112. The Carbonyl Group as Homoconjugated Electron-Releasing Substituent. Regioselective Electrophilic Additions at Bicyclo[2.2.1]hept-5-en-2-one, Bicyclo[2.2.2]oct-5-en-2-one, and Derivatives[1])

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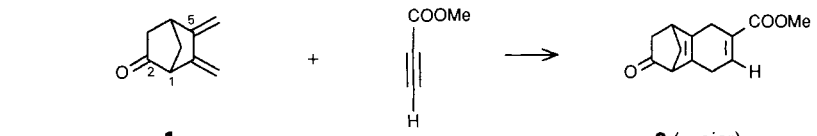
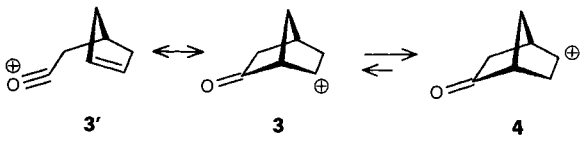
(3.V.89)

In $CHCl_3$, CH_3CN, or AcOH, benzeneselenenyl chloride (PhSeCl), bromide (PhSeBr), and acetate (PhSeOAc), 2-nitrobenzenesulfenyl chloride ($NO_2C_6H_4SCl$), and 2,4-dinitrobenzenesulfenyl chloride ($(NO_2)_2C_6H_3SCl$) added to bicyclo[2.2.1]hept-5-en-2-one (**5**) in an *anti* fashion with complete stereo- and regioselectivity, giving adducts **20**–**24** in which the chloride, bromide, or acetoxy substituent (X) occupies the *endo* position at C(6) and the Se- or S-substituent (E) the *exo* position at C(5). The addition **5** + $(NO_2)_2C_6H_3SCl \rightarrow$ **24** was accompanied by the formation of (1*RS*,2*RS*)-2-(2,4-dinitrophenylthio)cyclopent-3-ene-1-acetic acid (**25**). The latter was the major product in AcOH containing $LiClO_4$. The additions of PhSeCl and PhSeBr to bicyclo[2.2.2]oct-5-en-2-one (**6**) were less stereoselective (proportion of *exo vs. endo* mode of electrophilic attack was *ca.* 3:1) but highly regioselective giving adducts **27**/**28** and **29**/**30**, respectively, the regioselectivity being the same as that of the electrophilic additions of **5**. The reaction of PhSeCl with a 4:1 mixture of 2-*exo*-chloro- and 2-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-carbonitriles (**12**) was slower than addition **5** + PhSeCl; it gave adducts **31**/**32** (4:1) in which the PhSe moiety occupies the *exo* position at C(6) and the Cl atom the *endo* position at C(5). The addition of PhSeCl to 2-chlorobicyclo[2.2.1]oct-5-ene-2-carbonitriles (**13**) was very slow and gave adducts with the same regioselectivity as **12** + PhSeCl, but opposite with that of reactions of the corresponding enones **5** and **6**. PhSeX (X = Cl, Br, OAc) added to 2-cyanobicyclo[2.2.1]hept-5-en-2-yl acetates (**14**) with the same regioselectivity as **12** + PhSeCl. The additions of PhSeCl, PhSeBr, $NO_2C_6H_4SCl$, and $(NO_2)_2C_6H_3SCl$ to 2-(bicyclo[2.2.1]hept-5-en-2-ylidene)propanedinitrile (**49**) were not regioselective, showing that a dicyanomethylidene function is not like a carbonyl function when homoconjugated with a π system. The results are in agreement with predictions based on MO calculations suggesting that a carbonyl group homoconjugated with an electron-deficient centre can behave as an electron-donating, remote substituent because of favourable n(CO) $\leftrightarrow \sigma$C(1),C(2) $\leftrightarrow$ p(C(6)) hyperconjugative interaction.

Introduction. – In 1978, we reported that 5,6-dimethylidenebicyclo[2.2.1]heptan-2-one (**1**) adds to methyl propynoate with a relatively good *'para'* regioselectivity, giving the major adduct **2**. The results were in agreement with predictions based on the FMO theory [2] which considers the HOMO(diene)-LUMO(dienophile) orbital interaction to control the regioselectivity of the cycloaddition [1] [3]. The HOMO of **1** showed a significant difference in the size of the p atomic coefficients between those at C(5)=CH_2 and those at C(6)=CH_2 [3]. Furthermore, the shape of this HOMO suggested also an important hyperconjugative interaction of the type n(CO) $\leftrightarrow \sigma$(C(1),C(2)) $\leftrightarrow \pi$(C(5),C(6)) in **1** that makes the carbonyl group act as an electron-donating homoconjugated substituent. Semi-empirical calculations, first [4], and then *ab initio* STO 3G MO calculations [5], confirmed this hypothesis as it was found that the 6-oxobicyclo[2.2.1]hept-2-yl cation (**3**)

[1]) Presented at the autumn meeting of the Swiss Chemical Society in Berne, October 17, 1980; for a preliminary communication, see [1a].

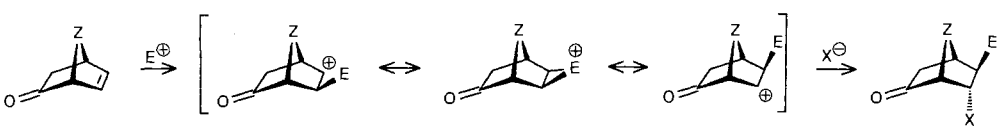




ΔE = +8.0 kcal/mol MINDO 3 [4]
+2.8 kcal/mol MNDO [4]
+3.0 kcal/mol AM1
+7.0 kcal/mol STO 3G [5]

is more stable than its 5-oxo isomer (**4**) (completely optimized geometries). The relatively long C(1)–C(6) and short C(1)–C(2) bond calculated for **3** were in agreement with the hypothetical hyperconjugative stabilizing interaction n(CO) ↔ σ(C(1),C(2)) ↔ p(C(6)) as represented by the limiting structures **3** ↔ **3'**. These features were not present in the case of 5-cyano- and 6-cyanobicyclo[2.2.1]hept-2-yl cations, the former ion being calculated to be more stable than the latter [5], as expected for carbocations remotely perturbed by an electron-withdrawing group such as the CN substituent (field effect [6]).

Following these calculations, we predicted that additions of electrophiles E^+X^- to the olefinic moieties of bicyclo[2.2.*n*]alk-5-en-2-ones **5**–**7** should be regioselective and give preferentially adducts **11** under conditions of kinetic control. In contrast, the synthetic precursors such as the corresponding chlorocarbonitriles **12** and **13** or cyano acetates **14** and **15** should give preferentially adducts **19**. A S- or Se-electrophile E^+ is expected to form the bridged cationic intermediates **9** [7] on reacting with enones **5**–**7**. Intermediates **9** are attacked then preferentially at C(6) by the counter-ion X^- because the limiting structures **10** contribute more than the corresponding structures **8**, the former being stabilized by the electron-donating ability of the homoconjugated carbonyl group. In the case of the electrophilic additions of **12**–**15**, the corresponding cationic intermediates **17** are expected to be attacked by X^- preferentially at C(5) because the limiting structures **18** should contribute more than the corresponding structures **16** because of the electron-withdrawing effect of the substituents at C(2). Alternatively, the regioselectivity of reac-



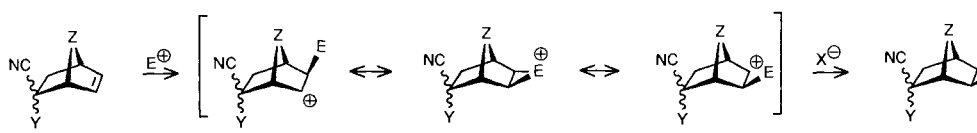
5 Z = CH_2
6 Z = CH_2CH_2
7 Z = O

8 Z = CH_2, CH_2CH_2, O

9 Z = CH_2, CH_2CH_2, O

10 Z = CH_2, CH_2CH_2, O

11 Z = CH_2, CH_2CH_2, O



12 Y = Cl, Z = CH_2
13 Y = Cl, Z = CH_2–CH_2
14 Y = OAc, Z = CH_2
15 Y = OAc, Z = O

16 Y = Cl, Z = CH_2, CH_2CH_2, O

17 Y = Cl, Z = CH_2, CH_2CH_2, O

18 Y = Cl, Z = CH_2, CH_2CH_2, O

19 Y = Cl, Z = CH_2, CH_2CH_2, O

tions **12**–**15** + EX → **19** could be governed by the bulk of the *endo* substituents at C(2), this in the case of *exo* mode of additions only. Completely optimized geometries obtained by the *ab initio* STO 3G technique for model 2,3-episulfoniobicyclo[2.2.1]heptanes confirmed our hypotheses [5]. They were also in agreement with preliminary results on the regioselective electrophilic additions of **5** and **6** [1], **7** [8], **12** and **13** [1], and **14** and **15** [8] [9]. We report here the full experimental details for the additions of several electrophilic agents onto the C=C bond of **5**, **6**, **12**, **14** and 2-(bicyclo[2.2.1]hept-5-en-2-ylidene)-propanedinitrile (**49**; see below).

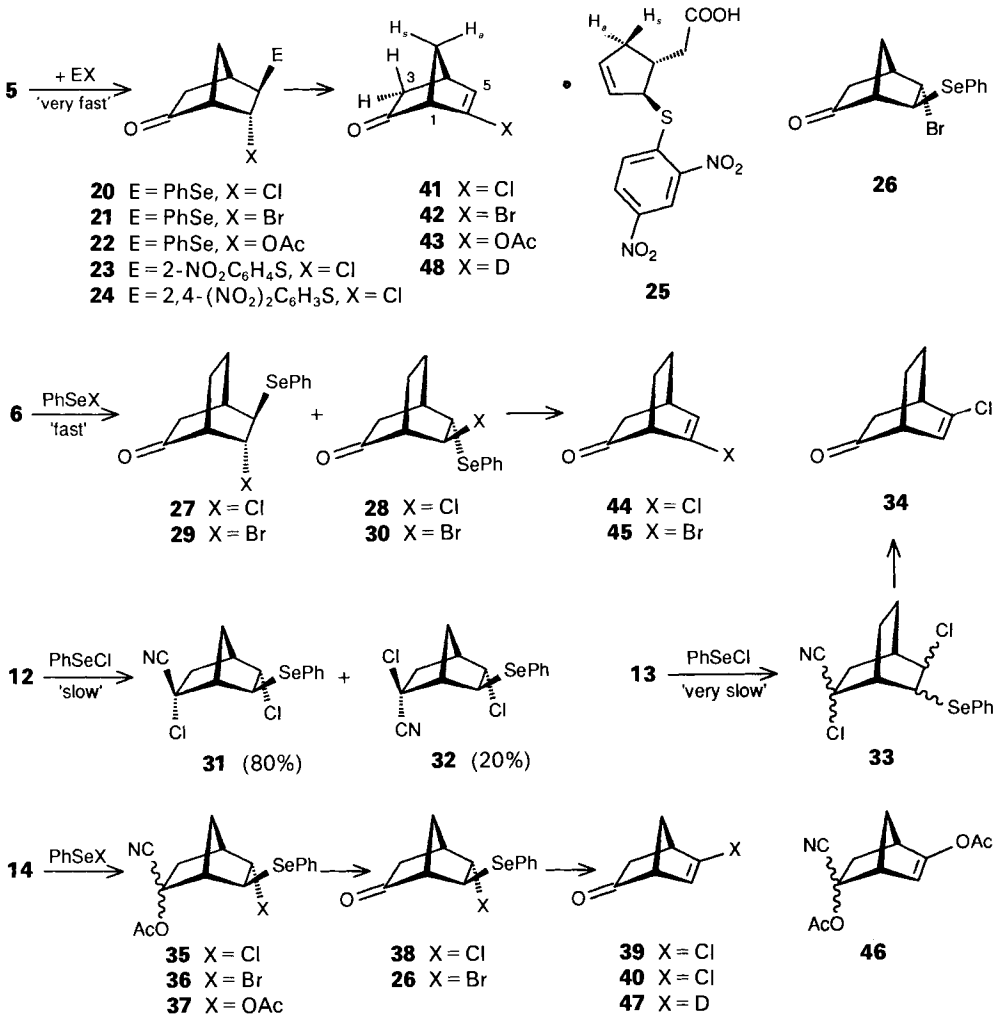
Results. – With benzeneselenenyl chloride (PhSeCl) and benzeneselenenyl bromide (PhSeBr) in $CHCl_3$, CH_3CN, or AcOH, bicyclo[2.2.1]hept-5-en-2-one (**5**) gave adducts **20** (93%) and **21** (95%, isolated), respectively. At 20°, the reactions were 'instantaneous'. At –78° in THF, the addition of PhSeBr to **5** gave **21** nearly quantitatively in 2–5 h. With benzeneselenenyl acetate (PhSeOAc, prepared according to [10]), **5** gave adduct **22** which was not isolated, but directly treated with 1 equiv. of 3-chloroperbenzoic acid to afford the enol acetate **43** (see below; *Scheme 1*) in 59% yield. The 2-nitrobenzenesulfenyl chloride ($NO_2C_6H_4SCl$) and 2,4-dinitrobenzenesulfenyl chloride ($(NO_2)_2C_6H_3SCl$) in $CHCl_3$ added to **5** and afforded adducts **23** (93%, isolated) and **24**, respectively. In CH_3CN or AcOH, the addition of $(NO_2)_2C_6H_3SCl$ to **5** gave **24** (60–70%) together with the acid **25** (20–30%, isolated after aqueous workup). In AcOH + 2 equiv. of $LiClO_4$, **25** was the major product and could be isolated in 80% yield. No trace of any isomeric adducts could be detected in the crude reaction mixtures **20**–**24** and in the mother liquors after crystallization of **20**, **21**, **23**, and **24**, by 360-MHz ^{1}H-NMR and HPLC. Prolonged heating in CH_3CN (90°, 10 h) of the *a priori* most labile adduct **21** [10] led to the slow formation of isomer **26** (prepared independently from **14**, see below), **5** and polymers, thus confirming that the adducts **20**–**24** were formed under conditions of kinetic control.

The additions of PhSeCl and PhSeBr to bicyclo[2.2.2]oct-5-en-2-one (**6**) in $CHCl_3$ were slower than those to bicyclo[2.2.1]hept-5-en-2-one (**5**). While the reactions were completed in a few seconds in the latter case at 20°, 12 h were required for completion in the former case. They furnished mixtures of the *exo* and *endo* adducts **27**/**28** (73:27, > 90%) and **29**/**30** (75:25, > 90%), respectively[2]).

As expected for olefins perturbed by electron-withdrawing groups such as CN and Cl, the addition of PhSeCl to the 2-chlorobicyclo[2.2.1]hept-5-ene-2-carbonitriles **12** (4:1 mixture of *exo*-CN/*endo*-CN) were much slower (20°, 48 h, $CHCl_3$) than those of bicyclo-[2.2.1]hept-2-ene and of enone **5**. They gave a 4:1 mixture of adducts **31**/**32** in good yield. Similarly, the 2-chlorobicyclo[2.2.2]oct-5-ene-2-carbonitriles **13** added PhSeCl very slowly (6 days, reflux in CH_2Cl_2, large excess of PhSeCl) giving a mixture **33** of adducts. Treatment of this mixture with $NaIO_4/NaHCO_3$ in $MeOH/H_2O$ [10] or H_2O_2 in THF gave the 2,5-dichlorobicyclo[2.2.2]oct-5-ene-2-carbonitriles which were directly transformed to 5-chlorobicyclo[2.2.2]oct-5-en-2-one (**34**). Less than 3% of the corresponding 6-chlorobicyclo[2.2.2]oct-5-en-2-one (**44**; see below) were detected in the 360-MHz ^{1}H-NMR and 90-MHz ^{13}C-NMR spectra of the crude reaction mixture, thus demonstrating the high regioselectivity of reaction **13** + PhSeCl → **33**. It is the same as that of addition **12** + PhSeCl → **31**/**32**, but opposite to that of reactions **5** + EX and **6** + PhSeX

[2]) We use the words *exo* and *endo* for electrophile attack onto the face of the C=C bond from the same and opposite side, respectively, as the *n* bridge of the bicyclo[2.2.*n*]alk-5-en-2-yl systems.

Scheme 1



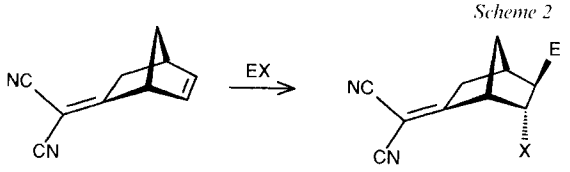
(Scheme 1). With PhSeCl, PhSeBr and PhSeOAc, the cyano acetates **14** afforded the corresponding adducts **35**, **36**, and **37**, respectively.

On saponification (K_2CO_3/MeOH/H_2O), followed by treatment with formaline, the adducts **35** and **36** gave ketones **38** and **26**, respectively. Oxidative elimination of the Se-containing substituent [10] afforded the corresponding chloro- and bromoenones **39** and **40**, respectively. No trace of the isomeric 6-chloro- and 6-bromobicyclo[2.2.1]hept-5-en-2-ones (**41** and **42**, resp.) could be detected in the 360-MHz ^{1}H-NMR of the crude reaction mixtures. Under similar conditions ($NaIO_4$/$NaHCO_3$/MeOH/H_2O, 20° [10], adducts **20**, **21**, **22**, **27**/**28**, and **29**/**30** furnished the 6-substituted bicyclo[2.2.*n*]alk-5-en-2-ones **41**, **42**, **43**, **44**, and **45**, respectively, in good yield, thus demonstrating the high regioselectivity of the electrophilic additions of the bicyclic enones **5** and **6**. Oxidative

elimination of the PhSe substituent from adducts **37** gave the diacetates **46**. On treatment of the bromoenones **40** and **42** with a zinc-copper couple in THF/D_2O and dioxane/D_2O [11], the corresponding deuterated enones **47** and **48** were obtained stereospecifically (> 95% D_1 by MS and 360-MHz ^{1}H-NMR). The results demonstrate the reversal of the regioselectivity of the electrophilic additions of the bicyclic olefins when going from the β,γ-unsaturated ketones **5**, **6** to their synthetic precursors, the chlorocarbonitriles **12**, and **13** or cyano acetates **14**.

In contrast with the high regioselectivities observed with the electrophilic additions of *Scheme 1*, the reactions of PhSeCl, PhSeBr, $NO_2C_6H_4SCl$, and $(NO_2)_2C_6H_3SCl$ with 2-(bicyclo[2.2.1]hept-5-en-2-ylidene)propanedinitrile (**49**; prepared by *Knoevenagel* condensation of **5** with malonodinitrile) were not regioselective. They led to the adduct mixtures **50**/**51**, **52**/**53**, **54**/**55**, and **56**/**57**, respectively *(Scheme 2)*. The product ratios

Scheme 2



49

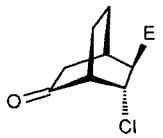
50 E = PhSe, X = Cl	(68:32)	**51** E = PhSe, X = Cl
52 E = PhSe, X = Br	(65:35)	**53** E = PhSe, X = Br
54 E = 2-$NO_2C_6H_3S$, X = Cl	(55:45)	**55** E = 2-$NO_2C_6H_4S$, X = Cl
55 E = 2,4-$(NO_2)_2C_6H_3S$, X = Cl	(58:42)	**57** E = 2,4-$(NO_2)_2C_6H_3S$, X = Cl

were determined by 360-MHz ^{1}H-NMR of the crude reaction mixtures. No other products could be detected. Although the carbonyl and dicyanomethylidene group have been considered to have very similar substituent effects when directly attached to a π system [12] [13] ($-I$, $-M$ effects), they behave quite differently when homoconjugated with the endocyclic double bond of bicyclo[2.2.1]hept-2-ene.

The structures of the new products presented here were deduced from their elemental analysis and their spectral data (see *Exper. Part*). Signal attributions in the 360-MHz ^{1}H-NMR spectra were based on double-irradiation experiments and measurements of nuclear *Overhauser* effects (NOE's). The *trans* relationship between the E and X groups in the adducts was expected for reactions of PhSeCl, PhSeBr, $NO_2C_6H_4SCl$, and $(NO_2)_2C_6H_3SCl$ with bicyclic olefins [7] [8]. The distinction between *exo* and *endo* protons[2]) at C(5) and C(6) in the 2-functionalized bicyclo[2.2.1]heptanes **20**–**24**, **26**, **31**, **32**, **35**–**38**, and **50**–**57** was established by their vicinal coupling constants with the adjacent bridgehead protons H–C(4) and H–C(1), respectively [14]. Distinction between *H*–C–X (X = Cl, Br) and *H*–C–E (E = SePh, SAr) signals was made easily on comparing the NOE's observed for these signals by irradiating the aromatic-proton signals of the PhSe and ArS substituents: significantly larger NOE's were observed for the *H*–C–E than for the *H*–C–X signals.

The regioselectivity of the additions of PhSeX to enones **5** and **6** was confirmed by the oxidative elimination of the PhSe substituent which gave the substituted enones **41**–**45**. The regioselectivity of the additions of PhSeX to the cyano acetate **14** was confirmed also by the oxidative eliminations of the PhSe substituent which gave exclusively the substi-

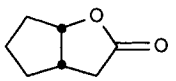
tuted enones **39** and **40**, regioisomeric with **41** and **42**, respectively. The 360-MHz ^{1}H-NMR spectra of **39–45** allowed unambiguous attribution of their structures. Further confirmations were given by the reduction of the bromoenones **40** and **42** into the deuterated enones **47** and **48**, respectively. Interestingly, *Adam* and coworkers reported recently that bicyclo[2.2.2]oct-5-en-2-one (**6**) added to *p*-toluenesulfenyl chloride to give adduct **58** as major product; oxidation of **58** with 3-chloroperbenzoic acid afforded the sulfoxide **59** whose structure was established rigorously by means of single-crystal X-ray crystallography [15]. This result also confirms our proposed structures and our ^{1}H-NMR analyses.



58 E = 4-MeC$_6$H$_4$S
59 E = 4-MeC$_6$H$_4$SO

60

61



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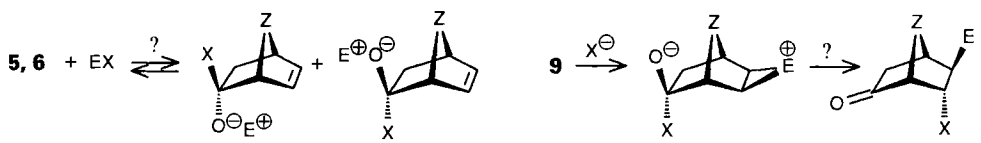
The high regioselectivity of the additions of enones **5** and **6** to the soft electrophiles PhSeX, $NO_2C_6H_4SCl$, and $(NO_2)_2C_6H_3SCl$ contrasts with the lack of regioselectivity reported by *Krieger* [16] for the H_2SO_4-catalyzed addition of AcOH to bicyclo[2.2.1]hept-5-en-2-one (**5**). Indeed, in the latter case, the reaction yielded mostly polymeric material and less than 16% of volatile, neutral adducts **60** and **61** in *ca.* equal amounts [16]. Unless very strong acids such as CF_3SO_3H [17] or HSO_3F [18] are used as catalysts, acids such as HCl, HBr, H_2SO_4, or CH_3SO_3H in AcOH lead to additions following a concerted Ad_E-3 type of mechanism [19], thus avoiding the formation of cationic intermediates of the type generally involved in conditions of halide and ester solvolyses or in conditions of the additions of PhSeX, $NO_2C_6H_4SCl$, and $(NO_2)_2C_6H_3SCl$ to olefins. We thus have investigated the AcOH addition to **5** catalyzed by CF_3SO_3H and HSO_3F. As in the case of the H_2SO_4-catalyzed addition [16], the reactions were slow (3–4 h, 110–120°) yielding mostly polymers[3]). Careful analysis of the crude reaction mixtures by 360-MHz ^{1}H-NMR showed, however, that lactone **62** was the major compound initially formed, but it decomposed more rapidly than acetate **60** [20], a minor compound formed competitively under our strongly acidic conditions. Lactone **62** has been prepared independently by oxidation of **5** with peracetic acid, followed by catalytical hydrogenation [21].

Discussion. – The high *exo*-face selectivity of the electrophilic additions of the C=C bond in bicyclo[2.2.1]hept-5-en-2-one (**5**), in its synthetic precursors **12** and **14**, and in derivative **49** was expected [23]. The possibility to influence the regioselectivity of the electrophilic addition of 2-functionalized bicyclo[2.2.*n*]alk-5-enes by the substituents at C(2) was suggested by several reports [7] [24]. The relatively high regioselectivity of additions **5** + EX → **20–24** is in agreement with our predictions based on MO calculations [4] [5]. Obviously, this agreement alone does not prove that the carbonyl group in **5** and **6** acts as an electron-donating rather than an electron-withdrawing group. Nevertheless and as we shall see, the latter interpretation is the most reasonable that we feel can be

[3]) When **5** was dissolved at −90° in HSO_3F/SO_2ClF, only the corresponding protonated ketone was formed; no adducts of HSO_3F could be observed between −80 and 50° [22].

adopted at this moment. One could invoke the hypothesis that the electrophilic agents EX add first to the carbonyl group of **5** and **6** to give adducts of type **63** or/and **64** in a reversible fashion. Then **63** or/and **64** would add a second equiv. of EX onto the endocyclic C=C bond. The regioselectivity of the latter reaction being opposite to that observed for the additions of **12**–**14** to PhSeX would imply that the alcoholate functions in **63** and **64** act as electron-donating remote substituents, capable of overwhelming the effect of the bulk of the substituents at C(2) which is expected to lead to the opposite regioselectivity then that observed for reactions **5** or **6** + EX. This hypothesis appears unlikely as the regioselectivity was the same in $CHCl_3$ (non-polar, non-nucleophilic) or CH_3CN (polar, non-nucleophilic) and AcOH (polar, nucleophilic solvent [25]).



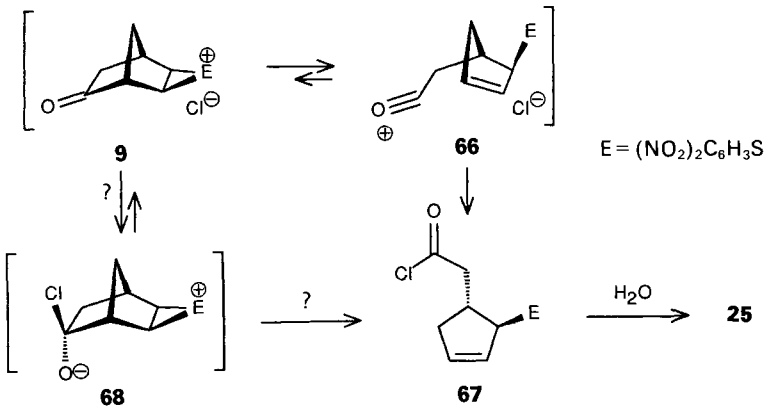
63 **64** **65** **11**

Another hypothesis would be to assume that the counter-ions X^- add to the carbonyl group of intermediates **9** to give the corresponding zwitterions **65**. The latter would then give the observed adducts following facile 1,3-shifts of type **65** → **11**. The fact that the same regioselectivity was observed for both the *exo* and *endo* mode of electrophilic additions[2]) of enone **6** militates against this interpretation.

Steric hindrance to the approach of X^- has been invoked to interprete the regioselectivity of the addition of arenesulfenyl chlorides to bicyclo[3.2.0]hept-2-en-6-ones [26], the CH_2 group being assumed to be more bulky than the CO function. If such a hypothesis should be retained in the case of reactions **5** + EX → **20**–**24** and **6** + PhSeX → **27**, and **29** (*exo* mode of electrophilic attack), it is not acceptable for **6** + PhSeX → **28** and **30** (*endo* mode of attack). Furthermore, if a steric effect should dominate the regioselectivity of the reactions of **5** and **6**, the same high regioselectivity should be observed for the electrophilic additions of the dicyanomethylidene derivative **49**. This was not the case.

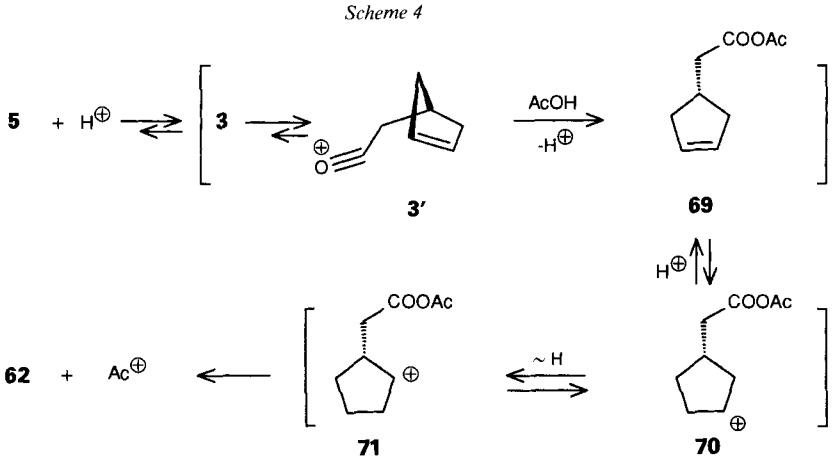
The observation of product **25** in the addition of $(NO_2)_2C_6H_3SCl$ to **5** can be interpreted by invoking the formation of the acylium-ion intermediate **66** resulting from σ(C(1), C(2)) bond cleavage in intermediate **9** (Z = CH_2; *Scheme 3*). The acylium ion **66** is then quenched by the counter-ion Cl^- to give product **67**, consistently with the 360-MHz ^{1}H-NMR spectra of the crude reaction mixture. Workup with H_2O decomposes the acyl chloride **67** to give the corresponding acid **25**. Another interpretation would be to invoke the addition of Cl^- to the carbonyl group of the cationic intermediate **9** affording zwitterion **68**. The latter could undergo a *Grob* fragmentation with production of the acyl chloride **67**. Intermediate **68** could also be formed by electrophilic attack of the hypothetical intermediate **63** (Z = CH_2, X = Cl). However, the solvent effect observed on the proportion of products **24** and **25** arising from reaction of **5** with $(NO_2)_2C_6H_3SCl$ was not consistent with the intermediacy of **68**. Indeed, the latter should be favoured in non-ionizing solvent such as $CHCl_3$ on one hand and disfavoured in an ionizing solvent such AcOH and in the presence of ClO_4^- ions on the other hand. We have found that

Scheme 3



$5 + (NO_2)_2C_6H_3SCl \rightarrow 25$ was the most competitive with $5 + (NO_2)_2C_6H_3SCl \rightarrow 24$ in AcOH containing $LiClO_4$, an observation which is not consistent with mechanism $9 \rightarrow 68 \rightarrow 67$. Furthermore, products of $\sigma(C(1), C(2))$ bond cleavage have been observed only with the 'hardest' electrophilic agents ($(NO_2)_2C_6H_3S^+$, H^+). This fact is consistent with mechanism $9 \rightarrow 66 \rightarrow 67$ rather than with mechanism $9 \rightarrow 68 \rightarrow 67$. If intermediate **68** should be formed with $(NO_2)_2C_6H_3SCl$, similar intermediates should also exist with the softer electrophiles $NO_2C_6H_4SCl$ and PhSeX. The higher the ionizing power of the medium and the higher the electron demand of the electrophile, the more facile is the bond cleavage of type $9 \rightarrow 66$. This relates to the *Grob* fragmentation [27] and the frangomeric effect [28] which can be interpreted with limiting structures $9 \leftrightarrow 10$ ($Z = CH_2$) $\leftrightarrow 66$. This hyperconjugative interaction [29] is proposed as a possible mechanism. It implies that the carbonyl group can act as an electron-donating homoconjugated substituent when the electron demand is sufficiently large. The same mechanism is believed to intervene in making acyl-group migrations in *Wagner-Meerwein* rearrangements to be more facile than alkyl-group migrations [30].

Scheme 4



This hyperconjugative interaction can also be invoked to interpret the protic acid promoted rearrangement of bicyclo[2.2.1]hept-5-en-2-one (**5**) into the bicyclic lactone **62**, the major product formed initially on treating **5** with AcOH and HSO_3F or CF_3SO_3H *(Scheme 4)*. From our MO calculations [4] [5], protonation of the C=C bond of **5** is expected to yield preferentially 6-oxobicyclo[2.2.1]hept-2-yl cation (**3**). In absence of a good nucleophile, the latter undergoes σ(C(1), C(2)) bond cleavage giving the acylium ion **3′** which reacts then with AcOH and affords the mixed anhydride **69**. Under the strongly acidic conditions used for that reaction, protonation of the C=C bond of **69** occurs and gives the cyclopentyl-cation intermediate **70** *(Scheme 4)*. A nearly degenerate 1,2-hydride shift leads to the isomeric cation **71** which is then quenched internally by the carboxylic function and gives the observed lactone **62** and acetyl cation.

The additions of bicyclo[2.2.2]oct-5-en-2-one (**6**) to PhSeX were significantly slower than those of bicyclo[2.2.1]hept-5-en-2-one (**5**). This observation was consistent also with the hypothesis of the carbonyl group acting as an electron-donating, remote substituent because of the hyperconjugative interaction of type **3**↔**3′**. The latter is expected to be more important in cationic intermediates **9** derived from **5** than from **6** because of a more favourable overlap between the σ(C(1), C(2)) bond and the forming empty p orbital at C(6) (see the *Fig.*) in bicyclo[2.2.1]heptyl than in bicyclo[2.2.2]octyl structures (smaller bond angle between C(2), C(1), and C(6) in the former than in the alter systems [31]). Alternatively, the better reactivity of bicyclo[2.2.1]hept-2-ene derivatives compared with that of corresponding bicyclo[2.2.2]oct-2-ene derivatives might be attributed to the non-planarity of the double bond in the former systems [31b].

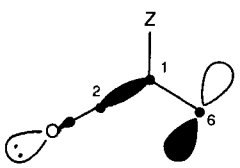


Figure. *Representation of the n(CO), σ(C(1),C(2)), and the empty p orbital at C(6)*

The additions of PhSeCl to the chlorocarbonitriles **12** and **13** were much slower than reactions **5** + PhSeCl and **6** + PhSeCl, respectively. This is consistent with our hypothesis of the carbonyl function in **5** and **6** acting as electron-donating substituent (polarizability effect overwhelming the field effect), whereas the Cl and CN moieties in **12** and **13** act as electron-withdrawing groups and thus retard the electrophilic additions because of their field effects (permanent dipole effect overwhelming the polarizability effect [32]). The opposite regioselectivity of additions of **12**, **13**, and **14** compared with that of additions of the corresponding enones **5** and **6** is consistent with the above hypothesis. Nevertheless, one cannot exclude that a steric effect of the *endo* substituents at C(2) in **12**–**14** also controls the regioselectivity of the reactions, at least in the case of the *exo* mode of electrophilic attack at C(5)=C(6).

The lack of regioselectivity of the addition of 2-(bicyclo[2.2.1]hept-5-en-2-ylidene)-propanedinitrile (**49**) can be interpreted in terms of a competing electron-withdrawing field effect ($-M$, $-I$) and a possible homoconjugative, electron-donating effect. The $C{=}C(CN)_2$ group does not behave like the C=O group as a homoconjugated function because it lacks the n electron pairs which interact with the σ(C(1), C(2)) 'relay' bond.

Conclusion. – Electrophilic reagents add to the endocyclic double bond of 2-functionalized bicyclo[2.2.*n*]alk-5-ene derivatives regioselectively. The sense of the regioselectivity can be controlled by the nature of the substituents at C(2), under conditions of kinetic control. While bulky or electron-withdrawing substituents at C(2) (*e.g.* CN + Cl or CN + OAc) lead to adducts in which the electrophile E^+ is attached at C(6) and the counter-ion X^- at C(5), a CO function at C(2) leads to adducts with opposite regioselectivity in which E is attached at C(5) and X at C(6). Contrary to a carbonyl group, the dicyanomethylidene moiety at C(2) does not induce good regioselectivities. The results are consistent with predictions based on MO calculations [4] [5] suggesting that a carbonyl function homoconjugated with an electron-deficient centre can behave as an electron-donating, remote substituent because of favourable $n(CO) \leftrightarrow \sigma(C(1), C(2)) \leftrightarrow p(C(6))$ hyperconjugative interaction. This phenomenon is related to the overlapping of the n(CO) orbital with the π orbital of the ground state of the C=C bond in non-planar β,γ-unsaturated ketones, invoked already in 1959 by *Labhart* and *Wagnière* [33] to interpret the unusual strength of their $n \rightarrow \pi^*$ transitions. It is believed also to influence the chiroptical properties [34] and radical-cation states of β,γ-unsaturated ketones [29b].

We are grateful to *F. Hoffmann-La Roche & Co. AG,* Basel, the *Fonds Herbette,* Lausanne, and the *Swiss National Science Foundation* for financial support. We thank also Miss *F. Berchier, A. Lettieri, M. Leuppi,* and *N. Larbi* for their technical assistance.

Experimental Part

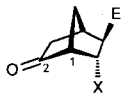
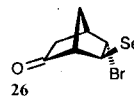
General. See [35]. Several experiments reported in the text were run in sealed NMR tubes and the mixtures directly analyzed by 360-MHz ^{1}H-NMR; they will not be described here. Only the procedures allowing the isolation of new compounds will be given. None of the procedures reported have been optimized. ^{1}H-NMR and ^{13}C-NMR data are given in *Tables 1* and *2*.

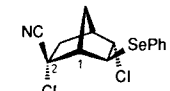
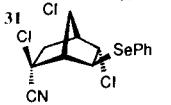
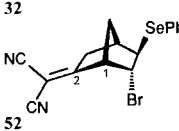
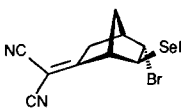
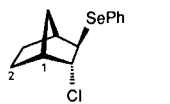
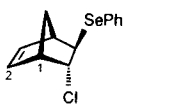
5-exo-*Benzeneselenenyl-6*-endo-*chlorobicyclo[2.2.1]heptan-2-one* (**20**). A soln. of PhSeCl (3.55 g, 18.5 mmol) in $CHCl_3$ (5 ml) was added portionwise to a soln. of **5** (prepared according to [36]; 2 g, 18.5 mmol) in $CHCl_3$ (10 ml). Discolouration was instantaneous at 20°. After stirring for 5–10 min at 20°, the soln. was evaporated and the residue recrystallized from petroleum ether/Et_2O 1:1 giving 5.15 g (93%), colourless crystals. M.p. 64–65°. UV (95% EtOH): 217 (10300), 241 (3510), 268 (2400). UV (dioxane): 220 (13400), 240 (6925), 266 (3250), 271 (3100). IR (KBr): 2980, 1760, 1580, 1480, 1440, 1290, 1160, 1140, 1085, 1070, 1020, 1000, 980, 940, 920, 820, 770, 750. ^{1}H-NMR: *Table 1.* ^{13}C-NMR: *Table 2.* MS (70 eV): 302 (3), 301 (2), 300 (7), 299 (1), 298 (4), 297 (1), 296 (2), 178 (2), 158 (9), 157 (7), 156 (5), 154 (5.5), 153 (3.3), 152 (2), 149 (9), 143 (4), 107 (17), 102 (4), 79 (100), 77 (95). Anal. calc. for $C_{13}H_{13}ClOSe$ (299.66): C 52.11, H 4.37; found: C 51.93, H 4.46.

5-exo-*Benzeneselenenyl-6*-endo-*bromobicyclo[2.2.1]heptan-2-one* (**21**). A soln. of PhSeBr (4.85 g, 18.5 mmol) in $CHCl_3$ (5 ml) was added portionwise to a soln. of **5** (2 g, 18.5 mmol) in $CHCl_3$ (10 ml). The purplish soln. was discoloured instantaneously. After stirring for 5–10 min at 20°, the soln. was evaporated and the residue recrystallized from petroleum Et_2O/Et_2O 1:1: 6.03 g (95%), colourless crystals. M.p. 65–66°. UV (EtOH): 218 (11150), 240 (3830), 275 (1930). UV (dioxane): 218 (13150), 247 (5100), 275 (5000). IR (KBr): 2980, 1750, 1570, 1480, 1440, 1390, 1300, 1285, 1260, 1220, 1210, 1180, 1160, 1145, 1130, 1080, 1060, 1015, 980, 955, 930, 910, 870, 740, 690. ^{1}H-NMR: *Table 1.* ^{13}C-NMR: *Table 2.* MS (70 eV): 348 (1.1), 347 (0.9), 346 (5.3), 345 (1.2), 344 (6), 343 (1.3), 342 (3.3), 341 (0.7), 340 (0.9), 266 (1), 223 (2), 189 (3), 187 (4), 158 (10), 157 (12), 156 (6), 155 (8), 154 (5), 153 (3), 147 (5), 145 (6), 107 (21), 97 (4), 95 (3), 93 (3), 91 (3), 79 (100), 77 (40), 66 (23). Anal. calc. for $C_{13}H_{13}BrOSe$ (344.11): C 45.38, H 3.81; found: C 45.48, H 3.92.

6-endo-*Acetoxy-5*-exo-*benzeneselenenylbicyclo[2.2.1]heptan-2-one* (= *3*-exo-*Benzeneselenenyl-6-oxobicyclo[2.2.1]hept-2*-endo-*yl Acetate;* **22**). PhSeBr (21.85 g, 92.6 mmol) was added portionwise to a soln. of AgOAc (15.46 g, 92.6 mmol) in $CHCl_3$ (100 ml). After stirring at 20° (10 min), the soln. was filtered to eliminate the AgBr formed. The filtrate was added dropwise to a soln. of **5** (5 g, 92.6 mmoles) in $CHCl_3$ (20 ml). After stirring for 60 h under reflux, the soln. was evaporated and the residue purified by column chromatography on silica gel (CH_2Cl_2).

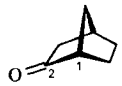
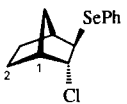
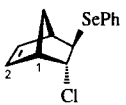
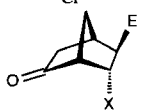
Table 1. *^{1}H-NMR* (360 MHz) *Data of* **20–24**, **26–28**, **31**, **32**, **52**, **53** *and of the PhSeCl Adducts to Bicyclo[2.2.1]hept-2-ene and Bicyclo[2.2.2]hepta-2,5-diene.* δ(H) in ppm in $CDCl_3$, internal ref. TMS; attributions confirmed by selective double irradiation experiments; J(H, H) in Hz, *x = exo, n = endo, s = syn, a = anti.*

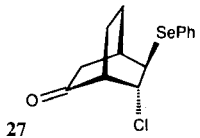
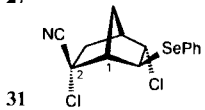
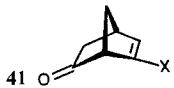
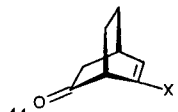
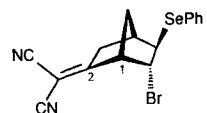
	H–C(1)	H_{exo}–C(3)	H_{endo}–C(3)	H–C(4)	H–C(5)	H–C(6)	H_{syn}–C(7)	H_{anti}–C(7)	arom. H	H_{syn}–C(8)	H_{anti}–C(8)
	2.87 (*dm*) $J(1,6) = 4.8$	2.3 (*dd*) $J_{gem} = 18.4$	2.05 (*dd*) $J(3n,7a) = 3.5$	2.74 (*dm*) $J(4,3x) = 7.8$	3.45 (*dd*) $J(5,7s) = 3.0$	4.3 (*dd*) $J(5,6) = 3.2$	1.87 (*ddm*) $J_{gem} = 11.4$	2.21 (*ddm*)	7.62; 7.32		
20 E = PhSe, X = Cl											
21 E = PhSe, X = Br	2.87 (*dm*) $J(1,6) = 4.8$	2.3 (*dd*) $J_{gem} = 18.4$	2.06 (*dd*) $J(3n,7a) = 3.5$	2.74 (*dm*) $J(4,3x) = 4.8$	3.57 (*dd*) $J(5,7s) = 3.0$	4.26 (*dd*) $J(5,6) = 3.2$	1.84 (*ddm*) $J_{gem} = 11.4$	2.20 (*ddm*)	7.62; 7.30		
23 E = $NO_2C_6H_4S$, X = Cl	2.97 (*dm*) $J(1,6) = 4.5$	2.44 (*dd*) $J_{gem} = 18.1$	2.24 (*dd*) $J(3n,7a) = 3.2$	2.83 (*dm*) $J(4,3x) = 4.5$	3.6 (*dd*) $J(5,7s) = 2.8$	4.28 (*dd*) $J(5,6) = 3.2$	1.95 (*ddm*) $J_{gem} = 14.0$	2.33 (*ddm*)	7.62; 8.2; 7.4		
24 E = $(NO_2)_2C_6H_3S$, X = Cl	2.88 (*dm*) $J(1,6) = 4.8$	2.43 (*dd*) $J_{gem} = 18.3$	2.28 (*dd*) $J(3n,7a) = 3.5$	2.82 (*dm*) $J(4,3x) = 4.8$	3.8 (*dd*) $J(5,7s) = 3.0$	4.44 (*dd*) $J(5,6) = 3.3$	2.0 (*ddm*) $J_{gem} = 12.4$	2.14 (*ddm*)	7.85; 8.01; 8.42[a])		
 **26**	2.93 (*m*)	2.18 (*m*) $J_{gem} = 18$	2.73 (*dd*) $J(3n,7a) = 3.5$	2.68 (*dm*) $J(4,5x) = 4.5$	4.98 (*ddd*) $J(5,3x) = 1.8$	3.44 (*dd*) $J(5,6) = 4.0$	1.95 (*dm*) $J(6,7s) = 2.8$	2.20 (*m*)	7.61; 7.32		
 **27**	2.3 (*dt*) $J(1,6) = 3.4$	1.88 (*dd*) $J_{gem} = 18$ $J(3x,4) = 2.5$	1.99 (*ddd*) $J(3n,4) = 2.0$	1.78 (*m*) $J(4,5) = 2.5$	3.62 (*dd*) $J(5,8s) = 1.5$	3.93 (*dd*) $J(5,6) = 4.0$	1.3 (*m*) $J(1,7) = 2.0$	1.3 (*m*) $J(1,7) = 2.0$	7.5; 7.0	0.85 (*m*) $J(5,8s) = 1.5$	1.73 (*m*)[b]) $J(3n,8a) = 3.0$
 **28**	2.52 (*dt*) $J(1,6) = 3.4$	2.14 (*ddd*) $J_{gem} = 18$ $J(3x,4) = 2.6$	2.69 (*ddd*) $J_{gem} = 18$ $J(3n,8a) = 2.4$	2.23 (*ddd*) $J(4,5) = 2.8$ $J(4,3n) = 2.2$	3.62 (*ddd*) $J(5,6) = 4.2$ $J(5,3x) = 1.0$	4.17 (*ddd*) $J(6,7s) = 1.5$	1.74	2.26 $J(1,7a) = 2.0$	7.57; 7.28	1.74	1.74

 **31**	2.5 (br. *s*)	1.8 (*ddd*) $J_{gem} = 15.2$	2.2 (*dd*) $J(3n,7a) = 3.0$	1.6 (*ddm*) $J(4,5x) = 4.5$	3.7 (*ddd*) $J(5,3x) = 1.8$	3.8 (*dd*) $J(5,6) = 4.0$	1.4 (*m*) $J(6,7s) = 2.8$	1.4 (*m*)	7.4; 6.9[b]
 **32**	2.67 (br. *s*)	*ca.* 2.45 (*m*)	*ca.* 2.45 (*m*)	2.56 (br. *s*) $J(4,5) \approx 4.5$	4.1 (*ddd*) $J(5,7s) \approx 1.5$	3.53 (*dd*) $J(5,6) = 4.0$	2.01 (*m*) $J(6,7s) = 2.5$	2.01 (*m*)	7.55; 7.3
 **52**	3.67 (*dm*) $J(1,6) = 4.6$	2.74 (*dd*) $J_{gem} = 20.0$	2.57 (*dd*) $J(3n,7a) = 3.4$	2.71 (*dm*) $J(4,3x) = 4.8$	3.28 (*dd*) $J(5,7s) = 3.1$	4.31 (*dd*) $J(5,6) = 4.1$	1.74 (*ddm*) $J_{gem} = 11.8$	2.2 (*ddm*)	7.6; 7.34
 **53**	3.4 (br. *s*)	2.6 (*ddd*) $J_{gem} = 18$	3.22 (*dd*) $J(3n,7a) = 3.5$	2.86 (*ddm*) $J(4,3x) = 4.8$	4.1 (*ddd*) $J(4,5) = 4.8$ $J(5,3x) = 1.8$	3.19 (*dd*) $J(6,7s) = 3.2$ $J(5,6) = 4.0$	1.8 (*dd*) $J_{gem} = 11.8$	2.2 (*dd*)	7.6; 7.36
	2.43 $J(1,6) = 3.2$	1.3–2.1 (CH_2(2),CH_2(3))		2.37 $J(4,5) = 0.0$	3.06 $J(5,7s) = 2.8$	4.15 $J(5,6) = 4.0$ $J(6,2x) = 0.8$	1.57	1.57[c]	
	3.2 $J(1,6) = 3.2$	6.24, 6.36 (H–C(2), H–C(3)) $J(2,3) = 6.5$		3.1 $J(4,5) = 0.3$	3.05 $J(5,7s) = 3.6$	4.3 $J(5,6) = 3.6$	1.76	1.76[d]	

[a]) In CD_3CN. [b]) In C_6D_6. [c]) See [37], arbitrary numbering. [d]) See [38], arbitrary numbering.

Table 2. *^{13}C-NMR Data of Bicyclo[2.2.1]heptan-2-one* [39], *Bicyclo[2.2.1]hept-5-en-2-one* [40] (**5**), *and Bicyclo[2.2.2]oct-5-en-2-one* [41] (**6**) *of Adducts of PhSeCl to Bicyclo[2.2.1]hept-2-ene* [37] *and Bicyclo[2.2.1]hepta-2,5-diene* [38], *and of* **20**–**24**, **27**, **31**, **34**, **40**–**42**, **44**, **45**, *and* **52**. δ(C) in ppm, $^1J \pm 1$ Hz in parentheses; solvent $CDCl_3$, internal ref. TMS; attributions confirmed by 'off-resonance' ^{1}H-decoupling experiments [42].

		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(1′)	C(2′)	C(3′)	C(4′)	C(5′)	C(6′)
		49.4	216.1	44.6	35.1	27.0	23.6	37.2							
5		55.8	212.8	36.7	40.0	143.0	130.8	50.8							
6		48.6	212.4	40.4	32.4	136.8	128.3	24.3	22.5						
		44.5	21.5	29.6	44.3	50.6	67.9	36.2[a])							
		49.6	134.9	137.0	49.5	50.6	64.9	46.3[a])							
20		57.2 (153)	209.3 –	44.5 (136)	42.1 (148)	51.9 (156)	60.4 (164)	35.4 (140)		128.4 –	134.0 (164)	129.1 (162)	127.8 (162)	129.1 (162)	134.0 (164)
21		57.4 (154)	209.4 –	44.2 (134)	42.5 (148)	52.5 (155)	48.7 (168)	35.5 (140)		128.3 –	134.3 (165)	129.1 (162)	128.0 (168)	129.1 (162)	134.3 (165)
23		56.9 (154)	208.8 –	43.7 (135)	41.2 (148)	55.8 (158)	59.7 (162)	35.3 (138)		134.5 –	146.4 –	125.7 (164)	128.5 (164)	133.7 (164)	126.0 (164)
24		57.1 –	209.0 –	43.5 –	41.7 –	55.5 –	59.5 –	35.0 –		– –	– –	121.4 –	– –	127.5 –	129.4[b])

 **27**	61.4 (150)	209.4 –	44.5 (136)	34.0 (143)	51.0 (154)	21.8 (136)	21.8 (136)	19.3 (134)	–	134.3 (164)	129.1 (161)	128.0 (160)	129.1 (161)	134.3 (164)
 **31**	56.1 (154)	58.2 –	39.6 (140)	44.4 (152)	64.5 (164)	45.0 (154)	35.8 (138)	– –	– –	133.6 (163)	129.2 (164)	128.0 (163)	129.2 (164)	133.6[c]) (163)
34	49.5 (146)	209.7 –	39.6 (132)	41.3 (145)	137.9 –	122.7 (172)	27.1 (235)	24.7 (135)						
40	56.8 (156)	211.0 –	35.4 (135)	48.5 (150)	133.4 –	128.3 (178)	49.8 (138)							
 **41**	61.2 (158)	211.6 –	36.0 (138)	40.1 (152)	135.9 (175.0)	134.5 –	50.0 (136)							
42	62.6 (158)	211.4 –	35.7 (136)	41.4 (152)	141.0 (177)	121.1 –	50.4 (135)							
 **44**	56.4 (147.5)	208.6 –	39.6 (132)	33.0 (140)	130.9 (173)	130.9 –	24.3 (132)	22.8 (132)						
45	57.8 (148)	208.4 –	39.3 (130)	34.1 (142)	135.7 (171)	117.4 –	24.0 (132)	22.8 (138)						
 **52**	54.6 (154)	183.3 –	40.3 (140)	43.5 (152)	51.3 (150)	51.2 (156)	37.6 (138)		127.7 –	134.6 (164)	129.3 (162)	128.3 (162)	129.3 (162)	134.6[d]) (164)

[a]) Arbitrary numbering. [b]) In CD_3CN. [c]) CN at 119.5 ppm. [d]) $C{=}C(CN)_2$ at 84.2, 110.8, and 110.5 ppm.

The 1st fraction contained PhSeSePh, the 2nd 10.0 g (67%) of **22** (yellow oil, after evaporation). This fraction was directly used for the preparation of **43** (see below).

6-endo-*Chloro-5*-exo-*(2-nitrobenzenesulfenyl)bicyclo[2.2.1]heptan-2-one* (**23**). A soln. of 2-nitrobenzenesulfenyl chloride ($NO_2C_6H_4SCl$; 3.51 g, 18.5 mmol) in $CHCl_3$ (5 ml) was added to a soln. of **5** (2 g, 18.5 mmol) in $CHCl_3$ (10 ml). After stirring for 36 h at 20°, the soln. was evaporated and the residue recrystallized from $CHCl_3/Et_2O$ 1:1: 5.1 g (93%), yellow crystals. M.p. 164–165°. UV (CH_3CN): 220 (7050), 244 (14280), 270 (9800), 364 (3390). UV (dioxane): 220 (6410), 246 (15450), 262 (6170), 364 (3550). IR (KBr): 2960, 1750, 1590, 1560, 1510, 1450, 1405, 1335, 1300, 1250, 1245, 1195, 1140, 1100, 1080, 1050, 1040, 960, 940, 920, 885, 850, 790, 780, 730, 710. ^{1}H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. MS (70 eV): 299 (0.5), 297 (1), 262 (0.4), 198 (0.8), 156 (4), 147 (10), 107 (12), 101 (12), 91 (10), 78 (100), 76 (25). Anal. calc. for $C_{13}H_{12}ClNO_3S$ (297.76): C 52.44, H 4.06; found: C 52.34, H 4.05.

6-endo-*Chloro-5*-exo-*(2,4-dinitrobenzenesulfenyl)bicyclo[2.2.1]heptan-2-one* (**24**). A soln. of 2,4-dinitrobenzenesulfenyl chloride ($(NO_2)_2C_6H_3SCl$; 4.35 g, 18.5 mmol) was added to a soln. of **5** (2 g, 18.5 mmol) in CH_3CN (15 ml). After stirring for 36 h at 20°, the soln. was evaporated and the residue recrystallized from CH_3CN/Et_2O 1:1: 4.25 g (67%), yellow crystals. M.p. 191–192°. UV (CH_3CN): 220 (11300), 240 (sh, 8050), 270 (6770), 325 (11725). UV (dioxane): 220 (11160), 240 (sh, 8380), 270 (6785), 324 (11900). IR (KBr): 3100, 3000, 2980, 2960, 1755, 1595, 1510, 1450, 1400, 1390, 1380, 1300, 1250, 1150, 1135, 1100, 1050, 920, 890, 830, 820, 790, 770, 730. ^{1}H-NMR: *Table 1*. ^{13}C-NMR: see *Table 2*. MS (70 eV): 344 (0.5), 342 (1), 183 (1.5), 155 (4), 153 (11), 107 (19), 101 (11), 97 (11), 95 (9), 85 (15), 83 (16), 79 (100), 72 (29), 57 (54). Anal. calc. for $C_{13}H_{11}ClN_2O_5S$ (342.75): C 45.55, H 3.23; found: C 45.71, H 3.49.

*(1*RS,*2*RS)-trans-*2-[(2,4-Dinitrophenyl)thio]cyclopent-3-ene-1-acetic Acid* (**25**). The mother liquor of the above crystallization was evaporated and purified by column chromatography on silica gel (30 g, $CHCl_3$/acetone 95:5): 0.26 g (4.3%), yellow crystals, recrystallized from $CHCl_3$. M.p. 152–153°. UV (CH_3CN; insoluble in dioxane): 220 (9970), 270 (5500), 336 (10870). IR (KBr): 3100, 3000, 2940, 2910, 1710, 1595, 1510, 1440, 1425, 1410, 1330, 1300, 1260, 1240, 1130, 1090, 1040, 930, 910, 820, 725, 680. ^{1}H-NMR (360 MHz, CD_3CN): 9.05 (*d*, *J* = 2.5, 1 H), 8.4 (*dd*, *J* = 2.5, 9.0, 1 H), 7.8 (*d*, ^3J = 9.0, 1 H, 3 arom. H); 6.1 (*m*, H–C(4)); 5.84 (*m*, H–C(3)); 4.3 (*m*, ^3J(H–C(1),H–C(2)) = 3.2, ^4J(H–C(2),H–C(4)) = ^4J(H–C(2),H_a–C(5)) ≈ 2.0, H–C(2)); 2.93 (*dddd*, ^2J = 17, ^3J(H–C(1),H_a–C(5)) = 7.5, ^4J(H–C(2),H_a–C(5)) = 2.0, ^4J(H–C(2),H_a–C(5)) = 2.0, ^4J(H–C(3),H_a–C(5) ≈ 2, H_a–C(5)); 2.81 (*dtdd*, ^3J(H–C(1),H_a–C(5)) = 7.5, ^3J(H–C(1),H–C(2)) = 7.7, ^3J(H–C(1),H_s–C(5)) = 3.2, ^3J(H–C(1),H–C(2)) = 3.2, H–C(1)); 2.7, 2.65 (2*dd*, ^2J = 16.3, ^3J(H–C(2),H–C(1)) = 7.7, CH_2(2)); 2.2 (*ddm*, ^2J = 7, ^3J(H–C(1),H_s–C(5)) = 3.2, ^4J(H–C(3),H_s–C(5) = 2.0, H_s–C(5)). ^{13}C-NMR ($CDCl_3$): 176.5 (*s*, CO); 146.1 (*s*); 145.9 (*s*); 144.3 (*s*); 135.5 (*dm*, ^1J(C,H) = 170, C(3)); 128.4 (*d*, ^1J(C,H) = 168, arom. C); 127.7 (*dm*, ^1J(C,H) = 169, C(4)); 126.7 (*dd*, ^1J(C,H) = 171, ^3J(C,H) = 7, arom. C(5)); 121.5 (*dd*, ^1J(C,H) = 172, ^3J(C,H) = 7, arom. C); 56.3 (*d*, ^1J(C,H) = 151.2, C(2)); 40.53 (*d*, ^1J(C,H) = 136, C(1)); 38.3 (*t*, ^1J(C,H) = 131); 37.8 (*t*, ^1J(C,H) = 130). MS (70 eV): 323 (0.05), 280 (2.7), 265 (8.5), 256 (25), 125 (70), 79 (34), 57 (90), 44 (100). Anal. calc. for $C_{13}H_{12}N_2O_6S$ (324.31): C 48.15, H 3.73, N 8.64; found: C 47.95, H 3.69, N 8.74.

Reaction of $(NO_2)_2C_6H_3SCl$ and **5** *in AcOH in the Presence of $LiClO_4$.* To a soln. of **5** (2 g, 18.5 mmol) in AcOH (15 ml) were added successively $LiClO_4$ (3.94 g, 37 mmol) and $(NO_2)_2C_6H_3SCl$ (4.35 g, 18.5 mmol). After stirring at 20° for 36 h, the soln. was evaporated, yielding a 1:4 mixture **24**/**25**. The same products were obtained in similar proportion when the reaction was run in CD_3COOD.

Addition of PhSeCl to Bicyclo[2.2.2]oct-5-en-2-one (**6**). A soln. of PhSeCl (6.38 g, 33.3 mmol) in $CHCl_3$ (10 ml) was added to a stirred soln. of **6** [36] (4 g, 33 mmol) in $CHCl_3$ (20 ml). After stirring at 20° for 12 h, the soln. was evaporated and the residue purified by column chromatography on silica gel (AcOEt/hexane 1:2). The 1st fraction (0.9 g) contained several unidentified compounds, the 2nd one (1.5 g, 14%) **27**/**28**, and the 3rd one pure **27** (3.3 g, 32% after recrystallization from hexane/AcOEt). 360-MHz ^{1}H-NMR of the reaction mixture: **27** (< 66%), **28** (> 24%; identified by its ^{1}H-NMR, *cf. Table 1*), and unidentified compounds (< 10%).

*Data of (1*RS,*4*SR,*5*SR,*6*SR*)-5*-exo-*Benzeneselenenyl-6*-endo-*chlorobicyclo[2.2.2]octan-2-one* (**27**). Colourless crystals. M.p. 72–73°. UV (EtOH): 218 (9500), 250 (4425), 270 (3425). UV (dioxane): 220 (9125), 240 (3100), 274 (1950). IR (KBr): 2940, 2880, 1730, 1460, 1450, 1440, 1400, 1330, 1270, 1220, 1195, 1155, 1105, 1070, 1020, 1000, 965, 920, 880, 800, 770, 750. ^{1}H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. MS (70 eV): 316 (5), 315 (1.5), 314 (11), 312 (6), 311 (3), 310 (2), 160 (3), 159 (4), 158 (16), 157 (11), 156 (9), 155 (6), 154 (5), 153 (3), 115 (11), 111 (6), 93 (63), 78 (100), 77 (63). Anal. calc. for $C_{14}H_{15}ClOSe$ (313.686): C 53.60, H 4.82; found: C 53.54, H 4.82.

Addition of PhSeBr to **6**. A mixture of PhSeBr (5.9 g, 25 mmol) and **6** (3 g, 25 mmol) in $CHCl_3$ was allowed to stand at 20° for 12 h. On solvent evaporation, decomposition of the 3:1 (by 360-MHz ^{1}H-NMR) mixture **29**/**30** was observed. Thus, the above soln. in $CHCl_3$ was directly used for the oxidative elimation of the Se-containing moiety (see preparation of **45**).

*Addition of PhSeCl to 2-*exo*-Chloro- and 2-*endo*-Chlorobicyclo[2.2.1]hept-5-ene-2-carbonitriles* (**12**). A mixture of **12** (obtained by reaction of cyclopentadiene and α-chloroacrylonitrile [36]; 4:1 mixture *exo*-CN/*endo*-CN; 2 g, 13 mmol) and PhSeCl (2.5 g, 13 mmol) in $CHCl_3$ (10 ml) was stirred at 20° for 48 h. The solvent was evaporated and the residue recrystallized from $CHCl_3/Et_2O$ 1:1 yielding 3.23 g (72%) of pure, crystalline **31** and a soln. containing a 1:2.5 mixture **31**/**32**. Isolation of **32** was not attempted; its structure was deduced from the 360-MHz ^{1}H-NMR *(Table 1)* of the soln. of **31**/**32**.

*Data of 6-*exo*-Benzeneselenenyl-2-*endo*,5-*endo*-dichlorobicyclo[2.2.1]heptane-2-*exo*-carbonitrile* (**31**). Colourless crystals. M.p. 68–69°. UV (EtOH): 216 (9575), 240 (3550), 272 (3600). UV (dioxane): 216 (9900), 240 (4500), 272 (3800). IR (KBr): 3060, 2980, 2960, 2240, 1580, 1480, 1460, 1440, 1330, 1310, 1300, 1185, 1170, 1140, 1070, 1045, 1020, 990, 930, 920, 870, 820, 780, 720, 680. ^{1}H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. MS (70 eV): 349 (5), 347 (17), 345 (27), 343 (12.5), 341 (5), 310 (4), 295 (6), 293 (10), 291 (8), 158 (50), 157 (50), 156 (25), 155 (33), 154 (50), 152 (10), 151 (15), 115 (50), 79 (50), 78 (100), 65 (63), 64 (96), 51 (67). Anal. calc. for $C_{14}H_{13}Cl_2NSe$ (345.13): C 48.72, H 3.80; found: C 48.65, H 3.79.

*Addition of PhSeCl to 2-*exo*-Chloro- and 2-*endo*-Chlorobicyclo[2.2.2]oct-5-ene-2-carbonitrile* (**13**). A mixture of **13** (5.0 g, 29.8 mmol) and PhSeCl (6.6 g, 34.5 mmol) in $CHCl_3$ (30 ml) was heated under reflux for 5 d. After solvent evaporation, the crude mixture was purified by chromatography on a column of silica gel (petroleum ether/Et_2O 9:1) yielding 9.6 g (90%) of a complex mixture of stereoisomers **33**. Part of this mixture (4.0 g, 11.1 mmol) was dissolved in THF, and 30% H_2O_2 soln. (11 ml) was added at 0°. After 1 h at 0°, the soln. was stirred overnight at 20°. Then, H_2O (270 ml) was added and the soln. extracted with CH_2Cl_2 (60 ml, 5 times). The org. layer was washed with 5% Na_2CO_3 soln. (60 ml, 3 times), H_2O (60 ml), and sat. aq. NaCl soln. (60 ml, twice), dried ($MgSO_4$), and evaporated. The resulting yellow oil (2.0 g, 89%), a mixture of stereoisomers, was dissolved in DMSO (7 ml). A soln. of KOH (2 g) in H_2O (3 ml) was added dropwise. After stirring at 20° for 5 h, H_2O (33 ml) was added. The mixture was extracted with pentane (10 ml, 6 times), the org. layer washed with sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated, and the residue purified by column chromatography on silica gel (petroleum ether/Et_2O 4:1) and distilled: 750 mg (48.4%) of *5-chlorobicyclo[2.2.2]oct-5-en-2-one* (**34**), colourless oil. B.p. 80–90°/12 Torr. UV (95% EtOH): 222 (3020), 293 (194). UV (isooctane): 222 (3120), 285 (144), 296 (167), 306 (150), 317 (80). IR (film): 2960, 2900, 2880, 1730, 1610, 1150, 1090, 1030. ^{1}H-NMR (360 MHz, $CDCl_3$): 6.07 (*dd*, ^4J(H–C(4),H–C(6)) = 2.5, ^3J(H–C(1),H–C(6)) = 7.0, H–C(6)); 3.15 (*dt*, ^3J(H–C(1),H–C(6)) = 7.0, ^3J(H–C(1),H–C(7)) = 2.5, H–C(1)); 2.98 (*m*, ^4J(H–C(4),H–C(6)) = 2.5, ^3J(H_{endo}–C(3),H–C(4)) = 2.5, ^3J(H_{exo}–C(3),H–C(4)) = 3.0, ^3J(H–C(1),H–C(8)) = 2.5, H–C(4)); 2.23 (*dddd*, ^3J(H_{endo}–C(3),H–C(4)) = 2.5, ^4J(H_{endo}–C(3), H_{anti}–C(8)) = 2.2, ^2J = 18.7, H_{endo}–C(3)); 2.01 (*dd*, ^2J = 18.7, ^3J(H_{exo}–C(3),H–C(4)) = 3.0, H_{exo}–C(3)); 1.90–1.60 (*m*, CH_2(7), CH_2(8)). ^{13}C-NMR: *Table 2*. MS (70 eV): 159 (0.5), 158 (4.1), 157 (1.2), 156 (12.8), 117 (0.8), 116 (11.4), 115 (3.6), 114 (40.1), 113 (3.5), 112 (6.2), 91 (8.0), 80 (7.0), 79 (100.0), 78 (9.4), 77 (33.0), 65 (8.6), 64 (1.6), 63 (7.1), 52 (4.5), 51 (14.3), 50 (7.5). Anal. calc. for C_8H_9ClO (156.612): C 61.35, H 5.79; found: C 62.20, H 5.99.

*Additions of PhSeX to 2-*exo*-Cyano- and 2-*endo*-Cyanobicyclo[2.2.1]hept-5-en-2-yl Acetates* (**14**). *6-*exo*-Benzeneselenenyl-5-*endo*-bromobicyclo[2.2.1]heptan-2-one* (**26**). A mixture of **14** (1.9 g, 11 mmol) and PhSeBr (2.6 g, 11 mmol) in $CHCl_3$ (200 ml) was heated under reflux for 2 d. After solvent evaporation, the crude adduct was purified by chromatography on a column of silica gel (CH_2Cl_2), yielding 2.2 g (48%) of **36**, colourless oil. A 30% soln. of MeONa in MeOH (0.7 ml) was added to a stirred soln. of **36** (2.2 g, 5.3 mmol) in MeOH (7 ml). Formaline (40% CH_2O in H_2O; 5 ml) was added. After staying at 20° for 2 h, sat. aq. NaCl soln. (10 ml) and 5% aq. HCl soln. were added, and the mixture was extracted with CH_2Cl_2 (20 ml, 3 times). After drying ($MgSO_4$), the solvent was evapored and the residue purified by column chromatography on silica gel (CH_2Cl_2), yielding 1.1 g (60%), colourless oil. The product crystallized in Et_2O/hexane yielding white crystals. M.p. 61–62°. UV (95% EtOH): 202 (16000), 221 (10330), 287 (1340). UV (isooctane): 205 (10450), 220 (9110), 243 (3200), 282 (1205). IR (KBr): 2980, 2960, 2930, 1760, 1580, 1480, 1440, 1400, 1310, 1290, 1090, 1070, 1020, 990, 960, 940. ^{1}H-NMR: *Table 1*. MS (70 eV): 264 (0.2), 263 (0.4), 189 (2.7), 188 (6.1), 187 (2.0), 186 (5.1), 159 (3.0), 158 (5.6), 157 (15.7), 156 (11.0), 155 (6.7), 154 (7.4), 153 (4.0), 147 (3.3), 146 (1.7), 145 (2.9), 144 (1.5), 117 (2.4), 108 (2.8), 107 (18.6), 106 (2.5), 81 (1.1), 80 (8.8), 79 (100), 78 (11.0), 77 (41.7), 73 (3.2), 75 (2.5), 66 (20.8). Anal. calc. for $C_{13}H_{13}BrOSe$ (344.11): C 45.38, H 3.81; found: C 45.36, H 3.93.

5-Bromobicyclo[2.2.1]hept-5-en-2-one (**40**). A soln. of 3-chloroperbenzoic acid (3-$ClC_6H_4CO_3H$; 0.59 g, 3.1 mmol) in CH_2Cl_2 (22 ml) was added slowly to a stirred soln. of **26** (1.1 g, 3.1 mmol) cooled to −70°. After stirring at −70° for 2 h, the mixture was allowed to warm to 20° within *ca.* 1 h. The mixture was washed successively with sat. aq. $NaHCO_3$ soln. (10 ml, 3 times), sat. aq. NaCl soln. (10 ml, twice), and H_2O (10 ml, twice). After drying ($MgSO_4$) and solvent evaporation (with reflux), the residue was purified by column chromatography on silica gel (CH_2Cl_2). The crude **40** was distilled (b.p. 120°/14 Torr): 250 mg (43%), colourless oil. UV (isooctane): 220 (3710),

286 (281), 296 (382), 307 (423), 320 (272). IR (CH_2Cl_2): 3020, 2980, 2960, 2890, 1750, 1580, 1420, 1300, 1160, 1130, 1120, 1080, 1040, 970, 940, 820, 640. ^{1}H-NMR (360 MHz, C_6D_6): 5.80 (*dddd*, ^3J(H–C(1),H–C(6)) = 4.0, ^4J(H–C(4),H–C(6)) = 1.2, ^5J(H_{exo}–C(3),H–C(6)) = 1.0, ^4J(H_{syn}–C(7),H–C(6)) = 1.0, H–C(6)); 2.77 (*dm*, ^3J(H–C(6),H–C(1)) = 4.0, ^3J(H–C(7),H–C(6)) = 2.5, H–C(1)); 2.66 (*ddm*, ^3J(H_{exo}–C(3),H–C(4)) = 3.6, ^3J(H–C(7),H–C(4)) = 2.5, ^3J(H_{endo}–C(3),H–C(4)) = 0.5, H–C(4)); 1.89 (*m*, ^2J = 10.0, H_{anti}–C(7)); 1.85 (*dm*, ^2J = 17.0, H_{endo}–C(3)); 1.60 (*dm*, H_{endo}–C(3)); 1.35 (*dm*, H_{syn}–C(7)). ^{13}C-NMR: *Table 2*. Anal. calc. for C_7H_7BrO (187.042): C 44.95, H 3.77; found: C 44.99, H 3.81.

*6-*exo*-Benzeneselenenyl-5-*endo*-chlorobicyclo[2.2.1]heptan-2-one* (**38**). As for **14** → **36** → **26**, with **14** (1.9 g, 1.1 mmol), PhSeCl (2 g, 11 mmol), and $CHCl_3$ (200 ml): 3.3 g (81%) of **38**, colourless oil. Then with 30% soln. of MeONa in MeOH (1.16 ml), **38** (3.3 g, 9 mmol) in MeOH (4 ml), and formaline (40% CH_2O in H_2O; 8 ml): 1.7 g (63%), colourless oil. The product crystallized in Et_2O/hexane yielding white crystals. M.p. 26–27°. UV (95% EtOH): 203 (16800), 220 (11740), 243 (4360), 287 (1840). UV (isooctane): 205 (9150), 220 (7580), 242 (2880), 281 (1100). IR (KBr): 2980, 2960, 2920, 2880, 1760, 1580, 1480, 1440, 1400, 1390, 1300, 1200, 1160, 1150, 1090, 1070, 1020, 990, 960, 940. ^{1}H-NMR (80 MHz, $CDCl_3$): 7.7–7.3 (*m*, 5 arom. H); 4.4 (*ddd*, ^3J(H–C(4),H–C(5)) = 4.0, ^3J(H–C(6),H–C(5)) = 4.0, ^4J(H_{exo}–C(3),H–C(5)) = 1.5, H–C(5)); 3.3 (*dd*, ^3J(H_{syn}–C(7),H–C(6)) = 2.8, H–C(6)); 3.0–1.5 (*m*, H–C(1), H–C(4), H_{exo}–C(3), H_{endo}–C(3), H_{syn}–C(7), H_{anti}–C(7)). MS (70 eV): 248 (0.2), 240 (0.2), 159 (1.6), 158 (5.5), 157 (12.5), 156 (10.8), 155 (6.4), 154 (5.8), 153 (3.6), 144 (3.3), 143 (11.1), 142 (4.9), 117 (3.8), 116 (1.1), 115 (5.4), 114 (1.4), 108 (1.7), 107 (18.0), 106 (3.1), 103 (3.7), 102 (2.6), 101 (15.3), 100 (3.1), 79 (100), 78 (12.0), 77 (42.1), 76 (3.4), 65 (15.1), 52 (23.1). Anal. calc. for $C_{13}H_{13}ClOSe$ (299.66): C 52.11, H 4.37; found: C 52.02, H 4.30.

5-Chlorobicyclo[2.2.1]hept-5-en-2-one (**39**). A soln. of 3-$ClC_6H_4CO_3H$ (1.1 g, 5.7 mmol) in CH_2Cl_2 (41 ml) was added slowly to a stirred soln. of **38** (1.7 g, 5.7 mmol) in CH_2Cl_2 (41 ml). After stirring at −70° for 2 h, the mixture was allowed to warm to 20° within *ca.* 1 h and washed successively with 5% aq. $NaHCO_3$ soln. (10 ml, 3 times), sat. aq. NaCl soln. (10 ml, twice), and H_2O (10 ml, twice). After drying ($MgSO_4$), the solvent was removed by distillation under reflux. The residue was purified by column chromatography on silica gel (CH_2Cl_2) and distilled (b.p. 120°/14 Torr): 420 mg (52%), colourless oil. UV (95% EtOH): 218 (3260), 302 (360). UV (isooctane): 222 (3520), 287 (231), 296 (340), 306 (368), 320 (242). IR (film): 2980, 2940, 2880, 1740, 1560, 1410, 1290, 1250, 1110, 1040, 940, 810. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.86 (*dm*, ^3J(H–C(1),H–C(6)) = 4.0, H–C(6)); 3.18 (*m*, H–C(1),H–C(4)); 2.37 (*m*, H_{exo}–C(3)); 2.05–1.95 (*m*, H_{endo}–C(3), H_{syn}–C(7), H_{anti}–C(7)). Anal. calc. for C_7H_7ClO (142.586): C 58.97, H 4.95; found: C 58.79, H 4.99.

6-Chlorobicyclo[2.2.1]hept-5-en-2-one (**41**). To a soln. of **20** (2.5 g, 8.3 mmol) in MeOH (145 ml) at 20°, H_2O (24 ml), $NaHCO_3$ (0.84 g, 9.6 mmol), and $NaIO_4$ (4.15 g, 19.3 mmol) were added successively under vigourous stirring. After stirring at 20° for 2 h, the precipitate was filtered off and the soln. extracted with Et_2O/pentane 15:100 (100 ml). The org. extract was washed with sat. aq. $NaHCO_3$ soln. (80 ml), then with H_2O (100 ml). The aq. layers were extracted with Et_2O (50 ml, 3 times). The org. phases were dried ($MgSO_4$) and evaporated. The residue was chromatographed on a short silica-gel column (AcOEt/hexane 1:2) and distilled (b.p. 80–90°/12 Torr): 1.1 g (92%), colourless oil. UV (95% EtOH): 217 (2950), 298 (117), 304 (119). UV (isooctane): 220 (2930), 225 (2810), 288 (151), 298 (205), 309 (227), 322 (144). IR (CH_2Cl_2): 2980, 2940, 2880, 1750, 1585, 1430, 1300, 1170, 1130, 1050, 985, 880, 840, 820. ^{1}H-NMR ($CDCl_3$): 6.35 (*ddd*, ^3J(H–C(4),H–C(5)) = 2.8, ^4J(H_{exo}–C(3),H–C(5)) = 1.0, ^4J(H–C(1),H–C(5)) = 1.0, H–C(5)); 3.34 (*m*, ^3J(H–C(4),H–C(5)) = 2.8, J(H_{exo}–C(3),H–C(4)) = 3.0, H–C(4)); 2.97 (*m*, ^4J(H–C(1),H–C(5)) = 1.0, H–C(1)); 2.48 (*dm*, ^2J = 10, ^4J(H_{endo}–C(3), H_{anti}–C(7)) = 2.2, H_{anti}–C(7)); 2.05 (*m*, CH_2(3)); 2.0 (*m*, H_{syn}–C(7)); attributions in agreement with those of *Krieger et al.* for methylbicyclo[2.2.1]hept-5-en-2-ones [43], confirmed by NOE measurements. ^{13}C-NMR: *Table 2*. MS (70 eV): 145 (0.5), 144 (4.5), 143 (1.1), 142 (13) 120 (2), 115 (0.6), 113 (1), 102 (30), 101 (6), 100 (100), 79 (20), 77 (7), 66 (4), 65 (46), 64 (5), 63 (7), 62 (3). Anal. calc. for C_7H_7ClO (142.585): C 58.97, H 4.95; found: C 59.17, H 5.10.

6-Bromobicyclo[2.2.1]hept-5-en-2-one (**42**). As for **20** → **41**, with **21** (3 g, 8.7 mmol) in MeOH (155 ml), H_2O (26 ml), $NaHCO_3$ (0.88 g), and $NaIO_4$ (4.36 g, 20.3 mmol; 3 h at 20°): 1.46 g (90%), colourless oil. B.p. 80–90°/12 Torr. UV (95% EtOH): 222 (3030), 304 (260). UV (isooctane): 222 (3375), 288 (158), 300 (234), 310 (267), 324 (174). IR (CH_2Cl_2): 2980, 2940, 2880, 1750, 1730, 1575, 1420, 1300, 1160, 1130, 1125, 1090, 1035, 980, 870, 825. ^{1}H-NMR ($CDCl_3$): 6.52 (*ddd*, ^3J(H–C(4),H–C(5)) = 2.6, ^4J(H_{exo}–C(3),H–C(5)) = ^4J(H–C(1),H–C(5)) = 1.0, H–C(5)); 3.2 (*m*, ^3J(H–C(4),H–C(5)) = 2.6, ^3J(H_{exo}–C(3),H–C(4)) = 2.8, H–C(4)); 2.97 (*m*, ^3J(H–C(1),H–C(5)) = 1.0, H–C(1)); 2.4 (*dm*, ^2J = 10, J(H_{endo}–C(3), H_{anti}–C(7)) = 1.2, H_{anti}–C(7)); 1.95 (*m*, CH_2(3)); 1.90 (*m*, H_{syn}–C(7)). ^{13}C-NMR: *Table 2*. MS (70 eV): 188 (8), 186 (8), 149 (11), 146 (44), 144 (47), 86 (53), 85 (31), 84 (88), 83 (38), 81 (25), 80 (22), 78 (47), 72 (59), 70 (66), 57 (100), 55 (75). Anal. calc. for C_7H_7BrO (187.03): C 44.95, H 3.77; found: C 44.74, H 3.83.

6-Acetoxybicyclo[2.2.1]hept-5-en-2-one (= *6-Oxobicyclo[2.2.1]hept-2-en-2-yl Acetate;* **43**). A soln. of 3-$ClC_6H_4CO_3H$ (3.1 g, 16 mmol) in CH_2Cl_2 (128 ml) was added slowly to a stirred soln. of **22** (5.1 g, 16 mmol) cooled to −70° under N_2. After stirring at −70° for 2 h, the mixture was allowed to warm to 20° within *ca.* 1 h. The mixture was washed successively with sat. aq. $NaHCO_3$ soln. (150 ml, 3 times), sat. aq. NaCl soln. (120 ml, twice), and H_2O (150 ml, twice). After drying ($MgSO_4$), the mixture was heated under reflux for *ca.* 8 h. The reaction time was carefully monitored by NMR on aliquots in order to avoid unwanted derivatives of **43**. After evaporation, the mixture was purified by column chromatography on silica gel (CH_2Cl_2) and the residue distilled (b.p. 50°/5·10^{-1} Torr): 1.2 g (45.2), colourless oil. IR (CH_2Cl_2): 3000, 2960, 2940, 2900, 1780, 1760, 1640, 1610, 1380, 1310, 1200, 1180, 1120, 1110, 1010, 990, 910, 810. ^{1}H-NMR (80 MHz, $CDCl_3$): 6.0 (*dm*, ^3J(H–C(4),H–C(5)) = 4.0, H–C(5)); 3.1 (*m*, H–C(4)); 2.9 (*m*, H–C(5)); 2.4 (*dm*, ^2J = 18, H_{exo}–C(3)); 2.1 (*s*, CH_3CO); 2.0–1.7 (*m*, H_{endo}–C(3), H_{syn}–C(7), H_{anti}–C(7)). MS (70 eV): 167 (0.6), 166 (9.6), 165 (1.2), 149 (0.6), 147 (0.8), 125 (0.9), 124 (11.3), 123 (2.2), 97 (2.1), 96 (4.9), 95 (5.2), 83 (6.5), 82 (100), 81 (4.9), 56 (10.5), 55 (43.6), 54 (14.9), 53 (17.1). Anal. calc. for $C_9H_{10}O_3$ (166.178); C 65.05, H 6.07; found: C 64.96, H 5.90.

6-Chlorobicyclo[2.2.2]oct-5-en-2-one (**44**). The crude reaction mixture of **6** (4.8 g, 25 mmol) and PhSeCl (3 g, 25 mmol) in $CHCl_3$ (15 ml, 20°, 12 h) was diluted with MeOH (430 ml). Under vigourous stirring, H_2O (73 ml), $NaHCO_3$ (2.53 g, 28.9 mmol), and $NaIO_4$ (12.5 g, 58.1 mmol) were added successively. After 2 h at 20°, the precipitate was filtered off and the soln. extracted with Et_2O/pentane 15:100 (300 ml). The org. extract was washed with sat. aq. $NaHCO_3$ soln. (240 ml), then with H_2O (100 ml). The aq. phases were extracted with Et_2O (150 ml, 3 times). The org. phases were dried ($MgSO_4$) and evaporated. The residue was rapidly chromatographed on silica gel (AcOEt/hexane 1:2). The crude **44** was distilled (b.p. 140–150°/12 Torr): 3.2 g (82%), colourless oil. UV (95% EtOH): 207 (3450), 295 (119). UV (isooctane): 212 (3200), 287 (82), 298 (98), 307 (90), 320 (46). IR (CH_2Cl_2): 2960, 2920, 2880, 1730, 1620, 1470, 1450, 1410, 1130, 1210, 1180, 1150, 1100, 1080, 1040, 980, 870, 840. ^{1}H-NMR ($CDCl_3$): 6.38 (*dd*, ^4J(H–C(1),H–C(5)) = 2.0, ^3J(H–C(4),H–C(5)) = 6.7, H–C(5)); 3.24 (*dt*, ^3J(H–C(1), H–C(5)) = 2.0, ^3J(H–C(1),H–C(7)) = 2.0, H–C(1)); 3.08 (*m*, ^3J(H–C(4),H–C(5)) = 6.7, ^3J(H_{endo}–C(3), H–C(4)) = 2.2, ^3J(H_{exo}–C(3), H–C(4)) = 2.6, H–C(4)); 2.10 (*ddd*, ^3J(H_{endo}–C(3),H–C(4)) = 2.2, ^4J(H_{endo}–C(3),H_{anti}–C(8)) = 2.2, ^2J = 18.8, H_{endo}–C(3)); 2.03 (*dd*, ^2J = 18.8, ^3J(H_{exo}–C(3),H–C(4)) = 2.6, H_{exo}–C(3)); 1.8–1.95 (*m*, CH_2(7)); 1.72 (*m*, H_{syn}–C(8)); 1.61 (*m*, H_{anti}–C(8)). ^{13}C-NMR: *Table 2*. MS (70 eV): 160 (3), 158 (1.9), 157 (0.6), 156 (4.2), 117 (0.9), 116 (7.3), 115 (3), 114 (25), 113 (3), 112 (4), 100 (2), 91 (5), 85 (3), 83 (3), 80 (9.5), 79 (100), 78 (8), 77 (40), 65 (11), 63 (8), 53 (6), 52 (6), 51 (20), 50 (8), 49 (9). Anal. calc. for C_8H_9ClO (156.61): C 61.35, H 5.79; found: C 61.12, H 5.83.

6-Bromobicyclo[2.2.2]oct-5-en-2-one (**45**). The crude reaction mixture of **6** and PhSeBr (see above) was diluted in MeOH (430 ml). Successively, H_2O (73 ml), $NaHCO_3$ (2.53 g, 28.9 mmol), and $NaIO_4$ (12.5 g, 58.13 mmol) were added under vigourous stirring. After 2 h at 20°, the precipitate was filtered off and the soln. extracted with Et_2O/pentane 15:100 (300 ml). The org. phases were extracted with Et_2O (150 ml, 3 times). The org. extract was washed with sat. aq. $NaHCO_3$ soln. (240 ml), then with H_2O (100 ml). The aq. phases were dried ($MgSO_4$) and evaporated. The residue was chromatographed on a short silica-gel column (AcOEt/hexane 1:2) and purified by distillation (b.p. 140–150°/12 Torr): 4 g (80%), colourless oil. UV (95% EtOH): 206 (4000), 278 (353). UV (isooctane): 214 (3850), 290 (100), 298 (125), 309 (19), 320 (64). IR (CH_2Cl_2): 2960, 2920, 2880, 1730, 1610, 1470, 1450, 1410, 1340, 1330, 1260, 1220, 1210, 1180, 1150, 1100, 1015, 1000, 980, 870, 840. ^{1}H-NMR ($CDCl_3$): 6.64 (*dd*, ^3J(H–C(4),H–C(5)) = 7.2, ^4J(H–C(1),H–C(5)) = 2.0, H–C(5)); 3.35 (*dt*, ^3J(H–C(1),H–C(5)) ≈ ^3J(H–C(1), H–C(7)) ≈ 2, H–C(1)); 3.1 (*m*, ^3J(H–C(4),H–C(5)) = 7.2, ^3J(H_{endo}–C(3),H–C(4)) = ^3J(H_{exo}–C(3), H–C(4)) = 2.5, H–C(4)); 2.15 (*ddd*, ^3J(H_{endo}–C(3),H–C(4)) = 2.5, ^4J(H_{endo}–C(3),H_{anti}–C(8)) = 2.2, ^2J = 18.2, H_{endo}–C(3)); 2.05 (*dd*, ^2J = 18.2, ^3J(H_{exo}–C(3),H–C(4)) = 2.5, H_{exo}–C(3)); 1.9 (*m*, CH_2(7)); 1.7 (*m*, H_{syn}–C(8)); 1.6 (*m*, H_{anti}–C(8)). ^{13}C-NMR: *Table 2*. MS (70 eV): 202 (2.5), 200 (2.7), 160 (11.5), 158 (16), 92 (10), 80 (100), 78 (55), 65 (13), 63 (10), 53 (6), 52 (8), 51 (17), 50 (10). Anal. calc. for C_8H_9BrO (201.063): C 47.79, H 4.51; found: C 47.89, H 4.58.

*Mixture of 5-*exo*-Cyano- and 5-*endo*-Cyanobicyclo[2.2.1]hept-2-ene-2,5-diyl Diacetates* (**46**). PhSeBr (6.6 g, 28.2 mmol) was added portionwise to a soln. of AgOAc (9.4 g, 28.2 mmol) in $CHCl_3$ (100 ml). After stirring at 20° (10 min), the soln. was filtered to eliminate the AgBr formed. The filtrate was added dropwise to a soln. of **14** (5.0 g, 28.2 mmol) in $CHCl_3$ (20 ml). After 2 d of heating under reflux, 2 equiv. of PhSeOAc were added. After stirring for 7 d, under reflux, the soln. was evaporated and the residue purified by column chromatography on silica gel (CH_2Cl_2). The 1st fraction contained PhSeSePh, the 2nd 8.2 g (74%) of **37** (yellow oil, after evaporation). The crude **37** (5.0 g, 12.8 mmol) was then treated with 3-$ClC_6H_4COI_3H$ (2.5 g, 12.8 mmol) in CH_2Cl_2 (100 ml) as described for **22** → **43** (b.p. 50°/5·10^{-1} Torr): 1.9 g (64%) of **46**, colourless oil as a *ca.* 4:1 mixture of stereoisomers. IR (film): 2980, 2960, 1750, 1630, 1610, 1440, 1370, 1330, 1230, 1190, 1140, 1120, 1030. ^{1}H-NMR (80 MHz, $CDCl_3$) for the major isomer: 5.5 (*dm*, ^3J(H–C(1),H–C(6)) = 4.0, H–C(6)); 3.7 (*m*, H–C(1)); 2.9 (*m*, H–C(4)); 2.6 (*dm*,

^2J = 17, H_{exo}–C(3)); 2.1 (*s*, CH_3CO); 2.0 (*s*, CH_3CO); 2.1 1.6 (*m*, H_{endo}–C(3), H_{syn}–C(7), H_{anti}–C(7)). MS (70 eV): 236 (0.3), 235 (5.2), 234 (0.4), 219 (2.2), 208 (1.4), 207 (5.9), 203 (1.9), 193 (16.3), 192 (1.0), 191 (4.3), 175 (1.8), 152 (1.6), 151 (14.2), 150 (4.3), 133 (2.5), 124 (15.9), 123 (8.6), 96 (4.4), 95 (2.7), 91 (2.2), 83 (7.3), 82 (100), 81 (2.0), 80 (1.2), 79 (1.6), 74 (6.5), 67 (10.6), 60 (58.3), 58 (30), 56 (28.1). Anal. calc. for $C_{12}H_{12}NO_4$ (235.242): C 61.27, H 5.57; found: C 61.29, H 5.59.

(5-^{2}H)Bicyclo[2.2.1]hept-5-en-2-one (**47**). Zn-Cu couple: an acid soln. of $CuCl_2$ (22 ml of a soln. of $CuCl_2$ (20 g in 1 l 5% HCl soln.)) was added to a suspension of powered Zn (6.5 g, 100 mmol) in H_2O (10 ml) under N_2. After the end of H_2 evolution, the suspension was filtered under N_2 and washed successively with D_2O (10 ml, twice), anh. acetone (10 ml), and anh. Et_2O (10 ml). The black powder was heated at 100° under vacuum for 1 h and kept under Ar. Under Ar, **40** (300 mg, 1.6 mmol) was added to a soln. of Zn-Cu (1 g) in anh. THF (10 ml) and D_2O (2 ml). The soln. was stirred under reflux for 43 h. Zn-Cu (1 g in THF (3 ml) and D_2O (1.5 ml)) was added after 12 h and again after 30 h. After filtration, the soln. was extracted with CH_2Cl_2 (10 ml, twice), and the org. layer washed with H_2O (10 ml, twice). After drying ($MgSO_4$), the soln. was concentrated under reflux and the product isolated by prep. GC (*Carbowax 20 M*, 120° isotherm): 95 mg (53%) of colourless liquid. IR ($CDCl_3$): 3010, 2980, 2230, 1730, 1425, 1340, 1150, 840. ^{1}H-NMR (80 MHz, $CDCl_3$): 6.1 (*d*, ^3J(H–C(1), H–C(6)) = 4.0, H–C(6)); 3.1 (*m*, H–C(4)); 3.0 (*m*, H–C(1)); 2.1–1.7 (*m*, 2 H–C(7), 2 H–C(3)). MS (70 eV): 110 (0.6), 109 (6.4), 107 (0.2), 80 (8.7), 79 (2.3), 78 (4.6), 77 (2.6), 67 (100), 66 (15.1), 65 (2.5).

(6-^{2}H)Bicyclo[2.2.1]hept-5-en-2-one (**48**). Under Ar, **42** (1.0 g, 5.3 mmol) was added to Zn-Cu (3.2 g) in anh. dioxane (3.2 ml) and D_2O (6 ml). The soln. was stirred under reflux for 4 d. Zn-Cu (3.2 g in dioxane (25 ml) and D_2O (5 ml)) was added after 1 d and again after 3 d. After filtration, the soln. was extracted with CH_2Cl_2 (10 ml, 3 times) and the org. layer washed with H_2O (10 ml, 4 times). After drying ($MgSO_4$), the soln. was concentrated under reflux and the product isolated by prep. GC (*Carbowax 20 M*, 120° isotherm): 230 mg (40%) of colourless liquid. IR ($CDCl_3$): 3000, 2980, 2220, 1740, 1425, 1340, 1150, 840. ^{1}H-NMR (80 MHz, $CDCl_3$): 6.50 (*d*, ^3J(H–C(4), H–C(5)) = 3.0, H–C(5)); 3.1 (*m*, H–C(4)); 3.0 (*m*, H–C(1)); 2.10–1.70 (*m*, 2 H–C(7), 2 H–C(3)). MS (70 eV): 110 (1.6), 109 (16.8), 108 (0.5), 80 (13.0), 79 (4.1), 78 (6.5), 68 (6.1), 67 (100), 66 (18.4), 65 (3.0).

2-(Bicyclo[2.2.1]hept-5-en-2-ylidene)propanedinitrile (**49**). Malonodinitrile (5.5 g, 83.3 mmol) and piperidine (1 ml) were added to **5** (9 g, 83.3 mmol) in MeOH (50 ml). After heating under reflux for 1 h, the mixture was evaporated and the residue distilled (b.p. 91–92°/0.5 Torr): 7.8 g (60%), colourless oil. UV (95% EtOH): 238 (7000), 260 (4100). UV (isooctane): 238 (7850), 260 (4850). IR (film): 3080, 3000, 2960, 2240, 1620, 1570, 1450, 1420, 1320, 1290, 1160, 1140, 995, 985, 940, 920, 850, 820, 780, 720. ^{1}H-NMR ($CDCl_3$): 6.56 (*dd*, ^3J(H–C(5), H–C(6)) = 5.6, ^3J(H–C(4), H–C(5)) = 2.8, H–C(5)); 6.1 (*ddd*, ^3J(H–C(5), H–C(6)) = 5.6, ^3J(H–C(1), H–C(6)) = 2.8, ^5J(H_{exo}–C(3), H–C(6)) ≈ 1, H–C(6)); 3.95 (*dd*, ^3J(H–C(1), H–C(6)) = 2.8, ^3J(H–C(1), H_{syn}–C(7)) = 1.6, H–C(1)); 3.27 (*dm*, ^3J(H–C(4), H–C(5)) = 2.8, ^3J(H–C(4), H_{syn}–C(7)) ≈ 1, H–C(4)); 2.6 (*ddd*, ^2J = 18.4, ^3J(H_{exo}–C(3), H–C(4)) = 4.0, ^5J(H_{exo}–C(3), H–C(6)) = 1.0, H_{exo}–C(3)); 2.38 (*dd*, ^2J = 18.4, ^4J(H_{endo}–C(3), H_{syn}–C(7)) = 3.8, H_{endo}–C(3)); 2.0 (*dddd*, ^2J = 11, ^3J(H–C(4), H_{syn}–C(7)) = 1.0, ^3J(H–C(1), H_{syn}–C(7)) = 1.6, ^4J(H_{endo}–C(3), H_{syn}–C(7)) = 3.8, H_{syn}–C(7)); 1.7 (*dm*, ^2J = 11.0, H_{anti}–C(7)). ^{13}C-NMR ($CDCl_3$): 188.9 (*s*, C(2)); 142.5 (*d*, *J* = 176, C(5)); 129.9 (*d*, *J* = 176, C(6)); 111.5 (*s*, CN); 111.2 (*s*, CN); 79.0 (*s*, $C(CN)_2$); 51.9 (*d*, *J* = 152, C(1)); 51.1 (*t*, *J* = 138, C(3)); 41.4 (*d*, *J* = 152, C(4)); 38.3 (*t*, *J* = 136, C(7)); signal attributions based on the comparison with the ^{13}C-NMR spectra of 5-methylidenebicyclo[2.2.1]hept-2-ene [44] and acrylonitrile [45]. MS (70 eV): 157 (56), 156 (100), 149 (19), 141 (33), 129 (35), 128 (23), 111 (23), 109 (20), 102 (26), 98 (44), 96 (26), 91 (48), 69 (59), 67 (74), 57 (63), 55 (67). Anal. calc. for $C_{10}H_8N_2$ (156.187): C 76.90, H 5.16, N 17.94; found: C 76.82, H 5.35, N 17.99.

Electrophilic Additions of **49**. PhSeCl, PhSeBr, $NO_2C_6H_4SCl$, and $(NO_2)_2C_6H_3SCl$ (0.32 mmol) were added to a soln. of **49** (50 mg, 0.32 mmol) in $CDCl_3$ or CD_3CN (1 ml, in 5-mm NMR tube). After 24 h staying at 20°, 360-MHz ^{1}H-NMR analyses were made. No trace of other products than adducts **50**–**57** could be observed in the NMR spectra.

*2-(5-*exo*-Benzeneselenenyl-6-*endo*-bromobicyclo[2.2.1]hept-2-ylidene)propanedinitrile* (**52**). A soln. of PhSeBr (3.02 g, 12.82 mmol) in $CHCl_3$ (5 ml) was added to **49** (2 g, 12.82 mmol) in $CHCl_3$ (10 ml). After stirring at 20° for 12 h, the purple soln. was discoloured. The soln. was evaporated and the residue recrystallized from Et_2O/petroleum ether 1:1 (**52** crystallized before its isomer **53**, the latter could not be purified): 3.66 g (55%), colourless crystals. M.p. 112–113°. UV (95% EtOH): 221 (25830), 240 (23750), 280 (3650). UV (dioxane): 222 (22250), 240 (21600), 280 (4350). IR (KBr): 3010, 2920, 2240, 1630, 1575, 1475, 1440, 1410, 1320, 1295, 1275, 1240, 1230, 1195, 1180, 1160, 1100, 1060, 1020, 985, 970, 935, 870, 730, 680. ^{1}H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. MS (70 eV): 396 (2), 394 (8), 392 (9), 390 (6), 315 (1), 313 (45), 312 (4), 311 (4), 310 (2), 238 (5), 236 (6), 235 (6), 234 (3), 233 (3), 232 (3), 231 (2), 187 (3), 186 (3), 185 (10), 184 (4), 183 (6), 182 (4), 181 (3), 160 (4), 159 (10), 156 (27), 157 (48), 156 (20), 155 (59), 154 (17), 153 (9), 128 (15), 127 (18), 78 (100), 51 (56). Anal. calc. for $C_{16}H_{13}BrN_2Se$ (392.157): C 49.00, H 3.34; found: C 48.88, H 3.74.

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