cyclohexenone was produced in a 95% yield together with a 3% yield of cyclohexanone. 2-Cyclohexenone was isolated in about 85% yield by column chromatography on silica gel eluting with benzene.

$Pd^{II}(OAc)_2$-catalyzed dehydrosilylation of other silyl enol ethers (1) was similarly carried out. The reaction time is indicated in the Table I. Products of α,β-unsaturated carbonyl compounds were identified by comparison of their IR and NMR spectra with those of authentic samples. The stereochemistry of (*E*)-2-cyclododecenone (**2g**) and (*E*)-2-hexenal (**2i**) was convincingly confirmed by comparison of their IR and NMR spectra with those of authentic samples.[10] The stereochemistry of (*E*)-3-nonen-5-one (**2h**) was determined by the NMR coupling constant (J_{H-H} = 15.6 Hz) of the olefinic protons.

Preparation of 2-Cyclohexenone by $Pd^{II}Cl_2$-$(C_6H_5CN)_2$-Catalyzed Dehydrosilylation of 1-Trimethylsilyloxy-1-cyclohexene (1b). A mixture of 54 mg (0.5 mmol) of *p*-benzoquinone and 192 mg (0.5 mmol) of $Pd^{II}Cl_2$-$(C_6H_5CN)_2$ was dissolved in 4 mL of benzene with stirring. To the homogeneous solution, 170 mg (1.0 mmol) of 1-trimethylsilyloxy-1-cyclohexene (**1b**) was added, and then the reaction mixture was stirred at room temperature for 3 h. The product of 2-cyclohexenone was isolated by column chromatography on silica gel eluting with benzene.

Registry No.—(*Z*)-**1g**, 55314-46-0; (*E*)-**1g**, 55314-44-8; (*Z*)-**1h**, 64682-31-1; (*E*)-**1h**, 64682-32-2; (*Z*)-**1i**, 64728-30-9; (*E*)-**1i**, 64682-33-3.

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Structure and Reactivity.[1] 2.
2-*tert*-Butyl-3-cyano-7-oxabicyclo[4.1.0]heptane Stereoisomers: Pseudoaxial *tert*-Butyl Conformer and Epoxidation Reaction Path

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The stereoselectivities of alkene epoxidations are sometimes rather difficult to rationalize;[2] for the two examples given in Figure 1, the inhibited syn attact is obviously related to steric hindrance, the cyano group being also rather bulky in syn-1,3 situations; the electrostatic interaction of this group may also play a part in this stereoselectivity.

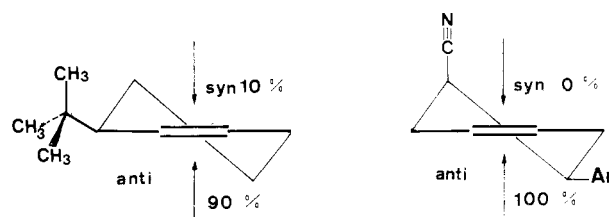When the cyano group is equatorial, no stereoselectivity

Figure 1. Induced stereoselectivities in the epoxidation of 3-*tert*-butylcyclohexene[3] and 4-cyano-5-arylcyclohexene.[4]

occurs: 50% of anti attack on *trans*-4-cyano-5-phenylcyclohexene in 1,2-dichloroethane as a solvent.[4]

Taking into account these results and the observed stereoselectivity for 4-cyanocyclohexene, 82 to 90% of anti attack,[5] and also the conformational populations for this compound ($\Delta G° \simeq 0$),[6] one can predict the ratio of the rates of anti attack ($k(a)$) on each conformer (a and e)

$$3,5 < (k_a(a)/k_e(a)) < 8$$

This result lacks in precision, but it shows a faster attack on the conformer with an axial cyano group. This analysis is based on the reasonable assumption, first made by Rickborn and Lwo,[7] that the transition state conformation must be very similar to that of the starting alkene; the use of the ground state populations is then possible without violating the Curtin–Hammet principle.[8]

The problem of the epoxidation of *cis*- and *trans*-3-*tert*-butyl-4-cyanocyclohexenes must be also related to their conformational behavior:

(a) For the cis isomer, there is only one conformer at room temperature, the one with a pseudoequatorial *tert*-butyl group and an axial cyano substituent; the ring is in a half-chair conformation; this information has been established by NMR study[9] and an x-ray crystal structure analysis.[10]

(b) For the trans isomer, NMR[9] and vibrational[11] studies agree with two equally populated conformers.

(c) The "pseudoequatorial *tert*-butyl" conformer of this trans isomer has a *sofa* conformation similar to the one which has been determined in the crystallographic study of *trans*-1-acetoxy-3-*tert*-butyl-4-cyanocyclohexene;[12] the ring dihedral angles are $\phi_{12} = -4.3°$, $\phi_{23} = -1.1°$, $\phi_{34} = +29.4°$, $\phi_{45} = -58.6°$, $\phi_{56} = +53.3°$, $\phi_{61} = -23.5$; the dihedral angle of the *tert*-butyl and the cyano C–C bonds is 86.5°.

(d) For the second conformer of the trans isomer ("pseudoaxial *tert*-butyl") we can reasonably expect another *sofa* conformation in which the axial character of the *tert*-butyl group would be less pronounced than in a half-chair conformation.

These conformational data are sufficiently uncommon to justify a study of the reactivity of these compounds; the epoxidation reaction is especially interesting owing to the relative simplicity of the reaction path (one-step reaction).

Results and Discussion

The epoxidation of *cis*-3,6,6-trideuterio-3-*tert*-butyl-4-cyanocyclohexene by *p*-nitroperbenzoic acid in chloroform gives only one compound **1**, which is proved by gas chromatography and NMR spectroscopy. Except small differences in chemical shifts and in coupling constants, the NMR spectra of **1** and of its parent cyclohexene are quite identical.

The corresponding set of NMR parameters is reported in Table I. Long-range coupling constants (^4J) are observed between each of the two bridgehead protons (H_1 and H_6) and a proton located near the cyano group (H_3 and H_4, respectively); the difference between these two coupling constants is small but sufficient to allow the identification of transitions of protons H_1 and H_6. The coupling between H_6 and one of the

Table I. NMR Parameters [a] of Deuteriated 2-*tert*-Butyl-3-cyano-7-oxabicyclo[4.1.0]heptanes

		1			2			3	
		b	c	d	b	c	d	b	c	d
$(CH_3)_3C$		1.14	1.13	1.10	1.08	1.08	1.08	1.08	1.08	1.08
H_{3c}		2.86	2.97	2.68				2.66	2.71	2.59
H_{3t}					2.14	2.43	2.11			
H_{4c}		1.57	1.50	1.48	1.85	1.86	1.84	1.81	1.89	1.80
H_{4t}		1.78	1.71	1.66	1.68	1.78	1.65	1.54	1.64	1.52
H_1		3.16	3.10	2.93	2.95	3.04	2.89	3.10	3.13	3.04
H_6		3.31	3.19	3.08	3.05	3.12	2.99	3.16	3.22	3.20
^3J	1–6	3.9	4.0	3.9	4.0	4.0	4.2	4.2	4.2	4.0
	3_c–4_c	2.6	2.9	2.9				4.2	4.0	4.1
	3_c–4_t	4.2	4.1	4.2				4.6	4.9	4.9
	3_t–4_c				12.9	12.8	12.7			
	3_t–4_t				3.9	3.8	4.0			
	3_t–D						1.4			
^2J	4_c–4_t	−13.4	−13.6	−13.6	−13.2	−13.3	−13.2	−13.6	−13.2	−13.8
^4J	6–4_t	0.8	0.8	0.9						
	1–3_c	1.0	1.0	1.0						

[a] Me_4Si as a reference for the chemical shifts δ; T = 303 K. [b] Solvent $CDCl_3$. [c] Solvent $(CD_3)_2CO$. [d] Solvent CS_2.
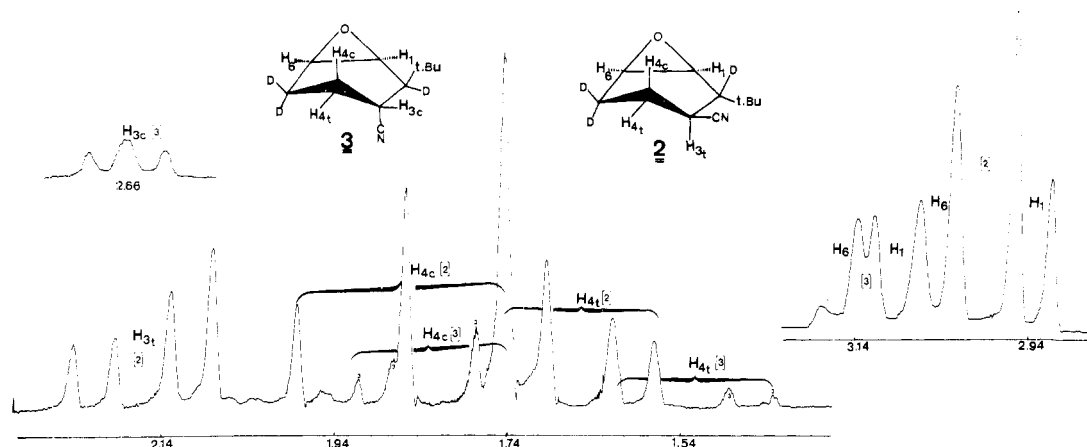

Figure 2. Deuterium decoupled 100-MHz NMR spectrum of a mixture of isomer epoxides **2** and **3**.

H_4 protons involves an equatorial situation of the latter; the vicinal coupling constants (^3J) between H_3 and H_4 protons (2.9 and 4.2 Hz) require an equatorial H_3 proton.

Our assumption that the epoxy bridge of **1** is trans with respect to the two other substituents is supported by the stereoselectivity of the reaction (Figure 1), the syn approach of the peroxy acid being hindered by the two substituents.

The epoxidation of *trans*-3,6,6-trideuterio-3-*tert*-butyl-4-cyanocyclohexene gives a mixture of isomers, where **2** is the major one (87% estimated by GC). In the NMR spectrum of this mixture (Figure 2), the identification of the lines corresponding to **2** is straightforward; thus, when the deuterium decoupling is stopped, the four lines at δ 2.14 give four triplets ($^3J_{HD}$ = 1.4 Hz); therefore, we have a proof that this proton is coupled to only one deuterium, and the value $^3J_{HD}$ (equivalent to $^3J_{HH} \simeq 9$ Hz) agrees with an anti relationship of the two nuclei; then, these lines are those of proton H_3, this one being preferentially axial. The splitting at $\delta \simeq 1.85$ results from two large couplings and the three lines are attributed to the axial H_4 proton. The attribution of protons H_1 and H_6 is allowed by the observation of a difference between the half-height line widths (^4J coupling between H_6 and H_{4t}) and by the examination of the spectrum without deuterium decoupling (triplets for H_1 lines).

The NMR spectrum (Figure 2) of the minor isomer **3** is clear enough to obtain all its parameters, the overlap of the spectra being limited. The low-field lines (δ 2.66) are attributed to the

H_{3c} proton, the equatorial situation of which is strongly suggested by the high chemical shift and by the narrowness of the signal (8.8 Hz). Once again, the axial and equatorial positions of H_{4c} and H_{4t} respectively are proved by examination of the spectrum without deuterium decoupling (H_{4c} lines being broader than H_{4t} ones); further, the effect of Eu(fod)$_3$ is 1.6 times stronger for H_{4c} than for H_{4t}.

The NMR parameters obtained after LAOCOON analysis of the spectra of **2** and **3** are reported in Table I; the vicinal coupling constants of **3** are small ($^3J_{34} \simeq 4.2$ Hz), which is a proof of the larger stability of the conformer with an axial cyano group (equatorial H_3); this conformer must have a pseudoaxial *tert*-butyl group.

Our assumption about the relative positions of the epoxide ring (Figure 3) can be justified: (a) by the stereoselectivity of the epoxidation which is mainly governed by the hindrance of the *tert*-butyl group (no effect of the equatorial cyano group in the starting cyclohexene); and (b) by the conformational equilibrium of **3**, only possible with a trans relationship between the epoxide ring and the axial cyano group. For the opposite assumption the two dipoles of these groups would be roughly parallel and would display a repulsive electrostatic interaction, the importance of which can be estimated to 0.9 kcal mol^{-1}.[13]

For compound **1**, the 4.2 Hz value of the ^3J coupling constant between the trans protons H_{3c} and H_{4t} is consistent with a large proportion of the conformer with the *tert*-butyl and
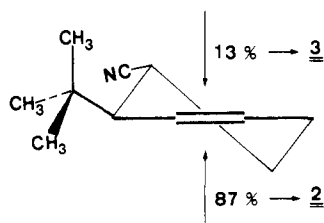
Figure 3. Stereoselectivity in the epoxidation of *trans*-3-*tert*-butyl-4-cyanocyclohexene.

cyano groups pseudoequatorial and axial, respectively, just as in the parent cyclohexene.[9]

For compound **2**, the trans coupling constant (between H_{3t} and H_{4c}) has the same magnitude (12.8 Hz) as the specific coupling constant of a diequatorial conformer. Thus, we observe an important difference with the parent cyclohexene in which the two conformers are equally populated; this difference can be ascribed to the unfavorable electrostatic interaction between the epoxy and cyano groups in the diaxial conformer of **2**.

The most striking result is obtained with epoxide **3** for which the diequatorial conformer is much less populated than the diaxial one, in spite of the steric interaction between the *tert*-butyl and epoxide groups in this latter conformer. To explain this fact, we cannot argue that there is a balancing between this *tert*-butyl epoxide interaction and a stronger *tert*-butylcyano gauche interaction (in the diequatorial conformer) because this latter interaction, acting alone in the parent cyclohexene, only leads to a 1:1 conformational equilibrium.

To explain the conformational equilibrium of **3**, we must investigate the possibilities of minimization of the different steric interactions by ring distortions. In the diequatorial conformer, the evolution from a *half-chair* to a *sofa* conformation relieves the *tert*-butylcyano gauche interaction, but the *tert*-butyl group is taking an isoclinal position[14] which increases its interaction with the oxygen atom.[15] Thus, the diequatorial conformer presents conflicting interactions which are not operative in the diaxial conformer; in that one, the evolution to a *sofa* conformation decreases the axiality of the *tert*-butyl group, relieving the *tert*-butyl epoxide interaction which is not outweighed by any other steric interaction.

In this coherent interpretation, the terms pseudoequatorial and pseudoaxial are meaningless in describing the conformational positions of the *tert*-butyl group. These terms are still useful as we initially make reference to half-chair conformers.

Reaction Paths

For the epoxidation of *trans*-3-*tert*-butyl-4-cyanocyclohexene, an energy profile is proposed (Figure 4) which points out the equal stabilities of the ee′ and aa′ cyclohexene conformers and, for the minor product **3**, the energy difference between the two conformers.

The two reaction paths leading to this product proceed through transition states whose relative energies reflect more or less those of the conformers of **3** according to the nature of these transition states, $\Delta G^{\ddagger}$ being zero for a reactant-like transition state or being equal to $\Delta G°$ (**3**) for a product-like transition state. At least, the reaction path which takes off from the aa′ cyclohexene is responsible for 50% in the formation of **3**, but that extreme situation corresponds to the unlikely assumption of a reactant-like transition state; moreover, this reaction path is favored by the axial position of the cyano group (see the introductory section).

Therefore, the epoxide **3** is mainly obtained from the aa′ cyclohexene conformer; this conclusion elucidates why the
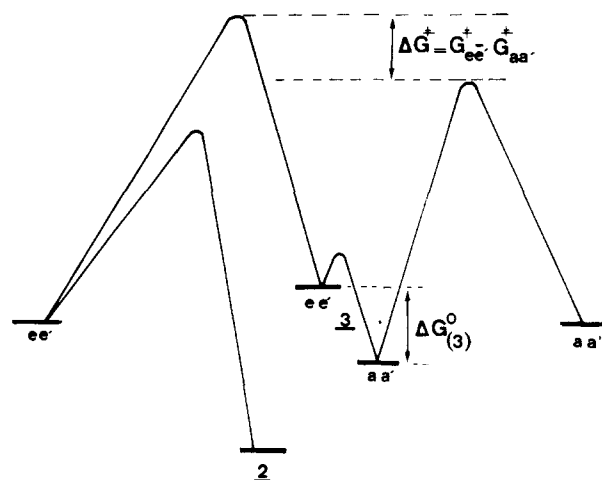

Figure 4. Energy profile of the epoxidation of *trans*-3-*tert*-butyl-4-cyanocyclohexene (product-like transition state hypothesis).

stereoselectivity is only 74% which is lower than that of the 3-*tert*-butylcyclohexene epoxidation (80%). A higher stereoselectivity (>80%) was effectively expected for the epoxidation of the ee′ conformer of *trans*-3-*tert*-butyl-4-cyanocyclohexene; with respect to a syn attack, the *tert*-butyl group of its *sofa* conformation causes greater hindrance to syn attack than the same group in the half-chair conformation of 3-*tert*-butylcyclohexene.

Conclusion

This study of the epoxidation of strongly strained molecules shows that a good knowledge of energetical and geometrical data on the reactants and on the products is a prerequisite to any interpretation of the stereoselectivity.

Experimental Section

NMR spectra were recorded on a Varian XL 100 spectrometer equiped with an heteronuclear spin decoupler.

Epoxidations were achieved according to ref 16. The ratios of epoxides **2** (retention time: 50 min) and **3** (retention time: 22 min) were determined by gas chromatography with a digital integrator (LTT 4200) operating at the output of a Girdel 300 chromatograph (column Reoplex 10% on Chromosorb W 60/80 non-Acid Washed, at 120 °C).

For epoxide **1** (retention time: 23 min) mp 50–51 °C (uncorrected).

Registry No.—**1**, 64683-03-0; **2**, 64726-48-3; **3**, 64726-49-4; *cis*-3,6,6-trideuterio-3-*tert*-butyl-4-cyanocyclohexene, 63125-70-2; *trans*-3,6,6-trideuterio-3-*tert*-butyl-4-cyanocyclohexene, 63125-66-6.

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