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THE STEREOCHEMISTRY OF THE $S_{RN}1$ REACTION IN SOME CYCLOHEXANE DERIVATIVES

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Abstract—The substitution reactions of nitrocyclohexanes **8**, **9**, **12** and **23** with various nucleophiles were studied and were found to proceed by the electron-transfer initiated $S_{RN}1$ mechanism. Epimeric products were formed and the proportion of epimers under both thermodynamic and kinetic control normally reflected the bulk of the incoming nucleophile relative to the substituent which was present at the reaction site. In the reaction of **23** with relatively high concentrations of PhS^- in HMPA the reaction proceeded with high stereoretention. The results of these reactions are discussed in terms of the stability of radical configuration and the rate and mode of radical anion dissociations and associations.

Electron transfer processes play a key role in the free-radical nucleophilic substitution reaction, whose initiation and propagation steps are given in generalized form in eqns (1)–(4). This reaction, which has been given the designation $S_{RN}1$,[1] readily occurs at saturated carbons which bear a nucleofuge and in addition, nitro[2,3]

$$RX + e \longrightarrow [RX]^{-\cdot} \quad (1)$$

$$[RX]^{-\cdot} \longrightarrow R^{\cdot} + X^- \quad (2)$$

$$R^{\cdot} + A^- \longrightarrow [RA]^{-\cdot} \quad (3)$$

$$[RA]^{-\cdot} + RX \longrightarrow [RX]^{-\cdot} + RA \quad (4)$$

or a *p*-nitrophenyl group.[2]

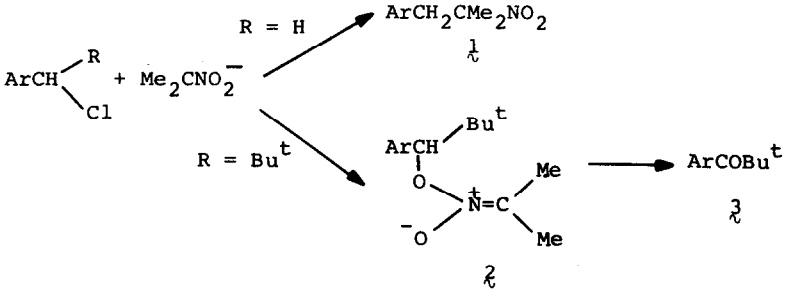
We have been interested in the stereochemical features of this reaction. For example we have found that steric factors may influence the regiochemistry of the association step (3). Thus the reaction of *p*-nitrobenzyl chloride with 2-nitro-2-propanide ion gives the *C*-alkylate (**1**),[2] whereas the α-t-Bu analogue (a neopentyl derivative) gives the *O*-alkylate (**2**), which subsequently yields the ketone (**3**),[4] as shown in Scheme 1.[a]

We decided to investigate the stereochemistry of the $S_{RN}1$ reaction at saturated carbon in some conformationally fixed cyclohexane derivatives, i.e. R· in eqns (1)–(4) would be a substituted cyclohexyl radical. Determination of the stereochemistry and hence relative proportion of the products formed in such reactions would give the relative importance of axial and equatorial attack by anions on the intermediate cyclohexyl radical(s) in the association step (3). A further point of interest is the nature of the intermediate cyclohexyl radical.

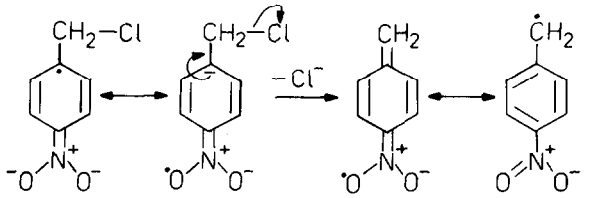
Cyclohexyl radicals are normally considered to be effectively planar. Thus a large body of experimental data, both EPR and product studies, indicate that cyclohexyl radicals are either planar or exist in non-planar conformations in which the energy barrier to inversion at the radical site is quite small.[5–7] The latter proposal has been supported by *ab inito* calculations,[8] which further confirmed the tendency of electron withdrawing substituents at the radical site to increase the degree of nonplanarity of cyclohexyl radicals. The cyclohexyl radicals involved in $S_{RN}1$ processes will have a nitro group or a *p*-nitrophenyl group attached to the radical site. As a consequence, particularly in the latter case where the radical is also benzylic, the conformation of the intermediate radicals will be subject to two opposing influences, an electronegativity effect and a conjugative effect.

The radical intermediates in *p*-nitrobenzylic substrates are normally assumed to be planar[2] and this appears to follow from the representation of the dissociation of the radical anions of both *p*-nitrobenzyl[2] and *p*-methoxycarbonylbenzyl[9] derivatives as essentially an elimination process.[2] The representation for the dissociation of the radical anion of *p*-nitrobenzyl chloride is given in eqn (5).[2] Indeed, evidence which appears to support formation of a planar intermediate benzylic radical has been presented. Optically active **4** gives racemic products **5** when treated with azide, benzenesulfinate, ben-

[a]In this scheme and elsewhere in this paper the abbreviation Ar stands specifically for the p-$O_2NC_6H_4$ moiety.



Scheme 1.



(5)

zenethiolate and 2-nitro-2-propanide ions.[10] These experiments need not be definitive however, since with certain anions ($A^- = NO_2^-$, N_3^-, $PhSO_2^-$), which have been shown to be nucleofuges under $S_{RN}1$ conditions,[2] the reactions will be readily reversible. If the rate of collapse of an initially formed pyramidal radical, which would give

$$\underset{\text{NO}_2}{\overset{|}{\text{ArCMeEt}}} + A^- \longrightarrow \underset{\text{A}}{\overset{|}{\text{ArCMeEt}}} + NO_2^-$$

4 **5**

products with retained configuration, to an effectively planar radical, which would give racemized products, were in the same order as the rate of radical-anion association, each successive replacement reaction would decrease the proportion of the product with retained configuration. Racemized products would eventually ensue. In cases where the reaction is effectively irreversible ($A^- = PhS^-$, $Me_2CNO_2^-$), the demonstrated ability of the nitrite ion, produced in the course of the reaction, to racemize the starting material **4**,[10] might further negate the validity of the results.

An alternative approach to the radical anion dissociation step, has been invoked by Rossi *et al.*[11] in order to explain the difference in stability (with respect to dissociation) of the radical anion of naphthylacetonitrile, $(NapCH_2CN)^{-\cdot}$, relative to that of phenylacetonitrile $(PhCH_2CN)^{-\cdot}$. One possible explanation for this difference was given in terms of formation of alternative radical anions **6** and **7** wherein the additional electron is accommodated in an antibonding orbital principally associated with the aryl moiety and the nitrile group respectively.

$$^{-\cdot}\text{ArylCH}_2\text{CN} \qquad \text{ArylCH}_2\text{CN}^{-\cdot}$$

6 **7**

The above rationalization suggested to us the possibility that steps (1) and (2) in the general $S_{RN}1$ process might sometimes be replaceable by eqns (6)–(8):

$$RX + e \longrightarrow {}^{-\cdot}R - X\ (\pi^*) \qquad (6)$$

$$^{-\cdot}R - X \longrightarrow R - X^{-\cdot}\ (\sigma^*) \qquad (7)[11]$$

$$R - X^{-\cdot} \longrightarrow R^{\cdot} + X^- \qquad (8)$$

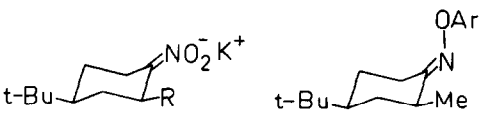
When the work, which is presented in this paper,[12] was nearing completion, a report by Neta and Behar appeared which supported this approach.[13] Thus the formation and dissociation of the radical anions of nitrobenzyl halides is presented in terms of original acceptance of an electron by the nitro group, then an intramolecular electron transfer to the halogen followed by dissociation.

This type of dissociation process might conceivably lead to a pyramidal radical, rather than the planar one expected[2] from descriptions such as that given in eqn (5) and this possibility, together with the consequent possibility of $S_{RN}1$ reactions proceeding with retention of configuration added further impetus to our study in cyclohexyl systems.[14]

RESULTS AND DISCUSSION

The ^1H NMR data and assigned structures (including stereochemistry) for the cyclohexane derivatives **8–30** prepared in this study are collected in Table 1.

The epimeric chloro nitro compounds **8** and **9** were prepared by the standard route,[15,16] *viz* conversion of 4-t-butylcyclohexanone to its oxime followed by chlorination and oxidation with ozone. The epimers were separated by chromatography on silica gel.[17] Reduction of **8** and/or **9** with $NaBH_4$ in ethanol in the presence of 10% Pd/C[17] gave a mixture of *cis* and *trans*-4-t-butyl-1-nitrocyclohexane which was converted to the potassium salt, **31**, with KOH in ethanol. Reaction of **31** with *p*-dinitrobenzene[18] in DMSO gave an 88% yield of **12**. Similarly *cis*-2-methyl-4-t-butylcyclohexanone[20] was converted to potassium salt, **32**, which on reaction with



31 R = H
32 R = Me

33

p-dinitrobenzene gave **23** (24% yield) and the expected by-products **33** (12%) and *p*-nitrophenol.[16]

The reaction of the nitrocyclohexanes **8**, **9**, **12** and **23** with various nucleophiles is collected in Table 2.

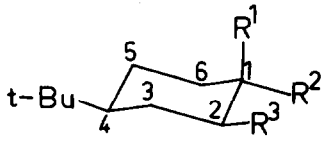
Assignment of stereochemistry

The assignment of stereochemistry at C1 in **8** and **9** (and analogously **10** and **11**) was based on the well-established shielding properties of the nitro group in conformationally fixed cyclohexanes,[21,22] namely that an equatorial nitro group shields vicinal protons whereas an axial nitro group deshields vicinal, equatorial protons. The assignment of the broad downfield doublets in the spectra of **8** and **10** to the equatorial protons on C2 and C6 (i.e. H2e and H6e) was also confirmed by width-at-half-height measurements (see footnote *b*, Table 1).

In the remaining compounds the presence of an aryl substituent at C1 is an added complication, since a phenyl group is expected to display similar characteristics to a nitro group.[22] For example in both **12** and **23**, nitro *and p*-nitrophenyl groups are present at C1.

The problem of assignment of relative stereochemistry at C1 was solved as follows. The reaction of **12** with NaN_3 (Table 2, entry 3) gave a mixture of two azides **13** and **14**. The major isomer, when subjected to the original reaction conditions, gave the same mixture of azides as above, consistent with the previously discussed nucleofugacity of azide in $S_{RN}1$ reactions. The major and minor isomers can be assigned the structures **13** and **14** respectively by three independent arguments. First, the less sterically demanding azido group can be expected to adopt an axial position in the more stable isomer.

Table 1. ^{1}H NMR data and structural assignments for cyclohexane derivatives



Entry	Compound	R_1	R_2	R_3	^{1}H NMR chemical shifts (δ)[a] Bu^t	H $2e_b$, H $6e_b$	Me (R_3)
1	8	NO_2	Cl	H	0.82	3.06	
2	9	Cl	NO_2	H	0.92	—[c]	
3	10	NO_2	CMe_2NO_2	H	0.81	2.68	
4	11	CMe_2NO_2	NO_2	H	0.84	—[c]	
5	12	NO_2	Ar	H	0.87	3.13	
6	13	N_3	Ar	H	0.92	—[c]	
7	14	Ar	N_3	H	0.76	2.65	
8	15	Ar	SO_2Tol	H	0.69	2.65	
9	16	SO_2Tol	Ar	H	0.94	3.10	
10	17	SPh	Ar	H	0.96	—[c]	
11	18	Ar	SPh	H	0.70	2.36	
12	19	SO_2Ph	Ar	H	0.93	3.10	
13	20	Ar	SO_2Ph	H	0.70	2.68	
14	21	Ar	CMe_2NO_2	H	0.67	2.53	
15	22	Ar	$C(CN)_2Et$	H	0.76	2.74	
16	23	NO_2	Ar	Me	0.90	2.84	1.07
17	24	N_3	Ar	Me	0.92	—[c]	0.61
18	25	Ar	SO_2Tol	Me	0.72	—[c]	1.70
19	26	SPh	Ar	Me	0.93	—[c]	0.84
20	27	Ar	SPh	Me	0.74	2.84	
21	28	SO_2Ph	Ar	Me	0.90	2.88	1.59
22	29	Ar	SO_2Ph	Me	0.72	—[c]	1.70
23	30	Ar	$C(CN)_2Et$	Me	0.71	2.72	

[a]At 100 MHz; the remaining protons on the cyclohexane ring and appropriate resonances for protons in groups R^1 and R^2 were also present; a detailed analysis of the 400 MHz spectra of some of these compounds will appear elsewhere. [b]Width at half-height for each component of the broad doublet (J 12-14 Hz) assigned to these protons was in the range 5-8.5 Hz. [c]Unassigned; under cyclohexane envelope δ 1.0-2.5.

Secondly, the major isomer does *not* have a downfield broad doublet (see entries 6 and 7, Table 1) and hence is assigned the structure with an equatorial *p*-nitrophenyl group. Finally, inspection of molecular models of **13** and **14** reveal that only in **14** (axial *p*-nitrophenyl group) is the t-Bu group in the shielding zone of the aromatic ring; the t-Bu resonance in the minor isomer is 0.16 ppm upfield of that in the major.

This latter observation is in fact quite general. Where pairs of epimers were formed, one had a t-Bu group near δ 0.9 and the other had a t-Bu group near δ 0.7 (Table 1). This difference combined with the relative intensity and sharpness of the t-Bu peaks allowed ready identification and estimation of epimers at C1 in the crude reaction mixtures (Table 2). Furthermore axial phenylthio and arenesulfonyl groups do not cause this upfield shift in the t-Bu resonance. The nitro compounds **12** and **23** with t-Bu group at δ 0.87 and 0.90 respectively are readily seen to have equatorial *p*-nitrophenyl groups at C1.

Further confirmatory observations on the relative configurations of groups at C1 can be gleaned from the NMR data in Table 1. The broad doublet attributable to H2e and/or H6e can only be discerned when a *p*-nitrophenyl, nitro or arenesulfonyl group is in an axial position at C1. Consequently oxidation of sulfides **17** and **18** (an inseparable mixture) to the corresponding sulfones **19** and **20** respectively (**17** : **18** = **19** : **20**) produced a downfield doublet in the NMR spectrum of **19** absent in that of **17**.

Mechanism of the substitution reactions

The substitution processes reported in this work can really only be expected to occur by an $S_{RN}1$ mechanism since they involve substitution at tertiary sites bearing electron withdrawing groups and involve normally poor nucleofuges such as NO_2^- and N_3^-. All these factors disfavour S_N1 and S_N2 processes but are typical substrate conditions for $S_{RN}1$ processes.[2,3] Nevertheless inhibition studies were performed.[12] Oxygen completely inhibited the formation of substitution products, e.g. the reactions in Table 2, entries 1, 8, 13 and 15 were com-

Table 2. Epimer ratios and conditions for reactions of **8**, **9**, **12** and **23** with nucleophiles. Unless otherwise stated reactions were performed at 55° in an atmosphere of nitrogen with sunlamp irradiation and substrate (0.5 mmol) in DMSO (10 ml). The epimer ratio was determined by ^{1}H NMR or glc (entries 1 and 2)

Entry	Substrate	Salt[a]	Reaction Time[b]	Ratio of C 1 epimers[c]
1	8	$LiCMe_2NO_2$ (3)	30 min	9:91
2	9	$LiCMe_2NO_2$ (3)	30 min	10:90
3	12	NaN_3 (2-4)	20-25 h	87:13
4	12	$TolSO_2Na$ (4)	24 h	15:85
5	12	PhSNa (4-32)	1-5 h	56:44
6	12	PhSNa (16-32)[d]	<5 min	55:45
7	12	$Bu_4NCMe_2NO_2$ (2)	20-40 min	<5:95[e]
8	12	$Et(CN)_2CNa$ (4-20)	10-30 min	<5:95[e]
9	23	NaN_3 (8)	*c.* 10 d	>95:5[e]
10	23	$TolSO_2Na$ (4)	24 h	<5:95[e]
11	23	PhSNa (4-32)	30-60 min	53:47
12	23	$TolSO_2Na$ (4)[d,f]	24 h	<5:95[e]
13	23	NaN_3 (8)[d]	1 h	>95:5[e]
14	23	$Et(CN)_2CNa$ (20)[d]	20 h	<5:95[e]
15	23	PhSNa (8-32)[d]	<5 min	>95:5[e]
16	23	PhSNa (3)[d,g]	3-4 h	60:40

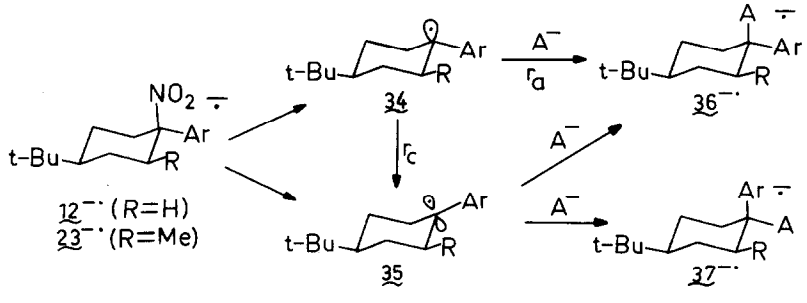
[a]The molar ratio of salt to substrate is given in parenthesis; Tol is *p*-MeC_6H_4. [b]Estimated by TLC; reaction times in excess of five hours may be longer than necessary. [c]Isolated yields for typical reactions are given in the Experimental; the epimer ratio corresponds to the ratio **36** : **37** (Scheme 2), i.e. gives first the epimer in which the nucleophile has assumed an axial position. [d]**23** (0.25 mmol) in HMPA (5 ml). [e]No detectible amount of minor isomer by PLC and NMR. [f]Entrained with $LiCMe_2NO_2$ (0.25 mmol). [g]**23** (0.25 mmol) in HMPA (30 ml).

pletely suppressed when a gentle stream of O_2 was passed through the mixture. *p*-Dinitrobenzene also effectively prevented the reaction of **12** with NaN_3. The reaction time (but *not* the product distribution) for the reaction of **12** with sodium *p*-toluenesulfinate, was reduced to less than one hour (see entry 4, Table 2) in the presence of the lithium salt of 2-nitropropane, well known as an initiator of $S_{RN}1$ reactions.[2]

Stereochemistry of the substitution reactions

The reaction of **8** and **9** with lithium 2-nitropropanide in DMSO (and indeed in a variety of other solvents),[12] gave identical proportions of the *C*-alkylates **10** and **11**, with the former product greatly predominating (Table 2, entries 1 and 2). Clearly the same effectively planar radical intermediate is involved in both cases and the less sterically hindered product **10**, in which the CMe_2NO_2 group is equatorial, is formed.

In the case of reactions of **12** and **23**, the corresponding epimers at C1 were not synthetically available and the following approach was adopted. The possible reaction pathways relating the radical anions $\mathbf{12}^{-\cdot}$ and $\mathbf{23}^{-\cdot}$, the pyramidal radical **34**, effectively planar radical **35** and the radical anions of the two possible epimeric products **36** and **37** are given is Scheme 2. If the pyramidal radical **34** is produced, the ratio **36** : **37** may vary with the concentration of the nucleophile A^-. This would be a



Scheme 2.

result of the rate of conversion of **34** into **35** being a unimolecular process (rate of collapse, $r_c \alpha [34]$), independent of $[A^-]$, whereas the rate of association of the radical **34** with anion A^- is dependent on the concentration of the latter ($r_a \alpha [34][A^-]$). Clearly if $r_c \gg r_a$ product ratio **36**:**37** will be effectively independent of $[A^-]$.

The reactions involving azide and *p*-toluenesulfinate are reversible (see above) and the ratio of products from these reactions merely reflect the relative stabilities of general products **36** and **37**. Inspection of the data in Table 2 (entries 3, 4, 9, 10, 12 and 13) reveals that the azido group prefers an axial position whereas the more bulky *p*-toluenesulfonyl group prefers to be equatorial with respect to the *p*-nitrophenyl group.

The other reactions in Table 2 can reasonably be expected to be irreversible.[23] With the notable exception of entry 15 (Table 2), the reactions of both **12** and **23** give products which are independent of nucleophile concentration and appear to be the result of attack on an effectively planar cyclohexyl radical to give products in which the bulkier substituents predominantly and often exclusively occupy the equatorial position at the reaction site (C1).

The reaction with PhS^- gave nearly equal proportions of epimers at C1 even at quite high thiolate concentrations (up to 1.6M) except in the reactions of **23** with HMPA as solvent. These reactions (Table 2, entries 15 and 16) showed a striking dependence on benzenethiolate concentration. These experiments were quite reproducable and the percentage of isomer **27** formed at the higher PhS^- concentrations was less than 2%. This result can be interpreted[14] in terms of formation of the radical **34** (R = Me; Scheme 2) which is trapped by PhS^- ion before it collapses to radical **35**. The failure of the system without a 2-Me group (Scheme 2, R=H) to display this phenomenon is explicable by two alternatives. The first explanation is that the radical anion $12^{\cdot -}$ loses nitrite forming the radical **35** (R=H) directly. The second is that in absence of a 2-Me group, which can be seen, at least by inspection of molecular models, to hinder the transformation **34**→**35**, the collapse (r_c) of **34** (R = H) is still much faster than the rate of trapping (r_a) by the extremely efficient PhS^- ion, even in the excellent solvent HMPA.

Even if the first of the above explanations is correct, the retention of configuration at C1 (in the conversion **23**→**26**), at relatively high thiolate concentrations, "implicates the formation and trapping of a pyramidal benzylic radical."[14]

It would appear that the observation of stereoretention in substitutions occurring by the $S_{RN}1$ mechanism may well be limited to substrates for which the conversion to the effectively planar intermediate radicals such as **35** is a relatively difficult process. It would also appear that the results involving optically active substrate **4** are consistent with the simple explanation originally proposed,[10] with the provision that an initially formed pyramidal radical may be involved. Indeed the vital question as to whether *all* $S_{RN}1$ processes involve a pyramidal radical is not definitively answered by the above experimental results.

The formation and trapping of pyramidal benzylic radicals in suitably hindered situations may well be a general phenomenon and it is our intention to design and prepare substrates which on appropriate treatment will give rise to this class of radical.

EXPERIMENTAL

Instrumentation, purification of solvents and general workup and isolation procedures are as previously reported.[4,16,26,27] All ^1H NMR data were recorded on a Varian HA 100 spectrometer with $CDCl_3$ as solvent (Table 1). Glc was performed on a Pye 402 instrument using a column containing 2.5% Carbowax 20M on chromasorb G.

The lithium and tetrabutylammonium salts of 2-nitropropane, *sodium benzenethiolate and the sodium salt of 2-ethyl-malononitrile* were prepared as previously described,[26,27] the *latter two being generated in situ using sodium hydride.*

t-4-t-Butyl-r-1-chloro-1-nitrocyclohexane (**8**) *and c-4-t-butyl-r-1-chloro-1-nitrocyclohexane* (**9**). A mixture of **8** and **9** was prepared from 4-t-butylcyclohexanone oxime (15.5 g, 0.09 mol) by chlorination followed by oxidation with O_3, using the usual method.[15,16] The crude yellow oil (19.0 g) was separated by chromatography on silica gel with light petroleum as eluent to give **8** (4.0 g, 20%) as white crystals (light petroleum) m.p. 57–58° (lit.[17] 56–57°), and **9**, as an oil (12.4 g, 63%), b.p. 84–86°/0.1 mm. (Found: C, 55.1; H, 8.3; N, 6.3; Cl, 16.6. Calc. for $C_{10}H_{18}NO_2Cl$: C, 54.7; H, 8.2; N, 6.4; Cl, 16.2%).

c-4-t-Butyl-r-1-nitro-1-(P-nitrophenyl)cyclohexane (**12**). In a typical experiment,[17] a mixture of **8** and **9** (2 g, 9 mmol) in EtOH (100 ml) was treated with a slurry of excess $NaBH_4$ (0.5 g, 13 mmol) in ethanol (100 ml), in the presence of 10% Pd/C (100 mg) at room temp. After stirring for an hour the mixture was filtered and then acidified (glacial AcOH). Workup by dilution with water and extraction with ether in the usual fashion gave a mixture of crude *cis*- and *trans*-4-t-butyl-1-nitrocyclohexane (1.6 g). Excess of a 15% soln of KOH in EtOH (3.5 ml) was then added to this mixture. The soln was allowed to stand at 0° for 1 hr, after which the precipitated **31** (1.4 g, 73%) was filtered off, washed with ether, and dried. *p*-Dinitrobenzene (1.26 g, 7.5 mmol) was added with stirring to an excess of **31** (2.23 g, 10 mmol) in DMSO (100 ml) at room temp. After 24 hr, water was added, and the crude products were extracted into EtOAc, washed with NaOH aq, washed twice with water, then with brine, dried ($MgSO_4$) and the solvent was evaporated. Recrystallization (EtOH) yielded pale yellow plates of *c-4-t-butyl-r-1-nitro-1-(p-nitrophenyl)cyclohexane* (**12**) (2.04 g, 88%) m.p. 166–168°. (Found: C, 62.8; H, 7.2; N, 8.8. Calc. for $C_{16}H_{22}N_2O_4$: C, 62.7; H, 7.2; N, 9.1%). IR ($CHCl_3$) ν_{max}: 1540, 1520, 1365 cm^{-1}. UV (MeOH) λ_{max}: 260 (ε 11300) nm.

c-4-t-Butyl-c-2-methyl-r-1-nitro-1-(p-nitrophenyl) cyclohexane (**23**) and *(E)-cis-4-t-butyl-2-methylcyclohexanone oxime O-(p-nitrophenyl) ether* (**33**). *cis*-4-t-Butyl-2-methylcyclohexanone[20] was converted into its oxime and then treated in the sequence above to give **32** in 35% overall yield. *p*-Dinitrobenzene (1.85 g, 11.7 mmol) was added in a stirred soln of excess **32** (5.1 g, 27.5 mmol) in dry DMSO (250 ml). After 24 hr, water (150 ml) was added and the mixture was worked up as above to give an oil containing **23**, **33** and other unidentified products. Partial separation was achieved by column chromatography on silica, eluting with 2% EtOAc/light petroleum. Separation of the resultant mixture was completed by PLC using the same solvent, to give less polar **33** as white needles (ethanol) (390 mg, 12%), m.p. 126–128°. (Found: C, 67.2; H, 7.6; N, 9.2. Calc. for $C_{17}H_{24}N_2O_3$: C, 67.1; H, 7.9; N, 9.2%). ^1H NMR ($CDCl_3$): δ 0.90 (s, 9H, t-Bu), 1.23 (d, 3H, Me, *J* 6.5 Hz), 1.10–2.56 (m, 7H, cyclohexyl H), 3.35 (m, 1H, H6e), AA'XX' system: 7.28 (2H *meta* to NO_2), 8.20 (m, 2H *ortho* to NO_2), $J_{AX}+J_{AX'}$ 9.3 Hz. IR ($CHCl_3$) ν_{max}: 1585, 1500, 1480, 1350 cm^{-1}. UV (MeOH) λ_{max}: 314 (ε 15300) nm. The more polar product was recrystallized twice (ethanol) to yield white needles of **23** (840 mg, 24%), m.p. 133–134°. (Found: C, 63.9; H, 7.5; N, 8.7. Calc. for $C_{17}H_{24}N_2O_4$: C, 63.8; H, 7.5; N, 8.8%). IR ($CHCl_3$) ν_{max}: 1535, 1515, 1365 cm^{-1}. UV (MeOH) λ_{max}: 266 (ε 11200) nm.

The base extracts, combined with the water layers of the original extraction were shown to contain *p*-nitrophenol (*c.* 10%) in the usual way.[16]

Products from reaction of **8**, **9**, **12** *and* **23** *with nucleophiles.* The following compounds were isolated (entry numbers refers to Table 2). The crude reaction products were obtained by extraction with ethyl acetate.

c-4-*t*-*Butyl*-1-(1-*methyl*-1-*nitroethyl*)-r-1-*nitrocyclohexane* (**10**) (*entry* 1 *or* 2). Recrystallization of the crude product from acetone yielded white plates of pure **10** (40–60%), which darkens and decomposes above 200°. (Found: C, 57.6; H, 8.5; N, 10.0. Calc. for $C_{13}H_{24}N_2O_4$: C, 57.3; H, 8.9; N, 10.3%). IR ($CHCl_3$) ν_{max}: 1550, 1380, 1350 cm^{-1}. UV (MeOH) λ_{max}: 283 (ϵ 90) nm. Preparative glc of the mother liquors together with repeated fractional crystallization yielded **10**, and its isomer, t-4-*t*-*butyl*-1-(1-*methyl*-1-*nitroethyl*)-r-1-*nitrocyclohexane* (**11**), in a 3:2 mixture. (Found: C, 57.1; H, 8.6; N, 10.4%).

r-1-*Azido*-c-4-*t*-*butyl*-(p-*nitrophenyl*)*cyclohexane* (**13**) and its *epimer* (**14**) (*entry* 3). Recrystallization (EtOH) of the crude yielded pale yellow needles of **13** (110 mg, m.p. 94–95°. (Found: C, 63.6; H, 7.4; N, 18.4. Calc. for $C_{16}H_{22}N_4O_2$: C, 63.6; H, 7.3; N, 18.5%). IR ($CHCl_3$) ν_{max}: 2100, 1520, 1370 cm^{-1}. UV (MeOH) λ_{max}: 215 sh (ϵ 7600), 271 (ϵ 10900) nm. Repeated fractional crystallization of the mother liquors with EtOH, MeOH, and light petroleum as solvents also gave r-1-*azido*-*t*-4-*t*-*butyl*-1-(p-*nitrophenyl*)*cyclohexane* (**14**) as a pale yellow crystalline solid (4.5 mg, 3%) m.p. 100–105° (decomposes at m.p.). Elemental analysis was performed on a mixture of the two isomers for which **13**:**14** was approximately 1:2 (Found: C, 63.8; H, 7.5; N, 18.5%). Spectral data (^1H NMR and IR) were obtained with the epimerically pure sample of (**14**). IR ($CHCl_3$) ν_{max}: 2095, 1520, 1370 cm^{-1}.

t-4-*t*-*Butyl*-1-(p-*nitrophenyl*)-r-1-p-*toluenesulfonylcyclohexane* (**15**) *and its epimer* (**16**) (*entry* 4). Plc of the crude mixture (2% EtOAc/light petroleum) followed by recrystallization (EtOH) of the appropriate fraction, yielded cream crystals of a mixture of the isomers **15** and **16** in 45% yield. These were separated by further PLC (5% EtOAc/light petroleum) and separately recrystallized (EtOH). The more polar isomer, **15**, was obtained as a pale yellow crystalline solid (66 mg, 32%) m.p. 224–226°. (Found: C, 66.2; H, 7.1; N, 3.2; S, 8.0. Calc. for $C_{23}H_{29}NSO_4$: C, 66.5; H, 7.0; N, 3.4; S, 7.7%). IR ($CHCl_3$) ν_{max}: 1515, 1360, 1150 cm^{-1}. UV (MeOH) λ_{max}: 228 (ϵ 18200) 276 (ϵ 13700) nm. The less polar minor isomer **16**, was obtained as a white crystalline solid, in very low yield (*c.* 3 mg, 1%), which contained traces of impurity. Elemental analysis was performed on a mixture of the two isomers (**16**:**15** approximately 1:3). (Found C, 66.5; H, 6.7; N, 3.3: S, 7.8%). IR ($CHCl_3$) ν_{max}: 1520, 1365, 1315, 1150 cm^{-1}.

Sulfides **17** *and* **18** (entry 6). The crude was recrystallized (EtOH) to yield white crystals of a 6:4 mixture of the epimers **17** and **18** (148 mg, 80%). (Found: C, 71.3; H, 7.2; N, 3.8; S, 8.5. Calc. for $C_{22}H_{27}NO_2S$: C, 71.5; H, 7.4; N, 3.8, S, 8.7%). The NMR spectrum showed two separate t-Bu peaks at δ 0.70 and 0.96 as well as cyclohexyl and aromatic protons in the expected ratio. IR ($CHCl_3$) ν_{max}: 1515, 1365 cm^{-1}. Repeated preparative layer chromatography with a wide range of solvent polarities resulted only in decomposition of these compounds, without separation. These sulfides were therefore characterized as their respective sulfones.

A mixture of the above sulfides (300 mg, 0.81 mmol) was dissolved in CH_2Cl_2 (15 ml) and excess *m*-chloroperbenzoic acid (344 mg, 2 mmol) was added. The soln was stirred until the reaction was complete by tlc (15 min). The organic layer was washed with $NaHCO_3$ aq, then brine, and dried ($MgSO_4$). Evaporation of the solvent gave a quantitative yield of a 6:4 mixture of the sulfones **19** and **20**, which were separated by plc (5% EtOAc/light petroleum). Recrystallization (EtOH) of the less polar isomer gave white crystals of r-1-*benzenesulfonyl*-c-4-*t*-*butyl*-1-(p-*nitrophenyl*)-*cyclohexane* (**19**) (148 mg, 42%) m.p. 199–200°. (Found: C, 65.9; H, 7.0; N, 3.3; S, 8.3. Calc. for $C_{22}H_{27}NO_4S$: C, 65.8; H, 6.8; N, 3.5; S, 8.0%). IR ($CHCl_3$) ν_{max}: 1520, 1368, 1320, 1154 cm^{-1}. UV (MeOH) λ_{max}: 268 sh (ϵ 10800), 273 (ϵ 11000) nm. Recrystallization (EtOH) of the more polar sulfone gave white crystals of r-1-*benzenesulfonyl*-t-4-*t*-*butyl*-1-(p-*nitrophenyl*)*cyclohexane* (**20**) (113 mg, 32%) m.p. 173–174°. (Found: C, 65.6; H, 7.0; N, 3.2; S, 8.3%). IR ($CHCl_3$) ν_{max}: 1520, 1368, 1320, 1158 cm^{-1}. UV (MeOH) λ_{max}: 268 sh (ϵ 11300) 273 (ϵ 11600) nm.

t-4-*t*-*Butyl*-r-1-(1-*methyl*-1-*nitroethyl*)-1-(p-*nitrophenyl*) *cyclohexane* (**21**) (*entry* 7). Recrystallization (EtOH) of the crude gave pure **21**, a yellow crystalline solid (148 mg, 85%), m.p. 215–217° (Found: C, 65.2; H, 7.9; N, 7.8. Calc. for $C_{19}H_{28}N_2O_4$: C, 65.5; H, 8.1; N, 8.0%). IR ($CHCl_3$) ν_{max}: 1530, 1520, 1365 cm^{-1}. UV (MeOH) λ_{max}: 271 (ϵ 11600) nm.

2-[t-4-*t*-*Butyl*-1-(p-*nitrophenyl*)*cyclohexyl*]-2-*ethylmalononitrile*, (**22**), (*entry* 8). Recrystallization (EtOH) of the crude mixture yielded yellow crystals of **22**, (157 mg, 89%) m.p. 153–155°. (Found: C, 71.1; H, 7.6; N, 11.7. Calc. for $C_{21}H_{27}N_3O_2$: C, 71.4; H, 7.7; N, 11.9%). IR ($CHCl_3$) ν_{max}: 1530, 1375 cm^{-1}. UV (MeOH) λ_{max}: 266 (ϵ 11340) nm.

r-1-*Azido*-c-4-*t*-*butyl*-c-2-*methyl*-1-(p-*nitro*-*nitrophenyl*) *cyclohexane*, **24** (*entry* 9). Recrystallization (EtOH) of the crude yielded yellow crystals of **24** (134 mg, 85%) m.p. 140–142°. (Found: C, 64.7; H, 7.7; N, 17.8. Calc. for $C_{17}H_{24}N_4O_2$: C, 64.5; H, 7.7; N, 17.7%). IR ($CHCl_3$) ν_{max}: 2110, 1525, 1320 cm^{-1}. UV (MeOH) λ_{max}: 220 sh (ϵ 6700), 274 (ϵ 11700) nm.

t-4-*t*-*Butyl*-t-2-*methyl*-1-(p-*nitrophenyl*)-r-1-p-*toluenesulfonylcyclohexane*, (**25**), (*entry* 12). Plc of the crude (7% ethyl acetate/light petroleum) followed by recrystallization (EtOH) yielded pale crystals of **25** (95 mg, 44%) m.p. 231–231.5°. (Found: C, 66.7; H, 7.4; N, 3.3; S, 7.1. Calc. for $C_{24}H_{31}NO_4S$: C, 67.1; H, 7.3; N, 3.3; S, 7.5%). IR ($CHCl_3$) ν_{max}: 1520, 1365, 1310, 1155 cm^{-1}. UV (MeOH) λ_{max}: 228 (ϵ 16000), 275 (ϵ 12800) nm.

Sulfides **26** *and* **27** *and derived sulfones* **28** *and* **29** (*entry* 11). Since the oily mixture of sulfides **26** and **27** could not be separated by plc, oxidation with *m*-chloroperbenzoic acid was carried out, in the same fashion as compounds **17** and **18** above. The resulting sulfones **28** and **29** were separated by plc (3% ethyl acetate/light petroleum). Recrystallization of the less polar isomer yielded white needles of r-1-*benzenesulfonyl*-c-4-*t*-*butyl*-c-2-*methyl*-1-(p-*nitrophenyl*) *cyclohexane* (**28**) m.p. 193–193.5°. (Found: C, 66.7; H, 6.9; N, 3.3; S, 7.8. Calc. for $C_{23}H_{29}NO_4S$: C, 66.5; H, 7.0; N, 3.4; S, 7.7%). IR ($CHCl_3$) ν_{max}: 1525, 1365, 1320, 1145 cm^{-1}. UV (MeOH) λ_{max}: 268 (ϵ 11300) 275 (ϵ 11700) nm. Recrystallization of the more polar sulfone yielded pale yellow plates or r-1-*benzenesulfonyl*-t-4-*t*-*butyl*-t-2-*methyl*-1-(p-*nitrophenyl*) *cyclohexane* (**29**) m.p. 190–191°. (Mixed m.p. with **28**, 161–64°). (Found: C, 66.5; H, 6.9; N, 3.4; S, 7.5%). IR ($CHCl_3$) ν_{max}: 1525, 1365, 1315, 1155 cm^{-1}. UV (MeOH) λ_{max}: 269 (ϵ 12500), 275 (ϵ 13100) nm.

2-[t-4-*t*-*Butyl*-t-2-*methyl*-1-(p-*nitrophenyl*). *cyclohexyl*]-2-*ethylmalononitrile* (**30**) (*entry* 14). The crude product was purified by plc (5% EtOAc/light petroleum). Recrystallization of the most polar component (98 mg) from EtOH yielded pale crystals of **30** (53 mg, 29%), m.p. 128–130°. (Found: C, 72.2; H, 8.1; N, 11.4. Calc. for $C_{22}H_{29}N_3O_2$: C, 71.9; H, 8.0; N, 11.4%). IR ($CHCl_3$) ν_{max}: 1520, 1365 cm^{-1}. UV (MeOH) λ_{max}: 268 (ϵ 11500) nm. The other plc fractions contained by-products, but none of the isomeric adduct was detected.

c-4-*t*-*Butyl*-c-2-*methyl*-1-(p-*nitrophenyl*)-r-*phenyl*-*thiocyclohexane*, (**26**) (*entry* 15). Purification by plc (light petroleum) of the product from one reaction in which the [PhS] was 1.6 M gave **26** (containing less than 2% **27**) as an oil in 95% yield. (Found: C, 72.1; H, 7.8; N, 4.0; S, 8.5. Calc. for $C_{23}H_{29}NO_2S$: C, 72.0; H, 7.6; N, 3.7; S, 8.4%). IR ($CHCl_3$) ν_{max}: 1520, 1365 cm^{-1}. UV (MeOH λ_{max}: 267 (ϵ 13400) nm. The sulfide **26** was oxidized to the corresponding sulfone, using *m*-chloroperbenzoic acid, in the manner described for mixtures of **26** and **27**. The product was identical in all respects to compound **28** previously prepared above.

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