Diels-Alder-Adducts of Dichloromethylenepropanedinitrile; Reactions with Nucleophiles

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Dedicated with Best Wishes to Professor Horst Kunz on the Occasion of his 60th Birthday

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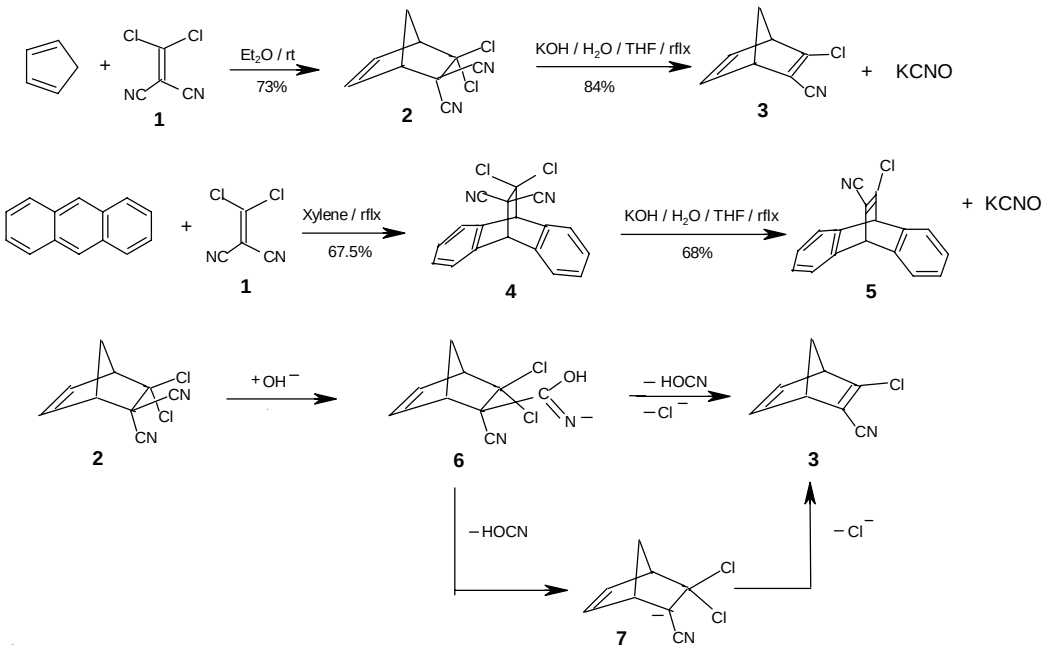
Abstract. Upon treatment with aqueous alkali, the Diels–Alder adducts **2** and **4** of dichloromethylenepropane-dinitrile (**1**) with cyclopentadiene and anthracene resp. are converted into 3-chloro-bicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile (**3**) and 12-chloro-9,10-dihydro-ethenoanthracene-11-carbonitrile (**5**), resp. The reaction may be brought about by other nucleophiles as well and involves the fragmentation of an intermediate β-chloroimidate anion. **3** is a educt for substituted norbornenes such as cyanoketone **18**.

Some 2- or 3-heterosubstituted cyanoethenes such as the ketene equivalent 2-chloroacrylonitrile [1] have found interest as dienophiles. Depending on further synthetic aims, the value of Diels–Alder reactions with good dienophiles such as TCNE and other polycyanoethenes may be diminished by difficulties encountered during chemical transformations of the polycyano adducts. Thus, with these compounds it may prove difficult to remove a particular nitrile group by a hydrolysis-decarboxylation sequence or by a β-elimination reaction because cyano groups are, as a rule, sluggish leaving groups.

We were interested in chemical transformations of Diels–Alder adducts of dichloromethylenepropanedinitrile (**1**) [2], especially in the applicability of **1** as a cyanoketene equivalent. By treating its cyclopentadiene adduct 3,3-dichlorobicyclo-[2.2.1]hept-5-ene-2,2-dicarbonitrile (**2**) [3] with potassium hydroxide in tetrahydrofuran-water at reflux temperature, we observed a smooth conversion, obtaining 3-chlorobicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile (**3**) in 84% yield. This reaction proved also useful in converting 12,12-dichloro-9,10-dihydro-ethanoanthracene-11,11-dicarbonitrile (**4**), the anthracene adduct of **1**, into a 68% yield of 12-



Scheme 1 Reaction of the dichlorodicyanoethano bridges in **2** and **4** with aqueous alkali

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chloro-9,10-dihydro-ethenoanthracene-11-carbonitrile (**5**). In both cases potassium cyanate was isolated from the reaction mixture. This result suggested a tentative mechanism formulated for the reaction **2** → **3** in scheme 1. For steric reasons we assume the nucleophilic attack of OH^- at the *exo* nitrile group giving the imidate anion **6**, which in analogy to the alkaline elimination of hydrogen halides in *trans*-2,3-dichloronorbornane [4] either *syn*-fragmentates in one step to give **3** and cyanate or reacts *via* the nitrile-stabilized carbanion **7** to give **3**.

In order to prove the involvement of an imido intermediate in the conversion **2** → **3**, we studied the reactions of other nucleophiles with compound **2**. In a base-catalyzed Pinner reaction [5], supported by the electron-withdrawing effect of the other nitrile group, one equivalent of sodium methoxide in boiling methanol could be added to the *exo*-nitrile group affording 71% of imido ester **8**. By refluxing with dilute hydrochloric acid **8** was converted into the methyl ester **9** in 79% yield.

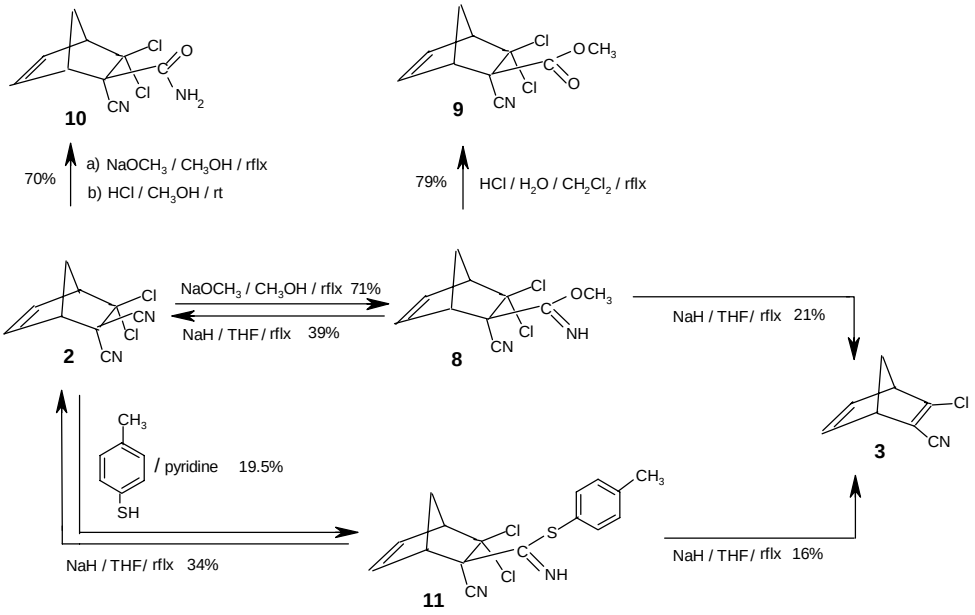
The signals of the ^1H and ^{13}C NMR spectra of **2** and **9** were assigned unambiguously by homo- and heteronuclear decoupling. H-7a and H-7s could be identified by their coupling to the olefinic protons and to C-2/C-3 and C-5/C-6 resp.. The fully coupled ^{13}C NMR spectrum of **2** shows doublets for both CN-groups. Selective decoupling provided the coupling constants ^3J(CN-*exo*, H-1) = 2.1 Hz and ^4J(CN-*endo*, H-7a) = 1.9 Hz, and allowed to differentiate between H-1 and H-4. The signals of the carbonyl group as well as of the cyano group in **9** are doublets (with additional splitting to quartets for CO due to OCH_3). Selective decoupling provided the coupling constants ^3J(CO, H-1) = 1.6 Hz and ^4J(CN, H-7a) = 1.9 Hz, thus verifying the *exo* position of the ester group in **9** and of the imidoester group in precursor **8**.

Additionally **8** with hydrogen chloride in methanol at *r.t.* gave the *exo*-carboxamide **10** in 70% yield. The addition of 4-mercaptotoluene in pyridine at *r.t.* to the *exo* nitrile in **2** yielded 19% of *p*-tolyl 3,3-dichloro-2-*endo*-cyanobicyclo[2.2.1]hept-5-ene-2-*exo*-thiocarboximidate (**11**), the *exo* position of the thioimido function is assumed for reasons of analogy.

Under the weakly basic conditions of their formation, compounds **8** and **11** turned out to be reasonably stable, but conversion into their respective anions by sodium hydride in refluxing tetrahydrofuran yielded in both cases mixtures of compounds **2** and **3** as shown in scheme 2.

The formation of norbornadiene **3** both from **8** and **11** thus strongly supports the existence of intermediates such as **6** in the reactions of compounds **2** and **4** with aqueous base. Whereas the base-induced reversal of the imido ester synthesis from nitrile and alcohol is a common reaction [7], the corresponding cleavage of a thioimido ester has not been reported to our knowledge.

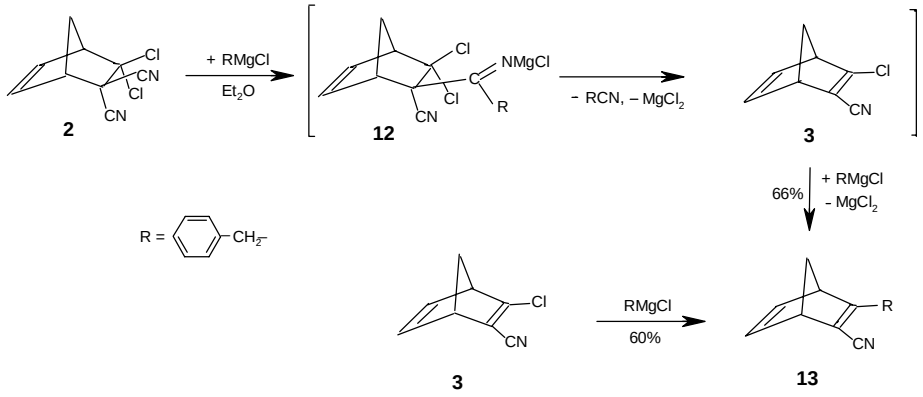
The intermediate formation of **3**, probably *via* a ketimine, is a key step in the reaction of **2** with a Grignard reagent. With slightly more than three equivalents of benzylmagnesium chloride compound **2** gave a 66% yield of 3-benzylbicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile **13**. If we accept the above mechanism, the irreversibility of the first addition step should favour the fragmentation of the anion of ketimine **12** to give compound **3** together with benzyl cyanide. The latter then would consume a second equivalent of Grignard reagent and the nucleophilic vinylic substitution of the chlo-



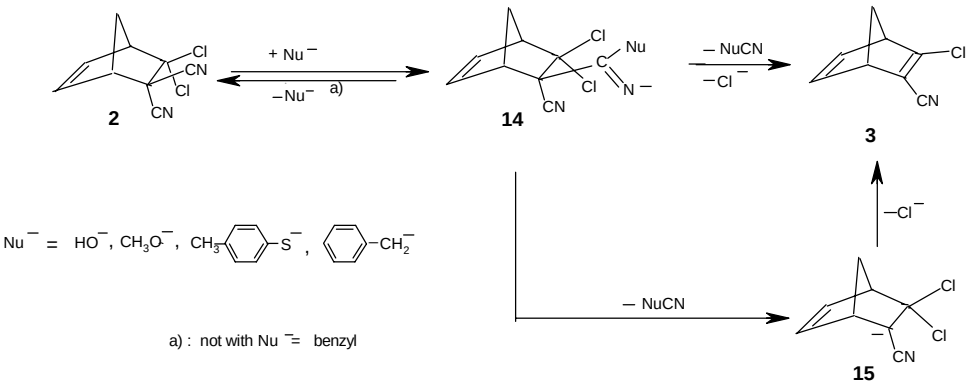
Scheme 2 Conversions of the *exo*-nitrile group in **2** *via* imidate formation

ro substituent by a third molecule of Grignard reagent would yield the observed product **13** (scheme 3). Although we did not prove the formation of benzyl cyanide by isolating dibenzyl ketone after the aqueous work-up, the suggested mechanism is supported by the independent synthesis of **13** from **3** and one equivalent of benzyl Grignard reagent in 60% yield and by the observation, that reaction **2** → **13** needs three equivalents of Grignard reagent to go to completion.

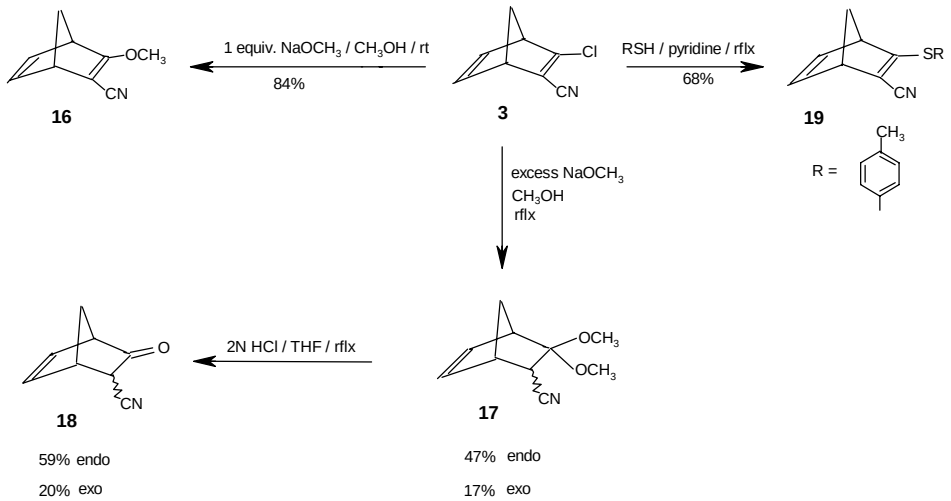
Summarizing the above results, scheme 4 gives a general mechanism for the conversion of **2** into **3** by the nucleophiles studied. A possible alternative to the *syn*-



Scheme 3 Reaction of **2** with Grignard reagent



Scheme 4 General mechanism of the reaction of **2** with nucleophiles



Scheme 5 Reactions of **3** with nucleophiles

fragmentation **14** → **3** could be the formation of an internediate nitrile-stabilized anion **15**.

The applicability of **1** as a cyanoketene equivalent could by demonstrated by the synthesis of 3-cyanobicyclo-[2.2.1]hept-5-en-2-one (**18**), an interesting starting compound for the 2,3-annelation of heterocycles to norbornadienes. Treatment of norbornadiene **3** with one equivalent of sodium methoxide at *r.t.* afforded the methoxy compound **16** in 84% yield. An excess of the reagent in boiling methanol gave the dimethyl ketal **17** as a mixture of 47% *endo*- and 17% *exo*-nitrile. Cleavage of **17** by dilute hydrochloric acid eventually afforded the cyanoketone **18** in 79% yield. Another example of nucleophilic substitution is the reaction of **3** with *p*-thiocresol to give 68% of the thioether **19**.

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Experimental

IR: Perkin-Elmer 298. – NMR: Varian A 60D and Bruker WM 400 (400 and 100.6 MHz for ^{1}H and ^{13}C, resp.); *m.p.* (uncorrected): Dr. Tottoli apparatus of Fa. Büchi. Flash chromatography on silica gel, Macherey & Nagel, 0.063–0.2 mm or 0.04–0.063 mm.

3,3-Dichlorobicyclo[2.2.1]hept-5-ene-2,2-dicarbonitrile (**2**) *[3]*

2.45 g (40 mmol) of freshly distilled cylopentadiene were added to a stirred solution of 4.9 g (33.3 mmol) of sublimed dichloromethylenepropanedinitrile (**1**) [2] in 50 ml of abs. diethyl ether. After 4 h at *r.t.* the slightly concentrated solution yielded a precipitate, which after recrystallization from dichloromethane afforded 5.15 g (73%) of product, *m.p.* 151–152 °C (*m.p.* Lit. [3] 149–151 °C). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ/ppm = 2.15 (dt, 1H, H-7a), 2.33 (d, 1H, H-7s), 3.74 (m, 1H, H-4), 3.82 (m, 1H, H-1), 6.49 (q, 1H, H-6), 6.52, (q, 1H, H-5). – ^{13}C NMR ($CDCl_3$), 100.6 MHz): δ/ppm = 46.25 (C-7), 53.25 (C-2), 56.58 (C-1), 61.13 (C-4), 90.05 (C-3), 112.59 (CN-*endo*), 113.03 (CN-*exo*), 135.04 (C-6), 139.18 (C-5); ^3J(CN-*exo*, H-1) = 2.1 Hz, ^4J(CN-*endo*, H-7a) = 1.9 Hz.

$C_9H_6Cl_2N_2$	Calcd.:	C 50.73	H 2.84	Cl 33.28	N 13.15
(213.1)	Found:	C 50.96	H 2.75	Cl 33.05	N 13.46.

3-Chloro-bicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile (**3**)

To a solution of 10.0 g (46.9 mmol) of **2** in 75 ml of tetrahydrofuran was added a solution of 7.7 g KOH in 15 ml of water and the mixture was stirred under reflux for 3.5 h. After cooling to *r.t.* and addition of 20 ml of water the mixture was extracted with three 30 ml portions of diethyl ether. The combined organic layers were dried over Na_2SO_4, the solvents evaporated and the dark oily residue chromatographed (silica gel, $CHCl_3$/CCl_4 1:2) to give 4.9 g (84%) of product **3** and 1.8 g of recovered educt **2**. The product was further purified by distillation; $b.p._{.14}$ 104 °C, n_D^{23} 1.5206. – IR (neat): ν/cm^{-1} = 2960, 2210, 1590, 1290, 1270, 1100, 1045, 1010, 810, 780, 720). – ^{1}H NMR ($CDCl_3$, 90 MHz): δ/ppm = 2.28 (q, 2H), 3.56 (m, 1H), 3.80 (m, 1H), 6.82 (m, 2H). After the ether extraction, the aqueous layer was nearly evaporated and the residue treated with ethanol. The filtrated solution was slightly acidified with acetic acid and a saturated ethanolic solution of cobalt-II-acetate was added. Concentration of the solution yielded blue crystals of $K_2[Co(NCO)_4]$.

C_8H_6ClN	Calcd.:	C 63.38	H 3.99	Cl 23.38	N 9.24
(151.6)	Found:	C 63.10	H 4.23	Cl 23.39	N 9.22.

12,12-Dichloro-9,10-dihydro-ethanoanthracene-11,11-dicarbonitrile (**4**)

A solution of 2 g (11.2 mmol) of anthracene and of 1.65 g (11.2 mmol) of freshly sublimed dichloromethylenepropanedinitrile (**1**) in 40 ml of abs. xylene was refluxed, until TLC (silica gel, CH_2Cl_2) showed no more **1**. After cooling the solution deposited needles which were filtered off and recrystallized from dichloromethane to give 2.46 g (67.5%) of the product **4**, *m.p.* 191–192 °C. An analytical sample was obtained by preparative TLC. – IR (KBr): ν/cm^{-1} = 2920, 2 260 (very weak), 1460, 1170, 900, 850, 760, 640, 630, 610. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 4.96 (s, 1H), 4.97 (s, 1H), 7.31–7.38 (m, 4H), 7.44–7.52 (m, 4H).

$C_{18}H_{10}Cl_2N_2$	Calcd.:	C 66.48	H 3.10	Cl 21.80	N 8.61
(325.2)	Found:	C 66.24	H 2.99	Cl 21.93	N 8.64.

12-Chloro-9,10-dihydro-ethenoanthracene-11-carbonitrile (**5**)

To a solution of 1.0 g (3.07 mmol) of **4** in 100 ml of tetrahydrofuran was added a solution of 5.0 g KOH in 40 ml of water and the mixture was stirred under reflux for 5 h. After cooling to *r.t.*, the precipitate was filtered off, air-dried and extracted with dichloromethane. After evaporation of the solvent the residue was recrystallized from dichloromethane/chloroform, 0.55 g (68%); *m.p.* 203–205 °C. – IR (KBr): ν/cm^{-1} = 3070, 2910, 2200, 1600, 1580, 1460, 1260, 1160, 1050, 980, 770, 730, 700, 630. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 5.15 (s, 1H), 5.27 (s, 1H), 7.03–7.13 (m, 4H), 7.34–7.42 (m, 4H). $K_2[Co(NCO)_4]$. could be prepared from the evaporated filtrate.

$C_{17}H_{10}ClN$	Calcd.:	C 77.42	H 3.82	Cl 13.44	N 5.31
(263.7)	Found:	C 77.16	H 4.22	Cl 13.67	N 5.26.

Methyl 3,3-Dichloro-2-endo-cyanobicyclo[2.2.1]hept-5-ene-2-exo-carboximidate (**8**)

To a solution of 2.5 g (11.7 mmol) of **2** in 50 ml of abs. methanol was added a solution of 0.27 g (11.7 mmol) of sodium in 10 ml of abs. methanol. The mixture was refluxed for 1 h, followed by evaporation of the solvent, addition of 30 ml of water to the residue and extraction with three 30 ml portions of diethyl ether. The combined ether layers were dried over Na_2SO_4 and evaporated. After recrystallization of the residue 2.04 g (71%) of **8** were obtained; *m.p.* 95 °C. – IR (neat): ν/cm^{-1} = 3340, 3000, 2240, 1670, 1430, 1340, 1060, 1040, 900, 840, 740. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.04 (d, 1H), 2.32 (d, 1H),3.52 (d, 1H), 3.79 (d, 1H), 3.90 (s, 3H), 6.46 (m, 1H), 6.57 (m, 1H), 7.69 (m, 1H).

$C_{10}H_{10}Cl_2N_2O$ Calcd.: C 49.04 H 4.12 Cl 28.92 N 11.43
(245.1) Found: C 48.78 H 4.08 Cl 28.64 N 11.33.

Methyl 3,3-Dichloro-2-endo-cyanobicyclo[2.2.1]hept-5-ene-2-exo-carboxylate (**9**)

A mixture of 2.0 g (8.2 mmol) of **8**, 40 ml of dichloromethane and 40 ml 2N HCl was refluxed for 30 min and the organic phase then separated. The aqueous layer was extracted with two 20 ml portions of dichloromethane, the combined organic layers were washed with saturated $NaHCO_3$ and dried over Na_2SO_4. Evaporation of the solvent and recrystallization from diethyl ether afforded 1.6 g (79%) of colourless crystals; *m.p.* 92 °C. – IR (KBr): ν/cm^{-1} = 3000, 2960, 2220, 1750, 1440, 1330, 1250, 1230, 1040, 960, 920, 900, 840, 790, 730, 690. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ/ppm = 2.01 (dt, 1H, H-7a), 2.39 (d, 1H, H-7s), 3.52 (m, 1H, H-1), 3.56 (m, 1H, H-4), 3.91 (s, 3H, OCH_3), 6.42 (q, 1H, H-5), 6.51 (q, 1H, H-6). – ^{13}C NMR ($CDCl_3$), 100.6 MHz): δ/ppm = 46.64 (C-7), 51.55 (C-1), 54.02 (OCH_3), 60.81 (C-4), 63.33 (C-2), 91.69 (C-3), 116.40 (CN), 138.16 (C-5), 165.23 (CO), ^3J(CO, H-1) = 1.6 Hz, ^4J(CN, H-7a) = 1.9 Hz.
$C_{10}H_9Cl_2NO_2$ Calcd.: C 48.80 H 3.69 Cl 28.81 N 5.69
(246.2) Found: C 48.75 H 3.66 Cl 28.61 N 5.66.

3,3-Dichloro-2-endo-cyanobicyclo[2.2.1]hept-5-ene-2-exo-carboxamide (**10**)

In a 100 ml round-bottomed flask equipped with gas inlet and reflux condenser, 2.5 g (11.7 mmol) of **2** were dissolved in 50 ml of abs. methanol and a solution of 0.27 g (11.7 mmol) of sodium in 8 ml of abs. methanol was added. After stirring under reflux for 1 h the solution was cooled to *r.t.* and a slow stream of HCl gas, dried over conc. H_2SO_4, was bubbled through the solution for 20 min. After removal of the solvent under reduced pressure the residue was taken up in dichloromethane and water and the aqueous phase was extracted with two portions of dichloromethane. The combined organic phases were dried over Na_2SO_4 and evaporated to give a solid which after recrystallization from chloroform afforded 1.9 g (70%) of **10**; *m.p.* 177 °C (darkening above 170 °C). – IR (KBr): ν/cm^{-1} = 3410, 3300, 3210, 1700, 1620, 1350, 840, 730. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.01 (d, 1H), 2.52 (d, 1H), 3.57 (m, 2H), 6.28 (broad d, 2H), 6.47 (m, 1H), 6.56 (m, 1H).
$C_9H_8Cl_2N_2O$ Calcd.: C 46.77 H 3.49 Cl 30.68 N 12.12
(231.1) Found: C 46.85 H 3.50 Cl 30.43 N 12.13.

p-Tolyl 3,3-Dichloro-2-endo-cyanobicyclo[2.2.1]hept-5-ene-2-exo-thiocarboximidate (**11**)

In a 250 ml round-bottomed flask equipped with gas inlet, reflux condenser, drying tube and bubbler 6.4 g (30.0 mmol) of **2** and 3.8 g (30.6 mmol) of 4-mercaptotoluene were dissolved under nitrogen with stirring in 60 ml of abs. pyridine. Stirring was continued under nitrogen at *r.t.* for 17 h, then 150 ml of 3N HCl were added to the red solution with external cooling and the mixture extracted with three 100 ml portions of diethyl ether. The combined organic layers were washed with saturated $NaHCO_3$ and dried over Na_2SO_4. Evaporation of the solvent gave a dark solid which was chromatographed on silica gel with ligroin/diethyl ether 3:2 to yield 2.3 g of educt and 1.26 g (19.5%) of **11** after recrystallization from ligroin/diethyl ether 3:1; *m.p.* 146 °C (with darkening above 125 °C). – IR (KBr): ν/cm^{-1} = 3260, 3000, 2900, 2230, 1630, 1600, 1490, 1450, 1380, 1250, 1200, 830, 780, 740, 720. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.96 (d, 1H), 2.45 (s, 3H), 2.5 (d, 1H), 3.60 (m, 1H), 3.72 (m, 1H), 6.49 (m, 1H), 6.65 (m, 1H), 7.36 (m, 4H), 9.53 (s, 1H).
$C_{16}H_{14}Cl_2N_2S$ Calcd.: C 56.97 H 4.19 Cl 21.02 S 9.50
(337.3) Found: C 57.19 H 4.20 Cl 20.57 S 9.23.

Reaction of 8 with Sodium Hydride

In a 250 ml round-bottomed flask equipped with reflux condenser, drying tube and bubbler 0.57 g (23.9 mmol) of sodium hydride was added with stirring to a solution of 3.9 g (15.9 mmol) of **8** in 50 ml of abs. THF. After the hydrogen evolution had ceased the mixture was refluxed for 1–2 h until TLC monitoring showed the disappearance of the educt. After cooling, 30 ml of water were added and the THF removed under reduced pressure. The remaining aqueous mixture was extracted with diethyl ether, the combined organic phases washed with water and dried over Na_2SO_4. Removal of the solvent and chromatography on silica gel with ligroin/diethyl ether 3:2 furnished 0.51 g (21%) of 3-chlorobicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile (**3**) and 1.32 g (39%) of 3,3-dichlorobicyclo[2.2.1]hept-5-ene-2,2-dicarbonitrile (**2**), which were characterized as described above.

Reaction of 11 with Sodium Hydride

In a 50 ml round-bottomed flask equipped with reflux condenser, drying tube and bubbler 40.5 mg (1.7 mmol) of sodium hydride was added with stirring to a solution of 0.52 g (1.54 mmol) of **11** in 10 ml of abs. THF. After the hydrogen evolution had ceased the mixture was refluxed for 30 min. cooled down and 40 ml of water were added. The mixture was extracted with three 20 ml portions of diethyl ether, the combined organic phases washed with water and dried over Na_2SO_4. Removal of the solvent and chromatography on silica gel with ligroin/diethyl ether 3:2 furnished a small amount of 4-mercaptotoluene, 37 mg (16%) of 3-chloro-bicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile (**3**) and 110 mg (34%) of 3,3-dichlorobicyclo[2.2.1]hept-5-ene-2,2-dicarbonitrile (**2**), which were characterized as described above. The original reaction mixture showed the IR absorption of the isothiocyanto function at 2150 cm^{-1}.

3-Benzylbicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile (**13**)

A Grignard solution, prepared from 1.6 g (67 mmol) of magnesium and 9.0 g (71 mmol) of benzyl chloride in 25 ml of diethyl ether, was added within 20 min to a solution of 4.1g (19 mmol) of **2** in 30 ml of abs. diethyl ether. After refluxing for 2 h a yellow precipitate had formed and the cooled mixture was treated portionwise with 10 ml 2N HCl, then with 20 ml 6N HCl. The aqueous phase was extracted with three portions of diethyl ether and the combined organic layers were washed with saturated $NaHCO_3$ solution and dried over Na_2SO_4. Evaporation gave a yellow oil which was purified by chromatography on silica (diethyl ether/ligroin 3:2) and yielded 2.6 g (66%) of **13**, $b.p._{0.2}$ 117 °C, n_D^{22} 1.5582. Vacuum distillation caused considerable loss of product. – IR (neat):

ν/cm^{-1} = 3020, 2990, 2970, 2200, 1620, 1600, 1500, 1450, 1300, 830, 750, 730, 700, 640. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.03 (m, 1H), 2.12 (m, 1H), 3.43 (m, 1H), 3.79 (m, 3H), 6.46 (m, 1H), 6.77 (m, 1H), 7.10 (m, 2H), 7.29 (m, 3H). The benzyl compound **13** was also obtained in 60% yield by adding a slight excess of the Grignard solution to a solution of **2** in diethyl ether, refluxing for 30 min and working up as described above.

$C_{15}H_{13}N$	Calcd.:	C 86.91	H 6.33	N 6.76
(207.2)	Found:	C 86.72	H 6.56	N 6.85.

3-Methoxybicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile (**16**)

In a 100 ml round-bottomed flask equipped with dropping funnel and drying tube a solution of 0.30 g (13.1 mmol) of sodium in 30 ml of abs. methanol was slowly added with stirring to a solution of 2.0 g (13.2 mmol) of **3** in 20 ml of abs. methanol. To prevent the formation of ketal **17**, there should always be a slight excess of **3** during the reaction. After 2.5 h the precipitated NaCl was filtered off and the filtrate evaporated to give a pale yellow oil, which was purified by the chromatography on silica gel with dichloromethane (distillation may cause considerable loss of product); yield 1.6 g (84%); $b.p._{.0.1}$ 48 °C, n_D^{21} 1.5157). – IR (KBr): ν/cm^{-1} = 3000, 2960, 2200, 1610, 1450, 1440, 1340, 1300, 1150, 970, 810, 730. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.04 (m, 1H), 2.24 (m, 1H), 3.30 (m, 1H), 3.65 (m, 1H), 4.03 (m, 3H), 6.65 (m, 1H), 6.97 (m, 1H).

C_9H_9NO	Calcd.:	C 73.48	H 6.15	N 9.52
(147.2)	Found:	C 73.36	H 6.24	N 9.64.

3,3-Dimethoxybicyclo[2.2.1]hept-5-ene-2-dicarbonitrile (**17**)

In a 100 ml round-bottomed flask equipped with reflux condenser and drying tube to a solution of 1.44 g (60 mmol) of sodium in 60 ml of abs. methanol was added with stirring 4.0 g (26.25 mmol) of **3**. After 1.5 h reflux the precipitated NaCl was filtered off and the filtrate evaporated to give a yellow oil, which was purified by distillation to afford 2.9 g (64%) of **17** (47% *endo*-nitrile/17% *exo*-nitrile); $b.p._{.0.05}$ 72 °C, n_D^{23} 1.4879. – IR (KBr): ν/cm^{-1} = 3030, 2980, 2240, 1450, 1340, 1260, 1180, 1140, 1100, 1060, 830, 770, 730. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.76 (m, 2H), 2.97 (d, 1H), 3.05 (m, 1H), 3.21 (m, 1H), 3.30 (d, 6H), 6.30 (dd, 1H), 6.43 (dd, 1H).

$C_{10}H_{13}NO_2$	Calcd.:	C 67.00	H 7.32	N 7.82
(179.2)	Found:	C 66.82	H 7.33	N 8.07.

3-Cyanobicyclo[2.2.1]hept-5-en-2-one (**18**)

A mixture of 3.57 g (20 mmol) of **17**, 30 ml of THF and 20 ml of 2N HCl was stirred under reflux for 30 min. The solution was concentrated under reduced pressure and extracted with three 20 ml portions of diethyl ether. The combined etheral phases were washed with saturated $NaHCO_3$ and dried over Na_2SO_4. Removal of the solvent under reduced pressure gave a colourless oil which was distilled to give 2.1 g (79%) of **18** (59% *endo*-nitrile/20% *exo*-nitrile), $b.p._{.0.05}$ 84 °C, n_D^{23} 1.4920. – IR (KBr): ν/cm^{-1} = 3000, 2970, 2230, 1760, 1450, 1180, 1140, 1100, 1060, 780, 740. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.03 (d, 1H), 2.35 (m, 1H), 2.87/3.07 (dd, 1H), 3.30 (m, 1H), 3.52 (m, 1H), 6.29 (m, 1H), 7.66 (m, 1H).

C_8H_7NO	Calcd.:	C 72.15	H 5.31	N 10.15
(133.2)	Found:	C 71.93	H 5.63	N 10.41.

3-(4-Methylphenyl)sulfanylbicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile (**19**)

In a 100 ml round-bottomed flask equipped with dropping funnel, gas inlet, reflux condenser and bubbler 3.32 g (21.9 mmol) of **3** were dissolved in 30 ml of abs. pyridine. Under a slow stream of nitrogen a solution of 2.5 g (21.9 mmol) of 4-mercaptotoluene was added with stirring and the mixture was refluxed for 3 h. The precipitated pyridine hydrochloride was filtered off with suction and the deep red solution was treated with 180 ml 6N HCl. After extraction with three 50 ml portions of diethyl ether the combined etheral layers were washed with saturated $NaHCO_3$, dried over Na_2SO_4 and evaporated under reduced pressure. The remaining red oil was purified by chromatography on silica gel with dichloromethane (vacuum distillation caused a loss in yield of ca. 40%) to give 3.55 g (68%) of **19**, $b.p._{.0.05}$ 145 °C, n_D^{21} 1.5887. – IR (KBr): ν/cm^{-1} = 3010, 3000, 2960, 2200, 1600, 1560, 1540, 1490, 1450, 1300, 1260, 1010, 810, 780, 730. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.03 (m, 1H), 2.17 (m, 1H), 2.40 (s, 3H), 3.46 (m, 1H), 3.84 (m, 1H), 6.64 (m, 1H), 6.83 (m, 1H), 7.20 (m, 2H), 7.30 (m,2H).

$C_{15}H_{13}NS$	Calcd.:	C 75.27	H 5.48	N 5.85	S 13.39
(239.4)	Found:	C 75.28	H 5.43	N 5.79	S 13.12.

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