-20-0.

Addition of Tri-*n*-butyltin Hydride to Conjugated *p*-Menthadienes

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The addition reaction of tri-*n*-butyltin hydride is here adapted to the conjugated 1,3- and 2,4(8)-*p*-menthadienes. The yields of the adducts are considerable for these conjugated *p*-menthadienes. Eight new organotin adduct compounds have been separated and their structures determined by IR and NMR spectra, which show one double bond as in the *p*-menthene ring, as well as the tri-*n*-butylstannyl group. An addition scheme is postulated in which 1,2-addition of tri-*n*-butyltin hydride to the original *p*-menthadienes is favored, followed by isomerization from the original. 1,4-Addition then occurs.

The addition of tri-*n*-butyltin hydride to β-pinene, limonene, and 1(7)-*p*-menthene has been previously reported by the present authors.[1] In these cases, the tri-*n*-butylstannyl group attaches to the outer carbon of the *p*-menthene ring, and the adducts are simple compositions.

In this paper, further investigation, using these techniques, on the conjugated *p*-menthadiene adducts such as 1,3- and 2,4(8)-*p*-menthadienes is presented. In these cases, however, the compositions of adduct mixtures are complex, and thus careful separation and analytical techniques are needed.

It has been found that by using a Golay column we could analyze these organotin adduct components without decomposition even at temperatures as high as 190 °C if proper operating conditions were chosen. Moreover, each component was purified sufficiently to permit the determination of its structure by a combination of two separation techniques, vacuum distillation with a spinning-band column followed by several repetitions of liquid chromatography using a column packed with silica gel at room temperature.

As it was difficult to obtain these terpenes[2] at high purity as starting material, they were used as mixtures containing several percent of other terpenes such as *p*-menthene, *p*-cymene, and 1,4-[3] and 1,4(8)-*p*-menthadienes in which mono- and unconjugated double bonds were absent or far less active in this reaction.

The conditions used for the addition reaction were the same as those in the previous report:[1] azobis(isobutyronitrile) (AIBN) and heating at 200 °C for 24 h or more in a sealed glass tube.

The determination of the structure of each component was made possible by examining the IR and NMR spectra of the purified samples and referring to its retention time in GC and stability in the acid and iodine cleavage reactions.

Experimental Section

The precise GC analysis of the organotin components was carried out on a Hitachi K-53 gas chromatograph with a Golay column of Z-45 (silicone grease SE-30, 0.25 mm i.d. × 45 m, column temperature 190 °C, He 1.0 atm, injection quantity of sample 0.2–0.4 mL). *p*-Menthanes, methenes, methadiens, and iodo-*p*-menthanes were also analyzed by a Golay column of R-45 (polypropylene glycol, up to 140 °C) and HB-2000 (polyethylene glycol, up to 160 °C). A spinning-band fractionation column having 40 theoretical plates was used under a vacuum of 1.0 torr, and high reflux ratios were used for the separation of each com-

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(2) P. de Mayo, "Mono- and Sesquiterpenoids", Vol. II, Interscience, New York, 1959, p 60. On this page, it is mentioned that α-terpinene (1,3-*p*-menthadiene) has not been obtained in pure form.

(3) The adduct yield for 1,4-*p*-menthadiene was only 9.1% under the same conditions as those used for the other conjugated menthadienes. The dehydrogenation tendency to *p*-cymene of this menthadiene was strongest, and the adduct components were almost the same as those in 1,3-*p*-menthadiene with regard to formation ratios and kinds. Thus, it may be isomerized first to 1,3-*p*-menthadiene in this reaction system and can add Bu_3SnH, but owing to simultaneous side reactions this is consumed and changes to ditin, which causes a low yield.

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