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RADICAL CYCLISATION OF α,ω-DINITROALKANES

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Summary: *2,6-Dinitroalkanes have been cyclised to yield vicinal dinitrocyclopentanes via stereoselective intramolecular addition of nitronate anions to α-nitroalkyl radicals. A "cyclohexane type" transition state is proposed for this radical anion cyclisation.*

Radical coupling reactions[1,2] between nitro compounds, e.g. $S_{RN}1$ reactions, have been extensively investigated in recent years. Similarly, the intramolecular addition reactions of alkenyl radicals have become a key area of modern synthetic organic chemistry.[3,4] Radical cyclisations of α,ω-difunctional chains have proved successful, e.g. acyloin condensation and iodine oxidation of α,ω-di(ß-carbonyl)-dianions, and therefore, we sought to investigate the radical cyclisation of α,ω-dinitroalkanes. Two different radical coupling methods of nitro-compounds proceeding by intermolecular addition of nitronate anions to α-nitroalkyl radicals are of particular value (see Scheme 1).

SCHEME 1: $S_{RN}1$[1,2]

$$R_2C(X)NO_2 + R_2C{=}NO_2^- \longrightarrow [R_2C(X)NO_2]^{\cdot-} + R_2\dot{C}NO_2$$
$$[R_2C(X)NO_2]^{\cdot-} \longrightarrow R_2\dot{C}NO_2 + X^-$$
$$R_2\dot{C}NO_2 + R_2C{=}NO_2^- \longrightarrow [R_2C(NO_2)C(NO_2)R_2]^{\cdot-}$$
$$[R_2C(NO_2)C(NO_2)R_2]^{\cdot-} + R_2C(X)NO_2 \longrightarrow R_2C(NO_2)C(NO_2)R_2 + [R_2C(X)NO_2]^{\cdot-}$$

Oxidative addition[1,5]

$$R_2C{=}NO_2^- + Fe(III) \longrightarrow R_2\dot{C}NO_2 + Fe(II)$$
$$R_2\dot{C}NO_2 + R_2C{=}NO_2^- \longrightarrow [R_2C(NO_2)C(NO_2)R_2]^{\cdot-}$$
$$[R_2C(NO_2)C(NO_2)R_2]^{\cdot-} + Fe(III) \longrightarrow R_2C(NO_2)C(NO_2)R_2 + Fe(II)$$

Intramolecular $S_{RN}1$ reactions *via* aryl radicals[6] have been reported and therefore should also be applicable to suitably functionalised α,ω-dinitroalkanes. Likewise, several examples of oxidative cyclisation *via* α-nitroalkyl radicals have been reported; α,ω-dinitronate anions[7,8] and a 1,6-nitronate-phenolate dianion.[9] The successful synthesis of vic-dinitrocycloalkanes has synthetic potential because of the facile conversion of nitro groups to other functional groups. In this paper we report the successful studies of the cyclisation of 1,5-dinitroalkanes and our failure with 1,3- and 1,4-dinitroalkanes. Preliminary results have been reported.[10]

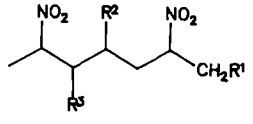
1,5- and 1,6-Dinitroalkanes should cyclise most easily, i.e. to 5- and 6-membered rings respectively.

Initially, 1,5-dinitropentane and 1,6-dinitrohexane were readily prepared by literature methods. Attempted oxidative cyclisation of the dinitronate dianions failed, e.g. oxidation of the dinitronate dianion of 1,5-dinitropentane, using potassium ferricyanide [$K_3Fe(CN)_6$], or catalytic $K_3Fe(CN)_6$, with sodium persulphate[5a] to reoxidise Fe(II) to Fe(III), gave 70-80% recovery of unaltered 1,5-dinitropentane and no cyclised material. Iodine oxidation, which had proved successful for the 1,3-cyclisation of the dinitronate dianion of 2,4-dinitropentane,[7] also gave largely unaltered 1,5-dinitropentane. Primary nitronates, therefore, appeared unsuitable for further studies. Several synthetic approaches to secondary 2,7-dinitro-octanes were attempted without success and therefore cyclisation to 6-membered rings could not be studied.

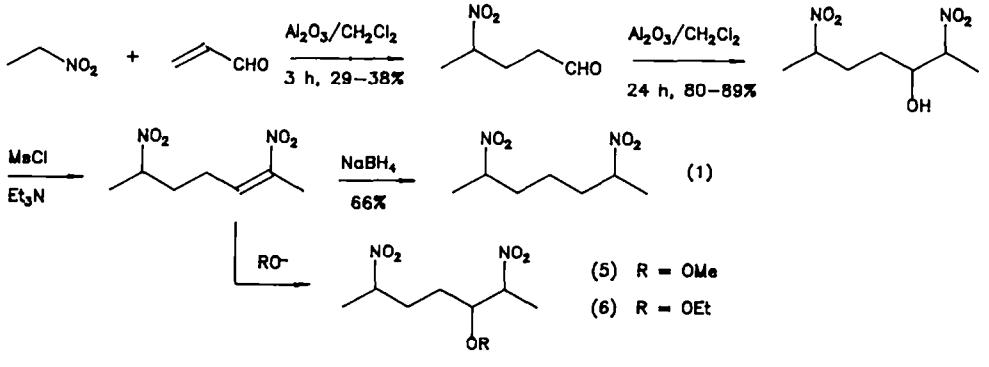
Preparation of 2,6-dinitroalkanes

The secondary nitroalkanes (1)-(6) were successfully prepared in 20-25% yield as exemplified in Scheme 2 for 2,6-dinitroheptane. The method of Rosini et al[12] was adapted for the preparation of 4-nitroaldehydes and for carrying out the Henry reactions (step 2).[12,13] The ß-nitroalchols were dehydrated using mesyl chloride and triethylamine.[13] High yields were consistently obtained if a slight excess of mesyl chloride and a three hold excess of triethylamine, were used. Some of the non-conjugated ß,γ-nitroalkenes were also formed by isomerisation from the α,ß-nitroalkene. Reduction of the nitroalkenes with sodium borohydride using dioxan/ethanol[14] rather than tetrahydrofuran (THF)/methanol (MeOH)[16] as solvent gave highest yields. Addition of nucleophiles to the intermediate nitroalkenes[16] provides a facile method of introducing a variety of substituents. In several of the syntheses, certain intermediates were not fully purified due to the number of diastereoisomers and the instability of the compounds.

SCHEME 2. PREPARATION OF 2,6-DINITROALKANES



(1) $R^1 = R^2 = R^3 = H$
(2) $R^1 = Me, R^2 = R^3 = H$
(3) $R^1 = R^3 = H, R^2 = Me$
(4) $R^1 = R^2 = H, R^3 = Me$
(5) $R^1 = R^2 = H, R^3 = OMe$
(6) $R^1 = R^2 = H, R^3 = OEt$

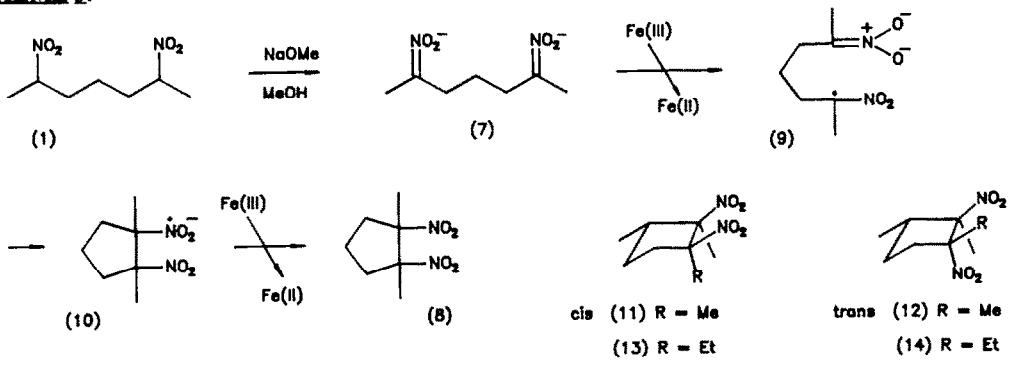


Oxidative cyclisation of 2,6-dinitroalkanes

Iodine oxidation[7] of the secondary dinitronate dianion (7) gave a low yield of products which included the two diastereoisomers of 1,2-dimethyl-1,2-dinitrocyclopentane (8). Oxidation of the dinitronate (7) with an excess of $K_3Fe(CN)_6$ in a two phase system [water and diethyl ether (Et_2O)][5] under an atmosphere of nitrogen gave a rapid reaction and yielded the cyclised vicinal dinitrocyclopentane, (8), in 71-85% yield.

The putative mechanism for the oxidative cyclisation is shown in Scheme 3. Loss of an initial electron from the dinitronate dianion (7) yields the radical anion (9), which can react further by either of two routes. The most favourable route entails a **unimolecular** cyclisation of (9) to the cyclised radical anion (10). which subsequently looses a second electron to yield the cyclised product (8). The unimolecular reaction is more likely than a **bimolecular** reaction between the radical anion and ferricyanide to yield a diradical. The addition of nitronate anions to α-nitroalkyl radicals (see Scheme 1) is the proposed mechanism for bimolecular couplings and is likely for the unimolecular coupling as well. There is considerable evidence that α-nitroalkyl radicals do not dimerise[1] although in one sterically constrained molecule a diradical coupling appears to be the most likely mechanism.[8]

SCHEME 3:



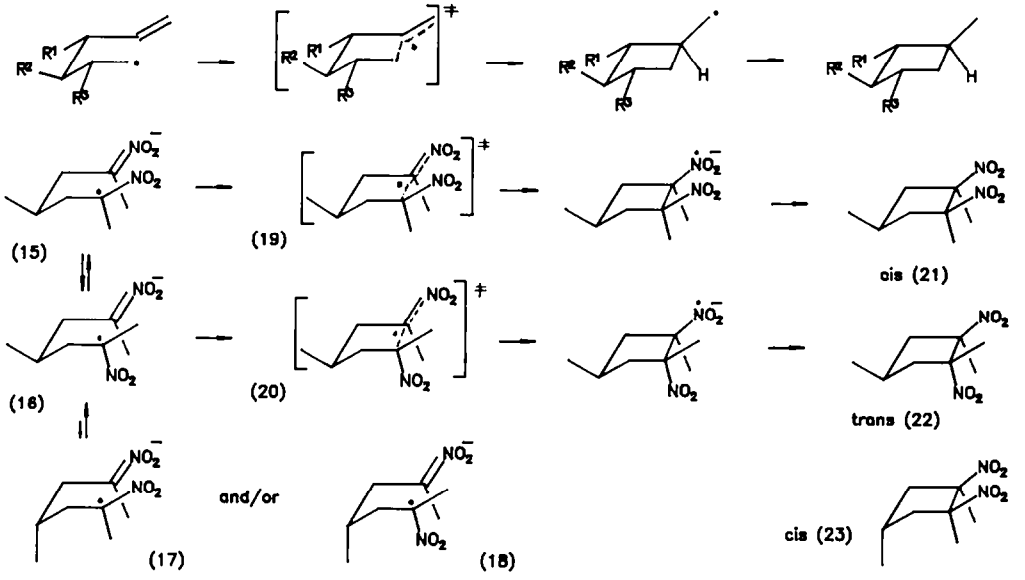
Oxidation of the dinitronate (7) in the presence of a large excess of benzenesulphinate gave an unaltered yield of the cyclised product (8) with no bimolecular trapping of the intermediate α-nitroalkyl radicals (9), *i.e.* no α-nitrosulphones. Benzenesulphinate is the most efficient anion for adding to α-nitroalkyl radicals in these oxidative couplings[1,5] and therefore, suggests that bimolecular reactions are not favoured.

The cyclisation of 2,6-dinitroheptane (1) gave both the *cis* and *trans* diastereoisomers, (11) and (12), in a *cis:trans* ratio of 60:40. On purely steric grounds a majority of the *trans* diastereoisomer would be predicted, but the differences in A-values[7,19] are small (methyl = 1.7 and nitro = 1.1). In contrast, the 1,3-cyclisation of the dinitronate dianion of 2,4-dinitropentane[7] gave only the *trans* diastereoisomer but is reported to proceed by a different mechanism. 2,6-Dinitro-octane (2) was also oxidatively cyclised using the same procedure, to yield the two diastereoisomers of 1,2-dinitro-1-ethyl-2-methylcyclopentane, (13) and (14), in 85% yield with a *cis:trans* ratio of 65:35.

Whereas the cyclisation of (1) and (2) showed little stereoselectivity, the cyclisation of (3) gave largely only two of the three possible diastereoisomers of 1,2,4-trimethyl-1,2-dinitrocyclopentane, in 90%

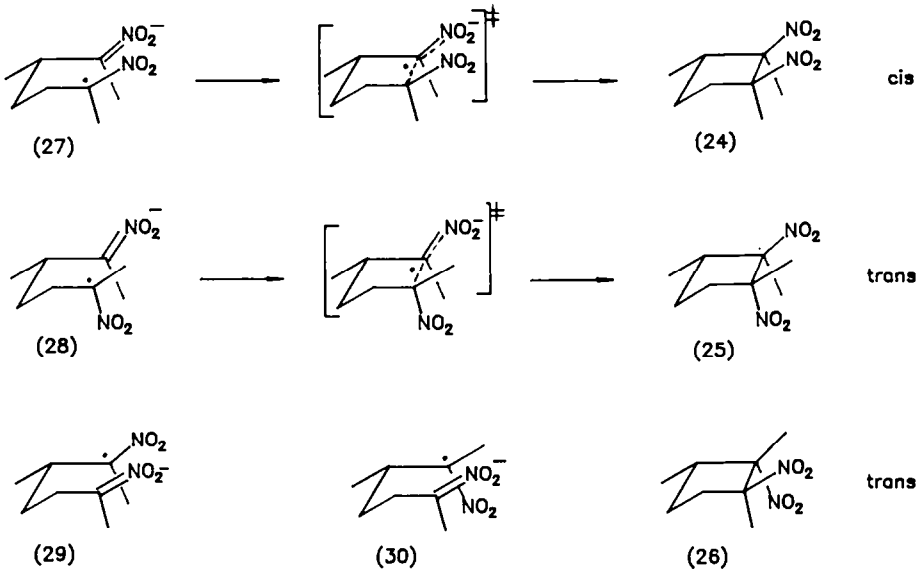
yield. Analysis of the mixture of isomers using ^{1}H NMR spectroscopy showed a ratio of 40:60 for the *cis:trans* ratio of (21):(22). The other isomer (23) was observed in less than 5%. Similarly, the cyclisation of (4) gave exclusively only two of the possible four diastereoisomers, in 93% yield with a *cis:trans* ratio [(24):(25)] of 50:50. The observed stereoselectivity can be explained by proposing transition states for cyclisation *via* radical anions (as exemplified in Scheme 2) akin to those proposed by Beckwith and co-workers[3,20] for the cyclisation of hex-5-en-1-yl radicals (Scheme 4). We have assumed that the nitronate double bond behaves similarly to an alkene in radical cyclisations. The cyclisation of the dinitronate dianion of (3), using the Beckwith model, is shown in Scheme 4. The dianion is oxidised to yield an intermediate radical anion which has four possible conformations, (15)-(18). Cyclisation *via* transition states which have "cyclohexane-chain" conformations with the 4-methyl in an equatorial position, (19) and (20), will be favoured over those with the 4-methyl axial, thereby giving largely (21) and (22), and not (23), as products. Cyclisation *via* a transition state from the radical anion (18) would yield (22).

SCHEME 4: BECKWITH MODEL FOR THE RADICAL ANION CYCLISATION OF (3)



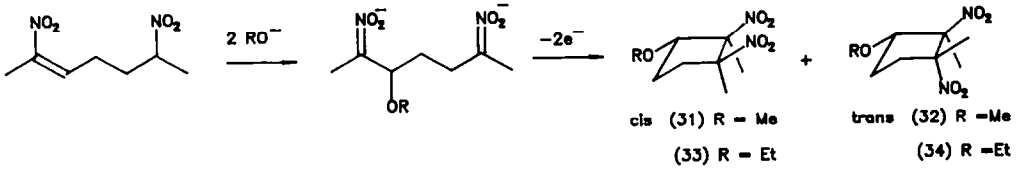
Using our interpretation above of the Beckwith model for the oxidative cyclisation of the dinitronate anion of 2,6-dinitro-3-methylheptane (4); three diastereoisomers, (24), (25) and (26), are predicted as products (Scheme 5). Only (24) and (25), formed *via* transition states from the radical anion conformations, (27) and (28), were observed. Products formed *via* transition states from (29) and (30) should also be formed because the rate of oxidation of the two different nitronates should be similar [(29) would give the product (24), but (30) would yield (26)]. Transition states with the 3-methyl in an axial conformation have been excluded, but some would yield the same products as observed. The absence of products resulting from (30) [and possibly (29)] is probably explained by assuming that some extra minor steric effect also controls the stereoselectivity.[10]

SCHEME 5:



Further evidence for the above conclusions is given by the oxidative cyclisation of the 3-alkoxy-2,6-dinitroheptanes, (5) and (6), which also only yield the two analogous diastereoisomers (equation 1) [R = OMe (66%); *cis* (31):*trans* (32) = 55:45, and R = OEt (72%); *cis*(33):*trans* (34) = 50:50]. The dianions of (5) and (6) were generated *in situ* by addition of methoxide and ethoxide respectively to 2,6-dinitrohept-2-ene. We propose that the stereoselectivity observed in these oxidative cyclisations is explained by our use of the Beckwith model for the radical anion intermediate and would not be observed in a diradical mechanism.

(1)

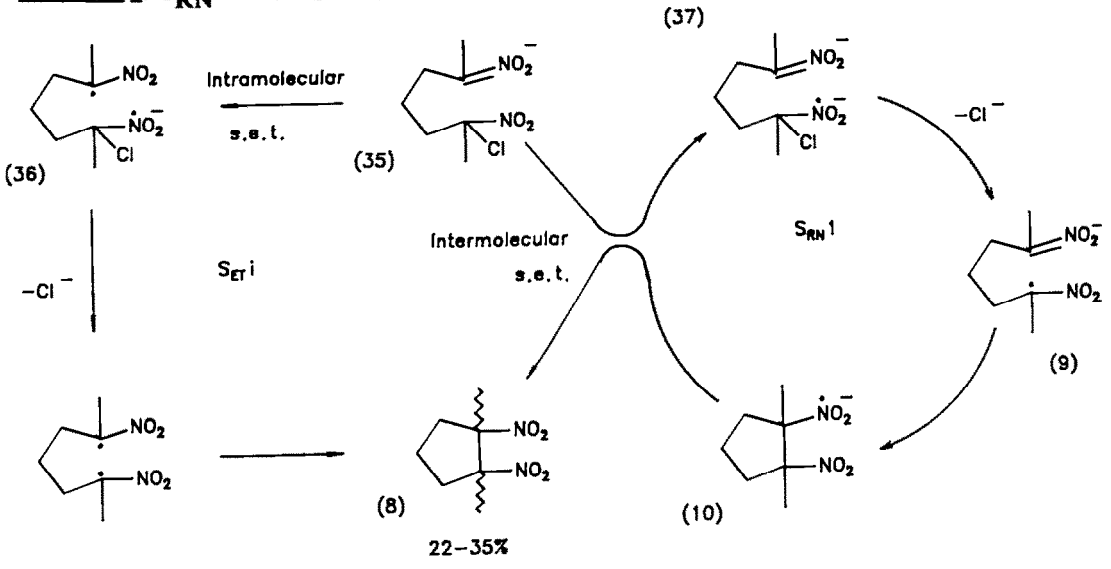


$S_{RN}1$ cyclisation

The key step in the oxidative cyclisation (Route A, Scheme 3), intra-molecular addition of a nitronate to an α-nitroalkyl radical, is the same step that would be required for an intramolecular $S_{RN}1$ reaction [(9) to (10) in Scheme 6]. To this aim the anion of 2-chloro-2,6-dinitroheptane (35) was photolysed under conditions favouring $S_{RN}1$ reactions to give the expected dinitrocyclopentane (8) (22-35%). The *cis:trans* ratio (60:40) was the same as that observed as for the oxidative cyclisation, indicating a similar transition state of cyclisation. Normal diagnostic methods[1] for the radical-chain $S_{RN}1$ mechanism indicated a chain

mechanism ($S_{RN}1$) rather than a non-chain $S_{ET}i$ mechanism (substitution, electron transfer, intramolecular)[1,7,21] as shown in Scheme 6. Slight inhibition was observed (18% yield) with a strong electron acceptor (p-dinitrobenzene) and complete inhibition when carried in the absence of light and under an atmosphere of oxygen in place of nitrogen. The intramolecular s.e.t. from (35) to yield the diradical anion species (36) in the non-chain $S_{ET}i$ mechanism appears to be slower than the bimolecular s.e.t. to yield the radical dianion (37) in the chain $S_{RN}1$ mechanism (Scheme 6).

SCHEME 6: $S_{RN}1$ CYCLISATION



Determination of the structure of the products

The stereochemistry of the products was assigned using high resolution NMR spectroscopy, including COSY, $^{13}C/^{1}H$ Shift Correlation, and NOESY techniques. A brief summary of NMR spectroscopic data is presented in the experimental. The assignment of symmetrical *cis*-dinitrocyclopentanes, (12) and (21), were obvious. The methyls in the *trans* compounds were shifted downfield by the adjacent nitro groups as compared to the *cis* diastereoisomers, allowing assignment of the dimethyl-dinitro portion of the molecules. The downfield shift in the ^{1}H NMR spectra due to deshielding of hydrogen(s) by adjacent *cis* nitro group(s) was particularly helpful in assigning the equatorial nature of 3-substituents. X-Ray crystallography[22] was used to assign the structures (21) and (22).

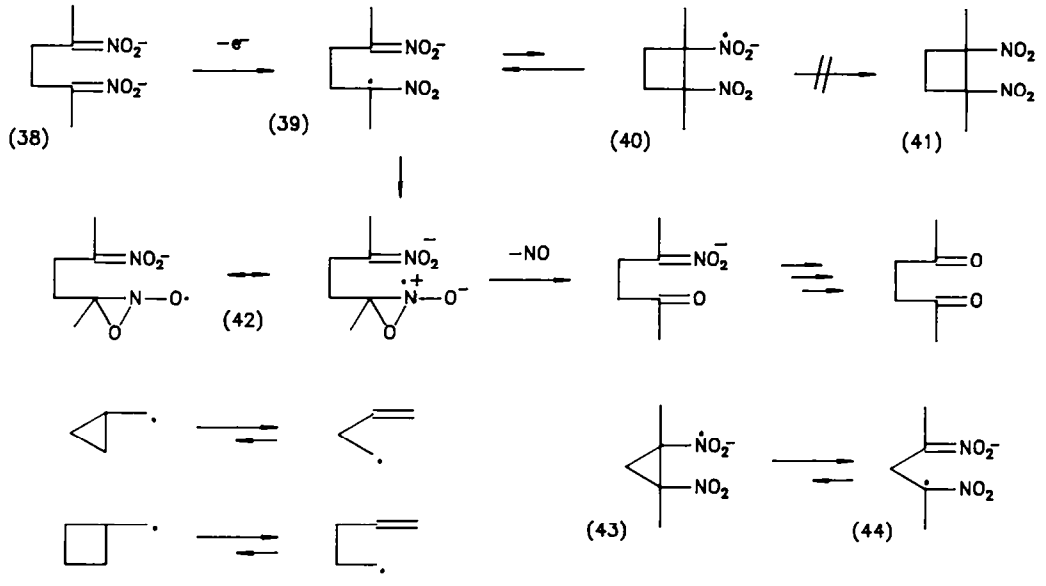
Attempted cyclisations of 1,3- and 1,4-dinitronate dianions

The dinitronate dianion of 2,4-dinitropentane was prepared from sodium hydroxide (standard procedure), sodium methoxide, or dimsyl sodium[7] and oxidised with $K_3Fe(CN)_6$. All three reactions gave low yields of intractable material and not any 1,2-dimethyl-1,2-dinitrocyclopropane. The successful oxidative cyclisation[7] of the dianion of 2,4-dinitropentane using iodine in DMSO is reported to proceed *via* initial iodination to yield the 4-nitronate of 2,4-dinitro-2-iodopentane which then cyclises *via* a di-(α-nitroalkyl)

diradical by a $S_{ET}i$ mechanism, analogous to that shown in Scheme 6. The $S_{ET}i$ mechanism has also been proposed[21] for the 1,3-cyclisation of the anions of (3-chloro-3-nitro)-esters, -ketones, and -nitriles.

The dinitronate dianion of 2,5-dinitrohexane (**38**) gave hexan-2,5-dione in 50% yield and no products from oxidative cyclisation [*e.g.* (**41**)]. An oxidative cyclisation using $K_3Fe(CN)_6$ of a 1,4-dinitronate dianion has been reported[8] for a very favourably constrained 1,3-bishomocubyl ring system, which indicates that 1,4-oxidative cyclisation only takes place when sterically favoured. We have observed[23] that α-nitroalkyl radicals (in the absence of oxygen) rearrange to ketones when competing reactions/reagents are not present. A nitroxide type radical [*e.g.* (**42**)] has been proposed[23,24] to explain the rearrangement of α-nitroalkyl radicals to ketones. Therefore, because cyclisation of the radical anion (**39**) to the dinitro-cyclobutane radical anion (**41**) is unfavoured, rearrangement *via* (**42**) takes place to eventually yield hexan-2,5-dione. A mechanism *via* cyclisation of the nitronate oxygen onto the radical centre in (**39**) would yield a 6-membered ring nitronic ester which could hydrolyse to hexan-2,5-dione, should also be considered.

SCHEME 7



We suggest that the failure of 1,3- and 1,4-cyclisation *via* the radical anions, (**43**/**44**) and (**40**/**39**) respectively, is explained by comparison with the analogous pent-1-en-5-yl and but-1-en-4-yl radicals[3,4] (Scheme 7). Ring opening is much faster than cyclisation for 3- and 4-membered rings and cyclisation is strongly favoured for 5- and 6-membered rings. Therefore, the well-known alkenyl alkyl radical cyclisations[3,4] provide good models for cyclisation of α,ω-dinitro radical anions and explain both the propensity for cyclisation and the stereoselectivity.

Acknowledgements

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EXPERIMENTAL

General Procedures

60 MHz ^{1}H- and ^{13}C-NMR spectra were recorded with a Varian EM360A and a Bruker WP-80 (80 MHz) spectrometer, respectively, and 400 MHz ^{1}H- and ^{13}C-NMR spectra (cyclisation products) with a Bruker AMX400 spectrometer. NMR spectra were carried out in $CDCl_3$ with TMS as internal standard. IR spectra were recorded with a Pye PU 9516 spectrometer. Flash sinter chromatography was carried out using May and Baker Sorbsil C60 (40-60H microns) silica gel using light petroleum (b.p. 40-60°C) and ethyl acetate as eluants. Solvents were dried and purified by standard procedures. Pure compounds not submitted for combustion analysis were homogeneous on two t.l.c. systems and showed no impurities by ^{1}H NMR spectroscopy. 2,4-Dinitropentane was prepared by Michael addition of nitroethane to 2-nitropropene by the reported procedure[7,12] to give two diastereoisomers.

2,6-Dinitroheptane

(a) **4-Nitropentanal: General procedure for Michael and Henry reactions**: The literature procedures were used for the Michael additions[12] (acrolein and nitroethane) and for the Henry reactions[12,13] (4-nitropentanal and nitroethane), except that CH_2Cl_2 was used as a solvent, to yield 4-nitropentanal (29%) and 2,6-dinitroheptan-3-ol (89%) respectively. 2,6-Dinitroheptan-3-ol was also prepared directly from nitroethane (5 molar excess) and acrolein using the same procedure for 17 h in 39% yield.

(b) **2,6-Dinitrohept-2-ene: General procedure for dehydrations**: Triethylamine (Et_3N) (3.25 mol. equiv.) was added dropwise to a solution of 2,6-dinitroheptan-3-ol (16.00 g, 77.6 mmol) and methanesulphonyl chloride (12.53 g, 1.4 mol equiv.) in CH_2Cl_2 (160 ml) at reflux. After the addition, the solution was cooled and washed with water, 2M hydrochloric acid, and brine. The CH_2Cl_2 solution was dried and evaporated to yield almost pure 2,6-dinitrohept-2-ene (11.73 g, 80%); IR 1546 and 1336 cm^{-1}; δ_H 1.60 (3 H, d, MeCHNO$_2$), 2.17 (3 H, s, MeC=C), 1.90-2.90 (4 H, m, CH_2CH_2), 5.00 (1 H, m, $CHNO_2$), and 7.05 (1 H, t, CH=C).

(c) **2,6-Dinitroheptane: General procedure for reduction of nitroalkenes**: Crude 2,6-dinitrohept-2-ene (11.23 g) was dissolved in dry dioxan (100 ml) and added dropwise to a solution of sodium borohydride (9.28 g, 4 mol. equiv.) in dry dioxan/dry ethanol (100:30) at 0°C. The suspension was stirred for 1 h, acidified with hydroxylamine hydrochloride, and the excess borohydride destroyed by careful addition of 50% aqueous acetic acid. The organic solvents were removed by evaporation and the residual aqueous solution extracted with dichloromethane. The CH_2Cl_2 extracts were dried and evaporated to dryness to yield crude 2,6-dinitroheptane (9.10 g). Flash chromatography gave pure 2,6-

dinitroheptane (7.55 g, 61%); IR 1546 and 1360 cm^{-1}; δ_H 1.52 (6 H, 2xd, Me), 1.00-2.40 (6 H, m, CH_2), and 4.61 (2 H, sextet, C<u>H</u>NO_2). ^1H NMR spectroscopy and TLC indicated two diastereoisomers.

2,6-Dinitro-octane

The procedure for Henry reactions was used with 1-nitropropane and 4-nitropentanal for 24 h to yield virtually pure 2,6-dinitro-octan-5-ol (57%); δ_H 0.95 (3 H, t, <u>Me</u>CH_2), 1.56 (3 H, d, <u>Me</u>CHNO_2), 1.20-2.85 (6 H, m, CH_2), 3.35 (1 H, brs, O<u>H</u>), 3.75-5.00 (3 H, m, C<u>H</u>NO_2 and C<u>H</u>OH). Dehydration using the general procedure gave 2,6-dinitro-oct-5-ene which was reduced without purification. The crude 2,6-dinitro-octane was treated with a solution of bromine in CH_2Cl_2 to remove 2,6-dinitro-oct-4-ene. Flash sinter chromatography gave pure 2,6-dinitro-octane (16% from the nitroalcohol); δ_H 0.94 (3 H, t, C<u>H</u>$_3CH_2$), 1.55 (3 H, d, <u>Me</u>CHNO_2), 1.15-2.35 (8 H, m, CH_2), 4.55 (2 H, m, $CHNO_2$).

2,6-Dinitro-4-methylheptane

The general procedures were used to prepare:

(a) **2-methyl-4-nitropentanal**: (Methacrolein in place of acrolein) (82%).

(b) **2,6-Dinitro-4-methylheptan-3-ol**: (30 h reaction time, four diastereoisomers); 90% yield; δ_H 0.75-1.30 (3 H, m, Me), 1.35-1.70 (3 H, m, <u>Me</u>CHNO_2), 1.30-2.25 (3 H, m, CH_2CH), 3.00-3.45 (1 H, brs, OH), 3.55-4.35 (1 H, brs, C<u>H</u>OH), and 4.35-5.10 (2 H, m, $CHNO_2$).

(c) **2,6-dinitro-4-methylheptane**: The alcohol was dehydrated to yield crude 2,6-dinitro-4-methylhept-2-ene; δ_H 6.92 (1 H, d, C<u>H</u>=CNO_2); with no impurities of the 3-ene. The crude olefin was immediately reduced to yield the crude heptane. Purification using flash sinter chromatography gave pure 2,6-dinitro-4-methylheptane as a mixture of 4 diastereoisomers (43% from the alcohol); IR 1548 and 1358 cm^{-1}; δ_H 0.85-1.15 (3 H, m, <u>Me</u>CH), 1.52 and 1.54 (6 H, dd, <u>Me</u>CHNO_2), 1.15-2.35 (5 H, m, CH_2CHCH_2), and 4.40-5.05 (2 H, m, C<u>H</u>NO_2).

2,6-Dinitro-3-methylheptane

(a) **2,6-Dinitro-5-methylheptan-3-ol** was prepared directly as follows: Nitroethane (4.39 g, 4.1 mol. equiv.) was added to a solution of lithium (365 mg) in dry MeOH (30 ml). Crotonaldehyde (1.00 g, 14.3 mmol) was added, the reaction stirred for 5 min, acidified with 50% aqueous acetic acid, and extracted with CH_2Cl_2. The organic extracts were washed with water, dried and evaporated to dryness to yield crude 2,6-dinitro-5-methylheptan-3-ol (1.98 g, 63%); δ_H 1.03 (3 H, d, Me), 1.55 (6 H, dd, <u>Me</u>CHNO_2), 1.20-2.90 (3 H, m, $CHCH_2$), 3.28 (1 H, brs, O<u>H</u>), 3.70-5.00 (3 H, m, $CHNO_2$ and C<u>H</u>OH).

(b) **2,6-Dinitro-3-methylheptane** (Four diastereoisomers): 2,6-Dinitro-5-methylhept-2-ene was prepared from the nitroalcohol using the general procedure, and reduced immediately. The crude product was purified using flash sinter chromatography to give pure 2,6-dinitro-3-methylheptane (54% from nitroalcohol); δ_H 0.97 (3 H, m, Me), 1.49, 1.51 and 1.56 (6 H, 4xd, <u>Me</u>CHNO_2), 1.10-2.70 (5 H, $CHCH_2CH_2$), 4.54 and 4.59 (1 H, m, C<u>H</u>NO_2); δ_C 1.32, 14.44, 14.99, 15.77, 15.91, 15.96, 19.12, 19.30, 19.48 (Me), 28.22, 29.25, 32.16, 32.29, 32.47 (CH_2), 37.26, 37.40 (CH), 83.44, 87.15, 87.53 and 87.45 ppm (<u>C</u>HNO_2).

General procedure for oxidative cyclisation of 2,6-dinitroalkanes

The reaction was carried out under an atmosphere of nitrogen. The 2,6-dinitroalkane (2-4 mmol) was added to a solution of sodium methoxide (3 mol. equiv. of sodium) in MeOH (5-10 ml) to form the dianion. H_2O (10-15 ml) and diethyl ether (25-50 ml) were added, the reaction stirred for 5 min, and a saturated aqueous solution of $K_3Fe(CN)_6$ (5 mol. equiv.) was added. The two phase mixture was stirred for 20 min, extracted with diethyl ether, and the ether fractions dried and evaporated to dryness to yield oils of virtually pure dinitrocyclopentanes. Diastereoisomers were separated by flash sinter chromatography.

(a) **1,2-Dimethyl-1,2-dinitrocyclopentane** (71-85%): ***cis*-Diastereoisomer (11)**; m.p. 110°C (d) (EtOH/H_2O); (Found: C, 44.5; H, 6.4; N, 14.7. $C_7H_{12}N_2O_4$ requires C, 44.7; H, 6.4; N, 14.9%); IR 1550 and 1348 cm^{-1}; δ_H 1.60 (3 H, s, Me), 2.25 (4 H, m, 4-H_2, 3-H and 5-H *trans* to NO_2), and 2.69 (2 H, m, 3-H and 5-H *cis* to NO_2); δ_C 20.42 (Me), 21.51, 37.23 (CH_2), and 97.40 ppm (CNO_2). ***trans*-Diastereoisomer (12)**; m.p. 70°C d (light petroleum, b.p. 40-60°C); (Found: C, 44.5; H, 6.5; N, 14.7%); IR 1546 and 1357 cm^{-1}; δ_H 1.83, 2.02 (2 H, m, 4-H_2), 1.84 (3 H, s, Me), 2.18 (2 H, ddd, 3-H and 5-H *trans* to NO_2), and 2.87 (2 H, ddd, 3-H and 5-H *cis* to NO_2); δ_C 17.76, 36.58 (CH_2), 22.62 (Me), and 96.59 ppm (CNO_2).

(b) **1,2-Dinitro-1-ethyl-1-methylcyclopentane** (85%): ***cis*-Diastereoisomer (13)**; m.p. 32-33°C (EtOH/H_2O); (Found: C, 47.49; H, 6.76; N, 13.60. $C_8H_{14}N_2O_4$ requires C, 47.52; H, 6.98; N, 13.85%); δ_H 0.99 (3 H, t, CH_2Me), 1.43 (1 H, sextet, MeC$\underline{H}^1$), 1.60 (3 H, s, $MeCNO_2$), 2.06-2.24 (4 H, m, 4-H_2, 3-H and 5-H *trans* to NO_2), 2.37 (1 H, sextet, MeC$\underline{H}^2$), and 2.67-2.78 (2 H, m, 3-H and 5-H *cis* to NO_2); δ_C 8.79 ($\underline{Me}CH_2$), 21.11 ($MeCNO_2$), 21.65 (4-C), 26.93 ($\underline{C}H_2Me$), 33.48, 37.52 (3,5-C), 98.47, and 103.19 ppm (CNO_2). ***trans*-Diastereoisomer (14)**; an oil; (Found: C, 47.50; H, 7.03; N, 13.78%); δ_H 0.94 (3 H, t, $CH_2\underline{Me}$), 1.66-1.81 (2 H, m, 4-H *trans* to 2-NO_2, MeC$\underline{H}^1$), 1.87 (3 H, s, $MeCNO_2$), 2.00-2.10 (2 H, m, 4-H *trans* to 2-NO_2, 5-H *cis* to 2-NO_2), 2.18 (1 H, ddd, 3-H *trans* to 2-NO_2), 2.37 (1 H, sextet, MeC$\underline{H}^2$), 2.65 (1 H, m, 5-H *cis* to 2-NO_2), and 2.95 (1 H, m, 3-H *cis* to 2-NO_2); δ_C 8.24 ($\underline{Me}CH_2$), 18.17 (4-C), 20.99 ($MeCNO_2$), 28.79 ($\underline{C}H_2Me$), 30.61 (3-C), 36.93 (5-C), 98.24, and 100.30 (CNO_2).

(c) **1,2-Dinitro-1,2,4-trimethylcyclopentane** (90%). ***cis*-Diastereoisomer (21)**; m.p. 42-42.5°C (EtOH/H_2O); (Found: C, 47.51; H, 7.05; N, 13.89. $C_8H_{14}N_2O_4$ requires C, 47.52; H, 6.98; N, 13.85%); δ_H 1.14 (3 H, d, CH$\underline{Me}$), 1.81 (6 H, s, $MeCNO_2$), 2.29 (3 H, m, 4-H, 3,5-H *trans* to NO_2), and 2.57 (2 H, m, 3,5-H *cis* to NO_2); δ_C 20.59, 23.49 (Me), 27.60 (CH), 45.44 (CH_2), and 98.29 ppm (NO_2). ***trans*-Diastereoisomer (22)**; m.p. 36-37°C (EtOH/H_2O); (Found: C, 47.46; H, 7.10; N, 13.75%); δ_H 1.26 (3 H, d, CH$\underline{Me}$), 1.61, 1.63 (6 H, $MeCNO_2$), 1.82 (1 H, dd, 3-H *trans* to 2-NO_2), 3.33 (1 H, dd, 5-H *cis* to 2-NO_2), 2.50 (1 H, dd, 5-H *trans* to 2-NO_2), 2.69 (1 H, m, 4-H), and 2.88 (1 H, dd, 3-H *cis* to 2-NO_2); δ_C 20.11 (C_4-$\underline{Me}$), 21.79, 22.37 ($MeCNO_2$), 30.36 (4-C), 45.49 (5-C), 45.77 (3-C), 98.08, and 98.24 ppm (CNO_2).

(d) **1,2-Dinitro-1,2,3-trimethylcyclopentane** (91%): ***cis*-Diastereoisomer (24)**; m.p. 110.5-111.4°C (EtOH/H_2O); (Found: C, 47.51; H, 7.10; N, 13.75. $C_8H_{14}N_2O_4$ requires C, 47.52; H, 6.98, N, 13.85%); δ_H 1.03 (3 H, d, CH$\underline{Me}$), 1.49, 1.71 (6 H, 2s, $MeCNO_2$), 1.59 (1 H, m, 4-H *trans* to NO_2), 2.00-2.15 (2 H, m, 4-H *cis* to NO_2, 5-H *trans* to NO_2), 2.93 (1 H, m, 5-H *cis* to NO_2), and 3.21 (1 H, m, 3-H); δ_C 14.15 C_3-$\underline{Me}$), 15.79 (C_2-$\underline{Me}$), 24.53 (C_1-$\underline{Me}$), 27.23 (4-C), 34.34 (5-C), 40.27 (3-C), 96.97, and 97.63 ppm (CNO_2). ***trans*-Diastereoisomer (25)**; m.p. 103.5-104.5°C (light petroleum, b.p. 80-100°C); (Found: C, 47.52; H, 6.82; N, 13.73%); δ_H 1.14 (3 H, d, CH$\underline{Me}$), 1.62, 1.83 (6 H, 2s, $MeCNO_2$), 1.38 (1 H, m, 4-H *cis* to 2-NO_2), 1.99 (1 H, ddd, 5-H *cis* to 2-NO_2), 2.26 (1 H, m, 4-H *trans* to 2-NO_2), 2.77 (1 H, ddd, 5-H *trans* to 2-NO_2),

and 3.24 (1 H, m, 3-H); δ_C 15.12 (C_3-Me), 18.18, 21.76 ($MeCNO_2$), 27.80 (4-C), 35.30 (5-C), 39.62 (3-C), 96.93, and 99.29 ppm (CNO_2).

(e) **1,2-Dimethyl-3-methoxy-1,2-dinitrocyclopentane** (66%): 2,6-Dinitrohept-2-ene (1.06 g, 5.64 mmol) in MeOH (20 ml) was added dropwise to a solution of NaOMe in MeOH (20 ml) and stirred for 10 min. The resulting dianion was reacted using the general procedure for oxidative cyclisation. ***cis*-Diastereoisomer (31)**; (Found: C, 44.12; H, 6.44; N, 12.65. $C_8H_{14}N_2O_5$ requires C, 44.04; H, 6.49; N, 12.84%); δ_H 1.59, 1.73 (6 H, 2s, $MeCNO_2$), 1.20-3.30 (4 H, m, CH_2), 3.40 (3 H, s, OMe), and 4.55-5.00 (1 H, t, CHOMe). ***trans*-Diastereoisomer (32,)**; (Found: C, 44.16; H, 6.49; N, 12.90%); δ_H 1.75, 1.84 (6 H, 2s, $MeCNO_2$), 1.00-3.00 (4 H, m, CH_2), 3.46 (3 H, s, OMe), and 4.45-4.80 (1 H, m, CHOMe).

(f) **1,2-Dimethyl-1,2-dinitro-3-ethoxycyclopentane** (72%): The preparation was carried out as above with NaOEt in place of NaOMe. ***cis*-Diastereoisomer (33)**; (Found: C, 44.67; H, 6.94; N, 11.90. $C_9H_{16}N_2O_5$ requires C, 46.55; H, 6.94; N, 12.06%); δ_H 1.15 (3 H,t, CH_2Me), 1.58, 1.70 (6 H, 2s, $MeCNO_2$), 1.50-3.30 (4 H, m, CH_2CH_2), 3.51 (2 H, q, OCH_2), and 4.80 (1 H, t, CHOEt). ***trans*-Diastereoisomer (34)**; (Found: C, 46.61, H, 6.92; N, 11.93%); δ_H 1.20 (3 H, t, CH_2Me), 1.77, 1.84 (6 H, 2s, $MeCNO_2$), 1.45-3.15 (4 H, m, CH_2CH_2), 3.63 (2 H, q, OCH_2), and 4.50-4.85 (1 H, dd, CHOEt).

2-Chloro-2,6-dinitroheptane

2,6-Dinitroheptane (1.19 g) was converted to the dianion with sodium methoxide (3 equiv.) in dry methanol and treated with N-chlorosuccinimide (1.1 equiv.) for 30 min. Water was added and extracted with CH_2Cl_2 to remove 2,6-dichloro-2,6-dinitroheptane. The aqueous layer was acidified with hydroxylamine hydrochloride and extracted with CH_2Cl_2. The CH_2Cl_2 solution was dried and evaporated to an oil which was treated with Girards Reagent P to remove 6-chloro-6-nitroheptan-2-one. Flash sinter chromatography gave pure 2-chloro-2,6-dinitroheptane as two diastereoisomers (640 mg); IR 1548, 1358 and 1340 cm^{-1}; δ_H 1.53 (3 H, d, $MeCHNO_2$), 2.12 and 2.15 (3 H, 2xs, MeCCl), 1.20-2.80 (6 H, m, CH_2), and 4.60 (1 H, sextet, $CHNO_2$).

$S_{RN}1$ cyclisation using 2-chloro-2,6-dinitroheptane

2-Chloro-2,6-dinitroheptane (114 mg, 0.5 mmol) was dissolved in a solution of NaOMe (3 mol. equiv.) in dry MeOH. The MeOH was removed, dimethylformamide (20 ml) added and the solution irradiated under nitrogen for 2 h with fluorescent lamps (2 x 150 W, mercury blended tungsten universal mounted, emitting maximally at 430 nm). The reaction mixture was poured into water and extracted with diethyl ether (3 x 40 ml). The ether extracts washed with H_2O (7x), dried, and evaporated to dryness. The amount of 1,2-dimethyl-1,2-dinitrocyclopentane was measured using ^1H NMR spectroscopy with p-dimethoxybenzene as an internal standard to give yields of 22, 35 and 37% in separate runs. The reaction was repeated: a. with 25 mol.% p-dinitrobenzene (18%); b. in air, with exclusion of light (10%); c. under oxygen, with exclusion of light (0%).

2,5-Dinitrohexane

5-Nitrohexan-2-one was prepared as reported[12] and converted to the oxime using hydroxylamine hydrochloride in sodium carbonate solution. The oxime was treated with chlorine[25] to give a high yield of a

crude blue liquid of 2-chloro-2-nitroso-5-nitrohexane; IR 1584, 1548, and 1360 cm^{-1}; δ_H 1.58 (3 H, d, MeCHNO$_2$), 1.86 (3 H, s, MeCCl); 1.70-2.85 (4 H, m, CH_2), and 4.60 (1 H, sextet, $CHNO_2$). The nitroso-compound was immediately oxidised with ozone[25] to yield 2-chloro-2,5-dinitrohexane; b.p. 120-125°C/0.5 mm; IR 1548, 1360, and 1242 cm^{-1}; δ_H 1.61 (3 H, s, MeCHNO$_2$), 2.16 (3 H, s, MeCCl), 1.75-2.80 (4 H, m, CH_2), and 4.67 (1 H, sextet, $CHNO_2$). Reduction[26] of the chloronitro compound with dihydrobenzylnicotinamide and purification using flash sinter chromatography gave 2,5-dinitrohexane; δ_H 1.59 (3 H, d, Me), 1.75-2.50 (4 H, m CH_2), and 4.30-4.95 (2 H, m, $CHNO_2$).

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