# *exo* to *endo* Isomerisation of the Nitrile Group in 3-Nitrobicyclo[2.2.1]hept-5-ene-2-carbonitrile

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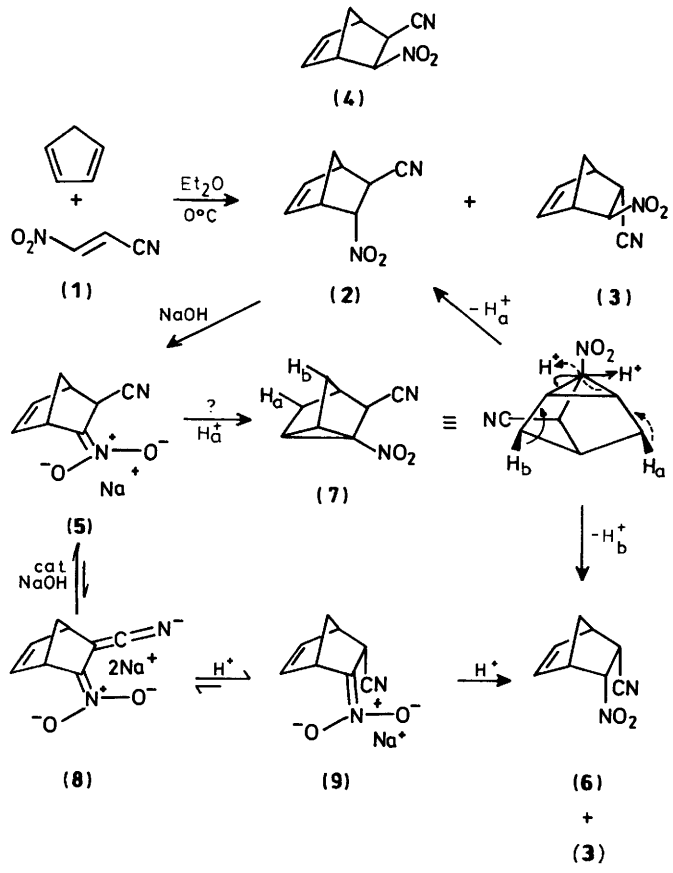
The Diels–Alder reaction of (*E*)-3-nitropropenenitrile (**1**) and cyclopentadiene yields a 9:1 mixture of 3-*endo*-nitrobicyclo[2.2.1]hept-5-ene-2-*exo*-carbonitrile (**2**) and the 3-*exo*-nitro-2-*endo*-carbonitrile isomer (**3**). On treatment with aqueous sodium hydroxide followed by reacidification, the adduct is isomerised to a mixture of (**2**), (**3**), and 3-*endo*-nitrobicyclo[2.2.1]hept-5-ene-2-*endo*-carbonitrile (**6**) in a ratio of *ca.* 46:22:32. The stereochemistry of the nitrile group appears to be established in a rapidly attained equilibrium during the deprotonation phase. Deuteriation studies rule out an isomerisation pathway involving skeletal rearrangement by way of a tricyclo[2.2.1.$0^{2,6}$]heptane intermediate; instead, the isomerisation probably proceeds through a dianion intermediate. Compound (**6**) itself isomerises to the same mixture of products under identical conditions, but produces (**3**) after contact with silica gel.

Derivatives of (*E*)-3-nitropropenoic acid readily participate in Diels–Alder reactions to give adducts that may themselves undergo a variety of transformations. Adducts with both cyclic and acyclic dienes have, for example, served as intermediates in the synthesis of natural products;[1-4] and we have ourselves used the adducts with various cyclopentadienes in studying aspects of the chemistry of nitronorbornenes.[5-7] Reactions with cyclopentadiene itself were originally reported by Russian workers,[8] but the results were surprisingly poor. The reaction of cyclopentadiene with (*E*)-3-nitropropenenitrile (**1**), for instance, was performed both at room temperature and under reflux in benzene to give a product, m.p. 142—142.5 °C, in 24—25% yield. No spectroscopic data were reported, and the stereochemical outcome was not investigated. In this paper we comment further on the stereochemistry of the Diels–Alder adduct from (*E*)-3-nitropropenenitrile (**1**) and cyclopentadiene, and on the isomerisation of this adduct.




Scheme.

We found that reaction between the substrates in ether occurred rapidly (2 h) at 0 °C, giving a chromatographically homogeneous adduct, m.p. 119—125 °C (98%). $^1$H N.m.r. spectroscopy showed the product to be a 9:1 mixture of two isomers. Although we were unable to separate these compounds, the $^1$H n.m.r. spectrum of the adduct mixture (see Figure, spectrum *a*), in conjunction with decoupling experiments, allowed assignment of their stereochemistries. The appropriate data appear in Tables 1 and 2. The diagnostic signals are those due to 3-H, the proton geminal to the nitro group. In the major isomer, this proton is responsible for a triplet at 5.64, *J* 3.8 Hz (in [$^2H_6$]acetone); coupling is to the vicinal protons on C-2 and C-4, and the magnitude of the latter indicates an *exo* disposition of 3-H.[9] 2-H Shows a long-range W-coupling[9] of 3.1 Hz to anti-7-H. The major isomer is thus 3-*endo*-nitrobicyclo[2.2.1]hept-5-ene-2-*exo*-carbonitrile (**2**), as one would expect from the greater secondary orbital interactions involving the nitro group in the nitroalkene substrate.[10] In the minor isomer, 3-H is a double double doublet at δ 4.78 ([$^2H_6$]acetone). Coupling to the bridgehead proton 4-H is very small indeed (*J* 0.7 Hz), as expected for an *endo*-H, but a long-range W-coupling (*J* 1.4 Hz) to the *anti*-7-H is again observed. The isomer is therefore 3-*exo*-nitrobicyclo[2.2.1]hept-5-ene-2-*endo*-carbonitrile (**3**). Isolation of this compound from a different reaction will be discussed below.

We failed to prepare a compound with a m.p. in the range 142—142.5 °C by repeating the reaction in refluxing benzene as originally described;[8] nor was there any change in product composition or isomer ratio when the (**2**)/(**3**) isomer mixture prepared in ether as described above was heated under reflux in benzene for 5 h. We suspected that the product originally reported[8] might merely be a stereoisomer of the kinetically formed adducts (**2**) and (**3**). If so, the bis-*exo* compound (**4**), perhaps formed by way of the *aci*-nitro tautomer of (**2**), is likely to be thermodynamically favoured. We accordingly set out to prepare this compound by deliberately trying to induce *endo*-to-*exo* isomerisation of the nitro group in (**2**).

Ouellette and Booth demonstrated the *exo*-preference of nitro groups in nitronorbornenes, and developed conditions (potassium t-butoxide 0.1 equiv., t-butyl alcohol, 80 °C) under

**Table 1.** $^1$H Chemical shifts (p.p.m. from TMS) and multiplicities at 200.13 MHz for three isomers of 3-nitrobicyclo[2.2.1]hept-5-ene-2-carbonitrile *

| | 1 | 2x | 2n | 3x | 3n | 4 | 5 | 6 | 7s | 7a |
|---|---|---|---|---|---|---|---|---|---|---|
| *endo*-$NO_2$-*exo*-CN (**2**), $CDCl_3$ | 3.46, m | — | 3.13, m | 5.23, t | — | 3.76, m | 6.22, ddd | 6.45, ddd | 1.87, m | |
| *endo*-$NO_2$-*exo*-CN (**2**), $CD_3COCD_3$ | 3.40, m | — | 3.20, t | 5.64, t | — | 3.74, m | 6.10, dd | 6.44, dd | 1.86, dm | 1.77, dm |
| *endo*-$NO_2$-*exo*-CN (**2**), $CD_3OD$ | 3.34, m | — | 3.15, t | 5.56, t | — | 3.69, m | 6.07, dd | 6.45, dd | 1.84, dm | 1.77, dm |
| *exo*-$NO_2$-*endo*-CN (**3**), $CDCl_3$ | 3.45, m | 3.68, t | — | — | 4.56, dt | 3.59, m | 6.40, ddd | 6.53, dd | 1.83, m | |
| *exo*-$NO_2$-*endo*-CN (**3**), $CD_3COCD_3$ | 3.46, m | 3.82, t | — | — | 4.78, ddd | 3.62, m | 6.46, ddd | 6.51, ddd | 1.79, m | |
| *endo*-$NO_2$-*endo*-CN (**6**), $CDCl_3$ | 3.43, m, | 3,55, dd | — | 5.22, dd | — | 3.60, m | 6.48, dd | 6.54, dd | 1.46, dm | 1.76, dt |
| *endo*-$NO_2$-*endo*-CN (**6**), $CD_3COCD_3$ | 3.41, m | 3.94, dd | — | 5.63, dd | — | 3.58, m | 6.44, ddd | 6.48, ddd | 1.63, m | |

* x = *exo*, n = *endo*, a = *anti*, s = *syn*.

**Table 2.** Selected proton-proton coupling constants (Hz) for three isomers of 3-nitrobicyclo[2.2.1]hept-5-ene-2-carbonitrile in [$^2H_6$]acetone solution

| | 1, 2n | 1, 2x | 1, 5 | 1, 6 | 2, 3 | 2n, 7a | 3n, 4 | 3x, 4 | 3n, 7a | 4, 5 | 4, 6 | 5, 6 | 7a, 7s |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *endo*-$NO_2$-*exo*-CN (**2**) | 0.5 | — | 0.7 | 3.2 | 3.8 | 3.1 | — | 3.8 | — | 2.9 | 0.8 | 5.7 | 9.9 |
| *exo*-$NO_2$-*endo*-CN (**3**) | — | 3.5 | 0.9 | 2.8 | 3.7 | — | 0.7 | — | 1.4 | 3.3 | 0.6 | 5.8 | — |
| *endo*-$NO_2$-*endo*-CN (**6**) | — | 3.5 | 0.9 | 2.8 | 9.5 | — | — | 3.4 | — | 2.7 | 0.9 | 5.7 | — |

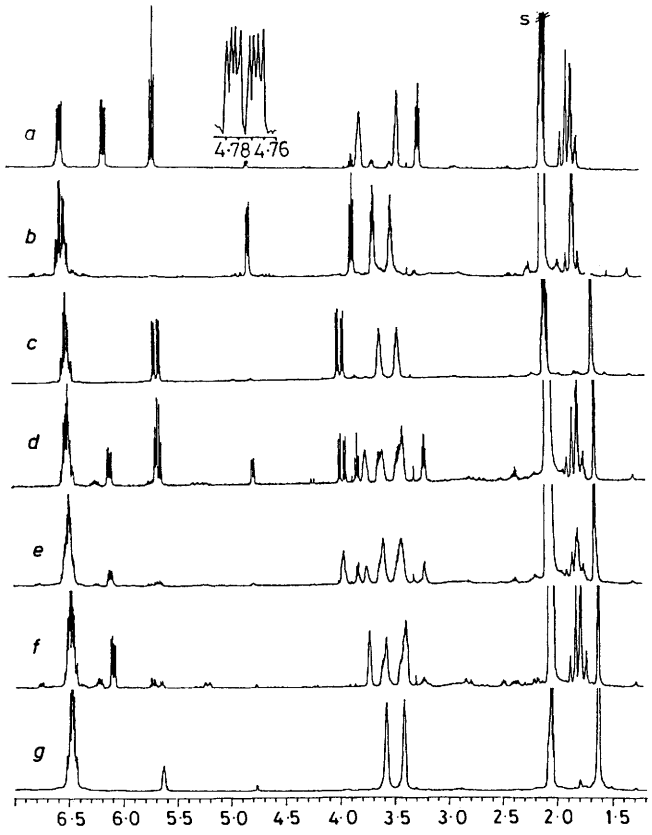



**Figure.** $^1$H N.m.r. spectra recorded at 200.13 MHz in [$^2H_6$]acetone (S = Solvent). (*a*) Diels–Alder adduct of (*E*)-3-nitropropenenitrile (**1**) and cyclopentadiene; 9:1 mixture of 3-*endo*-nitrobicyclo[2.2.1]hept-5-ene-2-*exo*-carbonitrile (**2**) and 3-*exo*-nitrobicyclo[2.2.1]hept-5-ene-2-*endo*-carbonitrile (**3**). Inset: expansion of δ 4.78 signal of (**3**). (*b*) 3-*exo*-Nitrobicyclo[2.2.1]hept-5-ene-2-*endo*-carbonitrile (**3**). (*c*) 3-*endo*-Nitrobicyclo[2.2.1]hept-5-ene-2-*endo*-carbonitrile (**6**). (*d*) Mixture of (**2**), (**3**), and (**6**) (46:20:34) obtained by sequential treatment of (**2**)/(**3**) adduct mixture with NaOH and HCl. (*e*) 3-Monodeuteriated mixture of (**2**), (**3**), and (**6**) obtained by sequential treatment of (**2**)/(**3**) adduct mixture with NaOH and DCl. (*f*) 2,3-Dideuteriated mixture of (**2**), (**3**), and (**6**) obtained by sequential treatment of (**2**)/(**3**) adduct mixture with NaOD and DCl. (*g*) 2-*exo*,3-*exo*-Dideuterio-3-*endo*-nitrobicyclo[2.2.1]hept-5-ene-2-*endo*-carbonitrile [$^2H_2$]-(**6**)

which equilibrium could be established.[11] When these conditions were applied to the Diels–Alder adduct mixture of (**2**) and (**3**), there was no noticeable change in isomer ratio, and no $^1$H n.m.r. evidence for the formation of a new compound. Other attempts at inducing isomerisation under conditions of thermodynamic control with stoicheiometric or catalytic quantities of weak organic bases [1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), triethylamine] were unsuccessful.

In an alternative strategy, we prepared the nitronate salt (**5**) of the Diels–Alder adduct mixture *in situ* with aqueous sodium hydroxide at room temperature over 10 min, the expectation being that a small but detectable quantity of the desired product (**4**) would be formed on reprotonation of the nitronate. We were aware that reprotonation should largely be from the *exo* direction,[12] a fact attributed to kinetically controlled attack of the protonating species during the quenching process.[11] We were also aware of the need to avoid concentrated acid as the proton source, since this might effect Nef reaction, or, as seems to be common with nitronorbornenes, skeletal cleavage.[13] In the event, dropwise treatment of a dilute solution (0.5M) of the nitronate (**5**) with cold concentrated hydrochloric acid produced a mixture of three isomers (93%) in the ratio 46:20:34, readily determined from the $^1$H n.m.r. spectrum in [$^2H_6$]acetone (see Figure, *d*). The first two corresponded to the Diels–Alder adducts (**2**) and (**3**) respectively; the third, which could be separated from the others by column chromatography, was a solid, m.p. 139—141 °C. The product ratio appears to be dictated, at least in part, by thermodynamically controlled events occurring during deprotonation: when contact with aqueous sodium hydroxide was maintained at 65 °C for 5 h before quenching with acid, essentially the same product ratio (45:22:33) and yield (88%) were found. It was important in these experiments to avoid an excess of sodium hydroxide, otherwise the nitrile group was partially hydrolysed.

Surprisingly, the new product was not the expected product (**4**), but instead the bis-*endo* isomer (**6**). The diagnostic features of the $^1$H n.m.r. spectrum (see spectrum *c* in Figure, and Tables 1 and 2) are the signals for 2-H and 3-H; both are double doublets that couple not only with each other (*J* 9.5 Hz), but also with the bridgehead protons 1-H and 4-H respectively. The sizes of the coupling constants, 3.5 Hz and 3.4 Hz respectively, support incontrovertibly this stereochemical assignment.[9] We have, in fact, never succeeded in forming the bis-*exo* isomer (**4**).

How is this unexpected bis-*endo* compound (**6**) formed? Base-induced equilibration of a 2-cyano group on the otherwise

unsubstituted norbornyl system is known to give a *ca.* 1:1 mixture of *exo*- and *endo*-CN isomers.[14] In our case, a dianion intermediate would have to be invoked, and we were reluctant to believe that a weak base such as sodium hydroxide could accomplish the transformation so readily. Our thoughts turned to skeletal rearrangement instead. It has been proposed[15] that resonance stabilisation of norborn-5-ene-2-nitronate anion by C=C involvement in the formation of a tricyclo[2.2.1.0$^{2,6}$]-heptane species might occur during abnormal Nef reactions on nitronorbornenes. We wondered whether reprotonation of nitronate intermediate (**5**) might not to some extent be at the C=C bond (Scheme, attachment of $H_a$). If so, the tricyclic intermediate (**7**) formed can collapse back to (**2**) by concerted reversal of the process (loss of $H_a$ and protonation α to $NO_2$; dotted arrows), the C=C double bond being effectively regenerated in an antiperiplanar elimination as the cyclopropane ring opens during $S_E2$ reprotonation with inversion. However, since (**7**) is symmetrical apart from the nitrile group, an alternative antiperiplanar elimination involving loss of $H_b$ (solid arrows) is now feasible, and product (**6**) results. The original C-7 of (**2**) becomes C-6 of (**6**) and *vice versa*, and what appears to be an *exo*-to-*endo* epimerisation of the nitrile substituent in fact arises from skeletal rearrangement of the system. The increased proportion of the minor Diels–Alder isomer (**3**) may then arise from further epimerisation of (**6**).

This intriguing hypothesis was tested by forming the nitronate (**5**) with aqueous sodium hydroxide as described above, isolating and drying the salt, and then treating a solution of it in deuterium oxide with deuterium chloride. If the hypothesis is correct, all products should be deuteriated α to the nitro group, and (**6**), if not (**3**), should also bear deuterium at C-7. In fact, all three compounds in the isomer mixture turned out to be monodeuteriated exclusively α to the nitro group (see Figure, *e*). This rules out tricycloheptane formation as a possible process on protonation of the nitronate. It does not rule out tricycloheptane formation (rather than simple isomerisation) *before* protonation, however; that is, equilibration of the nitronates themselves by way of a tricyclic anionic intermediate, as proposed by Wildman and Saunders.[15] This possibility was tested by forming the nitronate salt with sodium deuteroxide in deuterium oxide over 10 min, then quenching with deuterium chloride. All three products in the isomer mixture were found by $^1$H n.m.r. to be dideuteriated (see Figure, *f*), but again there was no deuterium incorporation at C-7 in (**6**). Instead, the labels were α to the nitro and nitrile groups. Isolation of a pure sample of compound (**6**) from this reaction provided clear proof of dideuteriation at C-2 and C-3 (see Figure, *g*).

The epimerisation of the nitrile group must thus occur simply by equilibrium deprotonation and reprotonation at its α position. This has been confirmed by conducting the experiment in an n.m.r. tube with [$^2H_4$]methanol as solvent. On addition of sodium deuteroxide (1 equiv.), both the 2-H and the 3-H signals disappeared in the time required to acquire the spectrum (*ca.* 6 min). Furthermore, the resulting spectrum showed the presence of two compounds, presumably the C-2 deuteriated nitronates (**5**) and (**9**). The implication is that a short-lived, resonance-stabilised dianion intermediate (**8**) is involved, and that this reprotonates at C-2 with equal facility at either face, exactly as the literature analogy[14] would suggest. The nitronates (**5**) and (**9**) themselves seem to undergo subsequent protonation—possibly kinetic—preferentially on the less hindered *exo* face.

Further evidence for the proposed sequence of events came after subjecting the bis-*endo* isomer (**6**) to our standard isomerisation conditions. The product mixture (91% recovery) contained the three compounds (**2**), (**3**), and (**6**) in the ratio 45:22:33, indicating a common set of intermediates. However, when (**6**) was left in contact with silica gel for 16 h prior to column chromatography, the nitro group was partially epimerised to the *exo* position; on elution, a relatively pure sample of the minor Diels–Alder adduct (**3**) was obtained as a gum, and its identity could be confirmed by $^1$H n.m.r. spectroscopy (see Figure, *b*). The physical properties of the three isomers we have described therefore lead us to suggest that the compound isolated by the Russian workers[8] was most probably (**6**), though the factors responsible for its formation in the earlier work remain unclear.

## Experimental

Routine measurements were made on Kofler micro hot-stage (m.p.), Pye-Unicam SP3-300 (i.r. in KBr dispersion), AEI MS-9 (m.s.), and Varian EM-360A and Bruker AC200 FT (n.m.r.) spectrometers. T.l.c. was on pre-coated silica gel plates (Merck F254), and column chromatography was on Merck Kieselgel 60 (particle size 0.063—0.200 mm).

*Diels–Alder Reaction of Cyclopentadiene and* (E)-3-*Nitropropenenitrile* (**1**).—Freshly cracked cyclopentadiene (813 mg, 12.3 mmol) was added dropwise to a solution of the nitrile[16] (1.00 g, 10.2 mmol) in diethyl ether (45 ml) at 0 °C. The mixture was kept for 2 h at this temperature and at room temperature for a further 3 h. Removal of the solvent gave a chromatographically homogeneous (t.l.c.) solid (1.64 g, 98%), m.p. 119—125 °C, $R_F$ 0.44 (hexane–ethyl acetate 3:1), which consisted of a mixture (9:1) of 3-endo-*nitrobicyclo*[2.2.1]*hept*-5-*ene*-2-exo-*carbonitrile* (**2**); $\nu_{max.}$(KBr) 3 070, 2 980, 2 880, 2 240 (CN), 1 545, 1 367, and 721 cm$^{-1}$; for $^1$H n.m.r. data see Tables 1 and 2; $\delta_c$($CDCl_3$) 137.92 (C-6), 133.25 (C-5), 119.54 (CN), 87.93 (C-3), 48.24 (C-1), 47.59 (C-4), 47.10 (C-7), and 33.54; $\delta_C$([$^2H_6$]acetone) 139.52 (C-6), 134.36 (C-5), 120.98 (CN), 89.26 (C-3), 49.53 (C-1), 48.67 (C-4), 47.88 (C-7), and 34.81 (C-2), and 3-exo-*nitrobicyclo*-[2.2.1]*hept*-5-*ene*-2-*endo*-*carbonitrile* (**3**); for data see below.

3-endo-*Nitrobicyclo*[2.2.1]*hept*-5-*ene*-2-endo-*carbonitrile* (**6**).—A mixture of aqueous sodium hydroxide (0.5M; 2.1 ml, 1.05 mmol) and the above adducts (**2**)/(**3**) (164 mg, 1.0 mmol) was shaken, with brief periods of sonication to ensure rapid reaction, at room temperature for 10 min. The bright yellow solution thus formed was diluted with water to *ca.* 8 ml, and cold concentrated hydrochloric acid was added dropwise until the solution was just acidic. The solution lost colour, and a precipitate was formed immediately. After 15 min the mixture was extracted with dichloromethane (2 × 5 ml). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure to yield a mixture of the isomers (**2**), (**3**), and (**6**) (153 mg, 93%) in the ratio 46:20:34 ($^1$H n.m.r.). Partial separation of a similar isomeric mixture (573 mg, from 537 mg Diels–Alder adduct) was achieved by column chromatography on silica gel with hexane–ethyl acetate mixture as eluant. A mixture of isomers (**2**) and (**3**) (248 mg, 46%) was recovered, together with 3-endo-*nitrobicyclo*[2.2.1]*hept*-5-*ene*-2-endo-*carbonitrile* (**6**) (165 mg, 31%) as colourless needles, m.p. 139—141 °C (from ethanol) (Found: C, 58.8; H, 4.9; N, 16.85. $C_8H_8N_2O_2$ requires C, 58.53; H, 4.91; N, 17.06%); $R_F$ 0.16 (hexane–ethyl acetate 3:1); $\nu_{max.}$(KBr) 3 010, 2 245 (CN), 1 545, and 1 377 cm$^{-1}$; for $^1$H n.m.r. data see Tables 1 and 2; $^{13}$C n.m.r. ([$^2H_6$]acetone) 137.35 and 137.20 (C-5, C-6), 118.97 (CN), 88.13 (C-3), 48.02 (C-1), 47.33 (C-4), 46.87 (C-7), and 35.62 (C-2).

*Deuteriation Studies on Diels–Alder Adducts* (**2**)/(**3**).—(*i*) A mixture of aqueous sodium hydroxide (0.5M; 2.4 ml, 1.2 mmol) and Diels–Alder adducts (**2**)/(**3**) (176 mg, 1.07 mmol) was shaken, with brief periods of sonication, for 8 min at room temperature. The solvent was removed at 1 mmHg, yielding the

nitronate (**5**) as a pale yellow sticky solid (241 mg); $\nu_{max.}$(KBr) 2 240 and 1 620 $cm^{-1}$. This was dissolved in deuterium oxide (2 ml). Deuterium chloride (38% solution in $D_2O$) was added dropwise until the solution was just acidic. A precipitate formed immediately. After 10 min the mixture was diluted to 10 ml with water and then extracted with dichloromethane (2 × 8 ml). The extracts were dried ($MgSO_4$) and evaporated under reduced pressure to yield a mixture of 3-monodeuteriated isomers of (**2**), (**3**), and (**6**) (163 mg, 92%) in the ratio 27:23:50. For $^1H$ n.m.r. data see Figure, spectrum *e*.

(*ii*) A suspension of adduct mixture (**2**)/(**3**) (151 mg, 0.92 mmol) in deuterium oxide (2.0 ml) was shaken with sodium deuterioxide (40% in $D_2O$, 0.097 ml, *ca.* 0.97 mmol) at room temperature for 8 min until a clear yellow solution had formed. Deuterium chloride (38% in $D_2O$) was added dropwise until the solution was just acidic. After 10 min, the mixture was extracted with dichloromethane (3 × 1 ml). The extracts were dried ($MgSO_4$) and evaporated to yield a mixture of 2,3-*bis-deuteriated* isomers of (**2**), (**3**), and (**6**) in the ratio 43:22:35 (135 mg, 88%). For $^1H$ n.m.r. data see Figure, spectrum *f*. Partial separation of a similar isomer mixture (from 608 mg of Diels–Alder adduct) was achieved by column chromatography on silica gel with hexane—ethyl acetate mixtures. A mixture of 2,3-dideuterio isomers of (**2**) and (**3**) (304 mg, 49%) was obtained, together with 2-exo,3-exo-*dideuterio*-3-endo-*nitrobicyclo*-[2.2.1]*hept*-5-*ene*-2-endo-*carbonitrile* [$^2H_2$]-(**6**) as colourless needles after recrystallisation from ethanol (224 mg, 36%), m.p. 131—134 °C; $\delta_c$([$^2H_6$]acetone] 137.32 and 137.15 (C-5, C-6), 118.94 (CN), 87.73 (C-3, t, $^1J_{C-D}$ 20.0 Hz), 47.89 (C-1), 47.21 (C-4), 46.83 (C-7), and 35.32 (C-2, t, $^1J_{C-D}$ 22.4 Hz) (Found for $M^+ - NO_2$: 120.0765. $C_8H_6D_2N$ requires 120.0780).

*Isomerisation of* 3-endo-*Nitrobicyclo*[2.2.1]*hept*-5-*ene*-2-endo-*carbonitrile* (**6**).—(*i*) A suspension of (**6**) (82 mg, 0.5 mmol) in aqueous sodium hydroxide (0.5M; 1.06 ml, 0.53 mmol) was shaken at room temperature with brief periods of sonication for 10 min until an amber-coloured solution formed. Water (4 ml) was added, followed by conc. hydrochloric acid (6 drops). The colour disappeared, and a white precipitate formed. After 10 min the mixture was extracted with dichloromethane (2 × 5 ml). The extracts were dried ($MgSO_4$) and concentrated to yield a mixture of isomers (**2**), (**3**), and (**6**) (75 mg, 91%) in the ratio 43:22:35.

(*ii*) A solution of (**6**) (23.0 mg, 0.14 mmol) in acetone (0.5 ml) was dried onto Merck Kieselgel 60 (particle size 0.063—0.200 mm, 100 mg). The powder was kept at room temperature for 16 h prior to elution on a column of silica gel (2.0 g) with hexane–ethyl acetate mixtures. Compound (**6**) (11.0 mg, 47.8%) was recovered along with 3-exo-*nitrobicyclo*[2.2.1]*hept*-5-*ene*-2-endo-*carbonitrile* (**3**) as a gum (10.7 mg, 46.5%); $R_F$ 0.44 (hexane–ethyl acetate 3:1); $\nu_{max.}$($CHCl_3$) 3 045, 2 250(CN), 1 550, and 1 365 $cm^{-1}$; for $^1H$ n.m.r. data see Tables 2 and 3; $\delta_C$($CDCl_3$) 138.92 (C-6), 135.64 (C-5), 119.25 (CN), 88.65 (C-3), 50.04 (C-4), 45.87 (C-7), 45.69 (C-1), and 34.95 (C-2) (Found for $M^+ - NO_2$: 118.0641. $C_8H_8N$ requires 118.0657).

*Detection of the Nitronates* (**5**) *and* (**9**) *by* $^1H$ *N.m.r. Spectroscopy*.—A solution of the adduct mixture (**2**)/(**3**) (33 mg, 0.2 mmol) in [$^2H_4$]methanol (0.4 ml) was treated with sodium deuterioxide (40% in $D_2O$, 0.02 ml, *ca.* 0.2 mmol), and an n.m.r. spectrum was taken immediately of the yellow solution thus formed. The C-2-deuteriated nitronates (**5**) and (**9**), were formed (1:1), and the following signals (tentative assignments given) were observed: 6.54 [0.5 H, dd, *J* 5.5 and 3.0 Hz, 6-H of (**5**)], 6.43 [1 H, m, 5-H and 6-H of (**9**)], 6.30 [0.5 H, dd, *J* 5.5 and 3.0 Hz, 5-H of (**5**)], 3.79 (1 H, m, 4-H), 3.37 (1 H, m, 1-H), 1.97 [0.5 H, dt, *J* 9.2 and 1.5 Hz, 7a-H of (**9**)?], 1.1 [1 H, 9 lines, observable *J* 8.8 and 1.8 Hz, 7-H of (**5**)?], and 1.67 [0.5 H, dt, *J* 9.1 and 1.5 Hz, 7s-H of (**9**)?].

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## References

1 G. Just, A. Martel, K. Grozinger, and M. Ranjeesingh, *Can. J. Chem.*, 1975, **53**, 131; G. Just, T. J. Liak, M. Lim, P. Potvin, and Y. S. Tsantrizos, *ibid.*, 1980, **58**, 2024.
2 S. Danishefsky, M. P. Prisbylla, and S. Hiner, *J. Am. Chem. Soc.*, 1978, **100**, 2918.
3 P. A. Grieco, R. E. Zelle, R. Lis, and J. Finn, *J. Am. Chem. Soc.*, 1983, **105**, 1403.
4 I. Fleming, in 'New Trends in Natural Product Synthesis,' eds. Atta-ur-Rahman and P. W. Le Quesne, Elsevier, Amsterdam, 1986, pp. 83—93.
5 N. F. Blom, D. M. F. Edwards, J. S. Field, and J. P. Michael, *J. Chem. Soc., Chem. Commun.*, 1980, 1240.
6 J. C. A. Boeyens, L. Denner, and J. P. Michael, *J. Chem. Soc., Perkin Trans. 2*, 1984, 767.
7 J. P. Michael, N. F. Blom, and J. C. A. Boeyens, *J. Chem. Soc., Perkin Trans. 1*, 1984, 1739.
8 S. S. Novikov, G. A. Shvekhgeimer, and A. A. Dudinskaya, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 1961, 690; English translation in *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1961, 640.
9 A. P. Marchand, 'Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems,' Verlag Chemie International, Deerfield Beach, 1982.
10 M. Kakushima and D. G. Scott, *Can. J. Chem.*, 1979, **57**, 1399.
11 R. J. Ouellette and G. E. Booth, *J. Org. Chem.*, 1965, **30**, 423.
12 F. G. Bordwell and K. C. Yee, *J. Am. Chem. Soc.*, 1970, **92**, 5939.
13 W. E. Noland, J. H. Cooley, and P. A. McVeigh, *J. Am. Chem. Soc.*, 1959, **81**, 1209; S. Ranganathan, D. Ranganathan and R. Iyengar, *Tetrahedron*, 1976, **32**, 961.
14 P. Wilder, Jr. and D. B. Knight, *J. Org. Chem.*, 1965, **30**, 3078.
15 W. C. Wildman and D. R. Saunders, *J. Org. Chem.*, 1954, **19**, 381.
16 H. Schechter, F. Conrad, A. L. Daulton, and R. B. Kaplan, *J. Am. Chem. Soc.*, 1952, **74**, 3052.

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